

Testing the time-invariance of fundamental constants using microwave spectroscopy on cold diatomic radicals

Hendrick L. Bethlem* and Wim Ubachs

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The recently demonstrated methods to cool and manipulate neutral molecules offer new possibilities for precision tests of fundamental physics theories. We here discuss the possibility of testing the time-invariance of fundamental constants using near degeneracies between rotational levels in the fine structure ladders of molecular radicals. We show that such a degeneracy occurs between the $J = 6$, $\Omega = 1$ and the $J = 8$, $\Omega = 0$ levels of the various natural isotopomers of carbon monoxide in its $a^3\Pi$ state. As a result, the 2-photon transition that connects these states is 300 times more sensitive to a variation of m_p/m_e than a pure rotational transition. We present a molecular beam apparatus that might be used to measure these transitions with a fractional accuracy of 10^{-12} . Ultimately, the precision of an experiment on metastable CO will be limited by the lifetime of the $a^3\Pi$ state. We will discuss other possible molecules that have a suitable level structure and can be cooled using one of the existing methods.

Introduction

The equivalence principle of general relativity postulates that the outcome of any non-gravitational experiment is independent of position and time. In theories that attempt to unify gravity with other fundamental forces, on the other hand, violation of the equivalence principle may occur and can be consistently described. The Kaluza–Klein theories from the 1920s as well as modern string theories, for instance, introduce additional compactified dimensions, and the size of these—yet unobserved—dimensions determines the strength of the fundamental forces. If the size of these dimensions should happen to change over time, the strength of the forces in four-dimensional space–time would change as well. Such a change would manifest itself as a change of the coupling constants and particle masses.¹

From an experimental perspective, it is most practical to search for variation of dimensionless quantities. The fine structure constant, α , representing the strength of the electro-weak force, and the proton–electron mass ratio, $\mu = m_p/m_e$, which is a measure for the strength of the strong force, are the prime targets of modern research in this area. Possible variations can be detected from a wide variety of physical phenomena, but the extreme accuracy that can be obtained in the determination of frequencies or wavelengths of spectral lines in atoms and molecules makes spectroscopy the ideal testing ground for searches of varying α and μ .² The proton–electron mass ratio is of particular interest as theoretical models predict that the variation of μ could be significantly larger than the variation of α . Calmet and

Laser Centre Vrije Universiteit, de Boelelaan 1081, NL-1081 HV Amsterdam, The Netherlands

Fritsch, for instance, predict that the variation of μ is 38 times larger than the variation of α .³

Recent astrophysical data suggest that the fine structure constant, α , has increased over cosmological time. The combined analysis over more than 100 quasar systems has produced a value of a relative change of $\Delta\alpha/\alpha = -0.57 \pm 0.10 \times 10^{-5}$, which is at the 5σ significance level.⁴ Based on the spectral lines of molecular hydrogen in two quasar systems at redshifts of $z = 2.6$ and $z = 3$, an indication was found of a relative decrease of the proton–electron mass ratio, μ , of two parts in 10^5 over cosmological time.⁵ If one assumes that the constants change linearly over time, this implies a fractional change on the order of 10^{-15} per year. To test the time-variation of fundamental constants in the current epoch, frequency standards based on different atomic and molecular transitions are being compared as a function of time. As these standards have in general a different dependence on α and μ , a possible time-variation of α and/or μ will lead to a frequency shift. In contrast to astrophysical observations, which measure the constants' value over a significant fraction of the age of the universe, laboratory tests cover only a short time span. Their advantage, however, is their great accuracy, reproducibility and unequivocal interpretation.

Currently, laboratory experiments have found no indications for the time-variation of any fundamental constant. The most stringent limit is set by a comparison between an optical mercury ion clock and a caesium fountain clock over 6 years. Assuming invariance of other constants, this results in a limit for the variation of $\Delta\alpha/\alpha < 1.3 \times 10^{-16} \text{ yr}^{-1}$.⁶ The most stringent *independent* test of the time-variation of μ is set by comparing vibrational transitions in SF₆ with a caesium fountain over 2 years, which has resulted in a limit for the variation of $\Delta\mu/\mu < 5.6 \times 10^{-14} \text{ yr}^{-1}$.⁷

The sensitivity of any experiment looking for a frequency shift, $\Delta\nu$, due to the time-variation of a fundamental constant, X , depends both on the size of the shift, *i.e.*, the inherent sensitivity of the atomic or molecular transition, and on the ability to measure this shift. As a measure for the inherent sensitivity of a transition, we introduce a sensitivity coefficient, K , *via*:

$$\frac{\Delta\nu}{\nu} = K_X \frac{\Delta X}{X}$$

Generally, two strategies can be followed: (i) one uses a system that is naturally suitable for precision measurements—*i.e.*, a system that can be well controlled by *e.g.*, laser cooling techniques, offers a high Q -factor, a high signal to noise, *etc.*—but has typically a sensitivity on the order of unity. (ii) one uses a system that has a large sensitivity, but that is not necessarily ideal for precision measurements. At present, most currently running and proposed⁸ experiments take the first approach. A notable exception is the experiment of Cingöz *et al.* on atomic dysprosium.⁹

Atomic dysprosium has a unique property of an accidental near degeneracy between two high lying energy levels that have a different symmetry and move in opposite directions if α varies. As a result, the rf transition between the two levels has a fractional sensitivity to a variation in α of about 10^6 . Note that, given a certain change of α , the resulting absolute frequency shift of the energy levels in dysprosium is comparable to that in, for instance, the mercury ion. However, whereas in the mercury ion this shift needs to be measured on an optical frequency, in dysprosium this shift can be measured on an rf frequency. The latter is usually much simpler. For example, the fractional frequency uncertainty of the current best optical standard—the mercury ion clock—is on the order of 10^{-17} , which corresponds to an absolute frequency uncertainty of 10 mHz.⁶ The current best microwave standard—the caesium fountain clock—has a fractional frequency uncertainty of 10^{-16} , which corresponds to an absolute frequency uncertainty of 1 μHz .¹⁰

Whereas in atoms a near degeneracy between levels of different symmetry is very rare, in molecules this happens rather frequently. DeMille *et al.*¹¹ proposed a test

based on a near degeneracy between the $a^3\Sigma_u^+(v = 37)$ and the $X^1\Sigma_g^+(v = 138)$ in Cs_2 . Flambaum¹² proposed to use diatomic molecules with unpaired electrons, such as LaS, LaO, LuS, LuO, YbF and similar ions, that have a cancellation between their hyperfine and rotational interval. Kozlov and Flambaum¹³ proposed to use diatomic molecules that have a cancellation between their fine structure and vibrational interval and identified Cl_2^+ , CuS, IrC, SiBr and HfF^+ as suitable candidates.¹⁴ These cancellations occur in heavy molecules which, however, do not lend themselves well to the recent developed cooling and manipulation techniques based on time-varying electric or magnetic fields.¹⁵

In this paper we propose another system that is suitable for detecting μ -variation in a laboratory experiment, in this case because of a near degeneracy between rotational levels in the fine structure ladders of a $^2\Pi$ or $^3\Pi$ state. Such a degeneracy is shown to occur in the various natural isotopomers of carbon monoxide in its $a^3\Pi$ state, which is metastable. We discuss the precision that might be obtained using metastable CO and discuss other (including ground-state) molecules that have a suitable level structure.

The sensitivity of molecular transitions to a variation of α or μ

In the Born–Oppenheimer approximation, the motion of the molecule is separated into an electronic and nuclear part. The physical basis of this separation is that the nuclei are much heavier than the electrons and hence move at much slower speeds. The nuclear motion can be further separated into a vibrational part and a rotational part. The energy difference between electronic states is much larger than the energy difference between vibrational states within an electronic state, and the energy difference between vibrational states is correspondingly larger than the energy difference between rotational states. We thus have a hierarchy of states which reveals itself in electronic, vibrational and rotational spectra of molecules. The energy of a closed shell diatomic molecule can be written as;

$$E_{v,J} = T_e + \omega_e(v + 1/2) + \omega_e x_e(v + 1/2)^2 + \dots + B_e J(J + 1) - D_e J^2(J + 1)^2 + \dots - \alpha_e(v + 1/2)J(J + 1) + \dots$$

with T_e being the electronic energy, ω_e and $\omega_e x_e$ being the harmonic and anharmonic vibrational constant, B_e and D_e being the rotational constant and the centrifugal distortion constant, and v and J are the vibrational and rotational quantum numbers, respectively. α_e is the lowest order coupling term between the vibrational and rotational motion in the molecule.^{16,17}

In order to determine the sensitivity of a certain molecular transition to a possible change of the proton to electron mass ratio, μ , we must determine the dependence of the molecular constants to μ . If we assume that the neutron to electron mass ratio changes at the same rate as the proton to electron mass ratio, we find that:

$$\frac{\Delta\mu}{\mu} = \frac{\Delta\mu_N}{\mu_N}$$

with μ_N being the reduced nuclear mass of the molecule. Thus, the dependence of the molecular constants on μ can be found by using the well known scaling relations upon isotopic substitution—the favorite method of the spectroscopist to aid the assignment of molecular spectra. The following relations hold¹⁶

$$T_e \propto \mu^0, \quad \omega_e \propto 1/\sqrt{\mu}, \quad \omega_e x_e \propto 1/\mu \\ B_e \propto 1/\mu, \quad D_e \propto 1/\mu^2, \quad \alpha_e \propto 1/\mu^{1.5}$$

Thus we see that pure electronic transitions do not depend on μ (but do depend on α). Transitions between low lying vibrational levels have $K_\mu = 1/2$, while K_μ is below

$\frac{1}{2}$ for transitions between higher vibrational levels due to anharmonicity. Transitions between low lying rotational states have $K_\mu = 1$, while K_μ is below 1 for transitions between higher lying rotational states where centrifugal distortion becomes significant. Note that in more complex molecules, additional degrees of freedom and intramolecular motions play a role which may lead to an enhancement of the sensitivity to a variation in μ . The inversion frequency in the ground state of ammonia, for instance, has a sensitivity equal to $K_\mu = 4.6$.^{18,19}

Let us now turn to diatomics with open shell electronic states—so called free radicals. The interaction between the electronic orbital angular momentum, L , the spin angular momentum, S , and the rotational angular momentum, R , give rise to additional structure as compared to a closed shell molecule. Two cases can be distinguished:^{16,17} (i) Hund's case (a); L is strongly coupled to the internuclear axis and S couples to the electronic orbital angular momentum vector *via* spin-orbit interaction. (ii) Hund's case (b); the S is decoupled from the internuclear axis, the orbital angular momentum couples to R to form N , which then couples to S .

We will be interested in molecular states that are well described by Hund's case (a) coupling scheme for reasons that will become obvious. In Hund's case (a), molecular levels are labeled by the total angular momentum, J , by the projection of L on the internuclear axis, A , by the projection of S on the internuclear axis, Σ , and by the projections of J on the internuclear axis, Ω , and on the space fixed axis, M . There are $2S + 1$ fine structure levels, characterized by their Ω values. These levels have energies of $A_e A \Sigma$, with A_e being the spin-orbit constant. Each fine-structure state has a pattern of rotational levels with energies given by $B_e J(J + 1) - D_e J^2(J + 1)^2 \dots$, with $J = \Omega$ being the lowest level. In light molecules, A_e is comparable to B_e , whereas in heavy molecules A_e becomes comparable to ω_e . In Hund's case (a), the electronic motion can in first order be separated from the nuclear motion; that is, the energy differences between the different Ω -manifolds depend on α but not on μ . This has as interesting consequence that when two rotational levels of different Ω -manifolds have a near degeneracy, the sensitivity of a transition connecting these two levels to a variation of α and μ is enhanced by a factor A_e/ν , with ν being the frequency of the transition in energy units. As an example we will study such near degeneracies in metastable CO.

Metastable CO

The metastable $a^3\Pi$ state in CO is one of the most extensively studied triplet states of any molecule. It has been studied using rf,²⁰ microwave²¹ and UV-spectroscopy.²² The lifetime of the $a^3\Pi$ state depends strongly on the rotational level and ranges from 2.6 ms in the $v = 0, J = 1, \Omega = 1$ level to 140 ms in the $v = 0, J = 2, \Omega = 2$ level. Rotational levels in the $v = 0$ and $v = 1$ of the $a^3\Pi$ state can be directly excited using laser radiation around 206 and 199 nm, respectively.²³ Due to its favorable properties, metastable CO was used in the first demonstration of Stark deceleration.²⁴ Recently, metastable CO was trapped in an electrostatic trap and its lifetime directly measured by monitoring the trap-decay.²⁵

We have calculated the excitation energy of the rotational levels of the $a^3\Pi$ state using the model of Field *et al.*²² In this model, the wavefunctions are a superposition of pure Hund's case (a) wavefunctions.²⁶ The energies of the lower rotational levels are shown in Fig. 1. The component of the total electronic angular momentum along the internuclear axis Ω takes on the values $A + \Sigma = 0, 1, 2$, resulting in three Ω -ladders. Each J -level is split by the A -doubling into two components with opposite parity. The A -doubling in the $\Omega = 0$ state is large and relatively independent of J . The A -doubling in the $\Omega = 1$ state is much smaller and in the $\Omega = 2$ state even smaller still.

For pedagogic reasons, we will first examine 1-photon transitions between the different Ω -manifolds. We are looking for transitions with as small a frequency as

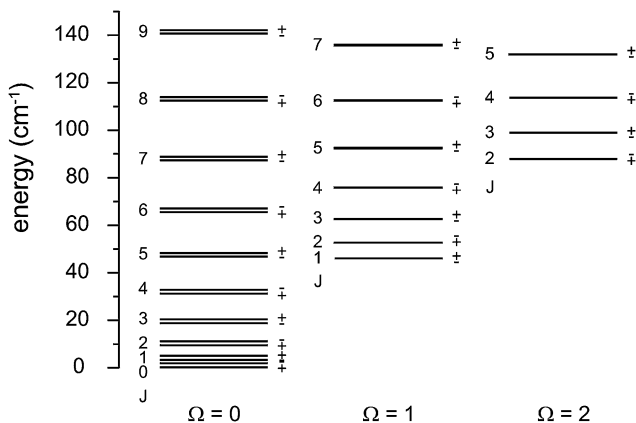


Fig. 1 Energy of the lowest rotational levels of the $a^3\Pi$ ($\nu = 0$) state of $^{12}\text{C}^{16}\text{O}$.

possible, hence we look at transitions $J - 1, \Omega = 2 \rightarrow J, \Omega = 1$ and $J, \Omega = 1 \rightarrow J + 1, \Omega = 0$. As the total parity changes sign in a 1-photon transition, transitions only connect upper Λ -doublet levels to upper Λ -doublet levels and lower Λ -doublet levels to lower Λ -doublet levels. Hence, for every J , we have a total of 4 transitions. These 4 transitions are shown in the upper panel of Fig. 2 as a function of J . Naively, we expected a minimum transition frequency to occur when $A_e \approx 2B_e J$. For the $a^3\Pi$ state of $^{12}\text{C}^{16}\text{O}$, $A_e = 41.45 \text{ cm}^{-1}$ and $B_e = 1.68 \text{ cm}^{-1}$,²² thus, we expected a minimum transition frequency when $J \approx 12$. From the figure, we see that although the energy difference initially becomes rapidly smaller as J increases—as is obvious from the tangent at low J shown as dashed lines—the energy difference converges to a constant. We can understand this as a transition from a Hund's case (a) to a Hund's case (b) coupling scheme. At higher J , the spin becomes uncoupled from the internuclear axis and the electronic and nuclear motion can no longer be separated. As a consequence the sensitivity to a μ -variation for transition between the different Ω -manifolds at high J is similar to pure rotational transitions.

Let us now turn to 2-photon transitions, *i.e.*, transitions from $J - 2, \Omega = 2 \rightarrow J, \Omega = 1$ and $J, \Omega = 1 \rightarrow J + 2, \Omega = 0$. Again transitions only connect upper Λ -doublet levels to upper Λ -doublet levels and lower Λ -doublet levels to lower Λ -doublet levels because parity is conserved in a 2-photon transition. Hence, we have 4 transitions for every J . These 4 transitions are shown in the lower panel of Fig. 2 as a function of J . A minimum energy difference is now expected when $A_e \approx 4B_e J$; *i.e.*, when $J \approx 6$, as is indeed observed.

In Fig. 3, the transitions from $J = 4, \Omega = 2 \rightarrow J = 6, \Omega = 1$ and $J = 6, \Omega = 1 \rightarrow J = 8, \Omega = 0$ are shown for the most common isotopomers of CO. Here the effects of nuclear spin and hyperfine structure have been neglected. The molecular constants are obtained *via* isotope scaling of the constants of $^{12}\text{C}^{16}\text{O}$ *via* the relations discussed earlier. The large isotope shift of the transitions is indicative of a large sensitivity to a variation of μ . The solid lines plotted in the figure, follow the relation $E = \text{constant} + \mu_{\text{N}} \times 72.5 \text{ [GHz amu}^{-1}\text{]}$, with μ_{N} being the reduced nuclear mass. From this we can determine the sensitivity, $K_{\mu} = 2\mu_{\text{N}} \times 72.5 \text{ [GHz amu}^{-1}\text{]}/\Delta E$, with ΔE being the energy difference between the two near degenerate levels. Similar calculations have been performed for the $\nu = 1$ state (not shown). Due to the smaller B constant in the $\nu = 1$, the energy differences of the different transitions are slightly larger (more positive). As a result, in the $\nu = 1$ state the $J = 6, \Omega = 1$ lies slightly above the $J = 8, \Omega = 0$, whereas in the $\nu = 0$ state the $J = 6, \Omega = 1$ lies slightly below the $J = 8, \Omega = 0$.

All transitions with frequencies below 25 GHz are listed in Table 1 together with their sensitivity to a variation of μ . Particularly interesting are the two transitions in

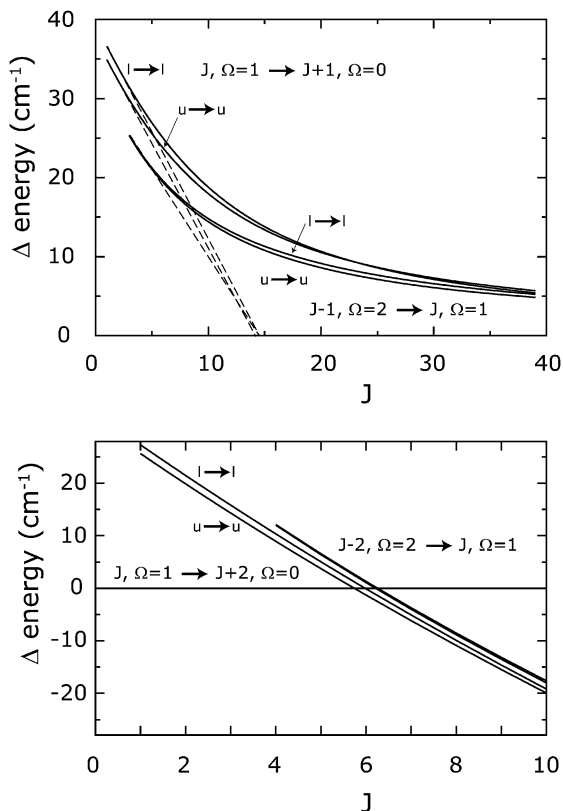


Fig. 2 Energy difference between $J - 1, \Omega = 2$ and $J, \Omega = 1$ levels and between $J + 1, \Omega = 0$ and $J, \Omega = 1$ levels (1-photon transitions) (upper panel) and energy difference between $J - 2, \Omega = 2$ and $J, \Omega = 1$ levels and between $J, \Omega = 1$ and $J + 2, \Omega = 0$ levels (2-photon transitions) (lower panel) in the $a^3\Pi$ ($v = 0$) state of $^{12}\text{C}^{16}\text{O}$.

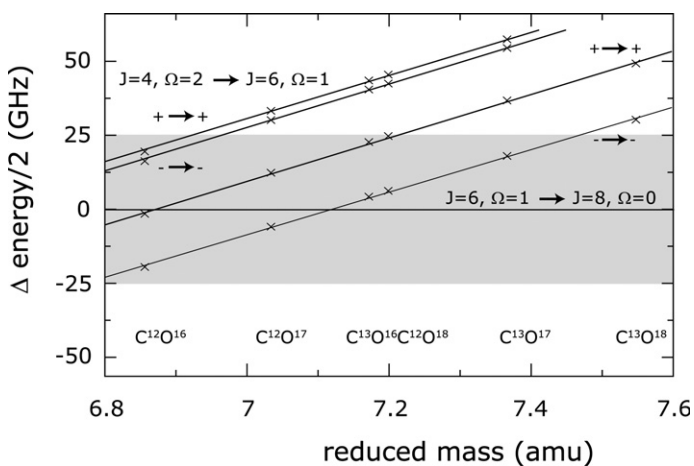


Fig. 3 Energy of selected 2-photon transitions in the $a^3\Pi$ ($v = 0$) state of (different isotopomers of) CO. The sensitivity for a change of μ is apparent from the large isotope shift of the transition.

Table 1 Frequencies of selected 2-photon transitions in the $a^3\Pi$ state of (different isotopomers of) CO together with their sensitivity to a μ -variation

ν/GHz	Isotope	Transition	Sensitivity, K_μ
1	1.648	$\text{C}^{12}\text{O}^{16}$ $\nu = 0, J = 6, \Omega = 1, + \rightarrow \nu = 0, J = 8, \Omega = 0, +$	-302
2	1.9	$\text{C}^{12}\text{O}^{17}$ $\nu = 1, J = 6, \Omega = 1, - \rightarrow \nu = 1, J = 8, \Omega = 0, -$	-264
3	2.459	$\text{C}^{12}\text{O}^{16}$ $\nu = 1, J = 6, \Omega = 1, + \rightarrow \nu = 1, J = 8, \Omega = 0, +$	202
4	4.1	$\text{C}^{13}\text{O}^{16}$ $\nu = 0, J = 6, \Omega = 1, - \rightarrow \nu = 0, J = 8, \Omega = 0, -$	126
5	6.0	$\text{C}^{12}\text{O}^{17}$ $\nu = 0, J = 6, \Omega = 1, - \rightarrow \nu = 0, J = 8, \Omega = 1, -$	-86
6	6.1	$\text{C}^{12}\text{O}^{18}$ $\nu = 0, J = 6, \Omega = 1, - \rightarrow \nu = 0, J = 8, \Omega = 0, -$	86
7	8.0	$\text{C}^{13}\text{O}^{16}$ $\nu = 1, J = 6, \Omega = 1, - \rightarrow \nu = 1, J = 8, \Omega = 0, -$	65
8	10.0	$\text{C}^{12}\text{O}^{18}$ $\nu = 1, J = 6, \Omega = 1, - \rightarrow \nu = 1, J = 8, \Omega = 0, -$	52
9	12.2	$\text{C}^{12}\text{O}^{17}$ $\nu = 0, J = 6, \Omega = 1, + \rightarrow \nu = 0, J = 8, \Omega = 0, +$	42
10	16.040	$\text{C}^{12}\text{O}^{16}$ $\nu = 0, J = 6, \Omega = 1, - \rightarrow \nu = 0, J = 4, \Omega = 2, -$	31
11	16.1	$\text{C}^{12}\text{O}^{17}$ $\nu = 1, J = 6, \Omega = 1, + \rightarrow \nu = 1, J = 8, \Omega = 0, +$	32
12	17.8	$\text{C}^{13}\text{O}^{17}$ $\nu = 0, J = 6, \Omega = 1, - \rightarrow \nu = 0, J = 8, \Omega = 0, -$	30
13	19.253	$\text{C}^{12}\text{O}^{16}$ $\nu = 0, J = 6, \Omega = 1, + \rightarrow \nu = 0, J = 4, \Omega = 2, +$	26
14	19.470	$\text{C}^{12}\text{O}^{16}$ $\nu = 0, J = 6, \Omega = 1, - \rightarrow \nu = 0, J = 8, \Omega = 0, -$	-26
15	19.917	$\text{C}^{12}\text{O}^{16}$ $\nu = 1, J = 6, \Omega = 1, - \rightarrow \nu = 1, J = 4, \Omega = 2, -$	25

$^{12}\text{C}^{16}\text{O}$ at 1.648 GHz and 2.459 GHz (#1 and #3 of Table 1). When μ changes, the frequencies of these two transitions will change in opposite directions, *i.e.*, when μ becomes larger, the transition frequency in the $\nu = 0$ will decrease while the transition frequency in the $\nu = 1$ will increase. Combined these two transitions have a sensitivity which is 500 times larger than an ordinary rotational transition. It is instructive to compare the sensitivity to what one would expect in a pure Hund's case (a). For the transition at 1.648 GHz we expect a sensitivity of $-A/\nu = -41.45 \times 29.979/1.648 = -754$ which is 2.5 times larger than calculated using the model that includes the coupling between the different Ω -ladders. This is a warning that neglecting relevant couplings leads to an overestimation of the sensitivity.

Transitions between levels of different Ω -ladders are sensitive to variations of both μ and α . As the spin orbit energy scales as α^2 ,^{12,13} in a pure Hund's case (a) the sensitivity of the 2-photon transitions to a variation of α is given by $2 A/\nu$. Mixing between different Ω -ladders will decrease the sensitivity to a variation of α . To first order, K_α will decrease in the same way as K_μ , hence, for the different transitions listed in Table 1, K_α is estimated to be two times larger than K_μ .

A proposed experiment in metastable CO

In this section we will present a molecular beam machine that is currently under construction at the Laser Centre Vrije Universiteit to measure 2-photon microwave transitions in metastable CO, and estimate the accuracy that may be achieved. We will focus on the $J = 6, \Omega = 1, + \rightarrow J = 8, \Omega = 0, +$ transitions in the $\nu = 0$ and $\nu = 1$ of $^{12}\text{C}^{16}\text{O}$ at 1.648 GHz and the 2.459 GHz, respectively, as these offer the highest sensitivity and are located in a convenient frequency range. Furthermore, $\text{C}^{12}\text{O}^{16}$ is the most abundant isotope (99%) and both C^{12} and O^{16} have a nuclear spin equal to zero. As both transitions differ only in vibrational energy (and sensitivity coefficient), systematic shifts due to stray magnetic or electric fields will be similar, and hence will cancel to first order. The other transitions listed in Table 1, as well as Λ -doublet transitions that are located in the same frequency range might be used to check for various systematic errors.

As mentioned, astronomical observations suggest that $\Delta\mu/\mu$ might change by $2 \times 10^{-15} \text{ yr}^{-1}$.⁵ The most stringent laboratory test of μ -variation is set by comparing vibrational transitions in SF_6 with a caesium fountain over 2 years, which has

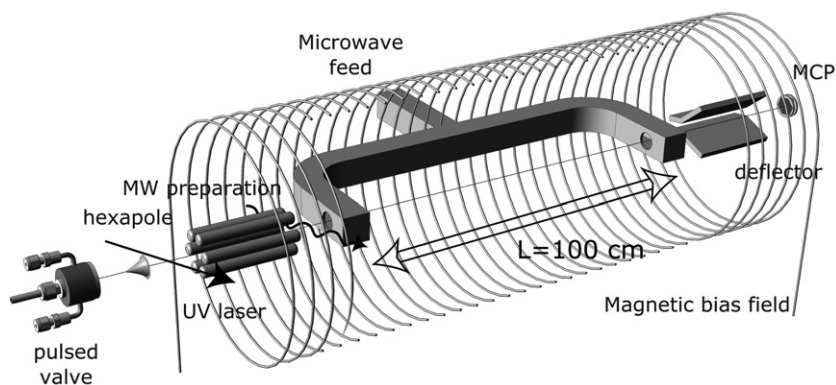


Fig. 4 Schematic view of a molecular beam apparatus to measure 2-photon microwave transitions in metastable CO.

resulted in a limit for the variation of $\Delta\mu/\mu < 5.6 \times 10^{-14} \text{ yr}^{-1}$.⁷ In order to achieve a sensitivity in the order of 10^{-15} yr^{-1} the 2-photon transitions should be measured with a fractional accuracy of 10^{-12} . Although demanding, this seems possible.

Fig. 4 shows a schematic of a molecular beam apparatus that will be used to measure 2-photon microwave transitions in metastable CO. The machine is largely similar to the familiar magnetically deflected cesium beam clock²⁷—clocks that have routinely reached fractional accuracies below 10^{-13} —the main difference being that the inhomogeneous magnetic fields are replaced by inhomogeneous electric fields. Due to its large vapor pressure and small polarisability, it is straightforward to produce an intense beam of CO molecules. Using pulsed laser light around 206 or 199 nm, the spin forbidden $a^3\Pi_1(v=0, J=6, -) \leftarrow X^1\Sigma^+(J=6)$ or $a^3\Pi_1(v=1, J=6, -) \leftarrow X^1\Sigma^+(J=6)$ is driven. These states are the upper components of the $J=6, \Omega=1$ state and have a positive Stark shift. Hence molecules in these states can be focused into the microwave cavity using either a quadrupole or hexapole or a combination of the two. Before the molecules enter the cavity they are driven to the lower component of the $J=6, \Omega=1$ state by inducing the A -doubling transition using pulsed microwave radiation around 6.5 GHz.

The 2-photon transition is measured using Ramsey's separated oscillatory fields method.²⁸ In the first cavity a coherent superposition of the lower component of the $J=6, \Omega=1$ and $J=8, \Omega=0$ state is created. During free flight between the two cavities, the phase of this coherent superposition will evolve. If there is no phase difference between the wavefunction and the microwave field—the microwave field is exactly at resonance—all molecules will be driven to the $J=8, \Omega=0$ state. If there is a π difference between the phase of the microwave field and the wavefunction, molecules will be driven to $J=6, \Omega=1$ state. Thus, if the frequency of the microwave field is scanned, an interference pattern is observed. The width of the fringes is determined by the time it takes for the molecules to pass the distance between the two cavities. If the distance between the cavities is taken to be a meter and the molecules have a velocity of about 500 m s^{-1} , the fringes will have a width of about 250 Hz. A homogeneous magnetic field is applied throughout the beam tube, to shift all resonances out of resonance, except for the $M=0 \rightarrow M=0$. Note that, as this magnetic field is perpendicular to the electric field, the magnetic field does not influence the pre and post state-selection. After the microwave cavity the molecules pass an inhomogeneous electric field that will deflect molecules in the $J=6, \Omega=1$ state while it will not influence the trajectories of molecules in the $J=8, \Omega=0$ state. Metastable CO molecules are detected by letting them impinge onto a multichannel plate (MCP) detector. The 6 eV internal energy of the metastable CO molecules is sufficient to free electrons at the surface of the MCP detector. These electrons are

multiplied and accelerated towards a phosphor screen. Subsequently, a digital camera is used to record the image on the phosphor screen.²⁹ The possibility to record the number of molecules in the $J = 6, Q = 1$ and $J = 8, Q = 0$ state *simultaneously* makes it possible to normalize the beam on a shot to shot basis which increases the signal to noise ratio. Note that any molecules remaining in the upper component of the $J = 6, Q = 1$ will be deflected in the opposite direction to molecules in the lower component and hence will not cause any background signal.

A frequency measurement is characterized by its statistical uncertainty and its accuracy—how well the measured frequency agrees with the unperturbed molecular frequency. A measure of the statistical instability as a function of measurement time is provided by the Allen variance,²⁷

$$\sigma_y(\tau) = \frac{1}{Q} \frac{1}{\sqrt{N\tau/\tau_c}}$$

where Q is the quality factor of the transition given by the transition frequency over the measured linewidth, $\nu/\Delta\nu$, N is the number of metastable molecules detected per cycle, τ is the measurement time and τ_c is the duration of a single cycle. As mentioned, if we assume that the two cavities are separated by a distance of 1 m, and the velocity of the beam is on the order of 500 m s^{-1} , the interaction time is 2 milliseconds and the measured linewidth will be about 250 Hz. This corresponds to a Q -factor of 1×10^7 . We estimate that it should be possible to detect 1000 or more molecules per cycle. At a repetition frequency of 10 Hz, we find $\sigma_y = 1 \times 10^{-9} \tau^{-1/2}$. This implies that a measurement time of about 1 h is required to reach an accuracy of 2×10^{-11} , and 300 h to reach an accuracy of 1×10^{-12} .

Ultimately, the precision will be limited by systematic shifts. With a careful design it should be feasible to keep errors due to the second order Zeeman and Stark shifts and blackbody radiation below 10^{-12} . Note that in caesium fountain clocks¹⁰ these systematic effects are compensated at the level of 10^{-16} . Moreover, as the two transitions that will be compared differ only in vibration, we expect that most systematic errors will—to a very large extent—cancel. An open question is if the high power, necessary to induce the 2-photon transitions, leads to unacceptably large light shifts. Again, the shifts in both transitions are expected to be similar and they will partly cancel.

Other molecules

The precision that will be obtained on measuring the proposed 2-photon transitions in metastable CO will be limited by the lifetime of the metastable CO, which is on the order of 3 milliseconds for the $J = 6, Q = 1$ and $J = 8, Q = 0$ state. In this section we will discuss a number of other molecules where a cancellation of the fine structure and rotational interval might be expected to occur. We are particularly interested in molecules that can be decelerated using time-varying electric fields, such that the transition can be measured in a slow molecular beam^{17,30} or in a molecular fountain.¹⁸ In Bethlem *et al.*³¹ a list of candidate molecules for Stark deceleration was presented. Most molecules on that list have by now indeed been decelerated. If we discard all polyatomic molecules—which are interesting in their own right—we are left with CH, CF, CO ($a^3\Pi$), LiH, NH ($a^1\Delta$), NO, OH, OD, SH. In what follows, we will discuss the suitability of these molecules to detect μ -variation using near degenerate rotational levels in different Q -manifolds.

CH

The ground state of CH is $^2\Pi$. The spin orbit constant and rotational constant are $A = 27.95 \text{ cm}^{-1}$ and $B = 14.457 \text{ cm}^{-1}$, respectively.³² Due to the small ratio of A to B

the molecule is best described by a Hund's case (b) coupling scheme even for low J , and no degeneracies will occur. For CD, the spin orbit constant and rotational constant are $A = 27.95 \text{ cm}^{-1}$, and $B = 7.8 \text{ cm}^{-1}$. Although the ratio of A to B is increased by a factor of 2 compared to CH, CD is still very much case (b) even in the lowest J .

CF

The ground state of CF is $^2\Pi$. The spin orbit constant and rotational constant are $A = 77.12 \text{ cm}^{-1}$ and $B = 1.417 \text{ cm}^{-1}$, respectively.³² Due to the large ratio of A to B , CF is well described by Hund's case (a). The two Ω -manifolds are expected to have a near-degeneracy at $J \approx 13$. More detailed calculations are needed to determine the frequency of the 2-photon transition and its sensitivity. However, the fact that the degeneracy occurs at high J , makes CF less suitable.

LiH

The ground state of LiH is $^1\Sigma$. As $\Lambda = 0$, it follows a Hund's case (b) coupling scheme.

NH

NH can be decelerated in the long lived $a^1\Delta$ state. This state is best described in Hund's case (b).

NO

The ground state of NO is $^2\Pi$. The spin orbit constant and rotational constant are $A = 123.26 \text{ cm}^{-1}$ and $B = 1.672 \text{ cm}^{-1}$, respectively.³² Due to the large ratio of A to B , NO is well described by Hund's case (a). For $^{14}\text{N}^{16}\text{O}$ the two Ω -manifolds have near-degeneracies at $J = 18.5$ and $J = 19.5$. The smallest frequencies are around 70 GHz, which results in an enhancement of about 60. Smaller frequencies and correspondingly larger enhancement might be obtained with other isotopes of NO, however, the high J at which the degeneracy occurs is a disadvantage.

OH

The ground state of OH is $^2\Pi$. The spin orbit constant and rotational constant are $A = -139.21 \text{ cm}^{-1}$ and $B = 84.881 \text{ cm}^{-1}$, respectively.³² Due to the negative A constant the $^2\Pi_{3/2}$ lies below the $^2\Pi_{1/2}$ state. If this would not have been the case, no near-degeneracies would have occurred due to the small A to B ratio. However, as a result of spin-orbit inversion, a near-degeneracy occurs between the $J = 7/2$, $\Omega = 3/2$ and $J = 3/2$, $\Omega = 1/2$ states with a 2-photon transition frequency of 220 GHz and an estimated enhancement to a μ -variation of about 10. The situation might be more favorable in OD.

SH

The ground state of SH is $^2\Pi$. The spin orbit constant and rotational constant are $A = -376.9 \text{ cm}^{-1}$ and $B = 9.461 \text{ cm}^{-1}$, respectively.³² Due to the large ratio of A to B , SH is well described by Hund's case (a). The two Ω -manifolds are expected to have a near-degeneracy at $J \approx 12$. More detailed calculations are needed to determine the frequency of the 2-photon transition and its sensitivity.

Conclusions

In this paper we have shown that the sensitivity to a variation of the proton-electron mass ratio, μ , and the fine-structure constant, α , is enhanced due to near degeneracy

between rotational levels in the fine structure ladders of molecular radicals. This is an extension to the work of Flambaum¹² and Flambaum and Kozlov,¹³ who showed that the relative sensitivity to a variation of μ and α is enhanced due to cancellation of hyperfine intervals with rotational intervals and cancellation of fine structure intervals with vibrational intervals. Whereas the cancellations discussed in ref. [12] and [13] occur in heavy molecules, the cancellations discussed in this paper occur in light molecules. As techniques to manipulate and cool molecules are more adapted to light molecules, a higher precision might be expected for these molecules.

We have presented a detailed calculation, including all relevant couplings, that show that a degeneracy occurs in the various natural isotopomers of carbon monoxide in its $a^3\Pi$ state. The most suitable transitions are the $J = 6, Q = 1, + \rightarrow J = 8, Q = 0, +$ transitions in the $v = 0$ and $v = 1$ of $^{12}\text{C}^{16}\text{O}$ at 1.648 GHz and the 2.459 GHz, respectively, which have a combined sensitivity to a μ -variation on the order of 500, and an estimated combined sensitivity to an α -variation of 1000. It seems possible to measure the 2-photon transitions with a fractional precision on the order of 10^{-12} , which would result in a limit for μ -variation on the order of 10^{-15} yr^{-1} .

The enhanced sensitivity due to the near-degenerate fine-structure levels should occur in many other light molecules as well. It is our hope to identify a molecule that has a suitable level structure and that can be cooled using one of the existing cooling techniques. We have performed a check for a number of seemingly promising molecules. But it turned out that these molecules all have either a too small A/B ratio—such that the molecule is no longer well described in a Hund's case (a) coupling scheme—or a too large A/B ratio—in which case the near degeneracy occurs at high J . We encourage the attendants of the Faraday meeting to come forward with suggestions for suitable molecules.

Acknowledgements

We thank Giel Berden and Gerard Meijer for many stimulating discussions on metastable CO and Sam Meek for useful discussions on the Zeeman effect. We thank Ruud van Putten for help with the calculations. H. L. B acknowledges financial support from the Netherlands Organisation for Scientific Research (NWO) *via* a VIDI-grant and from the European Research Council *via* a Starting Grant.

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General discussion

Dr Lane opened the discussion of the paper by Professor Herschbach: Chemists are particularly interested in the transition state region of a reaction. What prospects do you see for ultracold molecules in this area of research? Would their usefulness depend on whether the reaction has an early or late barrier?

Professor Herschbach replied: The transition state of a reaction, as Dr Lane points out, is indeed a chief concern of chemists. It refers to a critical stage that the transient liaison of the reactants must reach in order to metamorphose into products. Most often, the transition state is considered to be at the crest of an activation energy barrier separating the entrance and exit valleys of the potential energy surface. The barrier is termed “early” if its crest lies in the entrance valley, “late” if in the exit valley. Traversing an early barrier requires reactant translational kinetic energy at least slightly in excess of the barrier height, whereas a similar level of reactant vibrational excitation is ineffective. In contrast, for crossing a late barrier reactant vibrational excitation is highly effective but translation is not. This pattern, and more nuanced aspects, was demonstrated particularly well by John Polanyi and his colleagues in extensive classical trajectory simulations of reactions on a variety of potential surfaces.¹

In ultracold collisions, chemical reactions cannot be expected to occur at an appreciable rate unless an activation energy barrier is lacking (as in the reactions of open-shell atoms or free radicals mentioned in my paper) or tunneling through the barrier is unusually facile (as for $F + H_2$, enhanced by very small reduced mass, low and narrow barrier, and strong resonance). There would thus seem to be no practical prospect of ultracold probing of transition states of the sort usually considered, located at barrier crests. However, that may hold only if translational kinetic energy is required to reach the crest. The crest region could instead be accessed in reactions of ultracold reactant molecules prepared in a vibrationally excited state. (Now achieved for alkali dimers, but not pertinent here as their reactions are barrierless.) According to the Polanyi pattern, this would be expected to enable reactions governed by a late barrier but not by an early barrier. That pattern was demonstrated in the classical realm, so invites a theoretical study to see whether or not it holds also for ultracold collisions.

¹ J. C. Polanyi, *Chem. Scr.*, 1987, **27**, 229; J. C. Polanyi, *Science*, 1987, **236**, 68.

Professor Stwalley addressed Professor Herschbach: I wanted to point out that in the reactions of ultracold molecules, the uppermost final rotational state populated can be limited because of angular momentum rather than energy constraints. For example,¹ in consideration of the reaction of translationally ultracold $KRb(v = 0, j = 0)$ with K , the exoergicity to form $K_2(v' = 0, j' = 0)$ is 225 cm^{-1} . If the exoergicity is put into rotation instead, K_2 molecules with j' up to 62 could be formed. However, since the initial collisional angular momentum l must be small (say $l < 4$) at ultracold temperatures to surmount the centrifugal barriers in the entrance channel and since $j = 0$, the total angular momentum (excluding spins) must be small; consequently, a final $j' = 62$ must be accompanied by a final l' of ~ 60 to conserve the small total angular momentum. However, the exit channel centrifugal barrier for $l' \sim 60$ is then likely to be sufficiently large to prevent the products [$Rb + K_2(v' = 0, j' = 62)$] from separating.

¹ D. Wang *et al.*, *Eur. Phys. J. D*, 2004, **31**, 165.

Professor Herschbach responded: For $A + BC$ reactions of low exoergicity that proceed *via* an attractive short-range potential well, the product departure is often

inhibited by centrifugal barriers in the exit valley. The inhibition introduces a characteristic form factor in the product kinetic energy distribution.¹ As Professor Stwalley points out, the exit angular momentum constraint, $l = -j'$, imposed in the ultracold limit might be expected to suppress to some extent the population of rotational states of the AB product molecule.

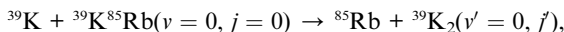
The maximum value of the product rotational excitation $E_{R'}(j') = B_v' j'(j' + 1)$ and corresponding momentum allowed by energy conservation is given by $\Delta E \geq E_{R'}(j')$, where ΔE is the reaction exoergicity to form the product vibrational state v' , with $j' = 0$, and B_v' is the rotational constant of the AB molecule in the v' state. The question is whether a substantially lower limit on j' results from the requirement that the product translational kinetic energy, $E_{T'} = \Delta E - E_{R'}(j')$, exceeds the exit centrifugal barrier $V_{CB}(l)$, with the exit orbital momentum specified by $l = j'$.

Pertinent evidence and estimates indicate that for ultracold reactions of alkali atoms with dimers, the allowed range of j' is generally not much affected by the centrifugal barrier. In a review of quantum dynamics calculations,² Hutson and Soldán display product rotational distributions resulting from inelastic/reactive vibrational quenching collisions of spin-polarized $M + M_2(v = 1, j = 0) \rightarrow M + M_2(v' = 0, j')$. These occur on quartet surfaces with deep attractive wells. Both for $M = Na$ and K , the rotational distributions extend to the maximum j' allowed by energy conservation: 20 and 24, respectively. Subject to symmetry restrictions (only even j' for bosons, odd for fermions), all accessible levels are populated. These results are consistent with the usual formula for estimating $V_{CB}(l)$ for an R^{-6} exit potential,

$$V_{CB}(l) = 0.38[l(l + 1)/\mu']^{3/2} C_6^{-1/2},$$

where V_{CB} is in cm^{-1} , the $AB + C$ reduced mass μ' in amu and the van der Waals coefficient C_6 in atomic units (hartree-bohr⁶). For the Na case, $V_{CB}(20) = 0.70 \text{ cm}^{-1}$ (with $C_6 \sim 6000 \text{ a.u.}$), whereas $\Delta E = 23.5 \text{ cm}^{-1}$. For the K case, $V_{CB}(24) = 0.44 \text{ cm}^{-1}$ (with $C_6 = 9050 \text{ a.u.}$), whereas $\Delta E \sim 16 \text{ cm}^{-1}$.

The reaction considered by Stwalley,



occurs on the ground singlet surface, also likely subject to a strongly attractive well. With $\Delta E = 225 \text{ cm}^{-1}$ and $B_0 = 0.05666 \text{ cm}^{-1}$, energy conservation allows K_2 levels up to $j' = 62$. A value for $C_6(\text{Rb-K}_2)$ is not available; however, it is surely larger than $C_6(\text{Rb-K}) \sim 4200 \text{ a.u.}$ ³ Thus the latter value can be used to obtain an upper bound: $V_{CB}(62) < 6 \text{ cm}^{-1}$. Deducting the requisite $E_{T'} \sim 6 \text{ cm}^{-1}$ from ΔE would then at most reduce the maximum allowed rotational excitation of K_2 to $j' = 61$.

1 S. A. Safron, N. D. Weinstein, D. R. Herschbach and J. C. Tully, *Chem. Phys. Lett.*, 1972, **12**, 564.

2 J. M. Hutson and P. Soldán, *Mol. Phys.*, 2007, **26**, 1.

3 H. L. Kramer and D. R. Herschbach, *J. Chem. Phys.*, 1970, **53**, 2792.

Dr Hudson opened the discussion of Dr Bethlem's paper: I wonder about systematic errors in the proposed measurement. Consideration of statistical sensitivity is important for establishing a bound on the experiment's sensitivity. But it is essential to also carefully consider possible systematic effects to truly estimate an experiment's potential. In particular, it would be interesting to make a quantitative estimate of the effect of the Stark shift and the consequent level of electric field control required.

The variety of transitions on offer in a molecule might in this respect be advantageous. As you suggest, one can imagine finding transitions whose frequencies can be combined in a way that eliminates the Stark effect. It would be interesting, then, to expand upon Table 1 by showing each transition's relative Stark shift.

It might be particularly useful to consider systematic effects in the context of choosing an ideal molecule. The relative merits of candidate molecules could appear somewhat different in this light.

Dr Bethlem answered: The Stark shift decreases rapidly as a function of J . For the considered transitions it is on the order of 1 Hz per $(\text{V}/\text{cm})^2$. Note that the Stark shift is similar for all transitions in the table as all these transitions involve the same rotational levels – although being in different vibrational states or in different isotopes. In order to monitor the residual electric field we plan to use (1-photon) Δ -doublet transitions in a low J level. Note that in the proposed experiment we compare transitions in the $v = 0$ and $v = 1$ state such that residual Stark shifts will in fact cancel to first order, as will many other systematic effects.

Professor Dr van der Avoird enquired: In the considerations in your paper you assume that the frequencies of the molecular vibrations and rotations are purely determined by the nuclear masses. It has been shown, however, both by theory¹ and by computations of Schwenke and Tennyson on H_2O , that due to non-Born–Oppenheimer effects these frequencies are not determined by the masses of the bare nuclei, but by atomic masses in which the mass of the electrons has to be included to some extent. What makes things complicated is that the effective atomic masses turn out to be different for different vibrations and again different for the rotations. If the ratio of the atomic masses and the nuclear masses were constant, this would not affect your results, I presume, but if this ratio varies even by a small extent (due to a time variance of the electromagnetic interactions, for example) this is perhaps a serious problem in the determination of the proton/electron mass ratio. Have you considered this problem?

1 W. Kutzelnigg, *Mol. Phys.*, 2007, **105**, 2627.

Dr Bethlem responded: In principle such considerations should be taken into account. However one should realize that knowledge of the K-sensitivity coefficients beyond accuracies of a few percent is not necessary as long as no variation is detected. For the case of H_2 the influence of non-Born–Oppenheimer (rotational-electronic interactions between the $\text{B}^1\Sigma_u^+$ and $\text{C}^1\Pi_u$ states) effects was included in the derivation of sensitivity coefficients. In addition the influence of adiabatic (mass-dependent) effects in the H_2 molecule on the resulting values for the K-coefficients was explicitly calculated and found to be less than 1% of the actual K values.¹

The representation of the level energies is a separate issue. In virtually all cases the experimental accuracy on level energies of molecules is better than their *ab initio* representations. One strategy for determining K values may start from a semi-empirical representation of level energies (*e.g.* in a Dunham expansion); the intrinsic problem is then how the coefficients of the model scale with varying proton to electron mass ratio. In the case of a Dunham model this is well-known, even for the mass-scaling of ro-vibrational coupling terms. An alternative strategy for determining K values is to compute level energies over a range of values for m , as was done by Meshkov *et al.*² for H_2 , and by Ivanov *et al.*³ for HD. Here the shortcoming is that the representation of level energies is not as good, specifically for hydrogen at the 1 cm^{-1} accuracy level. For the example of H_2 both methods^{1,2} compare to the few percent accuracy level.

1 W. Ubachs, R. Buning, K. S. E. Eikema and E. Reinhold, *J. Mol. Spectrosc.*, 2007, **241**, 155.

2 V. V. Meshkov, A. V. Stolyarov, A. Ivanchik and D. A. Varshalovich, *JETP Lett.*, 2006, **83**, 303.

3 T. I. Ivanov, M. Roudjane, M. O. Vieitez, C. A. de Lange, W. U. L. Tchang-Brillet and W. Ubachs, *Phys. Rev. Lett.*, 2008, **100**, 093007.

Dr Küpper asked: In your paper you discuss the sensitivity of change of μ and suggest the use of transitions between different Ω -ladders in CO. Did you consider transitions between different nuclear spin ladders? I understand these transitions are weak, but you are looking for narrow transitions to reach high resolution anyway. What would be the sensitivity for microwave-transitions between rotational levels in different nuclear spin symmetry ladders, *i.e.*, in molecules like ammonia?

Dr Bethlem replied: The energy level schemes of symmetric top molecules look – at a first glance – very similar to those of molecular radicals. However, whereas in radicals the energy difference between the different rotational manifolds (Ω -ladders) is due to the motion of the electrons, in symmetric top molecules the energy difference between different rotational manifolds (K-ladders) is due to the rotation along the different symmetry axes of the molecule. The energy difference between different K-ladders and the energy difference between rotational levels within a single K-ladder have the same dependence on the fundamental constants. As a consequence, transitions between different K-ladders do not show an anomalously large isotope shift as was explicitly checked for different isotopes of ammonia.

Mr Lemeshko addressed Dr Bethlem: You assume that the neutron-to-electron mass ratio changes at the same rate as the proton-to-electron one. Is it also predicted by theories beyond the Standard Model?

Dr Bethlem said: The proton and neutron are much heavier than the quarks they are composed of; the main contribution to their mass comes, in fact, from the interaction between the quarks – the number of gluons present inside the proton and neutron, if you like. As a consequence, the proton and neutron masses are a measure of the strength of the strong force and are expected to change at the same rate, at least in first order. Note that the electron is not a composite particle, and its mass arises from the electroweak sector. Hence, the proton to electron mass ratio probes phenomena of the hadronic sector with respect to those of the electroweak sector.^{1,2}

1 V. V. Flambaum, private communication.

2 V. V. Flambaum, D. B. Leinweber, A. W. Thomas, and R. D. Young, *Phys. Rev. D*, 2004, **69**, 115006.

Professor Meijer remarked: The metastable state of CO is close to the $v = 27$ and 28 of the electronic ground-state. Would it be possible to make a $X^1\Sigma^+ \leftarrow a^3\Pi$ transition, or are the Franck–Condon factors for this prohibitively low?

Dr Bethlem replied: As already mentioned, a near degeneracy between a highly excited vibrational level in the ground state and a vibrational level in an excited electronic state potentially leads to a very large enhancement of the sensitivity to a variation of the proton-to-electron mass ratio. The sensitivity of the transition mentioned is enhanced by a factor of 100 000. Moreover, as both levels have a relatively long lifetime, the linewidth of the transition may be quite narrow. Unfortunately however, the two electronic states have a minimum at nearly the same internuclear distance which results in a Franck–Condon factor for the $X^1\Sigma^+(0) \leftarrow a^3\Pi(27,28)$ below 10^{-20} , so it seems hardly feasible to drive this transition.

Dr Vanhaecke asked: Have you considered the possibility of using an additional source of photons to dress one of the states involved in the transition you want to measure? Could it constitute an additional parameter which could be used to better characterize the transition?

Dr Bethlem answered: We have not considered such opportunities yet, for the reason that it may further complicate the experiment. Particularly, if the final

precision depends on the intensity or frequency of the additional source of photons, it will only shift the problem.

Professor Ye said: It would be interesting to explore a much larger energy range where one can compare two molecular levels with vastly different dependence on (me/mp). The maximal enhancement factor obtained is through the measurement of an entire molecular potential. Can one think of optical 2-photon transitions to explore much higher vibrational levels of one potential and compare it against the lower vibrational levels of a different potential?

Dr Bethlem responded: It is important to distinguish the *absolute* sensitivity of a transition, *i.e.*, the frequency shift, $\delta\nu$, due to a certain variation of a fundamental constant from the *relative* sensitivity, *i.e.*, the relative shift, $\delta\nu/\nu$, due to a possible variation of a fundamental constant. Ideally both are large, but most systems that are currently being discussed have either a large absolute sensitivity or a large relative sensitivity.

As you mention, a large absolute sensitivity can be obtained through the measurement of an entire molecular potential using optical 2-photon transitions – as is also discussed in your paper on Sr₂,¹ however, the relative sensitivity of optical transitions is rather small. For comparison, the absolute sensitivity of the optical transitions in Sr₂ is about 10 times larger, but the relative sensitivity is about 1000 times smaller than the microwave transitions in CO discussed in our paper.

I T. Zelevinsky, S. Kotochigova, and J. Ye, *Phys. Rev. Lett.*, 2008, 100, 043201.

Professor Ye asked: What is the required level of control of residual electric fields, considering that the two molecular levels have a differential Stark shift? A drifting electric field could limit the achievable sensitivity as an important source for systematic error.

Dr Bethlem replied: The Stark shift of the considered transitions is on the order of 1 Hz per (V/cm)². For a measurement with a fractional uncertainty below 10⁻¹², we need to keep residual electric fields below 50 mV cm⁻¹, which seems feasible. Moreover, we will compare transitions in the $\nu = 0$ and $\nu = 1$, which have near identical Stark shifts (the dipole moment in the $\nu = 1$ is only 5 · 10⁻⁴ larger than in the $\nu = 0$), so these will cancel.

Dr Tarbutt commented: The sensitivity enhancement of these proposed experiments is based on the notion that it is easier to measure a given frequency shift using a low-frequency transition than a high-frequency transition. The underlying assumption here is that the precision of the experiment is limited by the relative precision of the frequency measurement so that you get a better absolute precision by measuring a smaller frequency. That will sometimes be the case, but certainly not always. I think you already make this point in your paper, but I want to emphasize it here because I think it's an important one. For example, an experiment may well be limited by a systematic error that has a certain absolute size, irrespective of whether the measurement is made on a large or a small interval. In such cases, the sensitivity enhancement does not improve the experiment at all. The characterization of certain systems by a "sensitivity factor" can be useful, but there is an inevitable temptation to think that bigger is always better, which would be very misleading indeed. In fact, a system with an enormous sensitivity factor may make a far worse experiment than one with a small factor, because it happens to suffer from a particularly severe systematic effect. A related point is that the absolute precision of a frequency measurement tends to bottom out as the frequency is lowered. In going from optical to microwave the precision improves, but once the transition is already in the microwave region, there is little to be gained from going to still lower frequencies.

Dr Bethlem responded: We fully agree. It is generally not easier to measure a certain frequency shift at 100 MHz than at 1 GHz. But, it is certainly easier to measure a certain frequency shift at 2 GHz than at 1.2 THz – which is the ‘effective’ energy difference that is being probed in our proposed experiment. On your remark on systematic errors; in our paper we propose to compare two transitions in the $v = 0$ and $v = 1$ of the $a^3\pi$ state in CO, which shift in opposite directions when the proton-to-electron mass ratio changes. This will greatly reduce systematic errors and may turn out to be more important than the increased fractional sensitivity.

Professor Tennyson addressed Dr Bethlem: I have two questions/comments.

First you compare the (prospective) observations of shifts in laboratory experiments recorded over less than a decade in the current epoch with astronomical results where the major sensitivity comes from observations of objects billions of years ago. Is this a like-for-like comparison? Do theories predict that any change in fundamental constants is linear with time or would one expect greater changes in the early universe?

Second I note microwave electronic spectra recorded some years ago by Carrington *et al.*¹ These workers observed transitions from the highest vibrational state of the $X^2\Sigma_g^+$ ground state of H_2 to the ground vibrational state of the $A^2\Sigma_u^+$ state. The two electronic states converge to the same asymptote; the excited state is basically repulsive but has a shallow minimum which supports a long-range vibrational state. This observation provides a means of observing electronic state in near degeneracy. The H_2^+ system has the advantage of being amenable to *ab initio* calculations which reach experimental precision.² This means that the effect of changing any fundamental constant can be thoroughly and accurately investigated *a priori*. To this end I made a quick calculation on the effect of changing the proton to electron mass ratio. Increasing the proton mass by 0.1% lowers the vibrational ground state by 0.6 cm^{-1} but only lowers the last bound vibrational state by 0.02 cm^{-1} .

While on this topic I note that many of the rare gas dimers being prepared at ultracold temperatures, such as Rb_2 , are often prepared in the highest vibrational state of the system. Rb_2 is electronically similar to H_2 and therefore these high-lying vibrational states of the $X^1\Sigma_g^+$ ground state could undergo electronic transitions at very long wavelengths to low-lying states of the first excited $a^3\Sigma_u^+$ state, which again only has a shallow minimum. This is of course a singlet–triplet transition so may not be expected to be as strong as those observed in H_2^+ . To achieve the equivalent spin-allowed transitions using alkali metal dimers one would have to prepare ions such as Rb_2^+

- 1 A. Carrington, I. R. McNab and C. A. Montgomerie, *Chem. Phys. Lett.*, 1989, **160**, 237.
2 C. A. Leach and R. E. Moss, *Ann. Rev. Phys. Chem.*, 1995, **46**, 55.

Dr Bethlem replied: To the first question, indeed there are theories which predict variation of fundamental constants occurs only during some cosmological episodes. In the model by Barrow *et al.*¹ the fundamental constants change only during the cosmological epoch of the matter-dominated universe; in the radiation era before $z \sim 1000$ there is no variation, nor is there any variation in the present epoch of accelerated expansion, which may have started at $z = 0.5-1$. In such a scenario no variations would occur on laboratory time scales. On the other hand, if the variation of the fundamental constants is somehow connected to the size of the universe they might be changing still. The fact of the matter is that laboratory measurements – needed to convince most of us – can only be performed now. It is noted that recent laboratory measurements already put tighter constraints on rates of change of the fine-structure constant^{2,3} than observations on cosmological time scales do.⁴

In answer to the second question, a near degeneracy between a highly excited vibrational level in the ground state and a vibrational level in an excited electronic state potentially leads to a very large enhancement of the sensitivity to a variation

of the proton-to-electron mass, as the enhancement scales with the energy difference between the two electronic states divided by the energy between the two near degenerate levels. However, for vibrational levels near the dissociation energy the sensitivity is much reduced due to the anharmonicity of the potential wells – as indeed follows from your calculations as well. A test based on a near degeneracy between the $a^3\Sigma_u^+(v = 37)$ and the $X^1\Sigma_g^+(v = 138)$ in Cs_2 was proposed by DeMille *et al.*⁵ The enhancement factor in their proposal is on the order of 1000 – again lower than one would naively expect due to anharmonic terms in the potential well. The Rb_2 system is similar to Cs_2 and similar arguments hold.

1 J. D. Barrow, H. Sandvik, and J. Magejjo, *Phys. Rev. D*, 2002, **65**, 063504.

2 A. D. Ludlow *et al.*, *Science*, 2008, **319**, 1805.

3 T. Rosenband *et al.*, *Science*, 2008, **319**, 1808.

4 M. T. Murphy, J. K. Webb, V. V. Flambaum, *Month. Not. Roy. Astron. Soc.*, 345 (2003) 609.

5 D. DeMille, S. Sainis, J. Sage, T. Bergeman, S. Kotochigova, and E. Tiesinga, *Phys. Rev. Lett.*, 2008, **100**, 043202.

Professor Herschbach commented: In the analysis of rotational spectra, it is generally assumed that the molecule consists of neutral atoms, each represented as a point mass that includes all its electrons. That is unrealistic, although adequate for many purposes. However, in early precision measurements of isotope mass ratios in diatomic molecules by microwave spectroscopy, the cloud-like electron distribution and its distortion during rotation was found to appreciably affect the molecular moment of inertia.¹ For LiBr and LiI , it proved possible in effect to “weigh an electron,” as the rotational spectra for the ^6Li and ^7Li isotopes showed that one electron had indeed been transferred from lithium to the halogen atom.² Effects of the electron distribution evidently are not considered to handicap testing the time-invariance of the proton-electron mass ratio. Is that so because the fractional change in the p-e mass ratio is taken to be equal to the change in the reduced nuclear mass of the molecule? As Dr Bethlem points out, that equality requires the neutron-electron mass ratio to change at the same rate as the p-e mass ratio.

1 C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy*, McGraw-Hill Book Company, New York, 1955.

2 A. Honig, M. Mandel, M. L. Stich and C. H. Townes, *Phys. Rev.*, 1954, **96**, 629.

Dr Bethlem responded: For testing variation of the proton-to-electron mass ratio in the case of molecules other than H_2 we simply take the scaling of the proton-to-electron mass ratio μ to be similar to that of the reduced mass of the molecule. This implies that we do not make a distinction between protons and neutrons (see above), nor do we care about the effects of electrons, since those are at the 10^{-3} level. The important issue at stake is that in experiments testing μ -variation the variation over time is measured on a relative scale $\Delta\mu/\mu$. It is not the aim of such experiments to measure a value of μ or to bring a theoretical model of a molecule (*ab initio* or otherwise) in agreement with an experimental determination.

We note that there exists an ongoing activity of high-precision molecular spectroscopy with the aim of determining μ .¹ This is pursued in the simplest existing molecular entity H_2^+ . In this case of course all the subtleties of masses should be accounted for.

1 S. Schiller and V. Korobov, *Phys. Rev. A*, 2005, **71**, 032505.

Dr Pinkse opened the discussion of Dr Tarbutt’s paper: Would a square box potential trap solve or reduce the depolarization caused by the geometric phase in a harmonic trap?

Dr Hudson responded: On the bottom of a square box potential one could hope to better control the geometric phase. The problem will come at the wall. Here one

would expect to generate large geometric phases, or even drive non-adiabatic transitions between states. Fundamentally, the difficulty is that, at around a kelvin, the molecule's kinetic energy is comparable to the depth of a realistic trapping potential. Changing the shape of the potential can't avoid this fact.

Dr Bethlem asked: You show that inhomogeneous geometrical phase shifts are a problem for doing an EDM experiment in an electrostatic trap. Is there any hope that these problems are less severe in a 2D-guide. Particularly, do you think it will be possible to do a sensitive EDM experiment in a guided fountain?

Dr Hudson replied: In a 2D-guide the field could, ideally, be confined to lie in a plane. A field rotating in a plane, returning exactly to its starting point, introduces no geometric phase shift. This is essentially the idea behind controlling the geometric phase in the nascent trapped ion EDM measurement in Eric Cornell's group.

Consider though, to set the scale of the problem, that in our current EDM measurement we measure phase shifts of order μrad . This would set very stringent limits on both the mechanical tolerances of the guide and the level of field control. I am sceptical that it will prove possible to make a sensitive EDM measurement in a guided fountain, but it is certainly worth investigating further.

Mr Zeppenfeld enquired: In how far could the geometric phase which dephases the spin precession caused by the EDM for EDM measurements in an electric trap be compensated by using a second pair of states as a reference?

Dr Hudson responded: There are no such states in the electronic ground state of YbF, but such states do exist. Ω -doubling, found in molecular states with a non-zero projection of electronic angular momentum on to the internuclear axis, results in pairs of states that acquire equal geometric phases, but have oppositely signed EDM interactions. ThO, for instance, is a promising molecule for EDM measurement with an Ω -doubled metastable state, which is being investigated by the ACME collaboration.

Using these Ω -doublet states to suppress the effect of the geometric phase in a trap, however, would be difficult. The Ω -doublet states Stark shift oppositely in an electric field. As the geometric-phase induced dephasing is an inhomogeneous effect it would be necessary to prepare a superposition of Ω -doublet states. The superposition would be very rapidly decohered across the molecular ensemble by the spatially inhomogeneous trapping electric field.

Dr Küpper commented: In the Miller group it was observed that $(\text{HCN})_3$ is a linear chain inside helium droplets, but nevertheless the field-free rotationally resolved ν_n -band shows a Q-branch.¹ This might be attributed to electric fields (anisotropic interactions) inside the droplets.²

Of course, in an alternative approach we have routinely applied external electric fields of 20–100 kV cm⁻¹ to create pendular states and to observe the connecting 'pendular spectra'.

1 K. Nauta, PhD thesis, University of North Carolina, Chapel Hill, NC, USA, 2000.

2 K. Nauta, D. T. Moore and R. E. Miller, *Faraday Discuss.*, 1999, **113**, 261.

Dr Mudrich opened the discussion of Professor Jäger's paper: What motivates the assumption of a droplet-size dependent line width (besides the similarity of the line shape with log-normal distribution), given the fact that at all studied conditions the nanodroplets are much larger than any solvation layer surrounding the molecules?

What could be the origin of the observed fast rotational relaxation, given the superfluid nature of the He environment? Is a "critical rotational velocity"

(in analogy with Landau's critical velocity) conceivable, which may lead to damping in dependence of the rotational excitation J ?

Professor Jäger answered: We initially speculated that the observed line shapes are a result of a droplet size dependence of the B rotational constant. For smaller clusters with up to 70 helium atoms, such dependence was indeed observed.¹ It is unclear however, which physical mechanism could be responsible for such behaviour in the larger helium nanodroplets. Our studies with different droplet sizes (see Fig. 9 in our paper) also clearly indicate that a droplet-size dependence is not the main contributor to the overall line widths. In the microwave study of a pure inversion transition of ammonia embedded in helium nanodroplets, it was found that the overall line shape could be well reproduced by assuming a splitting of the molecular energy levels into energy level manifolds.² Such splitting could occur through, for example, coupling of the molecular rotation with a particle in a spherical box motion. In this case the droplet size determines the details of the energy level manifolds and influences the line width. There is also evidence that the angular momentum imparted to the droplet by the collision with the dopant molecule has significant effects on the spectroscopic signatures. This will clearly be droplet-size dependent.^{3,4} The existence of a critical rotational velocity at the microscopic level is an interesting thought. Pitaevskii and Stringari have treated superfluid effects in rotating helium clusters.⁵ They considered surface excitations of the clusters and determined a critical rotational frequency, in analogy to the critical velocity in bulk helium. Also in this case the droplet size would be important, as it determines the density of surface states. It is not clear, however, how the observed asymmetric line shapes could be rationalized with this model.

1 A. R. W. McKellar, Y. Xu, and W. Jäger, *Phys. Rev. Lett.*, 2006, **97**, 183401.

2 R. Lehnig, N. V. Blinov, and W. Jäger, *J. Chem. Phys.*, 2007, **127**, 241101.

3 N. Pörtner, A. F. Vilesov, and M. Havenith, *Chem. Phys. Lett.*, 2003, **368**, 458.

4 K. K. Lehmann and A. M. Dokter, *Phys. Rev. Lett.*, 2004, **92**, 173401.

5 L. Pitaevskii and S. Stringari, *Z. Phys. D*, 1990, **16**, 299.

Dr Küpper enquired of Professor Jäger: You describe the asymmetric line shapes and suggest they are due to droplet-size variations. From various experiments in the Miller group (and others) we know that surface effects can have a strong influence on the spectra of embedded molecules.

Is it feasible to suggest that the droplet-size dependence of your lines is due to the averaged or fractional interaction of the molecule with the surface? This would obviously scale such that the interaction is weaker for larger droplets.

Professor Jäger replied: That is an interesting point considering that both the rotation–translation coupling and impurity–rippion interactions increase as the dopant molecule approaches the surface. Lehmann has considered both these contributions and could simulate the experimental line shape of the R(0) infrared transition of OCS.¹ However, it was not possible to reproduce the increase in line width with increasing J quantum number. While this initial calculation assumed a Boltzmann distribution of the translational states of OCS in a helium droplet, Dokter and Lehmann later showed that the angular momentum resulting from the pick-up process needs to be considered.² They concluded that high angular momentum translational states may have substantially larger populations than predicted from a Boltzmann distribution at the droplet temperature. We are not aware of any line shape simulations based on this model.

1 K. K. Lehmann, *Mol. Phys.*, 1999, **97**, 645.

2 K. K. Lehmann and A. M. Dokter, *Phys. Rev. Lett.*, 2004, **92**, 173401.

Dr Küpper asked: In your article you discuss the differences between vibrational and rotational relaxation of molecules in helium droplets. One of the first and most extreme cases where such differences of behaviour were observed, is in HF.¹

Moreover, the rotational relaxation of HF ($\nu = 1$) leads to a line width of 0.43 cm^{-1} ($\sim 12.9 \text{ GHz}$), whereas your line widths are $< 1 \text{ GHz}$. How can this be rationalized?

Could you measure the pure $J = 1 \leftarrow 0$ rotational transition of HF to determine the rotational lifetime of $J = 1, \nu = 0$?

1 K. Nauta and R. E. Miller, *J. Chem. Phys.*, 2000, **113**, 9466.

Professor Jäger answered: It seems evident that there is not a single mechanism that is responsible for the observed widths and shapes of rotational and rovibrational transitions. In the case of HF, the rotational excitation is at about 40 cm^{-1} (1.2 THz) and at this energy there are more relaxation channels available, *i.e.* the bulk modes, than for the much heavier OCS molecule (only surface modes). The increased line width for HF is thus the result of faster relaxation rates.

We are quite interested in the measurement of pure rotational transitions of lighter molecules embedded in helium nanodroplets. We do have sources, so-called backward wave oscillators, which can produce radiation up to frequencies of about 1 THz and are in the process of implementing them into our instrument. The $J = 1 \leftarrow 0$ rotational transition of HF is currently out of reach.

Dr Küpper continued: In Fig. 4 of your paper you compare the sensitivity of mass spectrometric and bolometric detection. Already in ref. 1 we have argued that bolometric detection is the best choice for such experiments. What do you consider the advantage of a MS over a bolometer (besides running costs)?

1 J. Küpper and J. M. Merritt, *Int. Rev. Phys. Chem.*, 2007, **26**, 249; J. Küpper and J. M. Merritt, *Int. Rev. Phys. Chem.*, 2007, **26**, 288.

Professor Jäger responded: The reason why we first took spectra using the mass spectrometer was simply that it was implemented into our helium nanodroplet spectrometer and functional before the bolometer system. However, there are a number of reasons for using a mass spectrometer for detection. For example, the mass spectrometer can be used as diagnostics for the helium droplet beam and it makes it possible to verify that a specific molecular species has been picked up and transported by the helium droplet beam. With the mass spectrometer, it is possible to shine a laser beam coaxially and counter-propagating to the droplet beam. This increases the overlap between laser beam and droplet beam compared to a perpendicular intersection, although the use of a multipass cell can partially compensate for this. Roger Miller and his group have used optically selected mass spectrometry experiments to investigate electron ionization mechanisms and fragmentation patterns of dopants embedded in helium nanodroplets.¹

1 W. K. Lewis, B. E. Applegate, J. Sztray, B. Sztray, T. Baer, R. J. Bemish, and R. E. Miller, *J. Am. Chem. Soc.*, 2004, **126**, 11283.

Professor Stwalley asked: Traditionally, cold molecules were first studied using matrix isolation spectroscopy and then using supersonic molecular beams. Your beautiful experiments illustrate helium cluster spectroscopy, a very powerful merging of the matrix isolation and molecular beam technologies and traditions. What do you see as possible future applications for helium cluster spectroscopy in cold and ultracold molecular spectroscopy?

Professor Jäger replied: There have already been a number of contributions from helium nanodroplet experiments to the field of cold atoms and molecules, apart from

purely spectroscopic studies of molecules and clusters. Among the most exciting are studies of chemical reactions at low temperatures. Vilesov and coworkers, for example, have investigated the exothermic chemical reaction $\text{Ba} + \text{N}_2\text{O} \rightarrow \text{BaO} + \text{N}_2$ as it occurs at the low temperature of 0.38 K in helium droplets.¹ The Freiburg group looked at reactions of alkali metal clusters with water molecules embedded in helium droplets and used femtosecond photoionization. They found that Rb and Cs react completely with water in the cold droplet environment.² The Drabbel's research group has studied photodissociation reactions of CH_3I and CF_3I embedded in helium droplets.³ It would also be of significant interest to observe a reaction where quantum effects dominate the outcome, such as is expected for $\text{F} + \text{HD} \rightarrow \text{HF} (\text{DF}) + \text{D} (\text{H})$,⁴ at helium droplet temperatures.

The ultracold temperature regime cannot be reached in helium nanodroplet experiments, since the droplets attain (on the time scale of the experiment) final temperatures of 0.38 K and 0.15 K for ^4He and ^3He , respectively. However, important spectroscopic information can be obtained about systems that are relevant to ultracold physics and chemistry, such as alkali metal dimers and trimers. Examples are the formation and spectroscopic investigation of alkali dimers⁵ and mixed alkali dimers (*e.g.* LiCs).⁶

1 E. Lugovoj, J. P. Toennies, and A. Vilesov, *J. Chem. Phys.*, 2000, **112**, 8217.

2 S. Müller, S. Krapf, Th. Koslowski, M. Mudrich, and F. Stienkemeier, *Phys. Rev. Lett.*, 2009, **102**, 183401.

3 A. Braun and M. Drabbel's, *J. Chem. Phys.*, 2007, **127**, 114305.

4 N. Balakrishnan and A. Dalgarno, *J. Phys. Chem. A*, 2003, **107**, 7101.

5 F. Stienkemeier, W. E. Ernst, J. Higgins, and G. Scoles, *J. Chem. Phys.*, 1995, **102**, 615.

6 M. Mudrich, O. Bünermann, F. Stienkemeier, O. Dulieu, and M. Weidemüller, *Eur. Phys. J. D*, 2004, **31**, 291.

Dr Chandler addressed Professor Jäger and Dr Mudrich : Can a collision of a helium droplet with a trapped but internally hot molecular ion be used to cool the ion to sub kelvin temperatures without losing the ion from the trap?

Dr Mudrich replied: The idea of cooling the internal degrees of freedom of molecular ions stored in ion traps by shooting a beam of He nanodroplets into the trap appears to be very interesting. In order to answer the question, we have to estimate the following quantities: the cooling capacity of the droplets, the kinetic energy of the droplets, which is transferred to the new ion–droplet complex *versus* the trap depth, and the stability of the ion–droplet complex.

The cooling capacity due to evaporation of single He atoms amounts to about 5 K per He atom for a small droplet containing 1000 atoms, which gives about 0.4 eV in total. This is sufficient to efficiently cool small molecular ions down to 0.4 K. The kinetic energy of such a droplet propagating at 300 m s^{-1} is 1.9 eV, which is in the range of the trap depth of typical ion traps. In a real experiment, however, the fact that the evaporating ion–droplet complexes have different masses that change with time raises the issue of which trap parameters, *i.e.* RF-frequencies, *etc.*, to use for maintaining stable trapping conditions. Besides, multiple collisions with He droplets will eventually kick the ions out of the trap unless cooling of the translational motion is applied. Concerning the stability of ion–droplet complexes, we know from experiments that no fragmentation occurs when electrostatically extracting ion-doped He droplets using electric fields of order 1000 V cm^{-1} . Thus, the entire droplet would contribute to evaporative cooling. However, it is probable that a few He atoms will remain strongly bound to the ionic core forming “snowball” complexes.

Professor Jäger answered: This probably depends predominantly on the depth of the trap and the linear momentum that is transferred from the droplet to the ion. There is some control over the droplet linear momentum, simply by adjusting nozzle

temperature and backing pressure to change the average droplet size. Helium nanodroplets are very efficient heat baths and cooling rates for ions of 1016 K sec^{-1} have been reported.¹ Roger Miller and his group have reported the production of (untrapped) cooled ions by electron impact ionization of doped helium droplets.¹ The ionization process causes significant heating of the resulting ion. The rapid energy transfer to the helium environment leads to cooling, can close certain fragmentation channels,² and leads to evaporation of the entire helium droplet. However, it was noted that the ion cooling was far from complete.¹

1 W. K. Lewis, B. E. Applegate, J. Sztray, B. Sztray, T. Baer, R. J. Bemish, and R. E. Miller, *J. Am. Chem. Soc.*, 2004, **126**, 11283.

2 W. K. Lewis, C. M. Lindsay, and R. E. Miller, *J. Chem. Phys.*, 2008, **129**, 201101.

Dr Küpper said: I believe that there is strong overlap between the two fields with respect to the reactive processes, which have already been discussed for cold and ultracold systems. Helium droplets, on the other hand, provide great opportunities for studying potential energy surfaces through high resolution spectroscopy of entrance and exit channel complexes. For example, we have stabilised and investigated multiple structural isomers of HF, HCN, and HCCCN with halogen atoms.^{1,2,3} Moreover, you can even stabilise clusters containing two halogen atoms, providing chemical energy densities similar to TNT.³ Generally, the investigation of atoms, molecules and clusters in helium droplets can provide a variety of accurate information for experiments with ultracold atoms and molecules.⁴

1 J. M. Merritt, J. Küpper and R. E. Miller, *Phys. Chem. Chem. Phys.*, 2005, **7**, 67.

2 J. M. Merritt, J. Küpper and R. E. Miller, *Phys. Chem. Chem. Phys.*, 2007, **9**, 401.

3 J. Küpper and J. M. Merritt, *Int. Rev. Phys. Chem.*, 2007, **26**, 249; J. Küpper and J. M. Merritt, *Int. Rev. Phys. Chem.*, 2007, **26**, 288.

4 M. Mudrich, O. Bünermann, F. Stienkemeier, O. Dulieu and M. Weidemüller, *Eur. J. Phys. D*, 2004, **31**, 291.

Professor Gianturco commented on Professor Dr Willitsch's paper: Mario Tacconi and I have looked at the possibility of creating an experimental setup in which a cloud of ultracold, laser cooled Rb atoms are introduced in a Coulomb crystal arrangement where $\text{MgH}^+(\text{X}^1\Sigma^+)$ and $\text{Mg}^+(\text{S})$ along with the laser-cooling populated excited species $\text{MgH}^+(\text{A}^1\Sigma^+)$ and $\text{Mg}^+(\text{P})$ are contained. Our computational findings suggest the most likely pathways for a series of "reactive" events coming from the interaction of Mg^+ , MgH^+ and Rb mixtures within the trap. Details of the *ab initio* calculations could be found in ref. 1, where the low-lying electronic states of the MgHRb^+ ionic complex are described, while the MgRb^+ system, thought to be also present in the Coulomb crystal (CC), has been extensively discussed in ref. 2.

Fig. 1 reports the region of curve crossing and the final, lowest-lying state of the charge-exchange process. The corresponding details for the atomic cation and for the RbMg^+ complex are given in Fig. 2.

The global picture arising from our analysis of the bi-crystal processes is therefore:

* Within the trap environment we are considering here, the most likely way in which the MgH^+ molecular ion can react with neutral Rb is *via* the radiative charge transfer process from the upper levels (entrance channels) shown by Fig. 1

* The neutral, cold partner Rb can further directly interact with the crystallized Mg^+ ions: our calculations tell us that, in this case, the only relevant process available is spontaneous photoemission and that the Mg^+ can effectively compete with MgH^+ in the reaction with Rb atoms.

* Our computational analysis of the atomic and molecular competing processes predict that the reactive events which involve the molecular ion MgH^+ can have an

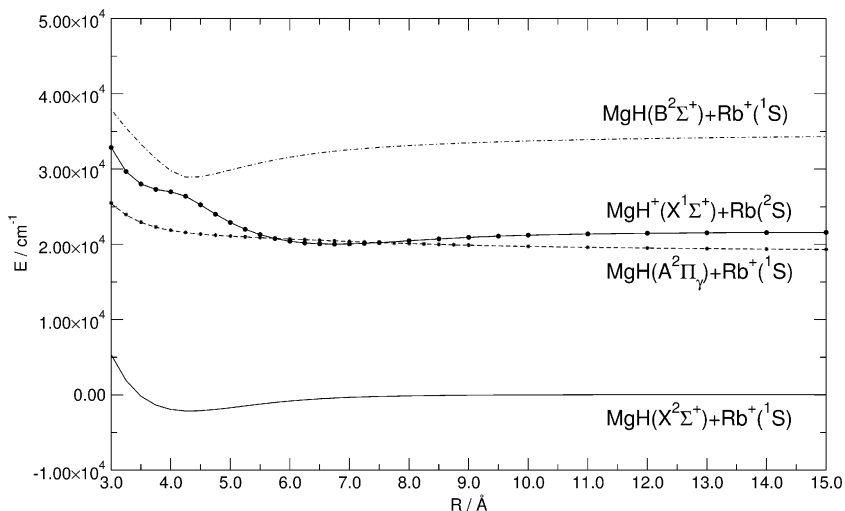


Fig. 1 Potential energy curves of MgH^+ interacting with Rb along the collinear geometry. Adapted from ref. 1.

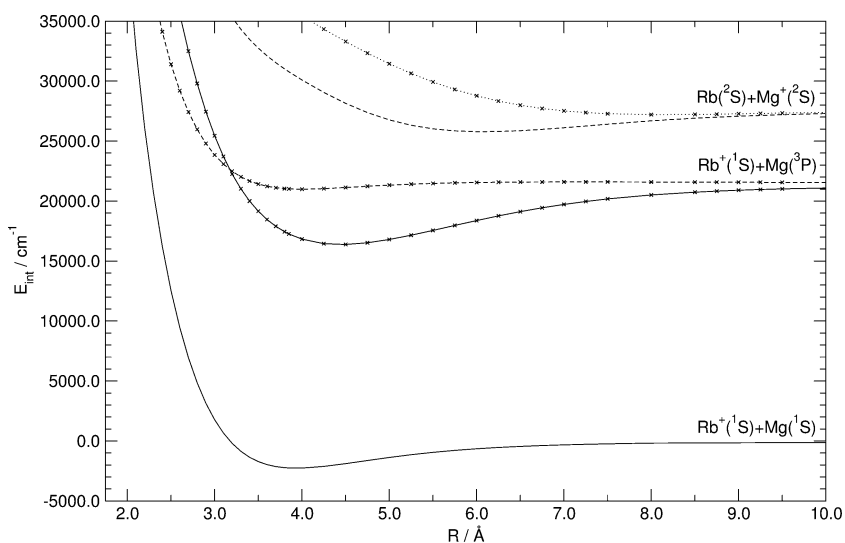


Fig. 2 Potential energy curves of Mg^+ interacting with Rb. Adapted from ref. 2.

efficiency which is comparable to that in which the ionic partner is the Mg^+ and that the Rb addition to the trap is very likely to produce sizable amounts of cold, trapped Rb^+ cations in the form of stable ionic complexes. We have also briefly considered the possibility of the Penning Ionization events whereby both couples of cations, *i.e.* MgH^+ plus Rb^+ and Mg^+ plus Rb^+ are produced. In our case we have tentatively provided an estimate of the expected rate coefficient K_P . Following ref. 3, one defines $K_P = f_W P_i K_C$, where f_W is the fraction of the collisions from which a continuum state can be reached without violating spin conservation (here $f_W = 1$ for both cases), P_i is the mean ionization probability per close collision, and K_C is the rate coefficient for the close collision. Thus, our estimates for

the Penning Ionization process could be $10^{-12} \lesssim K_p \lesssim 2.87 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, which is a fairly large value.

1 M. Tacconi and F. A. Gianturco., *Eur. Phys. J. D*, 2008, **46**, 443.

2 M. Tacconi and F. A. Gianturco., *Eur. Phys. J. D*, 2009, **54**, 31.

3 K. L. Bell, A. Dalgarno, and A. E. Kingston. *J. Phys. B*, 1968, **1**, 18.

Dr Wester opened the discussion of Professor Dr Gerlich's paper: Cryogenic radiofrequency multipole traps are a very useful tool to study negatively charged ions, their reactions and their interaction with light at temperatures between a few kelvin and room temperature. In particular the 22-pole ion trap¹ is employed, because it features a large trapping volume void of strong electric fields. The translational and rotational temperature of the trapped ions is controlled *via* buffer gas cooling with helium.

The dynamics of anion–molecule reactions are typically governed by a complex multi-well Born–Oppenheimer hypersurface. As a consequence, the reaction rate and the energy partitioning among the different translational and rovibrational degrees of freedom depends crucially on the complex few-body dynamics at short range.² Currently, open questions relate to the role of tunneling through the intermediate potential energy barrier and the importance of Feshbach scattering resonances.³ In this respect anion–molecule reactions are qualitatively different from many cation–molecule reactions, which occur at the Langevin or capture rate and are thus not influenced substantially by the short-range dynamics. Cross sections for chemical reactions and photodetachment processes are also important to understand the role of anions in interstellar molecular clouds, where several negatively charged species have recently been detected.⁴

In a study of a negative ion reaction at the lowest currently achieved temperatures, reaction rate coefficients have been obtained for the proton transfer reaction $\text{NH}_2^- + \text{H}_2 \rightarrow \text{NH}_3 + \text{H}^-$.⁵ Here the rate coefficient rises from 2 to 11% between room temperature and 20 K and decreases again for even lower temperatures down to 8 K. The increase may be explained by a classical complex-mediated reaction mechanism. The observed maximum at finite temperature, however, is currently unexplained. In this temperature regime only the lowest *para* and *ortho* angular momentum states of the two reactants are populated and only a small number of partial waves contribute to the reactive scattering. Furthermore the mean spacing of the Eigenstates of the reaction complex is larger than the temperature. Thus, quantum mechanics are assumed to dominate the reaction dynamics. Detailed scattering calculations are needed to clarify this and understand the low-temperature dynamics.

The most important light-matter interaction of negative ions is the photodetachment process. It is widely used in photoelectron spectroscopy to investigate the properties of both anions and neutrals. In plasmas the total cross section for photodetachment represents an important destruction mechanism for negative ions. In a 22-pole ion trap the absolute cross section can be measured with high systematic accuracy by observing the loss of ions in a radiation field.⁶ In this way, the absolute detachment cross sections for O^- and OH^- were obtained at different wavelengths and as a function of the buffer gas temperature.⁷ For O^- an overall relative accuracy of 5% was achieved. This benchmark result challenges state-of-the-art theoretical calculations, which currently deviate by about 35%.⁸ Photodetachment near threshold, thus using photon energies slightly larger than the electron affinity, has proven to be a useful tool to characterize the rotational state population of cold molecular anions in the ion trap. This will be explored in the future to study state-selected cold collisions, both inelastic and reactive.

Trapped negative chlorine anions, which are stable with respect to reactions with background gas and to black body-induced photodetachment, are useful to study

the trapping conditions in multipole rf traps. Specifically, the stability conditions in a 22-pole ion trap could be experimentally accessed and an experimental estimate for the maximum stability parameter could be deduced.⁹

- 1 D. Gerlich, *Phys. Scr.*, 1995, **T59**, 256.
- 2 J. Mikosch, S. Trippel, C. Eichhorn, R. Otto, U. Lourderaj, J. X. Zhang, W. L. Hase, M. Weidemüller and R. Wester, *Science*, 2008, **319**, 183.
- 3 S. Schmatz, *ChemPhysChem*, 2004, **5**, 600.
- 4 M. C. McCarthy, C. A. Gottlieb, H. Gupta and P. Thaddeus, *Astrophys. J. Lett.*, 2006, **652**, L141.
- 5 R. Otto, J. Mikosch, S. Trippel, M. Weidemüller and R. Wester, *Phys. Rev. Lett.*, 2008, **101**, 063201.
- 6 S. Trippel, J. Mikosch, R. Berhane, R. Otto, M. Weidemüller and R. Wester, *Phys. Rev. Lett.*, 2006, **97**, 193003.
- 7 P. Hlavenka, R. Otto, S. Trippel, J. Mikosch, M. Weidemüller and R. Wester, *J. Chem. Phys.*, 2009, **130**, 061105.
- 8 O. Zatsarinny and K. Bartschat, *Phys. Rev. A*, 2006, **73**, 022714.
- 9 J. Mikosch, U. Frühling, S. Trippel, D. Schwalm, M. Weidemüller and R. Wester, *Phys. Rev. Lett.*, 2007, **98**, 223001.

Professor Gianturco asked: We have recently studied the potential energy surfaces and the scattering behaviour at ultralow energies of an anionic species such as OH⁻ interacting with He and with Rb. In the latter case we have been able to compute not only the elastic cross sections but also the rotovibrational quenching cross sections at the nanokelvin regimes. As expected, the quenching cross sections for collisions with the Rb partner turned out to be much larger than in the case of He. They also appeared from calculations to markedly depend in size on the initial internal state of the anion. My question, therefore, is about the possibility of actually controlling the internal anionic temperatures in the experiments in order to reduce the importance of the quenching losses. Do you have any suggestion as to how this could be done and, at the same time, what sort of internal temperatures could be expected in the trapping of OH⁻?

Dr Wester answered: In current experiments with negative ions in cryogenic ion traps¹ translational as well as rotational temperatures of a few kelvin are achieved using helium buffer gas cooling. For trapped OH⁻ anions at 10 kelvin a population of about 99% in the $J = 0$ rotational ground state is reached. Preliminary work in our ion trap shows that the population of the higher rotational states can be increased in a controlled way by increasing the temperature of the buffer gas. Cryogenic ion traps should therefore provide good starting conditions for experiments on inelastic collisions of small molecular anions.

- 1 R. Wester, *J. Phys. B*, 2009, in press; arXiv:0902.0475.

Professor Softley asked Professor Dr Gerlich: In your paper you have commented; “especially at low collision energies, a collision complex usually utilizes the energy from all degrees of freedom, one should only call a bimolecular reaction *cold* if the *total energy* is below a few meV.” While we are grateful for this advice, we would argue that for many ion–molecule reactions it is valid to use the phrase “translationally cold” to describe reactions (as we have done in our paper) even where the reactants are internally warm. In the capture theory model of ion–dipole reactions, which has been shown to be valid for a number of reactions down to temperatures around 10 K, the translational and rotational effects on the reaction rate are physically quite distinct. Rotational effects are connected with the alignment of the dipole along the collision direction; as the rotational quantum number increases, this alignment becomes less pronounced leading to a possible decrease in the reaction rate. On the other hand the effect of translational cooling is attributable to the shift of the centrifugal barrier and how its height changes relative to the changing kinetic

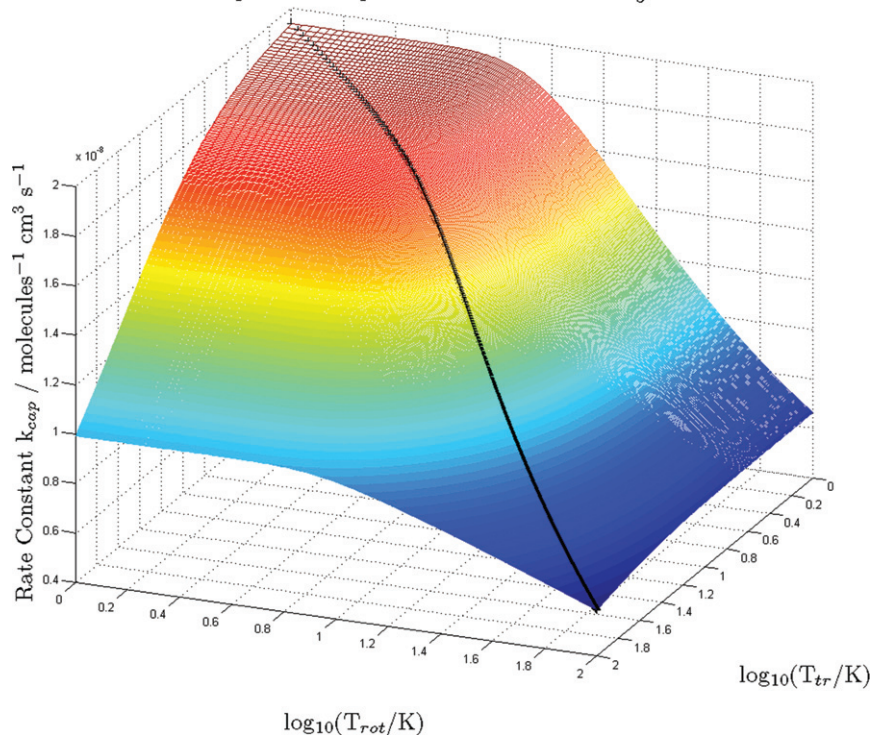


Fig. 3

energy. Fig. 3 shows an example rotationally adiabatic capture theory calculation¹ for the $\text{H}_3^+ + \text{HCl}$ reaction showing how the reaction rate constant varies with rotational and translational temperatures separately. We have also considered the difference between translationally cold reactions which are either rotationally warm or rotationally cold in Fig. 8 of our paper. While the effects of decreasing rotational temperature or decreasing translational temperature are qualitatively similar, they are quantitatively different.

However it is interesting to consider what is the most useful kind of rate constant measurement in this cold or ultracold regime. In some senses this is a completely artificial world where there are no natural environments with which we can compare thermal rate constants k_T for $T < 1$ K. In fact if the interest is really in identifying the dominance of quantum effects in this regime then ideally one would try to measure internal-quantum-state-selected experiments, to limit the number of channels that contribute to the reaction and therefore enhance the probability of observing resonant effects in the cross section *etc.*

Would you comment on why you consider that the measurement of rate constants for thermally equilibrated systems is an important objective in the sub-kelvin range?

¹ L Harper, M. T. Bell and T. P. Softley, Unpublished work.

Professor Dr Gerlich responded: Various discussions during the meeting have revealed that there is no general agreement concerning the meaning of cooling, ultracold molecules, cold chemistry, *etc.* My personal opinion has been summarized recently in the two chapters I contributed to Professor Smith's book.¹ Although

I do not intend to continue the discussion on this level, I am tempted to mention that the title of your paper contains misleading formulations such as “ion–molecule chemistry at very low temperatures” or “cold chemical reactions”. I agree with your formulation that you can study translationally cold collisions in your very interesting experiment, provided that the ions are really localized on the symmetry axis of the rf driven quadrupole and that the cold effusive beam traverses the ion cloud without hitting any surface which would create a 300 K neutral background.

I am in accord with the statement that the relative velocity determines the very first step of an ion–molecule reaction. Capture models have become quite popular in the past decades (see for example ref. 2). However, I do not know any chemical reaction where the outcome of a collision is just determined by the capture and is completely independent of the internal energy of the reactants. Our experience shows that the formation of products depends on many details of the collision dynamics. For example, very long lifetimes of the intermediate complex often lead to radiative association, sometimes even in competition with an exothermic product channel such as in $C_3^+ + H_2$.³ Many other effects influence the outcome of a reaction, e.g. zero point energies, tunneling through barriers, non-adiabatic coupling or restrictions due to symmetry selection rules in the case of identical atoms. All this makes the field of cold ion chemistry very interesting.

There is no final answer to your question on what the most useful experimental approach is for studying chemical reactions in the cold or ultracold regime. The various techniques including swarm methods, merged beams and various traps have been discussed recently.⁴ There is no doubt that it would be ideal to measure state to state cross sections over a wide range of translational energies, maybe even as a function of relative orientation. Photoionization methods in combination with supersonic beams and the merged beam technique are a step in this direction.⁵ On the other side there are many advantages to starting an experiment with a fully thermalized system since one knows precisely the population of the states. Temperature dependent studies allow one to record and assign, for example, unknown spectra (e.g. CH_5^+) or to determine state specific rate coefficients if only a few states are involved (e.g. H_3^+). Moreover, in a well-isolated finite ensemble of trapped ions, laser based strategies can be used to modify and tailor the thermal population, e.g. via hole burning.

Finally I want to comment on the statement that the sub-K regime is really an artificial world. Presently our universe is at 2.725 K; however, further expansion may lead to natural environments with $T < 1$ K. For predicting star formation in such regions, sub-K collisions are needed.

1 I. W. M. Smith (ed.), *Low temperatures and cold molecules*, World Scientific Publishing, ISBN 978-1-84816-209-9, 2008.

2 E. E. Nikitin and J. Troe, *Phys. Chem. Chem. Phys.*, 2005, **7**, 1540.

3 I. Savic and D. Gerlich, *Phys. Chem. Chem. Phys.*, 2005, **7**, 1026.

4 D. Gerlich, The study of cold collisions using ion guides and traps, in *Low temperatures and cold molecules*, World Scientific Publishing, ed. I. W. M. Smith, ISBN 978-1-84816-209-9, 2008, p. 121.

5 T. Glenewinkel-Meyer and D. Gerlich, *Isr. J. Chem.*, 1997, **37**, 343.

Dr Stoecklin commented: Concerning the possible use of the adiabatic capture theory for ion dipole reaction mentioned by Professor Softley, I would like to mention that the adiabatic capture theory cannot work in the very low collision energy range as it is based on a classical treatment of translation. However, an alternative approach was proposed by Dashevskaya *et al.*¹ where the Wigner regime is treated properly and the adiabatic capture approximation is used at higher energy.

1 E. I. Dashevskaya, A. I. Maergoiz, J. Troe, I. Litvin and E. E. Nikitin, *J. Chem. Phys.*, 2003, **118**, 7313.

Professor Sims addressed Professor Softley: In your comment, you asked why we should concern ourselves with the measurement of thermal rate coefficients when detailed measurements on single quantum states provide a more penetrating comparison with theory. While of course this would be true in an ideal world where it is possible to make such measurements of reactive or inelastic cross sections on an absolute basis, in practice this is extremely difficult to accomplish.¹ The advantage of thermal rate coefficient measurements at extremely low temperatures (indeed, at any temperature) is that the quantum state distributions of the colliding species are very well defined and known, and by the use of standard pseudo-first-order kinetics techniques, the absolute values of these rate coefficients can be reliably determined. This constitutes a significant advantage over many molecular beam techniques, and enables a more revealing comparison with theory than that possible with relative measurements alone. Of course, in the end, the two types of technique are highly complementary.

1 G. Scoles. In *Atomic and Molecular Beam Methods*; Scoles, G., Ed.; Oxford University Press: New York, Oxford, 1988; Vol. 1; p 4.

Dr Segal asked Professor Gianturco: Sympathetic cooling of molecular ions using laser cooled atomic ions is a well established technique. One well known limitation of this technique is that, while the long range Coulomb collisions are effective at equilibrating the translation temperatures of the co-trapped species, these collisions do not affect the internal degrees of freedom of the molecules. The molecular ions therefore remain rotationally hot and settle at a temperature close to that of the ambient black body field. One suggestion as a means of cooling the rotational motion is to co-locate cold atoms in a MOT (*e.g.* Rb) with a mixed cloud or Coulomb crystal of molecular ions and laser cooled atomic ions in an ion trap and then depend on relatively short range (r^{-4}) atom-ion collisions to cool the internal degrees of freedom of the molecules. In this context the chemical reactions described in your comment constitute loss channels *i.e.* the hope is that the rate of rotational cooling is sufficiently fast that it occurs on a timescale that is short in comparison with the timescale for the chemical reactions to take place. Are you able to calculate the rate of rotational cooling in order to be able to make this comparison?

Professor Gianturco replied: We have not done it as yet, although we have put together the relevant computational machinery to do so. However, one should also remember here that the “reaction” that entails a charge transfer process between MgH^+ and Rb is a strongly exothermic process as shown by our calculations and by the figures presented at the Discussion. Hence, what is important here is that the internally “hot” ion be able to cool its internal energy content with just a few collisions before charge exchange takes over. We already have some results for the rotational quenching of other ionic partners like OH^- and OH^+ but in collisions with He, which presents a less strong interaction with the molecules than Rb. However, the rotational relaxation rates for OH^+ , also a polar cation like MgH^+ , are already the largest exhibited by ultracold collisions with He and vary between 10^{-10} and 10^{-9} depending on the initial rotational state of OH^+ .¹ Thus, it is reasonable to expect that the rotational cooling of MgH^+ in the presence of Rb might occur on a faster timescale than that of the reactions we are discussing in our computational work.

1 L. Gonzalez-Sanchez *et al.*, *Eur. Phys. J. D*, 2007, **44**, 65.

Professor Dr Gerlich addressed Professor Sims: Your comment that flow systems (such as CRESU) work in a real thermal equilibrium, sounds like a general advantage; however, one certainly gets more information if one can extract state specific

(or state-to-state) rate coefficients from an experiment. Ion traps can be operated in various ways. With high buffer gas concentration (usually He), one gets near-thermal conditions. If one modifies the trapped cloud of ions (usually a few hundred) in a well-defined way, *e.g.* *via* laser induced processes, one can derive very specific information on elastic, inelastic or reactive collision processes.

Professor Dr Willitsch asked Professor Gianturco: The predominance of the Penning Ionisation channel over the direct-charge exchange reaction in excited $\text{Mg}^+/\text{MgH}^+ + \text{Rb}$ strikes me as quite remarkable. Do you expect a similar behaviour in other systems *e.g.* $\text{Ca}^+ + \text{Rb}$, as well?

Professor Gianturco answered: We were also surprised by the behaviour of the $\text{MgH}^+/\text{Mg}^+ - \text{Rb}$ system in terms of the expected efficiency of the Penning Ionization process in the trap, although we must consider the results as coming from a fairly simplified treatment of the PI dynamics, which definitely require further exploration. In relation to that process being just as important in the heavier cations, my presumption at the moment is that perhaps it should be just as important, since we have more excited states available and closer to each other; level congestion is usually a good reason for increasing couplings to the nearby continuum, which is the main cause for the more likely occurrence of PI events.

Dr Küpper asked Professor Dr Gerlich: On page 3 of your paper you discuss technical issues with the applied voltages to your rf traps. Already around 1970 the equivalence of rectangular wave forms and sinusoidal wave forms for ion-guides and traps was shown. Could you comment on their respective advantages and disadvantages, also with special emphasis on parasitic frequencies, heating of ions, and technical implementation details?

Professor Dr Gerlich replied: The motion of a system under the influence of a force varying in time and space is a rather fundamental subject, well studied in theoretical and experimental physics. One of the mathematical treatments for understanding the influence of the time dependent electric field in our applications is based on a special adiabatic approximation which has been discussed in textbooks of classical mechanics (*e.g.* ref. 1). This calculation reveals that the effective potential is proportional to the time average of the square of the field, *e.g.* to $\langle |E(t)|^2 \rangle$. Based on this it is obvious that, in principle, one can use any alternating field, *i.e.* any symmetric wave form. However, one can get problems with low frequency components since they can lead to parasitic heating of the ion motion while the high frequency components of rectangular pulses do not contribute much to the guiding force ($V^* \sim 1/\Omega^2$). Nonetheless, one should avoid them since they cause electronic noise. An important practical reason for using pure sinusoidal oscillations with a single frequency Ω is that we usually connect the electrode arrangement (equivalent to a capacitance) with a coil, resulting in a resonance circuit. As discussed in my contribution, we presently test low temperature traps with superconducting circuits. This will lead to very high quality circuits, to a very pure frequency and to extremely low power dissipation.

1 L. D. Landau and E. M. Lifshitz, *Theoretical Physics*, Pergamon, Oxford, 1960, vol. 1, p. 93.