

Laser Spectroscopic Studies of the $C^1\Sigma^+$, $v = 0$ and $v = 1$ States of CO

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Two laser spectroscopic investigations were performed on the $C^1\Sigma^+ - X^1\Sigma^+$ (1,0) and (0,0) bands of CO. In the first experiment, using 2 + 1 resonance-enhanced multiphoton ionization, information on highly excited rotational states up to $J \approx 50$ was obtained. In the second experiment, application of a narrow-band VUV laser provided highly accurate absolute calibrations. Molecular constants for $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, and, for the first time, $^{12}\text{C}^{17}\text{O}$ are derived.

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1. INTRODUCTION

The $C^1\Sigma^+ - X^1\Sigma^+$ bands are the strongest absorption features in carbon monoxide, which is the second most abundant molecular in outer space. Therefore these bands are of importance in astronomy, particularly since space-based vacuum ultraviolet detecting instruments, such as in the Copernicus satellite and the Hubble Space Telescope, have become available. Emission spectra of isotopomers of carbon monoxide in the vacuum ultraviolet are currently being investigated to further determine the fractionation of CO in diffuse interstellar clouds (see, e.g., Ref. (1)).

The $C^1\Sigma^+$ state has been the subject of various spectroscopic investigations, starting with the pioneering work of Hopfield and Birge (2). Tilford *et al.* (3) subsequently recorded $C^1\Sigma^+ - X^1\Sigma^+$ (1,0) and (0,0) bands for $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ at higher resolution and recently a similar study was performed by Eidelsberg and co-workers (4, 5) as well for $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{18}\text{O}$. Apart from these studies in the vacuum ultraviolet the $C^1\Sigma^+$ state was investigated via the $C^1\Sigma^+ - B^1\Sigma^+$ system in the infrared (6, 7) and via the $C^1\Sigma^+ - d^3\Delta$ (8) and $C^1\Sigma^+ - A^1\Pi$ (9) systems. In addition, highly accurate two-photon laser-induced transitions were observed, but only for low rotational states (10). Precise values for the rovibronic term values of the $C^1\Sigma^+$ state were collected in recent publications for $^{12}\text{C}^{16}\text{O}$ (11) and for $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ (12). In the present work we have investigated the $C^1\Sigma^+$, $v = 0$ and 1 states for various isotopomers via one- and two-photon laser excitation. New information on rotational states, as highly excited as $J \approx 50$, could be deduced; moreover, the $C - X$ system of $^{12}\text{C}^{17}\text{O}$ was observed for the first time from a sample of natural CO.

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2. EXPERIMENTAL

Two different experimental techniques were employed for the spectroscopic investigation of the $C^1\Sigma^+$, $v = 0$ and $v = 1$ states. Both methods have been described previously (13). First, two-photon studies were performed using the technique of 2 + 1 resonance-enhanced multiphoton ionization (REMPI) in a cell heated to 1000 K. In this arrangement high rotational states up to $J \approx 50$ are populated and excited. As only small samples of gas were required (the cell was filled to 3 Torr), spectra of natural CO and ^{13}C -enriched carbon monoxide could be recorded. Spectra were obtained for the $C-X$ (1,0) and (0,0) bands of $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$, while a frequency doubled dye laser was scanned over the wavelength range 218–212 nm. The excitation of CO molecules took place by focusing the UV light in between two capacitor plates and signals were obtained by monitoring the current. The fundamental blue wavelength was exploited for simultaneous recording of a $^{130}\text{Te}_2$ absorption spectrum, used for on-line frequency calibration (14). The linewidth of the rotationally resolved 2 + 1 REMPI feature of CO is about 1 cm^{-1} , which is partly due to laser linewidth, Doppler broadening, and some collisional broadening. Because of ac Stark effects in the focal zone the observed lineshapes were somewhat asymmetric.

In the second experimental setup one-photon excitation was performed in a different setup with a VUV laser and 1 VUV + 1 UV photoionization. The experimental configuration of the VUV laser and its spectroscopic application are described elsewhere in detail (13, 15, 16). Tunable vacuum ultraviolet radiation in the wavelength range 105–109 nm is produced by third-harmonic generation of the output of a frequency-doubled pulsed dye laser (~ 640 nm at the fundamental) in a gas jet expansion. Overlapping VUV and incident UV beams perpendicularly cross a molecular beam, thus allowing for collision-free and Doppler-free spectroscopic measurements. The linewidth in the VUV spectrum is 0.4 cm^{-1} . Frequency positions of CO features are calibrated against an I_2 absorption spectrum (17, 18) that was recorded simultaneously in the visible. Since the frequency scale in the VUV is directly related to the visible standard (via multiplication by a factor of 6), this results in an accurate *absolute* frequency calibration in the spectra of CO. As a result of the linewidths and intensity noise in the VUV spectra, a slight nonlinearity in the wavelength scan and a possible small Doppler shift due to imperfect alignment of the crossed beams, the calibration accuracy of the absolute frequency scale is estimated at 0.08 cm^{-1} in the VUV. Because the VUV spectra are obtained from a dense molecular beam only natural CO samples could be used. However, spectra for different isotopes can be obtained by making use of mass-selective ion detection after 1 VUV + 1 UV photoionization.

3. RESULTS AND DISCUSSION

Two-photon excitation spectra of the $C-X$ (0,0) band were obtained from samples of natural CO and ^{13}C -enriched CO. As an example we present the 2 + 1 REMPI spectrum of the $C-X$ (0,0) band of $^{13}\text{C}^{16}\text{O}$ in Fig. 1. In a two-photon excitation spectrum of a $^1\Sigma^+ - ^1\Sigma^+$ transition three branches are allowed. A very strong, largely unresolved Q branch is observed, but not included in Fig. 1. O ($\Delta J = -2$) and S ($\Delta J = +2$) branches are less intense by a factor of 1000. The intensity distribution in the well-resolved O and S branches follows a pattern determined by a Boltzmann distribution at 1000 K multiplied by two-photon linestrength factors. The $C-X$ (0,0) spectrum of $^{13}\text{C}^{16}\text{O}$ (Fig. 1) is contaminated by $^{12}\text{C}^{16}\text{O}$ lines that carry about 10%

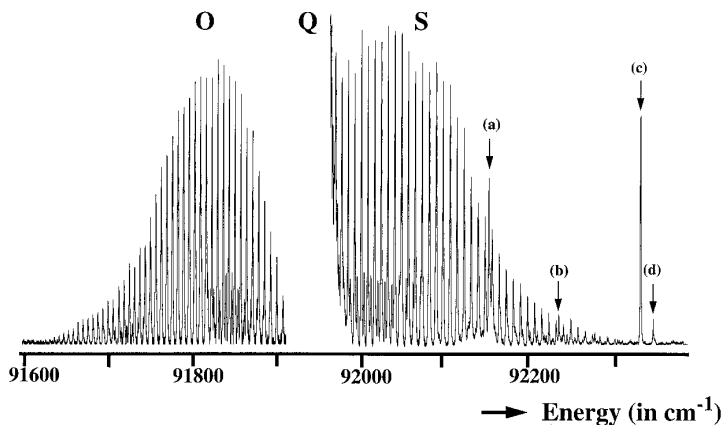


FIG. 1. Spectrum of the $C-X(0,0)$ band of $^{13}\text{C}^{16}\text{O}$ recorded by $2 + 1$ resonance-enhanced multiphoton ionization at a temperature of $T \approx 1000$ K. S- and O-branch lines could be discerned up to $J = 50$ and $J = 43$, respectively. The very strong unresolved Q branch is not plotted. Weak lines in the ranges $91\,700\text{--}91\,900\text{ cm}^{-1}$ and $92\,000\text{--}92\,100\text{ cm}^{-1}$ are due to $^{12}\text{C}^{16}\text{O}$ contamination. Lines (a), (b), and (c) are unidentified but related to ^{13}C . The feature marked (d) is related to ^{12}C (see text).

of the intensity. This contamination is caused by wall-sticking properties of carbon monoxide; once the cell has been filled with CO (of either the natural or the ^{13}C -enriched sample) it cannot be properly evacuated. Rotational lines up to O(47) and S(48) could be identified and calibrated against the tellurium standard. Moreover, Q -branch lines originating from $J = 46\text{--}48$ and 52 were well resolved. For $^{12}\text{C}^{16}\text{O}$ a similar spectrum was recorded, in which rotational lines up to O(43) and S(50) were observed.

For the $C-X(1,0)$ band $2 + 1$ REMPI spectra were recorded as well, but the signal intensities did not allow for recording of rotational lines $J > 30$ and were therefore not used in detailed spectroscopic analyses. However, from the observation of a Q branch in the $C-X(1,0)$ band of the $^{12}\text{C}^{17}\text{O}$ isotope, which had not been observed previously, a term value for the $C^1\Sigma^+, v = 1, J = 0$ state was derived: $94\,039.03 \pm 0.40\text{ cm}^{-1}$.

A second set of spectral data was obtained with the VUV laser source in combination with 1 VUV + 1 UV photoionization, time-of-flight mass separation, and ion detection techniques (13). A one-photon excitation spectrum of the $C-X(0,0)$ band of $^{12}\text{C}^{16}\text{O}$ obtained via these techniques is presented in Fig. 2. The typical signature of a missing Q branch in a $^1\Sigma^+ - ^1\Sigma^+$ one-photon transition is apparent. Due to the high sensitivity rotational lines up to $R(32)$ and $P(33)$ could be recorded even though the rotational temperature in the molecular beam was 250 K. Spectra of less abundant isotopomers were also measured from natural CO samples with abundances of 1% $^{13}\text{C}^{16}\text{O}$, 0.2% $^{12}\text{C}^{18}\text{O}$, and 0.037% $^{12}\text{C}^{17}\text{O}$. A simultaneously recorded spectrum of part of the R branch of the $C-X(0,0)$ band is shown in Fig. 3 for different ion masses. Because of the strong signals on the main $^{12}\text{C}^{16}\text{O}$ isotope these lines contaminate the spectra for the higher masses. Nevertheless the mass-29 channel clearly displays a spectrum for the $^{13}\text{C}^{16}\text{O}$ isotope from which rotationally resolved lines $R(2)\text{--}R(22)$ and $P(3)\text{--}P(23)$ were identified. Very weak lines in the mass-29 recording were observed, which can be assigned as the $C-X(0,0)$ band of $^{12}\text{C}^{17}\text{O}$. The average accuracy of the low

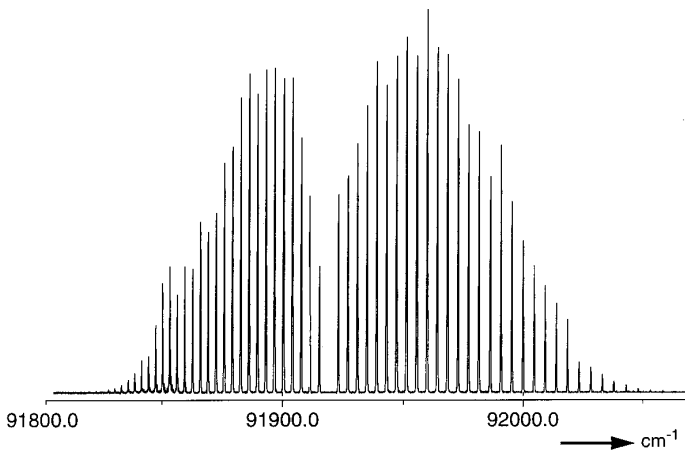


FIG. 2. One-photon excitation spectrum of the *C*-*X*(0,0) band of ¹²C¹⁶O recorded by 1 VUV + 1 UV photoionization.

signal-to-noise data is better than 0.15 cm⁻¹. Because these lines are observed for the first time, their transition frequencies are explicitly listed in Table I. The mass-30 channel shows the spectrum for the ¹²C¹⁸O isotope; lines up to *R*(19) were observed in the *R*-branch and *P*(5)–*P*(19) lines in the *P*-branch.

For the *C*-*X*(1,0) band similar VUV excitation spectra were recorded. Again for the ¹²C¹⁶O isotope rotational lines up to *P*(31) and *R*(27) were well resolved and analyzed. From the mass-29 channel frequencies of ¹³C¹⁶O lines were obtained up to *R*(15) and *P*(20). ¹²C¹⁸O lines were observed up to *R*(13) and *P*(10). No spectra of ¹²C¹⁷O could be obtained for the *C*-*X*(1,0) band from the VUV spectra.

The transition frequencies of VUV and 2 + 1 REMPI spectra were treated together in a least-squares minimization routine to determine molecular constants for each band and isotopomer. The data of the 2 + 1 REMPI spectra were adjusted with an offset parameter, to account for the asymmetric lineshapes. Values for the band origins were thus determined from the more accurate VUV data only. Excited state energies were expressed by:

$$E(J) = T_i + BJ(J + 1) - DJ^2(J + 1)^2.$$

Here T_i is the band origin and B and D are the rotational constants. The energies of ground state levels were calculated from the constants of Guelachvili *et al.* (19). Resulting values for the molecular constants are listed in Tables II–V, where they are compared with values from previous studies. Particularly for the C¹Σ⁺, *v* = 0 state of the main ¹²C¹⁶O isotope, for which 154 lines were included in the fit, the obtained molecular constants reach a level of accuracy as high as in the best previous studies. The improvement of the work lies in the incorporation of data for rotational states up to $J \approx 50$. This puts strong constraints on the value of the centrifugal distortion constant. Thus values for the centrifugal distortion parameters were deduced with much higher accuracy than in previous work, particularly for ¹²C¹⁶O and ¹³C¹⁶O. The internal consistency of the fit is such that the mean deviation between observed and calculated transition frequencies is better than 0.04 cm⁻¹ for ¹²C¹⁶O and ¹³C¹⁶O. The

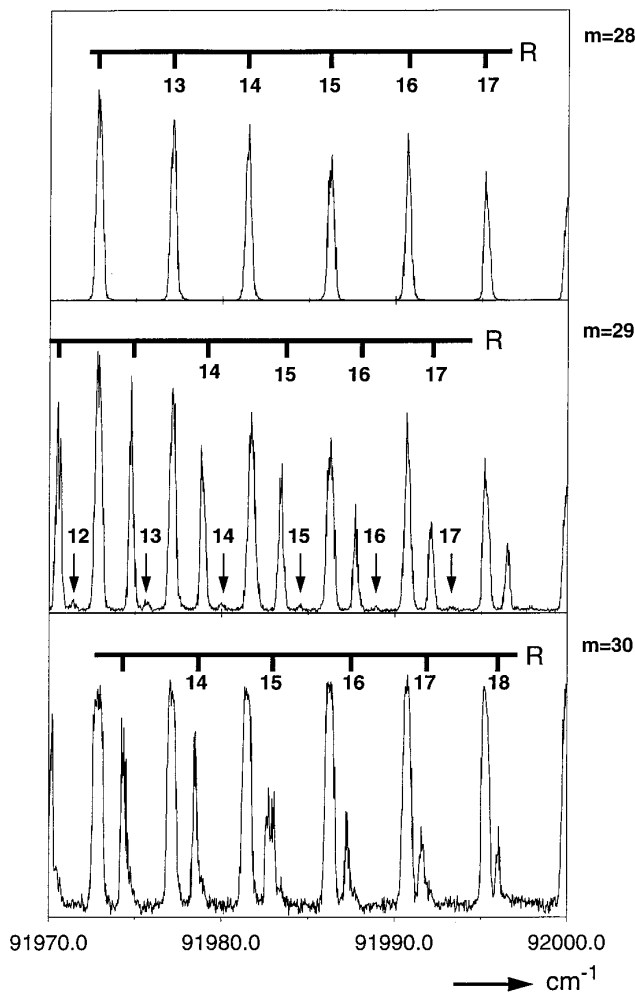


FIG. 3. Part of the R -branch spectrum of the $C-X(0,0)$ band recorded via 1 VUV + 1 UV photoionization; the upper, middle, and lower spectra are recorded simultaneously with time-of-flight separation of masses 28, 29, and 30, respectively. The strong lines related to $^{12}\text{C}^{16}\text{O}$ (upper spectrum) also leak into the other channels. In the middle spectrum $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{17}\text{O}$ (the latter indicated by the arrows) are discerned, while in the lower spectrum $^{12}\text{C}^{18}\text{O}$ lines are indicated.

accuracy of the values for T_i is, however, determined by the accuracy of the absolute frequency scale and the calibration procedure involving the VUV spectrum and I_2 reference spectrum. This yields an absolute accuracy of 0.08 cm^{-1} and correspondingly a systematic uncertainty of 0.08 cm^{-1} for the listed values of T_i in Tables II–V.

Since we found no indication of line shifts in any of the fitting routines that might be attributed to local perturbations, the parameters of Tables II–V straightforwardly represent the term energies from which transition frequencies can be calculated. For this reason it was decided not to reproduce lengthy tables of transition frequencies in the present paper. However, listings of line positions are available upon request from the authors.

TABLE I

Observed Transition Frequencies in the C–X (0,0) Band of ¹²C¹⁷O and Deviations from Calculated Values Obtained from a Least-Squares Fit (All Values in cm⁻¹)

J	R(J)		P(J)	
	obs.	obs.-calc.	obs.	obs.-cal.
10	91962.902	0.105	91883.306	0.042
11	91966.985	-0.053	91880.000	0.057
12	91971.357	0.037	91876.576	-0.089
13	91975.440	-0.202	91873.478	0.047
14	91979.872	-0.131	91870.274	0.033
15	91984.474	0.071	91867.045	-0.049
16	91988.959	0.116		
17	91993.337	0.015		

Apart from the isotopic contamination in the 2 + 1 REMPI spectra additional spectral features are observed that are marked (a)–(d) in Fig. 1. At 92 333.42 cm⁻¹ an unidentified Q-branch-like structure (feature c in Fig. 1) is found, which can be related to ¹³C. A corresponding feature for ¹²C at 10% of the intensity is found at 92 349.09 cm⁻¹ (feature d in Fig. 1). Similar sharp features are found at 92 150.38 cm⁻¹ (¹³C) (feature a) and 92 152.85 cm⁻¹ (¹²C) and at 92 234.68 cm⁻¹ (¹³C) (feature b) and 92 238.50 cm⁻¹ (¹²C). In addition to the three relatively strong features observed for both ¹²C and ¹³C isotopes, sequences of unidentified lines are found in the frequency domain 92 200–92 300 cm⁻¹. The relation to ¹²C and ¹³C isotopes was established by using natural and ¹³C-enriched samples in the cell. None of these lines could be

TABLE II

Molecular Constants for the C¹Σ⁺, v = 0 and v = 1 states of ¹²C¹⁶O

	this work	ref. [10]	ref. [7]	ref. [9]	ref. [6]	ref. [3]	ref. [4]	ref. [11]
v=0 T ₀	91919.041 (4) ^(e)	91919.072 (2) ^(a)			91919.11 (4)	91919.10	91919.11 (1)	91919.094 (4)
B	1.94344 (1)	1.9435 (1)	1.94337 (8)	1.94339 (2)	1.94338 (4)	1.9435	1.94338 (1)	1.94338 (1)
D	6.2234 (5) 10 ⁻⁶	6.172 10 ⁻⁶ ^(f)	6.3 (2) 10 ⁻⁶	6.16 (3) 10 ⁻⁶	6.172 (5) 10 ⁻⁶	6.3 10 ⁻⁶	6.2 (1) 10 ⁻⁶	6.28 (4) 10 ⁻⁶
v=1 T ₁	94065.60 (1) ^(e)				94065.64 (4)	94065.54	94065.57 (2)	
B	1.9239 (1)				1.9236 (2)	1.9239	1.9239 (1)	
D	6.37 (1) 10 ⁻⁶				5.0 (7) 10 ⁻⁶	6.1 10 ⁻⁶	6.3 (1) 10 ⁻⁶	

Note. All values in cm⁻¹. Errors represent one standard deviation.

^(a) Recalibration of Tellurium atlas accounted for.

^(f) Fixed in fitting routine.

^(e) Error as obtained from the fitting procedure; the estimated uncertainty in the absolute term value is 0.08 cm⁻¹.

TABLE III

Molecular Constants for the $C^1\Sigma^+$, $v = 0$ and $v = 1$ States of $^{13}\text{C}^{16}\text{O}$

		this work	ref. [3]	ref. [7]	ref. [4]
$v=0$	T_0	91919.017 (8) ^(e)	91919.10		91919.10 (3)
	B_0	1.85850 (2)	1.8590	1.85840 (5)	1.8584 (2)
	D_0	$5.70 (1) 10^{-6}$	$7.6 10^{-6}$	$5.6 (1) 10^{-6}$	$5.6 (2) 10^{-6}$
$v=1$	T_1	94018.42 (2) ^(e)	94018.46		94018.55 (4)
	B_1	1.8403 (2)	1.8389		1.8387 (3)
	D_1	$6.2 (6) 10^{-6}$	$6.1 10^{-6}$		$4.2 (3) 10^{-6}$

Note. All values in cm^{-1} . Errors represent one standard deviation.

^(e) Error as obtained from the fitting procedure; the estimated uncertainty in the absolute term value is 0.08 cm^{-1} .

identified as belonging to known spectroscopic features of CO, nor did we succeed in finding a rotational structure to interpret these spectral phenomena. These additional lines were not observed in the VUV molecular beam experiments. Because of selection rules the features might possibly be due to Δ states, which have not yet been observed in this energy range. The C -state lines observed close to the extra lines are not perturbed, so wavefunction mixing or intensity-borrowing effects may be excluded. From the observation it does not follow unambiguously that the extra lines originate in CO, although the relation to ^{12}C and ^{13}C is undeniable.

The rotational structure of the $C^1\Sigma^+$, $v = 0$ and $v = 1$ states is unperturbed up to the highest J values observed in the present study. Moreover, the intensity distributions in both the REMPI and the VUV spectra follow a regular pattern. In a previous study it was demonstrated how relative line intensities in $2 + 1$ and $1 + 1$ photoionization studies can be used as sensitive probes for accidental predissociation phenomena (13).

TABLE IV

Molecular Constants for the $C^1\Sigma^+$, $v = 0$ and $v = 1$ States of $^{12}\text{C}^{17}\text{O}$ as Derived in the Present Work

T_0	91918.83 (5) ^(e)
B_0	1.8950 (3)
D_0	$6.0 10^{-6}$ ^(f)
T_1	94039.03 (40)

Note. All values in cm^{-1} . Errors represent one standard deviation.

^(f) Fixed in the fitting routine.

^(e) Error as obtained from the fitting procedure; the estimated uncertainty in the absolute term value is 0.08 cm^{-1} .

TABLE V

Molecular Constants for the C¹Σ⁺, v = 0 and v = 1 States of ¹²C¹⁸O

	this work	ref. [4]	ref. [12]	ref. [7]
T ₀	91918.83 (2) ^(e)	91918.1 (2)	91918.86 (2)	
B ₀	1.8515 (2)	1.8535 (5)	1.8522 (5) ^(p)	1.85179 (7)
D ₀	6.0 (5) 10 ⁻⁶	6.9 (4) 10 ⁻⁶	5.72 10 ⁻⁶ ^(f)	6.9 (2) 10 ⁻⁶
T ₁	94014.26 (1) ^(e)	91014.39 (2)		
B ₁	1.8329 (2)	1.8321 (1)		
D ₁	4.0 10 ⁻⁶ ^(f)	4.0 (1) 10 ⁻⁶		

Note. All values in cm⁻¹. Errors represent one standard deviation.

^(f) Fixed in the fitting routine.

^(p) 1.8622 was listed in Ref. (12); we assume a printing error occurred.

^(e) Error as obtained from the fitting procedure; the estimated uncertainty in the absolute term value is 0.08 cm⁻¹.

Although fluctuations are present in the obtained intensities, a statistical analysis of intensities in multiple recordings does not show systematic deviations from a regular pattern. From this we conclude that the C¹Σ⁺, v = 0 and v = 1 states are not affected by accidental predissociations. In the same energy range the E¹Π, v = 0 and v = 1 states were found to be subject to accidental predissociations, caused by interactions with the k³Π state (13, 20, 21). For ¹²C¹⁶O the C¹Σ⁺, v = 0 rotational manifold crosses the k³Π, v = 1 state near J ≈ 5–10 and the k³Π, v = 2 state near J ≈ 35. Similarly, the C¹Σ⁺, v = 1 state crosses the k³Π, v = 4 state near J ≈ 20. No perturbations of the rotational structures are found at these locations, so obviously there is no interaction between the C¹Σ⁺ and k³Π states.

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