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Rotationally Resolved Photoionization with 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. The rotational state distributions for several linear cations (O_2, NO, OH(OD), HCl and N_2O) can be interpreted predominately on the basis of the near-threshold, one-electron photoionization dynamics; however, field-induced autoionization is often the dominate ionization pathway for rotational branches involving negative changes in core angular momentum. For photoionization of the H_2X (X = O, S) non-linear triatomic 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 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

Photofragment spectroscopy provides information on the dynamics of the fragmentation process by revealing the internal state distribution of the usually unobserved molecular fragment through the measurement of the kinetic energy distribution of the "light" or atomic fragments. In the same way, photoelectron spectroscopy reveals the photoionization dynamics through detection and momentum resolution of the ejected 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

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of cation *rotational* state distributions and hence, fully resolve quantum state distributions following photoionization.[1,2] 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 a number of small molecules in which we have explored the angular momentum constraints in rotational photoionization transitions.[3 - 9] 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 a summary of results of joint theoretical and experimental studies on several diatomic and triatomic molecules which demonstrate the utility of rotationally-resolved threshold photoelectron spectroscopy for examing photoionization dynamics.

2. Experiment

The photoelectron spectrometer and VUV source used for threshold photionization measurements is described in detail elsewhere.[10] 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 150 nm to 90 nm 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.[11] 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.[12] The diverging fundamentals (visible and UV) and harmonically generated VUV radiation are captured by a pyrex capillary tube (30 cm long; 1 mm i.d.) 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 capillary is also used as a gas filter which effectively separates the sum and difference VUV frequencies via total absorption of the high frequency radiation by a suitable rare gas injected into the center of the long capillary ($\leq$ 400 mTorr). 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}.

High-resolution threshold photoelectron spectra are obtained by the delayed, pulsed field ionization (PFI) method as first demonstrated by Reiser, *et al.*[13] 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).[14] The small 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 only the arrival time of the former depends on the pulse delay and voltage.

3. Threshold Photoionization of Linear Molecules

The ejection of a photoelectron with both spin and orbital angular momentum leads to selection rules for photoionization which look quite different compared to those of bound state spectroscopy. Photoabsorption takes place at short range where the excited electron strongly interacts with the ion core and where the general selection rule governing dipole transitions, i.e., $\Delta J = 0, \pm 1$, is valid. As the electron escapes the molecular ion potential, the interaction becomes weak and the coupling of angular momenta becomes more appropriate to a free photoelectron and well defined rovibronic level of the ion core. This uncoupling can be viewed as a scattering process in which the photoexcited electron exchanges energy and angular momentum with the ion core. The net result is that changes in core angular momentum well beyond $\Delta J = 0, \pm 1$ are possible. The conservation of angular momentum requires only that $\Delta J = J^+ - J'' = l + 3/2, l + 1/2, \ldots, -l - 3/2$, where l is the orbital angular momentum associated with s, p, d or higher outgoing waves.[15] For example, an outgoing d wave could result in eight rotational branches, with changes in the angular momentum of the core as large as $\pm 7/2$. The measurement of the relative branch intensities directly reflects the probability for the various partial waves of the outgoing electron. Such information is a sensitive probe of the ionization dynamics as the partial wave distribution can be strongly influenced by electron correlation and interactions of the photoexcited electron and the nuclear degrees of freedom, e.g., autoionization and shape resonances. Consequently, characterization of the quantum state distribution of the molecular ion and photoelectron pose challenges to theoretical descriptions of the photoionization process since both the electronic and nuclear wavefunctions must be accurately treated. Substantial progress has been made in theoretical approaches to photoionization and recent *ab initio* calculations using Hartree-Fock[4,16,17] and multichannel quantum defect theory (MQDT)[18,19] approaches have provided realistic cation rotational distributions for several molecules.

For the open shell diatomics, O_2[3] and NO, rotationally-resolved threshold photoelectron spectra obtained by the PFI technique were interpreted assuming that the observed branch intensities directly reflect the partial wave distribution of the ejected photoelectron at threshold. This approach is supported in both cases by one-electron, *ab initio* calculations which are in near quantitative agreement with the experimental spectra. For O_2, the calculations show that the observation of large changes in core rotation ($|\Delta J| \leq 9/2$) results from the presence of an $f\sigma(l = 3)$ shape resonance at the ionization threshold.[4] By contrast, threshold photoionization of NO results in a photoelectron continuum characterized by a broad partial wave distribution with $l = 0 - 3$ but with a propensity for small changes in core rotation ($|\Delta J| \leq 5/2$).

Unlike O_2 and NO, spectral simulations for N_2O^+ based on the Buckingham, Orr and Sichel photoionization line strength expressions[20] cannot reproduce a general feature of the data in which rotational branches with $\Delta J < 1/2$ have intensities uniformly larger than branches with $\Delta J \geq 1/2$.[5] Large differences in intensities between branches that only differ in the sign of ΔJ are not expected since only the magnitude of the angular momentum transfered to the core is relevant to determining line strengths (see equations (34)-(37), reference 20). Asymmetries in rotational branch intensities are also evident in the PFI spectra of the OH (OD) radical,[9] and particularly for HCl in which rotational branches with large negative changes in core angular momentum, $\Delta J = -5/2$ and $-7/2$, are relatively intense and, more importantly, they have no observable positive ΔJ counterparts. Such intensity asymetries have also been observed in the ZEKE-PES data of other laboratories as well, suggesting a mechanism which is general in origin.[2,21-24]

The most obvious source of complication in threshold measurements is from autoionization. Indeed, conventional threshold photoelectron spectroscopy using cw sources (e.g. synchrotron radiation) is often dominated by autoionizing states which yield low energy electrons. Such "resonant" autoionization processes have been well documented and lead to additional lines in non-Franck-Condon regions of the photoelectron spectrum.[25] The PFI technique used in our experiments discriminates against such electrons, but is susceptible to "forced" autoionization processes which are induced by the pulsed electric field.[26,27] Field-induced autoionzation involves the dipole coupling of high-n Rydberg states lying near the ionization threshold with near degenerate low-n Rydberg states converging to higher rotational limits.[28] Transitions to the low-n Rydberg states are strongly allowed and represent bound members of rotational branches with increasing ΔJ. Although the low-n Rydberg states lie too far below their respective thresholds to be field ionized, these levels can autoionize once the external field is applied and the high-n Rydberg levels become open ionization channels. For the most negative ΔJ branches, the number of posssible interactions with near-degenerate Rydberg levels is a maximum. Consequently, field induced autoionization can lead to substantial intensity enhancement

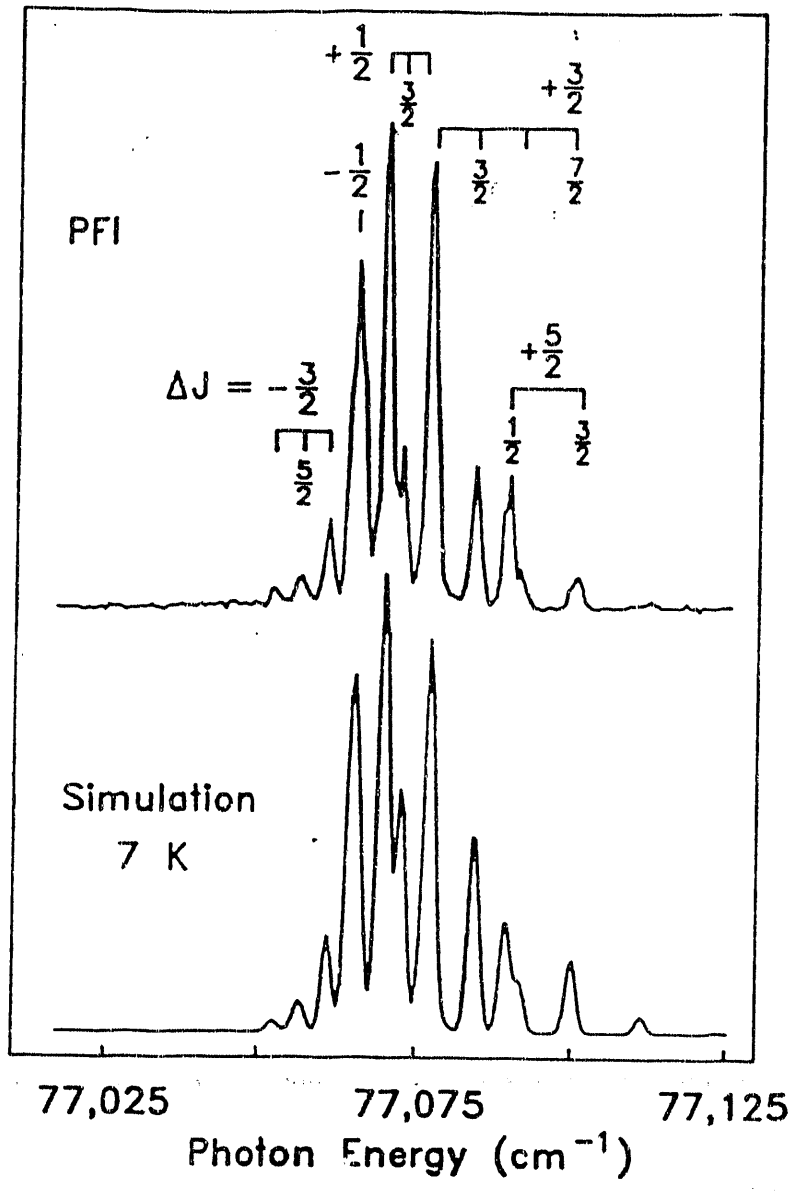

Figure 1: Upper trace: Pulsed field ionization spectrum of rotationally cold NO via $NO(\tilde{X}\ ^2\Pi_{1/2}, v'' = 0, J'') \rightarrow NO^+(X^1\Sigma^+, v^+ = 1, J^+) + e^-$ one-photon photoionization transitions. Lower trace: Simulated photoionization spectrum of NO at 7 K using best fit dynamical parameters in conjunction with the rotational photoionization line strength expressions of Buckingham, *et al* (see reference 20).

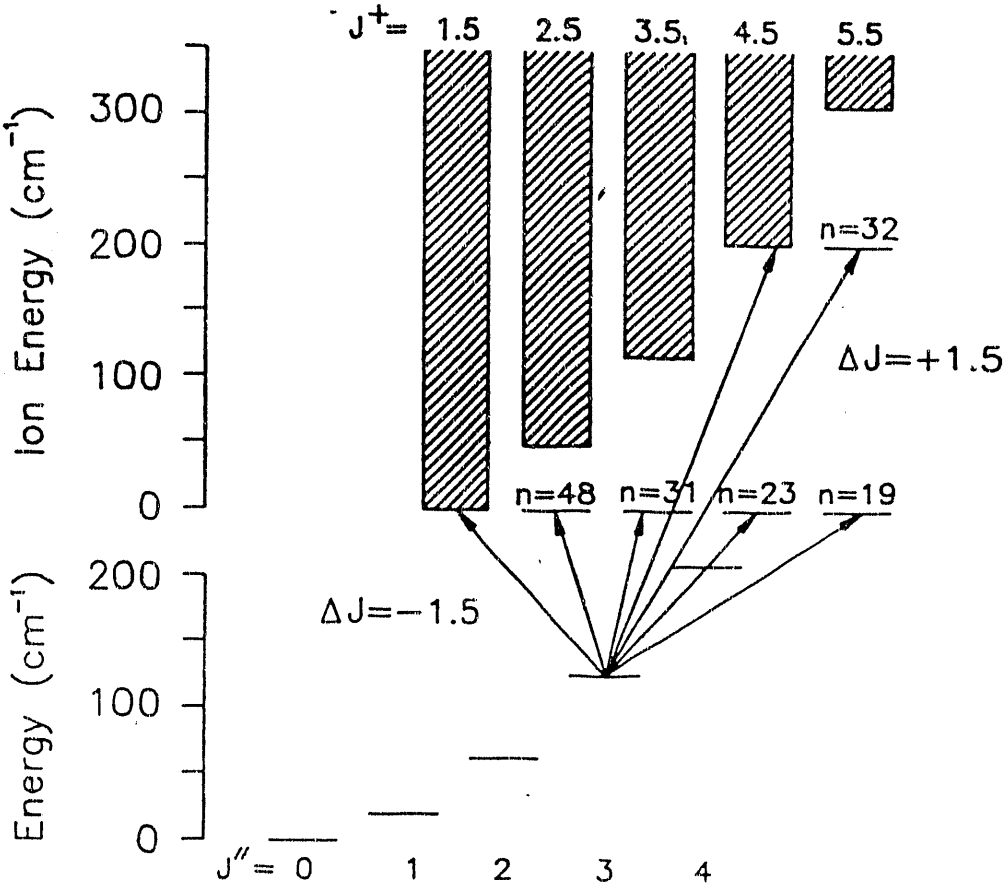

Figure 2: Upper trace: Scaled diagram illustrating field-induced autoionization in the PFI-ZEKE spectrum of HCl. The arrows mark transitions from $J'' = 3$ of the neutral ground state to Rydberg levels lying within 2 cm^{-1} of the ionization thresholds for $J^+ = 3/2$ ($\Delta J = -3/2$) and $J^+ = 9/2$ ($\Delta J = +3/2$). Principal quantum numbers for the low-n Rydberg states are estimated from accurate spectroscopic constants of HCl^+ and assuming zero quantum defect.

for branches with large negative ΔJ. By contrast, the number of possible Rydberg-Rydberg state interactions will be less for branches involving large positive ΔJ branches since there are fewer available low-n Rydberg states which can be optically connected to the ground rotational state. This mechanism is illustrated in Figure 2 for the specific case of HCl.

The implication of these results is that rotational line intensities obtained by ZEKE or PFI methods can be strongly influenced by Rydberg-Rydberg state interactions which ultimately result in autoionization. Since the experimentalist has some control over the sensitivity of PFI-ZEKE measurements to field-induced processes (delay, field strength, excitation bandwidth), this technique may give rise to

new opportunities to study multichannel interactions in molecules with very high selectivity.

4. 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 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.[6,8] 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 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.[19] These authors predict that photoionization will only involve a subset of type C transitions with $|\Delta K_c| = |K_a^+ - K_a''| = 1$ 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_x orbital. More recently, Gilbert and Child[28] 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 as discussed above 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 a very recent *ab initio*, Schwinger variational photoionization calculation on H_2O.[29] 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

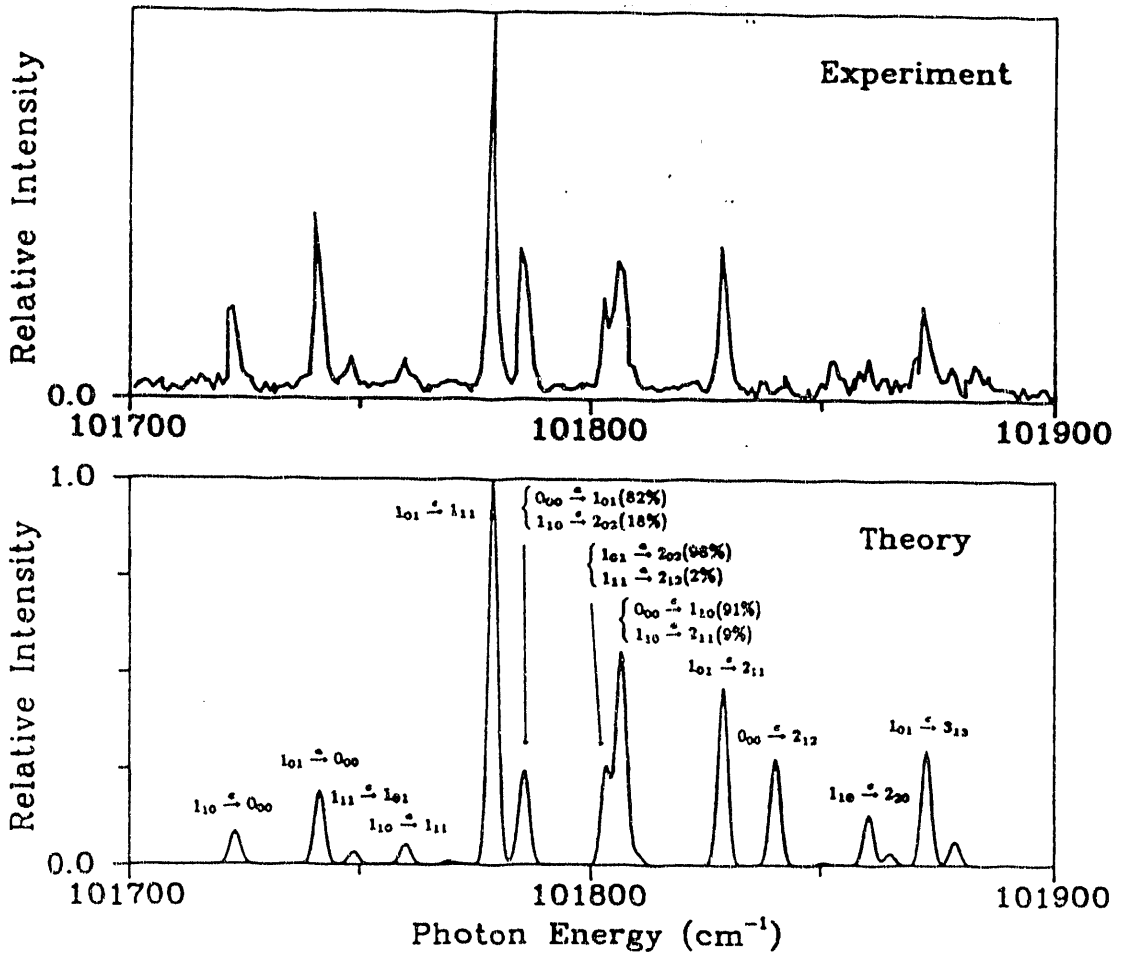

Figure 3: Experimental (top) and calculated (bottom) threshold photoelectron spectrum for photoionization from the $1b_1$ orbital of H_2O. The labels a and c refer to type A and type C rotational branch transitions.

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.

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