Lifetime measurements of the $E(1)\Pi$, $\upsilon=0$ and $\upsilon=1$ states of (CO)-C-12-O-16, (CO)-C-13-O-16, and (CO)-C-13-O-18

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LIFETIME MEASUREMENTS OF THE $E^\prime \Pi$, $v = 0$ AND $v = 1$ STATES OF $^{12}$C$^{16}$O, $^{13}$C$^{16}$O, AND $^{13}$C$^{18}$O

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ABSTRACT

In a laboratory investigation using tunable picosecond lasers in a pump-probe configuration, lifetimes of the $E^\prime \Pi$, $v = 0$ and $v = 1$ states of CO are experimentally determined. For $E^\prime \Pi$, $v = 1$, the lifetime is found to vary significantly for the isotopomers. Combining the data with existing oscillator strengths, predissociation probabilities within the range of 93.6%–98.6% result for $^{12}$C$^{16}$O, $^{13}$C$^{16}$O, and $^{13}$C$^{18}$O in the case of the $E^\prime \Pi$, $v = 1$ state, which is the state that predominantly influences the isotopic fractionation of CO in interstellar clouds.

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

1. INTRODUCTION

Carbon monoxide, the second most abundant molecule in the galaxy and the prototypical molecule for radio-astronomical studies, is a key ingredient in the chemistry of the interstellar medium. In the last decade, the photochemistry of CO and its isotopomers in diffuse and translucent clouds, as well as in photodissociation regions, has been clarified, to some extent, through modeling on the one hand (van Dishoeck & Black 1988; Viala et al. 1988) and laboratory experiments on the other. A number of spectroscopic overview studies (Letzelter et al. 1987; Edelsberg & Rostas 1990; Stark et al. 1991) in the wavelength range 91.2–110 nm, of interest for the photo-dissociation of CO in the interstellar medium, has yielded the general result that predissociation rather than continuum absorption is the main destruction mechanism for interstellar CO. The fact that predissociation, i.e., dissociation through bound states that are coupled to continuum states, is by its nature strongly wavelength dependent makes the photodissociation of CO a complicated problem. The richness of mutually interacting Rydberg and valence states is an additional complicating factor, particularly because the couplings appear to be strongly isotope dependent (Rostas et al. 1994). Following the first overview studies by classical and synchrotron techniques, narrow-band lasers are being used to unravel spectral features and predissociation phenomena in finer detail (Levett, Ubachs, & Hogervorst 1992; Eikema, Hogervorst, & Ubachs 1994; Drabbels et al. 1993; Komatsu et al. 1995; Ubachs et al. 1997). The progress via laser-based measurements has led to revised listings of spectral constants and predissociation rates (Ubachs et al. 1994; Morton & Noreau 1994).

In the advanced model of van Dishoeck & Black (1988), the effects of line broadening associated with predissociation, self-shielding of CO lines, shielding by atomic and molecular hydrogen lines, and isotope-selective shielding are examined extensively as a function of the depth in interstellar clouds. These photoinduced phenomena, as well as ion-molecule exchange reactions at low temperatures, result in strong isotope-dependent effects on the photodissociation rates. Thus, in the interior of interstellar clouds, larger effective photodissociation rates are found for the less abundant, heavier isotopomers. In particular, the excitation of the $E^\prime \Pi$ state at 107.61 nm for $v = 0$ and 105.17 nm for $v = 1$ seems to be of paramount importance, since these transitions have large oscillator strengths that coincide with a relatively high intensity of the interstellar radiation field. The predissociation probability of the $E^\prime \Pi$, $v = 1$ state is identified as the decisive parameter governing isotope selectivity in predissociation. In their conclusion, van Dishoeck & Black (1988) propose an independent measurement of the predissociation probabilities of the $E$–$X$ (0, 0) and (1, 0) bands to further validate their model.

Here we report on direct time-domain measurements of the lifetimes of the $E^\prime \Pi$, $v = 0$ and $v = 1$ states for the $^{12}$C$^{16}$O, $^{13}$C$^{16}$O, and $^{13}$C$^{18}$O isotopomers. The harmonic radiation generated by the picosecond laser of the Lund Laser Centre, previously used for lifetime measurements of He (Larsson et al. 1995), is used in a pump-probe configuration to detect time-delayed photoionization. The vacuum ultraviolet (VUV) radiation is tuned to resonance with the $E$–$X$ (0, 0) or (1, 0) band, while the second laser, at 355 nm and at a variable delay, induces photoionization. Resulting CO$^+$ ions are accelerated in a DC-electric field, mass-selected in a time-of-flight drift tube, and detected by an electron multiplier. The signal is registered on and read from a digital storage oscilloscope. The data on $^{12}$C$^{16}$O were obtained from CO gas in natural abundance. The $^{13}$C$^{16}$O and $^{13}$C$^{18}$O data are obtained from a 99% $^{13}$C-enriched sample of CO in which an amount of approximately 20% $^{13}$C$^{18}$O is found. Since the bands for the isotopomers overlap, the isotope selectivity of the time of flight is required for distinction between $^{13}$C$^{16}$O and $^{13}$C$^{18}$O signals.

2. EXPERIMENTAL METHOD AND RESULTS

A distributed-feedback dye laser (DFDL), tunable in the near-infrared, is pumped by the 532 nm output of an amplified mode-locked Nd-YAG laser, running at a 10 Hz repetition rate. The low-energy pulses of the DDFL are amplified in a titanium-sapphire crystal, which is pumped by a Q-switched Nd-YAG laser. The duration of the resulting infrared pulses is 50–70 ps, and via generation of the seventh harmonic in a pulsed jet of Xe atoms, a VUV pulse is produced with an estimated duration of 30 ps. The UV probe pulse at 355 nm is the third harmonic output of the same Nd-YAG laser, used to pump the dye laser. Its pulse duration was measured with a streak camera to be 60
the opening of the valve that delivers the molecular jet. From spectral analyses, it follows that the rotational distribution is colder earlier in the gas pulse. No dependence of the obtained lifetime on pressure, UV intensity, or rotational temperature is found, for either the (e) or the (f) parity state in E''II, v = 0; these states were independently probed by setting the laser on the Q- or P/R-branch. In Table 1, the resulting values for the lifetimes are listed with an estimated error. Although the error margins on the lifetimes for the 13C isotopomers are substantial, we find a definite indication of longer lifetimes for the 13C containing isotopomers.

In Figure 2, a pump-probe decay curve for the E''II, v = 1 state of 13C16O is presented with the UV radiation tuned to the Q-branch. Here the data show a much faster decay than in the case of v = 0. In view of the shorter lifetime and the weaker transition strength, both collisional effects and possible radiative trapping phenomena are less important. The systematic issue to address for the case of v = 1 is the deconvolution of the 80 ps instrument width. From a variation of the convolution parameter, it is found that indeed the estimated 80 ps leads to a minimum standard deviation in the fitting routine. The lifetimes obtained are listed in Table 1. In case of the E''II, v = 1 state, the lifetime of the main 12C16O isotopomer is found to be significantly shorter than that of 13C16O and 13C12O.

TABLE 1

<table>
<thead>
<tr>
<th>E''II</th>
<th>12C16O</th>
<th>13C16O</th>
<th>13C12O</th>
</tr>
</thead>
<tbody>
<tr>
<td>v = 0</td>
<td>912 ± 60</td>
<td>1350 ± 200</td>
<td>1250 ± 200</td>
</tr>
<tr>
<td>v = 1</td>
<td>118 ± 20</td>
<td>198 ± 25</td>
<td>270 ± 45</td>
</tr>
</tbody>
</table>

*For the E''II, v = 0 and v = 1 states of CO isotopomers.

3. DISCUSSION

Hitherto, only one lifetime measurement has been reported on the E''II state, the one on the v = 0 level by Smith (1978), which yields a value of \( \tau_0 = 1.5 \pm 0.2 \text{ ns} \), slightly higher than the present value. Eidelberg & Rostas (1990) give some rather crude estimates, based on fluorescence yield measurements. However, their results of \( 10^{-8} \text{ s} \) for E''II, v = 0 and \( 10^{-10} \text{ s} \)
for $E^1\Pi$, $v = 1$ closely match the present dedicated measurements.

An astrophysically important property is the competition between radiative and dissociative decay on excitation. The predissociation probabilities can be derived from the combined results of the present measurements and previously obtained oscillator strengths for the $E-X$ system. Following Morton & Noreau (1994), the oscillator strength $f_{\nu'\nu}$ is related to a decay rate $A_{\nu'\nu}$ via

$$
\frac{1}{2} f_{\nu'\nu} = \left( 4\pi\varepsilon_0 \frac{m_e c}{8\pi^2\varepsilon^2} \right) \chi_{\nu'\nu}^2 A_{\nu'\nu},
$$

where the factor of $\frac{1}{2}$ represents the twofold $\Delta$-doublet degeneracy of the upper state $E^1\Pi$. For clarity, we note that in this case, $f_{\nu'\nu}$ represents the total oscillator strength integrated over the $P_\nu$, $Q_\nu$, and $R_\nu$-branches of a $E-X (v', v)$ band. The value of the constant in parentheses can be evaluated to 1.4992 $\times 10^4$ m$^{-2}$ s. In the literature, a variety of oscillator strengths have been published. For the $E-X (0, 0)$ band, $f_{00}$ values range from 0.0365 (Eidelsberg & Rostas 1990) to 0.071 obtained in two independent electron-scattering experiments (Chan, Cooper, & Brion 1993; Ciocca, Kanik, & Ajello 1997). An intermediate value of 0.049 by Stark et al. (1992), obtained from high-resolution synchrotron radiation absorption, coincides with a value from ab initio calculations (Kirby & Cooper 1989). Since the purely radiative lifetime $\tau_0$ of the upper level $E^1\Pi$, $v = 0$ corresponds to a summation of partial decay rates,

$$
\frac{1}{\tau_0} = \sum_{\nu'\nu} f_{\nu'\nu} = \sum_{\nu'\nu} A_{\nu'\nu} = \sum_{\nu'\nu} A_{\nu'\nu} + \sum_{\nu'\nu} A_{\nu'\nu},
$$

an assumption has to be made on the decay in vibrational levels of the electronic ground state other than $X^1\Sigma^+$, $v' = 0$. For the absorptive transition originating in $v'' = 0$, it is found that 94% of the oscillator strength is in the $0, 0$ (0, 0) band (Eidelsberg & Rostas 1990; Kirby & Cooper 1989; Stark et al. 1992), and by applying sum rules, the same follows for the emission. The radiative decay into the $A^1\Pi$ and $B^1\Sigma^+$ electronic states, amounting to 8% (Kirby & Cooper 1989), should be included. This leads to a total rate $A_0$, which is 1.16 times the partial rate $A_{00}$. The predissociation probability $\eta$ then follows:

$$
\eta_{\text{pre}} = 1 - A_0 \tau,
$$

where $\tau$ is the true lifetime of the upper state, as measured in the present study. Using a number of published $f_{00}$ values, and deriving $A_0$ from these, the predissociation probabilities can be calculated. The results are listed in Table 2. For the $E^1\Pi$, $v = 1$ level, the same value for $A_0$ can be used, i.e., $A_1 = A_{10}$, since the total radiative decay of a vibrational series is constant to a very good approximation.

The value for the predissociation probability of the $E^1\Pi$, $v = 0$ state is found to vary in the range 69%–89%. Since the uncertainty in the lifetime measurements is a minor part of the uncertainty in $\eta$, we have not quoted errors in Table 2. Improved values for predissociation probabilities await the determination of more accurate, i.e., more reliable, oscillator strengths. In a recent study by Ciocca et al. (1997), direct electron-impact–induced emission from the $E^1\Pi$, $v = 0$ state was observed at high resolution. A higher fluorescence cross section for the $Q$-branch indicates a lower predissociation probability on the $E^1\Pi$–($f$) parity components. In the present study, this parity dependence is not found. For this purpose, a lifetime measurement was performed with the laser set on the $P$-branch, at a wavelength position where, even in view of the large bandwidth of the UV laser, no signal is obtained from the blue-degraded $Q$-branch in the (0, 0) band.

An interesting conclusion from a molecular physics point of view is that the lifetime of the $E^1\Pi$, $v = 1$ state is strongly dependent on the specific isotopomer. The reason for this effect is not yet clear. In two studies (Baker et al. 1993; Cacciari, Hogervorst, & Ubachs 1995), it was determined that a $k^1\Pi$ state causes an accidental predissociation near $J = 9$ for $^{13}C^1O$ and at a different $J$-value for the other isotopomers. Most likely, there is also an additional effect due to a coupling with a repulsive continuum that causes the predissociation. From an astrophysics viewpoint, these isotope-dependent effects are not decisive since it is firmly established in the present study that for the $E^1\Pi$, $v = 1$ state, for all isotopomers and for all oscillator strengths existing in the literature, the predissociation probability remains in the range 93.6%–98.6%, even when the large spread in published oscillator strengths is considered. In fact, the major assumption of van Dishoeck & Black (1988) that the predissociation does not significantly deviate from 100% is validated in the present experimental study.

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