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*Resonance Enhanced Multiphoton and
Single-Photon Ionization
of
Molecules and Molecular Fragments*

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I. Background and Objectives

Resonance enhanced multiphoton ionization (REMPI) utilizes pulsed laser radiation to prepare a molecule in an excited state via absorption of one or more photons and to subsequently ionize that level before it decays. A remarkable feature of REMPI is that the very narrow bandwidth of laser radiation makes it possible to select a specific rotational level in the initial (ground) state and to prepare the excited state of interest in a single rotational level. Thus, by suitable choice of the excitation step, it is possible to selectively ionize a species that may be present. *This conversion of optical selectivity into chemical selectivity makes REMPI one of the most powerful tools for ultrasensitive detection of trace and transient species.* On the more fundamental side, coupled with high-resolution photoelectron detection, REMPI provides ion rotational distributions for ionization of single rotational levels of excited electronic states. Such state-resolved spectra can clearly provide significant insight into the underlying dynamics of molecular photoionization. Other applications of REMPI include its use for studies of state-selective chemistry and for exploring excited-state chemistry at a quantum-state-specific level. Finally, although REMPI has the distinct advantage that a single rotational level of an excited electronic state is ionized and that it can be achieved with photon energies less than the ionization potential, studies of photoionization of jet-cooled molecules in their ground electronic states by a single photon of coherent vacuum ultraviolet (VUV) radiation are significant in their own right and highly complementary to those of REMPI.

The key objective of our effort is to carry out quantitative studies of REMPI of molecules and molecular fragments, as well as of single-photon ionization of these species by coherent VUV radiation, in order to provide a robust description of significant spectral features of interest in related experiments and needed insight into the underlying dynamics of these spectra. A major focus of our effort is joint theoretical and experimental studies of these ion rotational distributions which are being widely studied by the zero-kinetic-energy (ZEKE) technique. This technique, which is based on the detection of photoelectrons resulting from pulsed-field ionization of very high Rydberg states lying

just below an ion threshold, makes it possible to obtain cation distributions with sub-wavenumber resolution. The unprecedented resolution of this ZEKE technique is opening up entirely new vistas in studies of photoionization dynamics, ion spectroscopy, and state-selected ion-molecule reactions. Emerging applications built on the ultra-high resolution of this technique include its use for accurate determination of thermochemically important ionization energies, for characterization of ion rovibrational level structure of large organic molecules, of elemental clusters, and of weakly bound molecular complexes, for probing reactive fragments, and for pump-probe photoelectron studies of wavepacket dynamics.¹⁻⁵ This surge of experimental activity in ultra-high resolution studies of molecular photoelectron spectra continues to raise new theoretical challenges and has provided the stimulus for several of our collaborations with experimental groups in North America and Europe.

II. *Progress and Highlights*

We will now use a few examples to highlight the progress of our studies of ion rotational distributions from REMPI of excited electronic states of molecules and from single-photon ionization of ground state jet-cooled molecules by coherent VUV and extreme ultraviolet (EUV) radiation. Although we will not discuss the numerical and computational details of the procedures used to obtain the molecular photoelectron orbitals needed in these studies, it is essential to recognize that the quantitative determination of the ion rotational distributions of interest here requires the use of molecular photoelectron orbitals which correctly incorporate the angular momentum coupling present in these wave functions. In contrast to atomic photoelectron orbitals, molecular photoelectron orbitals are not angular momentum eigenfunctions but contain admixtures of angular momenta. This coupling of angular momenta is brought about by the torques associated with the nonspherical potentials of the molecular ions in which the photoelectron moves. This simply reflects the fact that as the photoelectron collides with the ion core, its angular momentum, as well as that of the molecular ion, changes. Such angular-momentum changing collisions between the photoelectron and the ion clearly play a crucial role in determining ion rotational distributions.

In our studies we take the photoelectron orbital to be a solution of a one-electron Schrödinger equation containing the Hartree-Fock potential of the molecular ion, $V_{ion}(\mathbf{r}, R)$,

$$\left(-\frac{1}{2}\nabla^2 + V_{ion}(\mathbf{r}, R) - \frac{k^2}{2}\right)\Psi_{\mathbf{k}}(\mathbf{r}) = 0, \quad (1)$$

where $k^2/2$ is the photoelectron kinetic energy. We obtain these orbitals numerically using an iterative procedure, based on the Schwinger variational principle, to solve the integral (Lippmann-Schwinger) equation associated with eq. (1). A significant feature of this procedure is that it avoids the integration of the coupled integro-differential equations which normally arise in the numerical solution of Schrödinger equations with nonspherical potentials, $V(\mathbf{r}, \theta, \phi)$. The computationally intensive steps of this procedure, which is numerically very stable even at the low photoelectron energies (≈ 0.05 eV) often of interest, are single-center expansions of a large number of multicenter basis functions and operators and subsequent use of these expansions in numerical quadratures of radial integrals.^{6,7}

(a) ZEKE Photoelectron Spectra of Sodium-Water and Sodium-Ammonia Complexes

The energetics, structure, dynamics, and spectroscopy of clusters consisting of neutral or ionic metal atoms and polar solvent molecules are of significant interest in studies of chemical reactions, electron solvation, corrosion, and a wide range of chemical and biological processes. Such clusters composed of a metal complexed with a variety of solvents, particularly those containing alkali metals, are interesting targets of study with ZEKE-PFI techniques. ZEKE-PFI spectra can be very useful in elucidating the molecular structure and intermolecular force fields of these small clusters. A combination of experimental studies and *ab initio* calculations can be very effective in unraveling these ZEKE spectra and, hence, in obtaining structural data from these spectra.

We have carried out such a joint study of the ZEKE photoelectron spectra of small $\text{Na}(\text{H}_2\text{O})_n$ and $\text{Na}(\text{NH}_3)_n$ clusters with Geoffrey Blake of our Department. Experimentally, it is straightforward to produce these clusters in sufficient quantities to detect with ZEKE-PFI, and the wavelengths required for their spectroscopic investigation are easily generated with dye lasers. We have concentrated on measurements of the ZEKE rotational band

contours in the sodium-water and sodium-ammonia complexes and on calculations of these rotational spectra. While agreement between the measured and calculated spectra is quite encouraging, the more significant implication of these results is that they demonstrate how essential calculated spectra are in accounting for the main features of the spectra and their potential for elucidating the molecular structure of the neutral and ionic clusters.⁸

Fig. 1 shows our measured and calculated ZEKE photoelectron spectra for ionization of the $3sa_1$ orbital of the $\tilde{X}^2A_1$ state of NaH_2O by single-photon coherent UV radiation.⁸ The calculated spectra were obtained for a photoelectron energy of 50 meV and were convoluted with a Gaussian detector function with a full-width at half-maximum (FWHM) of 2.2 cm^{-1} . The rotational constants used were derived from the calculated geometry of reference 9. These are $A = 14.157$, $B = 0.280$, and $C = 0.275\text{ cm}^{-1}$ for NaH_2O and $A^+ = 14.157$, $B^+ = 0.309$, and $C^+ = 0.296\text{ cm}^{-1}$ for NaH_2O^+ . Comparison of the measured ZEKE spectra with spectra calculated over a wide temperature range suggests a rotational temperature of about 100 K in these experiments. The spectra in Fig. 1 were calculated at this temperature.

Agreement between the measured and calculated spectra is encouraging. The dominant peak in these spectra belongs to P branch transitions ($\Delta N = -1$). The intensity of this peak is due to a band head. Analysis of the calculated spectra shows that $|\Delta N| = 0-4$ transitions contribute 13%, 62%, 15%, 7%, and 3% of the total cross section, respectively. The dominance of $|\Delta N| = 1$ transitions in the ZEKE spectra for photoionization of this $3sa_1$ orbital with its 91% s character is surprising and very nonatomiclike since, on the basis of angular momentum considerations, i.e., $|\Delta N| \leq \ell + 1$, the $s(\ell = 0)$ wave of the photoelectron drives $|\Delta N| = 1$ transitions. This $s \rightarrow s$ behavior is highly unusual for photoionization of an essentially 3s orbital of sodium where atomiclike propensity rules would suggest a strong p-wave photoelectron matrix element. In fact, our calculated photoelectron matrix elements show an *unusually strong s-wave component*. Even partial wave components of the photoionization matrix element account for about 70% of the total cross section. Our calculated rotationally resolved photoelectron spectra and the underlying dynamical coefficients account quite well for the principal features of these spectra.⁸

To explore the utility of studies of this kind in elucidating the molecular structure of these neutral and charged clusters, it is instructive to see how changes in the geometry influence the contour of the calculated ZEKE spectra. With such small B and C constants (the A constant does not play a role in determining the "end-over-end" rotational spacing), a slight change in B and C can lead to dramatic change in the spectral profile since, at a temperature of 100 K, more than 300 transitions contribute to the spectrum. The P branch peak intensity and its underlying band head make this an interesting case study. Fig. 2 shows the calculated spectrum for slight changes in the rotational constants to $B = 0.295$ and $C = 0.283 \text{ cm}^{-1}$ for NaH_2O and $B^+ = 0.298$ and $C^+ = 0.286 \text{ cm}^{-1}$ for NaH_2O^+ but with the previous value for the A and A^+ rotational constants. This change reflects about a 2% decrease in the $\text{Na}\cdots\text{O}$ bond length from 2.36 to 2.32 Å. These new rotational constants result in a shift of only about 2 cm^{-1} in the location of the peak of the rotational contour. However, the calculated spectrum shows a dramatically different profile. It is now the Q branch ($\Delta N = 0$) which has the highest peak intensity, even though it contributes only 13% of the cross section, since the similarity of the rotational constants in the neutral and ion precludes formation of P or R band heads. The apparent agreement between these calculated and measured spectra is quite good and may even suggest that the actual rotational constants may be close to these modified values. Comparison of experimental and calculated constants for such clusters can have large uncertainties due to excessive vibrational averaging, present in simple fits to spectra, but which would require an accurate knowledge of the global intermolecular potential energy surface to be included in theoretical treatments. In this context, both the intermolecular stretching and out-of-plane bending modes,¹⁰ may contribute to such certainties here in the rotational constants.

Fig. 3 shows measured and calculated ZEKE photoelectron spectra for ionization of the $3s a_1$ orbital of the $\tilde{X}^2 A_1$ state of NaNH_3 . The dominant peak in the measured and calculated spectra again belongs to P branch transitions and is also due to a band head. The calculated spectra also show a higher intensity profile at large photon energies than seen in the measured spectra. Overall agreement between these spectra, however, is quite good.

Comparison of these spectra with those of NaH_2O can reveal differences due to solvation effects. For example, the $3s a_1$ orbital of NaNH_3 has 69% s and 24% p character about the center-of-mass compared to values of 91% s and 7% p in the case of NaH_2O . This increased delocalization in NaNH_3 should lead to changes in the photoelectron spectra. Analysis of the calculated spectrum of Fig. 3 shows that $|\Delta N| = 0 - 4$ transitions contribute 14%, 45%, 23%, 10%, and 7% of the total cross section. Again the dominance of the $|\Delta N| = 1$ branches is due to a surprisingly strong and nonatomiclike s-wave component of the photoionization matrix element. Also, the close to 20% contribution from $|\Delta N| = 3$ and 4 transitions arises from f -wave ($\ell = 3$) components of the photoelectron matrix element. These $|\Delta N| \geq 3$ transitions are about twice as large in NaNH_3 than in the NaH_2O complex. Furthermore, with their large $\text{Na} \cdots \text{N}$ and $\text{Na} \cdots \text{O}$ bond lengths, one would expect photoionization of these complexes to occur mainly along the a principal axis. This is indeed the case of NaH_2O where 98% of the cross section is associated with transitions possessing no change in angular momentum about K_a , i.e., $\Delta K = 0$. However, with ammonia as a solvent, only about 60% of the cross section is associated with $\Delta K = 0$ transitions. Such differences provide useful insight into the structure of these complexes.

Improved resolution in the measured ZEKE-PFI spectra would provide even greater insight into the structure and dynamics of these clusters. Several routes to such spectra are being explored. For example, in contrast to the pick-up source currently used, laser vaporization offers colder rotational temperatures and would dramatically decrease the number of levels contributing to the ZEKE photoelectron signal. Alternatively, multiphoton ZEKE-PFI studies can be performed in which one laser selects an individual eigenstate of the neutral precursor, which is subsequently excited to a high- n Rydberg level and pulse-field ionized. For these clusters, the first step could involve either electronic excitation of the metal itself or vibrational excitation of intermolecular modes within the solvent. Such efforts are currently underway for these NaH_2O and NaNH_3 complexes.

(b) Energy-Dispersive High-Resolution Photoelectron Spectra of Polyatomic Molecules

While ZEKE photoelectron spectroscopy, with its subwavenumber resolution, can now provide ion rotational distributions for polyatomic molecules, the technique is restricted to the threshold region and does not permit studies at photoelectron energies away from the threshold region. Studies at higher photoelectron energies can display dynamical behavior not apparent in near-threshold studies. This is particularly true of features arising from Cooper minima. Energy-dispersive photoelectron analyzers have provided rotationally resolved spectra for light systems such as NO and high J levels of heavier diatomics, e.g., NO and OH, which have highlighted significant dynamical features of molecular photoionization in these systems. However, rotational resolution for non-threshold photoionization of a triatomic or larger molecule has been beyond the reach of conventional photoelectron analyzers. In a recent Communication,¹¹ we reported on the results of measurements and *ab initio* calculations of the first rotationally resolved, energy-dispersive photoelectron spectra for photoionization of water, a prototypical asymmetric top molecule. These spectra were the first rotationally resolved, REMPI photoelectron spectra for low rotational levels of any molecule other than H₂ at an energy significantly above threshold. We reported measured and calculated spectra for one rotational level (4₁₃) of the $\tilde{C}^1B_1$ (0,0,0) state of H₂O at a single photoelectron energy of 0.87 eV. Comparison of the measured spectra with calculated ion yield distributions was excellent and revealed very nonatomiclike behavior and the influence of *multiple Cooper minima* in the photoelectron channels. These Cooper minima can be clearly seen around 2 eV in the photoelectron matrix elements shown in Fig. 4.

To further explore the photoelectron dynamics of this polyatomic system in the region of these multiple Cooper minima, we have carried out calculations and measurements of these ion rotational distributions for a number of initial rotational levels of the $\tilde{C}$ (0,0,0) state at four different photoelectron energies ranging from 0.22 to 2.4 eV. Significant changes in the rotational distributions were seen in the measured spectra as the photoelectron energy was varied. Figs. 5 and 6 show these measured and calculated spectra for (2 + 1') REMPI of the 4₀₄ (N_{K_a,K_c}) rotational level at photoelectron energies of 0.87 and 2.4 eV, respectively. The dependence of these spectra on initial rotational level and photoelectron

energy is substantially reproduced in the calculations which properly account for the presence of multiple Cooper minima and strong nonatomiclike behavior of the photoelectron wavefunctions.

(c) Ion Rotational Distributions of the SH Radical

We have completed combined theoretical and experimental studies of the photoelectron spectra for REMPI of the SH radical via the $[a^1\Delta]3d\pi^2\Phi$ state.¹² These were the first studies of rotationally resolved photoelectron spectra of an excited electronic state of a diatomic hydride with high orbital angular momentum ($\Lambda' = 3$). These spectra display two very striking features. First, whereas up to ΔN (change in angular momentum, exclusive of spin, upon ionization) = ± 4 transitions are expected for photoionization of a $3d\pi$ orbital on the basis of angular momentum conservation, the largest ΔN transitions observed are ± 2 . Secondly, these photoelectron spectra show strong asymmetries between the $\Delta N = +1$ and -1 peaks and $\Delta N = +2$ and -2 peaks. Although minor asymmetries in ion rotational distributions are not exceptional, the strong asymmetry observed in these spectra is highly unusual.

Figs. 7(a) and (b) show the measured and calculated photoelectron spectra respectively for ionization of the $^2\Phi$ ($[a^1\Delta]3d\pi$, $v' = 0$, $N' = 11$) state of SH by (2+1) REMPI via the $S_{11}(19/2)$ rotational branch. Both calculated and measured spectra show only small changes in total angular momentum ($|\Delta N| \leq 2$) upon ionization. On the basis of conservation of angular momentum, i.e., $|\Delta N| \leq \ell + 1$, where ℓ is the photoelectron's angular momentum, *the observation of branches with $|\Delta N| \leq 2$ would imply that the photoelectron continuum is dominated by s and p partial waves.* This differs from expectations based on the calculated magnitudes of the photoelectron matrix element which show that the $\ell = 3$ partial wave is dominant in all three channels for ionization of this $3d\pi$ orbital, i.e., $3d\pi \rightarrow k\sigma, k\pi$, and $k\delta$. That larger changes (up to $\Delta N = \pm 4$) in angular momentum are not seen in these spectra, in spite of the significant magnitude of the f wave photoelectron matrix element, is due to interference between the $f(\ell = 3)$ waves in the different (σ , π ,

and δ) photoelectron continua. For example, an arbitrary change in the phase of one of these photoelectron continua resulted in spectra with strong $\Delta N = \pm 4$ peaks.

These spectra also show strong asymmetries between the $\Delta N = \pm 1$ peaks and between the $\Delta N = \pm 2$ peaks. These asymmetries represent unusually large deviations from the classical picture which would predict that gaining or losing angular momentum upon ionization should occur with equal probability. To provide further insight into the underlying dynamical reasons for these asymmetries. Fig. 8 shows calculated spectra for individual $e \rightarrow e$ ($f \rightarrow f$) and $e \rightarrow f$ ($f \rightarrow e$) parity transitions. These spectra along with parity selection rules¹³ show that $\Delta N = \text{even}$ transitions are expected when there is no parity change between the resonant and ionic states ($e \rightarrow e$ and $f \rightarrow f$ transitions) while $\Delta N = \text{odd}$ transitions are expected when there is a change of parity. Strong asymmetries for losing ($\Delta N < 0$) or gaining ($\Delta N > 0$) angular momentum clearly occur in both parity transitions. *The calculated spectra of Fig. 8 show that the measured spectra of Fig. 7, in fact, directly provide the contributions of the specific parity components of this transition.*

The nonclassical asymmetries seen in the spectra of Figs. 7 and 8 are essentially due to the large component of electronic orbital angular momentum along the internuclear axis ($\Lambda' = 3$) associated with a Φ state and the relatively low rotational angular momentum (≈ 10) of the molecule. To reach the classical limit for this large Λ' requires a correspondingly large rotational angular momentum. In such a limit, one would expect an almost symmetrical profile. In fact, calculated spectra for rotational levels up to $J' = 50$ revealed very symmetrical patterns at high J' 's.

(d) Rotationally Resolved Photoelectron Spectroscopy of the Vanadium Dimer

The elucidation of the electronic and geometric structure of transition metal clusters remains a challenging problem. Although a wealth of spectroscopic information has been obtained on neutral transition metal dimers,¹⁴ very little is known about trimers and higher clusters. Moreover, with regard to transition metal cluster cations, there is a severe lack of gas-phase spectroscopic data, even for diatomics.

ZEKE photoelectron spectroscopy is a powerful technique for addressing these problems. Recently Yang *et al.*¹⁵ have exploited this technique to study the electronic structure of the vanadium dimer cation. Rotationally resolved ZEKE spectra were obtained by $(1+1')$ REMPI of the $A\ ^3\Pi_u$ excited state of V_2 . Striking differences were observed in the ion rotational spectra recorded through the $^3\Pi_{1u}$ spin-orbit component and those recorded through the $^3\Pi_{2u}$ component, where a wide range of J^+ values are accessed, as opposed to only two in the case of the $^3\Pi_{1u}$ component.

To provide a quantitative description of the underlying dynamics of these features, we have calculated the ZEKE photoelectron spectra of the $X\ ^4\Sigma_g^-$ ground state of V_2^+ for $(1+1')$ REMPI of the $A\ ^3\Pi_u$ state. Figs. 9 and 10 show calculated and measured ZEKE photoelectron spectra for the $A\ ^3\Pi_{1u}$ state of V_2 with the excitation laser tuned to the R(7) line in the $A\ ^3\Pi_{1u} \leftarrow X\ ^3\Sigma_{0g}^-$ band and for the $A\ ^3\Pi_{2u}$ state with the excitation laser tuned to the R(6) line in the $A\ ^3\Pi_{2u} \leftarrow X\ ^3\Sigma_{1g}^-$ band, respectively. Agreement between these measured and calculated spectra is quite encouraging. Due to selection rules, the photoelectron spectra of Fig. 9 for the $A\ ^3\Pi_{1u}$ state show transitions only to the $^4\Sigma_{\frac{1}{2}g}^-$ spin-orbit component of the ion. Furthermore, since on the basis of parity selection rules,¹³ only the *e* parity component of the $J' = 8$ rotational level is accessed in this R(7) excitation, the number of J^+ rotational levels for the $X\ ^4\Sigma_g^-$ state of V_2^+ is significantly reduced. The agreement between the measured and calculated spectra is reasonable except for the 6.5(*f*) and 9.5(*e*) peaks, where our calculated intensities are somewhat stronger than the measured values.

Fig. 10 shows the calculated and measured ZEKE photoelectron spectra for $(1+1')$ REMPI of the $A\ ^3\Pi_{2u}$ state of V_2 with the excitation laser tuned to the R(6) line in the $A\ ^3\Pi_{2u} \leftarrow X\ ^3\Sigma_{1g}^-$ band. For this $A\ ^3\Pi_{2u}$ spin-orbit component, both the $X\ ^4\Sigma_{\frac{1}{2}g}^-$ and $X\ ^4\Sigma_{\frac{3}{2}g}^-$ components of the cation are accessible. Agreement with the measured and calculated spectra is encouraging except for the peak for the $J^+ = 8.5$ (*e*) and 6.5(*f*) levels which shows a weaker intensity in the calculated spectra. Since the $X\ ^3\Sigma_{1g}^-$ spin-orbit component of the ground state contains both *e* and *f* parities for each rotational level, which are assumed to have equal populations, both the *e* and *f* parities of the $J' = 7$

rotational level of the $A\ ^3\Pi_{2u}$ component are excited. *A wider range of J^+ rotational levels would hence be expected to arise here than for excitation via the $A\ ^3\Pi_{1u}$ component.*

(e) Photoion Rotational Distributions from Near-Threshold to Deep in the Continuum

While there have been widespread and successful efforts to probe rotationally resolved aspects of photoionization, work to date has been geared primarily towards understanding the rotational dynamics in the threshold or near-threshold region. Extension of such studies to higher photoelectron energies can potentially display dynamical behavior which may not be apparent from near-threshold studies. The requirement of extensive spectral coverage presents a serious obstacle for studying rotational distributions in molecular photoionization. For example, energy spacings between adjacent rotational levels, even for favorable diatomic systems, are on the order of 4 cm^{-1} ($500\ \mu\text{-volts}$). Hence, to achieve rotational resolution at 200 eV, resolving powers in excess of 10^6 are required. This is many orders of magnitude beyond the limits of the highest resolution photoelectron spectroscopy at comparable energies. *The strategy of choice for generating such rotationally resolved data over a broad spectral range is clearly detection of dispersed fluorescence from excited photoions.* Furthermore, by observing fluorescence, the detection bandwidth is uncoupled from, and therefore not limited by, the excitation bandwidth, thus making it possible to exploit the broad tunability of synchrotron radiation.

Poliakoff and his coworkers have recently exploited this strategy to carry out the first measurements of ion rotational distributions for photoionization over an extended range [$0 \leq E_K \leq 200\text{ eV}$ for $\text{N}_2\ (2\sigma_u^{-1})$ and $3 \leq E_K \leq 125\text{ eV}$ for $\text{CO}\ (4\sigma^{-1})$]. These results offered the first indication that truly molecular aspects and even chemically specific aspects may persist far from the ionization threshold. For example, the N_2 ion rotational distributions were seen to change dramatically over this energy range, indicating characteristically molecular behavior deep in the photoelectron continuum. In addition, the N_2 and CO results show a strikingly different dependence on energy. We seized this opportunity to use our procedures to calculate these ion rotational distributions for N_2 and CO over this broad spectral range. The agreement between the measured and calculated ion rotational

distributions is excellent.¹⁶ These calculations show that the observed behavior arises from the presence of Cooper minima in the $2\sigma_u \rightarrow k\sigma_g$ continuum in the case of N_2 and from an f -wave shape resonance in the $4\sigma \rightarrow k\sigma$ channel in CO. These studies also indicate that the photoions retain significant alignment even at high energies.

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

Relative Intensity

Relative Intensity

Fig. 5

Relative Intensity

Relative Intensity

Fig. 6

Measured and calculated photoelectron spectra for ionization of the $^2\Phi([a^1\Delta]3d\pi, v'=0, N'=11)$ state of SH by (2+1) REMPI via the $S_{11}(19/2)$ rotational branch.

The $e \rightarrow e(f \rightarrow f)$ and $e \rightarrow f(f \rightarrow e)$ parity contributions to the photoelectron spectra for ionization of the ${}^2\Phi([a'\Delta]3d\pi, v'=0, N'=11)$ state of SH by (2+1) REMPI via the S_{11} (19/2) rotational branch.

The (a) measured and (b) calculated PFI-ZEKE photoelectron spectra for (1+1') REMPI via the R(7) line of the $A^3\Pi_{1u} \leftarrow X^3\Sigma_{0g}^-$ band. The e/f labels indicate the parity of the ion rotational levels.

The (a) measured and (b) calculated PFI-ZEKE photoelectron spectra for (1+1') REMPI via the R(6) line of the $A^3\Pi_{2u} \leftarrow X^3\Sigma^-_{1g}$ band. The e/f labels indicate the parity of the ion rotational levels. The calculated spectrum is convoluted with a Gaussian detection function with an FWHM of 1.75 cm^{-1} and assumes a kinetic energy of 50 meV.

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IV. *Presentations Based on this Research:*

1. Presentation: *Studies of Molecular Photoelectron Spectra at Close-to-Threshold Energies*, Invited Talk at the International Workshop on New Theoretical Concepts in ZEKE Spectroscopy, Kreuth, Germany, July 1997.
2. *Rotational Distributions at Near-Threshold Photoelectron Energies*, Invited Talk in the Symposium on State-to-State Scattering Studies in the Production and Reactivity of Molecular Photons, National ACS Meeting, New Orleans, LA, March 1996.
3. *Highly State-Resolved Studies of Molecular Photoelectron Spectra*, Invited Talk at the Department of Chemistry, UCLA, Los Angeles, CA, May 1996.
4. Presentation: *Ion Rotational Distributions at Near-Threshold Photoelectron Energies*, Invited Talk at the University of Amsterdam, The Netherlands, September 1996.
5. Presentation: *State-Resolved Studies of Molecular Photoionization*, Invited Talk at the University of Utrecht, Utrecht, The Netherlands, September 1996.
6. Presentation: *Ion distributions at Low-Photoelectron Energies*, Invited Talk at the International Workshop on Photoionization Dynamics, Rydberg States and Large-Amplitude Motion, York, United Kingdom, November 1996.

7. Presentation: *Ab initio ZEKE Spectra*, Invited Talk at the Ciba Foundation/Royal Society Discussion Meeting on The Future of Rydberg Spectroscopy, London, United Kingdom, November 1996.
8. Invited seminar entitled *Rotational Distributions at Near-Threshold Photoelectron Energies*, Emory University (Atlanta, GA), March 31, 1995.
9. Invited lecture entitled *Ion Rotational Distributions at Low and High Photoelectron Energies*, at the International Symposium on Atomic and Molecular Dynamics in Photoionization (Quebec, Canada), July 19-22, 1995.
10. Invited lecture entitled *Ion Rotational Distributions at Low Photoelectron Energies*, at the Twenty-third International Symposium on Free Radicals (Victoria, Canada), August 13-18, 1995.
11. Invited lecture entitled *Rotationally Resolved Molecular Photoelectron Spectra*, at the European Workshop on Photoionization and Ion Spectroscopy (Rottach-Egern, Bavaria, Germany), September 25-29, 1994.
12. Invited lecture entitled *High-Resolution Laser Induced Photoionization in Molecules*, at the International Workshop on Photoionization (San Francisco), October 23-27, 1994.