UV photoabsorption cross sections of CO, N$_2$, and SO$_2$
for studies of the ISM and planetary atmospheres

Peter L. Smith, J. Rufus, K. Yoshino and W. H. Parkinson
Harvard-Smithsonian Center for Astrophysics

Glenn Stark
Physics Department, Wellesley College

Juliet C. Pickering and A. P. Thorne
Blackett Laboratory, Imperial College, London

Abstract

We report high-resolution laboratory measurements of photoabsorption cross sections of CO, N$_2$, and SO$_2$ in the wavelength range 80 to 320 nm. The motivation is to provide the quantitative data that are needed to analyze observations of absorption by, and to model photochemical processes in, the interstellar medium and a number of planetary atmospheres. Because of the high resolution of the spectrometers used, we can minimize distortion of the spectrum that occurs when instrument widths are greater than the widths of spectral features being measured. In many cases, we can determine oscillator strengths of individual rotational lines – a unique feature of our work. Abstract text here.

1. Carbon Monoxide (CO)

CO is the second most abundant interstellar molecule after H$_2$. Because CO is readily observed, it is used as a tracer of molecular material. However, estimates of abundances of CO are poorly determined observationally and not well understood theoretically. Incomplete or inconsistent molecular parameters contribute to many of the difficulties. Consequently, the acquisition of improved photoabsorption cross section and spectroscopic data for CO at VUV wavelengths has been a major focus of our research program in the past few years (Smith et al. 1994; Yoshino et al. 1995; Stark et al. 1999a).

Recently, we have studied the absorption spectrum of five weaker intersystem (spin-changing) bands in order to provide line oscillator strengths (f-values) for absorption features seen by Federman et al. (1994) and Sheffer et al. (2002). f-values can be difficult to calculate for these weak bands because each upper level is perturbed by a number of vibrational levels of the $A$ state. Therefore, we have emphasized direct measurements with the 6.65-m 6VOPE normal-incidence spectrometer at the Photon Factory, a synchrotron radiation source in Tsukuba, Japan. This spectrometer has a resolving power of about 170,000 and an order-sorting disperser that greatly reduces spurious signal. An example of our data is shown in Figure 1; the instrument resolution was greater than the Doppler dominated width of the spectral lines, so the line shapes are somewhat distorted in this spectrum.

Our line f-values for the d(7)-X(0) and e(4)-X(0) bands are given by Stark et al. (2002). These are the first direct measurements of individual line f-values for an intersystem band of CO. Our measured values generally confirm the band simulations of Rostas et al. (2000) and those determined by Sheffer et al. (2002) from observations of interstellar absorption.
2. Molecular Nitrogen (N₂)

The strongest band of N₂, c′(0) - X(0) at 95.9 nm, is in the FUSE wavelength range and is not blended with CO or H₂ features. The most prominent EUV emission features in the airglows of Titan and Triton, where N₂ is the major atmospheric constituent, originate from the c′ 1Σ⁺ₚ(v′ = 0) level. Like many of the VUV lines of N₂, those of the c′ - X band are extremely sharp, with natural line widths much less than the Doppler widths. Line f-values cannot be reliably calculated from band f-values and Hönl-London factors because of perturbations: measurements are required. The highest possible resolving power is necessary to minimize distortions of the spectrum and concomitant obscuration of saturation effects.

We again used the 6.65-meter spectrometer at the Photon Factory. Data for the c′(0) - X(0) band of N₂ are shown in Figure 2. Our results (Stark et al. 2000) are the first measurements of individual line f-values for this band. Our data are available in our N₂ data archive at http://cfa-www.harvard.edu/amdata/ampdata/N2ARCHIVE/n2home.html. We have also measured band f-values and line widths for a number of the ~100 bands of N₂ in the 80 to 100 nm wavelength region. These bands are important for understanding the temperature-density profiles of the atmospheres of Titan and Triton. Analysis of these data is in progress.

3. Sulfur Dioxide (SO₂)

Analysis of the UV spectrum of Io and modelling of the chemical composition and photochemical processes in its atmosphere require knowledge of the photoabsorption cross section of SO₂ over a wide wavelength range at temperatures from 110 to ~500 K. Our laboratory program, which also supports HST observations of the atmosphere of Venus, is producing such data over the wavelength range 190 to 325 nm with orders of magnitude higher resolving power than previous work.

The ultraviolet spectrum of SO₂ is dominated by two broad regions of absorption: 175 to 230 nm, which is the stronger, and 250 to 320 nm. Because the upper electronic states participating in these transitions are strongly perturbed, no comprehensive rotational analyses exist or are likely in the near future. This means that the temperature dependence of the SO₂ absorption spectrum, needed for analyses of planetary atmospheres, cannot be reliably
modelled but must be measured. The region is exceedingly complex at room temperature; previous photoabsorption measurements have been unable to fully resolve it.

We used the VUV Fourier transform (FT) spectrometer at Imperial College, London (Thorne et al. 1987) for two sets of measurements. Cross section data for the 198 to 220 nm region have been published (Stark et al. 1999); results for the region 220 to 235 nm are reported here (see also Rufus et al. 2002). Figure 3 shows recent data plotted on linear and log scales; note that the structure (see inset) is essentially all real, i.e., not noise. Our data are compared to those of Manatt & Lane (1993) and Wu et al. (2000) over a limited spectral region in Figure 4.

Figure 3. Photoabsorption cross section of SO₂ at 295 K measured with a resolution of 4 to 32 mA. Inset shows structure in a 0.2 nm region. Note that the SNR for this measurement was about 100, so the structure shown in the inset is real.

Fig. 4.— Comparison of our results (highly structured line) with those of Manatt and Lane [1993] (dashed line) and Wu et al. [2000] (smooth solid line with white border). Note that, on the average, the data roughly agree, but that our values for the peak cross sections are about a factor of two larger.
Acknowledgments

This work was supported in part by NASA Grant NAG5-4348 to Harvard University and NAG5-9059 to Wellesley College, by PPARC of the UK, and by a NATO Collaborative Research Grant. JCP is supported by a Royal Society University Research Fellowship. The authors thank D. S. Leckrone, G. Nave, and W. H. Parkinson for encouragement and assistance. We thank C. Y. R. Wu and A. L. Lane for providing SO$_2$ data in electronic form.

REFERENCES