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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. 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 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

This letter reports the first application of rotationally resolved photoelectron spectroscopy to a resonantly prepared 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. The main configuration of this state essentially consists of a \(3d\pi\) Rydberg electron with an \(a \,^1\Delta\) excited ionic core.

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resulting partial waves of the photoelectron matrix element would be of \( kp \) \((l=1)\) and \( kf \) \((l=3)\) character, from which a rotational 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 \( \pm 4 \) 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 \( ab \) \textit{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 3\( d \pi \) 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 \( H_2 S \) 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.

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 \( \pm 2 \) 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 continua. To test this assumption, we arbitrarily varied the phase factor in one of the photoelectron continua. To test this assumption, we arbitrarily varied the phase factor in one of the photoelectron continua. To test this assumption, we arbitrarily varied the phase factor in one of the photoelectron continua. To test this assumption, we arbitrarily varied the phase factor in one of the photoelectron continua. To test this assumption, we arbitrarily varied the phase factor in one of the photoelectron continua. To test this assumption, we arbitrarily varied the phase factor in one of the photoelectron continua. To test this assumption, we arbitrarily varied the phase factor in one of the photoelectron continua. To test this assumption, we arbitrarily varied the phase factor in one of the photoelectron continua. To test this assumption, we arbitrarily varied the phase factor in one of the photoelectron continua. To test this assumption, we arbitrarily varied the phase factor in one of the photoelectron continua. To test this assumption, we arbitrarily varied the phase factor in one of the photoelectron continua. To test this assumption, we arbitrarily varied the phase factor in one of the photoelectron continua. To test this assumption, we arbitrarily varied the phase factor in one of the photoelectron continua. To test this assumption, we arbitrarily varied the phase factor in one of the photoelectron continua.

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 \( \Delta J + \Delta \delta + \Delta p = l = \text{even}^{11,12} \) 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, \( \Delta N = \pm 2 \) 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 \( \Lambda’ \) requires a cor-

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

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 \( ^3 \Phi (\{ a^1 \Delta \} 3d \pi, \nu’ = 0, N’ = 11) \) state of SH by \((2 \pm 1)\) REMPI via the \( S_{11}(19/2) \) rotational branch.
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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