



6 May 1994

**CHEMICAL
PHYSICS
LETTERS**

Chemical Physics Letters 222 (1994) 161–166

Dispersed fluorescence from CO($B^1\Sigma^+$) excitation in He and Ar

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Received 3 December 1993; in final form 10 February 1994

Abstract

Two striking effects were observed between 158 and 175 nm in the dispersed laser-induced fluorescence spectrum resulting from excitation of CO($B^1\Sigma^+$). In the presence of Ar the intensity of the CO($X^1\Sigma^+$, $v' \leftarrow A^1\Pi$, $v' = 0$) progression was doubled. Also, an unresolved emission appeared over the entire spectrum. The former is attributed to a CO–Ar complex that undergoes an electronically non-adiabatic transition. Since collisionally induced intersystem crossing can account for only a fraction of the broadband emission, we speculate that most of this feature originates from a metastable triatomic complex.

1. Introduction

Electronically excited molecules may relax by a variety of mechanisms. The isolated molecule may emit a photon or undergo a radiationless transition to another potential energy surface. Both of these processes may be enhanced by collisions with an inert partner. The relative importance of these relaxation mechanisms is a sensitive function of the intra- and inter-molecular potential energy surfaces.

A case in point is the $B^1\Sigma^+$ Rydberg state of CO. In the absence of collisions the only relaxation mechanism is fluorescence, with 88% [1,2] of the molecules undergoing a vacuum UV transition to the $X^1\Sigma^+$ ground electronic state ($\nu_{00} = 86916 \text{ cm}^{-1}$ [3]) and 12% of the molecules undergoing a visible transition to the $A^1\Pi$ valence state ($\nu_{00} = 22171 \text{ cm}^{-1}$). Because of the larger internuclear distance of the valence state, the A–B emission spectrum dis-

plays a vibrational progression. Molecules in the A state in turn undergo a UV transition to the ground state ($\nu_{00} = 64748 \text{ cm}^{-1}$), with each of the upper vibrational levels producing its own vibrational progression.

In the presence of a bath gas a variety of radiationless processes can also occur. In an unpublished study Huang and Gordon [1] measured the quenching rates of CO($B^1\Sigma^+$) by eleven gas-phase collision partners. For some (e.g. Kr and Xe) it was found that the quenching cross section was gas kinetic, while for others (e.g. He, Ne, and Ar) it was too small to detect, in qualitative agreement with the earlier work of Comes and Fink [4]. The large quenching cross sections of Kr and Xe are readily understood, since these atoms have low-lying states which can accept energy from CO(B), with the energy defect going into translational motion. To gain more insight into the quenching mechanism, the fluorescence was passed through a filter which completely blocked all B–X emission (i.e. the resonant fluorescence) while transmitting the A–X fluorescence. The effect of the filter on the fluorescence was predictable for all of the quenching gases except for Ar. With the filter in place,

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Ar was the only gas to have the anomalous effect of *increasing* the non-resonant fluorescence [1].

This anomaly shows that collisions with Ar cause some of the CO(B) population to be transferred to some other state or states which fluoresce at wavelengths detected by our apparatus. The source of this fluorescence cannot be the bath gas since the lowest excited state of Ar is too high to accept energy from CO(B). One possible mechanism is a collisionally induced non-adiabatic transition to a different fluorescing state of CO. A second possibility is that some of the enhanced fluorescence originates from a metastable CO(B)–Ar complex. It is possible to distinguish between these mechanisms by dispersing the fluorescence. The present Letter is a preliminary report of such a study.

2. Experimental

A detailed description of the experimental method will be presented in a later publication. A cubical cell was filled with 3 Torr of a 1:1000 CO/He mixture, to which various pressures of Ar were added statically. The gases (CO, Linde, 99%; He, AGA 99.995%; Ar, Matheson, 99.995%) were used directly without further purification. The $J' = 9$ or $J' = 16$ levels of the B state of CO ($v' = 0$) were populated by irradiating the mixture with a laser tuned to 114.957 and 114.921 nm, respectively. This radiation was produced by generating 345 nm with a tunable dye laser, followed by frequency tripling in a Xe/Ar mixture optimized for 115 nm.

The fluorescence was observed from two ports along axes mutually perpendicular to the laser beam. The undispersed fluorescence from one of the windows was detected with a solar-blind photomultiplier tube (EMR 541G-08-17). A CaF₂ window (which has a cutoff at 125 nm), set between the cell and the PMT, allowed measurement of the emission in the region of the A–X band without interference from the B–X band. The second observation port was sealed with a 7.5 cm MgF₂ focal length lens, which focused the fluorescence onto the aperture of a one meter vacuum UV monochromator. The dispersed fluorescence was detected with a second solar-blind PMT (EMR 541G-09-17-03900).

3. Results and discussion

Fig. 1 shows the undispersed fluorescence as a function of added Ar pressure. The signal grows monotonically, and at 15 Torr it reaches a plateau of ≈ 2.5 times the zero pressure value.

The dispersed fluorescence spectra obtained with 3 Torr of the He/CO mixture, and 0 or 15 Torr of added Ar, are shown in Figs. 2 and 3, respectively. Because of the very low collection rate of photons it was necessary to combine many scans to achieve an acceptable signal/noise ratio. The spectra in Figs. 2 and 3 are the sums of twenty scans, each taking ≈ 1 h. The apparent noise in these spectra is the response of the PMT to individual photons, and is an indication that these spectra have not yet reached the limit of statistical photon counting.

The fluorescence peaks from CO without Ar (Fig. 2) correspond to vibronic progressions originating from CO(A, $v' = 0-5$). The intensities of the bands are well modeled assuming population transfer through the B–A fluorescence and no vibrational relaxation within the A state. The emission band intensity (defined as the number of photons emitted per second) is given by [5]

$$S_{v'v''} = \frac{64}{3} \pi N_{v'} \nu^3 \langle R_e^2 \rangle q_{v'v''} / h, \quad (1)$$

where h is Planck's constant, $N_{v'}$ is the population of the upper level, ν is the frequency of the emitted photon, R_e is the transition moment, and $q_{v'v''}$ is the Franck–Condon factor. In the present case the A state is populated by the B $^1\Sigma^+$, $v = 0 \rightarrow A$ $^1\Pi$, v' transition

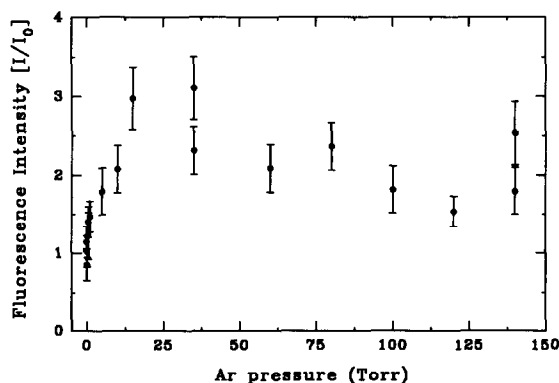


Fig. 1. Pressure dependence of the undispersed fluorescence, for a fixed pressure of 3.0 Torr of a 1000:1 He/CO mixture. Error bars are a single standard deviation.

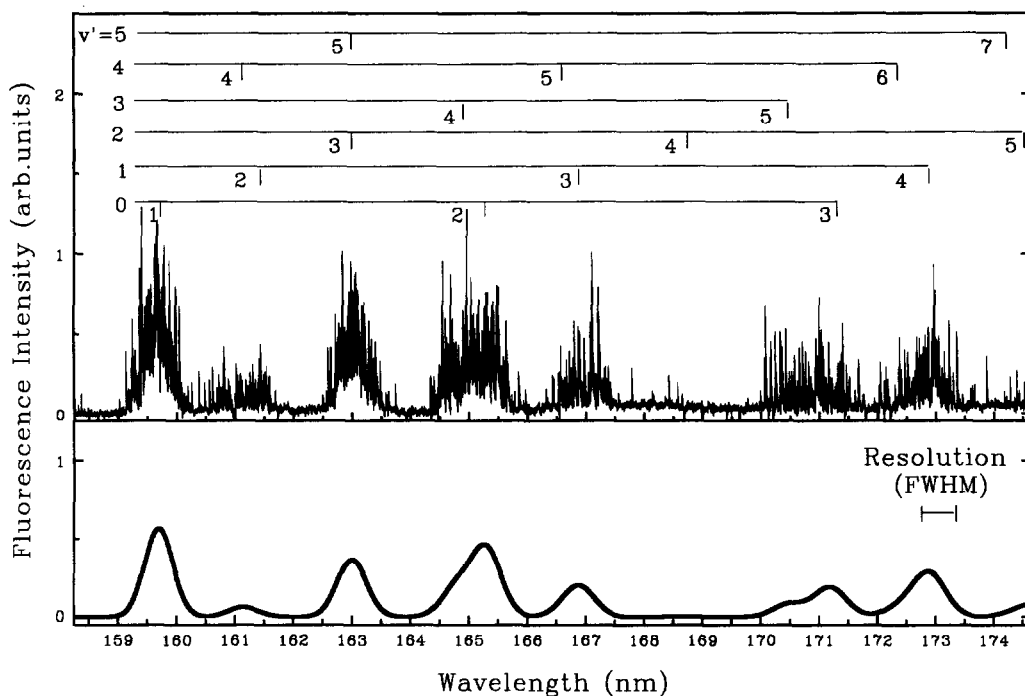


Fig. 2. Dispersed fluorescence spectrum of CO in the absence of Ar. Upper panel: experimental data, consisting of the sum of 20 individual scans, for 3.0 Torr of a 1000:1 He/CO mixture. Vibrational progressions originating in CO(A $^1\Pi$, $v'=0-5$) are indicated. Lower panel: simulation, using spectroscopic constants for the A-X band and the instrument response function. The resolution of the monochromator is indicated.

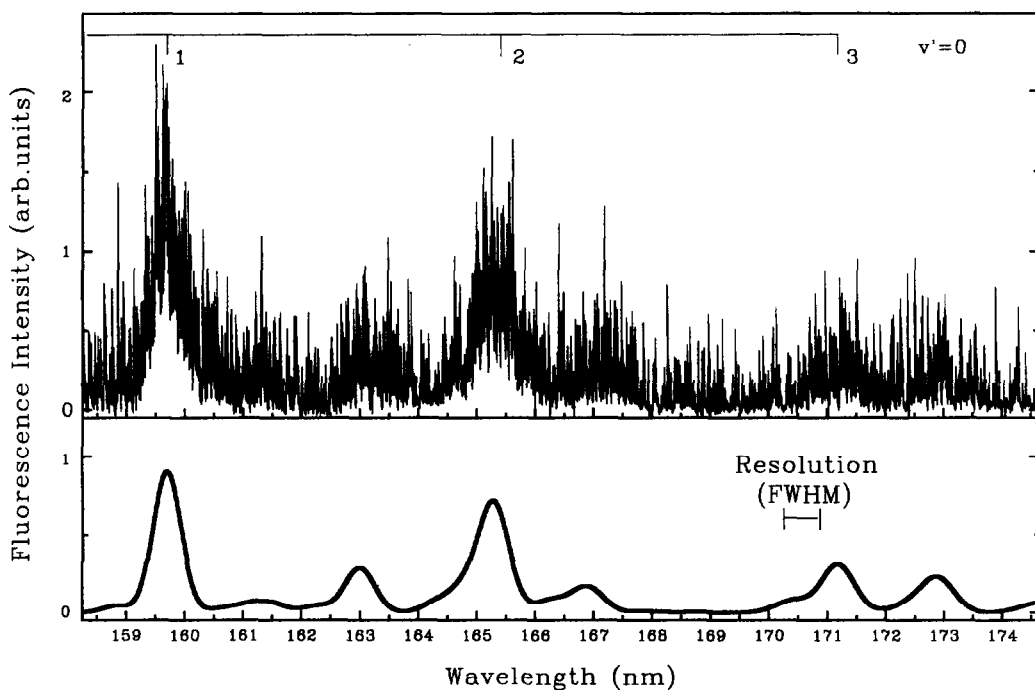


Fig. 3. Same as Fig. 2, only in the presence of 15 Torr of added Ar. Only the $v'=0$ progression is indicated in the upper panel. The simulation in the lower panel includes also emission from the $e^3\Sigma^-$, $d^3\Delta$, $a^3\Sigma^+$ states, as explained in the text.

at frequency ν' , and the detected photon is generated by the secondary $A^1\Pi, \nu' \rightarrow X^1\Sigma^+, \nu''$ transition at frequency ν'' . Under our experimental conditions the vibrational bands have the same shape as the experimentally measured monochromator slit function (0.5 nm fwhm), which is too wide to resolve the rotational structure. The detected signal is given by

$$S(\nu)_{A \rightarrow X} \propto P(\nu) \sum_{\nu', \nu''} q_{\nu\nu'} q_{\nu'\nu''} R(\nu - \nu'') \nu'^3 \nu''^3. \quad (2)$$

In Eq. (2) $P(\nu)$ is the frequency response of the PMT provided by the manufacturer, $R(\nu - \nu'')$ is the slit function, and the Franck–Condon factors were calculated using known spectroscopic constants [3]. The simulated spectrum is shown in the lower panel of Fig. 2.

In the presence of Ar the spectrum (Fig. 3) changes in two striking ways. First, the vibrational peaks originating from CO(A, $\nu' = 0$) are doubled in intensity. This increase in the A–X emission amounts to one third of the total enhancement observed in the undispersed pressure scan (Fig. 1). Since the progressions corresponding to $\nu' > 0$ do not decrease in intensity, the increase in $\nu' = 0$ cannot be caused by vibrational relaxation. Second, there is a broad emission over the entire spectrum ('grass') which is featureless within our 0.5 nm resolution. The grass is especially evident at 167.7–169.7 nm and 158.25–159.0 nm, where the baseline in the bare CO spectrum is flat. If the Ar is replaced by an equal amount of He (i.e. at a He pressure of 18 Torr) there is no enhancement of the non-resonant fluorescence and there is no evidence of grass.

The growth of the vibrational peaks in the presence of Ar can be explained by a non-adiabatic transition from a Rydberg to a valence potential energy surface. The essential elements of this mechanism are shown schematically in Fig. 4. In the absence of Ar, the only decay route for CO(B) is fluorescence to either the ground state or to the A state. When Ar is present, long-range attractive forces may produce a deep well in the CO(B)–Ar surface, allowing it to interact with the CO(A)–Ar surface. If we assume that the CO(B)–Ar and CO(A)–Ar surfaces intersect, then some fraction of the CO(B, $\nu' = 0$) population may end up in the CO(A, $\nu' = 0$) state, following an electronically non-adiabatic, vibrationally adiabatic transition.

What is unique about Ar as a collision partner, and

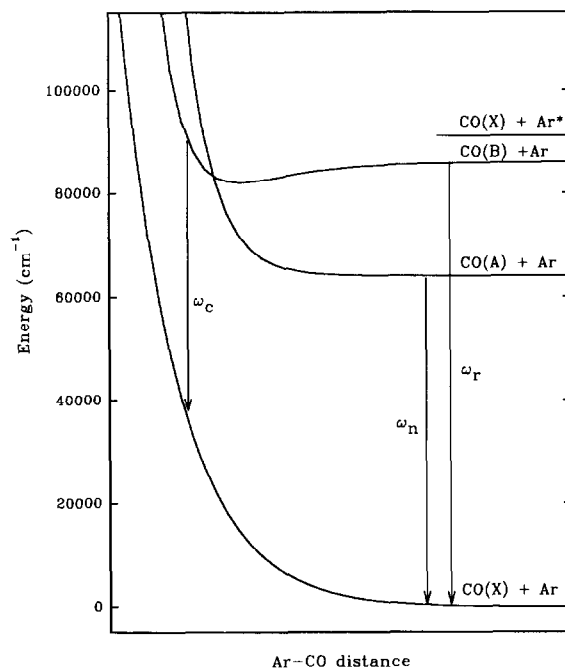


Fig. 4. Simplified model showing one-dimensional cuts of hypothetical potential energy surfaces. The arrows indicate discrete resonant (ω_r) and non-resonant (ω_n) fluorescence from the isolated CO molecule, as well as continuous 'grass' (ω_c) from the complex.

why should the CO(B) + Ar potential be especially attractive? Consider the other rare-gas atoms. The first excited states of He and Ne lie many eV above CO(B) and barely interact with it. In contrast, the corresponding states of Kr and Xe lie below CO(B $^1\Sigma^+$), and there are numerous states which may remove energy from CO. Ar is unique in that while its lowest accessible state is too energetic to accept energy from CO, it lies only $\approx 6500 \text{ cm}^{-1}$ above CO(B $^1\Sigma^+$, $\nu' = 0$), and the two states may be strongly mixed. B $^1\Sigma^+$ is the lowest Rydberg state of CO, having a ($^2\Sigma^+$) $3s\sigma$ configuration with the charge localized on the carbon atom. To a very crude approximation CO(B) + Ar may be compared with CO⁺ + Ar. In the latter case, CO⁺ + Ar and CO + Ar⁺ interact strongly [6]. The potential energy surfaces are anisotropic, with CO⁺ + Ar having a well depth of $\approx 0.5 \text{ eV}$ for a T-shaped configuration with $\Omega = \frac{1}{2}$.

What is the origin of the 'grass' in Fig. 3? The broadband emission disappears entirely in the absence of either CO or Ar, showing that both gases must

be present. During the fluorescence lifetime of CO(B) the number of collisions between each CO molecule and all Ar impurities is $<2 \times 10^{-4}$, ruling out the possibility that the grass comes from fluorescence of impurities in Ar. Rayleigh scattering is also ruled out as a possible mechanism. Two remaining possibilities are (i) emission from some other electronically excited state of CO, and (ii) emission from a triatomic species.

There are three triplet states which perturb CO(A $^1\Pi$) ($e^3\Sigma^-$, $d^3\Delta$, and $a'^3\Sigma^+$, designated collectively as CO(T)) [7]. Collision-induced intersystem crossing (CIISC) to these states is a highly efficient process for CO [8]. It is quite likely that energy is transferred to and from perturbing triplet states, and radiation from the many different triplet states would appear to be continuous.

In fact we have strong evidence that CIISC does occur. Although there was insufficient signal to measure the lifetime of the dispersed fluorescence, the undispersed fluorescence displays a decay time of 100–150 ns following the initial rapid decay of the singlet states. The rotationally averaged radiative lifetimes of different vibrational levels CO(A) are ≈ 10 ns [9], while the corresponding lifetimes of the CO(T) are several microseconds [10]. Near a perturbation, however, intensity and lifetime borrowing both occur, and the lifetimes of the triplet states fall to tens of nanosecond for specific rotational levels [10]. Our observed lifetime could result from reversible energy transfer between the singlet and triplet 'doorway states'. While most of the emission comes from CO(A), the triplets act as a reservoir which increases the emission lifetime, which is a strong indication of intersystem crossing.

While triplet to ground state emission (T–X) is a likely cause of some of the grass, it cannot explain all of it. The triplet states are populated by intersystem crossing that is caused by perturbations of the A state. The populations of individual vibronic levels could be calculated by solving the master equation if the full rate constant matrix were known. Since not all the rate constants are known, we made the simplifying approximation that the perturbed triplet states are equally populated with a branching fraction f . The observed spectrum is then given by

$$S_{\text{obs}}(\nu) = (1-f)S(\nu)_{\text{A}\rightarrow\text{X}} + fS(\nu)_{\text{T}\rightarrow\text{X}}. \quad (3)$$

The maximum value f could have from detailed balancing is 0.75 [11]. Even in this extreme case there is no predicted emission between 167.7 and 169.7 nm, contrary to observation. From our simulated spectra we know that f must be smaller than the statistical limit. For f as large as 0.4 some of the triplet \rightarrow singlet emission would appear as discrete peaks which we do not observe. A kinetic model which reproduces the singlet emission and fits the pressure dependence of the total signal gives a value of $f=0.2$. The simulated spectrum using this value is shown in Fig. 3b. In this calculation we assumed that the intensity of the $\nu'=0$ progression of the A–X band was double in the presence of Ar to correspond with our experimental observation. We conclude from our simulations that triplet emission accounts for only a small part of the grass.

Since emission from the triplets (or any other state of CO) cannot account for all of the grass, at least part of it must be due to emission from a different species. An intriguing possibility is that the grass is emission from a metastable COAr* complex. The 22 ns [12] lifetime of CO(B) provides a natural 'clock' for forming a triatomic complex. At low Ar pressure the probability of forming such a complex increases linearly with pressure. The leveling off of the enhanced fluorescence at 15 Torr in Fig. 2 is consistent with every CO(B) undergoing a collision with a bath atom with a capture cross section of 15 \AA^2 . The internal clock of the complex assures that the triatomic species is not stabilized by a second collision before redissociating^{#1}. Any emission from the triatomic must therefore be from a metastable species. We estimate from the spectrum that one third of the dispersed fluorescence comes from this species. We further calculate that this fraction corresponds to 10% of all the metastable complexes formed. While the fluorescence lifetime of the complex is unknown, a value ten times the dissociative lifetime is not unreasonable.

Continuous emission from a highly excited triatomic of comparable mass has been observed before [13]. What makes our present observations especially interesting is the possibility that for CO(B) + Ar

^{#1} A simple RRK calculation for a well depth of 4000 cm^{-1} and a dissociation frequency of 100 cm^{-1} gives an upper estimate for the dissociation lifetime of 130 ps.

the emission may be from a *metastable* complex. Additional experiments are planned to confirm this interpretation of the data. We have not as yet measured the spectrum outside of the region of the A–X emission, and it is possible that we underestimated the contribution of the grass to the total increase in fluorescence. On the other hand, our assumption that the broadband emission is uniform over the entire spectrum may overestimate its contribution. A higher resolution spectrum capable of revealing structure in the grass would be especially informative.

The present data are the first indication that a CO($B^1\Sigma^+$)–Ar van der Waals complex could be formed, if the pressure were high enough for stabilizing collisions to occur. A complex between CO(X) and Ar has been observed [14], but attempts to produce CO(B)–Ar by irradiation of the ground state complex at 115 nm were unsuccessful [15]. If the CO($B^1\Sigma^+$) + Ar surface is strongly anisotropic, and/or if the well is located at a small CO–Ar distance (see Fig. 4), Franck–Condon overlap at 115 nm would be very poor.

4. Conclusions

Using the method of vacuum UV laser-induced fluorescence, we studied the relaxation of the $B^1\Sigma^+$ Rydberg state of CO in the presence of He and Ar. The experimental results are as follows: (i) The undispersed non-resonant fluorescence is enhanced by the presence of Ar, increasing by a factor of 2.5 at a bath gas pressure of 15 Torr. (ii) The undispersed fluorescence displays a non-exponential decay, with a rapid initial falloff followed by a long lifetime of 100–150 ns. (iii) The dispersed fluorescence between 158 and 175 nm displays A–X vibronic progressions. The progression originating from $A^1\Pi(v'=0)$ is doubled in intensity by the Ar bath. (iv) The dispersed fluorescence also displays a continuous ('grass') emission over the entire measured spectrum.

These observations indicate that several mechanisms operate simultaneously. The enhanced discrete emission is attributed to a non-adiabatic transition from a Rydberg to a valence potential energy

surface of the triatomic COAr complex. The slow decay is caused by collision-induced intersystem crossing. While part of the continuous spectrum may be due to emission from triplet states, most of the grass originates from some other source. We speculate that this additional source is a metastable COAr* complex.

Acknowledgement

We wish to thank Professor Victoria Buch, Professor Eric Gislason, and Professor Philip Brooks for helpful discussions. Support by the Petroleum Research Fund administered by the American Chemical Society and by the National Science Foundation is gratefully acknowledged.

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