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ACCURATE DETERMINATION OF PREDISSOCIATION RATES AND TRANSITION FREQUENCIES FOR CARBON MONOXIDE

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ABSTRACT

By making use of two different laser spectroscopic techniques involving narrowband pulsed lasers in the visible, ultraviolet, and extreme-ultraviolet wavelength ranges, highly accurate data on absolute transition frequencies and predissociation rates were obtained for a number of excited states of CO and its isotopes. These data are combined, reanalyzed, and presented here in concise form.

Subject headings: ISM: molecules — molecular data — techniques: spectroscopic

The calculated abundance ratio of CO/H_2, as well as the abundancies of various neutral and ionized species in the interstellar medium, are found to depend largely on the photopredissociation processes of carbon monoxide induced by extreme-ultraviolet (EUV) radiation in the range 90–115 nm (van Dishoeck & Black 1988 and references therein). At the boundaries of dark clouds and in translucent clouds, CO is dissociated by the interstellar radiation field. Deep inside molecular clouds EUV photons, produced by emissions of cosmic-ray–excited H_2, play a role in the photodestruction of CO (Prasad & Tarafdar 1983; Gredel, Lepp, & Dalgarno 1987). In order to identify coincidences between H_2 emissions and CO absorptions, accurate transition frequencies of CO are of importance. The spectroscopy, as well as the predissociation properties, of CO have therefore attracted interest in recent years. The vibronic structure was unraveled by making use of synchrotron radiation (Letzelter et al. 1987) and 43 band features were identified in the range 90–115 nm. Subsequently, rotationally resolved studies were performed (Eidelsberg & Rostas 1990; Stark et al. 1991), and, recently, an atlas of absorption frequencies for $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, and $^{13}C^{18}O$ has been published (Eidelsberg et al. 1991, 1992). Values for predissociation rates pertaining to the different vibronic states and for the four isotopes were determined by the Meudon group (Eidelsberg & Rostas 1990) with an accuracy of a factor of 3. Moreover, absolute absorption cross sections were obtained by the Harvard-Smithsonian Center for Astrophysics group for a number of vibronic states (Stark et al. 1991, 1992, 1993). Absorption cross sections were also determined in electron scattering experiments (Chan, Cooper, & Brion 1993). A review of molecular parameters of CO relevant to ultraviolet astronomy will be published (Morton & Noreau 1994).

Recently, in Amsterdam and Nijmegen, laser spectroscopic techniques were developed that allow for measurements of line positions, excited state lifetimes, and predissociation rates that are more acurate than those measured by previous nonlaser techniques. A new result following from both studies is that predissociation rates of the highly excited states of CO do not only depend on the particular vibronic states, but also on the rotational substates and even, in some cases, on the Λ-doublet component of $^1\Pi$-states.

In the Amsterdam group, a narrowband EUV laser source was constructed (Levelt 1992). Based on the nonlinear upconversion of pulsed laser radiation, the EUV laser is continuously tunable in the relevant wavelength range 90–100 nm. As the EUV radiation corresponds to the exact sixth harmonic of visible radiation, the EUV wavelength can be calibrated against the I_2-absorption standard (Gerstenkorn & Luc 1978, 1979). Computerized interpolation procedures yield an estimated accuracy of 0.13 cm^{-1} for the absolute transition frequencies of the well-resolved rotational lines. The line width of the EUV radiation was first estimated at 0.32 ± 0.06 cm^{-1} but later found to vary from 0.44 to 0.30 cm^{-1} over the range 90–96 nm (Ubachs, Eikema, & Hogervorst 1993). The EUV laser is used in a 1 EUV + 1 UV photoionization scheme that allows for highly sensitive detection of CO. Spectra were recorded from a crossed beam Doppler-free geometry with CO densities of 10^{-4}–10^{-5} torr (Eikema et al. 1994b). Moreover, by means of a time-of-flight mass separation zone, isotope selective spectra could be recorded simultaneously. First, this technique was used to record spectra of $^{12}C^{16}O$ and $^{13}C^{16}O$ from natural samples of CO, and later, for the recording of separate $^{13}C^{16}O$ and $^{13}C^{18}O$ spectra from a ^{13}C enriched sample. Excited state lifetimes were derived from effects of line broadening. Rotationally resolved lines were fitted to Voigt profiles, and the Gaussian laser profile was deconvolved to yield the lifetime broadening effect. It should be noted that for the 1 EUV + 1 UV photoionization detection method, the signal depends on the excited state lifetime. As a consequence, the intensity of lines that are broadened beyond 1.5 cm^{-1} rapidly decreases. This corresponds to a maximum detectable predissociation rate of 3×10^{11} s^{-1}. A minimum line broadening effect of 30% of the total line width may be discerned without ambiguity. After deconvolution of the instrumental width, this corresponds to a minimum detectable predissociation rate of 3×10^{10} s^{-1}. Thus, predissociation rates in a dynamic range 3×10^{10} s^{-1}–3×10^{11} s^{-1} can be determined with the EUV laser. Thirteen different vibronic states of Rydberg character were investigated for the main isotope $^{12}C^{16}O$, while some of these states were also studied for $^{13}C^{16}O$ and $^{13}C^{18}O$ isotopes (Levelt, Ubachs, & Hogervorst 1992a, 1992b; Eikema et al. 1994a, 1994b).

In Nijmegen, a nearly Fourier transform–limited pulsed laser system was constructed based on the principle of pulsed dye amplication (PDA) of a single mode ring dye laser (Drabbels 1993). Employing this laser in combination with a molecular beam, the $B\,{}^1\Sigma^+$ and $C\,{}^1\Sigma^+$ states of CO were studied by two-photon laser-induced fluorescence spectroscopy (Drabbels, Meerts, & ter Meulen 1993a). By calibrating the frequency of the continuous wave laser to the Te_2-absorption spectrum (Cariou & Luc 1980) absolute transition frequencies could be determined within 0.003 cm^{-1}. Recently, we became aware of the fact that the frequencies listed in the Te atlas have to be corrected by 0.002 cm^{-1} (Gillaspy & San-

TABLE 1

MOLECULAR CONSTANTS FOR EXCITED STATES OF CO

State		ν_0	B	D	q
$^{12}C^{16}O$:					
$^1\Pi, v=0$	{7A}	109564.58 ± 0.07	1.915 ± 0.006	5.9×10^{-5} [a]	...
$5p\sigma\ {}^1\Sigma^+, v=1$	{7B}	109481.03 ± 0.03	1.829[a]	1.0×10^{-5} [a]	...
$^1\Sigma^+, v=2$	{7D}	109448.97 ± 0.03	1.7781 ± 0.0007	5.4×10^{-5} [a]	...
$6p\sigma\ {}^1\Sigma^+, v=0$	{8B}	109173.68 ± 0.06	1.685 ± 0.005	1.0×10^{-4} [a]	...
$^1\Pi$, $v=2$ (homogeneous)[b]	{13}	107682.33 ± 0.06	1.936 ± 0.001	$3.1 \pm 0.3 \times 10^{-5}$	...
Perturber state[b]	...	107706 ± 1	1.64 ± 0.02	...	...
$^1\Pi$, $v=2$ (heterogeneous)[b]	{13}	107681.95 ± 0.08	1.936 ± 0.001	$3.1 \pm 0.3 \times 10^{-5}$	...
Perturber state[b]	...	107710.1 ± 0.8	1.604 ± 0.005	...	...
$5p\sigma\ {}^1\Sigma^+, v=0,$	{15C}	107174.44 ± 0.05	2.1248[a]	1.0×10^{-5} [a]	...
$^1\Sigma^{+}$ [c]	...	107365.87 ± 0.04	1.884 ± 0.004	$3.1 \pm 0.9 \times 10^{-4}$	...
$3s\sigma\ W\,{}^1\Pi, v=2$[d,e]	{18}	106250.90 ± 0.05	1.6224 ± 0.0004	$-1.3 \pm 0.6 \times 10^{-5}$	$-2.7 \pm 0.5 \times 10^{-3}$
$4d\sigma\ {}^1\Sigma^+, v=0$[f]	{19}	105676.30 ± 0.04	1.8952 ± 0.0002	$1.73 \pm 0.04 \times 10^{-5}$	...
$4p\pi\ L\,{}^1\Pi, v=0$[g]	{25}	103271.797 ± 0.003	1.9603 ± 0.0004	$0.70 \pm 0.08 \times 10^{-5}$	$2.17 \pm 0.03 \times 10^{-2}$
$3d\pi\ L'\,{}^1\Pi, v=1$[h]	{26}	103211.8 ± 0.2	1.754 ± 0.002	$1.0 \pm 0.3 \times 10^{-5}$	$3 \pm 2 \times 10^{-2}$
$4p\sigma\ K\,{}^1\Sigma^+, v=0$	{27}	103054.667 ± 0.006	1.9166 ± 0.0003	$5.99 \pm 0.08 \times 10^{-5}$	...
$3s\sigma\ W\,{}^1\Pi, v=0$[i]	{28}	102806.658 ± 0.004	1.5664 ± 0.0002	$9.7 \pm 0.2 \times 10^{-5}$	$-7 \pm 4 \times 10^{-4}$
$W'\,{}^1\Pi, v=2$[j]	{29}	102312.3 ± 0.4	1.5417 ± 0.0024	$8 \pm 7 \times 10^{-6}$	$-1.11 \pm 0.27 \times 10^{-2}$
$C\,{}^1\Sigma^+, v=5$[k]	{Perturber}	102328 ± 5	1.9	...	...
$3p\sigma\ C\,{}^1\Sigma^+, v=0$	{40}	91919.0719 ± 0.0020	1.943425 ± 0.000097	6.172×10^{-6} [m]	...
$3s\sigma\ B\,{}^1\Sigma^+, v=1$	{42}	88998.33 ± 0.03	1.921902[a]	7.4×10^{-6} [a]	...
$3s\sigma\ B\,{}^1\Sigma^+, v=0$	{43}	86916.1581 ± 0.0016	1.948173 ± 0.000028	$6.90 \pm 0.27 \times 10^{-6}$	...
$^{13}C^{16}O$:					
$^1\Pi, v=2$	{13}	107593.47 ± 0.03	1.850 ± 0.001	7×10^{-6} [a]	...
$3s\sigma\ W\,{}^1\Pi, v=2$[d,n]	{18}	106196.42 ± 0.06	1.5542 ± 0.002	$-1.4 \pm 1.0 \times 10^{-4}$	$-5.0 \pm 0.8 \times 10^{-3}$
$4p\pi\ L\,{}^1\Pi, v=0$	{25}	103248.85 ± 0.02	1.8922 ± 0.0002	$7.9 \pm 0.1 \times 10^{-5}$	...
$3d\pi\ L'\,{}^1\Pi, v=1$	{26}	103161.3 ± 0.1	1.69 ± 0.01	1.0×10^{-5} [a]	...
$K\,{}^1\Sigma^+, v=0$	{27}	103054.41 ± 0.03	1.8308 ± 0.0006	$1.02 \pm 0.02 \times 10^{-4}$	...
$3s\sigma\ W\,{}^1\Pi, v=0$	{28}	102775.77 ± 0.02	1.5019 ± 0.0003	$8.9 \pm 0.3 \times 10^{-5}$	$1.5 \pm 0.7 \times 10^{-3}$
$3s\sigma\ B\,{}^1\Sigma^+, v=0$	{43}	86916.8190 ± 0.0019	1.86274 ± 0.00044	6.2×10^{-6} [a]	...
$^{12}C^{18}O$:					
$3s\sigma\ B\,{}^1\Sigma^+, v=0$	{43}	86916.67127 ± 0.0019	1.85553[a]	6.2×10^{-6} [a]	...
$^{13}C^{18}O$:					
$4p\pi\ L\,{}^1\Pi, v=0$[o]	{25}	103262.45 ± 0.04	1.759 ± 0.001	1.0×10^{-5} [a]	...
$^1\Pi$[c]	{New}	103203.07 ± 0.03	1.7082 ± 0.0003	1.0×10^{-5} [l]	$-1.51 \pm 0.07 \times 10^{-2}$
$K\,{}^1\Sigma^+, v=0$[p]	{27}	103054.02 ± 0.04	1.7477 ± 0.0002	$1.43 \pm 0.03 \times 10^{-5}$	...
$^1\Pi$[p]	{Perturber}	103073.44 ± 0.15	1.507 ± 0.002	$2.3 \pm 0.2 \times 10^{-5}$	...
$3s\sigma\ W\,{}^1\Pi, v=0$	{28}	102743.26 ± 0.03	1.4313 ± 0.0006	$2.0 \pm 0.5 \times 10^{-5}$	$2.0 \pm 0.5 \times 10^{-3}$

NOTES.—Molecular constants for excited states of CO as obtained from least-squares fits. A spectroscopic assignment of the states as well as a numbering in braces is given following reference (Eidelsberg & Rostas 1990). All values are in cm^{-1}.

[a] These parameters were kept fixed in the minimization routines at the values of reference (Eidelsberg & Rostas 1990).

[b] A deperturbation analysis was performed under the assumption of a homogeneous as well as a heterogeneous perturbation, yielding interaction parameters for the two possibilities: $H_{\rm hom} = 3.03 \pm 0.07$ cm^{-1} and $H_{\rm het} = 0.35 \pm 0.01$ cm^{-1} and spectroscopic constants for the $^1\Pi$, $v = 2$ and the perturber state as given.

[c] This is a newly identified state.

[d] The negative value for the D constants is unphysical, and it indicates a perturbation of this state. The constants, however, represent the term energies.

[e] A local perturbation of the $\Pi_e(J = 8)$ state was observed.

[f] Local perturbations at $J = 8$, 12, and 22 in the form of anticrossings are observed. In the wavelength region of the band head of this band, narrow but weak lines were observed belonging to some yet unidentified band. For more detail see reference (Eikema et al. 1994b).

[g] The frequency of the $R(2)$ line of the $L\,{}^1\Pi$–$B\,{}^1\Sigma^+(0, 0)$ band was erroneously stated in reference (Drabbels et al. 1993b) and should read: 16367.745 cm^{-1}.

[h] The data of reference (Sekine, Iwata, & Hirose 1991) were included in the fit.

[i] Molecular constants valid up to $J = 16$. For $\Pi_e(J > 16)$ levels, an upward shift is found indicating a perturbation.

[j] Previously assigned as a $^3\Pi$ state (Eidelsberg & Rostas 1990). In the perturbation analysis of $W'\,{}^1\Pi$, $v = 2$ a heterogeneous perturbation is assumed with a parameter $H_{\rm het} = 1.2 \pm 0.1$ cm^{-1}.

[k] The assignment of this perturber state is tentative.

[l] This constant is kept fixed at an estimated value.

[m] Kept fixed at value from reference (Amiot, Roncin, & Verges 1986).

[n] The $P(9)$ line was observed as a doublet indicating a local perturbation of the $\Pi_e(8)$ state.

[o] Molecular constants valid for $J \leq 8$. For $J > 8$ a gradually increasing upward shift of energy levels was found amounting to 4.6 cm^{-1} at $J = 16$. This is an indication of a perturbation.

[p] Heterogeneous perturbation analysis with $H_{\rm het} = 1.018 \pm 0.003$ cm^{-1}. The perturber state is tentatively assigned as $E\,{}^1\Pi$, $v = 5$.

sonetti 1991). As the laser was frequency-doubled and used to excite a two-photon transition, this correction implies that the term values for the B and C state have to be increased by 0.008 cm^{-1} with respect to the values previously reported (Drabbels et al. 1993a). The lifetime of the $B\,^1\Sigma^+$, $v = 0$ state was determined from the observed fluorescence decay, whereas the lifetime of the $C\,^1\Sigma^+$, $v = 0$ state was derived from line broadening by fitting the observed line profile to a Voigt function. Higher lying Rydberg states were investigated through double-resonance fluorescence spectroscopy (Drabbels et al. 1993b). In a first step, a single rotational level of $B\,^1\Sigma^+$, $v = 0$ was populated by a pulsed laser, while in a second step the

TABLE 2

LIFETIMES AND PREDISSOCIATION RATES

State		τ (s)	k_0 (s^{-1})	k_J (s^{-1})
$^{12}C^{16}O$:				
$^1\Pi, v = 0^{a,b}$	{7A}	$>3 \times 10^{-11}$	$<3 \times 10^{10}$	...
$5p\sigma\ ^1\Sigma^+, v = 1^a$	{7B}	$1.2 \pm 0.3 \times 10^{-11}$	$8.7 \pm 2.5 \times 10^{10}$	...
$^1\Sigma^+, v = 2^a$	{7D}	$1.1 \pm 0.3 \times 10^{-11}$	$8.9 \pm 2.5 \times 10^{10}$	...
$6p\sigma\ ^1\Sigma^+, v = 0^{a,b}$	{8B}	$>3 \times 10^{-11}$	$<3 \times 10^{10}$	...
$^1\Pi, v = 2^{a,b}$	{9A}	$2.0 \pm 0.4 \times 10^{-12}$	$5 \pm 1 \times 10^{11}$	...
$^1\Pi, v = 2^c$	{13}	$2.9 \pm 1.3 \times 10^{-11}$	$3.5 \pm 1.5 \times 10^{10}$	...
$5p\pi\ ^1\Pi, v = 0\,(?)^a$	{15A}	$>3 \times 10^{-12}$	$<3 \times 10^{11}$	...
$5p\pi\ ^1\Pi, v = 0\,(?)^a$	{15B}	$3.7 \pm 0.5 \times 10^{-12}$	$2.7 \pm 0.4 \times 10^{11}$	...
$5p\sigma\ ^1\Sigma^+, v = 0^{b,d}$	{15C}	...	$3.4 \pm 2.0 \times 10^{10}$	$7.3 \pm 3.0 \times 10^{10}$
$^1\Sigma^{+a}$	{New}	$>3 \times 10^{-11}$	$<3 \times 10^{10}$	...
$3s\sigma\ W\ ^1\Pi, v = 2^e$	{18}	$8.3 \pm 0.8 \times 10^{-12}$	$1.21 \pm 0.10 \times 10^{11}$	...
$4d\sigma\ ^1\Sigma^+, v = 0^f$	{19}	$8 \pm 1 \times 10^{-12}$	$1.2 \pm 0.2 \times 10^{11}$	...
$4p\pi\ L\ ^1\Pi, v = 0^g$	{25}[h]	...	$1.3 \pm 0.2 \times 10^9$	$1.39 \pm 0.05 \times 10^9$
	{25}[i, j]	$5.5 \pm 0.4 \times 10^{-10}$	$1.83 \pm 0.13 \times 10^9$	...
$3d\pi\ L'\ ^1\Pi, v = 1$	{26}	$4.42 \pm 0.22 \times 10^{-12}$	$2.26 \pm 0.11 \times 10^{11}$	...
$4p\sigma\ K\ ^1\Sigma^+, v = 0^g$	{27}	$4.50 \pm 0.27 \times 10^{-11}$	$2.22 \pm 0.13 \times 10^{10}$	...
$3s\sigma\ W\ ^1\Pi, v = 0$	{28}[h]	...	$1.0 \pm 0.1 \times 10^{10}$	$2.1 \pm 0.1 \times 10^9$
	{28}[i]	$1.0 \pm 0.1 \times 10^{-10}$	$9.6 \pm 0.8 \times 10^9$	...
$W'\ ^1\Pi, v = 2$	{29}	$2.59 \pm 0.14 \times 10^{-12}$	$3.86 \pm 0.21 \times 10^{11}$	...
$C\ ^1\Sigma^+, v = 5^k$	{Perturber}	...	$2 \times 10^{10} < k_0 < 10^{12}$	...
$3p\sigma\ C\ ^1\Sigma^+, v = 0$	{40}	$4.8 \pm 1.2 \times 10^{-10}$	...	...
$3s\sigma\ B\ ^1\Sigma^+, v = 1$	{42}	$19.8 \pm 1.3 \times 10^{-9}$	...	...
$3s\sigma\ B\ ^1\Sigma^+, v = 0$	{43}	$29.8 \pm 1.2 \times 10^{-9}$	...	...
$^{13}C^{16}O$:				
$^1\Pi, v = 2^l$	{13}	$>3 \times 10^{-11}$	$<3 \times 10^{10}$	...
$3s\sigma\ W\ ^1\Pi, v = 2^m$	{18}	$1.3 \pm 0.3 \times 10^{-11}$	$7.5 \pm 1.5 \times 10^{10}$	...
$4p\pi\ L\ ^1\Pi, v = 0^n$	{25}[h]	$>3 \times 10^{-11}$	$<3 \times 10^{10}$	...
$3d\pi\ L'\ ^1\Pi, v = 1$	{26}	$3.7 \pm 1.3 \times 10^{-12}$	$2.7 \pm 0.9 \times 10^{11}$	...
$K\ ^1\Sigma^+, v = 0$	{27}	$>3 \times 10^{-11}$	$<3 \times 10^{10}$	...
$3s\sigma\ W\ ^1\Pi, v = 0$	{28}[h]	...	$<3 \times 10^{10}$	$1.3 \pm 0.2 \times 10^9$
	{25}[i]	$>3 \times 10^{-11}$	$<3 \times 10^{10}$	...
$3s\sigma\ B\ ^1\Sigma^+, v = 0$	{43}	$29.6 \pm 1.6 \times 10^{-9}$	...	...
$^{12}C^{18}O$:				
$3s\sigma\ B\ ^1\Sigma^+, v = 0$	{43}	$29.2 \pm 1.6 \times 10^{-9}$	...	...
$^{13}C^{18}O$:				
$4p\pi\ L\ ^1\Pi, v = 0$	{25}	$>3 \times 10^{-11}$	$<3 \times 10^{10}$	...
$^1\Pi$	{New}	$>3 \times 10^{-11}$	$<3 \times 10^{10}$	...
$K\ ^1\Sigma^+, v = 0^o$	{27}	$>3 \times 10^{-11}$	$<3 \times 10^{10}$	...
$3s\sigma\ W\ ^1\Pi, v = 0$	{28}	$>3 \times 10^{-11}$	$<3 \times 10^{10}$	...

NOTES.—Lifetimes τ and predissociation rates for a number of excited states of CO and its isotopes. In cases of a predissociation rate independent of J, a value for k_0 is given. When a linear proportionality is found, k_0 and k_J are given as obtained from a fit to eq. (3). In case of a parity-dependent rate in $^1\Pi$ states, separate values for Π_e and Π_f are given.

[a] No indication of a rotational dependent predissociation found.

[b] Only a few low-J rotational states observed.

[c] Only valid for $J \leq 3$. A sharp increase of predissociation rates for $J > 3$ is found with an accidental predissociation resonance at $J = 8$–9. For $J > 10$ again a decrease is found.

[d] The rotational state dependent predissociation is unambiguous and is confirmed by an analysis of line intensities.

[e] Valid for $J \leq 5$; $J > 5$ increasing predissociation rates observed. These results hold for both (e) and (f) parity components.

[f] Valid for $J \leq 5$. Strong accidental predissociations are found at $J = 8$, 12, and 22.

[g] Proven to be valid up to $J = 20$.

[h] Refers to the (e) Λ-doublet component.

[i] Refers to the (f) Λ-doublet component.

[j] Accidental predissociation of the $\Pi_f(J = 7)$ level observed.

[k] Estimated limits on the predissociation rates from the deperturbation analysis.

[l] Valid only for $J \leq 4$. From $J = 5$–10 a monotonic increase in predissociation rate is found up to 10^{11} s^{-1}.

[m] Valid for $J \leq 4$. For $J > 6$ an increase is found up to 5×10^{11} s^{-1}.

[n] Valid up to $J = 13$ only for (e) components. The (f) components, observed in the Q-branch, were not resolved.

[o] Valid only for $J \leq 5$; for $J > 5$ a strong accidental predissociation is found.

Rydberg states were probed by fluorescence-dip spectroscopy employing the narrowband PDA laser. By calibrating the frequency of this laser to the I_2-absorption spectrum, the energy levels were determined within 0.006 cm^{-1}. The previously reported transition frequencies of the Rydberg states are also corrected for the calibration shift of the Te_2 lines. The lifetimes of the individual rotational levels of the Rydberg states were derived from observed line-broadening effects. The bandwidth of the PDA system allows for the determination of lifetime broadening effects ranging from 0.003 cm^{-1} up to 5 cm^{-1}. This corresponds to lifetimes of 10^{-9} to 10^{-12} s.

Transition frequencies from the Amsterdam and Nijmegen experiments were accumulated and reevaluated in least-squares minimization routines, in which the data were combined to derive accurate molecular constants for the excited states of CO. Ground state energies were derived from accurate constants in the literature (Guelachvili et al. 1983). For $^1\Pi$ states the energies of (e) and (f) Λ-doublet components, observable in P or R and Q transitions respectively, are represented by

$$E_{\Pi_e}(J) = \nu_0 + BJ(J+1) - DJ^2(J+1)^2 + qJ(J+1)\,, \quad (1)$$

$$E_{\Pi_f}(J) = \nu_0 + BJ(J+1) - DJ^2(J+1)^2\,. \quad (2)$$

In the previous papers of the Nijmegen group, separate B_e and B_f constants were used that relate to the present definition as $B_f = B$ and $B_e = B + q$. Equation (2) is also used for a $^1\Sigma^+$ state. The molecular constants for the excited states as obtained from the fits are listed in Table 1. All necessary calibration corrections are included in these values. In several bands, accidentally perturbed lines are observed. These lines, mentioned in Table 1, were left out of the fits. In a few bands, where a perturbation of the rotational structure was observed, a deperturbation treatment was performed. A perturber state was postulated, and both a homogeneous perturbation with a constant off-diagonal matrix element H_{hom} and a heterogeneous coupling with a J-dependent off-diagonal matrix element were considered. For perturbations between $^1\Sigma^+$ and $^1\Pi$ states the matrix element were considered. For perturbations between $^1\Sigma^+$ and $^1\Pi$ states the matrix element is of the form $H_{\mathrm{het}}\sqrt{J(J+1)}$, while for interactions between $^1\Pi$ and $^1\Delta$ states, the matrix element is $H_{\mathrm{het}}\sqrt{J(J+1)-2}$.

Information on predissociation rates from both experiments is accumulated in Table 2. The recalibration of the EUV laser bandwidth at the short wavelength side 90–93 nm (Ubachs et al. 1993) is accounted for, and this results in small differences with previously published values. When the predissociation rate of a certain vibronic state is found to be independent of J, an average value is listed. In some cases, a linear dependence of the predissociation rate k_p with $J(J+1)$ is found (J being the angular momentum quantum number), and the results are fitted to a relation:

$$k_p(J) = k_0 + k_J J(J+1)\,. \quad (3)$$

In all the cases were a predissociation rate is specified, it is assumed that k_p is inversely proportional to the excited state lifetime and that the influence of the radiative channel is negligibly small. For the $B\,^1\Sigma^+$ and $C\,^1\Sigma^+$ states, which have much longer lifetimes, this assumption is not valid. For these states, the listed lifetimes are predominantly radiative. For the $^{13}C^{18}O$ isotope, no line broadening effects were discernable and only upper limits for the predissociation rates are given.

Highly accurate values for transition frequencies and rotationally dependent predissociation rates for a large number of excited states of CO and its isotopes are presented. For several bands the presently tabulated values slightly deviate from previously reported values. This is partly due to the wavelength and bandwidth recalibrations but also to the reanalysis based on the combined set of data obtained by the two groups. The information is not complete, in the sense that only a limited number of valence and Rydberg states in the astrophysically important wavelength range 90–115 nm have been investigated. Nevertheless, the collected data should be useful for the modeling of the radiative transfer and chemistry in the interstellar medium.

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