UV AND VUV SPECTROSCOPY AND PHOTOCHEMISTRY OF SMALL MOLECULES IN A SUPERSONIC JET

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ABSTRACT

UV and VUV absorption and emission spectroscopy is used to probe jet cooled molecules, free radicals, and clusters in the gas phase. Due to efficient cooling inhomogeneous effects on spectral line widths are eliminated. Therefore from these spectra, both structural and dynamical information is obtained. The photoproducts of these reactions are probed by resonance enhanced multiphoton ionization.

INTRODUCTION

In the last years an experimental research program has been developed in our laboratory which allows study of reactive small molecules, radicals, and their molecular aggregates. This program employs a combination of supersonic molecular beams for sample preparation with spectroscopic and photofragment techniques, used to characterize these reactive species.

RESULTS AND DISCUSSION

Jet cooled molecules such as NH_3, CS_2, OCS, and CH_3I have been studied during the last years by vacuum UV spectroscopy. [1-3] These improved spectra provided structural and dynamical models for the excited states of these small reactive molecules. Besides absorption features known for the isolated molecules, new absorption bands have been observed at high stagnation pressure. These bands have been assigned as dimer absorption bands. The experimental scope has been extended recently to high resolution UV spectroscopy in order to understand monomolecular reaction dynamics of photoreactive systems. This is accomplished

by using a Fourier transform spectrometer (FTS) with a free jet expansion. Compared to the best conventional free jet absorption technique,[1] the FTS offers a 15 times greater sensitivity and two orders of magnitude better spectral resolution. This technique has been applied to study reactive electronic states of chlorine dioxide (OClO).[4] Upon electronic excitation $(\tilde{A}(^2A_2) \leftarrow \tilde{X}(^2B_1)$, 260-480 nm) OClO predissociates into the fragments ClO + O. With rotational cooling in a supersonic expansion spectral congestion due to inhomogeneous effects can be reduced substantially. From the rotational envelopes of the vibrational bands a rapid increase in the line widths is observed as the energy of the transition is increased. Figure 1 shows a portion of the jet cooled $(\tilde{A}(^2A_2) \leftarrow \tilde{X}(^2B_1)$ absorption band of chlorine dioxide. The splittings in each band are caused by the ^{35}Cl and ^{37}Cl isotopes.
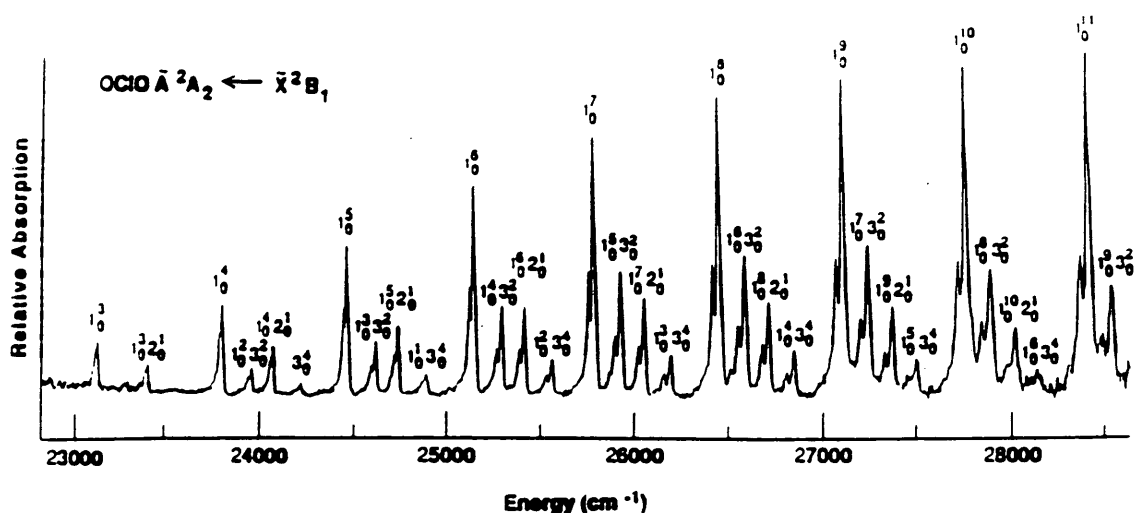

Figure 1: Portion of the jet cooled absorption spectrum of chlorine dioxide. Recorded at $5cm^{-1}$ resolution and 2 atm total stagnation pressure (3% OClO in He).

The Fourier transform technique can be also used for emission spectroscopy. This has been demonstrated for emission of jet cooled $CN(B\ ^2\Sigma)$ radicals.[5] The spectroscopic sample is formed in a continuous corona discharge. The $B \rightarrow X$ emission spectrum of CN is shown in Figure 2. The advantage of the corona discharge radical source is that high vibrationally excited levels can be studied in a relatively uncongested rotationally cold spectrum.[6] From the spectrum a vibrational temperature of 2200 K and a rotational temperature of 75 K has been deduced. New and more accurate rotational constants for the CN B-state have been obtained by the use of K values up to 62.
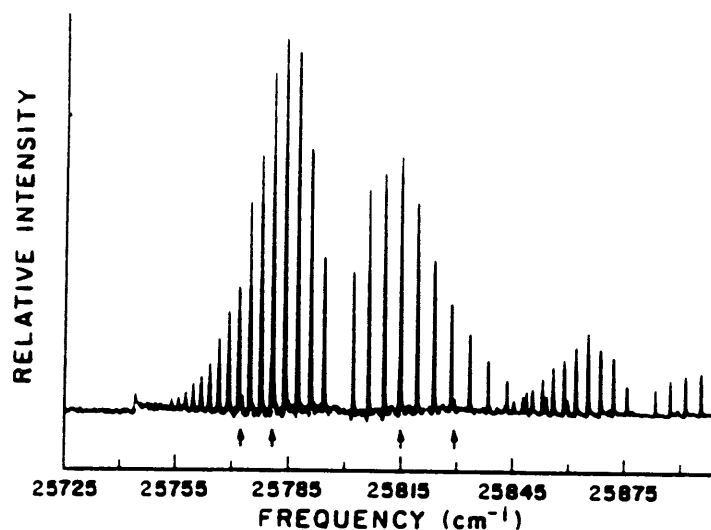
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Figure 2: CN (B→X) emission spectrum recorded at 0.25 cm^{-1} spectral resolution under stagnation conditions of 0.13 atm CH_3CN in 1 atm He. The spectrum includes both the 0-0 and 1-1 transitions. Arrows indicate perturbations from A-state rotational levels.

Besides spectroscopic probes we have employed mass spectrometry to analyze the products of reactive electronic states of jet cooled molecules. The technique used is resonance enhanced multiphoton ionization (REMPI). Chlorine dioxide has been studied in the spectral regime of $(\tilde{A}(^2A_2)\leftarrow\tilde{X}(^2B_1)$ transition.[7] The main products of the above mentioned predissociation is ClO + O. Chlorine oxide is probed in a (2+2) REMPI process, in which the $C(^2\Sigma)\leftarrow(^2\Pi)$ is accessed (see Figure 3a). All REMPI bands observed are due to vibrationally excited ClO $(X(^2\Pi)(v=3-6))$. The rotational profiles of the REMPI bands corresponds to a thermal Boltzmann population with T=100 K. At higher photon energy (around 340 nm) additional rotational fine structure of vibrationally excited ClO $(A(^2\Pi)\leftarrow X(^2\Pi))$ occurs in the REMPI spectrum of ClO^+. Besides predissociation of OClO we find evidence for photoisomerization of OClO $(\tilde{A}(^2A_2))$. A single resonance in the Cl^+ REMPI signal occurs at 362 nm (see Figure 3b). This agrees with matrix work on chlorine dioxide, where around 365 nm photoisomerization into ClOO was observed.[8]

Due to its low binding energy ClOO decays into Cl + O_2. Because of the low multiphoton ionization cross section of molecular oxygen we observe only a Cl^+ REMPI signal which suggests photoisomerization. We have recently discussed the potential importance of OClO photoisomerization with respect to polar ozone depletion.[9]
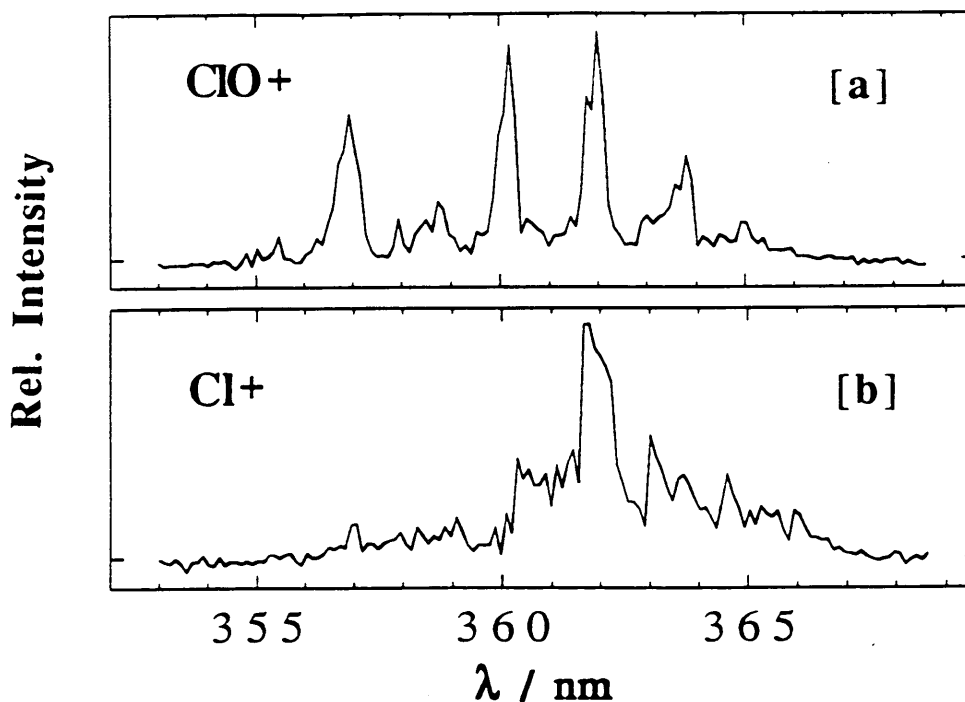
Figure 3: Resonance enhanced multiphoton ionization (REMPI) spectrum of ClO^+ [a], and Cl^+ [b] between 353 and 369 nm.

Currently we are extending our research program to small predissociating molecules which are of interest for planetary atmospheres, such as HCN, H_2S, and H_2O. We are also interested in the spectroscopy and photoreactivity of homogeneous and heterogeneous clusters of these species. Because cluster formation is enhanced at low temperatures, their photoreactivity might be important to understanding the chemistry of the atmospheres of outer planets.

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