On the Interaction of the S^- Ion with H_2 at low Collision Energies

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Potential energy functions have been calculated for the reactions $S^-(^2P) + H_2 \longrightarrow HS + H^-$ and $S^-(^2P) + H_2 \longrightarrow HS^- + H$ for low collision energies and collinear geometries. Unlike in the O^- + H_2 system, only very flat polarisation minima in the structures $S^-...H_2$ and $SH...H^-$ have been found. They are not deep enough to support the formation of a complex in the detachment, in the reactive detachment and in the reactive charge transfer processes of the S^- + H_2 collision system.

Introduction

The long lived negative ions H_2O^- and HDO^- have been detected experimentally using ion-molecule reactions and Fourier transform ion cyclotron resonance technique [1]. Previously, we have shown [2] that these species are the charge-quadrupole bound $O^-...H_2(HD)$ clusters rather than H_2O^- in the classical water structure. The low collision energy regions of the potential energy functions (PEF's) for the reactions $O^- + H_2 \rightarrow HO + H^-$ $(^2\Pi)$ and $O^- + H_2 \rightarrow HO^- + H$ $(^2\Sigma^+)$ have been mapped by ab initio calculations, and minima separated by barriers in the structures $O^-...H_2$ and $OH...H^-$ were found.

So far, no stable H_2S^- ion has been detected experimentally. Only the e + H_2S system has been extensively studied by electron impact experiments. Several resonances were observed : at 2 eV assigned to a $^2B_2$ state [3]-[6], at 5.3 eV assigned to a $^2B_1$ state [3], and at 6-8 eV assigned to a $^2A_1$ state [3]-[6]. The HS^- fragment was observed with a maximum efficiency around 2.2 eV [3], [6], [7], [8] whereas the S^- anion was detected for collision energies higher than 7.5 eV [9]. The H^- product together with the neutral HS radical has been observed with a maximum efficiency for a collision energy close to 5 eV [5]. Recently, an experimental study of the $S^- + H_2$ reaction [10], [11] showed that three competing channels: the simple detachment, the reactive detachment and the reactive charge transfer exist for collision energies extending from threshold to about 5 eV. The hydrogen transfer process could not be investigated. The results have been interpreted by symmetry arguments and the assumption that the shapes of the PEF's involved are similar to those of the H_2O^- system. The present study shows, however, that the bound collinear PEF's for the aforementioned reaction with sulphur are rather different. The $S^-...H_2$ and $SH...H^-$ polarisation minima are found to be very shallow, which could also explain the fact that the bound H_2S^- ion has not been detected experimentally.

1. Computational Method

The ab-initio calculations have been performed with the MOLPRO code [12] using a basis set of 165 primitive Gaussian functions contracted to 133 groups according to the general contraction scheme. The basis set consisted of a (16s, 11p, 3d, 2f) basis of T. H. Dunning [13] for sulfur augmented by one s diffuse function (exponent 0.048) and one p diffuse function (exponent 0.033). The basis set for hydrogen consisted of a (6s, 3p, 2d, 1f) set [13], augmented by two s (exponents 0.031, 0.011) and one p (exponent 0.10) diffuse functions contracted into [6s, 4p, 2d, 1f]. The PEF's for the $^2\Sigma$ and $^2\Pi$ states in collinear geometries were calculated using the complete active space self-consistent field (CASSCF) method [16] and the coupled electron pair approach in the version one (CEPA-1)[14]-[15]. In the preliminary full valence CASSCF computations the active space was augmented by one σ and one π molecular orbital. The active molecular orbitals (4σ-8σ and 2π-3π) varied smoothly over the whole range of investigated internuclear distances. The orbitals were optimized in state-averaged CASSCF calculations by minimizing the average energy of both states. These calculations

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Table 1. Comparison of the calculated[a] and experimental asymptotic energy differences relative to the lowest asymptote of H_2S^- (all values in eV).

Asymptote	SCF	CASSCF	CEPA	Experiment[b]
$SH(A^2\Sigma^+) + H^-(^1S)$	6. 40	5. 52	6. 08	6. 08
$SH(X^2\Pi) + H^-(^1S)$	2. 22	1. 53	2. 19	2. 23
$S(^3P) + H_2(^1\Sigma^+) + e^-$	0. 90	1. 44	1. 91	2. 077
$SH^-(X^1\Sigma^+) + H(^2S)$	0. 67	0. 71	0. 75	0. 67
$S^-(^2P) + H_2(^1\Sigma^+)$	0. 0[c]	0. 0[c]	0. 0[c]	0. 0

[a] calculated at the r_e values of the diatomic fragments taken from [20]. [b] All values are given at r_e's of the diatomic fragments; the experimental values used were: $D_0(SH) = 3.67$ eV [17], $AE(S) = 2.077$ eV [18], $AE_0(SH) = 2.317$ eV [19], $AE(H) = 0.754$ eV [18], $T_0(A^2\Sigma^+) = 3.85$ eV [20], $D_e(H_2) = 4.75$ eV [20]; the vibrational corrections were performed by using the data of [20]. [c] The calculated total energies were: SCF –398.673361 a. u., CASSCF –398.747621 a. u. and CEPA –398.907313 a. u.

showed that it is possible to compute the collinear PEF's with a method biased towards one leading configuration, but covering a larger portion of the electron correlation. In the following we discuss only the PEF's obtained from such CEPA-1 computations, in which all valence electrons have been correlated.

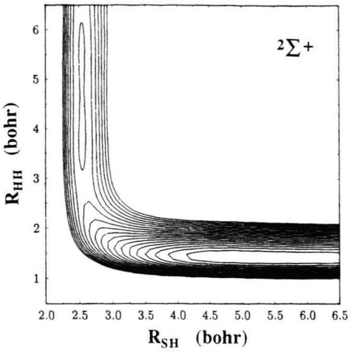

Fig. 1. Contour plot of the $^2\Sigma^+$ potential energy surface for the linear S...H...H geometries. The contours are in steps of 500 cm^{-1}.

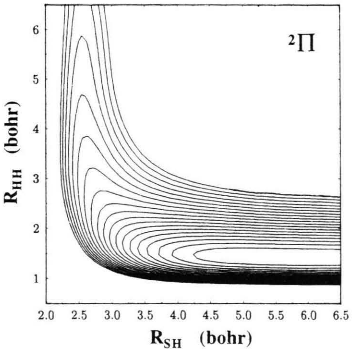

Fig. 2. Contour plot of the $^2\Pi$ potential energy surface for the linear S...H...H geometries. The contours are in steps of 1000 cm^{-1}.

2. Results and Discussion

The calculated SCF, CASSCF and CEPA energies for several asymptotes of the hypothetical H_2S^- ion are compared with the experimental values in Table 1. The CEPA-1 energy differences are found to be in very satisfactory agreement with the experimental values.

There are important differences between the asymptotic properties of the H_2S^- ion if compared to H_2O^-. In H_2O^- the lowest dissociation asymptote is the $OH^-(X^1\Sigma^+) + H(^2S)$, whereas in H_2S^- the lowest asymptote is $S^-(^2P) + H_2(^1\Sigma^+)$. The energy difference between the $OH(X^2\Pi) + H^-(^1S)$ and $OH^-(^1\Sigma^+) + H(^2S)$ asymptotes amounts to only 1.08 eV, whereas the corresponding value for the H_2S^- asymptotes amounts to 1.56 eV. The energy difference between $O^-(^2P) + H_2$ and $OH(X^2\Pi) + H^-(^1S)$ amounts to only 0.83 eV, whereas for sulphur this difference is much larger (2.23 eV, cf. Table 1). The changes of the energy positions of the asymptotes lead to changes in the charge-overlap effects for intermediate internuclear distances. Generally, the long range electrostatic forces in charged species lead to attractive interactions. In order to decide whether a negative ion can exist as a bound species in a cluster-like structure one has to investigate the shapes of the long range parts of the PEF's resulting from bound asymptotes. As in the oxygen species also the SH molecule has a permanent dipole (0.758 debye) with an excess of negative charge on sulphur. The approach of the H^- ion will lead to a repulsion for the H...SH structures and to an attraction for the SH...H structures with the R^{-2} distance dependence of the PEF. On the other hand, the charge-induced dipole interaction of SH^- and H has an R^{-4} dependence and is, therefore, very small. The strongest interaction between S^- and H_2 is of the charge-quadrupole type and has an R^{-3} dependence for the long range parts of the PEF's. All the asymptotic interactions will be influenced by charge-overlap effects, and qualitative arguments cannot be used to decide if the PEF's will exhibit sufficiently deep minima for different structures separated by barriers, which could lead to stable bound clusters. In the present study we have been interested only in the collinear SH...H cuts of the

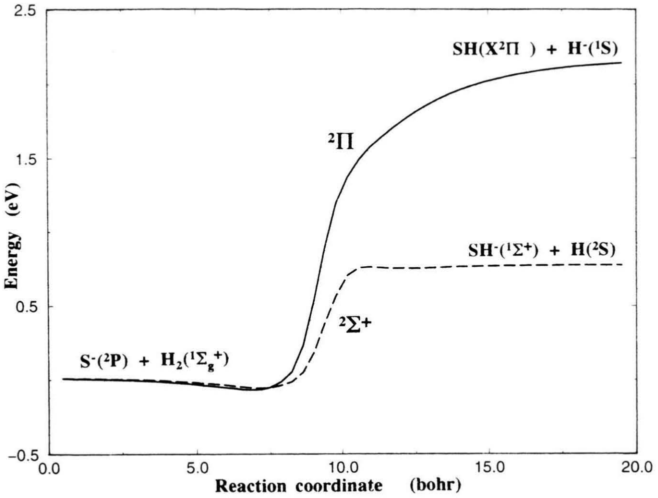

Fig. 3. Energy profile along the minimum energy paths between the $S^- + H_2$ and $[SH + H]^-$ asymptotes.

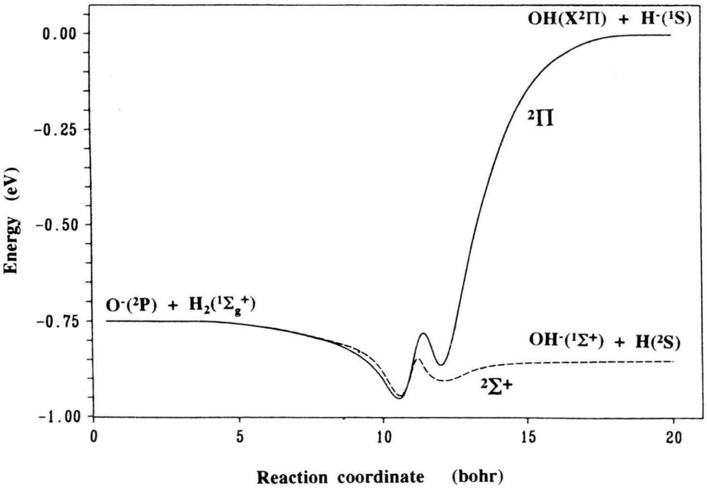

Fig. 4. Energy profile along the minimum energy paths between the $O^- + H_2$ and $[OH + H]^-$ asymptotes taken from [2].

$^2\Sigma^+$ and $^2\Pi$ PEF's correlating with the $S^-(^2P)$ + $H_2(^1\Sigma^+)$, $SH(X^2\Pi) + H^-(^1S)$ and $SH^-(^1\Sigma^+) + H(^2S)$ asymptotes, respectively. The two-dimensional contour plots of the CEPA PEF's are displayed in Figs. 1 and 2. Using this information, the PEF's along the $S^- + H_2$ reaction path have been evaluated; they are displayed in Figure 3. Similar PEF's for the $O^- + H_2$ reaction path, taken from [2], are shown in Figure 4. As can be seen from the shapes of the PEF's in Fig. 4, there are two rather deep long range minima in the structures $O^-...H_2$ and $OH...H^-$, separated by barriers. No such pronounced cluster structures exist for H_2S^-(cf. Figure 3). Expectedly, the strongest long range charge-dipole interaction is found for the $SH...H^-$ approach. The onset of the interaction occurs at longer distances than for $OH...H^-$, due to the more diffuse electron cloud in a second-row hydride. Contrary to the oxygen PEF's, the charge transfer between S^- and H^- occurs smoothly due to different charge-overlap effects. The main reason for the change of the charge-overlap in H_2S^- is the distinctly larger energy difference between the $S^- + H_2$ and $SH + H^-$ asymptote. As discussed previously, the H_2S^- PEF's exhibit charge-quadrupole ($S^- + H_2$ channel of both potentials) and charge-induced dipole ($SH^- + H$ channel of the $^2\Sigma^+$ potential) polarisation minima. Compared to H_2O^-, all three minima are very shallow. Their equilibrium geometries and the dissociation energies in Table 2 are not highly accurate since the basis superposition errors have not been taken into account in the present CEPA computations. In the entry channel of the $S^- + H_2$ reaction both PEF's will form a

Table 2. Calculated geometries and energies of the minima and barriers of the linear $^2\Pi$ and $^2\Sigma^+$ surfaces of H_2S^-.

State	R_{SH} [bohr]	R_{HH} [bohr]	Energy[a] [cm^{-1}]
Minima			
$^2\Sigma^+$	5.28	1.41_5	–620
	2.54	4.12	–186
$^2\Pi$	5.64	1.42	–707
Barrier			
$^2\Sigma^+$	2.56	3.10	–63

[a] The energies of the minima are given relative to the asymptotes, the barrier height relative to the minimum in the [SH^- ...H] channel.

conical intersection in lower symmetries, and the vibronic coupling will possibly not allow to distinguish which of the exit channels will be preferred before reaching the charge-quadrupole minimum. In C_s and C_{2v} symmetries the $^2\Pi$ PEF splits into two components coupled by the Renner-Teller effect. Since one of the A' components (A_1 in C_{2v} symmetry) correlates with the PEF of $H_2S(X^1A_1)$ + e, and since the long range parts of the PEF's have no barriers and only shallow minima, a bound negative cluster ion with the sum formula H_2S^- could exist only at very low temperatures in the structures of the polarisation minima. In the experimental study of the S^- + H_2 dynamics a complex formation has been postulated for the detachment, the reactive detachment and the charge transfer processes. The present theoretical results do not support this hypothesis. We can not exclude, however, that at higher energies and in other electronic states deeper minima on the PEF's could be present.

3. Conclusions

Using ab initio calculations, the collinear PEF's of the $^2\Pi$ and $^2\Sigma^+$ states of the S^- + H_2 system have been mapped. In contrast to the analogous oxygen system, only shallow polarisation minima for the cluster structures $S^-...H_2$ and $SH...H^-$ have been found, suggesting that the exothermic associative detachment yielding H_2S + e will proceed on a PEF without any significant barrier. This renders the experimental detection of the H_2S^- cluster very difficult. The differences between the oxygen and sulphur systems have been explained by different charge-overlap effects for intermediate distances of the SHH^- species.

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