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# High Resolution UV Emission Spectroscopy of Molecules Excited by Electron Impact

G. K. James, J. M. Ajello, L. Beegle, M. Ciocca[ψ], D. Dziczek, I. Kanik, C. Noren, C. Jonin and D. Hansen

*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA*
*[ψ] Department of Physics and Astronomy, University of Kentucky, Lexington KY 40506, USA*

Photodissociation via discrete line absorption into predissociating Rydberg and valence states is the dominant destruction mechanism of CO and other molecules in the interstellar medium and molecular clouds. Accurate values for the rovibronic oscillator strengths of these transitions and predissociation yields of the excited states are required for input into the photochemical models that attempt to reproduce observed abundances. We report here on our latest experimental results of the electron collisional properties of CO and $N_2$ obtained using the 3-meter high resolution single-scattering spectroscopic facility at JPL.

The Fourth Positive ($A\ ^1\Pi - X\ ^1\Sigma^+$) band system of CO is ubiquitously observed in astronomy, appearing in UV spectra from the sun, the planets, and the interstellar medium. We have measured laboratory emission spectra of CO at medium resolution (~0.03 nm full width at half maximum (FWHM)) produced by electron impact excitation at 20 eV and 100 eV in the wavelength range 130 to 205 nm. Features observed in these far-ultraviolet fluorescence spectra correspond to the Fourth Positive band system, atomic multiplets from C and O, together with their ions. The spectral region between 130 and 180 nm observed at 100 eV is shown in Figure 1. Electron impact emission cross sections measured in the present work (and listed in *Beegle et al.*, 1998) are about 10% higher than the previous measurements of *Aarts and de Heer* (1970), *Mumma et al.* (1971), and *Ajello* (1971). For example, the cross section at 100 eV for the entire Fourth Positive band system as reported by *Ajello* (1971) was ~31 x $10^{-18}$ $cm^2$, compared to a result of 34.4 x $10^{-18}$ $cm^2$ obtained in the present work. However, the value of the studies from 25 years ago which were in close agreement has been undermined by the different calibration standards employed, all of which have undergone substantial revision. In addition, the contribution of cascade to the emission cross section was underestimated in the earlier works.

The present CO Fourth Positive spectral data were used in combination with those of *DeLeon* (1989) to determine the dependence of the electronic transition moment ($R_e$) on the internuclear distance ($r_{v',v''}$). The transition moment data of *DeLeon* (1989) were normalized to our values of $R_e$ in the 1.35-1.40 Å region, as shown in Figure 2. The combined data set was then fitted with a polynomial out to an internuclear distance of 1.8 Å. This curve has the form:

$$R_e = 7.64\ (1-0.957\ r_{v'v''} + 0.2247\ r^2_{v'v''}),$$

and is in good agreement with recent work of others (*Federman et al.* (1997), *Smith et al.* (1994), *Chan et al.* (1993), and *Kirby and Cooper* (1989)). This agreement supports the conclusions of *Morton and Noreau* (1994) who recommended the use of the CO Fourth Positive band oscillator strengths measured by *Chan et al.* (1993).

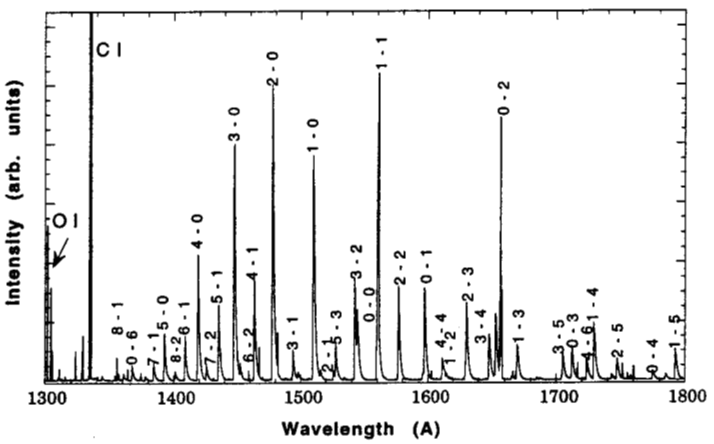


Fig. 1 CO emission spectrum at 100 eV.

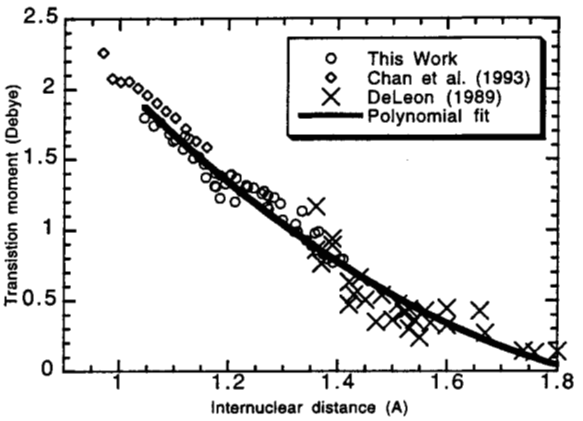


Fig. 2 Variation of electronic transition moment

High resolution measurements (0.0034 nm FWHM) of the CO (A-X) (5,1) and (3,0) bands show excellent agreement between the observed spectra and a synthetic model constructed to explain the high resolution rotational fine structure. Figure 3 shows this model in comparison with the experimental spectrum of the (3,0) band at 144.7 nm. There is some evidence of a small amount of self-absorption for Q3-Q7.

The energy dependence of the CO A $^1\Pi$ cross section was studied by measuring the excitation function of the strong A $^1\Pi$ (v'=0) - X $^1\Sigma^+$ (v''=1) band at 159.7 nm in the electron impact energy range from threshold to 750 eV. Relative excitation function data were put on an absolute scale by normalizing the intensity at 100 eV to an emission cross section value of 1.12 x $10^{-18}$ (*Beegle et al.*, 1998). The excitation function data are shown in Figure 4, together with the measurements of *Aarts and de Heer* (1970) and *Mumma et al.* (1971) renormalized to the present data at 200 eV. There is a significant contribution to the measured emission cross section due to

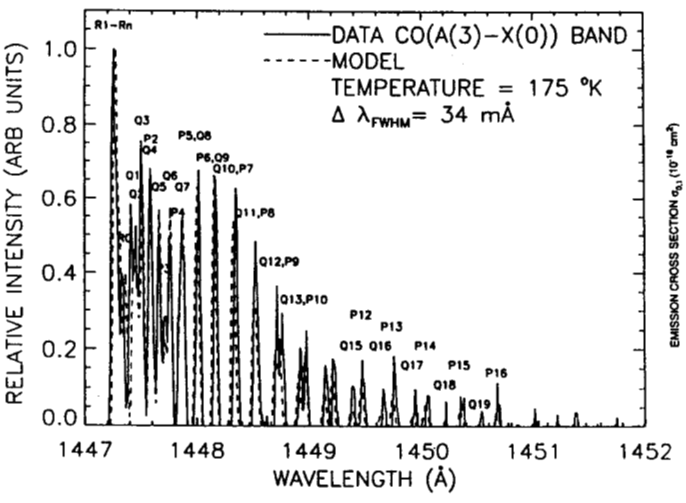


Fig. 3 CO A-X (3,0) band spectrum at 100eV

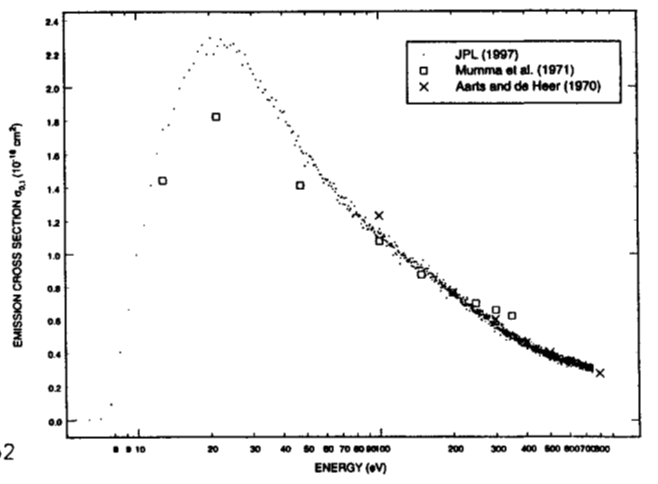


Fig. 4 Excitation function of CO A-X (0,1)

cascade from the higher lying B $^1\Sigma^+$ and C $^1\Sigma^+$ states populating the A $^1\Pi$ state. At 100 eV the ratio of the cascade cross section to the direct excitation cross section varies from 0.09 for v′ = 0 to 0.04 for v′ = 6. These estimates are based on available Franck Condon factors for the (B-A) and (C-A) band systems, the (B-A)/(B-X) and (C-A)/(C-X) branching ratios, and (B-X) and (C-X) excitation function data (*Kanik et al.* 1995).

We also report here on our latest experimental data for $N_2$. Figure 5 shows the high resolution (0.0036 nm FWHM), optically thin, extreme ultraviolet emission spectrum of the $N_2$ c′ $^1\Sigma_u^+$ (4,3) and (3,2) Rydberg bands produced by electron impact excitation at 100 eV. The remainder of the bands forming the v″ progressions (v″= 0 to 5) from v′= 3 and (v″ = 0 to 6) from v′ = 4 were also measured at 0.0064 nm (FWHM) resolution. Electron impact emission cross sections of the $N_2$ c′ levels at 175 °K were determined from the composite spectrum of the two progressions at 100 eV to be 7.9 x $10^{-19}$ cm$^2$ for v′=3, and 9.9 x $10^{-19}$ cm$^2$ for v′=4. A model of the perturbed rotational line intensity distribution of the bands (also shown in Figure 5) illustrates the effects of electronic state mixing between the c′ $^1\Sigma_u^+$ Rydberg state and the b′ $^1\Sigma_u^+$ valence state. By normalizing the model to the published predissociation yield for J′ =9 (*Walter et al.*, 1994) the laboratory spectrum can be used to determine the predissociation yields for each rotational level of v′ =3 and 4. It is found that the predissociation yields of the c′ v′ = 4 rotational levels increase with J′, as the percentage of b′ $^1\Sigma_u^+$ character increases. The predissociation yield is greater than 50% for J′ > 4 of v′ =4, and exceeds 80 % for J′ > 12, although we cannot acquire any data for J′ > 14. This important information on high J′ may be determined by photofragment spectroscopy. On the other hand, the predissociation yields of the c′ v′ = 3 rotational levels reach a maximum of ~50% for 5 < J′< 10 only. The mean predissociation yield for a Boltzmann thermal distribution of ground state $N_2$ molecules is a strong function of temperature, as illustrated by the calculation shown in Figure 6.

The observed emission from the v′=4 level of the $N_2$ c′ $^1\Sigma_u$ state will continually decrease as the temperature of the gas increases. However, emission from the v′=3 level will decrease with temperature to a minimum at ~ 150 °K and then increase at higher temperatures. These results give an important corollary to planetary atmospheres modeling. The emission cross section of the v′ =4

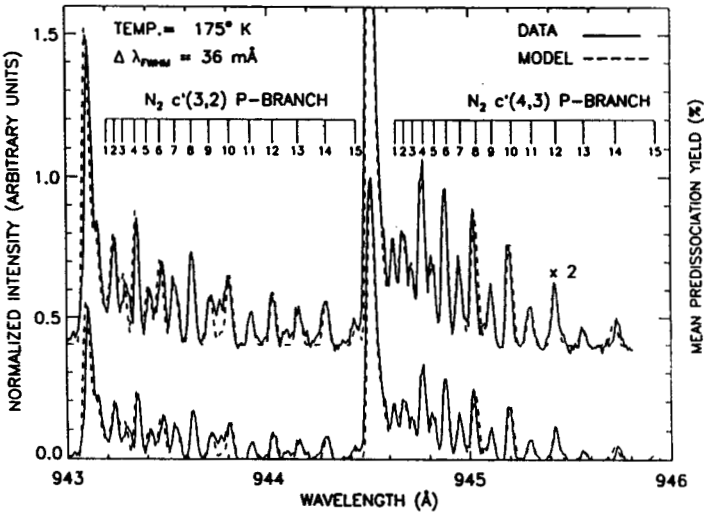


Fig. 5 $N_2$ c′ -X (3,2),(4,3) band spectrum at 100eV

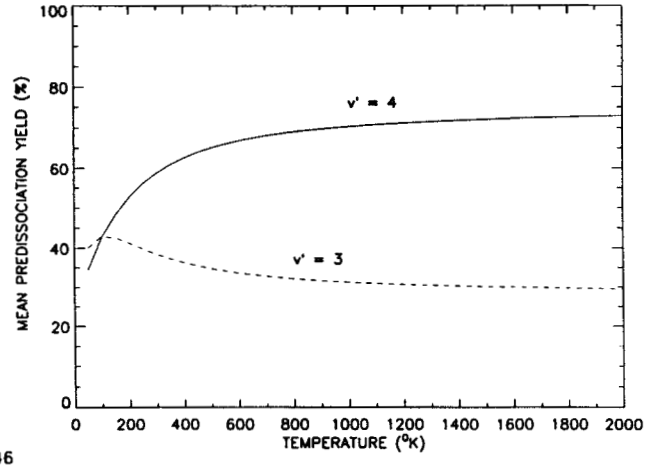


Fig. 6 $N_2$ c′ predissociation yield

level of the $N_2$ c' state will change with temperature, from very small in the Earth's atmosphere (where temperatures approach 1000 °K (*Hedin*, 1987)) to much larger in the atmospheres of Triton and Titan (where temperatures are about 50-200 °K). The opposite temperature trend will occur for the v' = 3 level. The results seem to establish a general trend of increasing mean predissociation yield with vibrational level by including in the study the mean 300 °K predissociation yield of 15% from our work on the c' v'=0 level (*Shemansky et al.*, 1995). The other strong levels, v'=.2 and 6, also need to be studied at high spectral resolution.

The excitation cross section at 100 eV can be calculated based on the emission cross section and the mean predissociation yield at 175 °K (42% and 50 % for v'= 3 and 4, respectively). The resulting total excitation cross section values are 13.6 x $10^{-19}$ $cm^2$ for v' = 3, and 19.8 x $10^{-19}$ $cm^2$ for v' =4. Although these absolute cross sections are dependent on normalization to the predissociation yield for J' =9 measured by *Walter et al.* (1994), the spectra obtained in this study are the first electron impact spectra to separate the effects of blending of the b' (v' = 10 and 13) levels with the c' (v' = 3 and 4) levels, respectively. The ratio of excitation cross sections c'(4)/c'(3) obtained here is 1.5. The corresponding excitation cross section ratio measured by *Geiger and Schroder* (1969) is 2.7, by *Chan et al.* (1993) is 2.6, by *Zipf and McClaughlin* (1978) is 2.9, and by *Carter* (1972) is 1.7. The last ratio was measured by high resolution absorption spectroscopy and the sets of former works were obtained by energy loss spectroscopy. The previously published cross section ratios from energy loss results must be viewed with caution, since the spectra did not resolve the structure from overlapping Rydberg and valence states.

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