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LETTERS TO THE EDITOR

The Letters to the Editor section is divided into four categories entitled Communications, Notes, Comments, and Errata. Communications are limited to three and one half journal pages, and Notes, Comments, and Errata are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 1995 issue.

COMMUNICATIONS

Rotationally resolved photoelectron spectroscopy of the $[a^1\Delta]3d\pi^2\Phi$ Rydberg state of the SH radical

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Results of calculated and measured photoelectron spectra via the $[a^1\Delta]3d\pi^2\Phi$ state of SH are reported. These spectra show a strong asymmetry away from classical expectations and only transitions up to $\Delta N = \pm 2$ are observed, in contrast to $\Delta N = \pm 4$ expected for photoionization of a $3d\pi$ orbital. Agreement between the calculated and measured spectra is excellent. © 1995 American Institute of Physics.

Resonance enhanced multiphoton ionization in combination with high-resolution photoelectron spectroscopy (REMPI-PES) constitutes a powerful tool for studying molecular excited states and their photoionization dynamics.^{1,2} Of particular interest is the application of the method to simple diatomic radicals which can be produced by photodissociation of commonly available precursors. Such transient species often play a crucial role as intermediates in atmospheric reactions under the influence of solar radiation and in combustion processes, and may occur as long-lived molecules in circumstellar space. Recently, we have employed REMPI-PES to characterize the spectroscopy and photoionization dynamics of the hitherto unobserved $[a^1\Delta]3d\pi^2\Phi$ state of SH radical.³ The main configuration of this state essentially consists of a $3d\pi$ Rydberg electron with an $a^1\Delta$ excited ionic core.

This letter reports the first application of rotationally resolved photoelectron spectroscopy to a resonantly prepared excited state in a diatomic hydride with high orbital angular momentum ($\Lambda' = 3$). This work reveals unprecedented asymmetries in the photoionization rotational branching ratios to the excited $a^1\Delta$ state of SH^+ , located at ~ 1.23 eV above the $X^3\Sigma^-$ ground ionic state.^{4,5} These asymmetries will be shown to arise from unusually large deviations from the classical picture which would predict that gaining or losing angular momentum on ionization should occur with equal probability. Furthermore, whereas up to $\Delta N = \pm 4$ transitions can be expected for photoionization of a $3d\pi$ orbital on the basis of angular momentum conservation, the largest ΔN transitions observed are ± 2 .

SH radicals are produced in their $^2\Pi(v'' = 0)$ ground state with a 3:2 population ratio⁶ in the 3/2 and 1/2 spin-orbit components via excitation of H_2S (99.6%, Messer Griesheim) to its first dissociative absorption band at 180–270 nm. Since the photodissociation efficiency appears to be a smooth function of the wavelength, the same pho-

tons can be used to perform REMPI spectroscopy. The $[a^1\Delta]3d\pi^2\Phi$ ($v' = 0$) Rydberg state is prepared via two-photon absorption from the radical ground state in the two-photon range between 77500 and 78500 cm^{-1} . A core-preserving ionization to the $a^1\Delta$ excited ionic state is subsequently achieved by absorption of one additional photon. Excitation spectra obtained by scanning the laser wavelength and collecting the core-preserving photoelectrons show a rich rotational structure from which accurate spectroscopic parameters for this $^2\Phi$ state can be derived. Rotationally resolved photoelectron spectra have been obtained for a large number of resonances by employing a sensitive magnetic bottle electron spectrometer. Despite the photoelectron line widths of approximately 12 meV arising from the fact that the radicals are produced with a significant degree of translational energy, the separation between rotational levels in the ion still exceeds this translational broadening if sufficiently high rotational quantum numbers N^+ can be accessed. Since the $^2\Phi$ state is strongly Rydberg in character, rotationally resolved photoelectron spectra can only be observed with sufficient counting statistics for transitions with $\Delta v = v^+ - v' = 0$.

Figure 1(a) shows the measured photoelectron spectrum for the $^2\Phi(v' = 0, N' = 11) \rightarrow a^1\Delta(v^+ = 0, N^+)$ transition of SH, obtained after excitation via the $S_{11}(19/2)$ rotational transition. A detailed discussion of transitions via other rotational branches will be the subject of a separate paper in which the photoionization dynamics via the $[a^1\Delta]5p\pi^2\Phi$ Rydberg state will also be discussed.⁷ The spectrum shows a relatively small $\Delta N = N^+ - N' = 0$ transition, while strong asymmetries between the $\Delta N = +1$ and -1 peaks and $\Delta N = +2$ and -2 peaks are apparent. Although minor asymmetries in rotational ion distributions are not exceptional,^{8–10} the present observation is highly unusual. Moreover, in an atomiclike picture one would expect that on removal of a $3d\pi$ Rydberg electron the

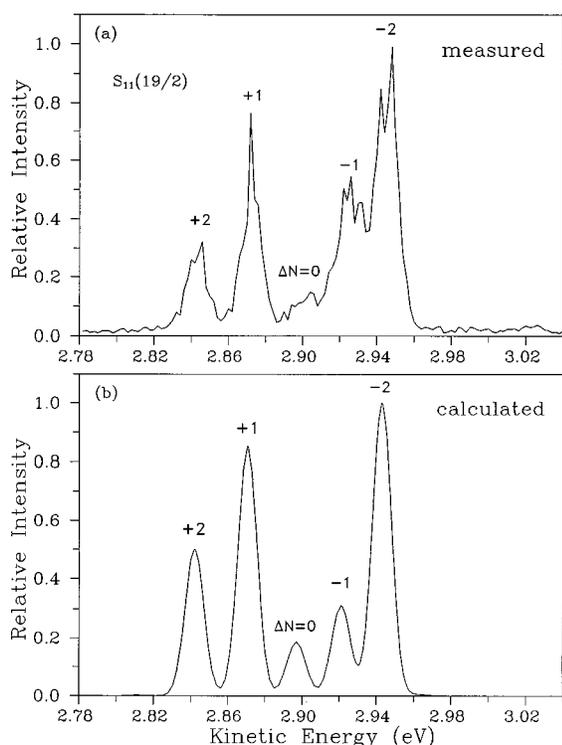


FIG. 1. Measured and calculated photoelectron spectra for ionization of the ${}^2\Phi([a^1\Delta]3d\pi, v'=0, N'=11)$ state of SH by (2+1) REMPI via the $S_{11}(19/2)$ rotational branch.

resulting partial waves of the photoelectron matrix element would be of kp ($l=1$) and kf ($l=3$) character, from which a rotationally resolved ion distribution with transitions up to $\Delta N=\pm 4$ would be predicted.^{11,12} From Fig. 1 it is clear that $\Delta N=\pm 3$ and ± 4 transitions have negligible intensities. An explanation of the underlying dynamics of these unusual features is clearly of interest.

Figure 1(b) shows the results of *ab initio* calculations of the rotationally resolved photoelectron spectrum for this ionization process. The calculated spectrum is convoluted with a Gaussian detector function with a full width at half maximum of 12 meV. In these calculations, the resonant intermediate state as well as the electronic continuum final state are treated at Hartree–Fock level employing multiplet-specific final-state ion potentials. A coupling scheme intermediate between Hund's cases (a) and (b) is used to describe the resonant and ionic states. At the internuclear distance of 2.6 a.u., the $3d\pi$ orbital of the $[a^1\Delta]3d\pi^2\Phi$ state has 5.04% p , 94.51% d , 0.39% f , and 0.05% g character, indicating a relatively pure Rydberg state. The rotational constants of the $a^1\Delta$ state of the ion and the ${}^2\Phi$ Rydberg state are 9.186 cm^{-1} and 8.855 cm^{-1} , respectively.³ The effects of alignment following the two-photon absorption to the excited ${}^2\Phi$ state have been included. Possible effects on the rotational ion distributions of ground state alignment in the SH fragments as the result of the H_2S photodissociation step have been neglected in our calculations. Agreement between experimental and calculated spectra is excellent. This level of agreement between measured and calculated spectra is seen for ionization via a large number of resonances.

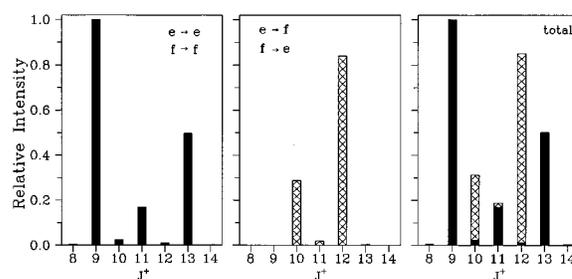


FIG. 2. The $e\rightarrow e$ ($f\rightarrow f$) and $e\rightarrow f$ ($f\rightarrow e$) parity contributions to the photoelectron spectra for ionization of the ${}^2\Phi([a^1\Delta]3d\pi, v'=0, N'=11)$ state of SH by (2+1) REMPI via the $S_{11}(19/2)$ rotational branch.

Both calculated and measured spectra of Fig. 1 show only small changes in total angular momentum ($|\Delta N|\leq 2$). From conservation of angular momentum, the observation of branches with $|\Delta N|\leq 2$ implies that the photoelectron continua are dominated by the s and p partial waves. This differs from expectations based on the calculated magnitudes of the photoelectron matrix element.⁷ These calculations show that the $l=3$ partial wave is dominant in the $3d\pi\rightarrow k\sigma, k\pi, k\delta$ channels for photoelectron kinetic energies of interest. That such large 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 probably due to interference between the f waves in the different photoelectron continua. To test this assumption, we arbitrarily varied the phase factor in one of the photoelectron channels (for example, a $1/4\pi$ phase shift in the $k\pi$ channel). The resulting spectra showed strong $\Delta N=\pm 3$ and ± 4 peaks. Such interference effects have also been observed in other diatomic systems.^{10,13}

The most striking feature of these photoelectron spectra is the strong asymmetries between the $\Delta N=\pm 1$ transitions and between the $\Delta N=\pm 2$ peaks. Even though slight discrepancies in intensities are expected in many molecular systems, such a large difference in intensities for losing or gaining the same angular momentum upon ionization is highly unusual and, to our knowledge, has not been previously observed. To provide some further insight into the underlying dynamics, Fig. 2 shows calculated spectra for individual $e\rightarrow e$ ($f\rightarrow f$) and $e\rightarrow f$ ($f\rightarrow e$) parity transitions. These spectra, along with the parity selection rule $\Delta J+\Delta S+\Delta p+l=\text{even}$,^{11,12} with p the parity index, indicate that the contribution from even waves of the photoelectron matrix element is minor. Since the f wave is dominant, $\Delta N=\text{even}$ transitions are expected when there is no parity change between resonant and ionic states (i.e., $e\rightarrow e$ and $f\rightarrow f$ transitions) while $\Delta N=\text{odd}$ transitions are expected when there is change in parity. Clearly, strong asymmetries for losing or gaining angular momentum occur in both parity transitions. Furthermore, comparison of Figs. 1 and 2 shows that the measured spectra, in fact, directly provide the contributions of specific parity components of this transition.

The resonant state has a large component of electronic orbital angular momentum ($\Lambda'=3$) along the internuclear axis, which could play an important role in these asymmetries. To reach the classical limit for large Λ' requires a cor-

respondingly larger rotational angular momentum. In this limit, one would expect an almost symmetrical spectral profile for high rotational levels. To test this idea, we have also calculated the photoelectron spectra for rotational levels up to $J' = 50$. Indeed, the spectra revealed very symmetrical patterns at these high J' 's. Therefore, the present study represents a situation which is rather different from that described by the classical picture of rotational motion. The strong asymmetries observed here underline the need for a full quantum mechanical description of the rotationally resolved photoionization process.

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