Photoionization Dynamics and Cation Spectroscopy with UV Coherent VUV Radiation

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Abstract: Pulsed field ionization (PFI) has been used in conjunction with coherent VUV radiation to investigate the rotational state distributions of molecular cations following single photon ionization. For photoionization of the H_2X (X = O, S) molecules, transitions between asymmetric top levels involving the rotational angular momentum projections, K_a and K_c, permit resolution of the photoelectron continua according to symmetry. The observed spectra also clearly demonstrate the importance of the non-spherical nature of the molecular ion potential which leads to photoelectron final states which are unexpected from atomic-like analogies.

1. Introduction

Photoelectron spectroscopy provides information on the dynamics of the photoionization process by revealing the internal state distribution of the molecular fragment (molecular cation) through the measurement of the kinetic energy distribution of the "light" fragment (photoelectron). The dynamics are considerably different than for neutral fragmentation, yet both involve similar concepts, especially as regards the evolution of a photoexcited "complex" into the observed asymptotic channels and the molecular forces which influence their branching ratios. With the development of laser-based, zero kinetic energy (ZEKE) and pulsed field ionization (PFI) techniques it is has now become possible to extend photoelectron spectroscopy to measurements of cation *rotational* state distributions and hence, fully resolve quantum state distributions following photoionization (Müller-Dethlefs 1991, Grant 1991). We have used the PFI technique in conjunction with a high-resolution VUV laser source to investigate the spectroscopy and one-photon ionization dynamics of several linear molecules (O_2, N_2O, Xe_2, HCl and OH(OD)) in which we have characterized the angular momentum constraints in rotational photoionization transitions (Tonkyn 1989, Braunstein 1990, Wiedmann 1991, Tonkyn 1991a, Tonkyn 1992, Wiedmann 1992b). Our concentration on one-photon processes arises from the extensive body of information which exists for molecular VUV photoionization using laboratory or synchrotron radiation sources, but for which only H_2 has been rotationally resolved. In this paper, we present results of recent studies on the H_2X (X = O, S) molecules which explore the symmetry properties of allowed rotational photoionization transitions in non-linear molecules.

2. Experiment

Figure 1 is a schematic diagram of the photoelectron spectrometer and VUV source which are described in detail elsewhere (Tonkyn 1989b). Briefly, we use a small, separately pumped frequency tripling chamber attached to a photoelectron/photoion time–of–flight (TOF) spectrometer. Tunable VUV radiation in the range 150nm to 90nm is produced by non-resonant third harmonic generation ($\omega_{vuv} = 3\omega_{uv}$) as well as resonant and non-resonant four-wave sum/difference frequency mixing ($\omega_{vuv} = 2\omega_{uv} \pm \omega_{vis}$) in free jet expansions of krypton, xenon and molecular nitrogen (Page 1987). The collinear laser beams ($\omega_{uv}, \omega_{vis}$) are focused by a 100 mm focal length achromatic lens into the tripling chamber and very near the 1 mm dia. exit nozzle of a piezoelectric pulsed-valve (Proch 1989). The diverging fundamentals (visible and UV) and harmonically generated VUV radiation are captured by a pyrex capillary tube (30 cm long; 1 mm id.) and directed into the TOF spectrometer, where it passes between two parallel plates which define the extraction field for the TOF spectrometer. The capillary acts as an efficient differential pumping barrier separating the VUV generation chamber ($\sim 10^{-3}$ Torr) and the spectrometer chamber ($\leq 1 \times 10^{-7}$ Torr), while also acting as a light guide which provides a collimated VUV beam without refocussing. The VUV intensity at the spectrometer is estimated to be $10^9 - 10^{10}$ photons per pulse, with an energy bandwidth of 0.7 cm^{-1}.

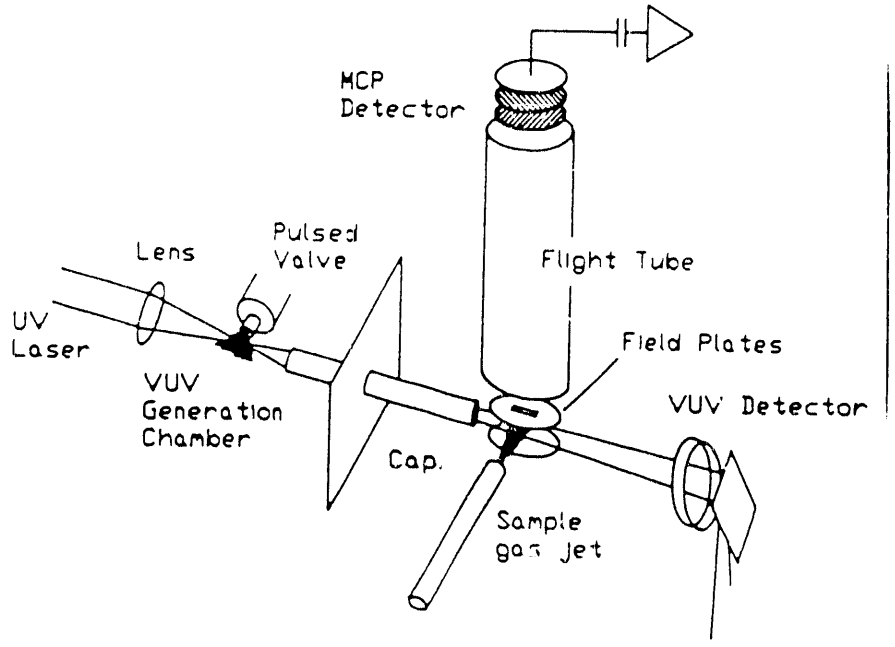

Figure 1. Schematic diagram of time-of-flight photoelectron spectrometer used for one-photon photoionization measurements.

High-resolution threshold photoelectron spectra are obtained by the delayed, pulsed field ionization (PFI) method as first demonstrated by Reiser, *et al* (1988). PFI takes advantage of the well known Stark shift of an ionization threshold in an external electric field (given by $\sim 6\sqrt{F}$ cm^{-1}, where F is the field strength in volts/cm). Bound Rydberg

levels very near the ionization threshold which are stable in a field free environment become open ionization channels when a Stark shift larger than their binding energy is applied. For fields used in these studies (0.3-0.5 V/cm) only Rydberg levels with $n \geq 150$ can be field ionized. Rydberg states with such high principal quantum numbers are very long lived due to rapid l mixing induced by a small DC electric field (~ 0.05 V/cm). The small positive DC voltage on the repeller (lower) plate also sweeps out any slow or near ZEKE photoelectrons produced directly by the laser pulse. After a delay of 700 ns, a fast, negative pulse ($0.3 - .5$ V) is applied to the repeller plate which field ionizes the metastable, high-n Rydberg states. Electrons produced by this pulsed field are readily distinquished from photoelectrons arising from direct ionization as the arrival time of the former depend only on the pulse delay and voltage.

3. Threshold Photoionization of H_2X (X = O, S)

High resolution (~ 1 cm^{-1}) threshold photoelectron spectra for jet-cooled (15 K) samples of H_2O and H_2S were obtained for rotational transitions between the

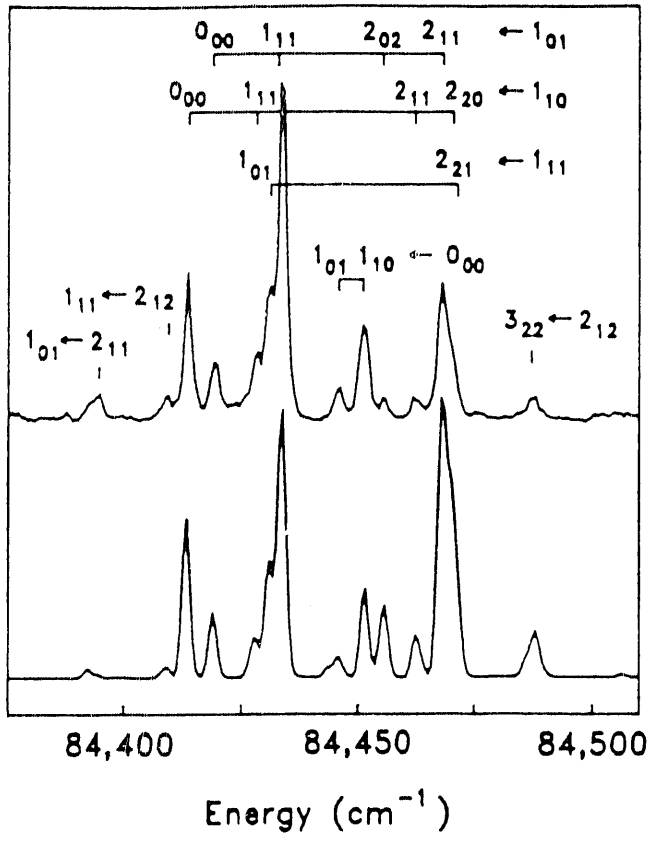

Figure 2. Upper trace: Rotationally resolved, pulsed field ionization spectrum for one-photon ionization of H_2S to the $\tilde{X}^2B_1$ (000) level of H_2S^+. Lower trace: Simulated photoionization spectrum of H_2S at 15 K including both type A ($\Delta K_c = \pm 1, \Delta K_a = 0$) and type C ($\Delta K_c = 0, \Delta K_a = \pm 1$) rotational transitions.

$X\,^1A_1$, (000) neutral ground state and the $\tilde{X}\,^2B_1$, $(\nu_1\nu_2\nu_3)$ vibrational levels of the ionic ground state (Tonkyn 1991b, Wiedmann 1992a). For H_2O, rotationally-resolved data were obtained for ionization into the (000), (100) and (010) vibrational levels, while for H_2S^+ only the (000) and (010) levels could be probed due to inefficient VUV production at wavelengths near the (100) symmetric stretch. The PFI spectrum for the $\tilde{X}^2B_1$, (000) level of H_2S^+ is shown in Figure 2. The H_2X^+ spectra could be readily assigned to two types of rotational photoionization transitions corresponding to specific changes in the asymmetric top angular momentum projection quantum numbers, K_a and K_c. Most of the stronger lines can be classified as type C rotational transitions $(\Delta K_c = 0, \Delta K_a = \pm 1)$ but type A $(\Delta K_c = \pm 1, \Delta K_a = 0)$ transitions are also clearly evident, particularly in the jet-cooled spectra. The utility of this classification stems from the fact that general symmetry arguments show that these rotational transitions are associated with only one photoelectron symmetry, i.e. ka_1 with type C and ka_2 with type A. The appearance of type A transitions with $\Delta K_a = 0$ is in variance with the predictions of a multichannel quantum defect theory (MQDT) analysis of photoionization of asymmetric top molecules by Child and Jungen (1990). These authors predict that photoionization will only involve a subset of type C transitions with $|\Delta K_a| = |K_a^+ - K_a''| = 1$ and $|\Delta N| = |N^+ - N''| \leq 1$, where N is the total angular momentum exclusive of spin. These limits on the changes of core angular momenta arise from the assumption that the $1b_1$ molecular orbital can be described exclusively in terms of an atomic p_z orbital. More recently, Gilbert and Child (1991) have presented a model based on field-induced autoionization in an effort to explain the appearance of type A transitions in the threshold spectra of H_2O. Although such rotational autoionization processes could give rise to the appearance of rotational final states which are nominally forbidden by optical selection rules, the specific application to H_2O also invokes an atomic-like description of photoexcitation from the $1b_1$ molecular orbital.

A more straightforward explanation for the appearance of type A transitions can be derived from very recent *ab initio*, Schwinger variational photoionization calculation on H_2O (Lee 1992). In this calculation, no assumptions concerning the atomic character of the initial and final states are made and the continuum is calculated in the full anisotropic potential of the ion core. The calculations predict the appearance of type A photoionization transitions without recourse to final state interactions (field-induced autoionization) and the calculated H_2O^+ rotational spectrum is in nearly quantitative agreement with experiment. A comparison of the H_2O^+ $\tilde{X}\,^2B_1$, (000) PFI spectrum and the theoretical near threshold photoionization calculation is shown in Figure 3.

A partial wave analysis shows that type A transitions are accompanied by nearly pure p wave photoelectrons. Furthermore, the type C transitions are not exclusively d partial waves as expected from the atomic analogies, but include significant and for some lines (e.g. $0_{00} \leftarrow 1_{10}$) dominant s wave character. These calculations emphasize the importance of the non-spherical nature of the molecular ion core which can "scatter" or torque the escaping photoelectron into different partial waves. For H_2S, we expect that similar dynamics are applicable since the $1b_1$ molecular orbital is primarily localized on the sulfur atom. However, the participation of the nominally unoccupied $3d$ levels centered on the heavier sulfur atom could lead to additional high l components in the continuum and modify the rotational line strengths.

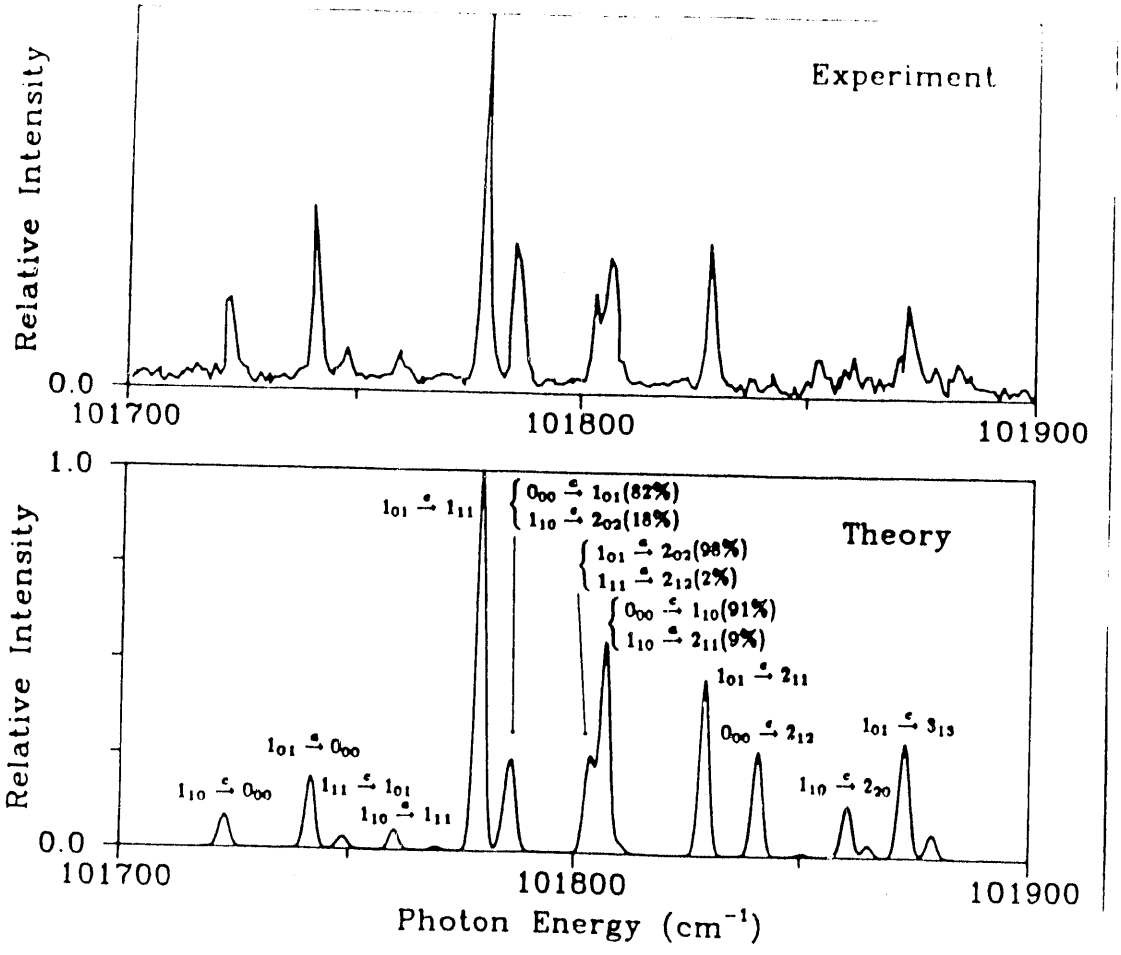

Figure 3. Experimental (top) and calculated (bottom) threshold photoelectron spectrum for photoionization from the $1b_1$ orbital of H_2O. The labels *a* and *c* refer to type A and type C rotational branch transitions.

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