Molecular radicals in the search for drifting constants

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VRIJE UNIVERSITEIT

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Chapter 1

Introduction

Even though the word 'constant' seems to imply otherwise, it can not be taken for granted that the fundamental numbers underlying all physical theories that physicists call constants are ever unchanging. Dirac was the first to realize this, when he noticed that the ratio between the electromagnetic and gravitational forces between and electron and a proton and the ratio between the mass of the universe and the mass of the proton are approximately equal to t and t^2 , respectively, with $t \approx 10^{39}$ the age of the universe expressed in atomic units [1]. Dirac assumed that this would not be coincidental, but a fundamental truth. By then, it was already known that the observable universe is expanding, which led Dirac to two conclusions: (1) the number of protons and neutrons in the universe must increase; and (2) the ratio between the strength of the electromagnetic and gravitational forces is a function of time. As the first point would lead to a much smaller relative change in the involved quantity than the second, it was concluded that it was the gravitational 'constant' (the quotes are his) that was changing [2]. Teller showed that any variation was much smaller than would be predicted by the theory from Dirac by explaining that the temperature on earth around 250 million years ago would be such that water would be either freezing or boiling, which conflicts with life being present at that time [2].

As will be discussed later, the constraints on a variation of fundamental constants have nowadays been set much tighter, and the coincidence seen by Dirac is now seen as just that, a coincidence. Nevertheless, the search for a time or position dependency of the value of fundamental constants is ongoing. The search is aimed only at dimensionless numbers, as a variation in dimensionful numbers can not be separated from a variation in the measurement system [3]. The dimensionless numbers that are most often targeted are the fine-structure constant, α , and the proton-to-electron mass ratio, μ , with the focus of this thesis being on the latter.

An intuitive way to search for a possible variation of a fundamental constant would be to measure that constant as precisely as possible a number of times over a time interval. However, as it is not possible to measure a fundamental constant directly, this is very inefficient. To find the value of α or μ , a measurement is performed and then calculations are used to extract the value of the constant itself. To experimentally find the value of a fundamental constant to a certain accuracy, one needs both measurements and calculations to this accuracy. To study whether a constant is changing over time¹, however, the exact value of the constant is not of interest. To find whether a fundamental constant is truly a constant, it is possible to directly use the results of a spectroscopic measurement, even if the dependency of the measured transition to the fundamental constant is known only to rather poor accuracy². To calculate how the energy of a transition depends on a constant to within a few percent is very much possible for molecular transitions (see, for example Chapter 6). This dependency is referred to as the sensitivity coefficient, K_X , and is defined as

$$\frac{\delta\nu}{\nu} = K_X \frac{\delta X}{X},\tag{1.1}$$

with X a fundamental constant. This means that any relative change in a fundamental constant, $\frac{\delta X}{X}$, is accompanied by a K_X times larger relative change in the transition frequency, $\frac{\delta \nu}{\nu}$. A constraint on the size of the relative rate of change of a fundamental constant can now be determined by measuring two transitions with a different K_X over a time interval, typically of the order of one year. Two transitions with a different K_X are needed, as otherwise the relative variation will be the same in both transition, and thus remain hidden. In practice, a cesium clock is often used as the reference transition [7].

The constraint that an experiment sets on the time variation of a fundamental constant is determined by the accuracy of the measurement, the sensitivity coefficient of the measured transition and the time over which a transition is monitored. K_X is typically of order 1, however, in special cases it can have very high values up to a few hundred [8–10]. A higher than normal sensitivity is most often the result of a near degeneracy between two levels that have a different dependence on the constant under consideration. In the case of the two-photon transition in the $a^3\Pi$ state of CO that will be discussed in this thesis, the energy of one of the two nearly-degenerate levels is purely rotational, while the energy of the other level is partially rotational and partially spinorbit. The rotational energy depends only on μ , while the spin-orbit energy depends only on α . A change in α or μ will result in one level shifting with respect to the other. A near degeneracy thus raises the sensitivity coefficient, and it moves the transition frequency into the microwave regime.

 $^{^{1}}$ A variation in space is equivalent to a variation in time, due to the movement of earth, and thus the laboratory, with respect to any outside reference frame. In this thesis, we will only discuss time variation.

²Spectroscopy is not the only way to study time variation of fundamental constants. For example, the evaluation of physical processes and the isotope ratios found in the Oklo natural fission reactor and the atomic abundances predicted by big bang nucleosynthesis have been used [4–6]. These methods however fall outside the scope of this thesis.

1.1 Astrophysical measurements

To make a search for a time-variation of a fundamental constant more sensitive, a very long time interval can be used. In laboratory studies this is not feasible, but it is being used in astrophysical measurements. When the light of a far-away light source travels through a interstellar gas cloud, the absorption features of the atoms and molecules that are present in the cloud are imprinted on the light. Those absorption features, that can be from the optical to the microwave regime, can be detected on earth and compared to laboratory measurements. All absorption features from the same gas cloud will be redshifted by the same relative amount. However, as not al transitions have the same sensitivity coefficient, absorption features will have shifted with respect to each other if a fundamental constant has shifted. For this purpose, absorption features of absorption in metal ions, e.g. Fe⁺ and Mg⁺ have been observed at high red shifts [11]. These observations were used to find a relative variation in α on the order of 10^{-5} [11]. After more data was collected and analyzed, this variation was interpreted as a spatial dipole in α , meaning that an increased α was found in one direction of the universe and a decreased α was found in the opposite direction [12].

To study a variation in μ using astrophysical observations, molecular hydrogen has been the main object of study. The transitions in hydrogen that were used is these studies, however, have a sensitivity coefficient of only order 0.01 [13]. Absorption in molecular hydrogen has been observed at redshifts corresponding to a look-back time of ~ 10¹⁰ years, leading to a constraint on the relative change of μ on the order of 10^{-5} [14, 15]. Recently, the observations of the inversion transition in ammonia ($K_{\mu} = -4.2$) [16–18] and torsion-rotation transitions in methanol (K_{μ} ranging from -33 to -1) [8, 19–21], at redshift 0.89 have resulted in more stringent limits on the variation of μ , with a most stringent limit of $\Delta \mu / \mu = (-1.0 \pm 0.8_{stat} \pm 1.0_{sys}) \times 10^{-7}$ [20] over a look-back time of 7.5 billion years.

One of the problems that faces astrophysical measurements is spatial segregation. Typically, transitions in different molecules are compared to find the most stringent constraint on a possible variation. However, if not all species are present in the same location, different conditions may apply to different molecules. To be unaffected by spatial segregation, one can use multiple transitions in one molecule that have a different sensitivity coefficient. An example of this is given in Chapter 6, where the lowest rotational transitions and lambda-doubling transitions in the lowest rotational levels of the ground state of CH are found to have very different sensitivity coefficients. Recently, these rotational transitions have been measured both in the laboratory [22] and at redshift z = 0.89 using ALMA [23].

1.2 α variation

The α dipole discussed before can in principle be confirmed by laboratory measurements, as earth is moving through space with respect to the α dipole. This movement through the dipole would result in $\dot{\alpha}/\alpha \approx 10^{-19} \text{ yr}^{-1}$ [24]. Here, we discuss a number of present and future laboratory experiments that search for a time variation of α .

One experiment is a comparison of two different ion-clocks, performed at NIST [25]. In this experiment, the relative frequency of a Hg⁺ and a Al⁺ clock are compared over a period of a year. As both clock transitions have a different dependence on α , a relative rate of change of α can be extracted from this experiment, and was found to be $\dot{\alpha}/\alpha = (-1.6 \pm 2.3) \times 10^{-17} \text{ yr}^{-1}$.

Another experiment is the dysprosium experiment performed in the Budker group at UC Berkeley. In this experiment, a near degeneracy between two hyperfine components of two different states of dysprosium is measured. Due to large, opposite-sign relativistic corrections to the energy of both states, this transition is highly sensitive to a variation of α [26]. As the sign of the sensitivity coefficient is opposite between 162 Dy and 164 Dy, the transition is measured in both isotopes to limit common-mode effects. The transition frequencies of 235 and 754 MHz, respectively, have been measured to an accuracy of better than a hertz over a period of two years, finding $\dot{\alpha}/\alpha = (-5.8 \pm 6.9) \times 10^{-17}$ yr^{-1} , consistent with zero. The accuracy of this experiment is limited by the very short, order microseconds, lifetime of one of the states, making the transition very broad. Even though the system under study in this experiment is much less ideal than the one in the ion clock comparison, the transitions in dysprosium are $\sim 10^6$ times more sensitive to a variation of α , so the final accuracy in $\dot{\alpha}/\alpha$ is of the same order of magnitude. However, these two experiments do not have the accuracy required to confirm or exclude the α dipole.

A new development that may reach the required accuracy is the thorium nuclear clock, based on a very narrow transition between nearly-degenerate nuclear states in ²²⁹Th [27]. This transition, with an energy of 7.8 ± 0.5 eV [28, 29], is very sensitive to a variation of α , as there is a cancellation between Coulomb and nuclear energies, which are both of order mega-electronvolt and depend differently on α [28, 30, 31]. It is also highly insensitive to external fields, as the nucleus couples to external electric and magnetic fields via the nuclear moments which are much smaller than the electronic equivalents. The electrons around the nucleus add an extra coupling via the hyperfine interaction, but this is still weaker than when electronic transitions are used. Furthermore, the Th³⁺ ion is alkali like, and thus amenable to laser cooling and trapping, making a single trapped ion experiment possible [27]. However, despite a search by a number of groups, this transition has not been directly observed yet [32, 33].

1.3 μ variation

In the scientific literature, many different clock comparisons can be found, for example the aforementioned comparison of Hg⁺-Al⁺ clocks [25] and a comparison between Hg⁺-Cs clocks [34]. Each of these comparisons measures the relative frequency of the two clocks involved over a time interval of order 1 year, and each relative frequency has a different dependence on α and μ . Under Grand Unification models, assumptions can be made about the relation between $\dot{\alpha}/\alpha$ and $\dot{\mu}/\mu$ [7]. Using the different dependencies on the fundamental constants, and the model-dependent relations, the relative rate of change of μ was found to be $\dot{\mu}/\mu = (0.7 \pm 2.9) \times 10^{-16} \text{ yr}^{-1}$ [7].

A model-free constraint on the time variation of μ is found from a comparison of a rovibrational transition in SF₆ with a cesium fountain clock [35] over a period of two years. The transition was measured in a two-photon spatial Ramsey experiment. A CO₂ laser around 10 μ m was used to detect Ramsey fringes with a periodicity of 200 Hz. A cavity was used to create a standing wave, effectively phase locking the two interrogation zones. As a vibrational transition in a molecule has a sensitivity coefficient of $K_{\mu} = 0.5$, the Cs clock a sensitivity coefficient of $K_{\mu} = -1$ and the dependence on the other constants is the same as in the Hg⁺-Al⁺ clock comparison, a constraint on the variation of μ could be extracted. The end result that was found is $\dot{\mu}/\mu = (3.8\pm5.6) \times 10^{-14}$ yr⁻¹ [35].

1.4 Near degeneracies

The idea of using a transition between nearly degenerate levels in the search for a possible variation of fundamental constants has been mentioned already, here we will discuss this in more detail. Near degeneracies between levels with a different dependence on a fundamental constant will lead to an enhancement of the sensitivity of the transition between these levels. This has the obvious advantage that a measurement of this transition can be less accurate, while still setting a tighter constraint on a varying constant than a measurement of a transition with a low sensitivity. Another advantage is that the same transition can have a very different sensitivity coefficient in a different isotope, thereby enabling a comparison of the two using the same experimental setup. In this way, common-mode effects can be monitored by comparing the relative rate of change of both transitions. A disadvantage is that a higher absolute accuracy needs to be reached, as a constraint is set using the relative accuracy of a measurement. This is not relevant in astrophysical measurements, as the accuracy of these measurements is limited by the Doppler width of the measured transitions, which is a relative effect. The main disadvantage is that the systems that exhibit the highest sensitivity coefficients are not necessarily systems that can be measured to high accuracy, as there are only very few highly sensitive transitions. Therefore, one will have to use a more complex system to measure, and use a more complex experimental setup.

Whereas in atoms near degeneracies are accidental and very rare, in molecules in states with S > 0 near degeneracies have a high probability of occurring. These states have multiple Ω manifolds, and the lowest rotational levels of each manifold are offset by the fine structure constant, A, and the rotational levels within a manifold are spaced by BJ(J+1), with B the rotational constant and J the rotational quantum number. As A depends only on α , and B depends only on μ , a change in one of these two constants will move the rotational ladders with respect to each other, theoretically leading to a rotational level in one manifold crossing a rotational level in another for the right values of Aand B. A near degeneracy between two levels with $\Delta J = 0$ will never lead to an increased sensitivity due to mixing of the Ω manifolds. A near degeneracy between two levels with $\Delta J = 1$ can happen in the case of a molecule with A = 4B, e.g. CD, but in this case the strength of this transition will unfortunately be zero, as will be shown in Chapter 6. For molecules where $A \neq 4B$. mixing of the different Ω manifolds prevents rotational levels with $\Delta J = 1$ from crossing. As there is no coupling between rotational levels in different Ω manifolds with $\Delta J = 2$, they can cross and thus become nearly degenerate. To first order, the sensitivity coefficient of a transition between these levels will be given by $K_X = E_c/\nu$, where ν is the energy difference between the two nearly degenerate levels, and E_c is the energy difference that is "canceled", i.e. the part of the energy of the two levels that has a different dependence on the fundamental constant under consideration. Here, it is equal to the energy of the fine-structure splitting, A.

In the above case, the near degeneracy is the result of a cancellation of spin-orbit and rotational energies. Cancellations between many other types of energy also occur in molecules, for example between vibrational and electronic energy [36] or between hyperfine and rotational energy [37]. An enhanced sensitivity coefficient can also be the result of a tunneling motion, as for example in ammonia [16]. This can be understood from the fact that the tunneling probability is heavily dependent on the mass that tunnels. The effects from a tunneling motion and a cancellation of different types of energy are combined in for example methanol, leading to sensitivity coefficients ranging from -40 to +50 [8].

1.5 Metastable CO as a probe for a variation of μ

Here, we will present an experiment in CO $a^3\Pi$ to test a possible time-variation of μ . Metastable CO has a number of features that make it uniquely suitable for precision measurements; (i) Producing an intense supersonic beam of CO is straightforward, and as the ground state is a ${}^{1}\Sigma$ state there will be very few clusters. (ii) Ground state molecules can be directly laser excited to the metastable $a^{3}\Pi$ state [38], using a narrow-band pulsed UV laser system, pro-



Figure 1.1: The J = 8, $\Omega = 0$ and J = 6, $\Omega = 1$ rotational levels of the CO $a^{3}\Pi$ state in the ${}^{12}C^{16}O$ and ${}^{13}C^{16}O$ isotopologues. The hyperfine splitting in ${}^{13}C^{16}O$ is neglected for clarity.

ducing a pure quantum state. (iii) Due to the long lifetime of 2.6 ms [39], transitions in this state have a low natural linewidth, on the order of a kilohertz. (iv) Excitation of the CO molecules with a pulsed nanosecond laser produces a well-defined packet of metastable molecules, both in time and in space, enabling a very precise determination of the molecular velocity. (v) Due to the high internal energy, 6 eV, of the metastable molecules, 2D detection can be performed using a multi-channel plate (MCP), a phosphor screen and a digital camera [40]. By gating the voltage on the MCP background from stray electrons and ions in the vacuum can be eliminated. (vi) Due to their high electric dipole moment, metastable CO molecules can be easily manipulated using electric fields, as for example used in the first Stark deceleration experiment [41]. (vii) ${}^{12}C^{16}O$ has no hyperfine structure.

Bethlem and Ubachs [9] studied the type of near degeneracy discussed in Sec. 1.4 for different molecules. It was found that the J = 8, $\Omega = 0$, the J = 6, $\Omega = 1$ and the J = 4, $\Omega = 2$ rotational levels of the $a^3\Pi$ state of CO are nearly degenerate, with the J = 8, $\Omega = 0$, +, the J = 6, $\Omega = 1$, + levels lying only 3.3 GHz apart, a factor 10^3 smaller separation than between consecutive rotational levels within one Ω manifold around this J value. These two rotational levels are shown in the left-hand panel of Fig. 1.1. This leads to a sensitivity coefficient of $K_{\mu} \approx A/\nu = 1243/-3.3 = -377$, in good agreement with the more accurate calculations in Chapter 2, where it is found that $K_{\mu} =$ -334, with the difference being due to mixing of the two Ω manifolds. As the J = 6, $\Omega = 1$ level is moving up with respect to the J = 8, $\Omega = 0$ level, the transition frequency decreases when μ increases, leading to a negative sensitivity coefficient.

As the reduced mass of ${}^{13}C^{16}O$ is ~5% larger than the reduced mass of ${}^{12}C^{16}O$, its rotational constant is ~5% smaller. This leads to a large shift of the nearly degenerate levels with respect to each other. This can be seen in the right-hand panel of Fig. 1.1 where the two nearly degenerate rotational levels in ${}^{13}C^{16}O$ are shown. Here, we see that the J = 8, $\Omega = 0$, - and J = 6, $\Omega = 1$, - levels are nearly degenerate. Here, the hyperfine splitting is neglected, the full calculation is given in Chapter 2. The ordering of the two rotational levels is inverted, leading to a positive sensitivity coefficient of $K_{\mu} = +128$. By studying both transitions in the same setup, common-mode effects can be studied and systematic shifts can be excluded. Instead of measuring in a different isotopologue, another vibrational level can be used. The J = 8, $\Omega = 0$, $+ \rightarrow J = 6$, $\Omega = 1$, + transition in the v = 1 level of ${}^{12}C^{16}O$ has a sensitivity coefficient of $K_{\mu} = 202$ [9].

1.6 Outline of this thesis

This thesis will present the progress towards setting a constraint on the possible time-variation of the proton-to-electron mass ratio using a measurement of a two-photon microwave transition in the $a^3\Pi$ state of CO. This transition between two nearly-degenerate rotational levels is highly sensitive to such a variation. In the planned experiment, a beam of metastable CO is prepared in a pure quantum state by expanding CO into vacuum and exciting the molecules using a narrow-band UV laser system. After passing two resonant microwave cavities that are separated by 50 cm, the molecules are state-selectively deflected and detected 1 meter downstream on a position sensitive detector.

In Chapter 2, to show that we have good control over the production of metastable CO, the $a^3\Pi$ state of CO is characterized by high-accuracy UV spectroscopy. We determined the frequency of the two-photon microwave transition with an accuracy of 0.5 MHz, reducing it's uncertainty by well over an order of magnitude. Furthermore, mass-scaling relations were used to calculate the sensitivity coefficients of a number of transitions between nearly-degenerate levels in different isotopologues. In Chapter 3, cavity ring-down spectroscopy is performed on the $a^3\Pi$ state of two isotopologues of CO, and it is found that the mass-scaling rules for the $a^3\Pi$ state can be used to predict the transition frequencies from v = 0, J < 8 in ¹²C¹⁶O to v = 1, J < 30 rovibrational levels in both ${}^{12}C^{18}O$ and ${}^{13}C^{16}O$ to within the experimental accuracy of 0.2 cm⁻¹. The design of the electro-static deflection field that is used to state-selectively deflect molecules in the microwave measurements is discussed in Chapter 4. Here, the theoretical description used for the design of the deflection field is also used to study two types of storage rings for molecules in high-field seeking states. In Chapter 5 we show that high precision microwave spectroscopy can be performed on CO $(a^3\Pi)$ in the planned setup. We measured the $\Omega = 1, J = 1$

lambda-doublet splitting around 394 MHz to an accuracy of 10 Hz, and discuss systematic effects that influence the result.

In Chapter 6 the sensitivity to a variation of α and μ is calculated for rotational transitions in the ground states of CH and CD molecules. It is shown that rotational levels with $\Delta J = 1$ in different Ω manifolds can become nearly degenerate, but the strength of transitions between the two levels converges to zero. This makes these near-degeneracies less interesting for the search for a variation of fundamental constants, leading to the conclusion that a two-photon transition is the best candidate.

In Chapter 7, an outlook towards measuring the highly sensitive two-photon microwave transition is given. A setup very similar to the molecular beam setup used in the one-photon microwave measurement is being planned, changes that need to be made to the setup are discussed in this chapter. As the highly sensitive transition is a two-photon transition, it requires a more intense microwave field. The transition strength is calculated, and a resonant microwave cavity is designed and tested. Also, a higher rotational level needs to be excited by the UV laser, resulting in a higher number of m_J^B sublevels, a smaller deflection and a lower population, the consequences of which are also discussed.

Chapter 2

UV frequency metrology on CO $(a^3\Pi)$

Abstract

UV frequency metrology has been performed on the $a^3\Pi$ - $X^1\Sigma^+$ (0,0) band of various isotopologues of CO using a frequency-quadrupled injection-seeded narrow-band pulsed Titanium:Sapphire laser referenced to a frequency comb laser. The band origin is determined with an accuracy of 5 MHz ($\delta \nu / \nu = 3 \cdot 10^{-9}$), while the energy differences between rotational levels in the $a^3\Pi$ state are determined with an accuracy of 500 kHz. From these measurements, in combination with previously published radiofrequency and microwave data, a set of molecular constants is obtained that describes the level structure of the $a^3\Pi$ state of ${}^{12}C^{16}O$ and ${}^{13}C^{16}O$ with improved accuracy. Transitions in the different isotopologues are well reproduced by scaling the molecular constants of ¹²C¹⁶O via the common mass-scaling rules. Only the value of the band origin could not be scaled, indicative of a breakdown of the Born-Oppenheimer approximation. Our analysis confirms the extreme sensitivity of two-photon microwave transitions between nearly-degenerate rotational levels of different Ω -manifolds for probing a possible variation of the proton-to-electron mass ratio, $\mu = m_p/m_e$, on a laboratory time scale.

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2.1 Introduction

The $a^3\Pi$ state of CO is one of the most extensively studied triplet states of any molecule. The transitions connecting the $a^3\Pi$ state to the $X^{1}\Sigma^{+}$ ground state were first observed by Cameron in 1926 [42]. Later, the $a^3\Pi$ state of the ${}^{12}C^{16}O$ isotopologue was studied using radio-frequency (rf) [43, 44], microwave (mw) [45–47], infrared [48, 49], optical [50] and UV spectroscopy [51]. The ${}^{13}C^{16}O$ isotopologue was studied using rf [52] and mw [45] spectroscopy. Recently, Bethlem and Ubachs [9] identified metastable CO as a probe for detecting a temporal variation of the proton-to-electron mass ratio, $\mu = m_p/m_e$, on a laboratory time scale. Two-photon microwave transitions between nearly-degenerate rotational levels in different Π_{Ω} spin-orbit manifolds were shown to be very sensitive to a possible variation of μ . As a measure of the inherent sensitivity of a transition to a drifting μ , the sensitivity coefficient, K_{μ} , is defined via:

$$\frac{\Delta\nu}{\nu} = K_{\mu} \frac{\Delta\mu}{\mu}.$$
(2.1)

Transitions between the J = 8, $\Omega = 0$, the J = 6, $\Omega = 1$ and the J = 4, $\Omega = 2$ levels display sensitivities ranging from $K_{\mu} = -300$ to +200 [9]. For an overview on the topic of varying physical constants, we refer the reader to [3] and [13].

In this paper, we present high-precision UV measurements of the $a^{3}\Pi$ - $X^{1}\Sigma^{+}$ (0,0) band in CO. In total 38 transitions in all six naturally occurring isotopes have been measured with MHz accuracy. All three Ω -manifolds have been probed, with J up to eight. A comprehensive fit of the optical data combined with previously published rf [44] and mw [46, 47] measurements was performed. The molecular constants found for ${}^{12}C^{16}O$ are mass scaled and compared with the measured transitions in other isotopologues.

2.2 Level structure of CO

The $a^3\Pi$ state is the first electronically excited state of CO, lying 6 eV above the $X^1\Sigma^+$ ground state. CO in the $a^3\Pi$ state has two unpaired electrons, leading to a nonzero electronic spin, \vec{S} , and orbital angular momentum \vec{L} . For low rotational levels, the $a^3\Pi$ state is best described in a Hund's case (a) coupling scheme, with the good quantum numbers Λ and Σ , the projection of \vec{L} and \vec{S} on the molecular axis, respectively. The projections of the total angular momentum \vec{J} on the molecular axis and on the space-fixed axis lead to the good quantum numbers Ω and M. The basis functions are $|n\Lambda\rangle|v\rangle|S\Sigma\rangle|J\Omega M\rangle$, representing the electronic orbital, vibrational, electronic spin and rotational components of the wave function, respectively. For higher rotational levels, the spin decouples from the electronic angular momentum and a Hund's case (b) coupling scheme becomes more appropriate. In Hund's case (b), the different Ω -manifolds are mixed.

The energies of the lower rotational levels of the $a^3\Pi$ and $X^1\Sigma^+$ states are shown in Fig. 2.1, together with selected transitions. The transitions are denoted by $\Delta J_{\Omega+1}(J^{"})$, where transitions with $\Delta J = -1, 0$ and 1 are denoted by P, Q and R, respectively. As the parity changes in a one-photon transition, the upper lambda-doublet component of rotational levels in the $a^3\Pi$ can only be reached via Q transitions, whereas the lower lambda-doublet components can only be reached via P or R transitions. The separation of the electronic motion and nuclear motion is not exact, leading to a splitting into lambda-doublet states of opposite parity, as indicated, not to scale, in Fig. 2.1. The lambda doubling in the $\Omega = 0$ state is large and relatively independent of J. The lambda doubling in the $\Omega = 1$ and $\Omega = 2$ manifolds is much smaller. In Fig. 2.1 the total parity, *i.e.*, the product of the symmetries of the rotational and electronic parts of the wavefunction, is indicated by the - and + signs. The electronic part of the wave function of the upper (lower) lambda-doublet levels has f(e) symmetry.

The spin-forbidden $a^3\Pi - X^1\Sigma^+$ system becomes weakly allowed due to spin-orbit mixing of singlet electronic character into $a^3\Pi$, most significantly of the $A^1\Pi$ state lying 2 eV above the $a^3\Pi$ state. As the $A^1\Pi$ state consists of a single, $\Omega = 1$, manifold, it only couples to the $\Omega = 1$ levels in $a^3\Pi$. Transitions to the $\Omega = 0, J > 0$ and $\Omega = 2$ manifolds become weakly allowed by mixing of the different Ω -manifolds. The $\Omega = 0, J = 0$ level is not mixed with the other Ω -manifolds, hence, the transition to this level, *i.e.* the $P_1(1)$, does not obtain transition strength via coupling to the $A^1\Pi$ state.

The $a^3\Pi$ (v = 0) state can only decay to the ground state, hence, the radiative lifetimes of the different rotational are inversely proportional to the transition strengths. The lifetimes are thus strongly dependent on J and Ω . For example the J = 2, $\Omega = 2$ level has a lifetime of 140 ms, whereas the J = 1, $\Omega = 1$ level has a lifetime of 2.6 ms [39].

Isotopes with an odd number of nucleons have a non-zero nuclear spin that leads to hyperfine structure. The two relevant odd-nucleon-number nuclei are ¹³C and ¹⁷O, with nuclear spin I = 1/2 and I = 5/2, respectively. Due to its zero electronic angular and spin momentum the hyperfine splitting in the ground-state of CO is small (≈ 50 kHz) [53]. The hyperfine splittings in the $a^{3}\Pi$ state vary between 30 and 500 MHz for the measured transitions.

2.3 Experimental setup

The molecular beam setup used for frequency metrology on CO is schematically depicted in Fig. 2.2. A pulsed beam of CO is produced by expanding CO gas into vacuum, using a solenoid valve (General Valve series 9). A backing pressure of 2 bar was used for recording transitions at low J, while for recording transitions at higher J, the backing pressure was reduced to 0.5 bar. For recording transitions in ¹³C¹⁶O, isotopically enriched CO (Linde Gas) was used. The enriched sample also contained slightly enhanced fractions of ¹³C¹⁸O and ¹³C¹⁷O, sufficient for obtaining signals. Spectra of ¹²C¹⁷O and ¹²C¹⁸O were measured using a natural CO sample.

After passing through a 1-mm skimmer, the molecular beam is crossed at right angles with laser radiation tunable near 206 nm. In the interaction region, a magnetic field of up to 200 Gauss can be applied by two coils in Helmholtz configuration. After being excited to the $a^3\Pi$ state, the molecules fly 60 cm downstream before being detected by an electron multiplier tube (EMT). The



Figure 2.1: Energy level diagram of the $X^1\Sigma^+$ (v = 0) ground state and the $a^3\Pi$ (v = 0) state of ${}^{12}C^{16}O$. Rotational quantum numbers and total parity are listed for each level. For the $a^3\Pi$ state, the value of the band origin, E_{Π} , is subtracted from the energy scale. The $a^3\Pi$ state has three Ω -manifolds, arising from spin-orbit coupling, and shows lambda-type doubling, as illustrated, not to scale. A number of transitions are indicated by the vertical arrows.



Figure 2.2: A schematic drawing of the experimental setup. A pulsed beam of CO is produced by expanding CO gas into vacuum, using a solenoid valve. After passing through a 1 mm skimmer, the molecular beam is crossed at right angles with laser radiation at 206 nm. After being excited to the $a^3\Pi$ state, the molecules fly 60 cm downstream before hitting an electron multiplier tube, where they are detected. The laser interaction region is built in a Sagnac interferometer to correct for Doppler shifts.

resulting signal is recorded using a digital oscilloscope and the integrated signal is stored. The absolute detection efficiency of this method for metastable CO (6 eV internal energy) is estimated to be on the order of 10^{-3} [54]. Note that the time of flight (750 μ s) is short compared to the lifetime of the metastable state (>2.6 ms). An adjustable slit is mounted in front of the EMT to limit the divergence of the beam that reaches the detector, thereby limiting the Doppler width of the recorded transitions.

The spectroscopic measurements are performed with a narrow-band frequency quadrupled titanium:sapphire (Ti:sapphire) pulsed laser described in detail by Hannemann *et al.* [55, 56]. A schematic drawing of the laser setup is shown in Fig. 2.3. A continuous wave (cw) Ti:sapphire ring laser (Coherent 899) produces around 700 mW of laser power tunable near 824 nm. Its



Figure 2.3: A schematic drawing of the laser system. A ring laser is used to injection seed an oscillator cavity, which is pumped by a Nd:YAG laser at 10 Hz. The produced IR pulses are amplified in a multipass amplifier and subsequently quadrupled in two consecutive BBO crystals. The absolute frequency of the cw seed laser is determined using a fiber comb laser. OI, optical isolator; GP, glass plate; OC, output coupler; HR, high reflective mirror; PA, piezoactuator; HC lock, Hänsch-Couillaud lock; SMF, single-mode fiber; AOM, acousto-optical modulator.

output is split into three parts, with all parts having approximately the same power. One part of the light is sent as a seed frequency to a pulsed Ti:sapphire ring oscillator that is pumped at 10 Hz with 50 mJ of pulsed 532 nm light from an injection seeded Nd:YAG laser (Spectra Physics LAB-170). The oscillator is locked to the cw seed light using a Hänsch-Couillaud scheme. The pulsed IR light emanating from the oscillator is amplified in a bow-tie multipass Ti:sapphire amplifier pumped with 300 mJ of pulsed 532 nm light from the same Nd:YAG laser that pumps the oscillator. After nine passes the laser power of the IR-beam is around 70 mJ in a 100 ns pulse. These pulses are then frequency doubled twice in two consecutive BBO crystals, resulting in pulses of 20 μ J at 206 nm.

In order to determine the absolute frequency of the cw Ti:sapphire ring laser, the cw light is mixed with the light from an erbium-doped fiber frequencycomb laser (Menlo systems MComb at 250 MHz repetition frequency) that is locked to a global positioning system (GPS) disciplined Rb-clock standard. The optical interference beat signal is measured with a photodiode and an Agilent 53132A counter. The obtained beat frequency is then transferred via ethernet to the central computer at which the data are analyzed. Further details on the absolute frequency calibration can be found in Sec. 2.5.4.

By making a small portion of the pulsed light interfere with part of the cw light, possible small differences between the frequencies of the cw seed laser and the central frequency of the pulsed output of the bow-tie amplifier are measured and corrected for [55]. In order to have a good fringe visibility, and to ascertain that the full wavefront of the pulsed output is mapped onto the cw reference beam, both beams are sent through a short single-mode fiber. The beat pattern is detected using a fast photodiode in combination with an oscilloscope and analyzed online.

The UV laser beam is split into two parts and sent through the molecular beam machine from opposite sides to limit the Doppler shift due to a possible imperfect perpendicular alignment of the laser beam. In order to ensure that the two beams are perfectly counterpropagating, the two laser beams are recombined after passing through the machine, forming a Sagnac interferometer. The paths through the molecular beam machine are aligned such that the two beams interfere destructively at the exit port (a dark fringe). The transition frequency is measured twice, using either the laser beam from the left- or right-hand side [57].

2.4 Experimental results

Isotopologue	Transition	Observed (MHz)	Residuals	Residuals
			fitted	scaled
$^{12}\mathrm{C}^{16}\mathrm{O}$	$R_1(0)$	$1452\ 065\ 305.5$	0.4	—
	$P_1(1)$	$1451 \ 857 \ 145.0$	0.9	

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Isotopologue	Transition	Observed (MHz)	Residuals	Residuals
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				fitted	scaled
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		$Q_1(1)$	$1452\ 002\ 039.3$	1.3	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$R_{1}(7)$	$1452\ 112\ 469.1$	2.1	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		$Q_1(8)$	$1451\ 232\ 745.8$	2.4	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		$R_{2}(0)$	$1453\ 348\ 525.5$	1.1	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		$Q_2(1)$	$1453\ 233\ 648.6$	1.2	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		$R_{2}(5)$	$1453\ 607\ 338.8$	-4.8	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		$Q_2(6)$	$1452 \ 922 \ 384.0$	-6.6	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		$P_{2}(7)$	$1452\ 109\ 212.5$	-6.2	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		$R_{3}(1)$	$1454\ 488\ 881.8$	1.8	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		$Q_{3}(2)$	$1454\ 258\ 350.7$	1.4	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		$R_{3}(3)$	$1454\ 683\ 187.7$	2.2	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		$Q_{3}(4)$	$1454\ 222\ 240.4$	2.7	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$^{12}\mathrm{C}^{18}\mathrm{O}$	$R_2(0)$	$1453 \ 498 \ 161.1$		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$^{13}\mathrm{C}^{16}\mathrm{O}$	$R_1(2)$	$1452 \ 325 \ 025.5$	-0.2	0.2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			$1452 \ 325 \ 217.9$	-0.3	0.7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$R_{1}(7)$	$1452\ 263\ 496.1$	-1.6	-13.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		- ()	$1452\ 263\ 906.8$	2.3	-8.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$Q_1(8)$	$1451 \ 425 \ 012.3$	-0.3	-9.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			$1451 \ 425 \ 321.6$	0.5	-10.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$R_{2}(0)$	$1453 \ 491 \ 411.3$	0.8	3.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		- ()	$1453 \ 491 \ 449.2$	1.8	4.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$Q_{2}(1)$	$1453 \ 381 \ 555.9$	0.4	2.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			$1453 \ 381 \ 613.6$	-0.2	2.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$R_{2}(1)$	1453 570 841.9	-0.5	3.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		- ()	$1453\ 570\ 876.4$	-0.6	3.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$R_{2}(5)$	$1453\ 740\ 818.2$	0.7	5.2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		- ()	$1453\ 740\ 854.3$	-0.9	2.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$Q_{2}(6)$	$1453\ 085\ 785.3$	-0.6	0.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			$1453\ 085\ 898.7$	-0.6	0.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$P_{2}(7)$	$1452 \ 308 \ 565.9$	-0.3	4.2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		- ()	$1452 \ 308 \ 602.9$	-0.9	2.8
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		$R_{3}(1)$	$1454 \ 635 \ 451.9$	-1.2	-3.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			$1454 \ 636 \ 019.2$	-1.0	-2.7
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		$R_{3}(3)$	$1454 \ 818 \ 557.3$	0.9	2.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			$1454 \ 818 \ 676.7$	0.8	2.6
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		$Q_{3}(4)$	1454 377 868.2	0.8	2.6
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			$1454 \ 377 \ 989.2$	0.1	2.0
1453 426 924 0	${}^{12}C^{17}O$	$R_2(0)$	$1453\ 426\ 677.0$		
1400 420 024.0			$1453\ 426\ 924.0$		
$1453\ 427\ 108.2$ — —			$1453\ 427\ 108.2$		
$R_{2}(0) = 1453\ 571\ 485.7$	$^{13}C^{17}O$	$R_2(0)$	1453 571 485 7		

Isotopologue	Transition	Observed (MHz)	Residuals	Residuals
			fitted	scaled
		$1453 \ 571 \ 732.5$		
		$1453 \ 571 \ 918.5$		
$^{13}C^{18}O$	$Q_1(3)$	1452 210 864.9		-12.3
		$1452\ 211\ 002.6$		-12.4
	$R_{2}(0)$	$1453\ 643\ 585.2$		-1.7
		$1453\ 643\ 626.6$		-1.4
	$Q_2(1)$	$1453 \ 539 \ 184.1$		-4.4
		$1453 \ 539 \ 244.9$		-4.6
	$R_{2}(5)$	$1453\ 882\ 578.9$		15.9
		$1453\ 882\ 612.1$		13.8
	$Q_2(6)$	$1453 \ 259 \ 995.8$		7.6
		$1453\ 260\ 099.7$		4.4
	$R_{3}(3)$	$1454 \ 963 \ 029.8$		-0.5
		$1454 \ 963 \ 165.2$		1.7
	$Q_{3}(4)$	$1454\ 544\ 280.2$		-2.6
	/	1454 544 414.5		-3.4

Table 2.1: Measured transition frequencies for various isotopologues of CO. The rightmost two columns are the residuals from the fit and the mass-scaling procedure discussed in Sec. 2.6.

In Table 2.1 the frequencies are listed for the measured transitions in the $a^3\Pi - X^1\Sigma^+$ (0,0) band. In view of the time-consuming measurement procedure, only a selection of transitions has been investigated. In total, 38 transitions have been recorded in all six stable isotopologues of CO. In ${}^{12}C^{16}O$, ${}^{13}C^{16}O$ and ${}^{13}C^{18}O$, we have recorded low J transitions to each Ω manifold and each parity level, to be able to give a full analysis of the level structure. In addition, transitions to the J = 8, $\Omega = 0$, J = 6, $\Omega = 1$ and J = 4, $\Omega = 2$, the near degenerate levels of interest to the search for μ variation, were measured. Furthermore, the $R_2(0)$ transition, the most intense line under our conditions, has been measured in the ${}^{12}C^{17}O$, ${}^{12}C^{18}O$ and ${}^{13}C^{17}O$ isotopologues. Note that the observed signal strengths for the different transitions varies over more than three orders in magnitude.

In Fig. 2.4 a typical recording of the $R_2(0)$ transition in ${}^{12}C^{16}O$ is shown. The upper and lower graph show the spectra obtained with the laser beam propagating through either path of the Sagnac interferometer. For each pulse of the pulsed laser, the frequency of the cw laser is determined using the fiber comb laser and a possible shift between the pulsed laser and the cw laser is determined using the online cw-pulse offset detection. Subsequently, these data are combined with the metastable CO signal from the EMT. Typically, the recorded scans are not perfectly linear, resulting in an uneven distribution of the data points along the frequency-axis. This has no influence on the peak



Figure 2.4: Recordings of the $R_2(0)$ transition in ${}^{12}C^{16}O$ measured using the laser beam propagating from the right-hand side (upper panel) and the left-hand side (lower panel). The frequency of the seed laser is scanned while the signal from the EMT is recorded. Each point represents a single laser pulse. For each pulse the beat frequency of both the fiber comb and the cw-pulse offset measurement setup are recorded. A single scan takes around 20 min.

determination. At the peak of the transition, the observed signal corresponds to typically a few thousand detected metastable CO molecules per laser pulse. Note that the fluctuations in the signal shown in Fig. 2.4 are due to pulseto-pulse variations of the molecular beam and the UV power and not due to counting (Poisson) statistics. The solid lines in the figure show a Gaussian fit to the spectra. The transition frequency of the $R_2(0)$ transition is determined by taking the average of the measurements taken with the laser beam propagating from either side.

Transitions to the six near-degenerate levels in both ${}^{12}C^{16}O$ and ${}^{13}C^{16}O$ were measured. For ${}^{13}C^{18}O$ transitions to four of the six near-degenerate levels were obtained. In Fig. 2.5 a recording of the $P_2(7)$ and $R_1(7)$ transitions in ${}^{12}C^{16}O$ is shown. Both transitions originate from the J = 7 ground state level,



Figure 2.5: Recording of the $P_2(7)$ transition and the $R_1(7)$ transition in ${}^{12}C{}^{16}O$. Both transitions originate from the same ground-state level and connect to one of two nearly degenerate levels. Therefore, the combination difference of these two transition frequencies corresponds to the frequency of the transition between the two nearly degenerate levels.

thus the combination difference is equal to the frequency of the $J = 6, \Omega = 1, + \rightarrow J = 8, \Omega = 0, +$ transition, which is measured to be 3256.6 MHz.

As the transition strengths of transitions in the spin forbidden $a^3\Pi - X^1\Sigma^+$ system originate from mixing of $a^3\Pi \ \Omega = 1$ with $A^1\Pi$ [39], the transition strengths of the different transitions are proportional to (the square of) the $\Omega = 1$ character of the final rotational level and the Hönl-London factor. From this, we expect the $P_2(7)$ to be 3.2 times more intense than the $R_1(7)$. Experimentally, we find a ratio of 2.4:1. The deviation is explained by the fact that the J = 8, $\Omega = 0$ has a longer lifetime than the J = 6, $\Omega = 1$ (15.7 ms vs. 3.5 ms), and consequently, a smaller fraction of the metastable molecules decays back to the ground state before reaching the EMT. Taking the lifetime into account, we expect a ratio of 2.7:1, in reasonable agreement with the experiment.

The J = 0, $\Omega = 0$ is the only J = 0 level, and is therefore not mixed with



Figure 2.6: A recording of the $P_1(1)$ transition in ${}^{12}C^{16}O$. If only the coupling to the $A^1\Pi$ state is considered, this transition has zero transition strength.

the $\Omega = 1$ and $\Omega = 2$ manifolds. Consequently, the $P_1(1)$ transition, connecting the $X^1\Sigma^+$ J = 1 with the $a^3\Pi$ $\Omega = 0, J = 0, +$ parity level does not obtain any transition strength from coupling to the $A^1\Pi$ state. Nevertheless, we were able to observe this transition, shown in Fig. 2.6, albeit with low signal to noise. From our measurements, we estimate that the $P_1(1)$ transition is about 65 times weaker than $Q_1(1)$ and about 10⁴ times weaker than $Q_2(1)$, resulting in a lifetime of 8(1) s [58]. The transition strength is ascribed to mixing of the $a^3\Pi$ state with a ${}^{1}\Sigma^{+}$ state, most likely the $X^{1}\Sigma^{+}$ ground state [59].

The rotational levels of isotopologues with one or two odd-numbered nuclei show hyperfine splitting. In Fig. 2.7 a recorded spectrum of the $Q_2(1)$ transition in ¹³C¹⁶O is shown. The transitions to the hyperfine sublevels F = J - I = 1/2and F = J + I = 3/2 of the excited state are clearly resolved.

2.5 Measurement uncertainties

In this paragraph the main sources of uncertainty in the transition frequencies are discussed. The uncertainty budget is summarized in Table 2.2.



Figure 2.7: A recording of the $Q_2(1)$ transition in ¹³C¹⁶O. The labels indicate the value of the total angular momentum $\vec{F} = \vec{J} + \vec{I}$ in the excited state.

2.5.1 Zeeman effect

The ground state of CO is a ${}^{1}\Sigma$ state, hence, its Zeeman shift is small. The $a^{3}\Pi$ state on the other hand has both electronic angular momentum and spin, and experiences a considerable Zeeman shift. In the $\Omega = 2$ state the effect due to the electronic angular momentum and due to spin will add up, whereas in the $\Omega = 0$ and $\Omega = 1$ state these effects will partly cancel. Hence, we expect the largest Zeeman shift to occur in the $\Omega = 2$ levels, in particular in the $J = 2, \Omega = 2$ level.

In Fig. 2.8 the recorded spectra are shown for the $R_1(1)$, $R_2(1)$ and $R_3(1)$ transitions in ¹²C¹⁶O in a magnetic field of 170 Gauss. In these measurements, the polarization of the 206-nm light is parallel to the applied magnetic field, hence, only $\Delta m_J = 0$ transitions are allowed. As all three measured transitions originate from the $X^1\Sigma^+$ J = 1 level only the $m_J = \pm 1, 0$ sublevels of the probed $a^3\Pi$ levels are observed. The Zeeman shift of the J = 2, $\Omega = 2$, $m_J = 1$ sublevel is 1.2 MHz/Gauss, while the shifts of the J = 2, $\Omega = 1$, $m_J = 1$ and J = 2, $\Omega = 0$, $m_J = 1$ sublevels are about 5 times smaller. It is observed that



Figure 2.8: The $R_1(1)$, $R_2(1)$ and $R_3(1)$ transitions in ${}^{12}C^{16}O$ measured in an applied magnetic field of 170 Gauss, showing Zeeman splitting.

the transitions to the $m_J = -1$ and $m_J = 1$ sublevels are approximately equally strong, implying that the polarization of the 206 nm is highly linear, estimated to be better than 95%, as expected from light that has been quadrupled in non-linear crystals. In the earth magnetic field, approximately 0.5 Gauss, the $J = 2, \Omega = 1, m_J = -2$ and $m_J = 2$ sublevels will be shifted in opposite directions by less than 1 MHz. As the polarization is nearly perfect, the shift of the line center is estimated to be less than 1 kHz.

2.5.2 Stark effect

The Stark shift in the ground state of CO is negligibly small as the dipole moment is only 0.1 Debye (corresponding to $0.17 \cdot 10^{-2} \text{cm}^{-1}/(\text{kV/cm})$) and mixing occurs between rotational levels. The Stark shift in the $a^3\Pi$ state on the other hand is larger as the dipole moment is 1.37 Debye and mixing occurs between the lambda-doublet components [40]. We estimate that the electric field in the excitation region is below 1 V/cm. This corresponds to a Stark shift of 30 kHz for the J = 2, $\Omega = 2$, $M\Omega = 4$ and less for all other levels.

2.5.3 AC-Stark effect

A priori, the AC-Stark shift is difficult to estimate. We have measured the $R_2(0)$ transition in ${}^{12}C^{16}O$ for different laser powers, reducing the laser power by over an order of magnitude, but found no significant dependence of the transition frequency on laser power. Thus, we estimate the AC-Stark shift to be less than 100 kHz.

2.5.4 Uncertainty in absolute frequency determination

The absolute frequency of the cw light is calibrated by mixing this light with the output of a frequency-comb laser and counting the resulting beat frequency f_{beat} . The frequency f_{cw} is then obtained by the relation,

$$f_{\rm wc} = n \cdot f_{\rm rep} + f_0 + f_{\rm beat}, \qquad (2.2)$$

with n the mode number of the frequency comb that is nearest to the frequency of the wc light, and $f_{\rm rep}$ and f_0 the repetition and the carrier-envelope offset frequencies of the frequency comb, respectively. $f_{\rm rep}$ is tunable over a small range around 250 MHz and f_0 is locked at 40 MHz. We infer that the sign of $f_{\rm beat}$ is positive from the observation that $f_{\rm beat}$ increases when the cw laser is scanned toward higher frequency. Likewise, the sign of f_0 is positive from the observation that $f_{\rm beat}$ increases when f_0 is decreased. The beat note is averaged over a period of 100 ms. On this time scale, the accuracy of the Rbclock standard is 10^{-10} , equivalent to 150 kHz at the used frequencies. This uncertainty enters separately in each data point taken in a frequency scan. As each scan is approximately 1000 data points, this uncertainty averages out.

The integer mode number n is determined by measuring the transition frequency of the $R_2(0)$ transition in ${}^{12}C^{16}O$ using the frequency comb at different repetition frequencies and then determining at which transition frequency these three measurements coincide. This method gives an unambiguous transition frequency provided that the change in repetition frequency is much larger than the measurement uncertainty [60]. In our case this condition is well met as the uncertainty between two consecutive measurements is on the order of 500 kHz, while the repetition frequency of the comb is varied by 2 MHz. The absolute value obtained for the $R_2(0)$ transition of ${}^{12}C^{16}O$ is used to calibrate a wavelength meter (Burleigh WA-1500, 30 MHz precision) on a daily basis. This wavelength meter is then used to determine the mode number for the measurements of the other transitions.

2.5.5 Doppler effect

In a molecular beam experiment, the first-order Doppler effect is reduced by aligning the laser-beam perpendicular to the molecular beam. Two residual effects remain: (i) The finite transverse temperature of the molecular beam



Figure 2.9: The $Q_2(1)$ transition measured using slit widths of 10 and 3 mm. When the width of the slit is decreased the transition becomes narrower, down to 23 MHz for a slit width of 3 mm. The 23-MHz spectral width is attributed to the linewidth of the UV laser.

leads to a broadening of the transition; (ii) a possible imperfect perpendicular alignment of the laser beam leads to a shift of the center frequency.

To limit the Doppler width, we have placed a variable slit in front of the EMT, which limits the divergence of the beam hitting the detector. In Fig. 2.9 recordings of the $Q_2(1)$ transition of ${}^{12}C^{16}O$ using a slit width of 10 mm and 3 mm are shown. When the slit width is reduced below 3 mm the width of the transition remains the same while the signal decreases further. The minimum full width at half maximum (FWHM) observed is 23 MHz, which is attributed to the linewidth of the UV radiation. In our measurements, we have used a slit width of 6 mm, as a compromise between signal intensity and linewidth.

In order to eliminate the Doppler shift in the measurement, the UV laser beam is aligned in the geometry of a Sagnac interferometer. The angle between the two counterpropagating laser beams may be estimated to be smaller than λ/d , with λ being the wavelength of the light in nm and d being the diameter of the laser beam in mm [57]. In our case this results in a maximum Doppler shift of 200 kHz. We have verified this by comparing measurements of the $R_2(0)$ transition of ${}^{12}C^{16}O$ in a pure beam of CO (velocity of 800 m/s) and a beam of 5% CO seeded in He (longitudinal velocity of 1500 m/s). The second-order Doppler shift is sub-kHz. The recoil shift is ≈ 25 kHz.

2.5.6 Uncertainty in peak determination

The number of metastable molecules detected (at the peak of) the $R_2(0)$ transition of ${}^{12}C^{16}O$, the strongest transition observed, is on the order of 10^4 per laser pulse, while at the $P_1(1)$ transition of ${}^{12}C^{16}O$, the weakest transition observed, it is only a few molecules per laser pulse. The ability to determine the line center from the measurement is limited by pulse-to-pulse variations of the molecular beam and the UV power. Typically, the uncertainty in the peak determination is 300 kHz (corresponding to 1% of the line-width).

2.5.7 Frequency chirp in the pulsed laser system

The frequency of the pulsed IR light differs slightly from the frequency of the cw seed laser mainly due to two effects: (i) Mode pulling in the oscillator and (ii) frequency chirp and shift in the amplifier. The pump laser induces a change of the refractive index of the Ti:sapphire crystal and therefore a variation of the optical path length of the cavity on a time scale much shorter than the response time of the electronic system used for locking the cavity. Therefore, at the instant the pulse is produced the cavity resonances are shifted from the frequency to which they are locked. The size of the frequency shift due to mode pulling depends on the pump power. The optical properties of the Ti:sapphire crystal in the bow-tie amplifier change depending on the population inversion, which decreases during the multistep amplification of the IR pulse. The combined effect of both phenomena results in a shift on the order of a few megahertz. We measure and compensate for these effects by making a part of the pulsed light interfere with part of the cw light. The cw-pulse offset can be determined within 200 kHz. However, as a result of wavefront distortions of the pulsed beam, it depends very critically on the alignment. We have measured the chirp at different positions in the wavefront by moving a small pinhole through the pulsed beam, and observed deviations of a few megahertz. These deviations are amplified in the harmonic generation stages. As it is unclear which part of the pulsed laser beam gives rise to the observed metastable CO signal, we cannot compensate for this effect. Consequently, we find rather large day-today deviations in the measurements; measured transition frequencies taken on the same day, with a specific alignment and setting of the Ti:sapphire oscillator and bow-tie amplifier, agree within a 500 kHz. Measured transition frequencies taken on different days, on the other hand, may deviate by a few megahertz. In order to compensate for this systematic effect, we chose the $R_2(0)$ transition in ¹²C¹⁶O as an anchor for each measurement session. With this anchoring, measurements of any given transition [other than the $R_2(0)$ transition] taken
Source	Uncertainty(MHz)
Relative:	
Zeeman effect	< 0.1
Stark effect	< 0.03
AC-Stark effect	< 0.1
Comb absolute frequency determination	$\ll 0.15$
Doppler effect	< 0.2
Peak determination	0.3
cw-pulse offset	0.2
Absolute:	
cw-pulse offset	5

Table 2.2: The uncertainty budget of the measured transitions.

on different days agree within 500 kHz, showing that the consistency of the positions of the rotational levels of $a^3\Pi$ is sub-megahertz. The relatively large systematic uncertainty due to mode pulling and chirp will only enter in the value of the band origin. The root-mean-square deviation of 14 measurements of the ${}^{12}C^{16}O R_2(0)$ transition is about 2 MHz. We have set the uncertainty of the $R_2(0)$ transition, and hence the systematic uncertainty on all transitions, conservatively at 5 MHz. Note that Salumbides *et al.* [61] have circumvented this systematic offset of the absolute calibration by putting a small pinhole in the pulsed beam, therewith selecting a portion of the laser beam with smaller wave-front distortions. We could not apply this method here, as it resulted in too large a decrease in signal.

2.6 Analysis

2.6.1 Effective Hamiltonian and least square fitting for ${}^{12}C^{16}O$ and ${}^{13}C^{16}O$

The effective Hamiltonian for a ${}^{3}\Pi$ state has been derived by several authors [51, 62]. We have used the effective Hamiltonian from Field *et al.* [51] with the additions and corrections discussed by Carballo *et al.* [46]. The matrix elements for this effective Hamiltonian are listed in Table 2.3. As discussed by Carballo *et al.* [46], this Hamiltonian is equivalent to the effective Hamiltonian derived by Brown and Merer [62], but the molecular constants used in these Hamiltonians have a slightly different physical meaning, which will have consequences for the mass scaling discussed in Sec. 2.6.2. In Table 2.4, relations between the constants in the Hamiltonian of Brown and Merer and those in the Hamiltonian of Field *et al.* are listed for clarity.

A least-squares fitting routine was written in MATHEMATICA to obtain the molecular constants of the effective Hamiltonian. We have verified that our

$$\begin{array}{l} \langle^{3}\Pi_{0}|H|^{3}\Pi_{0}\rangle & E_{\Pi}+B(x+1)-D(x^{2}+4x+1)-A-2A_{J}(x+1)\\ -C\mp C_{\delta}-\gamma+xB_{0}+(1\mp1)(4B_{1}^{+}-2B_{0}^{+}) \\ \\ \langle^{3}\Pi_{1}|H|^{3}\Pi_{1}\rangle & E_{\Pi}+B(x+1)-D(x^{2}+6x-3)+2C-2\gamma\\ -2B_{0}^{+}+4B_{1}^{+} \\ \\ \langle^{3}\Pi_{2}|H|^{3}\Pi_{2}\rangle & E_{\Pi}+B(x-3)-D(x^{2}-4x+5)+A\\ +2A_{J}(x-3)-C-\gamma+B_{0}^{+}(x-2) \\ \\ \langle^{3}\Pi_{0}|H|^{3}\Pi_{1}\rangle & -\sqrt{2x}\left[B-2D(x+1)-A_{J}-0.5\gamma+(1\mp2)B_{1}^{+}\right] \\ \\ \langle^{3}\Pi_{1}|H|^{3}\Pi_{2}\rangle & -\sqrt{2(x-2)}\left[2D\pm B_{0}^{+}\right] \\ \\ \langle^{3}\Pi_{1}|H|^{3}\Pi_{2}\rangle & -\sqrt{2(x-2)}\left[B-2D(x-1)+A_{J}-0.5\gamma+B_{1}^{+}\right] \end{array}$$

Table 2.3: The matrix form of the Hamiltonian used in the comprehensive fit; x = J(J + 1). Upper sign choice refers to *e* levels; lower sign choice to *f* levels.

Carballo <i>et al.</i>	Brown and Merer
E_{Π}	T + B - D - q/2
B	B - 2D - q/2
D	D
A	$A + A_D + \gamma + p/2$
A_j	$A_D/2$
C	$-2/3\lambda$
C_{δ}	0
γ	$\gamma + p/2$
B_0^+	q/2
B_1^+	p/4 + q/2

Table 2.4: The conversion factors between the molecular constants used in the effective Hamiltonian of Carballo *et al.* [46] and Brown and Merer [62].

fitting routine exactly reproduces the results of Carballo *et al.* [46] and that it is consistent with PGOPHER [63]. For ${}^{12}C^{16}O$, we have fitted our optical data simultaneously with lambda-doubling transition frequencies in the rf domain measured by Wicke *et al.* [44] and the rotational transition frequencies in the mw domain measured by Carballo *et al.* [46] and Wada and Kanamori [47]. The fitted set consists of 9 rf transitions, 28 mw transitions and 14 optical transitions. The different data sets were given a weight of one over the square of the measurement uncertainties, taken as 50 kHz for the mw and rf data and 1 MHz for the optical data. The molecular constants for the $X^{1}\Sigma^{+}$ state of ${}^{12}C^{16}O$ are taken from Winnewisser *et al.* [64]. As discussed by Carballo *et al.* [46], γ and A_{J} can not be determined simultaneously from data of a single isotopologue, therefore γ was fixed to zero. The first column of Table 2.5 lists the different constants obtained from our fit for ${}^{12}C^{16}O$. The deviations between the observed and fitted transition frequencies are listed in Table 2.1.

All measured transitions could be fitted to approximately their respective uncertainties. However, the total root mean square (rms) of the residuals of the rf and mw data is significantly increased when the optical data is included; Carballo reported rms residuals of 27 kHz, while we find rms residuals of 52 kHz. The rms of the residuals of the fitted $^{12}C^{16}O$ optical transitions is equal to 3.3 MHz.

The molecular constants found from the fit to the combined data agree well with the constants found from a fit to the rf and mw data alone, but with largely decreased uncertainties. The uncertainty of A, C and C_{δ} , which are poorly constrained by the rotational and lambda-doubling transitions alone, are reduced by more than a factor of 10. Somewhat unexpectedly, the uncertainty of several other constants, including B, are also substantially decreased by the fit to the combined data. This can be understood from the fact that the mw data does not constrain B, but rather a combination of A and B. This also explains why the uncertainty of B as obtained from a fit to the rotational and lambda-doubling transitions is ~ 300 kHz, whereas the rotational transitions have a quoted uncertainty of 5-8 kHz and are fitted with an rms uncertainty of 27 kHz [46]. Our optical data directly probe A, and the more precise value of A results in turn in a more precise value of B. Adding the optical data results in an uncertainty in B of 30 kHz, much closer to the value one would expect from the precision of the recorded mw transitions. Altogether, the new set of constants is more balanced and adequately describes the $a^3\Pi$ state.

As seen from Table 2.1, the residuals of the optical transitions probing the $\Omega = 1$ manifold are larger than those to the $\Omega = 0$ and $\Omega = 2$ manifolds, which is surprising as these transitions are the strongest transitions in the spectra and are measured with a higher signal-to-noise ratio than the other transitions. We have investigated whether this might be explained by perturbations arising from the $a'^{3}\Sigma^{+}$ or $D^{1}\Delta$ state. When perturbations with the $a'^{3}\Sigma^{+}$ state were included, using the perturbation parameters from Carballo *et al.* [46], the residuals decreased marginally. A slight improvement was obtained by including a perturbation with the $D^{1}\Delta$ state. However, as the perturbation parameters

Molecular	K^X_{μ}	$^{12}\mathrm{C}^{16}\mathrm{O}$	$^{13}\mathrm{C}^{16}\mathrm{O}$
$\operatorname{constant}$	μ	fitted	fitted
E	0	1453190243.1(8)	1453340486.4(7)
В	-1	50414.24(3)	48198.28(7)
D	-2	0.1919(3)	0.1861(13)
A	0	1242751.3(10)	1242807.6(10)
A_{j}	-1	-5.732(8)	-5.51(2)
\check{C}	0	-538.4(6)	-536.8(3)
C_{δ}	0	26040.4(14)	26042.6(11)
γ	-1	0	0
B_0^+	-2	0.841(9)	0.775(7)
B_1^+	-1	39.67(5)	37.81(4)
a			162.2(3)
b			638.0(6)
c			8.3(3)
d			107.3(10)
Molecular		$^{13}C^{16}O$	$^{13}C^{18}O$
$\operatorname{constant}$		scaled	scaled
E		1453340489.2(9)	1453500584(3)
B		48197.73	45797.49
D		0.1753	0.1582
A		1242806.1	1242866.7
A_j		-5.479	-5.206
C		-538.8	-539.5
C_{δ}		26044.6	26049.4
γ		0	0
B_0^+		0.768	0.693
B_1^+		37.94	36.08
a		161.9(10)	161.9
b		638(2)	638
c		8.5(10)	8.5
d		105(3)	105

Table 2.5: Molecular constants for the $a^3\Pi$ state of ${}^{12}C^{16}O$ and ${}^{12}C^{16}O$, obtained from a simultaneous fit to rf, mw, and optical data. γ is fixed at zero in the analysis. The one standard deviation uncertainty from the fits is listed after each value, in units of the last digit. The values for the band origins have an additional uncertainty of 5 MHz due to the cw-pulse offset in the present optical measurements. For ${}^{13}C^{16}O$ and ${}^{13}C^{18}O$, the table also lists the values that were obtained by scaling the constants of ${}^{12}C^{16}O$. For ${}^{13}C^{16}O$, when the constants are scaled, the hyperfine constants are fitted together with the value of the band origin, while the scaled constants are kept fixed, resulting in slightly different values for these constants. For ${}^{13}C^{18}O$ the hyperfine parameters of ${}^{13}C^{16}O$ are used.

of the coupling between the $a^3\Pi$ and $D^1\Delta$ states are unknown, it is unclear if this improvement is genuine.

A similar analysis has been performed for ${}^{13}C^{16}O$. We have included the hyperfine interaction in the effective Hamiltonian following Brown *et al.* [65]. Only terms that are diagonal in J were included, since contributions from off-diagonal terms are estimated to be smaller than 100 kHz [52]. We have fitted our optical data simultaneously with lambda-doublet transition frequencies measured by Gammon *et al.* [52] and the rotational transition frequencies measured by Saykally *et al.* [45]. The fitted set consisted of 19 rf transitions, 4 mw transitions and 24 optical transitions. The molecular constants for the $X^1\Sigma^+$ are taken from Klapper *et al.* [53]. The molecular constants resulting from the fit are listed in Table 2.5. The difference between the observed transition frequencies and the frequencies from the fit are listed in Table 2.1. The rms of the residuals of the fitted ${}^{13}C^{16}O$ optical transitions is equal to 0.9 MHz.

For ${}^{13}C^{18}O$, as for the other isotopologues, no previous measurements on the $a^{3}\Pi$ were found in the literature, except for four mw transitions in ${}^{12}C^{18}O$ [45]. Hence, no fit has been attempted.

2.6.2 Mass scaling

An important motivation for this work was to validate the mass scaling of the energy levels of the $a^3\Pi$ state, and to confirm the sensitivity to a possible variation of the proton-to-electron mass ratio for a selected number of level spittings. In the literature, the reduced mass of the molecule is frequently denoted by the symbol μ . In this paper, we will use μ to denote the proton-toelectron mass ratio, and will denote the reduced mass of the molecule by μ_{red} . As we will see in Sec. 2.6.3, μ_{red} is linearly proportional to μ which is defined for the various isotopologues ${}^{x}C{}^{y}O$ as

$$\mu_{red}^{x,y} = \frac{m_C^x \cdot m_O^y}{m_C^x + m_O^y}.$$
(2.3)

The molecular constants as determined from the fits are effective molecular constants for the v = 0 level of the $a^3\Pi$ state. In general, an effective molecular constant $X_{e,v}$ can be expressed as

$$X_{e,v} = X_e + \alpha_{X,1}(v + 1/2) + \alpha_{X,2}(v + 1/2)^2 + \dots \quad (2.4)$$

Note that for the constants A and B the second term of Eq. (2.4) has a minus sign by convention [48]. Thus, the mass dependence of every constant consists of the mass dependence of X_e and a correction due to the vibrational dependence of $X_{e,v}$. The second column of Table 2.5 lists the dependence of the molecular constants, X_e , on the reduced mass of the molecule, μ_{red} . The effective molecular constant, $X'_{e,v}$, of an isotopologue with a reduced mass μ'_{red} then becomes

$$X'_{e,v} = \left(\frac{\mu'_{red}}{\mu_{red}}\right)^{K_{\mu}^{X}} X_{e} + \left(\frac{\mu'_{red}}{\mu_{red}}\right)^{K_{\mu}^{X} + \frac{1}{2}} \alpha_{X,1}(v+1/2) + \left(\frac{\mu'_{red}}{\mu_{red}}\right)^{K_{\mu}^{X} + 1} \alpha_{X,2}(v+1/2)^{2} + \dots,$$
(2.5)

where X_e , $\alpha_{X,1}$, and $\alpha_{X,2}$ are the constants for the isotopologue with reduced mass μ_{red} and

$$K^X_\mu = \frac{\mu}{X_e} \frac{\partial X_e}{\partial \mu}.$$
 (2.6)

Note that we use μ in Eq. (2.6) rather than μ_{red} (see below).

As we have only measured transitions in the v = 0 band, the vibrational dependencies of the molecular constants cannot be extracted from our data. Hence, we have used the ratios between X_e , $\alpha_{X,1}$, and $\alpha_{X,2}$ determined by Havenith *et al.* [48] to scale our constants. The molecular constants for ${}^{13}C^{16}O$ and ${}^{13}C^{18}O$, found by scaling the constants of ${}^{12}C^{16}O$ via the outlined procedure, are listed in the third and fourth column of Table 2.5, respectively. For ¹³C¹⁶O, the value of the band origin and the hyperfine constants were determined by fitting the data while the other constants were fixed at the scaled values. For ${}^{13}C^{18}O$, the hyperfine constants were taken to be identical to those of ¹³C¹⁶O. The data for the $X^1\Sigma^+$ state were calculated from Puzzarini et al. [66] and only the value of the band origin was fitted. The differences between the observed transition frequencies and the frequencies calculated using the scaled molecular constants are listed in Table 2.1. As is seen the correspondence is satisfactory. The rms of the residuals of the ${}^{13}C^{16}O$ and ${}^{13}C^{18}O$ data with the frequencies found by scaling the molecular constants is equal to 5.1 MHz and 8.3 MHz, respectively.

Until now the value of the band origin, E_{Π} , was treated as a free parameter without considering its proper mass scaling. The value of the band origin consists of the following: (i) A pure electronic part, that scales as $(\mu_{red})^0$ except for a small correction due to the finite mass of the nuclei, known as the normal mass shift, or Bohr-shift, which is proportional to the reduced mass of the nuclei-electron system; (ii) a vibronic part that can be expanded in a power series of (v + 1/2) and contains the difference in zero-point energies in the $a^3\Pi$ and $X^1\Sigma^+$ states; (iii) a rotational part, equal to B - D, that was absorbed in the value of the band origin in our definition of the effective Hamiltonian; (iv) the specific mass shift, dependent on the electron correlation function; (v) nuclear-size effects, dependent on the probability density function of the electrons at the nucleus.



Figure 2.10: In the upper panel, the measured values of the band origins of the $a^3\Pi$ state of the six stable isotopologues of CO are plotted as a function of the reduced mass. The solid line shows the value of the band origin scaled with respect to ${}^{12}C^{16}O$. In the lower panel the difference between the measured and calculated values of the band origins are plotted.

In the upper panel of Fig. 2.10, the derived values of the band origin of the $a^3\Pi$ state of the six stable isotopologues of CO are plotted as a function of the reduced mass. The solid line shows how the value of the band origin scales when effects (i)-(iii), which are expected to be dominant, are included. The used formulas for the normal mass shift, the vibrational part and the rotational part are:

$$\Delta E_{\Pi} = \Delta E_{nms} + \Delta E_{vib} + \Delta E_{rot} \tag{2.7}$$

with

$$\Delta E_{nms} = E_{\Pi 0} \left[\left(\frac{\mu'_{red} \cdot m_{el}}{\mu'_{red} + m_{el}} \right) / \left(\frac{\mu_{red} \cdot m_{el}}{\mu_{red} + m_{el}} \right) - 1 \right], \tag{2.8}$$

$$\Delta E_{vib} = \frac{1}{2} \left(\omega_{e\Pi} - \omega_{e\Sigma} \right) \left(\left(\frac{\mu_{red}}{\mu'_{red}} \right)^{1/2} - 1 \right)$$
$$-\frac{1}{4} \left(\omega_{e\Pi} x_{e\Pi} - \omega_{e\Sigma} x_{e\Sigma} \right) \left(\frac{\mu_{red}}{\mu'_{red}} - 1 \right)$$
$$+\frac{1}{8} \left(\omega_{e\Pi} y_{e\Pi} - \omega_{e\Sigma} y_{e\Sigma} \right) \left(\left(\frac{\mu_{red}}{\mu'_{red}} \right)^{3/2} - 1 \right),$$
(2.9)

$$\Delta E_{rot} = B_0 \left(\frac{\mu_{red}}{\mu'_{red}} - 1\right) - D_0 \left(\left(\frac{\mu_{red}}{\mu'_{red}}\right)^2 - 1\right)$$
(2.10)

where ΔE_{Π} is the shift in the value of the band origin as a function of the reduced mass, μ'_{red} , with respect to a given isotopologue with reduced mass μ_{red} , band origin $E_{\Pi 0}$ and rotational constants B_0 and D_0 . m_{el} is the mass of the electron. The shift was calculated with respect to ${}^{12}C^{16}O$. For the $X^{1}\Sigma^{+}$ state the vibrational constants were obtained from fitting to the data from Coxon *et al.* [67], while for the $a^{3}\Pi$ state the constants from Havenith *et al.* [48] were used. In the lower panel, the difference between the experimental and calculated values of the band origins for the different isotopologues are plotted. The experimental and scaled values of the band origins deviate by a few gigahertz, which is more than expected given the precision of the data used in this analysis. Most surprising is the difference between the values of the band origins of ${}^{13}C^{16}O$ and ${}^{12}C^{18}O$, which have nearly equal reduced masses (7.18 vs. 7.21 amu, respectively). This suggests a breakdown of the Born-Oppenheimer approximation.

We have reanalyzed experimental data pertaining to all six stable isotopologues of CO for the E¹ Π (v = 1) state [68] and the C¹ Σ^+ (v = 1) state [69] and

Transition	Measured	MeasCalc.	K_{μ}
	(MHz)	(MHz)	
$^{12}C^{16}O$			
$(6, 1, +) \rightarrow (4, 2, +)$	19270.1	3.5	27.8
$(6,1,-) \to (4,2,-)$	16057.7	4.7	33.7
$(6,1,+) \to (8,0,+)$	-1628.3	-3.3	-334
$(6, 1, -) \to (8, 0, -)$	-19406.7	4.5	-27.3
$^{13}C^{16}O$			
$(6, 1, +, 6.5) \rightarrow (4, 2, +, 3.5)$	43005.8	0.1	12.9
$(6, 1, -, 6.5) \rightarrow (4, 2, -, 3.5)$	39988.0	0.7	12.2
$(6, 1, +, 5.5) \rightarrow (8, 0, +, 8.5)$	22329.6	6.0	23.5
$(6, 1, -, 5.5) \rightarrow (8, 0, -, 8.5)$	4003.4	5.0	128
$^{13}C^{18}O$			
$(6, 1, +, 6.5) \rightarrow (4, 2, +, 3.5)$	69062.0	-7.1	7.22
$(6, 1, -, 6.5) \rightarrow (4, 2, -, 3.5)$	66277.5	-3.6	7.60

Table 2.6: Measured level splittings between near-degenerate levels in CO $(a^{3}\Pi)$; States are listed as $(J,\Omega,\text{parity},F)$, F only where applicable. Frequencies are listed in terms of two-photon microwave transitions bridging the intervals. The Meas.-Calc. column lists the difference between the measured frequency and the frequency calculated using the constants listed in Table 2.5. The sensitivities to a possible variation of the proton-to-electron mass ratio are listed in the last column.

found a similar deviation as found for the $a^3\Pi$, both in size and in direction. This suggests that the ground state is probably the source of the discrepancy. Calculations using the LEVEL program [70] were performed to estimate the effects of the breakdown of the Born-Oppenheimer approximation in the ground state of CO following the approach by Coxon and Hajigeorgiou [67]. The calculated energy difference between the ${}^{12}C^{18}O$ and ${}^{13}C^{16}O$ isotopologues was approximately 50 times smaller than observed in our measurements and is thus insufficient to explain the observed effect [71].

The specific mass shift was not included in our analysis. It is however proportional to μ_{red} , and can thus not explain the observed large difference between ${}^{12}C^{18}O$ and ${}^{13}C^{16}O$. Nuclear size effects could in principle cause a similar isotope shift as observed, but the difference in nuclear charge radius between ${}^{17}O$ and ${}^{18}O$ is approximately 10 times larger than the difference between ${}^{16}O$ and ${}^{17}O$, whereas the observed difference between the values of the band origins in the isotopologues with these oxygen isotopes is similar in size [72]. It is therefore unlikely that the observed isotopic effect is due to a nuclear-size effect.



Figure 2.11: The frequencies of two-photon mw transitions between four near degeneracies as a function the reduced mass. The solid lines show the values obtained from mass scaling the molecular constants of ${}^{12}C{}^{16}O$. The crosses indicate the calculated frequencies of the transitions in the six stable isotopologues, whereas the boxes show the values obtained from differences between measured frequencies. The four different transitions are listed in the legend as they appear in the graph, from top to bottom.

2.6.3 CO ($a^{3}\Pi$) as a target system for probing $\partial \mu / \partial t$

In Fig. 2.11, the energies of the two-photon mw transitions between the neardegenerate levels of the different Ω -manifolds are shown as a function of μ_{red} . The solid lines show the values obtained from scaling the molecular constants of ¹²C¹⁶O using the mass-scaling relations discussed in Sec. 2.6.2. The crosses indicate the reduced masses of the six stable isotopologues, whereas the boxes show the values directly obtained from the measurements. The strong energy dependence on the reduced mass is indicative of a high sensitivity to the proton-to-electron mass ratio. The measured and calculated values for the twophoton microwave transitions between the nearly degenerate levels are listed in Table 2.6. Our measurements reduce the uncertainties of the two-photon transitions to ≈ 1 MHz, a factor 20 better than before. The mass of the proton is much larger than the masses of the constituent quarks, consequently, the mass of the proton is related to the strength of the forces between the quarks; Λ_{QCD} the scale of quantum chromodynamics [73]. As the same argument holds for the neutron-to-electron mass ratio, a possible variation of the proton-to-electron mass ratio is expected to be accompanied by a similar variation of the neutron-to-electron mass ratio [74]. With this assumption, it follows that

$$K_{\mu} = \frac{\mu}{\nu} \frac{\partial \nu}{\partial \mu} = \frac{\mu_{red}}{\nu} \frac{\partial \nu}{\partial \mu_{red}}.$$
 (2.11)

The sensitivity of a transition to a possible variation of the proton-toelectron mass ratio μ can now be calculated using the mass-scaling relations discussed before. The sensitivities for the two-photon microwave transitions are listed in the last column of Table 2.6. These coefficients have been calculated with an accuracy of 0.3-0.05%.

It is instructive to compare the sensitivity to what one would expect in a pure Hund's case (a). For the transition at 1628.3 MHz we expect a sensitivity of $K_{\mu} = A/2\nu = 1242751.3/2 \times 1628.3 \approx 382$ which is 12% larger than calculated using the model that includes the coupling between the different Ω -manifolds ¹.

2.7 Conclusion

UV-frequency metrology has been performed on the $a^3\Pi$ - $X^1\Sigma^+$ (0,0) band of various isotopologues of CO using a frequency-quadrupled injection-seeded narrow-band pulsed Ti:sapphire laser referenced to a frequency comb laser.

We have fitted our optical data for ${}^{12}C^{16}O$ together with the lambdadoubling transitions of Wicke *et al.* [44] and the rotational transitions of Carballo *et al.* [46] and Wada and Kanamori [47]. Adding the optical data resulted in a large decrease of the uncertainties of A, C and C_{δ} , and a smaller decrease in uncertainty in the other constants.

From our measurements we obtain the value of the band origin with an uncertainty of 5 MHz, a 30-fold improvement compared to the value obtained from absorption measurements by Field *et al.* [51]. We have also measured the value of the band origin in different isotopes and found an unexpected behavior of the isotope shifts, probably due to a breakdown of the Born-Oppenheimer approximation.

Our main motivation for this study was to obtain more accurate values for the two-photon transitions between near degenerate rotational levels in different Ω -manifolds and validate the large sensitivity coefficients predicted for these transitions. The calculated values of the transitions agree to within a few MHz with the measured values, giving confidence in the calculated values of K_{μ} .

¹Note that Bethlem and Ubachs [9] erroneously used $K_{\mu} = A/\nu$ instead of $K_{\mu} = A/2\nu$.

Chapter 3

Testing the mass-scaling relations in the $(a^3\Pi)$ state of ${}^{12}C^{18}O$ and ${}^{13}C^{16}O$

Abstract

Electronic spectra of the $a^3\Pi - X^1\Sigma^+$ (0-0) and (1-0) bands of ${}^{12}\text{C}{}^{18}\text{O}$, and the (1-0) band of ${}^{13}\text{C}{}^{16}\text{O}$ are measured by cavity ring-down spectroscopy in the 200 nm region. The experimental spectra are analyzed using the molecular constants predicted by mass-scaling relations. It is found that the mass-scaling rules for the $a^3\Pi$ state can be used to predict the transition frequencies from v = 0, J < 8 in ${}^{12}\text{C}{}^{16}\text{O}$ to v = 1and J < 30 rovibrational levels in both ${}^{12}\text{C}{}^{18}\text{O}$ and ${}^{13}\text{C}{}^{16}\text{O}$ within the experimental accuracy of 0.2 cm⁻¹.

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3.1 Introduction

The metastable lowest-lying triplet state of CO, $a^3\Pi$, has attracted much interest since the Cameron bands (the spin-forbidden $a^3\Pi - X^1\Sigma^+$ system) were detected in 1926 [42]. Extensive studies on the $a^3\Pi$ state of ${}^{12}C^{16}O$ have been performed in radio-frequency, microwave, infrared, optical and UV studies [10, 43–51]. Also, ${}^{13}C^{16}O$ and ${}^{12}C^{18}O$ have been studied using rf, mw and UV spectroscopy [10, 45, 52]. Recently, rotational transitions in metastable CO in its $a^3\Pi$ state have been identified as a sensitive probe to detect a possible time-variation of the proton-to-electron mass ratio, μ , on a laboratory time scale [9].

In our previous work on the UV-frequency metrology on the $a^3\Pi$ - $X^1\Sigma^+$ (0-0) band of CO [10] [Chapter 2], a number of transitions in various isotopologues were measured with an accuracy of 5 MHz. It was found that the transition frequencies in the higher mass isotopologues are well reproduced by scaling the molecular constants of ${}^{12}C^{16}O$ via the common mass-scaling rules. In this paper, the electronic spectra of the $a^{3}\Pi$ - $X^{1}\Sigma^{+}$ (0-0) and (1-0) bands of ${}^{12}C^{18}O$, and the (1-0) band of ${}^{13}C^{16}O$ have been experimentally recorded for the first time, by cavity ring-down spectroscopy (CRDS) in the 200 nm region. The aim of the present work is to test the common mass-scaling relations specifically in higher rovibrational levels ($v = 1, J \sim 30$) of the $a^{3}\Pi$ state of CO.

3.2 Experimental setup

The deep-UV spectra of CO are recorded in direct absorption using cavity ringdown spectroscopy (CRDS). Details of the experimental setup have been described in Refs. [75, 76]. Briefly, commercial isotopically-enriched gases (Sigma Aldrich, ${}^{12}C^{18}O$ purity $\sim 95\%$, and ${}^{13}C^{16}O$ purity $\sim 98\%$) are used. A 0.5 micron filter cleans the gas sample from dust and aerosol particles. The gas sample is kept at a stationary pressure of 20 mbar in a 48 cm long gas cell. Tunable deep-UV radiation in the 200 nm region is generated by frequency-tripling the output of a Nd:YAG (532 nm) pumped pulsed dye laser system (Sirah, Cobra Stretch) running near 600 nm at a repetition rate of 10 Hz. The UV light is focused into an optical cavity comprised of two highly reflective mirrors (reflectivity $\sim 99.5\%$ in the 195-210 nm range) mounted via precise alignment tools on opposite sides of the gas cell. The light leaking out of the cavity is detected by a photomultiplier tube (PMT). The PMT signal is subsequently digitized by an oscilloscope (LeCroy 9450, 1 GB sample rate and 350 MHz bandwidth) and the obtained data is analyzed to extract the ring-down time. Typical ring-down times in the present experiment are ~ 200 ns. Ten ring-down times are averaged to reduce the shot-to-shot noise. A full spectrum is obtained by recording the averaged ring-down time as a function of wavelength.

The bandwidth of the UV-radiation after frequency tripling is estimated to be $\sim 0.5 \text{ cm}^{-1}$. Since the laser bandwidth is larger than the Doppler linewidth, estimated to be 0.12 cm^{-1} for CO at room temperature, this may result in non-exponential decay transients of the ring-down signal, and consequently slightly unreliable absorption line intensities in the final experimental spectrum, as discussed by Jongma *et al.* [77]. It is noted that this effect only affects the intensity and does not change absorption line positions. It is relatively small for weak absorptions but may become pronounced in the case of strong absorptions.

The absolute frequency of the fundamental laser is calibrated by recording an iodine absorption spectrum simultaneously with the CRDS signal, using a small fraction ($\sim 5\%$) of the dye laser output split before frequency conversion. Transition frequencies in the CO absorption spectra are obtained by multiplying the dye laser frequency by three. The absolute accuracy of the transition frequencies is estimated to be 0.2 cm⁻¹ in the UV-spectrum (for strong and unblended lines it is estimated to be better than 0.1 cm⁻¹).

3.3 Results and discussion

Rotationally resolved spectra of the (0-0) and (1-0) bands of ${}^{12}C^{18}O$, at 206 and 199 nm, respectively, are recorded in this work, where 168 transitions with J values up to 32 are assigned in the (0-0) band, and 158 transitions with J values up to 31 are assigned in the (1-0) band. As an example, the experimental spectrum of the (0-0) band of ${}^{12}C^{18}O$ is shown in the upper trace (black) of Fig. 3.1(a). Fig. 3.1(b) shows a zoomed in region of the spectrum, with the reference I₂ spectrum shown as the lowest trace (blue). As high-precision spectroscopy of the (0-0) band of ${}^{13}C^{16}O$ has been performed by de Nijs *et al.* [10][Chapter 2], in the present work, only the (1-0) band at 199 nm is studied, and 139 transitions with J values up to 28 are assigned.

Using the previously reported molecular constants for the $a^3\Pi$ state of ${}^{12}C^{16}O$ and the mass-scaling model that is described in Section VI.B. of Ref. [10] [Chapter 2], the relevant molecular constants for the $a^3\Pi$ state of ${}^{12}C^{18}O$ and ${}^{13}C^{16}O$ are calculated, and listed in the second column (scaled) of Table 3.1. These mass-scaled constants are subsequently used in the analysis of the experimental spectra and for testing the mass-scaling model also for higher rovibrational levels in the $a^3\Pi$ state of CO.

Least-squares fits of the experimental spectra are performed using the Hamiltonian for a ${}^{3}\Pi$ - ${}^{1}\Sigma$ forbidden transition defined in the PGOPHER software [63]. The accurate molecular constants for the $X^1\Sigma^+$ ground state of both ${}^{12}\dot{C^{18}O}$ and ¹³C¹⁶O are taken from previous laboratory microwave work [53, 78] and fixed in the fits. The mass-scaled molecular constants for the $a^3\Pi$ state, listed in Table 3.1, are set as initial values in the fits. As noted in Ref. [10][Chapter 2], the values of the band origins, T_0 , depend not only on the reduced mass of the molecule but also exhibit an atom dependent energy shift at the GHz level. Similar shifts were observed in the $C^1\Sigma^+$ and $E^1\Pi$ states suggesting the discrepancy originates from the ground state, however, the exact source is not yet understood. This finding is confirmed here, therefore, as the first step of a fit, the value of the band origin is set as free parameter, while all other spectroscopic parameters are fixed at the mass-scaled values. The resulting values of T_0 are listed in Table 3.1. This procedure reproduces the experimental spectra well. The standard deviations of the observed-calculated line positions for all three bands are $\sim 0.2 \text{ cm}^{-1}$, of the order of the estimated accuracy for the measured line positions, and shows no increase for higher J values.

To further confirm the validity of the mass-scaling model, fits with the inclusion of T_0 , B, D, A, o, and p as free parameters are performed. Because a fit including the higher-order molecular constants, A_D , γ , λ , and q, results in standard errors much larger than their values these constants are kept fixed at the mass-scaled values. The resulting molecular constants for the $a^3\Pi$ state are shown in the third column (fitted) of Table 3.1. A simulated spectrum of the (0-0) band of ${}^{12}C^{18}O$, using the fitted molecular constants for the $a^3\Pi$ state and a rotational temperature of 300 K, is shown in the lower, red, trace of Fig. 3.1(a). Fig. 3.1(b) shows a zoomed-in region, with J > 20, of both experimental and



Figure 3.1: In panel (a), the measured, upper trace (black), and simulated, lower trace (red), spectrum of the 0-0 band of the a-X system of ${}^{12}C{}^{18}O$ are shown. For the simulated spectrum, calculated using PGOPHER [63], the fitted constants found in Table 3.1 and a temperature of 300 K were used. In panel (b), a zoomed in section of the measured and simulated spectra are shown, including the I₂ reference spectrum as the lowest trace (blue). The transitions shown in panel (b) correspond to rotational quantum numbers of $J \sim 20 - 25$.

	Molecular	Scaled	Fitted
	Constant	(MHz)	(MHz)
${}^{12}C{}^{18}O, v = 0$			
	T_0	$1.4533039(5) \cdot 10^9$	$1.4533033(10) \cdot 10^9$
	B	48015.57	48018(6)
	D	0.1740	0.176(8)
	A	1242822	$1.2421(9) \cdot 10^6$
	A_D	-10.92	-10.92^{f}
	λ	808.40	808.40^{f}
	γ	-74.077	-74.077^{f}
	0	26044	$2.44(12) \cdot 10^4$
	p	148.2	$1.2(6) \cdot 10^2$
	q	1.524	1.524^{f}
$^{12}C^{18}O, v = 1$			
	T_0	$1.5034867(5) \cdot 10^9$	$1.5034874(11) \cdot 10^9$
	B	47485.49	47474(7)
	D	0.1788	0.160(9)
	A	1237759	$1.2361(10) \cdot 10^6$
	A_D	-10.92	-10.92^{f}
	λ	818.07	818.07^{f}
	γ	-71.83	-71.83^{f}
	0	25897.3	$2.73(14) \cdot 10^4$
	p	143.7	$2.2(8) \cdot 10^2$
	q	1.512	1.512^{f}
${}^{13}C{}^{16}O, v = 1$			
	T_0	$1.5035732(5) \cdot 10^9$	$1.5035727(10) \cdot 10^9$
	B	47665.72	47668(9)
	D	0.1802	0.181(15)
	A	1237743	$1.2393(8) \cdot 10^6$
	A_D	-10.96	-10.96^{f}
	λ	818.32	818.32^{f}
	γ	-72.10	-72.10^{f}
	0	25897.5	$2.50(12) \cdot 10^4$
	p	144.2	$1.7(8) \cdot 10^2$
	q	1.524	1.524^{f}

Table 3.1: The molecular constants for the $a^3\Pi$ state in the ${}^{12}C^{18}O$ and ${}^{13}C^{16}O$ isotopologues, for the v = 0 and v = 1 vibrational states, in MHz. The second column gives the values that are obtained by scaling from the values for v = 0, ${}^{12}C^{16}O$ to higher reduced mass and/or vibrational quantum number, using the mass-scaling procedure explained by de Nijs *et al.* [10][Chapter 2]. The value of the band origin is fitted when the other values are fixed, as the value of the band origin cannot be properly mass-scaled. The third column gives the values obtained from a fit to the measured cavity ring-down spectra. The values indicated with an f are kept fixed at the mass-scaled value, the others are fitted.

simulated spectra, in the upper, black, and middle, red traces, respectively. This figure shows that the experimental spectrum is well reproduced using the fitted molecular constants.

This work shows that, with an accuracy of 0.2 cm^{-1} , the mass-scaling model reported in Ref. [10][Chapter 2] works well for the v = 1 and J < 30 rovibrational levels in the $a^3\Pi$ state of both ${}^{12}\text{C}{}^{18}\text{O}$ and ${}^{13}\text{C}{}^{16}\text{O}$. It should be noted that, although high-J rovibrational levels are observed, the spectral resolution in the present experiment limits the precision of the fitted molecular constants of the $a^3\Pi$ state. A spectroscopic study with a reduced laser bandwidth and Doppler width may yield a further constraint of the molecular constants and test the mass-scaling model at higher precision. The mass-scaling model can be used to predict line positions, limiting the range that needs to be scanned in such an experiment.

Chapter 4

On deflection fields, weak-focusing and strong-focusing storage rings for polar molecules

Abstract

In this paper, we analyze electric deflection fields for polar molecules in terms of a multipole expansion and derive a simple but rather insightful expression for the force on the molecules. Ideally, a deflection field exerts a strong, constant force in one direction, while the force in the other directions is zero. We show how, by a proper choice of the expansion coefficients, this ideal can be best approximated. We present a design for a practical electrode geometry based on this analysis. By bending such a deflection field into a circle, a simple storage ring can be created; the direct analog of a weak-focusing cyclotron for charged particles. We show that for realistic parameters a weak-focusing ring is only stable for molecules with a very low velocity. A strong-focusing (alternating-gradient) storage ring can be created by arranging many straight deflection fields in a circle and by alternating the sign of the hexapole term between adjacent deflection fields. The acceptance of this ring is numerically calculated for realistic parameters. Such a storage ring might prove useful in experiments looking for an EDM of elementary particles.

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4.1 Introduction

A neutral polar molecule in an inhomogeneous electric field experiences a force that is equal to its dipole moment times the gradient of the electric field strength. This force makes it possible to manipulate polar molecules using inhomogeneous electric fields in much the same way as that charged particles are manipulated using electric fields [79]. In contrast to the forces on charged particles, however, the forces on polar molecules do not obey strict symmetries; i.e., for charged particles $\nabla \vec{F} = 0$ everywhere in space, whereas for polar molecules this is only true in special cases [80]. As a consequence, manipulation tools for polar molecules suffer from aggravating non-linearities [81].

One of the simplest manipulation tools is the electric or magnetic¹ deflection field, dating back to the seminal experiments by Stern and Gerlach [82] in the 1920s, on deflecting a beam of silver atoms using an inhomogeneous magnetic field (for a discussion of the historical context and influence see Ref. [83]). Electric deflection of a beam of molecules was first proposed by Kallmann and Reiche [84] and demonstrated by Wrede [85].

Deflection fields are extensively used to determine the magnetic and electric properties of atoms, molecules and clusters, ranging from alkali atoms [86], fullerenes [87, 88] to water [89] and metal clusters [90]. Furthermore, magnetic and electric fields have been used to deflect atoms and molecules state selectively onto a detector; the so-called molecular beam magnetic or electric resonance method (see for instance Ref. [91]). Recently, deflection fields have been used to prepare samples of molecules in the lowest rotational levels for subsequent laser-induced alignment and orientation studies [92] as well as to separate individual conformers of large molecules [93].

The ideal electric deflection field for polar molecules exerts a strong, constant force in one direction, while the force in the other directions is zero. For a molecule that has a linear Stark shift in the applied field, this implies that the electric field magnitude in one direction is linearly dependent on its position, while it is constant in the other directions. Unfortunately, such an electric field is not allowed by Maxwell's equations. In order to obtain accurate values for the polarizability of atoms and molecules, it is necessary to know both the electric field magnitude and its gradient. In the early experiments, the two wire field geometry was used, as this field and gradient are directly calculable from the geometry, thus avoiding difficult and tedious measurements of these quantities [91]. With the advent of numerical methods to calculate electric fields from arbitrary electrode geometries, an analytical expression of the electric field is no longer necessary. Hence, one may wonder if a more suitable deflection field can be created.

Recently, Stefanov *et al.* [94] discussed the optimal shape of a deflection field and presented a optimized design. Although the analysis of Stefanov *et al.* results in a near-ideal field, it gives little insight into the underlying principles and limitations. In this paper, we analyze deflection fields in terms of a multipole expansion, following an approach similar to the one used in Kalnins *et al.* [95] and Bethlem *et al.* [96]. We find a simple expression for the resulting

 $^{^1 {\}rm In}$ this paper, we restrict ourselves to electric deflection fields, but this analysis also holds for magnetic deflection fields.

force, and show how it can be optimized by a suitable choice of the expansion coefficients.

Our motivation for this study stems from an experiment that is being planned at the VU University Amsterdam. In this experiment, 2-photon microwave transitions will be measured in a molecular beam of metastable CO molecules [9] (as discussed in the introduction of this thesis), with the ultimate goal to detect or limit a possible variation of the proton to electron mass ratio. The measured transitions are between a state which has a rather strong Stark shift and a state that has virtually no Stark shift. The deflection field will deflect the molecules in the initially populated state while it will not affect the molecules in the excited state. Hence, by using a position sensitive detector, the fraction of molecules that have made a transition can be recorded. In order to have sufficient signal to noise, we require a deflection field with a large aperture that gives a clear seperation between molecules in either state.

Our paper is organized as follows; in Sec. 4.2, we analyze deflection fields in terms of a multipole expansion and find a simple expression for the resulting force. We simulate the trajectories of metastable CO molecules through deflection fields with different expansion coefficients, and show how the expansion coefficients should be chosen. The deflection fields discussed in Sec. 4.2 can be used to create weak-focusing and strong-focusing (alternating-gradient) storage rings for polar molecules. In Sec. 4.3, we show that unwanted terms in the deflection field limit the velocity of the molecules that can be stored in weak-focusing storage ring. In Sec. 4.4, we present a simple design for a strong-focusing storage ring and calculate its acceptance.

4.2 Force on a polar molecule in a deflection field

In a region devoid of charges the electric field can be derived from the electrostatic potential Φ using $\vec{E} = -\vec{\nabla}\Phi$. In two dimensions, Φ may be represented by a multipole expansion [95, 96] as:

$$\Phi(x,y) = \Phi_0 \left[\sum_{n=1}^{\infty} \frac{a_n}{n} \left(\frac{r}{r_0} \right)^n \cos(n\theta) + \sum_{n=1}^{\infty} \frac{b_n}{n} \left(\frac{r}{r_0} \right)^n \sin(n\theta) \right].$$
(4.1)

Here $r = \sqrt{(x^2 + y^2)}$ and $\theta = \tan^{-1}\left(\frac{y}{x}\right)$ are the usual cylindrical coordinates. a_n and b_n are dimensionless constants. r_0 and Φ_0 are scaling factors that characterize the size of the electrode structure and the applied voltages, respectively. The electric field magnitude at the centre is given by $E_0 = (\Phi_0/r_0)\sqrt{a_1^2 + b_1^2}$. The n = 1 terms in Eq. (4.1) represent a constant electric field, while the n = 2 and n = 3 terms represent the familiar quadrupole and hexapole fields that have been used extensively to focus molecules in low-field seeking states [97].



Figure 4.1: Equipotential lines for two deflection fields with $\Phi_0 = 10$ kV, $r_0 = 1.7$ mm, $a_1 = 1$ and $a_2 = -0.2$ (left panel) and $\Phi_0 = 10$ kV, $r_0 = 1.7$ mm, $b_1 = 1$ and $b_2 = -0.2$ (right panel), all other coefficients are set to zero. The solid curves show the voltage in steps of 5 kV. At the center the voltage is 0. The fields can be created by placing an electrode at any of the potential lines. The bold curves shown in the left panel are the electrode surfaces chosen for our experiment at VU University Amsterdam. The origins of the graphs coincide with the molecular beam axis. The cross section of the molecular beam is indicated by the dashed circles.

Eq. (4.1) represents the most general form of the 2D electrostatic potential consistent with Laplace's equation. Now we choose suitable coefficients for making a deflection field. If we choose the molecules to be deflected in the horizontal direction, we can create a deflection field by setting all $b_n = 0$, and setting $|a_1| \gg |a_2| \gg |a_3|$. This geometry is depicted on the left hand side of Fig. 4.1. We will refer to this geometry as the 'AA' deflection field or 'conventional' deflection field. Alternatively, we may create a deflection field by setting all $a_n = 0$, and setting $|b_1| \gg |b_2| \gg |b_3|$. This geometry is depicted on the right of Fig. 4.1. We will refer to this geometry as the 'BB' deflection field or 'wedge' field. The solid curves in Fig. 4.1 show the voltage in steps of 5 kV. At the center the voltage is 0.

These fields can be created by placing an electrode at any of the potential

lines. The bold curves shown in the left panel are the electrode surfaces chosen for our experiment at VU University Amsterdam. The negative electrode is a cylinder with a radius of 10 mm, centered at x = -11.7 mm to which a voltage of -10 kV is applied. The positive electrode follows the contour $\Phi = 10$ kV exactly up to $y = \pm 12$ mm and is then rounded of with a radius of 10 mm. Because these electrodes do not match the equipotential exactly, higher order terms are introduced. A fit to the numerically calculated field shows that the coefficients are changed by less than 3%.

Although the resulting potentials and electric fields for the AA and BB geometries are different, the magnitude of the electric field and forces are the same. We can write the electrostatic potential for the AA field as:

$$\Phi(x,y) = \Phi_0\left(a_1\frac{x}{r_0} + a_2\frac{\left(x^2 - y^2\right)}{2r_0^2} + a_3\frac{\left(x^3 - 3xy^2\right)}{3r_0^3}\right).$$
(4.2)

From this potential, we can obtain the electric field magnitude, via:

$$E(x,y) = \sqrt{\left(\frac{\partial\Phi}{\partial x}\right)^2 + \left(\frac{\partial\Phi}{\partial y}\right)^2}.$$
(4.3)

In Fig. 4.2, the electric field magnitude is shown for three different electrode geometries, with $\Phi_0 = 10 \text{ kV}$, $r_0 = 1.7 \text{ mm}$, $a_1 = 1$, $a_2 = 0.2 \text{ and } a_3$ as indicated in the figure. The solid curves show the magnitude of the electric field in steps of 5 kV/cm. The electric field magnitude is 58.8 kV/cm at the center and it decreases towards the right.

From the electric field magnitude, we can obtain the Stark shift and the force on the molecules, via:

$$\vec{F}(\vec{r}) = -\vec{\nabla}W(E) = \mu_{\text{eff}}\vec{\nabla}E.$$
(4.4)

Here we assume that the molecules experience a linear Stark shift; $W = -\mu_{\text{eff}}(E_0)E$, in the applied field, with $\mu_{\text{eff}}(E_0)$ being the effective dipole moment of the molecule in the electric field at the center of the deflector. μ_{eff} is positive for molecules in high field seeking states and negative for molecules in low field seeking states. Note that the Stark shift is assumed to be linear only over a small range of electric fields, this is a rather good approximation even for molecules that have a quadratic Stark shift. Throughout the region $r < r_0$, we can expand the force resulting from Eq. (4.2) as:

$$F_{\text{Stark},x} = \mu_{\text{eff}} E_0 \left[\frac{a_2}{a_1} \frac{1}{r_0} + 2 \frac{a_3}{a_1} \frac{x}{r_0^2} - \left(\frac{1}{2} \left(\frac{a_2}{a_1} \right)^3 - 2 \frac{a_2}{a_1} \frac{a_3}{a_1} \right) \frac{y^2}{r_0^3} + \dots \right],$$
(4.5)



Figure 4.2: The electric field magnitude for three different electrode geometries, with $\Phi_0 = 10$ kV, $r_0 = 1.7$ mm, $a_1 = 1$, $a_2 = -0.2$ and a_3 as indicated in the figure. The solid curves show the magnitude of the electric field in steps of 5 kV/cm. The electric field magnitude is 58.8 kV/cm at the center and it decreases towards the right.

$$F_{\text{Stark},y} = \mu_{\text{eff}} E_0 \left[\left(\left(\frac{a_2}{a_1} \right)^2 - 2 \frac{a_3}{a_1} \right) \frac{y}{r_0^2} - \left(\left(\frac{a_2}{a_1} \right)^3 - 4 \frac{a_2}{a_1} \frac{a_3}{a_1} \right) \frac{xy}{r_0^3} + \dots \right].$$
(4.6)

Ideally, the deflection force is constant and strong in the x-direction, while it is zero along the y-direction. Thus, we would like to keep only the first term of Eq. (4.5) and set all other terms in Eq. (4.5) and Eq. (4.6) equal to zero. We see that the desired term scales as a_2/a_1 while the undesired terms scale as a_3/a_1 or as the second or third power of a_2/a_1 . Thus, the undesired terms can be made arbitrary small, by choosing $a_3 = 0$ and $a_2/a_1 \ll 1$, but at the expense of the strength of the deflection force. In practice, one usually cannot

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Figure 4.3: Simulated transverse distribution of a beam of CO $(a^3\Pi)$ molecules in the high-field seeking $J = 6, M\Omega = 6, \Omega = 1$ state after passing through the deflection fields shown in Fig. 4.2. In each panel, the distribution is shown with the field switched on (green dots) and off (black dots). When the fields are on, the beam is displaced from the molecular beam axis by about -5 mm over 1 meter of free flight.

afford to choose a_2/a_1 , much smaller than 1/5. The dominant undesired term in this case is the first term of Eq. (4.6). This term can be cancelled with an appropriate choice of a_3 , but this introduces other unwanted terms.

In order to study the influence of a_3 we have performed simulations of the trajectories of polar molecules though different deflection fields. In our simulations, we assume that a beam of molecules traveling with a forward velocity of 800 m/s passes two diaphragms with a diameter of 1 mm, spaced 50 cm from each other before entering a 30 cm long deflection field. After passing the deflection field, the molecules travel 100 cm further before being detected by a position sensitive detector. The trajectories within the deflector are calculated by numerical integration of the force derived from Eq. (4.5) and Eq. (4.6)(including all higher order terms) using a Runge-Kutta method. In these calculations, μ_{eff} is taken to be 0.2 D, corresponding to $0.33 \times 10^{-2} \text{ cm}^{-1}/(\text{kV/cm})$; the effective dipole moment of metastable CO in the J = 6, $M\Omega = 6$, $\Omega = 1$ in an electric field of 58.8 kV/cm. If no deflection field is used, the transverse distribution of the beam at the detector is perfectly symmetric and has a FWHM of 2.6 mm. The arrival position of the undeflected molecules are shown as the black dots in Fig. 4.3, whereas the arrival position of the deflected molecules are shown as the green dots. The three panels show the distributions when the three electrode geometries shown in Fig. 4.2 are used. The beams are deflected over an angle given by:



Figure 4.4: FWHM of the transverse distribution of a beam of CO ($a^{3}\Pi$) molecules in the high-field seeking (HFS) $J = 6, M\Omega = 6, \Omega = 1$ and low-field seeking (LFS) $J = 6, M\Omega = -6, \Omega = 1$ states as a function of the strength of the hexapole term a_{3} . The horizontal line shows the FWHM of the undeflected beam.

$$\theta = \tan^{-1} \left[\frac{\mu}{m} E_0 \left(\frac{a_2}{a_1} \right) \frac{L_{\text{deff}}}{r_0} \frac{1}{v_z^2} \right],\tag{4.7}$$

with L_{deff} being the length of the deflection field. In our case this corresponds to an angle of ~ -4.5 mrad which translates into a displacement from the molecular beam axis of -5.2 mm after 1 m flight distance (note that the beam is already displaced by 0.7 mm from the molecular beam axis at the exit of the deflector). From Fig. 4.3, it is seen that the shape of the beam is deformed by the unwanted terms present in the force field. When $a_3 = 0$, the dominant term is the term linear in y, which causes the beam to be defocused in the y direction. This is shown in the middle panel of Fig. 4.3. When a_3 is large and negative, the beam is focused in the x-direction and defocused in the y-direction, this is shown in the left panel of Fig. 4.3. When a_3 is large and positive the beam is focused in the y-direction and defocused in the x-direction, this is shown in the right panel of Fig. 4.3. In Fig. 4.4 the FWHM of the transverse distribution of a beam of CO $(a^{3}\Pi)$ molecules in the high-field seeking (HFS) J = 6, $M\Omega = 6$, $\Omega = 1$ and low-field seeking (LFS) J = 6, $M\Omega = -6$, $\Omega = 1$ states is shown as a function of a_{3} . Let us first turn to the distribution of the high-field seekers, shown as the solid lines in the figure. It is seen that the beam is focused in the x-direction when $a_{3}/a_{1} < 0$ and defocused when $a_{3}/a_{1} > 0$. In the y direction, the beam is focused when $a_{3}/a_{1} > 0.5(a_{2}/a_{1})^{2} = 0.02$ and defocused when $a_{3}/a_{1} < 0.5(a_{2}/a_{1})^{2} = 0.02$. The cross-section of the beam, proportional to the product of the two curves, is larger than that of the undeflected beam. Note that for molecules in low-field seeking states (shown as the dashed lines in Fig. 4.4) the situation is reversed; the cross-section of the beam is smaller, irrespectively of a_{3} . And, when $0 < a_{3}/a_{1} < 0.5(a_{2}/a_{1})^{2}$, low-field seekers are focused in both directions.

The optimal choice of a_3 depends to some degree on experimental details. If one works with high-field seekers only, one might choose a_3 to be slightly negative such that the separation between molecules in different states becomes larger. In our experiment on metastable CO, we will use both high-field seekers and low-field seekers and we chose a_3 to be close to zero. It is noted that in molecular beam deflection experiments that use a two-wire field, often the the molecular beam is chosen to be at the position where the field is most homogeneous in the y-axis. This is referred to as the 'Hamburg' geometry [91] and corresponds to choosing $a_3/a_1 = 0.5(a_2/a_1)^2$.

4.3 A weak-focusing storage ring for polar molecules

A simple storage ring for polar molecules in high-field seeking states can be formed by bending the deflection fields discussed in the previous session into a circle. Such a storage ring is the direct analogue of the weak-focusing cyclotron for charged particles demonstrated by Lawrence in 1933 [98]. In a cyclotron, a magnetic field is used to bend charged particles in a circle while they are accelerated using electric fields. It was shown by Bethe and Rose [99] and Kerst and Serber [100] that the trajectories in a cyclotron are only stable if the magnetic field drops off slightly as a function of its radius. In this section, we will calculate the required form of the electric field of a weak-focusing storage ring for polar molecules ¹.

Let us assume that a BB deflection field similar to the one shown in Fig. 4.1 is bent into a circle of radius, $R_{\rm ring}$ (we chose a BB deflection field as it seems easier to inject and detect molecules in such a geometry). The y-direction is chosen to be the vertical direction, while x is chosen to be in the plane of the ring, such that $x = r - R_{\rm ring}$. In order for the trajectories to be stable, two

¹After submission of this manuscript, we became aware of the work by Ketterle and Pritchard [101] who have analysed weak-focusing electric and magnetic storage rings for atoms. Their conclusions are in agreement with the outcome of our analysis as given in Sec. 4.3.

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conditions must be met; (i) the applied force must vanish at the equilibrium orbit (chosen to be at x = 0, y = 0) and, (ii) for small displacements, the force should tend to restore the particle towards the equilibrium orbit. In keeping with literature on cyclotrons, we introduce the so-called field index, n, via:

$$n(r) = -\frac{\partial F_{\text{Stark}}/F_{\text{Stark}}}{\partial r/r} = -\frac{r}{F_{\text{Stark}}}\frac{\partial F_{\text{Stark}}}{\partial r}.$$
(4.8)

For $r = R_{\text{ring}}$ and $F_{\text{Stark}} = \sqrt{F_{\text{Stark},x}^2 + F_{\text{Stark},y}^2}$ given by Eq. (4.5) and Eq. (4.6), this leads to:

$$n(r = R_{\rm ring}) = -2\frac{b_3}{b_2}\frac{R_{\rm ring}}{r_0}.$$
(4.9)

If we neglect terms that are non-linear in the position, the force in the x-direction is given by:

$$F_{x} = F_{\text{centrifugal}} + F_{\text{Stark},x}$$

$$= \frac{mv_{\varphi}^{2}}{R_{\text{ring}} + x} + \mu_{\text{eff}} E_{0} \left(\frac{b_{2}}{b_{1}} \frac{1}{r_{0}} + 2\frac{b_{3}}{b_{1}} \frac{x}{r_{0}^{2}}\right)$$

$$= \frac{mv_{\varphi}^{2}}{R_{\text{ring}}} \left(1 - \frac{x}{R_{\text{ring}}}\right) + \mu_{\text{eff}} E_{0} \left(\frac{b_{2}}{b_{1}} \frac{1}{r_{0}} + 2\frac{b_{3}}{b_{1}} \frac{x}{r_{0}^{2}}\right)$$

$$= \left[\frac{mv_{\varphi}^{2}}{R_{\text{ring}}} + \mu_{\text{eff}} E_{0} \frac{b_{2}}{b_{1}} \frac{1}{r_{0}}\right] - \left[\frac{mv_{\varphi}^{2}}{R_{\text{ring}}^{2}} - 2\mu_{\text{eff}} E_{0} \frac{b_{3}}{b_{1}} \frac{1}{r_{0}^{2}}\right] x,$$
(4.10)

with v_{φ} the longitudinal velocity. The first stability condition requires $F_x = 0$ at the equilibrium orbit. This leads to:

$$\frac{b_2}{b_1} = -\frac{mv_{\varphi}^2}{\mu_{\rm eff}E_0} \frac{r_0}{R_{\rm ring}}.$$
(4.11)

For the second stability condition we write F_x , as:

$$F_x \equiv -k_x x = -\left[\frac{m v_{\varphi}^2}{R_{\rm ring}^2} - 2\mu_{\rm eff} E_0 \frac{b_3}{b_1} \frac{1}{r_0^2}\right] x.$$
(4.12)

Thus, molecules will oscillate around the equilibrium axis with an angular frequency given by:

$$\omega_x = \sqrt{\frac{k_x}{m}} = \sqrt{\frac{v_{\varphi}^2}{R_{\text{ring}}^2} - 2\frac{\mu_{\text{eff}}E_0}{m}\frac{b_3}{b_1}\frac{1}{r_0^2}}$$

$$= \Omega\sqrt{1-n}.$$
(4.13)

with $\Omega = v_{\varphi}/R_{\text{ring}}$ being the cyclotron frequency, and n as defined in Eq. (4.9).

Similarly, the force in the y-direction can be written as:

$$F_{y} \equiv -k_{y}y = \mu_{\text{eff}}E_{0}\left(\left(\left(\frac{b_{2}}{b_{1}}\right)^{2} - 2\frac{b_{3}}{b_{1}}\right)\frac{y}{r_{0}^{2}}\right).$$
(4.14)

And thus:

$$\omega_y = \sqrt{\frac{k_y}{m}} = \sqrt{-\frac{\mu_{\text{eff}}E_0}{m} \left(\left(\frac{b_2}{b_1}\right)^2 - 2\frac{b_3}{b_1}\right)\frac{1}{r_0^2}}$$

$$= \Omega\sqrt{n - \frac{mv_{\varphi}^2}{\mu_{\text{eff}}E_0}}.$$
(4.15)

In order to have stable confinement, we require the oscillation frequencies in both directions to be real. This is the case when:

$$\frac{mv_{\varphi}^2}{\mu_{\rm eff}E_0} < n < 1.$$
(4.16)

Thus, for high-field seekers, stability is only possible when the Stark shift of the molecule is larger than two times the kinetic energy of the molecules, regardless of $R_{\rm ring}$. Hence a weak-focusing storage ring for polar molecules in high-field seeking states can only store beams at very low velocity. For instance, for CO (a³II) molecules in the $J = 1, M\Omega = 1, \Omega = 1$ state in an electric field of 58.8 kV/cm, the maximum velocity that can be stored is about 15 m/s. It should be noted that in this derivation we have used $R_{\rm ring} \gg r_0$. For smaller rings, the multipole expansion should be written in cylindrical coordinates [102]. This decreases the stability region by a factor of 1/3.

It is interesting to, once again, compare a weak-focusing storage ring for polar molecules in high-field seeking states with a cyclotron for charged particles. In a cyclotron, trajectories are stable when 0 < n < 1. Thus, the analogy would be complete, if it wasn't for the left-hand side of Eq. (4.16) being unequal to zero. This term arises from the fact that for polar molecules in electric fields, $\nabla \vec{F}$ is not necessarily equal to zero [80]. As a result of the extra term, the stability region for high-field seekers is decreased, while the stability region for low-field seekers is increased. Consequently, it is easy to construct a stable weak-focusing storage ring for low-field seekers [103] but near impossible to store high-field seekers in a weak-focusing ring.

As a final note, we consider the so-called wire traps, proposed by Sekatskii [104], Sekatskii and Schmiedmayer [105] and Jongma *et al.* [40]. These are based on the fact that the electric field between two coaxial electrodes scales with the distance r from the axis as 1/r. This implies that molecules with a linear Stark effect experience a force that scales as $1/r^2$, and will be captured in stable "planetary" orbits. By comparison with the stability criterion, Eq. (4.16), we see that the electric field in a wire trap drops too quickly (n = 2) and the motion is unstable according to the used definition. Molecules in a wire trap are not stably confined around a certain equilibrium orbit, they are merely confined around the wire. Consequently, cooling techniques, such as sympathetic or evaporative cooling, cannot be applied to molecules in a wire trap (or to molecules in a storage ring based on a toroidal wire [106]).

4.4 AG ring

In a cyclotron for charged particles, the trajectories are stable in the horizontal and vertical plane if the field index, n, is between 0 and 1. In this case the oscillation frequencies are always a fraction of the cyclotron frequency. It was shown by Courant and Snyder in 1953 [107], that much stronger confinement can be achieved by alternating the field index between a large positive and a large negative value. In this case, the particles are alternately focused and defocused in both planes. As the particles are, on average, further away from the equilibrium orbit when the field is focusing and closer to the equilibrium orbit when the field is defocusing, the trajectories are stable in both planes. These rings are called strong-focusing or alternating-gradient (AG) storage rings.

The application of AG focusing for polar molecules was first discussed by Auerbach et al. [80] and first demonstrated by Kakati and Lainé [108]. A storage ring for hydrogen atoms based on magnetic AG lenses was proposed by Thompson *et al.* [109]. More recently AG focusing was used for decelerating [96, 110] and guiding [111, 112] beams of heavy polar molecules. Nishimura et al. [102] presented a design for a three meter diameter AG storage ring capable of storing beams with a forward velocity of 30 m/s. This AG ring consists of eight octants, each one containing a bend element, a buncher and a pair of alternating-gradient focusing triplets. Here, we propose an AG ring consisting of 40 straight deflection fields arranged in a circle, similar to a storage ring for molecules in low-field seeking states that was recently demonstrated by Zieger *et al.* [113]. Each deflection fields contains a strong quadrupole (b_2) term to deliver the necessary centripetal force and a hexapole (b_3) term to focus the molecules. By alternating the sign of the b_3 term in subsequent sections, molecules are alternately focused and defocused in both planes, leading to stable trajectories.

In order to determine the stability of the ring, we use a computer code that was developed to simulate the trajectories through a storage ring for low-field seeking states (see Heiner [114] for details). In our calculation, we consider a storage ring with a radius, $R_{\rm ring}$, equal to 0.25 m, consisting of 40 straight segments with a length of ≈ 39 mm. The segments are chosen to be of the BBtype shown on the right hand side of Fig. 4.1, with $\Phi_0 = 10$ kV, $r_0 = 1.7$ mm, $b_1 = 1$ and $b_2 = -0.2$. The longitudinal velocity that can be confined in this ring follows from Eq. (4.11). For CO (a³II) molecules in the high-field seeking $J = 1, M\Omega = 1, \Omega = 1$ state with an effective dipole moment of 0.7D, corresponding to 0.011 cm⁻¹/(kV/cm), the maximum velocity is 92 m/s. If the segments are indexed by s, the hexapole term in the sth deflection fields is given by:

$$b_3 = b_{3c} + (-1)^s b_{3a} = \frac{b_2}{4} \left(\frac{r_0}{R_{ring}} + \frac{b_2}{b_1} \right) + (-1)^s b_{3a}, \tag{4.17}$$

with b_{3a} and b_{3c} an alternating and a constant hexapole term, respectively. In this way, molecules are focused in the x plane and defocused in the y plane in odd segments, and vice versa in the even segments. The constant hexapole term, b_{3c} , is added to ensure that the working conditions in the x and y plane are similar. In the calculation, typically 10^5 molecules are generated with a random initial position and velocity. The acceptance is then found by multiplying the fraction of surviving molecules after a set number of roundtrips by the phase space volume of the initial packet. The aperture in the vertical direction is determined by the electrodes and in the horizontal direction by the non-linear terms in the force field.

In Fig. 4.5 the transverse acceptance of the AG ring is plotted as a function of the alternating hexapole term, b_{3a} . We see that the acceptance peaks when b_{3a} is equal to about 0.08. This corresponds to the situation when the molecules make slightly less than halve an oscillation in a single segment, as expected from the theory on AG focusing [96]. If the b_{3a} is increased further the molecules are over-focused and the motion becomes unstable. At the optimal value of b_{3a} the acceptance is 40 (mm×m/s)². This corresponds to a trap depth of about 8 mK and an effective aperture of about 2×2 mm. The acceptance is about 200 times smaller than the acceptance calculated for the storage ring for low-field seeking states of Zieger *et al.* [113, 114], and about 4 times smaller than the acceptance calculated for an AG guide for CaF molecules [112]. It should be noted, however, that the acceptance of AG focusing devices is very sensitive for the mechanical alignment of the AG lenses, and numerical calculations usually greatly overestimate the acceptance [96].

4.5 Conclusion

In order to make optimal use of manipulation tools for polar molecules it is important to understand their possibilities and limitations. In this paper, we analyze deflection fields in terms of a multipole expansion and find a simple expression for the resulting force. It is found that the field contains a term that focuses molecules in low-field seeking state and defocuses molecules in highfield seeking states perpendicular to the deflection direction. This term arises from the fact that $\nabla \vec{F}$ is unequal to zero. It can be made small by choosing $a_2/a_1 \ll 1$, but this goes at the expense of the strength of the deflection force. The force in a two wire field in the 'Hamburg' geometry is homogeneous in the direction perpendicular to the deflection. This corresponds to a positive value



Figure 4.5: Transverse acceptance of metastable CO molecules in a 0.5 meter diameter alternating-gradient ring consisting of 40 deflection fields as a function of the alternating hexapole b_{3v} , with $\Phi_0 = 10$ kV, $r_0 = 1.7$ mm, $b_1 = 1$, $b_2 = -0.2$ and $b_3 = b_{3c} \pm b_{3a}$. The longitudinal velocity of the stored molecules is equal to 92 m/s.

for the hexapole term, a₃. From our simulations, we find that it is advantageous to choose a₃ to be close to zero or slightly negative.

By bending a deflection fields into a circle a simple storage ring for polar molecules in high-field seeking states can be created. It is shown that a weakfocusing storage ring for polar molecules can only store beams at low velocities and is of little practical relevance.

A strong-focusing (alternating-gradient) storage ring can be created by arranging many straight deflection fields in a circle and by alternating the sign of the hexapole term between adjacent deflection fields. The acceptance of such a ring is numerically calculated for realistic parameters and is found to be 40 $(\text{mm}\times\text{m/s})^2$. Further study is necessary to optimize the geometry and to investigate how varying the applied fields to confine the molecules in the longitudinal directions affects the acceptance in the transverse direction. One application of such a storage ring might be for performing an EDM measurement. The sensitivity of EDM measurements scales with the time that the molecules spend in the interaction zone, hence various labs are working on ways to increase this time by decelerating and possibly trapping the molecules [115]. It would seem possible to inject cryogenic beams [116, 117] of heavy polar molecules such as YbF, PbF or WC, with a velocity below 200 m/s directly into a 2 m diameter storage ring.

Chapter 5

Ramsey-type microwave spectroscopy on CO $(a^3\Pi)$

Abstract

Using a Ramsey-type setup, the lambda-doublet transition in the J = 1, $\Omega = 1$ level of the $a^3\Pi$ state of CO was measured to be 394 064 870(10) Hz. In our molecular beam apparatus, a beam of metastable CO is prepared in a single quantum level by expanding CO into vacuum and exciting the molecules using a narrow-band UV laser system. After passing two microwave zones that are separated by 50 cm, the molecules are state-selectively deflected and detected 1 meter downstream on a position sensitive detector. In order to keep the molecules in a single m_J^B level, a magnetic bias field is applied. We find the field-free transition frequency by taking the average of the $m_J^B = +1 \rightarrow m_J^B = +1$ and $m_J^B = -1 \rightarrow m_J^B = -1$ transitions, which have an almost equal but opposite Zeeman shift. The accuracy of this proof-of-principle experiment is a factor of 100 better than the previous best value obtained for this transition.

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5.1 Introduction

Measurements of transition frequencies in atoms and atomic ions nowadays reach fractional accuracies below 10^{-17} , making atomic spectroscopy eminently suitable for testing fundamental theories [25, 118, 119]. The accuracy obtained in the spectroscopic studies of molecules typically lags by more than three orders of magnitude, however, the structure and symmetry of molecules gives advantages that make up for the lower accuracy in specific cases [35]. Molecules are for instance being used in experiments that search for time-symmetry violating interactions that lead to a permanent electric dipole moment (EDM) of the electron [120, 121], tests on parity violation [122, 123], tests of quantum electrodynamics [124], setting bounds on fifth forces [125] and testing a possible time-variation of the proton-to-electron mass ratio [19, 35, 126, 127].

Here we present the result of high-resolution microwave spectroscopy on CO molecules in the metastable $a^3\Pi$ state. Metastable CO has a number of features that make it uniquely suitable for precision measurements; (i) CO is a stable gas that has a high vapor pressure at room temperature making it straight forward to produce a cold, intense molecular beam; (ii) The $a^3\Pi$ state has a long lifetime of ~2.6 ms [39] and can be excited directly to single rotational levels at a well-defined time and position using laser radiation around 206 nm [38]; (iii) The metastable CO can be detected position dependently on a microchannel plate detector [54], allowing for a simple determination of the forward velocity as well as the spatial distribution of the beam; (iv) The most abundant isotopologue of CO ($^{12}C^{16}O$, 99% natural abundance) has no hyperfine structure, while other isotopologues are available commercially in highly enriched form; (v) The $a^3\Pi$ state has a strong first order Stark and Zeeman shift, making it possible to manipulate the beam using electric or magnetic fields [39–41].

Recently, it was noted that the two-photon transition between the J = 8, $\Omega = 0$ and the J = 6, $\Omega = 1$ levels in the $a^3\Pi$ state is 300 times more sensitive to a possible variation of the proton to electron mass ratio (μ) than purely rotational transitions [9, 10] (As discussed in the introduction of this thesis). We plan to measure these transitions with high precision. Here, as a stepping stone, we present measurements of the lambda-doublet transition in the J = 1, $\Omega = 1$ level around 394 MHz using Ramsey's method of separated oscillatory fields.

5.2 Energy level diagram

The $a^3\Pi$ state of CO is one of the most extensively studied triplet states of any molecule. The transitions connecting the $a^3\Pi$ state to the $X^1\Sigma^+$ ground state were first observed by Cameron in 1926 [42]. Later, the $a^3\Pi$ state was studied using radio frequency [43, 44, 52], microwave [45–47], infrared [48, 49], optical [50] and UV spectroscopy [51]. We have recently measured selected transitions in the CO $a^3\Pi - X^1\Sigma^+$ (0-0) band using a narrowband UV laser [10][Chapter 2] resulting in a set of molecular constants that describes the level structure of the $a^3\Pi$ state with an absolute accuracy of 5 MHz with respect to the ground state and a relative accuracy of 500 kHz within the $a^3\Pi$ state.

Fig. 5.1 shows the levels relevant for this study. The CO molecules are excited to the $\Omega = 1$ manifold of the $a^3\Pi$ state from the J = 0 and J = 1 levels of the $X^1\Sigma^+$ state using either the $R_2(0)$ or the $Q_2(1)$ transitions, indicated by straight arrows. The excitation takes place in an electric field that splits both lambda-doublet components into two levels labeled by Ωm_J^E as shown on the left hand side of the figure. The microwave transition is recorded in a region that is shielded from electric fields, but that is subjected



Figure 5.1: Energy level diagram showing the levels relevant for this experiment. CO molecules are excited from either of the two lowest rotational levels of the $X^1\Sigma^+$ ground state to the upper or lower lambda doublet component of the $\Omega = 1, J = 1$ level of the $a^3\Pi$ state using a narrow-band UV laser, indicated by the vertical arrows. An electric field is applied to lift the degeneracy of the m_J^E sublevels, enabling the excitation of a single m_J^E sublevel. In a magnetic field that is perpendicular to the electric field, the four m_J^E sublevels correspond to six m_J^B sublevels as indicated. The wavy arrows indicate the two microwave transitions that are measured in this work.
to a homogeneous magnetic field. In a magnetic field, both lambda-doublet components are split into three levels labeled by m_J^B as shown on the right hand side of the figure. In the region between the excitation zone and the microwave zone the applied magnetic field is perpendicular to the electric field. In this case, the $m_J^E = 0$ sublevel of the upper lambda-doublet component corresponds to the $m_J^B = -1$ sublevel while the $m_J^E = 0$ sublevel of the lower lambdadoublet component corresponds to the $m_J^B = +1$ sublevel, as indicated by the dashed arrows [128]. The $\Omega m_J^E = +1$ and $\Omega m_J^E = -1$ sublevels correspond to the $m_J^B = 0, -1$ and $m_J^B = 0, +1$ sublevels, respectively. The $m_J^B = +1$ and $m_I^B = -1$ sublevels exhibit a linear Zeeman effect of ~1 MHz/Gauss, respectively, while the $m_I^B = 0$ sublevel does not exhibit a linear Zeeman effect. Ideally, we would therefore record the $m_J^B = 0 \rightarrow m_J^B = 0$ transition. However, this transition is not allowed via a one-photon electric or magnetic dipole transition. Instead, we have recorded the $m_I^B = +1 \rightarrow m_I^B = +1$ and $m_I^B = -1 \rightarrow m_I^B = -1$ transitions indicated by the wavy arrows in the figure. To a first-order approximation, these transitions do not display a linear Zeeman shift. However, the mixing of the different Ω manifolds is parity dependent and as a result the Zeeman shift in the upper and lower lambdadoublet components are slightly different. Hence, the $m_J^B = +1 \rightarrow m_J^B = +1$ and $m_J^B = -1 \rightarrow m_J^B = -1$ transitions show a differential linear Zeeman effect of $\sim 10 \text{ kHz/Gauss}$. This differential linear Zeeman effect is opposite in sign for the two recorded transitions, and is canceled by taking the average of the two.

5.3 Experimental setup

Fig. 5.2 shows a schematic drawing of the molecular beam-machine used in this experiment. A supersonic, rotationally cold beam of CO molecules is produced by expanding either pure CO or a mixture of 20% CO in He into vacuum, using a solenoid valve (General Valve series 9). The backing pressure is typically 2 bar, while the pressure in the first chamber is kept below 10^{-5} mbar. After passing a 1 mm skimmer, the molecular beam is crossed at right angles with a UV laser beam that excites the molecules from the $X^1\Sigma^+$ ground state to the $a^3\Pi$ state. Details of the laser system are described elsewhere [10, 55, 129]. Briefly, a Ti:sapphire oscillator is locked to a CW Ti:sapphire ring laser and pumped at 10 Hz with a frequency doubled Nd:YAG-laser. The output pulses from the oscillator are amplified in a bow-tie type amplifier and consecutively doubled twice using BBO crystals. Ultimately, 50 ns, 1 mJ pulses around 206 nm are produced, with a bandwidth of approximately 30 MHz.

In the laser excitation zone a homogeneous electric field of 1.5 kV/cm is applied along the *y*-axis which results in a splitting of ~500 MHz between the $\Omega m_J^E = \pm 1$ and $m_J^E = 0$ sublevels, large compared to the bandwidth of the laser. In addition, a homogeneous magnetic field of typically 17 Gauss is applied along the molecular beam axis by running a 2 A current through a 100 cm long solenoid consisting of 600 windings. The current is generated by



Figure 5.2: Schematic drawing of the molecular beam setup. A supersonic, rotationally cold beam of CO molecules is produced by expanding CO gas into vacuum using a solenoid valve. After passing a 1 mm diameter skimmer, the molecules are excited to the metastable $a^3\Pi$ state using laser radiation tunable near 206 nm. An electric field of 1.5 kV/cm is applied in the excitation zone. Perpendicular to this electric field, a bias magnetic field of typically 17 Gauss is applied. Microwave transitions are induced by two microwave zones separated by 50 cm, in a Ramsey type setup. After passing the second microwave zone, molecules are state-selectively deflected using an inhomogeneous electric field and are subsequently detected using a position sensitive detector.

a current source (Delta electronics ES 030-10) that is specified to a relative accuracy of 10^{-3} . In the absence of an electric field, the magnetic field would give rise to a splitting of the m_J^B sublevels of ~15 MHz. In a strong electric field perpendicular to the magnetic field, the orientation and m labeling is determined by the electric field and the magnetic field splitting is below 1 MHz, small compared to the bandwidth of the laser. In our experiments, we excite the molecules to the $m_J^E = 0$ sublevel of either the lower or upper lambdadoublet component via the $R_2(0)$ or the $Q_2(1)$ transitions using light that is polarized in the z or y-direction, respectively (see for axis orientation the inset in Fig. 5.2). Upon exiting the electric field, the $m_J^E = 0$ sublevel of the lower lambda-doublet component adiabatically evolves into the $m_J^B = +1$ sublevel, while the $m_J^E = 0$ sublevel of the upper lambda-doublet component adiabatically evolves into the $m_J^B = -1$ sublevel, see Fig.5.1.

The microwave measurements are performed in a Ramsey-type setup consisting of two microwave zones that are separated by ~ 50 cm. Each microwave zone consists of two parallel cylindrical plates spaced 20 mm apart, oriented perpendicularly to the molecular beam axis with 5 mm holes to allow the molecules to pass through. Tubes of 5 cm length with an inner diameter of 5 mm are attached to the field plates. The two interaction regions are connected to a microwave source (Agilent E8257D) that generates two bursts of 50 μ s duration such that molecules with a velocity close to the average of the beam are inside the tubes when the microwave field is turned on and off. The electric component of the microwave field is parallel to the bias magnetic field along the z-axis, allowing $\Delta m_J^B = 0$ transitions only. Directional couplers are used to prevent reflections from one microwave zone to enter the other. Grids, not shown in the figure, are placed upstream and downstream from the interrogation zone to shield it from external electric fields.

After passing the microwave zones, the molecules enter a 30 cm long electrostatic deflection field formed by two electrodes separated by 3.4 mm, to which a voltage difference of 12 or 20 kV is applied for pure CO and CO seeded in helium, respectively. Ideally, the deflection field exerts a force on the molecules that is strong and position-independent in the y-direction while the force in the x-direction is zero. It has been shown by de Nijs and Bethlem [130][Chapter 4] that such a field is best approximated by a field that contains only a dipole and quadrupole term while all higher multipole terms are small. The electric field is mainly directed along the y-axis, i.e. parallel to the electric field in the laser excitation region. Hence, molecules that were initially prepared in a $m_J^E = 0$ sublevel and have not made a microwave transition will not be deflected. In contrast, molecules that made a microwave transition will end up either in the $\Omega m_J^E = +1$ or $\Omega m_J^E = -1$ sublevels and will be deflected upwards or downwards, respectively.

Finally, after a flightpath of 80 cm, sufficient to produce a clear separation between the deflected and non-deflected molecules, the molecules impinge on a Microchannel Plate (MCP) in chevron configuration, mounted in front of a fast response phosphor screen (Photonis P-47 MgO). The phosphor screen is imaged using a Charged-Coupled Device (CCD) camera (PCO 1300). Molecules in the $a^3\Pi$ state have 6 eV of internal energy which is sufficient to liberate electrons, that are subsequently multiplied to generate a detectable signal. The quantum efficiency is estimated to be on the order of 10^{-3} [54]. The voltage on the front plate of the MCP is gated, such that molecules with a velocity of $\pm 3\%$ around the selected velocity are detected only, and background signal due to stray ions and electrons is strongly suppressed. The recorded image is sent to a computer that determines the total intensity in a selected area. A photomultiplier tube is used to monitor the integrated light intensity emitted by phosphor screen. This signal is used for (manually) correcting the frequency of the UV laser if it drifts away from resonance. Note that due to the Doppler shift in the UV transition, the beam will be displaced in the x-direction when the laser frequency is off resonance. As the flight path of the molecules through the microwave zones will be different for different Doppler classes, this may result in a frequency shift. In future experiments this effect may be studied by measuring the transition frequency while changing the area of the detector over which the signal is integrated. At the present accuracy this effect is negligible.



Figure 5.3: Frequency scan of the UV-laser around the $R_2(0)$ transition showing two peaks corresponding to the $\Omega m_J^E = 1$ (left-hand side) and $m_J^E = 0$ (right-hand side) sublevels, respectively. The black circles are recorded by integrating the signal of the undeflected beam, while the red squares are recorded by integrating the signal of the upwards deflected beam.

5.4 Experimental results

Fig. 5.3 shows the integrated intensity on the MCP detector as a function of the frequency of the UV laser tuned around the $R_2(0)$ transition. An electric field of 1.5 kV/cm is applied along the *y*-axis while a magnetic field of 17 Gauss is applied along the *z*-axis. The polarization of the laser is parallel to the *y*axis. The black curve shows the number of undeflected molecules while the red dashed curve shows the number of upwards deflected molecules. As the Stark effect in the $X^1\Sigma^+$ state is negligible, the frequency difference between the two observed transitions directly reflects the splitting between the $\Omega m_J^E = +1$ and $m_J^E = 0$ (lower lambda-doublet) sublevels in the $\Omega = 1, J = 1$ level of the a³II state. The two peaks are separated by ~500 MHz, as expected in the applied fields [40]. When a magnetic field of 17 Gauss is applied, about 98% of the molecules that were initially prepared in the $m_J^E = 0$ sublevel remain



Figure 5.4: Typical images recorded on the CCD camera showing the spatial distribution of the beam when the laser is resonant with transitions to different sublevels, as indicated. Molecules in the $\Omega m_J^E = +1$ and $\Omega m_J^E = -1$ sublevels are upwards or downwards deflected, respectively, while molecules in the $m_J^E = 0$ sublevel experience almost no force. The white boxes define the integration areas used in the analysis.

in this sublevel until entering the deflection field, while 2% of the molecules are non-adiabatically transferred to one of the $\Omega m_J^E = +1$ sublevels. At lower magnetic fields, the depolarization increases strongly. When no magnetic field is applied, only one third of the beam remains in the $m_J^E = 0$ sublevel. Note, that although the depolarization gives rise to a loss in signal, it does not give rise to background signal in the microwave measurements.

Fig. 5.4 shows a number of typical images recorded on the CCD camera when the frequency of the laser is resonant with a transition to (a) the $\Omega m_I^E = +1$ sublevel, (b) the $m_I^E = +0$ sublevel and (c) the $\Omega m_I^E = -1$ sublevel of the $a^3\Pi$ state. In this measurement, the exposure time of the CCD camera is set to be 1 s, i.e., each image is the sum of 10 shots of the CO beam. Each white spot in the image corresponds to the detection of a single molecule. As seen, molecules in the $\Omega m_J^E = +1$ sublevel are being deflected upwards, while at the same time they experience a slight defocusing effect in the x direction. In contrast, molecules in the $\Omega m_I^E = -1$ sublevel are being deflected downwards, while experiencing a slight focusing effect in the x direction. These observations are in agreement with the analysis given in de Nijs and Bethlem [130] [Chapter 4]. The white boxes also shown in the figures define the area over which is integrated to determine the upwards deflected, undeflected and downwards deflected signal. Note that for recording these images the Ramsey tube containing the two microwave zones have been taken out. In this situation, typically, 1000 molecules are detected per shot. When the microwave zones are installed, the number of molecules reaching the detector is decreased by about a factor of 5. Gating the detector to select a specific velocity reduces the number of detected molecules further by a factor of 4.

Fig. 5.5 shows a power dependence of the microwave transition from the $m_J^B = +1$ sublevel in the lower lambda-doublet component to the $m_J^B = +1$ sublevel in the upper lambda-doublet component of the $\Omega = 1, J = 1$ level in the $a^3\Pi$ state. The frequency of the microwave field is set to the peak of the



Figure 5.5: Power dependence of the $m_J^B = +1 \rightarrow m_J^B = +1$ lambda-doublet microwave transition at resonance. The signal corresponds to the ratio of the number of molecules in the initial and final states. The black circles and red squares are recorded using the first and second microwave zone, respectively, while the solid and dashed curves result from a fit to the data.

resonance. The signal corresponds to the ratio of the integrated signal over the boxes for the undeflected and deflected beam shown in Fig. 5.4. Note that in this way, any pulse-to-pulse fluctuations in the signal due to the valve and UV-laser are canceled. Typically, 50 molecules per shot are detected. The black circles and red squares are recorded using the first and second microwave zone, respectively. The curves also shown are a fit to the data using

$$F(P) = a_0 \exp(-a_1 \sqrt{P}) \sin^2(a_2 \sqrt{P}),$$
(5.1)

with P being the microwave power. The observed deviations between the data and the fit are attributed to the fact that a fraction of the molecules that are deflected hit the lower electrode and are lost from the beam. As seen, four Rabi flops can be made in the second microwave zone, without significant decrease of coherence. The required power to make a $\pi/2$ pulse in the first microwave zone is three times larger than that in the second microwave zone. This is attributed to a poor contact for the microwave incoupling. For the Ramseytype measurements presented in the next sections, we balance the power in the two microwave zones by adding an attenuator to the cable that feeds the second microwave zone.

The linewidth of the resonance recorded by a single microwave zone is limited by the interaction time, $\Delta f = 1/\tau = v/l$, where v is the velocity of the molecular beam and l is the length of the microwave zone. In our case this corresponds to about 40 kHz. In order to decrease the linewidth and thereby increase the accuracy of the experiment, one needs to use slower molecules or a longer microwave zone. Ramsey demonstrated a more elegant way to reduce the linewidth by using two separate microwave zones [131]. In the first microwave zone a $\pi/2$ pulse is used to create an equal superposition of the upper and lower level. While the molecules are in free flight from the first to the second zone, the phase between the two coefficients that describe the superposition evolves at the transition frequency. In the second microwave zone, this phase is probed using another $\pi/2$ pulse. If the frequency of the microwave field that is applied to the microwave zones is equal to the transition frequency, the second pulse will be in phase with the phase evolution of the superposition and all molecules will end up in the excited state. If the frequency is however slightly different, the second pulse will be out of phase with the phase evolution of the superposition, and only a fraction of the molecules end up in the excited state. The so-called Ramsey fringes that appear when the frequency of the microwave field is scanned, have a periodicity that is now given by v/L, where L is the distance between the two microwave zones.

The black curve in the top panel of Fig. 5.6 shows the result of a Ramseytype measurement of the transition from $m_J^B = +1$ in the lower lambda-doublet component to $m_J^B = +1$ in the upper lambda-doublet component. Ramseyfringes appear as a rapid cosine modulation on a broad sinc-like line shape. The width of the sinc is determined by the interaction time from each microwave zone separately, and is given by v/l=800/0.02=40 kHz. The period of the cosine modulation is determined by the flight time between the two zones and is v/L=800/0.5=1.6 kHz. The red curve results from a fit to the data using

$$y = a_1 \frac{\sin^2\left(\frac{X}{4}\right)}{X^4} \left[X \cos\left(\frac{X}{4}\right) \cos\left(\frac{a_4 x + a_2}{2}\right) - a_3 x \sin(X/4) \sin\left(\frac{a_4 x + a_2}{2}\right) \right]^2,$$
(5.2)

with $X = \sqrt{\pi^2 + (a_3 x)^2}$ [127]. The green curve in the middle panel shows the difference between the experimental data and the fit. The bottom panel shows a zoomed in part of the central part of the peak. The black data points show the experimental data while the red curve is a fit. The observed deviations between the data and the fit are attributed to the fact that a fraction of the molecules that are deflected hit the lower electrode and are lost from the beam.



Figure 5.6: Ramsey-type measurement of the $m_J^B = +1 \rightarrow m_J^B = +1$ transition. The black curve in the top panel shows the measured ratio of the number of molecules in the initial and final states, while the red curve results from a fit to the data. The green curve in the middle panel shows the difference between the experimental data and the fit. The lower panel shows a zoomed in part around the resonance frequency. The frequency axis is offset by 394 229 829 Hz.



Figure 5.7: A recording of the central fringe in a beam of pure CO (black circles) and a beam of CO seeded in helium (red squares). A difference between the frequencies of the central fringes can be observed. This is due to phase shifts, and it can be eliminated by extrapolating to zero velocity.

As the deviations are symmetric around zero, the obtained transition frequency is not affected.

In order to identify the central fringe, we have recorded the fringe pattern using beams at different velocities. Fig. 5.7 shows the central fringe recorded in a beam of pure CO (black circles) and a beam of CO seeded in helium (red squares). The curves also shown are a \sin^2 fit to the data points. As a result of the higher velocity of the CO in helium, the observed fringes are wider. The central fringe, however, is always found near (but not exactly at) the transition frequency. Note that in our setup, the two inner field plates are grounded. As a result the two zones have a π phase difference and the transition frequency corresponds to a minimum in the fringe pattern. As observed, there is a small frequency shift between the measurements due to a phase difference between the microwave zones. The true transition frequency is found by extrapolating to zero velocity.

To determine the transition frequency, we typically record two fringes around

the central fringe and fit a \sin^2 function to the data. Such a scan takes approximately 600 seconds and allows us to determine the central frequency with an statistical uncertainty of about 4 Hz for measurements in a pure beam of CO and about 8 Hz for measurements on CO seeded in helium. These uncertainties are close to the ones expected from the number of molecules that are detected in our measurements. Note that by simultaneously measuring the number of molecules in the initial and the final state, shot-to-shot noise from the pulsed beam and the laser is canceled. Hence, we expected to be limited by quantum projection noise only. Indeed, on time scales below a few minutes the uncertainty reaches the shot-noise limit. On longer time scales, however, the statistical uncertainty is larger than expected. We attribute this to fluctuations of the magnetic bias field (*vide infra*).

In order to quantify possible systematic effects, we have recorded many single scans while varying all parameters that may influence the transition frequency.

5.4.1 Linear and quadratic Zeeman shift

The frequency that we obtain from a single measurement depends on the strength of the magnetic bias field as the recorded transitions experience a (differential) linear Zeeman shift. The upper panel of Fig. 5.8 shows the $m_I^B = +1 \rightarrow m_I^B = +1$ and $m_I^B = -1 \rightarrow m_I^B = -1$ transitions at three different magnetic fields. The x-axis displays the average magnetic field over the flight path of the molecules. As observed, the $m_J^B = +1 \rightarrow m_J^B = +1$ and $m_I^B = -1 \rightarrow m_I^B = -1$ transitions experience an equal but opposite linear Zeeman shift of $\sim 10 \text{ kHz/Gauss}$. The solid line results from a calculation with PGOPHER [63] using the molecular constants from de Nijs *et al.* [10][Chapter 2] and the g-factor from Havenith et al. [48]. In order to determine the field free transition frequency, we take the average of the $m_J^B = +1 \rightarrow m_J^B = +1$ and $m_J^B = -1 \rightarrow m_J^B = -1$ transitions recorded at the same magnetic field. These averages are shown in the lower panel of Fig. 5.8. The solid line shows a calculation with PGOPHER. From this calculation, we find that the linear Zeeman effect cancels exactly while the quadratic Zeeman shift is 14 mHz/Gauss². We have performed most of our measurements at a bias magnetic field of ~ 17 Gauss; at this field the quadratic Zeeman shift is still only 4 Hz while depolarization of the beam is avoided.

5.4.2 Magnetic field instabilities

Due to the sensitivity of the two transitions to the strength of the magnetic field, any magnetic field noise is translated into frequency noise. As a result of these fluctuations, the decrease of the uncertainty in our measurement as a function of measurement time is smaller than expected from the number of molecules that are detected. Whereas fluctuations of the magnetic field on short timescales add noise, fluctuations on longer time scales may give rise



Figure 5.8: Recorded frequencies of the $m_J^B = -1 \rightarrow m_J^B = -1$ and the $m_J^B = +1 \rightarrow m_J^B = +1$ transitions as a function of the magnetic field (upper panel) and the averaged value of these two transitions (lower panel). The solid curve results from a calculation using PGOPHER. Both frequency axes are offset by 394 064 983.6 Hz.



Figure 5.9: Measurements of the transition frequency at different molecular beam velocities. The black, solid, curve shows a fitted linear slope, the red and green dashed curves show one and two standard deviation confidence bands, respectively.

to systematic shifts. In order to cancel slow drifts, we switch between the $m_J^B = +1 \rightarrow m_J^B = +1$ and $m_J^B = -1 \rightarrow m_J^B = -1$ transitions every 20 minutes, limited by the time it takes to change the frequency and polarization of the UV laser.

5.4.3 Phase offsets

If the cables that connect the two microwave zones are not of the same length, there will be a phase shift that gives rise to a velocity dependent frequency shift. As in our setup a difference in length as small as 1 mm results in a frequency shift of 3 Hz at 800 m/s, the phase shift needs to be measured directly. Therefore we have recorded the transitions at different molecular velocities and extrapolate to zero, as shown in Fig. 5.9. From a total of 20 scans, of the $m_J^B = +1 \rightarrow m_J^B = +1$ and $m_J^B = -1 \rightarrow m_J^B = -1$ transitions measured in a beam of pure CO, v=800 m/s, and in a beam of 20% CO in helium, v=1270 m/s, we find the extrapolated frequency to be equal to



Figure 5.10: Recorded frequencies of the $m_J^B = -1 \rightarrow m_J^B = -1$ transition as a function of the applied DC voltage in the first (black circles) and second (red squares) microwave zone. The solid black and dashed red curves result from quadratic fits to the data.

 $394\ 064\ 874(10)$ Hz. The velocity of the molecular beam is determined from the known dimensions of the molecular beam machine and the time-delay between the pulsed excitation laser and the gate-pulse applied to the detector. Note that uncertainties in the distance between the excitation zone and the detector are canceled when we extrapolate to zero velocity. In order to find the field-free transition, we have to account for a 4 Hz shift due to the the quadratic Zeeman shift in the magnetic bias field. Thus, finally the true transition frequency is found to be $394\ 064\ 870(10)$ Hz.

5.4.4 2nd order Doppler shift and motional Stark effect

The shift due to the motional Stark effect is estimated to be below 1 Hz. Moreover, it scales linearly with the velocity and is compensated by extrapolating to zero velocity. The second order Doppler is $\Delta \nu = \nu_0 (v/c)^2 \approx 3$ mHz and is negligible at the accuracy level of the experiment.

5.4.5 DC-Stark shift

Electric fields in the interaction region due to leakage from the excitation and deflection fields, patch potentials in the tube and contact potentials between the field plates of the microwave zone induce Stark shifts. As the Stark shifts in the $m_J^B = -1 \rightarrow m_J^B = -1$ and the $m_J^B = +1 \rightarrow m_J^B = +1$ transitions are equal and both positive, they are not canceled by taking the average of the two. The biggest effect may be expected as a result of contact potentials. We have tested possible Stark shifts in the microwave zones by adding a small DC component to the microwave field. Fig. 5.10 shows the resonance frequency of the $m_J^B = -1 \rightarrow m_J^B = -1$ transition as a function of the applied DC voltage in the first (black data points) and second (red data points) microwave zones. The black and red curves show a quadratic fit to the data. The Stark shift is almost symmetric around zero, the residual DC-Stark shift is estimated to be below 1 Hz.

5.4.6 AC-Stark shift

To study the effect of the microwave power on the transition frequency, we have varied the microwave power by over an order of magnitude. No significant dependence of the frequency on microwave power was found.

5.4.7 Absolute frequency determination

The microwave source used in this work (Agilent E8257D) is linked to a Rubidium clock and has an absolute frequency uncertainty of 10^{-12} , i.e., ~ 0.4 mHz at 394 MHz, negligible at the accuracy level of the experiment.

5.5 Conclusion

Using a Ramsey-type setup, the lambda-doublet transition in the J = 1, $\Omega = 1$ level of the $a^3\Pi$ state of CO was measured to be 394 064 870(10) Hz. Frequency shifts due to phase shifts between the two microwave zones of the Ramsey spectrometer are canceled by recording the transition frequency at different velocities and extrapolating to zero velocity. Our measurements are performed in a magnetic bias field of ~17 Gauss. Frequency shifts due to the linear Zeeman effect in this field are canceled by taking the average of the $m_J^B = +1 \rightarrow m_J^B = +1$ and $m_J^B = -1 \rightarrow m_J^B = -1$ transitions. The quadratic Zeeman effect gives rise to a shift of 4 Hz which is taken into account in the quoted transition frequency. Other possible systematic frequency shifts may be neglected within the accuracy of the measurement. The obtained result is in agreement with measurements by Wicke *et al.* [44], but is a 100 times more accurate.

An important motivation for this work is to estimate the possible accuracy that might be obtained on the two-photon transition connecting the J = 6, $\Omega =$ 1 level to the J = 8, $\Omega = 0$ level that is exceptionally sensitive to a possible time-variation of the fundamental constants [9, 10][Chapter 2]. An advantage of this transition is that the $m_J^B = 0 \rightarrow m_J^B = 0$ transition can be measured directly, thus avoiding the problems with the stability of the magnetic bias field. A disadvantage is that the population in the J = 5 level is much smaller than the population in the J = 1 level, reducing the number of molecules that is observed, while the Stark shift is considerable less, making it necessary to use a longer deflection field.

In order to obtain a constraint on the time-variation of μ at the level of 5.6 $\times 10^{-14}$ /yr, the current best limit set by spectroscopy on SF₆ [35], we would need to record the J = 6, $\Omega = 1 \rightarrow J = 8$, $\Omega = 0$ two-photon transition at 1.6 GHz with an accuracy 0.03 Hz over an interval of one year. To reach this precision within a realistic measurement time, say 24 hours, the number of detected molecules should be at least 2500 per shot, i.e., 50 times more than detected in the current experiment but now starting from the less populated J = 5 level. Although challenging, this seems possible by using a more efficient detector [41] and/or by using quadrupole or hexapole lenses to collimate the molecular beam [54].

Chapter 6

Sensitivity of rotational transitions in CH and CD to a possible variation of fundamental constants

Abstract

The sensitivity of rotational transitions in CH and CD to a possible variation of fundamental constants has been investigated. Largely enhanced sensitivity coefficients are found for specific transitions which are due to accidental degeneracies between the different fine-structure manifolds. These degeneracies occur when the spin-orbit coupling constant is close to four times the rotational constant. CH and particularly CD match this condition closely. Unfortunately, an analysis of the transition strengths shows that the same condition that leads to an enhanced sensitivity suppresses the transition strength, making these transitions too weak to be of relevance for testing the variation of fundamental constants over cosmological time scales. We propose a test in CH based on the comparison between the rotational transitions between the e and fcomponents of the $\Omega' = 1/2, J = 1/2$ and $\Omega' = 3/2, J = 3/2$ levels at 532 and 536 GHz and other rotational or lambda-doublet transitions in CH involving the same absorbing ground levels. Such a test, to be performed by radioastronomy of highly redshifted objects, is robust against systematic effects.

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6.1 Introduction

A possible variation of the fundamental constants can be detected by comparing transitions between levels in atoms and molecules that have a different functional dependence on these constants. The limit that can be derived from such a test is proportional to the relative accuracy of the experiment and inversely proportional to both the time interval covered by the experiment and the sensitivity of the transition to a possible variation. The duration of tests that are conducted in the laboratory is typically limited to a few years, but these tests have the advantage that one can choose transitions in atoms or molecules that are very sensitive to a variation, transitions that can be measured to an extremely high precision, or both. Tests over cosmological time scales, on the other hand, typically span 10^9 years, but have the disadvantage that only a limited number of molecular transitions are observed at high redshift, and the accuracy of the observed lines is relatively low.

Up to very recently, tests of the time-variation of the proton-to-electron mass ratio, $\mu = m_p/m_e$, over cosmological time scales were based exclusively on molecular hydrogen, the most abundant molecule in the universe and observed in a number of high redshift objects. The transitions in molecular hydrogen correspond to the transitions between different electronic states and exhibit sensitivity coefficients, K_{μ} , ranging from -0.05 to +0.01 [13, 14]. Recently, the observations of the inversion transition in ammonia ($K_{\mu} = -4.2$) [16–18] and torsion-rotation transitions in methanol (K_{μ} ranging from -33 to -1) [8, 21, 132], at high redshift, have resulted in more stringent limits on the variation of μ .

In this chapter, we discuss the sensitivity of rotational transitions in CH and its deuterated isotopologue, CD to a variation of the proton-to-electron mass ratio, μ , and the fine structure constant, α . CH is a small diatomic radical that is frequently targeted in astrophysical studies, as it is a well established and well understood proxy of H₂ [133]. These studies have been targeting primarily the interstellar medium in the local galaxy. However, a survey for CH at high redshift is currently being conducted at the Atacama Large Millimeter Array (ALMA) [23]. CH and CD have a spin-orbit coupling constant, A, that is close to two and four times their respective rotational constant, B. This leads to near degeneracies between rotational levels of different spin-orbit manifolds. As a result, the rotational transitions between the near-degenerate levels have an increased sensitivity to a variation of μ . The work presented in this chapter is complementary to that of Kozlov [134], who calculated the sensitivity coefficients of lambda-doublet transitions in CH and other diatomic radicals.

6.2 Energy level structure of a $^{2}\Pi$ state

In this chapter, we investigate CH and CD in their ${}^{2}\Pi$ ground state. Molecules in ${}^{2}\Pi$ states have three angular momenta that need to be considered; the electronic orbital angular momentum, **L**, the spin angular momentum, **S**, and the rotational angular momentum, **R**. Depending on the energy scales associated with these momenta, the coupling between the vectors is described by the different Hund's cases. In Hund's case (a), **L** is strongly coupled to the internuclear axis and **S** couples to **L** via spin-orbit interaction. States are labeled by J, the quantum number associated with the total angular momentum, and Ω , the sum of Λ and Σ , the projections of **L** and **S** on the internuclear axis, respectively. When the rotational energy becomes comparable to the energy of the spin-orbit interaction, **S** decouples from the internuclear axis, and Hund's case (b) is more appropriate. In this case the molecular levels are labeled by $N = R + \Lambda$, and J.

In heavy molecules at low J, the spin-orbit interaction is much larger than the rotational energy splitting. As a result, the energy level structure consists of two spin-orbit manifolds separated by an energy A, each having a pattern of rotational levels with energies given by Bz, with $z = (J + 1/2)^2 - 1$. In light molecules, $A \sim Bz$ already at low J. In this case the two manifolds are considerably mixed and the energies are not described by a simple formula. To describe a situation that is intermediate between Hund's case (a) and (b), the wavefunction of a state is written as a superposition of pure Hund's case (a) wavefunctions:

$$|\Omega', J\rangle = c_{\Omega', J, \Omega = 1/2} |\Omega = 1/2, J\rangle + c_{\Omega', J, \Omega = 3/2} |\Omega = 3/2, J\rangle$$
(6.1)

where $c_{\Omega',J,\Omega=1/2}$ and $c_{\Omega',J,\Omega=3/2}$ are coefficients signifying the $\Omega = 1/2$ and $\Omega = 3/2$ character, respectively, of the wavefunction of the state $|\Omega', J\rangle$. Note that Ω' is used to label the rotational levels of the different spin-orbit manifolds, while Ω is used to denote the pure Hund's case (a) wave functions. The coefficients are the eigenvectors of the Hamiltonian matrix that is given, for instance, by Amiot *et al.* [135]. When the lambda-doublet splitting, centrifugal distortion and hyperfine splitting are neglected, the Hamiltonian matrix reduces to [136]:

$$\begin{pmatrix} \frac{1}{2}A + Bz & -B\sqrt{z} \\ -B\sqrt{z} & -\frac{1}{2}A + B(z+2) \end{pmatrix}.$$
(6.2)

The first row represents the ${}^{2}\Pi_{\Omega=3/2}$ component, the second the ${}^{2}\Pi_{\Omega=1/2}$ component. Although most of our calculations use the extensive matrix, all relevant features can be understood from the simplified matrix.

The level scheme of CH is depicted in Fig. 6.1. In CH (A = 1.98B), the $\Omega' = 1/2, J = 3/2$ level lies about 200 GHz below the $\Omega' = 3/2, J = 5/2$ level, whereas in CD (A = 3.65B) the energy difference is only 30 GHz. In Fig. 6.1, the lambda-doublet splittings are exaggerated by a factor of 10. It was shown by Kozlov [134] that, as a result of an inversion of the lambda-doublet splitting in the $\Omega' = 3/2$ -manifold, the different components of the lambda doublet become near-degenerate at $\Omega' = 3/2, J = 3/2$ for CH, leading to enhanced sensitivity coefficients of the lambda-doublet transitions.

Let us now consider the sensitivity of rotational transitions to a possible variation of μ . The sensitivity coefficient of a transition is defined as

$$K_{\mu} = \frac{\mu}{\nu} \frac{\partial \nu}{\partial \mu} = \frac{\mu_{red}}{\nu} \frac{\partial \nu}{\partial \mu_{red}}$$
(6.3)



Figure 6.1: Level scheme of the ground state of CH, calculated using the Hamiltonian matrix from Amiot *et al.* [135] and the molecular constants given by McCarthy *et al.* [137]. Indicated are five different types of rotational transitions, labeled I through V. The lambda-doublet splitting is exaggerated by a factor of 10. Also indicated are the symmetries of the electronic part of the wave function, denoted by *e* and *f* and the total parity, denoted by + and -. Note: The *e* and *f* labels of the $\Omega = 1/2$ manifold were inverted in the published version, the correct version is shown above.

with

$$\nu = (E_{\Omega'_{t},J_{f}} - E_{\Omega'_{i},J_{i}})/h \tag{6.4}$$

the transition frequency, and μ_{red} the reduced mass of the molecule. Note that it is assumed here that the neutron and proton masses vary in the same way. The K_{μ} and K_{α} coefficients can now be calculated using the Hamiltonian matrix by including the dependence of the molecular constants on the reduced mass of the molecule and α , given, for instance, in Beloy *et al.* [138], and the values of the molecular parameters for CH from McCarthy *et al.* [137] and for CD from Halfen *et al.* [139]. As the effective Hamiltonian used for these molecules is an accurate physical representation, the sensitivity coefficients that are found in this way are very accurate. For instance, in previous work on CO, the transition frequencies in different isotopologues could be predicted to a relative accuracy well within 10^{-4} [10][Chapter 2]. However, for actual tests of the variation of fundamental constants, an accuracy of 1% is sufficient and the sensitivity coefficients will be given to this level only.

We have calculated K_{μ} and K_{α} for rotational transitions in CH and CD using both the extensive and the reduced matrix. For clarity, we separate the transitions into five different types, I through V, as shown in Fig. 6.1. The transitions from J to J + 1 within the $\Omega' = 1/2$ and $\Omega' = 3/2$ manifolds are labeled by I and II, respectively. The transitions from $\Omega' = 1/2$ to $\Omega' = 3/2$ with $\Delta J = -1, 0, +1$ are labeled by III through V, respectively. From the calculations, we found that for both CH and CD, transitions of types I and II have K_{μ} close to -1 and K_{α} close to 0. Transitions of types III through IV also have K_{μ} close to -1 and K_{α} close to 0, except for transitions involving the lowest rotational levels, which have K_{μ} between -0.5 and -1 and a K_{α} between 1 and 0. Interestingly, transitions of type V were found to be extremely sensitive to a variation of α and μ . The K_{μ} for these transitions are listed in the third column of Table 6.1 and range from -67 to 18 for CD and -6.2 to 2.7 for CH. The fourth column of Table 6.1 lists the values of K_{α} . Note, that K_{α} $\sim 2+2K_{\mu}$, a relation that is exact when lambda-type doubling is neglected.

The calculations are most easily understood by plotting the sensitivity coefficients for the different transitions as a function of A/B, as shown in Fig. 6.2. The upper panel shows the K_{μ} for transitions of types I through IV, while the lower panel shows K_{μ} for transitions of type V, calculated using the reduced matrix from Eq. (6.2). The black curves show the sensitivity coefficients for transitions starting from J = 3/2. To indicate the progression towards higher values of J, transitions starting from J = 7/2 and J = 15/2 are plotted in gray. We see that for large |A/B|, K_{μ} approaches -1 for transitions of types I and II and 0 for transitions of types III through V. This can be understood by realizing that for large |A/B|, a Hund's case (a) coupling scheme applies. Consequently, transitions of types I and II are pure rotational transitions which are proportional to B, while transitions of types III through IV are pure electronic transitions and proportional to A. When $A \sim Bz$, the manifolds become mixed



Figure 6.2: Sensitivity coefficient K_{μ} of transition types I through IV (upper panel) and V (lower panel) starting from J = 3/2, in black, and J = 7/2 and J = 15/2, in gray, calculated using the reduced matrix given in Eq. (6.2). The crosses indicate the sensitivity coefficients calculated for the transitions from J = 3/2 for the listed molecules using the complete matrix.

and the sensitivity of the different types of transitions is between 0 and -1. When A = 0, corresponding to a pure Hund's case (b), all types of transitions have a sensitivity coefficient K_{μ} of -1, as expected. When A = 2B the two spin-orbit manifolds are fully mixed, also causing K_{μ} to become -1. Another special case is when A = 4B. Here, $\Omega' = 3/2, J$ levels are degenerate with $\Omega' = 1/2, J + 1$ levels. This gives rise to an enhancement of the sensitivity coefficient for transitions that connect these levels (i.e., transitions of type V). The enhancement is expected to be on the order of A/ν [9, 140], which is in reasonable agreement with our calculations. Note, that the sensitivity coefficients found from the simplified model are almost independent of J.

The crosses, also shown in Fig. 6.2, are the values of K_{μ} calculated using a full set of molecular parameters for CH (A = 1.98B), CD (A = 3.65B), OH (A = -7.48B), [141] and OD (A = -14.1B) [142]. The correspondence between the simplified model and the full description is very good for transitions at low J, but less good for higher J when effects of the lambda-type doubling become increasingly important. The lambda-type doubling shifts the energy levels, leading to a decrease or increase of the energy difference between the $\Omega' = 1/2, J$ and $\Omega' = 3/2, J + 1$ levels, and henceforth to a corresponding increase or decrease of the sensitivity coefficients.

6.3 Transition strengths

To be relevant for astrophysical tests of the time-variation of the proton-toelectron mass ratio, the highly sensitive transitions in CH and CD discussed in the previous section need to be sufficiently strong. In Hund's case (a), the transitions between different Ω manifolds (i.e., transitions of types III through V) are forbidden. However, as discussed in the previous section, the Ω manifolds of CH and CD are mixed and transitions are allowed.

The transition strength of a transition between rotational states i and f, is given by $|\langle i|T|f\rangle|^2$, with $|i\rangle$ and $|f\rangle$ given by Eq. (6.1). The transition strength of a transition $i \to f$ is then given by:

$$\begin{aligned} |\langle i|T|f\rangle|^2 &= |c_{i,1/2} c_{f,1/2} \langle 1/2, J_i|T|1/2, J_f\rangle \\ &+ c_{i,3/2} c_{f,1/2} \langle 3/2, J_i|T|1/2, J_f\rangle \\ &+ c_{i,1/2} c_{f,3/2} \langle 1/2, J_i|T|3/2, J_f\rangle \\ &+ c_{i,3/2} c_{f,3/2} \langle 3/2, J_i|T|3/2, J_f\rangle|^2. \end{aligned}$$

$$(6.5)$$

The expressions $\langle \Omega, J_i | T | \Omega, J_f \rangle$ are the Hund's case (a) dipole transition matrix elements given in, for example, Brown and Carrington [143]. As a result of the Hund's case (a) selection rules, the second and third terms on the righthand side of Eq. (6.5) are zero. Using the simplified Hamiltonian matrix given in Eq. (6.2), we have calculated the amplitude of the remaining terms as a function of A/B. In Fig. 6.3, the transition strength is plotted for type V transitions starting from different J levels. It is seen that when |A/B| becomes smaller, the levels become increasingly mixed and the transition strength becomes larger. Near A = 4B the transition strength becomes smaller, due to the destructive interference between the two different paths that combine to form this transition. At A = 4B the two paths are equally strong, but due to the orthogonality of the eigenvectors they have a different sign and the transition strength becomes zero. The last column of Table 6.1 lists the transition strength, calculated using the full Hamiltonian, but neglecting hyperfine splitting. For comparison, note that purely rotational transitions have a transition strength of order unity. The crosses shown in Fig. 6.3 again correspond to a calculation for CH, CD, OH, and OD using a complete set of parameters and are in good agreement with the calculations using the reduced matrix. We have validated that these calculations are also in agreement with calculations using the PGOPHER software package [63]. Note, that the dipole moment is set to unity in the calculations.

6.4 Relevance for tests on drifting constants over cosmological time scales

In the previous section, we have shown that transitions of type V that have an enhanced sensitivity to a variation of μ are too weak to be observed in astrophysical objects at high redshift. The only transitions in CH that have a non-vanishing transition strength and a K_{μ} that deviates significantly from -1are the $\Omega' = 1/2$, J = 1/2 to $\Omega' = 3/2$, J = 3/2 transitions at 532 and 536 GHz that have $K_{\mu} = -0.2$. By comparing these transitions with a rotational transition, typically exhibiting $K_{\mu} = -1$, in any other molecule observed in the same object, a test of the time variation of μ over cosmological time scales can be performed. If μ varies, the transition frequency of a pure rotational transition will vary while the frequency of the discussed transition in CH will change five times less (i.e., the CH transition will act as an anchor line). Ideally, the CH anchor transitions are compared with other transitions in CH, and preferably with transitions from the same absorbing levels. This eliminates one of the main systematic effects that limits astrophysical tests, namely the effect of spatial segregation. Astrophysical tests rely on the assumption that the transitions that are being compared originate from the same space-time location and hence the same apparent redshift. Spatial segregation of the absorbers may mimic or hide frequency shifts due to a variation of μ [18].

We propose a test of the time variation of μ by comparing the CH anchor transitions to other rotational or lambda-doublet transitions in CH involving the same absorbing ground levels (i.e. to the $\Omega' = 1/2, J = 1/2$ to $\Omega' = 1/2, J = 3/2$ transition near 2 THz and/or the $\Omega' = 3/2, J = 3/2$ to $\Omega' = 3/2, J = 5/2$ transition near 1.5 THz that has $K_{\mu} = -1$ or to the lambdadoublet transition in the $\Omega' = 1/2, J = 1/2$ at 3.3 GHz that has $K_{\mu} = -1.7$ and the lambda-doublet transition in the $\Omega' = 3/2, J = 3/2$ near 700 MHz



Figure 6.3: Transitions strengths of type V transitions, following from Eq. (6.5), starting from different J levels. The transition strength is zero at A = 4B for all J, making the transitions with the highest sensitivity exceedingly weak. The crosses correspond to a calculation for CH, CD, OH, and OD using a complete set of parameters. The molecules are also indicated by the vertical gray lines.

that has $K_{\mu} = -6.2$ [134]). This test is based on transitions within the lowest four levels of a single species making it very robust against possible shifts due to spatial segregation of the absorbing molecules. The transitions that are relevant to this test are listed in Tables 6.3 and 6.4, including the hyperfine splitting, with their respective sensitivity coefficients and transitions strengths, calculated using PGOPHER [63]. Our values for the sensitivity coefficients of the lambda-doubling transitions correspond well to those found by Kozlov [134], but our sensitivity coefficients are more exact as we use a more complete set of molecular parameters.

6.5 Conclusion

In this chapter, we have analyzed the sensitivity to a possible variation of μ and α for rotational transitions in ² Π states, in particular for rotational trans-

J	freq. (MHz)	K_{μ}	K_{α}	Tr. Str.
e parity				
1/2	536772.4	-0.22	1.57	$6.6 \cdot 10^{-1}$
3/2	191101.3	-1.02	-0.0068	$2.1 \cdot 10^{-2}$
5/2	137163.5	-1.09	-0.041	$6.7 \cdot 10^{-3}$
7/2	115440.4	-1.20	-0.074	$3.0 \cdot 10^{-3}$
9/2	107620.7	-1.32	-0.10	$1.6 \cdot 10^{-3}$
11/2	107870.7	-1.44	-0.12	$9.7 \cdot 10^{-4}$
13/2	113649.5	-1.55	-0.14	$6.3 \cdot 10^{-4}$
15/2	123632.5	-1.65	-0.14	$4.3 \cdot 10^{-4}$
f parity				
1/2	532741.0	-0.20	1.59	$6.6 \cdot 10^{-1}$
3/2	178904.5	-0.94	0.039	$2.1 \cdot 10^{-2}$
5/2	111119.2	-0.85	0.020	$6.7 \cdot 10^{-3}$
7/2	71064.4	-0.64	-0.012	$3.0 \cdot 10^{-3}$
9/2	40500.9	-0.11	-0.086	$1.6 \cdot 10^{-3}$
11/2	13698.2	2.56	-0.42	$9.7 \cdot 10^{-4}$
13/2	11758.8	-6.40	0.68	$6.3 \cdot 10^{-4}$
15/2	37049.6	-3.16	0.27	$4.3 \cdot 10^{-4}$

Table 6.1: Transition frequencies, sensitivity coefficients to variation of μ and α and transition strengths of transitions from $\Omega' = 1/2$, J to $\Omega' = 3/2$, J + 1, type V transitions in CH, calculated using the Hamiltonian matrix from Amiot *et al.* [135] and the molecular constants given by McCarthy *et al.* [137] for CH and Halfen *et al.* [139] for CD. Note that the values of K_{μ} for transitions starting from $\Omega' = 1/2$, J = 1/2 are always between 0 and -1, as the $\Omega' = 1/2$, J = 1/2 is unmixed. The transition strengths are following from Eq. (6.5). freq.: Frequency, Tr. Str.: Transition Strength.

sitions in the ground states of CH and CD. For certain rotational transitions, we found a significantly enhanced sensitivity due to accidental degeneracies between rotational levels of different fine-structure manifolds. These degeneracies occur when the spin-orbit coupling constant is close to four times the rotational constant. CH (A = 1.98B) and particularly CD (A = 3.65B), match this condition closely (as discussed in the introduction of this thesis). The fact that enhancement occurs is unexpected, as it was shown by Bethlem and Ubachs [9] that in molecules such as CO, the transition from Hund's (a) to Hund's case (b) coupling scheme prohibits levels that are connected by one-photon transitions to be become near degenerate. Here we show that for $A \sim 4B$ this does not apply. Unfortunately, the same condition that leads to an enhanced sensitivity suppresses the transition strength. Thus, one-photon transitions between different spin-orbit manifolds of molecular radicals are either insensitive or too weak to be of relevance for tests of the variation of fundamental constants over

J	freq. (MHz)	K_{μ}	K_{α}	Tr. Str.
e parity				
1/2	439799.0	-0.46	1.09	9.5×10^{-1}
3/2	31493.8	-10.6	-19.1	4.1×10^{-4}
5/2	23326.3	-10.0	-17.9	$1.7{ imes}10^{-4}$
7/2	20438.4	-9.09	-15.8	$8.6 imes 10^{-5}$
9/2	20133.3	-7.91	-13.2	4.9×10^{-5}
11/2	21473.9	-6.74	-10.6	3.1×10^{-5}
13/2	24037.3	-5.71	-8.27	2.1×10^{-5}
15/2	27598.2	-4.89	-6.44	1.5×10^{-5}
f parity				
1/2	439262.1	-0.45	1.10	$9.5{ imes}10^{-1}$
3/2	29320.6	-11.1	-20.3	$4.2{ imes}10^{-4}$
5/2	17073.0	-12.7	-24.0	1.7×10^{-4}
7/2	8787.4	-18.0	-35.9	8.6×10^{-5}
9/2	1771.6	-67.1	-146	4.9×10^{-5}
11/2	4894.4	18.0	44.7	3.1×10^{-5}
13/2	11611.1	5.38	16.4	2.1×10^{-5}
15/2	18576.6	2.12	9.14	1.5×10^{-5}

Table 6.2: Transition frequencies, sensitivity coefficients to variation of μ and α and transition strengths of transitions from $\Omega' = 1/2$, J to $\Omega' = 3/2$, J + 1, type V transitions, in CD. For a full discription of the table, see caption of Table 6.1

cosmological time scales. However, the high sensitivity coefficients could possibly be used in laboratory tests (note that experiments are being planned to decelerate CH molecules using electric fields [148] which open the prospect of measuring its rotational and microwave spectrum at high resolution).

We propose a test in CH based on the comparison between the rotational transitions between the e and f components of the $\Omega' = 1/2, J = 1/2$ and $\Omega' = 3/2, J = 3/2$ levels at 532 and 536 GHz, which have $K_{\mu} = -0.2$, with other rotational or lambda-doublet transitions in CH. Such a test, to be performed by far infrared spectroscopy of highly redshifted objects, is robust against systematic effects.

Ω', J	F	freq	o-c	K_{μ}	K_{α}	Trans.
		(MHz)	(kHz)			Str.
$\frac{1}{2}, \frac{1}{2} f \to \frac{1}{2}, \frac{1}{2} e$	$0{\rightarrow}1$	3263.795^{a}	16	-1.71	0.58	0.33
	$1 {\rightarrow} 1$	3335.481^{a}	-10	-1.70	0.61	0.67
	$1 {\rightarrow} 0$	3349.194^{a}	6	-1.69	0.62	0.33
$\frac{1}{2}, \frac{3}{2} f \to \frac{1}{2}, \frac{3}{2} e$	$1 \rightarrow 2$	7275.004^{a}	15	-2.13	-0.26	0.14
	$1 {\rightarrow} 1$	7325.203^{a}	27	-2.12	-0.24	0.68
	$2 \rightarrow 2$	7348.419^{a}	-15	-2.12	-0.24	1.23
	$2 \rightarrow 1$	7398.618^{a}	-4	-2.11	-0.22	0.14
$\frac{1}{2}, \frac{5}{2} f \to \frac{1}{2}, \frac{5}{2} e$	$2 \rightarrow 3$	14713.78^{b}	190	-2.02	-0.04	0.04
	$2 \rightarrow 2$	14756.670^{a}	36	-2.01	-0.03	0.54
	$3 \rightarrow 3$	14778.962^{a}	-28	-2.01	-0.03	0.77
	$3 \rightarrow 2$	14821.88^{b}	-160	-2.01	-0.02	0.04
$\frac{3}{2}, \frac{3}{2} f \to \frac{3}{2}, \frac{3}{2} e$	$2 \rightarrow 2$	701.667^{c}	-8	-6.14	-8.28	1.17
	$1 \rightarrow 2$	704.008	_	-6.11	-8.23	0.13
	$2 \rightarrow 1$	722.452	_	-5.98	-7.96	0.13
	$1 \rightarrow 1$	724.788^{c}	3	-5.96	-7.92	0.65

Table 6.3: Transition frequencies, sensitivity to variation of μ and α and transitions strengths of specific lambda-doubling transitions in CH calculated using PGOPHER [63] with the molecular constants from McCarthy *et al.* [137], including hyperfine splitting. Measured frequencies are given where possible, the difference with calculations is given for these transitions. The letters correspond to references: a: McCarthy *et al.* [137]; b: Brazier and Brown [144]; c: Ziurys and Turner [145]; d: Amano [146]; e: Davidson *et al.* [147]. freq., Frequency; o-c, Observed - Calculated; Trans. Str., Transition Strength. Tab. 6.4 lists rotational transitions.

Ω', J	\mathbf{F}	freq	o-c	K_{μ}	K_{α}	Trans.
		(MHz)	(kHz)			Str.
$\frac{1}{2}, \frac{1}{2} f \to \frac{3}{2}, \frac{3}{2} f$	$1 {\rightarrow} 1$	532721.333^d	-314	-0.20	1.59	0.17
	$1 \rightarrow 2$	532723.926^d	-54	-0.20	1.59	0.85
	$0 \rightarrow 1$	532793.309^d	-50	-0.20	1.59	0.34
$\frac{1}{2}, \frac{1}{2} e \to \frac{3}{2}, \frac{3}{2} e$	$1 \rightarrow 2$	536761.145^d	-1	-0.22	1.57	0.86
	$1 {\rightarrow} 1$	536781.954^d	31	-0.22	1.57	0.17
	$0{\rightarrow}1$	536795.678^d	58	-0.22	1.57	0.34
$\frac{3}{2}, \frac{3}{2} f \to \frac{1}{2}, \frac{3}{2} e$	$2 \rightarrow 1$	1470689.444	_	-1.00	0.00	0.03
	$1 {\rightarrow} 1$	1470691.777	_	-1.00	0.00	0.17
	$2 \rightarrow 2$	1470739.632	_	-1.00	0.00	0.30
	$1 {\rightarrow} 2$	1470741.965	_	-1.00	0.00	0.03
$\frac{3}{2}, \frac{3}{2} e \to \frac{1}{2}, \frac{3}{2} f$	$1 {\rightarrow} 1$	1477292.168	_	-1.00	0.00	0.16
	$2 \rightarrow 1$	1477312.946	_	-1.00	0.00	0.03
	$1 \rightarrow 2$	1477365.614	_	-1.00	0.00	0.03
	$2 \rightarrow 1$	1477386.391	_	-1.00	0.00	0.30
$\frac{3}{2}, \frac{3}{2} f \to \frac{3}{2}, \frac{5}{2} f$	$2 \rightarrow 3$	1656961.185	_	-1.00	0.00	2.32
	$2 \rightarrow 2$	1656970.448	_	-1.00	0.00	0.17
	$1 \rightarrow 2$	1656972.781	_	-1.00	0.00	1.49
$\frac{3}{2}, \frac{3}{2} e \rightarrow \frac{3}{2}, \frac{5}{2} e$	$2 \rightarrow 3$	1661107.278	_	-1.00	0.00	2.32
	$1 \rightarrow 2$	1661118.045	_	-1.00	0.00	1.49
	$2 \rightarrow 2$	1661138.822	_	-1.00	0.00	0.17
$\frac{1}{2}, \frac{1}{2} \ e \to \frac{1}{2}, \frac{3}{2} \ e$	$1 {\rightarrow} 1$	2006748.915	_	-0.79	0.42	0.16
	$0 \rightarrow 1$	2006762.612	_	-0.79	0.42	0.32
	$1 {\rightarrow} 2$	2006799.103	_	-0.79	0.42	0.81
$\frac{1}{2}, \frac{1}{2} f \to \frac{1}{2}, \frac{3}{2} f$	$1 {\rightarrow} 1$	2010738.601	_	-0.79	0.42	0.16
	$0 {\rightarrow} 1$	2010810.46^{e}	150	-0.79	0.42	0.33
	$1 {\rightarrow} 2$	2010811.92^{e}	-130	-0.79	0.42	0.81

Table 6.4: Transition frequencies, sensitivity to variation of μ and α and transitions strengths of specific rotational transitions in CH. For a full description, see caption of Tab. 6.3

Chapter 7

Progress towards using CO $(a^3\Pi)$ as a probe into the possible time variation of μ

Abstract

A number of steps have been made to measure the two-photon transition in CO $a^3\Pi$ that is highly sensitive to a variation of the proton-toelectron mass ratio. A calculation of the transition strength has shown that, in order to obtain high enough power, a resonant microwave cavity is required, which has been designed and tested. Laser excitation of the $m_J^B = 0$ sublevel is studied, and a proposal is made to improve the detection scheme.

7.1 Introduction

In this chapter, our progress towards measuring the highly sensitive two-photon microwave transition between the $\Omega = 1$, J = 6, + and the $\Omega = 0$, J = 8, + rotational levels in the $a^3\Pi$ state of ${}^{12}C^{16}O$ is discussed.

In the introduction of this thesis, it was shown that a near degeneracy between three rotational levels occurs in the $a^3\Pi$ state of CO. Fig. 7.1 shows the energy level diagram of these three rotational levels, using the calculations from Chapter 2. The transitions between these levels have $\Delta J = 2$, and can be induced using two-photon electric dipole transitions. In Chapter 2, it was found that the $\Omega = 1$, J = 6, $+ \rightarrow \Omega = 0$, J = 8, + transition, with an energy of 3.3 GHz, has a sensitivity coefficient of $K_{\mu} = -334$.

The proposed method to measure the two-photon microwave transition is very similar to the one-photon transition measurement discussed in Chapter 5. In this chapter, the differences will be discussed, mainly resulting from the fact that the two-photon transition requires a more intense microwave field and involves highly excited rotational levels. In section 7.2 the transition strength is



Figure 7.1: The relevant rotational levels of the energy level diagram of the $a^3\Pi$ state of ${}^{12}C^{16}O$. The three nearly degenerate rotational levels are shown, with the rotational quantum number and the total parity indicated.

calculated and compared to the transition strength of the one-photon transition. In section 7.3 the design of a microwave cavity is presented. The obtained electric field is compared to the electric field that is required to induce the microwave transition. As the rotational levels involved have higher rotational quantum number, they have more m_J^B sublevels and a lower Stark effect, the consequences of which are discussed in section 7.4. We study the effect of perpendicular \vec{E} and \vec{B} fields on the $\Omega = 1, J = 6, +$ state to find which m_J^E sublevel needs to be populated, and which UV transition can be used to populate it. Furthermore, we will discuss the lower separation of the initial and final states on the MCP detector due to the lower Stark shift.

7.2 Transition strength

As the highly sensitive transition is a two-photon transition, it requires a more intense microwave field than the one-photon transition measured in Chapter 5. Here, we present an analysis of the transition strength of the transition between the $\Omega = 1, J = 6, +$ level and the $\Omega = 0, J = 8, +$ level¹.

The transition strength is given by:

$$\Omega_{Rabi}/2\pi = \sum_{j} \frac{\left(\frac{1}{2}\right)^{2} \cdot |E|^{2} \cdot \mu_{e}^{2}}{\left(\mathcal{E}_{j} - \frac{1}{2}\left(\mathcal{E}' + \mathcal{E}''\right)\right)} \\ \left\{ \left(J'+1\right) \sum_{i} g\left(\Omega_{i}, J'\right) \times c_{\Omega_{i},\Omega',J'} \times c_{\Omega_{i},\Omega_{j},J_{j}} \\ \times (J_{j}+1) \sum_{i} g\left(\Omega_{i}, J_{j}\right) \times c_{\Omega_{i},\Omega_{j},J_{j}} \times c_{\Omega_{i},\Omega'',J''} \right\}.$$

$$(7.1)$$

Here, the summation over j is over all intermediate states. In this case, there are three, the J = 7, – level in all three spin-orbit manifolds. However, the $\Omega = 2, J = 7$, – level couples weakly to both initial and final state, so this intermediate state is neglected. In this calculation, the Hamiltonian matrix and molecular constants found in Chapter 2 are used. The summation over i is over all three values of Ω , single primes indicate the initial state, double primes the final state. The *c*-coefficients are the squares of the eigenvectors of the Hamiltonian matrix, representing the amount of Ω_i character a level has, |E|is the absolute value of the electric field and μ_e is the electric dipole moment of the molecule. \mathcal{E} is the energy of the corresponding rotational level. $g(\Omega, J)$ is the Hönl-London factor of the transition, for $\Delta m = 0$ transitions, and is given by:

$$g(\Omega, J) = \frac{1}{J+1} \sqrt{\frac{(J+1)^2 - \Omega^2}{(2J+1)(2J+3)}}.$$
(7.2)

This leads to a transition strength of $T = 2.6 \times 10^{-3} \ (\mu_e \text{E})^2$ Hz, compared to 0.1 $\mu_e \text{E}$ Hz for the one-photon transition measured in Chapter 5, both with E in V/cm and μ_e in Debye. This transitions strength comes from two different intermediate levels, the $\Omega = 0, J = 7, -$ and $\Omega = 1, J = 7, -$ levels. Of these two, the coupling via the $\Omega = 0, J = 7, -$ level is approximately two times stronger than the coupling via the $\Omega = 1, J = 7, -$ level, but both couplings are opposite in sign.

 $^{^1{\}rm This}$ calculation was performed by Dr. W.L. Meerts (Radboud University Nijmegen, the Netherlands).



Figure 7.2: A schematic drawing of the microwave cavity, indicating the sizes and coordinates used in the text.

7.3 Microwave cavity

To enhance the strength of the applied microwave field, a resonant cavity is used. In this section, we will discuss the design and testing of such a cavity.

For the shape of the cavity we choose a cylindrical hole in a copper block, commonly known as a pillbox cavity². A schematic drawing is shown in Fig 7.2. We drive a Transverse Magnetic (TM) mode, meaning that the electric field of the microwave field is along the z-axis, parallel to the bias magnetic field, driving $\Delta m_J^B = 0$ transitions. For the TM modes, the resonance frequency of a pillbox cavity is given by:

$$\omega_{mnp} = c \sqrt{\frac{x_{mn}^2}{R^2} + \frac{p^2 \pi^2}{d^2}}.$$
(7.3)

where x_{mn} is the *n*-th root of $J_m(x) = 0$. The mode numbers m, n, p are the mode number in the ϕ -, r-, and z-directions, respectively. For the lowest order, and smallest, TM mode, the TM₀₁₀ mode, this equation simplifies to:

$$R_{cav} = \frac{cx_{01}}{2\omega_0} = \frac{2.405c}{2\pi f_0}.$$
(7.4)

For a frequency of 1.6283 GHz, this gives a radius of 70.47 mm, while the height of the cavity is not constrained by the resonant mode, and can thus be chosen freely. We have chosen a height of 50 mm.

The design of the cavity can be seen in Fig. 7.3. It is made out of three oxygen-free copper parts, one body and two 'lids', and four KF-flanges. The molecules pass through the flanges in the lids, while the other two flanges are

 $^{^{2}}$ We based our design and calculations on the work of van Oudheusden [149].



Figure 7.3: Technical drawing of the microwave cavity. The body and the two lids are made out of oxygen-free copper, to which four KF-flanges are attached. The molecules fly through the KF-flanges in the lids, along the z-axis of the cavity. The other two flanges are used for the microwave antenna and a copper plunger, that is used to tune the cavity in resonance with the microwave field. Drawing courtesy of Mr. F. Hendriks (FMI-workshop, Faculty of Sciences, VU University, Amsterdam).

used for the microwave input and a plunger, that can be used to tune the cavity resonance. The plunger is a 15 mm diameter copper cylinder, attached to a micrometer screw. It can be moved in and out of the cavity over a distance of ~ 15 mm, thereby affecting the field and shifting the resonance frequency. The resonance frequency of the cavity is measured using a directional coupler to split of the microwave signal that is reflected back from the cavity. This backreflected signal is fed into a microwave power meter, and the output of the power meter is recorded as a function of frequency. Typical measurements can be seen in Fig. 7.4, for three different settings of the plunger. The frequency of the microwave radiation is scanned, and when the input is resonant with the cavity a large fraction of the power is coupled into the cavity. Therefore the reflected power drops. From the figure we can see that the resonance frequency can be tuned over approximately 4 MHz. The frequency of the transition is known from the UV-measurements to be 1628.3(5) MHz, well within the tunable range of the cavity. To further maximize the intra-cavity power, the impedance of the cavity needs to be matched to the cable. This is done by rotating the antenna. From Fig. 7.4, it can be seen that more than 95% of the input microwave power can be coupled into the cavity. The Q-factor of the cavity is given by the ratio between the central frequency of the resonance and the width of the resonance, $Q = \nu/\Delta\nu = 1628/0.28 = 5.8 \times 10^3$.

Now that we know the electric-field build-up in the cavity, we can calculate

how much microwave power we need to input into the cavity to be able to drive the two-photon transition. We first write the required electric field

$$E_{req}^2 = \frac{2 \arcsin(\sqrt{p})}{2\pi\tau T \mu_E^2},\tag{7.5}$$

with p the requested probability that a molecule makes a transition, T as following from Eq. 7.1 and τ the time it takes molecules to fly through the microwave field. To calculate the electric field that is present in the microwave cavity, we use

$$E_{cav}^2 = \frac{2PQ}{Ac\epsilon_0},\tag{7.6}$$

with P the microwave power input into the cavity, Q the quality factor as above and A the surface area of the cavity. We need the electric field in the cavity to be equal or higher than the electric field required to drive the transition. To calculate how much input power we need, we write

$$P_{req} = \frac{E_{req}^2 A c \epsilon_0}{2Q}.$$
(7.7)

To find the required amount of input microwave power we use $\tau = l/v = 0.05/800 = 62.5 \times 10^{-6}$ s, $A = \pi R_{cav}^2 = \pi 0.0704^2 = 1.6 \times 10^{-2}$ m² as given by the cavity designed above and $\mu_e = 1.37$ D. For the 1.63 GHz transition, we find $E_{req} = 911$ kV/cm for a transition probability of 0.5. We now find that that P > 30 W.

7.4 Laser excitation

In the one-photon lambda-doublet transition measurement discussed in Chapter 5, the Zeeman shift caused by the bias magnetic field was canceled by averaging over two microwave transitions with opposite Zeeman shift, as the $m_J^B = 0 \rightarrow m_J^B = 0$ transition was not allowed. As a result, instability of the bias magnetic field was the largest contributing error. In the two-photon transition discussed here, the $m_I^B = 0 \rightarrow m_I^B = 0$ transition is allowed, greatly limiting the effect of magnetic fields on the measurement. In Chapter 5, the correspondence between m_J^B and m_J^E sublevels was studied. For the J = 6 level, 13 sublevels are present. The splitting of the ground state is much smaller than the laser bandwidth, and can thus be ignored. Meek et al. [128] describe the $\Omega = 1, J = 1$ level of CO $a^3 \Pi$ in perpendicular \vec{E} and \vec{B} fields. Here, we follow their description, and extend it to higher J levels. We choose the magneticfield vector along the z-axis and the electric-field vector in the xy-plane. States are labeled by the quantum number m_J^B , the projection of the total angular momentum on the z-axis. As ${}^{12}C^{16}O$ has zero nuclear spin, total angular momentum is given by J only. The magnetic field is parallel to the quantization axis, and therefore only couples sublevels with the same m_J^B and parity. The



Figure 7.4: Scans of the reflection of microwaves off the cavity as a function of frequency, measured by splitting off part of the reflected power using a directional coupler. The different scans are taken with different settings of the plunger.

electric field only couples sublevels with $\Delta m_J^B = \pm 1$ and opposite parity. We can now write the Hamiltonian matrices, one for each parity, using the matrix elements given by

$$\langle \Lambda S \Sigma J \Omega m | H_{\text{stark}} | \Lambda S \Sigma' J' \Omega' m' \rangle = \mu_e E(-1)^{m-\Omega+1} \sqrt{(2J+1)(2J'+1)} \begin{pmatrix} J & 1 & J' \\ -m & -1 & m' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ -\Omega & 0 & \Omega \end{pmatrix}$$

$$(7.8)$$

and

$$\langle \Lambda S \Sigma J \Omega m | H_{\text{zeeman}} | \Lambda S \Sigma' J' \Omega' m' \rangle = \mu_b B (-1)^{m-\Omega} \sqrt{(2J+1)(2J'+1)} \begin{pmatrix} J & 1 & J' \\ -m & 0 & m' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ -\Omega & \Omega - \Omega' & \Omega' \end{pmatrix}$$
(7.9)


Figure 7.5: Dependence of different m_J sublevels on the electric field in a perpendicular magnetic field of 50 Gauss.

for the electric and magnetic-field coupling, respectively. Here, μ_e and μ_b are the electric and magnetic dipole moments, E and B are the absolute values of the electric and magnetic fields, respectively.

Fig. 7.5 shows the energy shifts in combined, perpendicular \vec{E} and \vec{B} fields for the $\Omega = 1, J = 6, +$ level as a function of the electric field in a fixed magnetic field of 50 Gauss. As two m_J sublevels are degenerate in an electric field, two different m_J^B sublevels combine to form one m_J^E sublevel, where m_J^E is the projection of the total angular momentum on the electric field vector. In the experiment, we need to laser excite the $m_J^B = 0$ sublevel. Therefore, we need to adiabatically follow the $m_J^B = 0$ sublevel to high electric field, and see that it becomes the $m_J^E = 3$ sublevel. This sublevel can be reached from two ground state rotational levels, via the $R_2(5)$ and the $P_2(7)$ transitions. As the beam of CO molecules is rotationally cold, we would prefer to excite from as low a ground state rotational level as possible, and thus use the $R_2(5)$ transition. Unfortunately, this transition is overlapped with the $R_2(7)$ transition, as shown in Fig. 7.6, where a calculation of both transitions is plotted in an electric field of 15 kV/cm and a rotational temperature of 20 K. Note, that in this figure the intensity of the $R_2(7)$ transition is multiplied by a factor 25 for clarity. The $R_2(5)$ transition to the $m_J^E = 3$ sublevel for this electric field strength is in



Figure 7.6: A simulation using PGOPHER of the $R_2(5)$ and $R_2(7)$ transitions in an electric field of 15 kV/cm, with a rotational temperature of 20 K. The $R_2(7)$ transition is multiplied by a factor of 25 for clarity.

between the $R_2(5)$ transition to the $m_J^E = 2$ sublevel and the $R_2(7)$ transition to the $m_J^E = 0$ sublevel. Exciting in a higher electric field will give more energy separation between the different sublevels of the $R_2(5)$ transition, but starting from around 20 kV/cm the $R_2(7)$ transition will be excited as well, adding a small background to the undeflected signal.

As discussed, the $m_J^B = 0$ sublevel becomes the $m_J^E = 3$ sublevel. However, populating the $m_J^E = 3$ sublevel will also populate the $m_J^B = -1$ sublevel. Molecules in this sublevel will not make a microwave transition, therefore the population of the initial state will not be empty at the resonance of the microwave transition. This problem was circumvented in the one-photon measurement by exciting the $m_J^E = 0$ sublevel, which only leads to one m_J^B sublevel.

7.5 Current status and outlook

Microwave frequency scans have been performed to observe the two-photon transition, at two different occasions during the project, but they were ultimately unsuccessful. In the first run, a number of scans were done with the resonant cavity in place, but it was found that the observed spatial separation between the different m_J^E sublevels was insufficient; the depletion of the signal of the $m_J^E = 6$ sublevel induced by the microwave transition would be hidden in the background. In order to obtain a larger deflection, a new deflection field was constructed. This deflection field has a length of 60 cm instead of 30 cm and it was conditioned to 18 kV instead of 12 kV. These factors combined led to a factor 4 improvement of the observed deflection. Preliminary measurements were taken with the new deflection field, however, around this time calculations became available for the transition strength of the two-photon transition and it became clear that the microwave power delivered by our generator (200 mW) was smaller than required to make a Rabi flop (30 W), and a microwave amplifier was acquired. Due to time limitations, this amplifier was never used to search for the two-photon transition.

Even though it should be possible to observe the two-photon transition with the new deflection field and microwave amplifier, the number of detected molecules in the current experiment is probably too small to perform a competitive test of the time-variation of μ . The main reason for this is the small population of the J = 5 level of the ground state in the molecular beam. Improved signal on the $R_2(5)$ transition was achieved by lowering the pressure behind the valve from 2 bar to 0.5 bar, resulting in less rotational cooling in the expansion. The downside to this approach is that by raising the rotational temperature of the beam the $R_2(7)$ transition becomes stronger relative to the $R_2(5)$ transition. This leads to an increased background. Another reason for low signal is the small Stark shift of the J = 6 level which makes it necessary to use a long deflection field. The longer flight path leads to geometrical losses due to the divergence of the molecular beam scaling with the square of the length of flight. Furthermore, as a result of the longer flight path, a larger fraction of the molecules will decay back to the ground state before reaching the detector.

The signal could be improved in two ways. The geometric losses can be reduced by focusing the beam of molecules using quadrupole or hexapole lenses [54]. However, due to the low effective electric dipole moment of the involved states, this will require long lenses at a very high voltages. Another option to improve the signal would be to improve the detection efficiency. In the current experiments, the molecules are detected by letting the metastable molecules impinge on an MCP. This process has a quantum efficiency of only $\sim 10^{-3}$ [54], as the work function of the surface of the MCP is only slightly smaller than the 6 eV of internal energy of the metastable molecules. Increasing the efficiency of the detection would greatly improve the accuracy of the experiment, and could be achieved by letting the metastable molecules impinge on a gold surface, see Fig. 7.7 for a schematic overview. The deflected and undeflected beams of metastable molecules each impinge on a separate gold plate, freeing electrons that are collected by a high voltage grid and then detected. To further improve the detection, the gold plate could be heated, to anneal it in between measurements, or a sodium beam could be installed, to constantly



Figure 7.7: A schematic drawing of a possible design for an improved detector.

deposite a layer of sodium atoms on the surface. This would further lower the work function of the surface and keep the surface free from contamination.

To estimate the signal strength that is required for a competitive measurement, we use the Allan deviation, given by

$$\sigma(\tau) = \frac{1}{Q\sqrt{N\tau/\tau_c}},\tag{7.10}$$

with $\sigma(\tau)$ the final error on the measurement, Q the quality factor of the measurement, given by the transition frequency over the measured linewidth, $\nu/\Delta\nu$, N the amount of molecules that is detected per measurement cycle, τ the total measurement time and τ_c the time of one measurement cycle [150]. The quality factor that can be reached, as shown by the one photon measurement, is $1.6 \times 10^9/1.4 \times 10^3 \approx 1.1 \times 10^6$. From previous experiments we expect that replacing the mcp by the new detector will increase the number of detected molecules with a factor 100. Together with other improvements it should be possible to detect 1000 molecules per shot. The current best constraint on μ

variation is set by the SF₆ experiment of Shelkovnikov [35], with an accuracy of 5.6×10^{-14} . To be competitive with that measurement, an accuracy of 1.8×10^{-11} is required, as our planned experiment has a sensitivity coefficient of 330. This leads to a total measurement time of ~60 hours. This long measurement time makes searching for systematic effects challenging, but not impossible.

7.6 Conclusion

To measure the $\Omega = 1$, J = 6, $+ \rightarrow \Omega = 0$, J = 8, + transition, a resonant cavity has been designed and tested. The deflection has been enhanced by making a longer deflection field, that has been conditioned to higher voltages. Due to time limitations, we have not been able to search for the two-photon transition with the acquired microwave amplifier. Although it should be possible to detect the two-photon transitions in the present setup, it will be challenging to reach the necessary accuracy to improve the current limit on a possible time variation of the proton-to-electron mass ratio. For a competitive test it is necessary to implement a more sensitive detector and/or to use quadrupole or hexapole lenses to collimate the beam.

Appendix A

Cavity modes of the pulsed Titanium:Sapphire oscillator

The Titanium:Sapphire oscillator used in the pulsed UV laser system is locked to the seed light from a CW ring laser via a Hänsch-Couillaud locking scheme [151]. The feedback signal is fed into a piezo stage, on which one of the four mirrors of the oscillator-cavity is mounted. Aligning the seed-light into the cavity is done by scanning the piezo voltage, and monitoring the transmitted light. A typical signal is displayed in the black trace in Fig. A.1.

In this figure, we see one full scan of the free-spectral-range of the oscillator, covering ~ 750 MHz, corresponding to a cavity length of 40 cm. The two large peaks correspond to consecutive longitudinal modes, the smaller peaks are transverse modes. By properly aligning the seed light into the cavity, the smaller peaks can be decreased in intensity, to approximately 1000 times weaker than the main peaks. To study whether the main peak is the desired TEM_{00} mode, which has a Gaussian beam profile, we connect a voltage supply to the piezo stage. The seed-light that is transmitted through the oscillator cavity is split into two parts. One part is sent to a photodiode, to monitor the transmission signal, the other part is imaged using a CCD camera. To increase the visibility of the weaker peaks, we slightly misalign the incoupling, in which case the main peaks are approximately 25 times stronger than the weaker peaks. We manually scan the piezo voltage until we hit one of the cavity modes, and record the image with the camera. The results can be seen in the insets of Fig. A.1. The large inset shows the image taken at a large peak. The two traces show a cut through the middle of their respective direction, showing that the beam is well described by a Gaussian line-shape, and can thus be seen to be the desired TEM_{00} mode. The five smaller insets show images taken at the smaller peaks, with the positions indicated by the arrows. The two left-most small peaks can be identified as a TEM_{01} mode and a TEM_{10} mode, respectively, while the two right-most small peaks can be identified as a TEM_{02} mode and a TEM_{20} mode, respectively. The image taken in between the TEM_{02} mode and the TEM_{20} mode shows the combination of



Figure A.1: Scan of the length of the oscillator cavity over one free-spectral-range of ~ 750 MHz. The two large peaks correspond to TEM₀₀ modes, while the smaller peaks correspond to higher order modes. The images in the insets, obtained by a CCD camera in the output beam, are taken at the indicated positions. The curves overlayed on the top image are cuts through the centers of their respective directions.

both. From this analysis we can conclude that the cavity is in the desired TEM_{00} mode when it is locked to one the main peaks.

Samenvatting

Moleculaire radicalen in de zoektocht naar veranderende constanten

Het werk in dit proefschrift heeft één centraal thema: de zoektocht naar een mogelijke verandering van natuurconstanten. Dit is niet alleen taalkundig gezien tegenstrijdig, het is ook strijdig met de bekende natuurwetten. Toch zijn er experimentele aanwijzingen gevonden voor zo'n variatie. In deze samenvatting wordt uitgelegd waar precies naar gezocht wordt, hoe er gezocht wordt en wat de plaats van dit werk in deze zoektocht is.

Het universum wordt door natuurkundigen beschreven door middel van natuurwetten. Deze wetten vertellen welke verbanden er zijn tussen de verschillende grootheden. Een bekend voorbeeld hiervan is de wet van Newton. De zwaartekrachtswet van Newton beschrijft de kracht tussen twee massa's over een bepaalde afstand. Deze wet kan als volgt worden geschreven: $F_g = Gm_1m_2/r^2$. Hierin zijn m_1 en m_2 de twee massa's die elkaar aantrekken, over een afstand r. Het getal $G = 6,67 \times 10^{-11} N(m/kg)^2$, geeft aan hoe sterk twee massa's elkaar over een afstand aantrekken. Over dit soort constanten gaat het ook in dit proefschrift, om precies te zijn over de constanten α , die de sterkte van de elektromagnetische kracht beschrijft, en vooral over μ , de verhouding tussen de massa van een elektron en een proton.

Dit proefschrift gaat over de zoektocht naar een verandering in de waarde van μ in de loop der tijd. Eerder onderzoek heeft al laten zien dat, als er al zo'n verandering is, deze erg klein is. De huidige bovengrens voor deze verandering is $\dot{\mu}/\mu < 2 \times 10^{-13} \text{ yr}^{-1}$ [35]. Dat betekent dat van de waarde van μ hooguit het dertiende getal achter de komma elk jaar verandert. Toch zou zelfs zo'n kleine verandering van groot belang zijn voor de fundamentele wetenschap, omdat de huidig bekende natuurwetten hier geen ruimte voor laten en er dus nieuwe theorieën bedacht moeten worden.

B.1 Hoge gevoeligheid

Het werk in dit proefschrift gaat over het doen van spectroscopie om een eventuele variatie van een natuurconstante te vinden. Spectroscopie is het meten van de energie van een overgang in een atoom of molecuul, wat betekent dat het verschil in energie tussen twee energietoestanden gemeten wordt. Niet alle overgangen veranderen even snel als een constante verandert. De mate waarin een overgang verandert noemen we de gevoeligheid van die overgang voor een verandering van de constante. De overgangen die gebruikt zijn voor het vinden van de eerste aanwijzingen van variatie zijn bijvoorbeeld duizenden keren minder gevoelig dan een overgang in koolmonoxide, waar een deel van dit proefschrift over gaat. Deze hoge gevoeligheden zijn het gevolg van toevallige bijna-ontaardingen. Dit zijn twee energietoestanden in een molecuul die toevallig heel dicht bij elkaar liggen. Om dit te begrijpen, kun de zoektocht naar een variatie van een constante vergeleken worden met het meten van de snelheid waarmee continenten uit elkaar drijven. Dit is een heel kleine verandering van een heel grote afstand. Als er een punt zou zijn waar deze twee continenten vlakbij elkaar komen, zou het daar veel makkelijker zijn om het uit elkaar drijven te meten. Zo is het ook met de variatie van constanten: als er twee energietoestanden vlakbij elkaar liggen is de verandering verhoudingsgewijs veel groter en dus makkelijker te meten.

B.2 Zoekmethodes

Er zijn in hoofdlijnen twee methodes om spectroscopie in te zetten om eventuele variaties te vinden. Eén van de methodes werkt op basis van metingen aan licht dat miljarden jaren geleden is uitgezonden. Als dit licht door ver weg gelegen stofwolken reist, absorberen de atomen en moleculen in die wolken licht van specifieke golflengtes. Deze golflengtes zijn verschillend per atoom of molecuul en ze worden bepaald door de natuurconstanten. Zo laat de wolk dus een soort vingerafdruk achter in het licht. Dit licht kan op aarde worden waargenomen en de vingerafdruk die miljarden jaren geleden is achtergelaten kan worden vergeleken met metingen hier op aarde aan diezelfde atomen en moleculen. Uit afwijkingen hiertussen kan nu bepaald worden of de waarde van de constante tijdens het absorberen van het licht, miljarden jaren geleden, hetzelfde is als nu op aarde. Uit dit soort metingen zijn de eerste aanwijzingen voor een mogelijke variatie van α gevonden [11, 12]. Door de lange periode tussen absorptie en meting kunnen heel kleine verschillen toch gevonden worden.

Het grote nadeel van deze metingen is dat niet goed bekend is onder welke omstandigheden het licht is geabsorbeerd. Deze omstandigheden kunnen slecht bestudeerd worden, wat de analyse van de metingen moeilijk maakt.

Bij de tweede methode wordt gebruik gemaakt van heel precieze metingen in het laboratorium op aarde. Doordat deze experimenten hooguit een aantal jaar kunnen duren moeten de metingen veel preciezer zijn dan de astrofysische metingen. Een deel van dit verschil wordt goedgemaakt doordat metingen in het laboratorium veel beter onder controle zijn. Alle omstandigheden zijn bekend en de invloed van de verschillende factoren kan één voor één onderzocht worden. Een ander voordeel is dat in het laboratorium zelf gekozen kan worden aan welke atomen of moleculen gemeten wordt. In miljarden jaren oude wolken is maar een heel klein aantal soorten atomen en moleculen aanwezig, maar op aarde kan aan elk systeem, hoe ingewikkeld ook, gemeten worden. Hierdoor kunnen overgangen met een hoge gevoeligheid gezocht en gemeten worden. Deze strategie wordt gevolgd in het werk in dit proefschrift.

B.3 Moleculaire radicalen in de zoektocht naar veranderende constanten

In dit proefschrift wordt gesproken over moleculaire radicalen. Dit zijn moleculen met een ongepaard elektron. Dit betekent dat ze erg reactief zijn. Dit proefschrift richt zich op een andere eigenschap van moleculaire radicalen, namelijk dat ze een toestand waarin er een hogere kans is op een toevallige bijna-ontaarding. In hoofdstuk 6 wordt uitgelegd waarom dit kan leiden tot overgangen met een hoge gevoeligheid. Hier worden de moleculen CH en OH doorgerekend en wordt gevonden dat CH een goede kandidaat kan zijn voor het doen van astrofysische metingen om een variatie van natuurconstanten te vinden. De rest van het proefschrift richt zich op het doen van metingen aan metastabiel CO. Bethlem en Ubachs [9] toonden in de eerste aangeslagen toestand van CO een twee-foton-microgolfovergang met een hoge gevoeligheid voor een verandering van μ aan. Dit proefschrift richt zich op het zo precies mogelijk meten van deze overgang. In het geplande experiment wordt een bundel van metastabiel CO geprepareerd in een enkele kwantumtoestand door CO in vacuüm te expanderen en de moleculen aan te slaan met een smalbandige UV-laser. Na het passeren van twee resonante microgolftrilholtes, met een onderlinge afstand van 50 cm, worden de moleculen toestandselectief afgebogen en 1 meter verder gedetecteerd op een positiegevoelige detector.

In hoofdstuk 2 wordt aangetoond dat er goede controle is over het aanslaan van deze toestand door hoge precisie UV-spectroscopie te doen aan de $a^3\Pi$ toestand van CO. We hebben de frequentie van de twee-foton-microgolfovergang bepaald met een precisie van 0.5 MHz, een verkleining van de onzekerheid van meer dan een orde grootte. Ook worden massaschalingsformules toegepast om gevoeligheidscoefficiënten te berekenen van overgangen in andere isotopologen van CO. In hoofdstuk 2 wordt cavity-ring-down-spectroscopie toegepast op de $a^{3}\Pi$ toestand van twee isotopologen van CO en wordt er gevonden dat de massaschalingsformules gebruikt kunnen worden om de overgangsfrequenties te voorspellen van v = 0, J < 8 in ¹²C¹⁶O naar v = 1, J < 30 rovibrationale niveaus in ${}^{12}C^{18}O$ en ${}^{13}C^{16}O$ tot binnen de experimentele nauwkeurigheid van 0.2 cm^{-1} . In hoofdstuk 4 wordt het ontwerp van het elektrostatische afbuigveld dat gebruikt wordt om toestandselectief moleculen af te buigen in de microgolfmetingen besproken. Het theoretische model dat gebruikt werd voor het ontwerp is ook toegepast op het bestuderen van twee types opslagringen voor moleculen in hoogveldzoekende toestanden. In hoofdstuk 5 laten we zien dat het mogelijk is om hoge precisie microgolfspectroscopie te doen in de geplande opstellingen. We hebben de $\Omega = 1, J = 1$ lambda-doublet opsplitsing rond 394 Mhz gemeten met een nauwkeurigheid van 10 Hz en bespreken systematische effecten die het resultaat beïnvloeden.

In hoofdstuk 7 wordt een vooruitblik gegeven naar het meten van de zeer gevoelige twee-foton-microgolfovergang. Het hiervoor voorgestelde experiment is erg vergelijkbaar met het één-foton-experiment dat in hoofdstuk 5 beschreven is, de verschillen worden hier besproken. Omdat de zeer gevoelige overgang een twee foton overgang is, heeft deze een hogere microgolfintensiteit nodig. De overgangssterkte is berekend, een resonante microgolftrilholte is ontworpen en getest. Daarnaast moet een hoger rotationeel niveau aangeslagen worden door de UV-laser, waardoor er meer m_J^B subniveaus een rol spelen, de afbuiging kleiner is en de bezetting van de toestand lager is. De gevolgen van deze factoren worden ook besproken.

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