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Rotationally Resolved Threshold Photoionization of H_2S

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1. INTRODUCTION

Photoionization leading to a singly charged ion and free electron represents one the simplest molecular fragmentation processes and determination of the final states of the products (ion and photoelectron) provides a complete description of the photoejection dynamics. Quantum characterization of the molecular fragment requires resolution of the internal rovibronic state distribution which in turn reflects the exchanges of energy and angular momentum in the "scattering" of the photoexcited electron and the anisotropic molecular ion potential. With the recent development of zero kinetic energy threshold photoelectron spectroscopy (ZEKE-PES) by Müller-Dethlefs, Schlag and coworkers[1] it is now possible to take advantage of the high resolution capabilities of laser radiation and measure the rotational distributions of many small cations produced via photoionization.

We have used threshold photoelectron spectroscopy in conjunction with a VUV laser source to probe the rotational distributions of several molecular cations following one-photon VUV photoionization.[2-6] Spectra are obtained by the delayed, pulsed field ionization (PFI) method which is a variant of the ZEKE-PES technique as first demonstrated by Reiser, *et al.*[7] The PFI technique takes advantage of the similarity between the distribution of Rydberg levels populated 1–2 cm^{-1} below an ionization threshold and the partial wave distribution of the photoelectron with near zero kinetic energy. The narrowband ($\leq$1 cm^{-1}), tunable VUV radiation required for rotationally resolved photoionization measurements is produced by third harmonic or sum frequency generation of visible and/or near UV laser light in pulsed, free jet expansions of the rare gases (Ar, Kr, Xe) or the diatomic gases CO and N_2.[8,9]

In this paper, we report on the rotationally-resolved threshold photoelectron spectra of the non-linear triatomic H_2S. These measurements are an extension of our earlier study on H_2O which provided the first look at the symmetry properties of allowed rotational transitions in the photoionization of non-linear molecules.[5] For photoionization of asymmetric top systems, transitions between levels involving the rotational angular momentum projections (K_a, K_b, K_c) permit resolution of the photoelectron continua according to symmetry. For H_2O, 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 were observed and these were shown to be associated with ka_2 and ka_1 photoelectron continua, respectively. 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 based on the symmetry properties of the initial state[10] in which the near atomic-like nature of the outermost $1b_1$ molecular orbital is invoked. The PFI results are also the subject of two very recent theoretical calculations which draw very different conclusions concerning the near-threshold photoionization dynamics for H_2O.[11,12] The new spectra reported here for the (000) and (010) states of H_2S^+ exhibit both type A and type C rotational photoionization transitions and coupled

with the previous H_2O^+ results are interpreted as a clear demonstration of the *non-atomic* nature of photoionization from the $1b_1$ orbital in the H_2X (X=O, S) molecules.

2. EXPERIMENTAL

The photoelectron spectrometer and VUV source have been described in detail elsewhere.[9] Briefly, we use a small, separately pumped frequency tripling chamber attached to a standard photoelectron/photoion time–of–flight (TOF) spectrometer. Tunable VUV radiation in the range 118.6–117.0 nm required to reach the H_2S^+, $\tilde{X}^2B_1$ (000) and (010) vibrational bands was produced by $2\omega_{uv} + \omega_{vis}$ sum frequency mixing in Xe gas near the $5p \rightarrow 5d$ and $5p \rightarrow 7s$ atomic resonances, respectively.[13] As a result of poor conversion efficiency at shorter wavelengths, it was not possible to obtain the PFI spectrum for the (100) symmetric stretch. The collinear visible (593.0–583.5 nm; ~40 mj/pulse; 0.07 cm^{-1}, 20 Hz) and UV (296.5–291.8 nm; ~5 mj/pulse) laser beams were focussed by a 100 mm focal length achromatic lens (Optics for Research) inside the tripling chamber and into a pulsed, free jet expansion of Xe. The diverging fundamentals (visible and UV) and sum frequency 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 VUV intensity at the spectrometer is estimated to be $\sim 10^9$ photons per pulse, with an energy bandwidth of 0.7 cm^{-1}.

High-resolution threshold spectra were obtained by the delayed, pulsed field ionization (PFI) method as first demonstrated by Reiser, *et al.*[7] 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 this work (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 the weak interaction of the Rydberg electron and the ion core. A small positive DC voltage (~ 0.05 V) was maintained on the repeller (lower) plate to sweep out any slow or near ZEKE photoelectrons produced directly by the laser pulse. After a delay of 700 ns, a fast, negative pulse ranging in amplitude from $0.3 - 0.5$ volts was applied to the repeller plate. Electrons produced by this pulsed field were readily distinquished from photoelectrons arising from direct ionization as the arrival time of the former depend only on the pulse delay and voltage.

Rotationally cold PFI spectra for H_2S were obtained by expanding 300 Torr of a 5% mixture of H_2S in Ar into the source chamber ($\sim 5 \times 10^{-5}$ Torr) through a pulsed valve (Laser Technics) fitted with a 0.5 mm diameter nozzle. A 1 mm skimmer located 3 cm downstream of the valve collimated the beam so it passed cleanly through the TOF apparatus (background pressure with sample $\sim 2 \times 10^{-7}$). To obtain comparable signal levels for the weaker (010) vibrational band, the distance between the pulsed valve and skimmer was reduced to 1 cm. In assigning rotationally cold spectra, we assume that the populations in the nuclear spin states (ortho and para) do not redistribute during the expansion. For normal H_2S this fixes the ratio of ortho to para at 3:1, regardless of the final rotational temperature. The ortho and para nuclear spin manifolds are then treated separately, each with the same rotational temperature (relative to its lowest energy level) and then normalized to recover the overall 3(ortho):1(para) ratio.

The spectra were placed on an absolute energy scale by calibration to known transitions in H_2 detected via 2-photon (VUV+UV) resonant multiphoton ionization (REMPI).[9,14] and corrected for the small Stark-shift (1-2 cm^{-1}) introduced by the pulsed field. Uncertainties in the wavelength calibration and spectral peak location result in an overall uncertainty of ± 2 cm in the reported ionization energies.

3. RESULTS AND DISCUSSION

3.1 SYMMETRY AND PHOTOIONZATION OF ASYMMETRIC TOPS

For asymmetric tops, the rotational energy levels can be labeled by J_{K_a,K_c} (or $N^+_{K_a,K_c}$ for the cation) where J is the total angular momentum and K_a and K_c describe the projection of the total angular momentum on the symmetry axis for corresponding pure prolate and oblate top wavefunctions. For the ion, N^+ labels the angular momentum excluding spin, and a small spin-orbit splitting results in F_1 and F_2 levels (J=N+1/2 or N-1/2) which we generally do not resolve. We use the convention that the x, y and z axes correspond to the c, a and b molecular axes, where the molecular axes are defined such that $I_a < I_b < I_c$ ($A > B > C$). With this choice of axes, z is the C_2 axis and y the orthogonal in-plane axis. It should be noted that while the energy levels and rotational symmetry of an asymmetric top can be *labelled* with respect to the correlating symmetric top wavefunctions, K_a and K_c are not good quantum numbers, and the true asymmetric top wavefunction is a linear combination of symmetric top functions.

The highest occupied molecular orbital in H_2S is essentially a non-bonding sulfur $3p_x$ orbital pointing out of the molecular plane with b_1 symmetry. Since H_2S is a closed shell molecule, its ground electronic state is A_1 symmetry, and removal of one outer electron yields an ion with $^2B_1$ symmetry. Dipole selection rules require that the final state (ion core + electron) must have A_1, B_1 or B_2 electronic symmetry, corresponding to kb_1, ka_1, and ka_2 Rydberg (or continuum) electrons. Restricting the Rydberg electron to $l \leq 2$, the possible atomic orbitals of A_1 symmetry include s, p_z, d_{z^2} and $d_{x^2-y^2}$. Only d_{xy} orbitals have A_2 symmetry, while p_x and d_{xz} are of B_1 symmetry.

A more detailed analysis of the allowed dipole transitions must include the symmetry of the rotational wavefunctions as well. The overall selection rules were outlined in our earlier paper on H_2O,[5] where it was shown that for outgoing photoelectrons with ka_1 symmetry, $\Delta K_c = 0, \pm 2 \ldots; \Delta K_a = \pm 1, \pm 3 \ldots$, for outgoing ka_2 electrons, $\Delta K_c = \pm 1, \pm 3 \ldots; \Delta K_a = 0, \pm 2 \ldots$, and for outgoing kb_1 electrons, $\Delta K_c = \pm 1, \pm 3 \ldots; \Delta K_a = \pm 1, \pm 3 \ldots$. These transitions are called type C, type A and type B, respectively, corresponding to the axes along which the transition dipoles are located. Type B transitions were shown to be strictly forbidden since they connect ground and ionic state rotational levels of different nuclear spin symmetry.

3.2 PFI SPECTRA OF H_2S

The jet-cooled, PFI spectrum for the $\tilde{X}^2B_1$ (000) and (010) vibrational levels of H_2S^+ are shown in Figures 1 and 2, respectively. The rotational assignments are based on accurate spectroscopic constants for the neutral ground state[15] and the (000) and (010) vibrational levels of the $\tilde{X}^2B_1$ ionic ground state.[16] Transition energies were calculated using the parameterized Hamiltonians given by Townes and Schawlow for rotational energy levels of asymmetric top molecules.[17] Spin doubling of

the H_2S^+ rotational levels is generally smaller than our overall resolution ($\sim$2 cm^{-1}) so that the final ionic levels are labeled by core angular momentum exclusive of spin, *i. e.* $N^+_{K_a,K_c}$. The H_2S^+ spectra are similar to those obtained previously for the (000) and (100) levels of H_2O^+,[5] in that threshold photoionization is accompanied by only small changes in core angular momentum, *i. e.* $\Delta N = 0, \pm 1$ and $\Delta K_{a,c} = 0, \pm 1$ and *both* type C ($\Delta K_c = 0; \Delta K_a = \pm 1$) and type A ($\Delta K_c = \pm 1, \Delta K_a = 0$) transitions are observed. As noted earlier, type A transitions were not expected to appear in the H_2O spectra based on the near-atomic nature of the $1b_1(2p_O) \rightarrow kd$ photoionization transition.[10] Although the type A transitions are generally weaker than type C transitions, the H_2S^+ spectra clearly contain lines which can be unambiquously assigned to type A. Our results for both H_2O and H_2S suggest that the near-atomic nature of the initial state does not exclusively determine the ionization dynamics of the H_2X molecules.

The lower traces in Figs. 1 and 2 are simulations of the one-photon ionization spectra of the (000) and (010) vibrational states assuming uniform line strengths, a ground state rotational temperature of 15 K and a Gaussian line shape with a width of 1 cm^{-1}(FWHM). The absolute energy scales are fixed by taking the ionization potentials to be the energies of the nuclear spin forbidden $0_{00} \leftarrow 0_{00}$ transitions at 84,434 $\pm$ 2 cm^{-1} for the (000) level and 85,592 $\pm$ 2 cm^{-1} for the excited (010) state. These ionization energies can be compared to the rotationally unresolved PES values of 84,413 $\pm$ 2 cm^{-1} and 85,550 $\pm$ 3 cm^{-1} obtained by Karlsson, *et al* using a room temperature gas sample and the He I resonance line (21.2 eV).[18] A type C to type A intensity ratio of 4:1 is found to give the best overall simulations for both vibrational levels and these can be compared to a 2:1 ratio found for H_2O^+.[5] A 2:1 type C to type A intensity ratio for H_2O^+ was rationalized by noting that two da_1 (d_{z^2}, $d_{x^2-y^2}$) final states are allowed for type C transitions while there exists only one da_2 (d_{xy}) final state of the correct symmetry for type A transitions. As will be discussed below, this correlation between type A/type C transition strengths and the number of associated d final states is only fortuitous; type A photoionization transitions in H_2O are actually dominated by $kp(l = 1)$ partial waves which result from torques exerted on the photoexcited electron by the molecular ion potential. Overall, the reasonable agreement between the PFI spectra and the simulations provides confidence in the line assignments as well as in the characterization of the spectra as having nearly independent type C and weaker type A contributions.

Comparison of Figs. 1 and 2 shows that the $\tilde{X}^2B_1$ (000) vibrationless ground state and the (010) bending excited state have virtually identical PFI spectra. Small intensity differences between the $0_{00} \leftarrow 1_{10}$ and $0_{00} \leftarrow 1_{01}$ lines may reflect slightly different rotational temperatures as the (010) required a smaller nozzle-to-skimmer distance (1 cm) to obtain reasonable signal levels. A similar lack of vibrational state dependence was observed in the PFI spectra for the ground (000) and (100) excited symmetric stretch levels of H_2O^+.[5] These results indicate that near threshold photoionization for the H_2X molecules can be treated in a Franck-Condon model in which vibrational motion does not strongly influence the molecular ion potential experienced by the escaping photoelectron.

The absence of transitions with $|\Delta N| > 1$ in the (000) and (010) H_2S^+ spectra also suggests that little angular momentum is transferred between the photoelectron and the ion core, particularly with respect to rotation. Neglecting spin, the range of ΔN is given by $l + 1, \ldots, -l - 1$ and since $l = 2$ partial waves are expected to dominate, transitions with $|\Delta N|$ as high as 3 are possible. Such large changes in core angular momentum occur in the threshold photoionization spectrum of O_2 ($|\Delta N| \leq 5$) and are attributed to the presence of a near-threshold shape resonance which enhances the $l = 3(f\sigma_u)$ partial wave.[2,3] The sensitivity of the shape resonance potential to the

internulear distance also leads to a pronounced vibrational state dependence of the O_2^+ rotational state distribution. The relative simplicity of the H_2O^+ and H_2S^+ rotational spectra are consistent with the predictions of the "rotation spectator" model in which the photoelectron carries away the angular momentum of the incident photon.[19,20] This model was found to be adequate to describe the low resolution threshold photoelectron spectrum of HCl.[21]

3.3 GENERAL ASPECTS OF H_2X (X = O, S) PHOTOIONIZATION

The observation of 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 photoionization transitions in H_2O^+ and H_2S^+ is contrary to the original predictions of Child and Jungen[10] who used MQDT to analyze the high resolution photoionization spectrum of H_2O reported by Page *et al.*[22] Specifically, Child and Jungen predict only type C transitions and moreover, only those with $|\Delta K_a| = \pm 1$ and $|\Delta N| \leq 1$. The 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 with both l and its body fixed projection, λ, equal to one. Although the authors characterize these as propensity rules, they are predicted to become stronger as the upper state approaches the Hund's case (d) limit, *i. e.* as the Rydberg levels converge to the ionization threshold. Our own symmetry analysis of the selection rules for H_2X photoionization showed that, in general, only type B transitions are strictly forbidden (due to nuclear spin considerations) and that there was no *a priori* way to exclude type A transitions without a detailed knowledge of the partial wave distribution of the continuum.[5] Our analysis assumed that the molecular point group symmetry, C_{2v} in this case, was valid for determining the overall symmetry properties of the combined molecular ion core and photoexcited electron complex. This was based on the fact that the absorption process takes place near the ion core where a Hund's case (b) coupling scheme is appropriate for both the ground and ion core–photoelectron excited states. As noted above, the asymptotic, long-range ionization channels are better characterized in a Hund's case (d) basis where the orbital angular momentum l of the photoelectron is well defined. In this basis, symmetry considerations show that type A and type C transitions are associated with continua of a given parity, specifically $l = odd$ with type A and $l = even$ with type C transitions.[10,12] Consequently, $d(l = 2)$ partial waves cannot contribute to both types of transitions and one is left with the conclusions of Child and Jungen, *i. e.*, type A transitions are not likely due to the atomic p_x nature of the outer $1b_1$ orbital and the $\Delta l = \pm 1$ dipole selection rule for atoms.

In an effort to explain the observed PFI spectra of H_2O^+, Gilbert and Child[11] attributed the appearance of type A transitions to field-induced autoionization of nominally very weak np Rydberg states via dipole coupling with strongly allowed and near-degenerate $n'd$ Rydberg levels. This mechanism has many attractive features and has been invoked to explain the observation of anomalous rotational branch intensities in the PFI spectra of N_2O and HCl.[6] However, the PFI spectra for both H_2O^+ and H_2S^+ do not exhibit features which point to field-induced autoionization. The most obvious indication would be the observation of rotational branches with large *positive* changes of core angular momentum ($\Delta N > +1$). In the cases of N_2O[4] and HCl,[6] rotational branches with $\Delta J > 2$ were found to be relatively intense, whereas the corresponding rotational branches differing only in the sign of ΔJ were often not observed. Such unusual intensity distributions are not evident the PFI spectra of H_2O^+ and H_2S^+, neither of which exhibit strong features which can be confidently assigned to $|\Delta N| > 1$. Furthermore, such field-induced autoionization processes are expected to be very sensitive to the density of Rydberg states near successive ionization thresholds.[11] These will vary considerably from H_2O to H_2S which have rotational constants which differ by nearly

a factor two. The observed similarity between the H_2O^+ and H_2S^+ transition types would therefore be quite unexpected. It therefore seems unlikely that field-induced autoionzation is the cause of type A photoionization transitions in the H_2X molecules.

A more straightforward explanation for the appearance of type A transitions is due to a very recent *ab initio* calculation on H_2O by Lee, *et al*[12] using the Schwinger variational method which has been generalized to include cation rotational distributions. 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 results are surprising in that the type A photoionization transitions are predicted with intensities in nearly quantitative agreement with experiment and a partial wave analysis shows these transitions to be accompanied by nearly pure p wave continua. 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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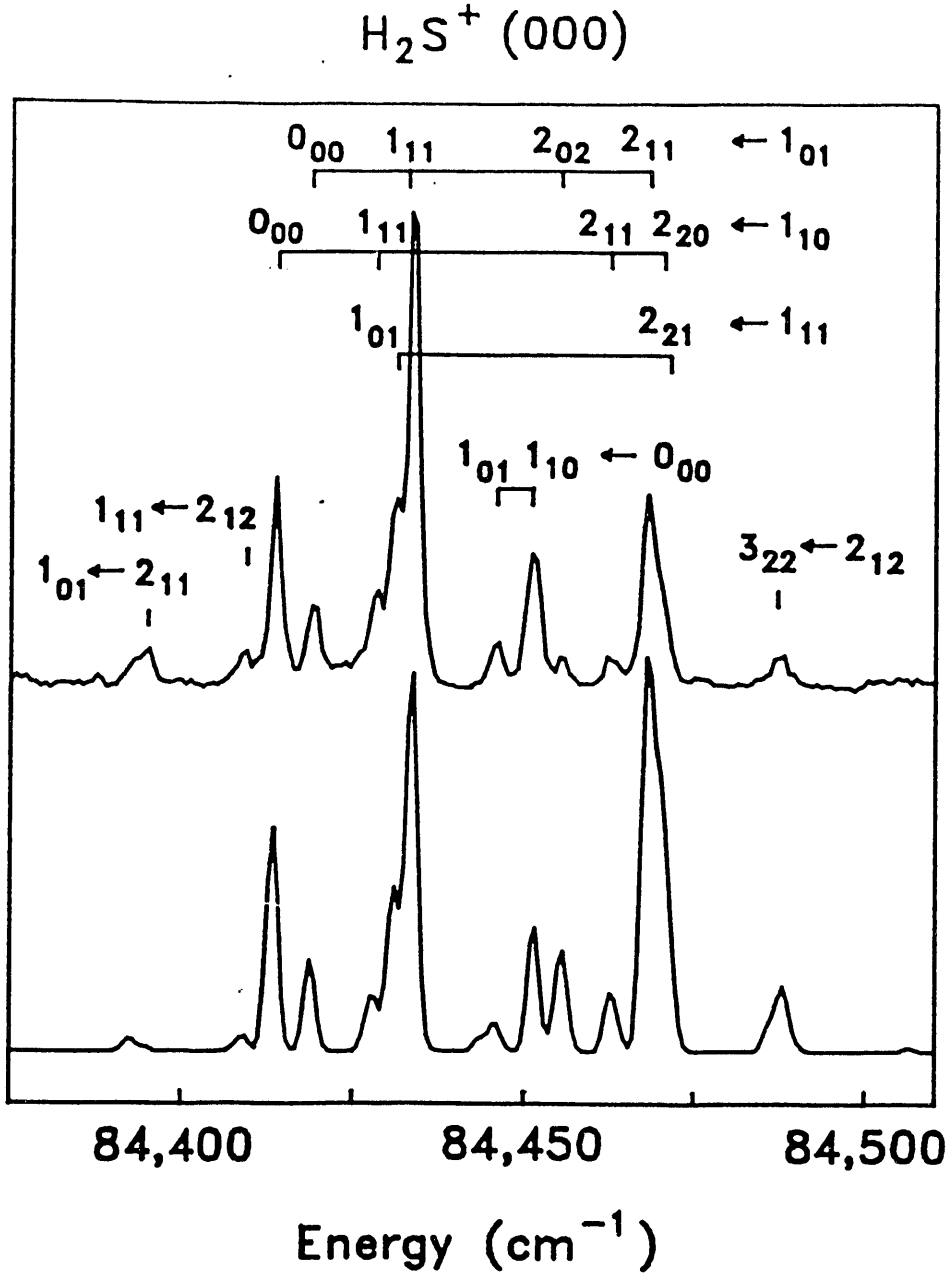

Figure 1: Upper trace: Rotationally-resolved, pulsed field ionization spectrum for one-photon ionization of H_2S to the $\tilde{X}^2B_1$ (000) level of H_2S^+. Lower trace: Simulated photoionization spectrum of H_2S at 15 K including both type A ($\Delta K_c = \pm 1$, $\Delta K_a = 0$) and type of C ($\Delta K_c = 0$; $\Delta K_a = \pm 1$) rotational transitions (1:4 ratio) and assuming ionization energy of 84,434 cm^{-1}.

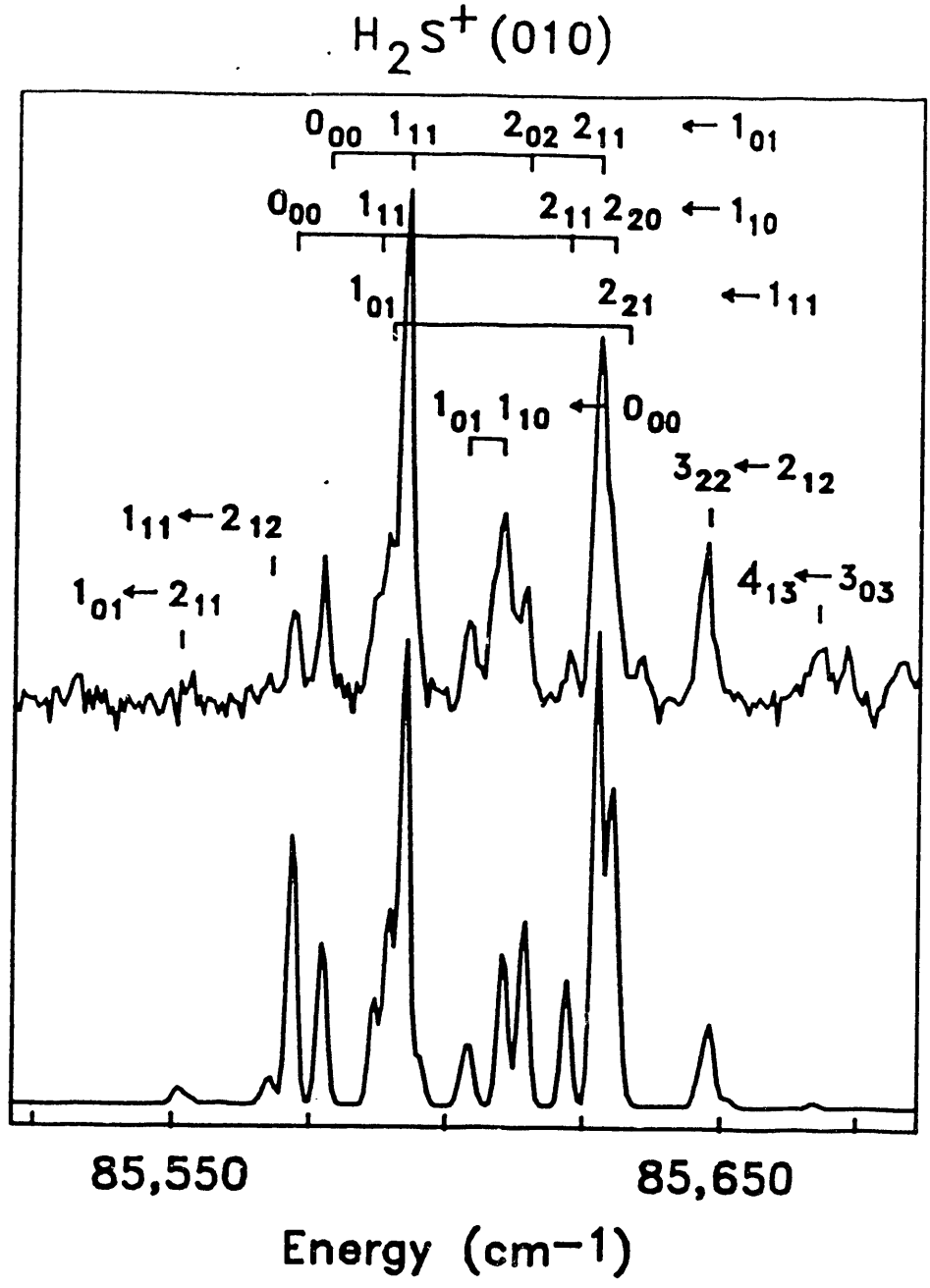

Figure 2: Upper trace: Rotationally-resolved, pulsed field ionization spectrum for one-photon ionization of H_2S to the $\tilde{X}^2B_1$ (010) excited bend level of H_2S^+. Lower trace: Simulated photoionization spectrum of H_2S at 15 K including both type A ($\Delta K_c = \pm 1$, $\Delta K_a = 0$) and type C ($\Delta K_c = 0$; $\Delta K_a = \pm 1$) rotational transitions (1:4 ratio) and assuming an adiabatic ionization energy of 85,592 cm^{-1}.

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