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Low energy electron collisions in H_2S and H_2Se: Structure in dissociative attachment cross-sections

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ABSTRACT

Dissociative electron attachment between 0 and 4 eV has been investigated in hydrogen sulfide and hydrogen selenide with an improved electron resolution (0.040 eV). HS^- and HSe^- cross-sections versus electron energy present vertical onsets revealing that the potential surfaces of the resonances which are reached around 2 eV are bound. A well-developed and intriguing structure is observed in HS^-, S^-, HSe^- and Se^- cross-sections. It could reveal interferences due to an attractive resonance having a lifetime of the order of one vibrational period. The strong similarity between the anion behaviour in H_2S and H_2Se is in contrast with H_2O where no dissociative attachment process occurs in this energy range.

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1. Introduction

Low energy electron scattering with H_2S have been the object of many studies during the last decades, both experimentally [1–8] and theoretically [9–15] implying several resonant states. If calculations are in rather good agreement with scattering measurements, many questions are still open to understand the dissociative processes. Very recently calculations have renewed the interest in the problem. R matrix calculations have been focussed on the elastic scattering and electronic excitation [12]. Using the local complex potential model, detailed dynamics calculations could reproduce the angular behaviour of H^- fragments in H_2O and H_2S [13]. More recent calculations by the same group, taking into account three resonant potential surfaces [14,15] were successful in reproducing qualitatively the dissociation data in H_2O concerning the major negative ions produced. These calculations could possibly be extended to similar processes at low energy in H_2S and H_2Se. It is well known that below about 10 eV, electron collisions with molecules are dominated by the temporary capture of the incident electron by the target, forming a short lived metastable anion ("resonance"), which can decay either by ejection of the incident electron, possibly leaving the molecule vibrationally excited, or by dissociation leading to a stable negative ion, and one or several neutral fragments

via the dissociative electron attachment (DEA) process. Therefore, the knowledge of the character (energy, symmetry, width) of the involved resonances is important to understand electron collisions in a given molecule.

In H_2S between 1 and 10 eV the DEA process is known [1–4] to give rise to HS^-, S^- and H^- anions. To explain the observation of HS^- around 2 eV a shape resonance of $^2A_1$ symmetry was originally proposed [3]. On the other hand, the vibrational excitation cross-section versus electron energy of the stretch modes 0 0 1 and 1 0 0 [5] was displaying, besides a peak at threshold, a structureless cross-section, peaking around 2.5 eV and extending up to 4 eV. It was also presenting an almost isotropic behaviour, in agreement with the proposed $^2A_1$ resonance symmetry.

Angular measurements of H^- anions around 5.5 and 7.5 eV [4], using the O'Malley–Taylor theory, demonstrated that these anions were produced by DEA through $^2B_1$ and $^2A_1$ resonant states. A few years later a theoretical study [10] found a $^2B_2$ resonance to take into account the 2–3 eV energy process, the 6–8 eV region being dominated by a $^2A_1$ resonance. Such a $^2B_2$ resonance was also reported in calculations of elastic scattering in H_2S and H_2Se [11] and also recently by Gupta and Baluja [12]. Despite the convincing assignment of Azria et al. [4] (only one partial wave was involved in their analysis), these authors [12] did not find any evidence of a $^2B_1$ resonance at 5.5 eV. Very recently, Haxton et al. [13] considering a $^2B_1$ resonance, and using the complex local potential model, were able to take into account the overall angular behaviour for the $H^- + HS$ $^2\Pi$ ($v = 0$) process at 5.5 eV, and even have a qualitative agreement for the behaviour of the process $H^- + HS$ $^2\Pi$ ($v = 1$).

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However, they do not mention any other resonance in H_2S, at lower or higher energy. The nature of the resonant states involved in H_2S from 1 to 10 eV appears therefore somewhat controversial and certainly needs to be clarified.

Using an improved electron energy resolution, the present paper deals with detailed observations of HS^- and S^- anion yields versus electron energy produced via DEA processes in the range 0–4 eV. An energy loss spectrum showing high-excited vibrational levels of H_2S is also presented. The well developed structure observed in DEA cross-sections may help to precise the nature of the involved resonant states, and its understanding could be a motivation for improved dynamics calculations on resonant potential surfaces. Similar results in H_2Se are also presented for comparison

2. Experimental

The experimental set up used to study HS^-, S^- and electron scattering in H_2S is an electrostatic electron spectrometer having two hemispherical energy analysers in tandem, both in the electron gun and the analyser section. The energy resolution ranges from 0.025 to 0.060 eV (FWHM) with electron currents ranging from 0.5 to 5 nA. Rotation of the analyser section allows angular behaviour of the scattered electrons. Mass analysis of anions and cations is performed by a time of flight system using a Mc Laren–Wiley geometry, the ions being collected onto microchannel plates. For anions studies, the electron beam is pulsed off during the mass analysis to avoid perturbation of the negative ion signal by the electrons. The energy scale is calibrated using SF_6^- anions at zero energy. H_2Se results have been performed using a magnetic mass spectrometer equipped with a trochoidal monochromator as electron gun [16]. Electron energy resolution used was 0.070 eV with current of about 10 nA. The energy scale was calibrated using the vertical onset of O^-/CO at 9.62 eV.

3. Results

3.1. H_2S

The existence of three separated peaks for S^- ions (Fig. 1) from 1 to 12 eV, as well as the observation of H^- ions at 5.5 and 7.5 eV [4] suggest the occurrence of at least three resonant states. The present study is focussed on HS^-, and S^- ions produced in the energy range 1–4 eV.
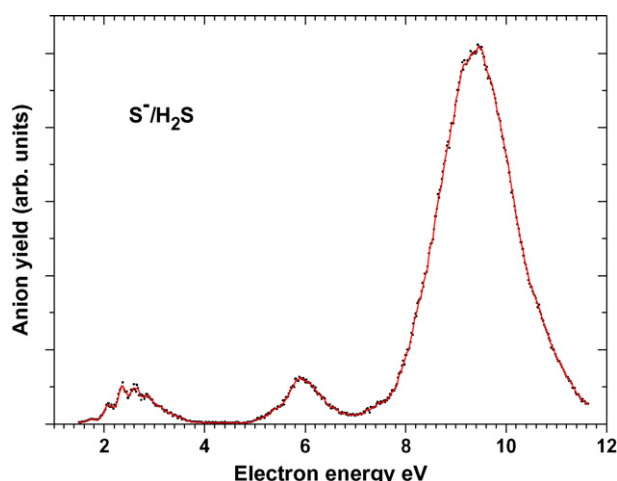

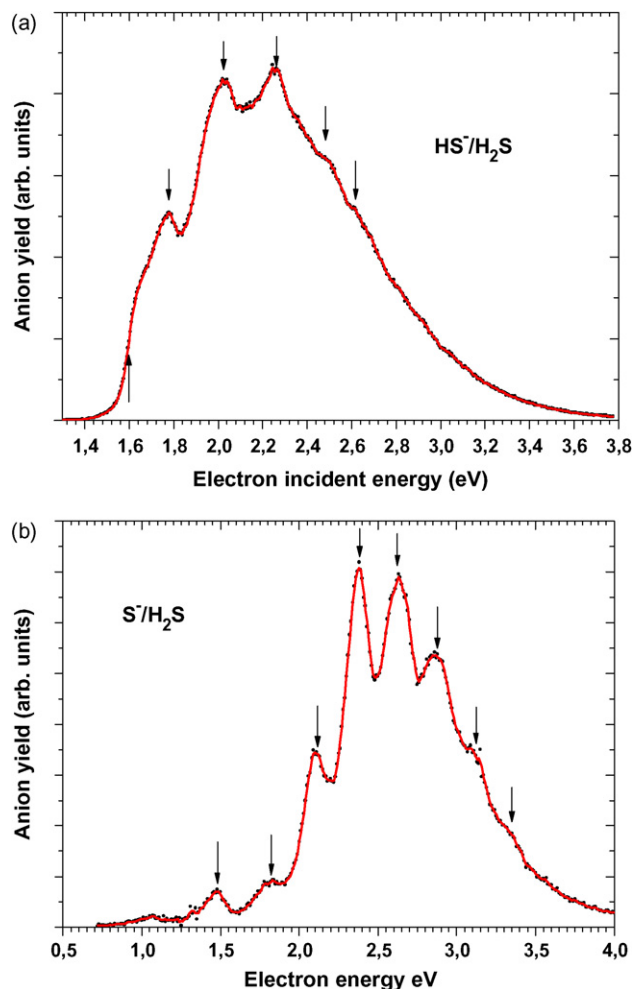**Fig. 1.** Anion yield of S^-/H_2S versus electron energy.

Fig. 2. Anion yields versus electron energy up to 4 eV for HS^-/H_2S (a) and S^-/H_2S (b). A vertical onset is observed for HS^- at 1.60 ± 0.02 eV. Peaks considered in the text are indicated by arrows. Cross-sections for S^- and HS^- at 2.4 eV are in the ratio 0.03:1, respectively.

Within the electron energy resolution (0.040 eV), HS^- cross-section versus electron energy (Fig. 2a), presents a vertical onset at 1.60 ± 0.02 eV (most probable value of the electron energy), a value in excellent agreement with the thermodynamical threshold (D–AE) = 1.58 eV, using HS electron affinity AE = 2.317 eV [17] and the dissociation energy $D(H_2S \rightarrow H\ ^2S + HS\ ^2\Pi) = 3.899$ eV [18]. In contrast with earlier results performed at lower electron energy resolution [3], the existence of a vertical onset is a clear indication that the potential surface reached at this energy is attractive. Several features are also observed at 1.78, 2.02, 2.26, 2.48 and 2.62 eV (all values ± 0.02 eV). No other appreciable signal of HS^- anions was observed up to 12 eV.

S^- (Fig. 2b) does not present a vertical onset; its observation begins at about 0.6 eV. Cross-sections for S^- and HS^- at 2.4 eV are in the ratio 0.03:1 respectively. Using $D(H_2S \rightarrow S\ ^3P + H_2\ ^1\Sigma^+_g) = 3.137$ eV [19] and AE (S) = 2.077 [17], the thermodynamical threshold for the limit $S^- + H_2$ is 1.06 eV. The S^- observation at lower energy is due to a small S^-/OCS impurity which is known to present a large cross-section around 1.2 eV [20]. Besides the peak at 1.2 eV due to the OCS impurity, a well-developed structure appears, presenting peaks at 1.49, 1.82, 2.11, 2.37, 2.63, 2.88, 3.12 and 3.35 eV (all values ± 0.02 eV). Spacing between peaks, ranging from 0.330 to 0.240 eV, is clearly evocating symmetric or antisymmetric vibra-

tional stretch modes of the neutral molecule $\nu_1 = 0.3242$ eV and $\nu_3 = 0.3256$ eV [21].

Among various possible processes, structures in HS^- and S^- anions could be due to the competition between vibrational excitation and DEA, like in the hydrogen halides [22–25], or to predissociation of a rather long lived resonance by another resonant dissociative potential surface. To check the validity of the first hypothesis we have recorded the electron energy loss spectrum to locate precisely the high energy vibrational levels of H_2S which could be involved in the opening of competing channels (Fig. 3). For HS^-, several energy loss peaks at 1.68, 1.77, 2.03, 2.15, and 2.27 eV could possibly be related to some small decreases or dips in the cross-section versus electron energy (Fig. 4a). However the correspondence is not always good, and it is not clear why we observe either clear dips or only very small decreases. For S^- no relationship could be found between the structure in the cross-section and the location of high-energy vibrational levels. The first interpretation is therefore not confirmed.

In the case of a predissociation, if the lifetime of the attractive resonance is long enough, one could expect that the vibrational levels would appear at the same energy in the cross-section for S^- and HS^-. Actually, the comparison between the two spectra (Fig. 4b) shows in contrast, that some of the first peaks observed in the S^- spectrum (1.82 and 2.11 eV) correspond to dips in the HS^- spectrum. This possibly indicates some competition between the two dissociation processes, originating from the same dissociative potential surface leading to two dissociation valleys. However, it is rather surprising that the more intense peaks in the S^- spectrum at 2.37 and 2.63 eV do not give rise to even larger dips in the HS^- signal. It appears therefore that none of the proposed interpretations seems satisfactory, the answer to the problem being certainly more complex. Note that if the lifetime of the attractive resonance is only of the order of the vibrational time, we may be dealing with "boomerang oscillations" like in N_2 [26], with no correspondence in S^- or HS^- cross-sections. The structureless vibrational excitation cross-section [5] indicates a rather short lifetime in the Franck–Condon region. However at larger internuclear distance, this lifetime could be slightly longer. More theoretical work on these dissociation processes appears therefore strongly needed.
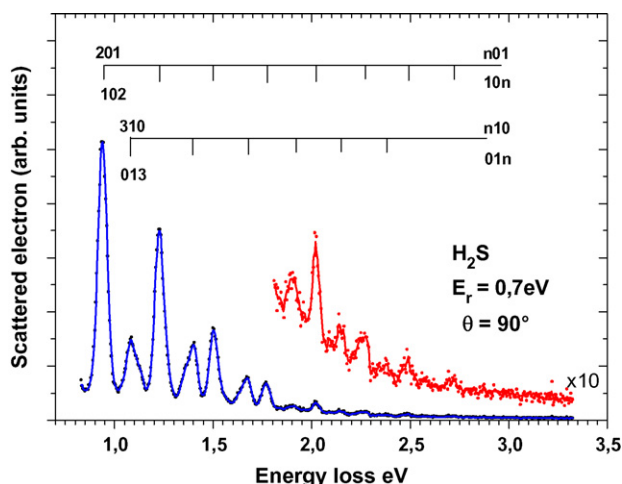

Fig. 3. Energy loss spectrum in H_2S recorded at residual energy $E_r = 0.7$ eV and at a scattering angle $\theta = 90°$. Only the high vibrational levels above 0.9 eV energy loss are shown. The series (n01 and 10n) and also (n10 and 01n) have been considered almost degenerate due to the limited resolution of the present work (0.040 eV, i.e., about 32 cm^{-1}).
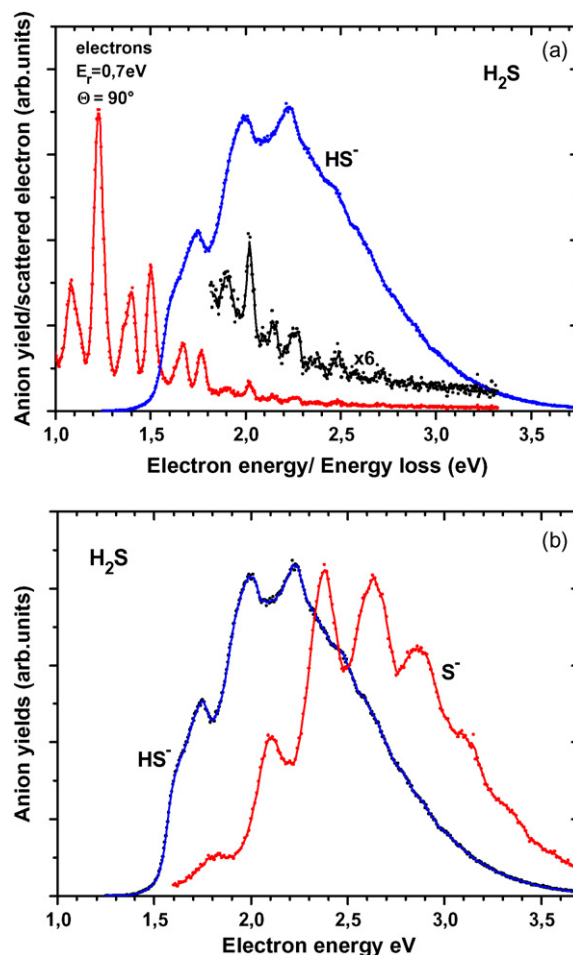

Fig. 4. (a) Comparison between the high-energy vibrational levels of H_2S and the HS^- structure (see text). (b) Comparison between S^- and HS^- structures. Peaks in S^- at 1.82, 2.11 and 2.37 eV correspond to dips or decreases in HS^- cross-section.

3.2. H_2Se

The results for H_2Se are very similar to H_2S concerning the low energy dissociation process. Both HSe^- and Se^- are observed (Fig. 5), the latter anion presenting also a well developed structure. For HSe^- a vertical onset is observed at 1.20 ± 0.04 eV. The thermodynamical threshold is calculated from $D(H_2Se \rightarrow HSe^- + H^+) = 14.81$ eV [27] to be 1.215 eV in excellent agreement with our experimental value. As for HS^-, a structure is observed with peaks or shoulders at 1.35, 1.57, 1.76 and 1.98 eV (all values ± 0.030 eV). The spacing between these features is again clearly evocating stretch vibrational modes of the neutral molecule ($\nu_1 = 0.2907$ eV and $\nu_3 = 0.2923$ eV [21].

Se^- like S^- does not present a vertical onset. Using the values AE $Se = 2.020$ eV (17), $D(HSe \rightarrow H + Se) = 3.2$ eV [28], and the values given above for HSe^-, the dissociation limit is calculated to be 0.127 eV. The observed onset around 0.9 eV is far above this value indicating that the potential surface reached in the Franck–Condon region is repulsive. The spectrum presents a series of well separated peaks at 1.09, 1.38, 1.65, 1.89, 2.12, 2.34 and 2.55 eV (shoulder), all values ± 0.020 eV. Like for S^-/H_2S, the peaks at 1.38, 1.65 and 1.89 eV correspond to dips in the HSe^- cross-section versus electron energy, indicating that the same observation in H_2S was not fortuitous.
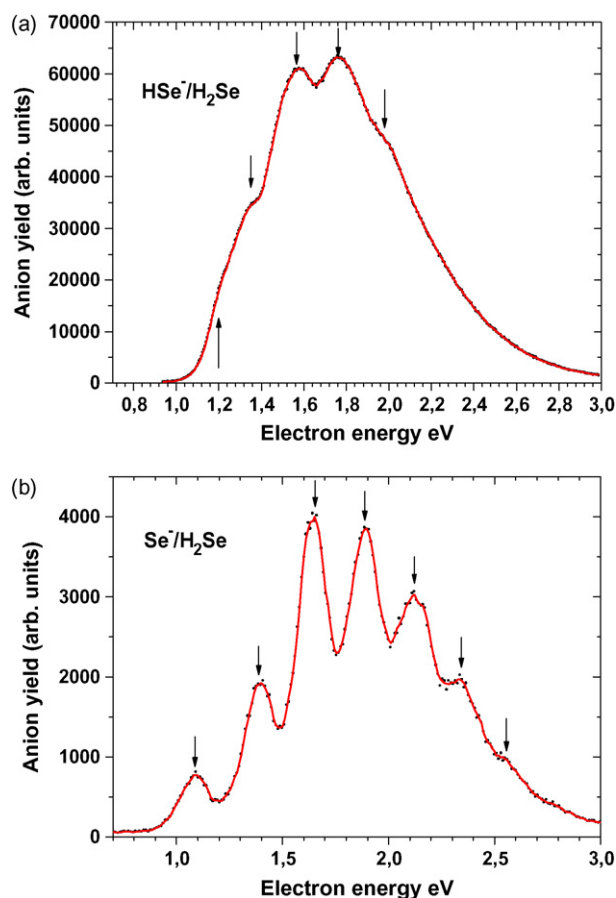
Fig. 5. Anion yields versus electron energy up to 3 eV for HSe^-/H_2Se (a) and Se^-/H_2Se (b). A vertical onset is observed for HSe^- at 1.20 ± 0.04 eV. Peaks considered in the text are indicated by arrows.

4. Discussion

Whereas DEA processes around 1–4 eV appear very similar in H_2S and H_2Se, the situation is totally different for H_2O. In this molecule, if the DEA leading to H^- anions resembles the H_2S case, observations for dissociations giving rise to O^- and OH^- ions are strongly different. Indeed, even if the thermodynamical threshold for $O^- + H_2$ is 3.57 eV [29], O^- ions are not observed below 7 eV. Furthermore, the dissociation limit for $OH^- + H$ is 3.29 eV [29], however OH^- is not observed via the direct DEA process, it is only observed due to the pressure dependent ion molecule reaction $(O^- + H_2O \rightarrow OH^- + OH)$, from 7 eV, following exactly the O^- formation process [29]. It appears therefore that the attractive resonant states responsible for the vertical onsets observed in H_2S and H_2Se do not exist or do not show up in H_2O. The absence of a resonant process around 2 eV is confirmed by a vibrational excitation study [30]. Indeed, the cross-section for excitation of H_2O vibrational stretch modes, besides a threshold peak, shows only a wide bump peaking around 7 eV, but does not present any evidence of a low energy resonant process in the energy range 2–4 eV.

H_2O, H_2S and H_2Se have isoelectronic valence shells. The ground electronic configuration of H_2S is: $\dots (4a_1)^2 (2b_2)^2 (5a_1)^2 (2b_1)^2$ X $^1A_1$. The first vacant orbitals $6a_1$ and $3b_2$ are very close in energy. The first shape resonances could hence be expected to have $^2A_1$ and $^2B_2$ symmetries. The first one was originally postulate to account for the HS^- process [3]. However it does not show up in the calculations and only the $^2B_2$ resonance appears to account for the low resonant energy scattering [10–12]. Concerning the Feshbach reso-

nances, it is interesting to look at the situation of the excited states which could be possible parents of these resonances. The lowest excited states responsible of the UV spectrum of H_2S from 4.59 to 8.06 eV [31] are $\dots (2b_1)^1 (3b_2)^1$ $^{1,3}A_2$ and $\dots (2b_1)^1 (6a_1)^1$ $^{1,3}B_1$ in C_{2v} symmetry. It has been shown that the B_1 surface is attractive whereas the A_2 is repulsive [32]. When the fragments HS and H are further away, these two states are A″ in Cs symmetry and are hence subject to non-adiabatic coupling, the B_1 surface being then pre-dissociated by the dissociative A_2 state. It is interesting to note that the situation is radically different in H_2O where only one surface is involved [33] and no predissociation process occurs. If the same situation occurs for Feshbach resonances associated to these excited states, it could explain the difference between the low energy DEA behaviour of H_2O and H_2S. However the first excited singlet state being located at 6.3 eV, even if the associated resonance is certainly at lower energy, it will not appear at energies as low as 2 eV. Our observations are therefore more likely to reveal low-lying shape resonances.

5. Conclusion

Using a better electron energy resolution we have observed a well-developed structure in the DEA cross-section versus electron energy (1–4 eV) for H_2S and H_2Se. The vertical onsets in HS^- and HSe^- reveal attractive resonant potential surfaces. The rather regular structure in S^- and Se^- cross-section from 1 to 4 eV could reveal a predissociation at large distance of these surfaces by dissociative states. At an energy as low as 2 eV, Feshbach resonances are not likely, shape resonances are more probably involved. These resonances are generally not long lived and the observed structure could then be interference oscillations like in the case of N_2 [26,34]. This interpretation is only conjectural and detailed calculations are strongly needed to really understand this process. The great similarity between DEA processes in H_2S and H_2Se is in contrast with H_2O. Reproduction of the observed structure and comparison between these molecules (some of the most simple triatomic molecules) is an interesting challenge for theoretical approaches like the one developed recently by Haxton et al. [14,15] for H_2O, to perform dynamics calculations on resonant potential surfaces.

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