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High resolution study of Q-branches in the $E^1\Pi$–$X^1\Sigma^+$ (0, 0) band of $^{12}C^{16}O$, $^{13}C^{16}O$, and $^{13}C^{18}O$☆

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Abstract

A tunable and narrowband vacuum ultraviolet laser system near $\lambda = 107.5$ nm is used to record Doppler-free molecular beam spectra of the $E^1\Pi$–$X^1\Sigma^+$ (0, 0) band for three isotopomers of carbon monoxide. The Q branches of the E–X (0, 0) bands in $^{12}C^{16}O$, $^{13}C^{16}O$, and $^{13}C^{18}O$ are fully resolved in this study, performed at a resolution of 0.02 cm^{-1} (FWHM). The newly obtained data are included in a comprehensive fitting routine with previous data to yield optimized molecular constants for the upper level.

The $E^1\Pi$ and $C^1\Sigma^+$ states, correlating with $3p\pi$ and $3p\sigma$ electronic orbitals, are the upper states of the strongest absorbing bands in the CO molecule. Because carbon monoxide is the second most abundant molecule in outer space, and the chemistry of interstellar clouds is largely governed by the photodissociation of CO [1], there is a continued interest in the spectroscopy involving these states. Starting with the early classical studies of Hopfield and Birge [2] a large number of studies were performed to unravel spectroscopic features in ever greater detail. After Baker et al. [3] had assigned the accidental predissociation phenomena in the $E^1\Pi, v = 0$ and $v = 1$ states to a singlet–triplet perturbation, a further quantitative analysis was performed, based on high resolution vacuum ultraviolet (VUV) laser studies by our group, for six natural isotopomers of CO [4,5]. Similarly laser spectroscopic studies of the $C^1\Sigma^+, v = 0$ and $v = 1$ states were also performed for various isotopomers [6,7]. Although the $E^1\Pi, v = 0$ state has been investigated in great detail, until now no report on the resolved Q-branches of the E–X (0, 0) bands have been published. Here we present measurements of fully rotationally resolved Q branches for three isotopomers of carbon monoxide performed with a narrowband and tunable VUV-laser, yielding transition frequencies more than an order of magnitude more accurate than all previous studies. The new data are incorporated in comprehensive fitting routines including all high resolution data for these bands, delivering updated molecular constants.

The experimental apparatus and the measurement procedures are the same as described in previous papers, where the use of the narrowband vacuum ultraviolet laser source and its application to the spectroscopy of CO was documented [5,8]. In the case of the E–X (0, 0) band spectral lines were recorded at a linewidth (FWHM) of ≈ 600 MHz or 0.02 cm^{-1}. Half of the broadening is determined by the excited state lifetime of $E^1\Pi, v = 0$, which was determined at 1 ns [9], while further the laser bandwidth (in the present setup using a pulsed-dye-amplification system and a continuous wave ring dye laser amounting to about 300 MHz after frequency sextupling to the VUV-domain) and some residual Doppler broadening in the crossed molecular beam configuration contribute. As in previous studies signal was obtained by the use of 1 VUV + 1 UV photoionization. In Fig. 1 an essential part of the spectral recordings is displayed. The figure represents data taken in two runs, one using natural CO gas yielding the $^{12}C^{16}O$ spectrum, and one using a ^{13}C isotopically enriched sample, yielding the $^{13}C^{16}O$ and $^{13}C^{18}O$ spectra;

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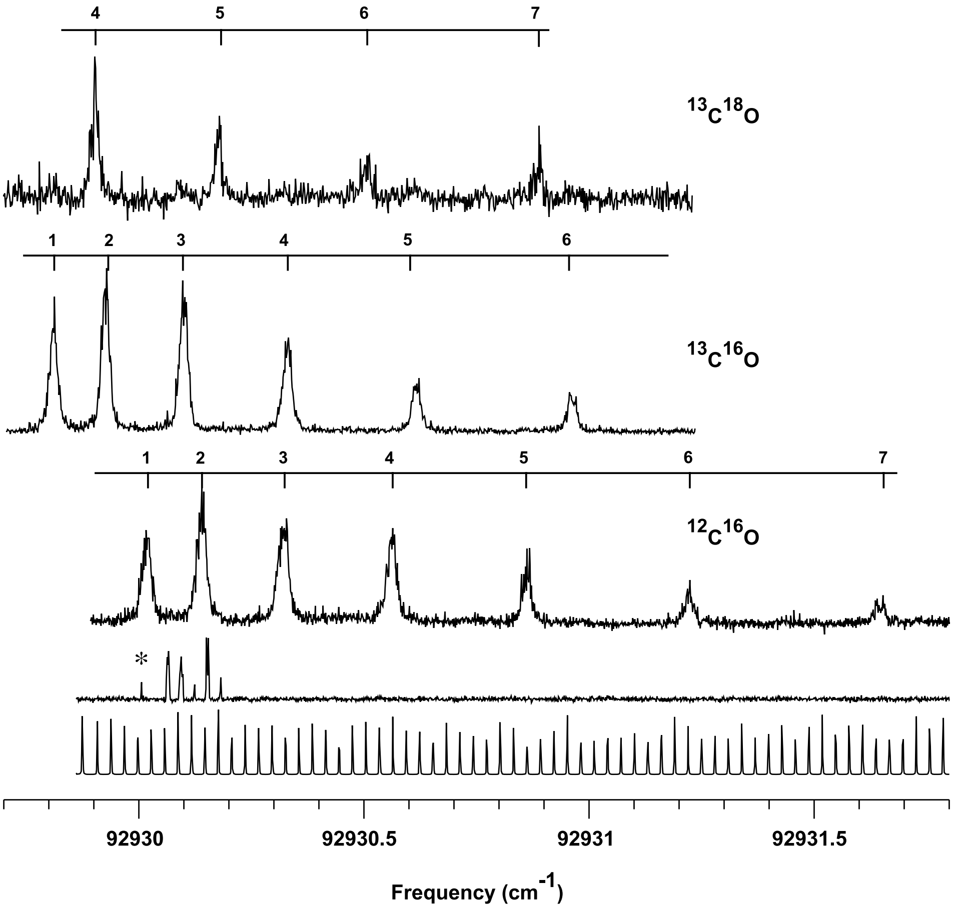

Fig. 1. High resolution spectra of the E–X (0, 0) band of CO for the three isotopomers of carbon monoxide as indicated. The lower traces represent the saturated I_2 spectrum and an étalon trace, recorded with the output of the cw ring-dye laser at the fundamental frequency, which are used for calibration purposes. The I_2 line marked by (*) is the t hyperfine component of the $R(48)$ line in the (7, 5) band at 15488.3344 cm^{-1}.

the latter two were unraveled by the use of a time-of-flight mass spectrometer and boxcars set at masses 29 and 31. For each recording transmission fringes of an étalon (FSR = 148.956 MHz), obtained in the visible domain at the fundamental laser wavelength, determine the relative frequency scale. The absolute scale is then determined by the location of a single hyperfine component of an I_2 line, in this case the t hyperfine component of the $R(48)$ line in the B–X (7, 5) band; its frequency, accurate to within 5 MHz, was obtained from the work of the Hannover group [10]. The spectra were recorded four times for most lines and the statistical uncertainty on the line positions is better than 0.001 cm^{-1}. However, the absolute accuracy is largely determined by systematic effects, the dominant being the frequency chirp in the pulse-amplification system, which may amount to 0.003 cm^{-1} [8]. The resulting transition frequencies, listed in Table 1, have therefore an estimated (absolute) uncertainty of 0.003 cm^{-1}.

The present data on the $^{12}C^{16}O$ isotopomer were included in a comprehensive fitting routine with the data obtained in previous laser based experiments on the E–X (0, 0) band [4]. Particularly the data on the 2 + 1 REMPI spectrum of heated static samples of CO are extensive, with recording of the two-photon O-branch up to $J = 51$, the P-branch up to $J = 32$, the R-branch up to $J = 42$ and the S-branch up to $J = 46$. The accuracy of these data is estimated at 0.06 cm^{-1} from a comparison with a simultaneously recorded Te$_2$-spectrum [14] using the fundamental wavelength ($\lambda = 430$ nm) of the laser

Table 1
Observed transitions frequencies for Q-branch lines in the E–X (0, 0) band of carbon monoxide for three isotopomers

Line	$^{12}C^{16}O$	$^{13}C^{16}O$	$^{13}C^{18}O$
$Q(1)$	92929.988	92929.804	92929.407
$Q(2)$	92930.109	92929.918	92929.516
$Q(3)$	92930.291	92930.092	92929.681
$Q(4)$	92930.532	92930.323	92929.902
$Q(5)$	92930.832	92930.610	92930.175
$Q(6)$	92931.194	92930.956	92930.504
$Q(7)$	92931.616	92931.358	92930.888
$Q(8)$	92932.098		

The uncertainty in the line positions on an absolute frequency scale is estimated at 0.003 and 0.001 cm^{-1} on a relative scale. Deviations between observed and calculated data from the least squares fitting routine are also 0.001 cm^{-1} or less.

output before frequency doubling. For the $2+1$ REMPI spectra the accuracy of the transition frequencies and the uncertainties therein, are determined by the fitting procedure and the widths of the spectral lines, which amounts to $1\,\mathrm{cm}^{-1}$, as a result of Doppler broadening at highly elevated temperatures (1000 K), laser bandwidth, collisional broadening, and the AC-Stark effect due to tight focusing of the UV-laser. The latter effect gives also rise to some asymmetry in the line shape and for this reason the absolute frequency in the $2+1$ REMPI data is not as accurate as the relative precision. A second set of data pertains to measurements of 1 VUV + 1 UV in a molecular beam with a tunable VUV source of $0.3\,\mathrm{cm}^{-1}$ bandwidth [4]. The calibration is performed by simultaneously recording an I_2 absorption spectrum, at the fundamental laser wavelength before frequency sextupling, under Doppler broadened conditions and comparison with the I_2 reference atlas [15]. Here the accuracy is estimated at $0.04\,\mathrm{cm}^{-1}$. Again a large data set is available with recordings of R-branch lines up to $J=34$ and P-lines up to $J=36$. Q-branch lines could be resolved in the range $J=9$–27. These data are included in the input deck of a weighted least-squares fitting routine together with the present data on the Q-branch lines, giving a total of 229 transition frequencies. The relative precision of the new Q-branch data is taken as $0.001\,\mathrm{cm}^{-1}$ although it is known that systematic effects due to frequency chirp in the dye amplifiers reduces the absolute accuracy to $0.003\,\mathrm{cm}^{-1}$ [8]. Transition frequencies are determined from excited state energies

$$E_{e,f} = T_0 + B_{e,f}J(J+1) - D_{e,f}J^2(J+1)^2, \qquad (1)$$

for (e) and (f) parity levels and from the highly accurate ground state constants by Varberg and Evenson [16]. The Λ-doubling parameters $q = B_e - B_f$ and $q_D = D_e - D_f$ are also determined. To accommodate the option of high precision and lower absolute accuracy the three data sets are taken with the possibility of a calibration offset, which is fitted as an independent parameter. It is known that the level structure of the $E^1\Pi, v=0$ state is perturbed by several vibrational levels of the $k^3\Pi$ state [3,4] and the levels affected by this perturbation are effectively left out of the fit by reducing their weigths. We have followed this procedure because the singlet–triplet perturbation was well treated and understood previously and the present highly accurate data at low J values do not warrant an improved deperturbation analysis at high J values. The molecular constants resulting from the fit are given in Table 2. The value for the band origin T_0 as resulting from the fit has an uncertainty of $0.0003\,\mathrm{cm}^{-1}$, although it should be considered that the uncertainty in the absolute frequency may be as large as $0.003\,\mathrm{cm}^{-1}$. Inclusion of a higher order centrifugal distortion parameter H did not result in an improved fit. From the fit it follows that the data set for the $2+1$

Table 2
Molecular constants for the $E^1\Pi, v=0$ state of carbon monoxide as derived from the presently obtained accurate data and the data listed in the electronic archive

Isotope		This work	Refs. [11–13]	Isotopic scaling
$^{12}C^{16}O$	T_0	92929.9285 (4)	92929.98 (1)	—
	B_e	1.96463 (2)	$=B_f+q$	—
	B_f	1.952672 (7)	1.95261 (2)	—
	q	0.01196 (2)	0.0118 (5)	—
	D_e	$6.55\ (1)\times10^{-6}$	$=D_f$	—
	D_f	$6.34\ (2)\times10^{-6}$	$6.5\ (1)\times10^{-6}$	—
	q_D	$0.21\ (2)\times10^{-6}$	—	—
$^{13}C^{16}O$	T_0	92929.7462 (6)	92929.91 (3)	—
	B_e	1.87782 (2)	$=B_f+q$	1.87775
	B_f	1.86678 (2)	1.866 23 (14)	1.86658
	q	0.01104 (3)	0.012 (5)	0.01117
	D_e	$6.00\ (1)\times10^{-6}$	$=5.8\ (1)\times10^{-6}$	6.12×10^{-6}
	D_f	$5.82\ (4)\times10^{-6}$	$=D_e$	5.93×10^{-6}
	q_D	$0.18\ (4)\times10^{-6}$	—	0.19×10^{-6}
$^{13}C^{18}O$	T_0	92929.3514 (7)	92929.37 (3)	—
	B_e	1.7842 (2)	1.784 23 (23)	1.78373
	B_f	1.77386 (3)	$=B_f$	1.77338
	q	0.0103 (3)	—	0.01035
	D_e	5.66×10^{-6} [a]	$5.9\ (2)\times10^{-6}$	5.66×10^{-6}
	D_f	5.49×10^{-6} [a]	$=D_f$	5.49×10^{-6}
	q_D	0.17×10^{-6} [a]	—	0.17×10^{-6}

The uncertainties for T_0 are the ones obtained from the fit; the real absolute calibration uncertainties amount to $0.003\,\mathrm{cm}^{-1}$. The third column gives the values calculated from the main isotopomer $^{12}C^{16}O$ constants by simple isotopic scaling laws. No uncertainties are repeated for these values. All values in cm^{-1}.

[a] Kept fixed.

REMPI data is offset by 0.08 cm^{-1}, which is reasonable in view of the asymmetry on the line shapes observed; the data obtained with the XUV-source based on a pulsed dye laser are offset by $-0.002\,\mathrm{cm}^{-1}$, which is a small number in view of the calibration procedures using the Doppler broadened I_2 spectrum. The χ^2 of the fit is 1.0 per data point, thus proving that the estimate on the uncertainties of the data points is appropriate. In Appendix I, submitted to the data archive of JMS, a listing of all line positions and their deviations from the fit is given.

For the $^{13}C^{16}O$ isotopomer the situation is quite similar as for the main isotope. Previously 2 + 1 REMPI and 1 VUV + 1 UV photoionization spectra were obtained from ^{13}C-enriched samples of carbon monoxide, although the amount of data is somewhat less; 194 transition frequencies are used in the analysis of $^{13}C^{16}O$. The ground state molecular constants are in this case obtained from Guelachvili et al. [17]. Again resulting constants are included in Table 2, while all data are listed in Appendix II in the data archive.

For the $^{13}C^{18}O$ isotopomer the amount of available data is much lower, and no laser-based data exist. Therefore the data of the classical absorption studies of Eidelsberg and Rostas [11–13] have been included in a combined fit. In those studies P- and R-branch lines were resolved up to $J = 15$, while also a single high-J transition was observed at $R(25)$. These data are taken in a weighted fit at an accuracy of 0.1 cm^{-1}, and the present data of Q-branch lines at an accuracy of 0.001 cm^{-1}. Compared to the previous cases in $^{12}C^{16}O$ and $^{13}C^{16}O$, the J values are not high enough to define the centrifugal distortion constant D. We choose to fix D using isotopic scaling laws, using μ, the reduced mass of the isotopomer, as a scaling parameter. The fit results in a χ^2 of 1.0 per data point with the parameters as given in Table 2. In view of the problems with the absolute calibration [13] we allowed for an offset on the classical data, which was determined at $+0.004\,\mathrm{cm}^{-1}$. The accurate data on the Q branches allow for a test of the validity of the isotopic substitution laws. From the constants for $^{12}C^{16}O$, those for $^{13}C^{16}O$ and $^{13}C^{18}O$ are calculated and compared with the experimental results (3rd column in Table 2).

In conclusion the $E^1\Pi, v = 0$ state has been investigated at the highest resolution hitherto reported, with a linewidth at twice the natural lifetime broadening, thus leaving only sparse room for further improvement. Since the previously obtained data from [4] have not yet been published, and we have used them, jointly with the present data in a comprehensive fitting procedure, we have deposited all data in the electronic archive of this journal. In Table 2 a comparison is made with the data from the VUV CO-atlas by Eidelsberg et al. [13]. A comparison of the band origins T_0 may shed some light on the calibration accuracy of the large amount of data for many bands, for which a recalibration was found to be necessary.

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References

[1] E.F. van Dishoeck, J.H. Black, Astrophys. J. 334 (1988) 771–802.
[2] J.J. Hopfield, R.T. Birge, Phys. Rev. 29 (1927) 922–922.
[3] J. Baker, J.L. Lemaire, S. Couris, A. Vient, D. Malmasson, F. Rostas, Chem. Phys. 178 (1993) 569–579.
[4] P. Cacciani, W. Hogervorst, W. Ubachs, J. Chem. Phys. 102 (1995) 8308–8320.
[5] W. Ubachs, I. Velchev, P. Cacciani, J. Chem. Phys. 113 (2000) 547–560.
[6] W. Ubachs, P.C. Hinnen, P. Hansen, S. Stolte, W. Hogervorst, P. Cacciani, J. Mol. Spectr. 174 (1995) 388–396.
[7] P. Cacciani, F. Brandi, I. Velchev, C. Lyngå, C.-G. Wahlström, W. Ubachs, Eur. J. Phys. D 15 (2001) 47–56.
[8] W. Ubachs, K.S.E. Eikema, W. Hogervorst, P.C. Cacciani, J. Opt. Soc. Am. B 14 (1997) 2469–2476.
[9] P.C. Cacciani, W. Ubachs, P.C. Hinnen, C. Lyngå, A. L'Huillier, C.-G. Wahlström, Astrophys. J. Lett. 499 (1998) L223–L226.
[10] The frequency was obtained with the program IodineSpec made available to us via H. Knöckel, Hannover University, Germany. See also: B. Bodermann, H. Knöckel, E. Tiemann, Eur. J. Phys. D 19 (2002) 31–44.
[11] M. Eidelsberg, F. Rostas, Astron. Astrophys. 235 (1990) 472–489.
[12] M. Eidelsberg, J.J. Benayoun, Y. Viala, F. Rostas, Astron. Astrophys. Suppl. Ser. 90 (1991) 231–282.
[13] M. Eidelsberg, J.J. Benayoun, Y. Viala, F. Rostas, P.L. Smith, K. Yoshino, G. Stark, C.A. Shettle, Astron. Astrophys. 265 (1992) 839–842.
[14] J. Cariou, P. Luc, Atlas du spectre d'Absorption de la Molecule de Tellure, CNRS, Paris, 1980.
[15] S. Gerstenkorn, P. Luc, Atlas du spectre d'Absorption de la Molecule de l'Iode entre 14 800–20 000 cm^{-1}, CNRS, Paris, 1978.
[16] T.D. Varberg, K.M. Evenson, Astrophys. J. 385 (1992) 763–765.
[17] G. Guelachvili, D. de Villeneuve, R. Farrenq, W. Urban, J. Vergès, J. Mol. Spectr. 98 (1983) 64–79.