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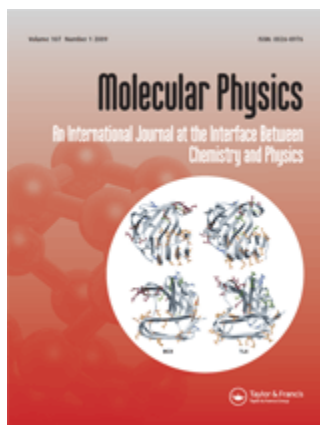
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### Spectroscopy and metastability of the HSS<sup>-</sup> anion

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**Spectroscopy and metastability of the HSS<sup>-</sup> anion<sup>#</sup>**

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<sup>#</sup> Dedicated to Prof. Pavel Rosmus for his retirement.

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**Abstract**

Accurate *ab initio* calculations on the potential energy surfaces (PESs) of the lowest electronic states of the neutral HSS and those of the electronic states of the HSS<sup>-</sup> negative ion correlating to the bound asymptotes of this molecular system, reveal that the ground state of HSS<sup>-</sup> (i.e.  $\tilde{X}^1A'$ ) and the long range parts of the anionic PESs are stable against the autodetachment processes. In light of these calculations, the [HS + S]<sup>-</sup> and [S<sub>2</sub> + H]<sup>-</sup> reactive systems are examined and found forming the HSS<sup>-</sup> ( $\tilde{X}^1A'$ ) ions either directly or after spin-orbit and / or vibronic and / or Renner-Teller couplings, in competition with fast electron loss processes. The three-dimensional PES of the unique bound electronic state of HSS<sup>-</sup> (i.e.  $\tilde{X}^1A'$ ) is generated using the coupled cluster approach and a large basis set. A set of spectroscopic parameters for HSS<sup>-</sup>/DSS<sup>-</sup> ( $\tilde{X}^1A'$ ) and their vibrational spectra up to 3700 cm<sup>-1</sup> are deduced from our 3D PES.

## I. Introduction

Little is known about the thiosulfeno negative ion ( $\text{HSS}^-$ ) in despite that its corresponding neutral molecule is widely studied [1]. These species as well as their positively charged ions are believed to play an important role in combustion and astrophysical chemistry and biochemistry [2-4]. The available experimental data for  $\text{HSS}^-$  are mostly due to the earlier photoelectron spectroscopic study of Moran and Ellison, who have determined the electron affinity (EA) of  $\text{HSS}$  to be  $1.907 \pm 0.023$  eV [5]. Such large EA is expected for sulfur containing species [6]. These authors have also found that attaching an extra electron to the  $\text{HSS}$  ground state results mainly in a lengthening of the SS bond.

By stretching the SH internal coordinate, the  $\text{HSS}^-$  negative ion possesses three bound asymptotes {i.e.  $\text{S}_2^-(\text{X}^2\Pi_g) + \text{H}(\text{S})$ ;  $\text{S}_2(\text{X}^3\Sigma_g^-) + \text{H}(\text{S})$ ;  $\text{S}_2(\text{a}^1\Delta_g) + \text{H}(\text{S})$ }, which are located below the  $\text{S}_2(\text{X}^3\Sigma_g^-) + \text{H}(\text{S})$  dissociation limit. The Wigner-Witmer correlation rules applied to the  $\text{HSS}^- \rightarrow [\text{S}_2 + \text{H}]^-$  molecular system show that the  $\text{HSS}^-$  ( $1^3\Pi$ ,  $1^1\Pi$ ,  $1^3\Sigma^-$  and  $1^1\Delta$ ) and their corresponding bent compounds should correlate to these three bound asymptotes. However, the lowest  $\text{HSS}^-$  ( $1^1\Sigma^+$ ) state correlates adiabatically to the unbound  $\text{S}_2(\text{b}^1\Sigma_g^+) + \text{H}(\text{S})$  limit, which is located at 0.22 eV above  $\text{S}_2(\text{X}^3\Sigma_g^-) + \text{H}(\text{S})$ . Along the SS coordinate, the  $\text{SH}^-(\text{X}^1\Sigma^+) + \text{S}(\text{P})$  and the  $\text{SH}(\text{X}^2\Pi) + \text{S}(\text{P})$  bound dissociation limits are located below the  $\text{SH}(\text{X}^2\Pi) + \text{S}(\text{P})$  neutral limit at 2.31 eV and 2.08 eV, respectively. In addition to the triatomic states given above, the  $1^1\Sigma^-$ ,  $1^3\Sigma^+$  and  $1^3\Delta$  states are also correlating to these two asymptotes at large SS separations (far from the molecular region). This high density of electronic states should favor their mutual couplings, resulting in mixing of their electronic wavefunctions.

In the present work, the metastability of the  $\text{HSS}^-$  electronic states with respect to the autodetachment leading to  $\text{HSS} + e^-$ , is discussed in light of their potential energy surfaces, their electronic configurations and those of the neutral  $\text{HSS}$  molecule. It is worth noting that several conditions should be fulfilled by an anionic electronic state to exist: (i) it should possess positive electron affinity with respect to its parent neutral state; (ii) it should exhibit slow depletion by spin-forbidden autodetachment for at least one fine structure component and by radiative depletion; and (iii) its wavefunction should undergo weak interaction with the electron continuum wave. Here, large basis sets and multiconfigurational methods are used. Such large computations are needed for a good description of the anionic wavefunctions. However, our approach is not valid to describe accurately the negative ion resonances [7-9] (i.e. the PES parts located above the autodetachment thresholds), so that, only the bound parts of these PESs will be presented and discussed in next sections. In the last

part of the manuscript, the three-dimensional PES of the  $\text{HSS}^-$  ground state is generated and its bound vibrational term values are calculated variationally.

## II. Computational methods

The electronic calculations were performed using the complete active space self-consistent field (CASSCF) approach [10] followed by the internally contracted multi-reference configuration interaction including the Davidson correction (MRCI+Q) method [11,12] and the Coupled Cluster technique including the quasi-perturbative treatment of the connected triple substitutions (CCSD(T)) [13], which are implemented in the MOLPRO program suite [14]. The sulfur atoms were described using a large basis set of *spdfgh* aug-cc-pV5Z quality [15] and the hydrogen was described with the *spdfg* aug-cc-pV5Z Dunning's basis set [16], resulting in 342 contracted Gaussian functions. In these calculations, the CASSCF active space included all configurations (CSFs configuration state functions) obtained after excitations of all valence electrons in valence orbitals. In the  $C_{2v}$  point group (collinear SS or SH elongations), this results in 172 (162), 130 (160), 130 (160) and 108 (148) CSFs for the singlets (for the triplets) in the  $A_1$ ,  $B_1$ ,  $B_2$  and  $A_2$  symmetries, respectively. Moreover, all electronic states with the same spin multiplicity have been averaged together using the CASSCF averaging procedure implemented in MOLPRO, where 3 (4)  $A_1$ , 2 (2)  $B_1$ , 2 (2)  $B_2$  and 3 (4)  $A_2$  components were considered for the singlets (for the triplets). For MRCI calculations, all configurations in the CI expansion of the CASSCF wavefunctions were taken as a reference. For  $\text{HSS}^-$ , this results in more than  $130 \times 10^6$  CSFs to be treated in the  $C_{2v}$  point group. All valence electrons were correlated. The present calculations were performed in both the  $C_{2v}$  (for the collinear PES cuts) and the  $C_s$  (for bent structures) point groups.

The three-dimensional PES of the  $\text{HSS}^-$  ( $X^1A'$ ) electronic ground state has been mapped in the internal coordinates of this anion corresponding to the SH ( $R_{\text{SH}}$ ), SS ( $R_{\text{SS}}$ ) stretchings and to the bending angle ( $\theta$ ), at the *spdfg(h)* aug-cc-pV5Z/CCSD(T) level of theory. The calculations were carried out for 45 different geometries, so that the near equilibrium and the bound parts of this PES are covered (up to  $\sim 10000 \text{ cm}^{-1}$  above the minimum). The calculated energies were fitted to a polynomial expansion (*cf. infra*). This analytical form was used later to calculate the quartic force field in internal coordinates, which has been transformed by the  $l$ -tensor algebra to quartic force field in dimensionless normal coordinates [17,18]. These data allow us to evaluate a set of spectroscopic properties using second order perturbation theory. The PES expansion was also used in variational calculations using the approach of Carter and Handy [19]. The vibrational energies up to  $3700 \text{ cm}^{-1}$  are deduced for  $\text{HSS}^- \tilde{X}$  and  $\text{DSS}^- \tilde{X}$ . The accuracy of the vibrational term values should be better than  $10\text{-}20 \text{ cm}^{-1}$  with comparison to similar works for other triatomic negative ions [21-22].

### III. Electronic States of $\text{HSS}^-$

The anionic states in interest here are obtained by attaching an extra electron to the  $3a''$  or to the  $14a'$  or to the  $15a'$  orbitals and present either the  $\text{HSS} (\tilde{X}^2A'')$  or the  $\text{HSS} (1^2A')$  as parent states. For further details readers are referred to Table I. Figure I depicts the MRCI+Q one-dimensional cuts of the three-dimensional potential energy surfaces of the electronic states of  $\text{HSS}^-$  for bent structures. Only the bound parts are presented. These curves are given in energy with respect to the  $\text{HSS} (\tilde{X}^2A'')$  minimum. They are obtained by varying the SS ( $R_{\text{SS}}$ , in A) and the SH ( $R_{\text{SH}}$ , in B) internal coordinates, where the bending angle is kept fixed at  $102^\circ$  and the  $R_{\text{SH}} = 2.5$  bohr or the  $R_{\text{SS}} = 3.9$  bohr ( $1 \text{ bohr} = 1 a_0 = 0.529 \text{ \AA}$ ) corresponding to their equilibrium values in  $\text{HSS}^- (\tilde{X}^1A')$  (see below). The dissociation limits are positioned using our dissociation energies ( $D_e$ ) for  $\text{HSS} (\tilde{X}^2A'')$ , the experimentally determined electron affinities (EA) of S ( $\sim 2.08 \text{ eV}$ ), of SH ( $\sim 2.31 \text{ eV}$ ), of  $\text{S}_2$  ( $\sim 1.670 \text{ eV}$ ) and of H ( $0.754 \text{ eV}$ ), and the electronic transition energies of  $\text{S}_2$  [6]. Our  $D_e$ 's are computed at the aug-cc-pV5Z/MRCI+Q level of theory including the Basis Set Superposition Error (BSSE). It is calculated  $2.76 \text{ eV}$  ( $2.86 \text{ eV}$ ) along the SS (SH) coordinate.

At large internuclear separations, Figure I shows a high density of electronic states for the  $\text{HSS}^-$  anion favoring their mutual couplings by vibronic (between the electronic states having the same spin multiplicity) and spin-orbit (between the singlets and the triplets), and complicating the computations for this molecular system. Some anionic states are lying so close in energy that one can not clearly distinguish them there. This is the case, for instance, for the  $2^3A'$ , the  $2^1A''$ ,  $2^3A''$  states (cf. Figure I A).

Figure II presents the MRCI+Q one-dimensional PES cuts evolution of the  $\text{HSS} (\tilde{X}^2A'', 1^2A'$  and  $1^4A''$ ) states and the bound parts of those of  $\text{HSS}^-$  along the bending coordinate. These curves are obtained by varying the bending angle ( $\theta$ ), where the stretches are set to  $R_{\text{SH}} = 2.5$  and  $R_{\text{SS}} = 3.9$ , in bohr. This figure shows that the neutral doublet states correlate to the same  $\tilde{X}^2\Pi$  state at linearity forming a bent/bent Renner-Teller system. The neutral quartet correlates to the lowest  $^4\Sigma^-$  state for  $\theta = 180^\circ$ . It is worth noting also that the  $\text{HSS}^-$  ground state is a singlet of  $A'$  symmetry species, correlating to the lowest  $^1\Sigma^+$  state at linearity. This ground state possesses a bent equilibrium geometry with a bending angle close to the equilibrium bending angle of  $\text{HSS} (\tilde{X}^2A'')$ . Moreover, the two lowest triplets form a linear/bent Renner-Teller pair, leading to the  $1^3\Pi$  state at linearity. Finally, the two upper singlets are coupled by Renner-Teller effect via the  $1^1\Pi$  state, which is however, found to be located above the autodetachment threshold for these internuclear distances.

Figure III displays the aug-cc-pV5Z/MRCI+Q one-dimensional cuts of the 3D PES of the electronic states of  $\text{HSS}^-$  and those of  $\text{HSS} (\tilde{X}^2\Pi \text{ \& } ^4\Sigma^-)$  for collinear configurations, along the SS stretching ( $R_{\text{SS}}$ , in Figure III A) and along the SH distance ( $R_{\text{SH}}$ , in Figure III B). Among the anionic electronic states depicted there, only the  $1^1\Sigma^+$  to which the  $\text{HSS}^- (\tilde{X}^1A')$  state correlates adiabatically, possesses a deep potential well along both the SS and SH internal coordinates. The other states are repulsive in nature at least when the SS distance is lengthened. In despite that several electronic states are located below the lowest neutral states for linear configurations, they will exhibit fast electron loss when the molecule is bent (cf. Figure II), exception should be made for the lowest singlet leading to  $\text{HSS}^- (\tilde{X}^1A')$  minimum.

Close examination of Figures I-III and Table I reveals that our anionic electronic states are bound at large internuclear distances since they are located below their respective parent states. The situation is, however, quite different in the molecular region and only the anionic electronic ground state {i.e.  $\text{HSS}^- (\tilde{X}^1A')$ } fully fulfills the metastability conditions given above. Indeed, this electronic state is located well below its parent state {i.e.  $\text{HSS} (\tilde{X}^2A'')$ } for both linear and bent configurations and it is located in energy far from the upper electronic states so that it is free from any interaction. In contrary, the anionic excited states are crossing the  $\text{HSS} (\tilde{X}^2A'')$  PES close to the molecular region where fast electron loss is expected to occur either directly (for those presenting the  $\text{HSS} (\tilde{X}^2A'')$  as parent state), or indirectly after spin-orbit and / or vibronic couplings (for those accessed by bending an extra electron to the  $\text{HSS}(1^2A')$ ). This is confirming the Photo Electron Spectroscopy results of Moran and Ellison, which found a unique stable electronic state for  $\text{HSS}^-$  [5]. Finally and by inspection of our data depicted in Figures I-III, the EA value of  $\text{HSS}$  is computed  $\sim 1.75$  eV at the *spdfg(h)* aug-cc-pV5Z/MRCI+Q level of theory, which is 0.16 eV lower than the experimental value ( $1.907 \pm 0.023$  eV [5]). Such differences between the experimental and the theoretical EA determinations are commonly admitted for similar calculations of this quantity. See Refs. [7-9, 23] for detailed discussions.

In light of the present theoretical results, we would like to discuss also the reactivity of  $\text{HS}/\text{HS}^-$  against  $\text{S}^-/\text{S}$  and its of  $\text{S}_2/\text{S}_2^- + \text{H}/\text{H}$ . When the reactants are taken in their electronic ground states, these reactions follow the PES of  $\text{HSS}^- (\tilde{X}^1A')$  for bent structures and lead directly to the formation of this negative ion. However, when the reactants are electronically excited and /or for collinear collisions, the reactions may follow first the PES of the  $\text{HSS}^-$  excited states, forming the electronically excited  $\text{HSS}^-$  ions transiently, which may be converted later into the  $\text{HSS}^- (\tilde{X}^1A')$  ions after spin-orbit and / or vibronic and / or Renner-Teller (for the doubly degenerate electronic states) interactions in competition with the autodetachment processes.



#### IV. Spectroscopy of the ground states of HSS<sup>-</sup> and of DSS<sup>-</sup>

A polynomial function of the form

$$V(Q_1, Q_2, Q_3) = \sum_{ijk} C_{ijk} (Q_1)^i (Q_2)^j (Q_3)^k$$

where  $Q_i = (R_i - R_i^{\text{ref}})/R_i$ , for  $i = 1, 2$

and  $Q_3 = \theta - \theta^{\text{ref}}$

The index 'ref' refers to the reference geometry used during the fit, which is taken the equilibrium geometry of HSS<sup>-</sup> ( $\tilde{X}^1A'$ ) here.  $R_1$ ,  $R_2$  correspond to the SS and the SH stretching coordinates respectively and  $\theta$  is the bending coordinate. The  $i, j, k$  exponents were restricted to  $i+j+k \leq 4$ . 35  $C_{ijk}$  coefficients were optimized using a least square procedure. These terms are given in Table II. The root mean square of the fit was less than  $8 \text{ cm}^{-1}$ .

Table III lists the quartic force fields of HSS<sup>-</sup> ( $\tilde{X}^1A'$ ) and of DSS<sup>-</sup> ( $\tilde{X}^1A'$ ) in dimensionless normal coordinates. It turns out from these values that some couplings do exist between the SH stretch and the bending modes, since both the third and fourth order force field terms relative to these modes (for instance  $\phi_{221} = 510.2 \text{ cm}^{-1}$  and  $\phi_{2211} = -527.1 \text{ cm}^{-1}$ ) have large values. However, only weak coupling is expected between the two stretching modes.

Table IV gives the equilibrium geometry of HSS<sup>-</sup> ( $\tilde{X}^1A'$ ) deduced from our 3D CCSD(T) PES. The  $R_{\text{eSS}}$  distance is computed  $2.091 \text{ \AA}$  and the  $R_{\text{eSH}}$  is calculated  $1.343 \text{ \AA}$ . The accuracy of our calculated equilibrium distances should be better than  $0.01 \text{ \AA}$ . The angles of HSS ( $101.74^\circ$  [24,25]) and of HSS<sup>-</sup> ( $101.8^\circ$ ) are close to each other. We have also done a systematic geometry optimization of the equilibrium geometry of this electronic state at the cc-pV6Z/CCSD(T) level of theory. The results are close to the one deduced from our 3D PES and those obtained by Owens et al [26] (cf. Table IV). Accordingly, the formation of HSS<sup>-</sup> ( $\tilde{X}^1A'$ ) by attaching an electron to HSS ( $\tilde{X}^2A''$ ) is accompanied by a lengthening of the SS bond ( $\Delta R_{\text{SS}} \sim 0.13 \text{ \AA}$ ) and a slight shortening of the SH distance ( $\Delta R_{\text{SH}} \sim 0.01 \text{ \AA}$ ) [24,25]. The changes are more significant for the SS distance in good accord with Moran and Ellison's Franck-Condon analysis of their PhotoElectron spectrum of HSS<sup>-</sup>. [5].

In Table IV are also listed the spectroscopic parameters of HSS<sup>-</sup> ( $\tilde{X}^1A'$ ) and of DSS<sup>-</sup> ( $\tilde{X}^1A'$ ) obtained using second order perturbation theory. They include the rotational constants ( $A_e, B_e, C_e$ ), the harmonic wavenumbers ( $\omega_i$ ) the vibration-rotation terms ( $\alpha_i$ ) and the anharmonicity terms ( $x_{ij}$ ). This table shows that HSS<sup>-</sup> is an asymmetric top molecule with  $B_e \sim C_e$ . Our harmonic wavenumbers are computed  $\omega_1 = 2594.4$  (SH stretching),  $\omega_2 = 829.8$  (bending) and  $\omega_3 = 484.6$  (SS stretching), in  $\text{cm}^{-1}$ ,

which are in good accord with the values of Ref. [26]. The variationally computed SH anharmonic wavenumber ( $\nu_1$ ) is calculated  $2453.6 \text{ cm}^{-1}$ . The SS stretch and the bending are calculated  $\nu_3 = 478.8 \text{ cm}^{-1}$  and  $\nu_2 = 808.8 \text{ cm}^{-1}$ , respectively, which are distinctly smaller than their corresponding values for HSS  $\tilde{X}$  (i.e.  $\nu_2 = 904 \pm 8 \text{ cm}^{-1}$  and  $\nu_3 = 595 \pm 4 \text{ cm}^{-1}$  [27]), where as the SH stretches for the anion and the neutral molecule ( $\nu_1 = 2463 \text{ cm}^{-1}$  [28]) are close to each other.

Table V gives the vibrational theoretical energies of HSS $^-$  ( $\tilde{X}^1A'$ ) and its isotopomer. The calculations are carried out for  $J=0$ . Here, anharmonic resonances can be found between their vibrational term values even for the ones located as low as  $2000 \text{ cm}^{-1}$  (they are marked by an asterisk in Table V). For example, the level of HSS $^-$   $\tilde{X}$  located at  $2538.5 \text{ cm}^{-1}$  is a mixture of (0,2,2), (0,1,3), (0,3,1) and (0,3,3) with the highest contribution from (0,2,2). Such resonances mix the vibrational wavefunctions of these levels making their assignment by quantum numbers quite difficult. For these reasons the attributions given in Table V are only tentative for energies  $>2000 \text{ cm}^{-1}$  with respect to the zero point vibrational energy (ZPE) except the levels involving the SH stretching. For DSS $^-$ , the isotopic shifts are calculated variationally to be  $\sim 662 \text{ cm}^{-1}$  for  $\nu_1$ , which is associated with the strongest reduction due to the H/D substitution; and  $\sim 220 \text{ cm}^{-1}$  for  $\nu_2$ . However, no significant change is found for  $\nu_3$  since it corresponds mainly to the SS elongation. These isotopic shift values are consistent with those observed for the neutral DSS and for the DSS $^+$  cation [6]. Since the Franck-Condon Factors (FCFs) for the H/DSS $^-$  ( $\tilde{X}^1A'$ ) +  $h\nu \rightarrow$  H/DSS ( $\tilde{X}^2A''$ ) +  $e^-$  process, correspond mostly to the excitation of the SS stretching mode ( $\nu_3$ ) and the isotopic shift for this mode is distinctly smaller than the PhotoElectron Spectroscopy experimental resolution (of  $\sim 160 \text{ cm}^{-1}$  [5]), the corresponding spectra for HSS $^-$  and for DSS $^-$  should have similar shapes with relatively few differences, which is consistent with the data given in Ref. [5].

## V. Conclusion

Accurate *ab initio* computations are performed on the HSS $^-$  electronic states correlating to the bound asymptotes of this molecular system and those of their respective neutral parent states. In light of these calculations, the stability of the electronic states of this anion has been treated, confirming the experimental findings that HSS $^-$  does possess a unique stable electronic state of  $^1A'$  symmetry. This electronic state is found to support several rovibrational levels located below the autodetachment threshold corresponding to the vibrational ground state of HSS ( $\tilde{X}^2A''$ ). The present theoretical predictions are also used for discussing the reactions leading to the formation of HSS $^-$  when S/S $^-$  (H/H $^-$ ) and SH/SH ( $S_2^-/S_2$ ) are colliding together, which are viewed to follow the PES of HSS $^-$   $\tilde{X}$  and the long range parts of the PESs of the HSS $^-$  electronic excited states. These reactions are occurring in

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2  
3 competition with the autodetachment processes. Finally, a set of accurate spectroscopic data are  
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5 computed for  $\text{HSS}^- \tilde{X}$  that should be helpful for identifying this triatomic negative ion in the  
6  
7 interstellar media and in laboratory.  
8

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11  
12  
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**Table I:** Dominant electron configurations of the electronic states of HSS<sup>-</sup> and HSS investigated presently. These configurations are quoted for  $R_{SS}=3.9$  bohr,  $R_{SH}=2.5$  bohr and  $\theta = 140^\circ$ .

State	Electron configuration
HSS( $\tilde{X}^2A''$ )	$\dots(13a')^2(14a')^0(15a')^0(2a'')^2(3a'')^1$
HSS( $1^2A'$ )	$\dots(13a')^1(14a')^0(15a')^0(2a'')^2(3a'')^2$
HSS( $1^4A''$ )	$\dots(13a')^1(14a')^1(15a')^0(2a'')^2(3a'')^1$
HSS <sup>-</sup> ( $\tilde{X}^1A'$ )	$\dots(13a')^2(14a')^0(15a')^0(2a'')^2(3a'')^2$
HSS <sup>-</sup> ( $2^1A'$ )	$\dots(13a')^1(14a')^1(15a')^0(2a'')^2(3a'')^2$
HSS <sup>-</sup> ( $1^1A''$ )	$\dots(13a')^2(14a')^1(15a')^0(2a'')^2(3a'')^1$
HSS <sup>-</sup> ( $2^1A''$ )	$\dots(13a')^2(14a')^0(15a')^1(2a'')^2(3a'')^1$
HSS <sup>-</sup> ( $1^3A'$ )	$\dots(13a')^1(14a')^1(15a')^0(2a'')^2(3a'')^2$
HSS <sup>-</sup> ( $2^3A'$ )	$\dots(13a')^1(14a')^0(15a')^1(2a'')^2(3a'')^2$
HSS <sup>-</sup> ( $1^3A''$ )	$\dots(13a')^2(14a')^0(15a')^1(2a'')^2(3a'')^1$
HSS <sup>-</sup> ( $2^3A''$ )	$\dots(13a')^2(14a')^1(15a')^0(2a'')^2(3a'')^1$

**Table II:**  $C_{ijk}$  coefficients of the 3D PES expansion of  $\text{HSS}^-$  ( $\tilde{X}^1A'$ ). See text.

$C_{200}$	1.1679279356	$C_{110}$	0.0814196421	$C_{011}$	-0.0440543365
$C_{020}$	0.8006828562	$C_{101}$	0.1323282354	$C_{210}$	-0.2403054745
$C_{002}$	0.0813695753	$C_{300}$	-1.5108646006	$C_{201}$	-0.2784954714
$C_{120}$	0.2954557506	$C_{030}$	-0.5414964790	$C_{102}$	-0.2160236364
$C_{111}$	0.0369662108	$C_{021}$	-0.0817846500	$C_{400}$	0.0049308279
$C_{012}$	-0.0113640627	$C_{003}$	0.0033473528	$C_{130}$	0.2993250306
$C_{310}$	0.0791335309	$C_{220}$	-0.4331797664	$C_{211}$	0.0523300287
$C_{040}$	-0.5020792556	$C_{301}$	-0.3118392838	$C_{202}$	0.0506992063
$C_{121}$	-0.0612625150	$C_{031}$	-0.0593922840	$C_{103}$	-0.0542080560
$C_{112}$	-0.0501480901	$C_{022}$	-0.0094558269	$C_{013}$	0.0571900248
$C_{004}$	-0.0176684380				

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**Table III:** Quartic force fields of  $\text{HSS}^- (\tilde{X}^1\text{A}')$  and  $\text{DSS}^- (\tilde{X}^1\text{A}')$  in dimensionless normal coordinates. All values are in  $\text{cm}^{-1}$ . See text for more details.

Quartic force field	$\text{HSS}^-$	$\text{DSS}^-$
$\omega_1$	2594.4	1863.9
$\omega_2$	829.8	600.2
$\omega_3$	484.6	484.4
$\phi_{333}$	-149.7	-149.3
$\phi_{222}$	6.83	4.21
$\phi_{111}$	-1780.78	-1082.2
$\phi_{332}$	-5.65	-6.68
$\phi_{322}$	-69.4	-51.3
$\phi_{331}$	7.2	9.79
$\phi_{221}$	510.2	290.6
$\phi_{312}$	-96.9	-72.3
$\phi_{311}$	71.9	51.7
$\phi_{211}$	-120.6	-77.0
$\phi_{3333}$	40.9	40.9
$\phi_{2222}$	297.6	131.3
$\phi_{1111}$	1003.4	516.4
$\phi_{3332}$	-0.76	-0.25
$\phi_{3222}$	-62.6	-36.7
$\phi_{3322}$	15.2	12.0
$\phi_{3331}$	3.6	3.2
$\phi_{2221}$	-71.3	-36.1
$\phi_{3321}$	-8.84	-7.0
$\phi_{3221}$	36.6	22.1
$\phi_{3311}$	-19.1	-16.1
$\phi_{2211}$	-527.1	-256.3
$\phi_{3211}$	94.2	60.5
$\phi_{3111}$	-38.8	-24.2
$\phi_{2111}$	96.9	52.6

**Table IV:** Structural and spectroscopic parameters of HSS $\tilde{(\tilde{X}^1A')}$  and DSS $\tilde{(\tilde{X}^1A')}$  deduced from our three-dimensional potential energy surface using second order perturbation theory and including the equilibrium geometry ( $R_{eSS}$ ,  $R_{eSH}$  and  $\theta_e$ ), rotational constants ( $A_e$ ,  $B_e$ ,  $C_e$ ), harmonic ( $\omega_i$ ) wavenumbers, vibration-rotation terms ( $\alpha_i$ ) and anharmonicity terms ( $x_{ij}$ ).

	HSS $\tilde{(\tilde{X}^1A')}$	DSS $\tilde{(\tilde{X}^1A')}$
$R_{eSS}/\text{\AA}$	2.091 2.089 <sup>a)</sup> 2.121 <sup>b)</sup> 2.101 <sup>c)</sup>	
$R_{eSH}/\text{\AA}$	1.343 1.346 <sup>a)</sup> 1.332 <sup>b)</sup> 1.348 <sup>c)</sup>	
$\theta_e/\text{degree}$	101.8 101.6 <sup>a)</sup> 101.0 <sup>b)</sup> 101.4 <sup>c)</sup>	
$A_e/\text{MHz}$	302035.8	157332.7
$B_e/\text{MHz}$	7050.1	6877.6
$C_e/\text{MHz}$	6889.3	6589.6
$\omega_1/\text{cm}^{-1}$	2594.4 2599 <sup>c)</sup>	1863.9
$\omega_2/\text{cm}^{-1}$	829.8 822 <sup>c)</sup>	600.2
$\omega_3/\text{cm}^{-1}$	484.6 478 <sup>c)</sup>	484.4
$\alpha_1^A/\text{MHz}$	9598.7	3472.9
$\alpha_2^A/\text{MHz}$	-6188.8	-2359.3
$\alpha_3^A/\text{MHz}$	226.5	129.1
$\alpha_1^B/\text{MHz}$	-27.1	-14.3
$\alpha_2^B/\text{MHz}$	19.2	6.4
$\alpha_3^B/\text{MHz}$	46.5	43.9
$\alpha_1^C/\text{MHz}$	-21.4	-7.7



$\alpha_2^C$ /MHz	31.1	19.5
$\alpha_3^C$ /MHz	46.1	45.0
$x_{11}$ /cm <sup>-1</sup>	-68.1	-35.1
$x_{22}$ /cm <sup>-1</sup>	-5.75	-2.9
$x_{33}$ /cm <sup>-1</sup>	-2.26	-2.2
$x_{12}$ /cm <sup>-1</sup>	-13.7	-7.1
$x_{13}$ /cm <sup>-1</sup>	2.31	1.7
$x_{23}$ /cm <sup>-1</sup>	-4.85	-3.7

- a) This work. Geometry optimized at the cc-pV6Z/CCSD(T) level of theory.
- b) *Spd* cc-pVDZ/SCF calculations. Ref. [29]
- c) Calculated at the aug-ccpVQZ/CCSD(T). Ref. [26].

**Table V:** Variationally computed vibrational term values of the electronic ground states of HSS<sup>-</sup> and of DSS<sup>-</sup>. The asterisk denotes anharmonic resonances (see text).

HSS <sup>-</sup> ( $\tilde{X}^1A'$ ) <sup>a)</sup>		DSS <sup>-</sup> ( $\tilde{X}^1A'$ ) <sup>b)</sup>	
( $v_1, v_2, v_3$ )	Energy/cm <sup>-1</sup>	( $v_1, v_2, v_3$ )	Energy/cm <sup>-1</sup>
(0,0,0)	0.0 <sup>c)</sup>	(0,0,0)	0.0 <sup>c)</sup>
(0,0,1)	478.8	(0,0,1)	478.9
(0,1,0)	808.8	(0,1,0)	588.9
(0,0,2)	953.0	(0,0,2)	953.4
(0,1,1)	1282.6	(0,1,1)	1064.0
(0,0,3)	1422.8	(0,2,0)	1172.0
(0,2,0)	1605.9	(0,0,3)	1423.4*
(0,1,2)	1751.8	(0,1,2)	1534.7*
(0,0,4)	1888.4	(0,2,1)	1643.1*
(0,2,1)	2074.5	(0,3,0)	1748.8*
(0,1,3)	2216.6*	(1,0,0)	1791.6
(0,0,5)	2350.5	(0,0,4)	1889.2*
(0,3,0)	2390.6	(0,1,3)	2000.9*
(1,0,0)	2453.6	(0,2,2)	2109.8*
(0,2,2)	2538.5*	(0,3,1)	2215.8*
(0,1,4)	2677.6*	(1,0,1)	2272.6*
(0,0,6)	2808.0*	(0,4,0)	2319.3
(0,3,1)	2853.9*	(0,0,5)	2351.1
(1,0,1)	2938.1	(1,1,0)	2374.2*
(0,2,3)	2998.2*	(0,1,4)	2463.5
(0,1,5)	3139.9*	(0,2,3)	2572.2*
(0,4,0)	3162.8	(0,3,2)	2678.5
(1,1,0)	3250.5	(1,0,2)	2750.4*
(0,0,7)	3264.5*	(0,1,4)	2782.3*
(0,3,2)	3312.6*	(0,0,6)	2809.2*
(1,0,2)	3414.9	(1,1,1)	2851.9
(0,2,4)	3455.5*	(0,5,0)	2883.6*
(0,1,6)	3593.7*	(0,1,5)	2925.5*
(0,4,1)	3620.9*	(1,2,0)	2951.3*
(0,0,8)	3732.7*	(0,2,4)	3031.9

a) Zero point vibrational energy ( $G_0$ ) = 1926.1 cm<sup>-1</sup>. c) Reference energy.

b) Zero point vibrational energy ( $G_0$ ) = 1459.4 cm<sup>-1</sup>.

**Figure Captions:**

**Figure I:** MRCI+Q one-dimensional cuts of the PESs of the electronic states of  $\text{HSS}^-$  (thin lines) together with those of  $\text{HSS}(\tilde{X}^2A''$  and  $1^2A')$  (thick lines) for bent structures. These curves are given along the SS ( $R_{\text{SS}}$ , in A) and SH ( $R_{\text{SH}}$ , in B) internal coordinates. The remaining coordinates are kept fixed at  $R_{\text{SH}} = 2.5$  bohr or  $R_{\text{SS}} = 3.9$  bohr and  $\theta = 102^\circ$  corresponding to their equilibrium values in  $\text{HSS}^- (\tilde{X}^1A')$ . These curves are given in energy with respect to the  $\text{HSS} (X^2A'')$  minimum.

**Figure II:** MRCI+Q one-dimensional cuts of the PESs of the electronic states of  $\text{HSS}^-$  (thin lines) together with those of  $\text{HSS} (\tilde{X}^2A''$  and  $1^2A')$  (thick lines) along the bending coordinate. The SH and SS distances are set to 2.5 and 3.9 bohr, respectively. These curves are given in energy with respect to the  $\text{HSS} (\tilde{X}^2A'')$  minimum.

**Figure III:** Collinear MRCI+Q one-dimensional cuts of the PESs of the electronic states of  $\text{HSS}^-$  (thin lines) together with those of  $\text{HSS}(\tilde{X}^2\Pi$  and  $^4\Sigma^-)$  (thick lines) along the SS ( $R_{\text{SS}}$ , in A) and SH ( $R_{\text{SH}}$ , in B) stretches. The remaining coordinates are kept fixed at their equilibrium values in  $\text{HSS}^- (\tilde{X}^1A')$ . These curves are given in energy with respect to the  $\text{HSS} (\tilde{X}^2A'')$  minimum.

Figure I A

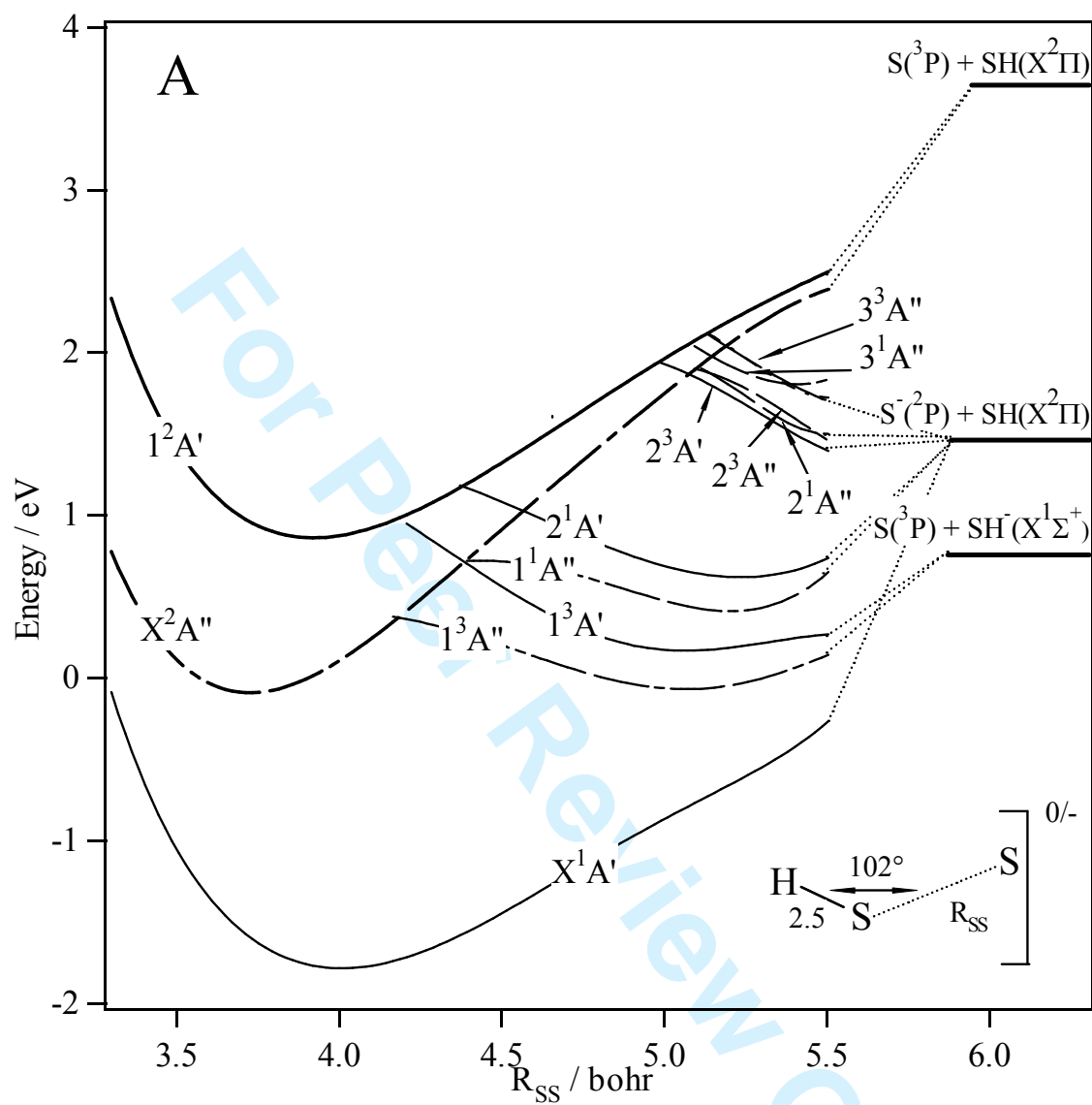


Figure I B

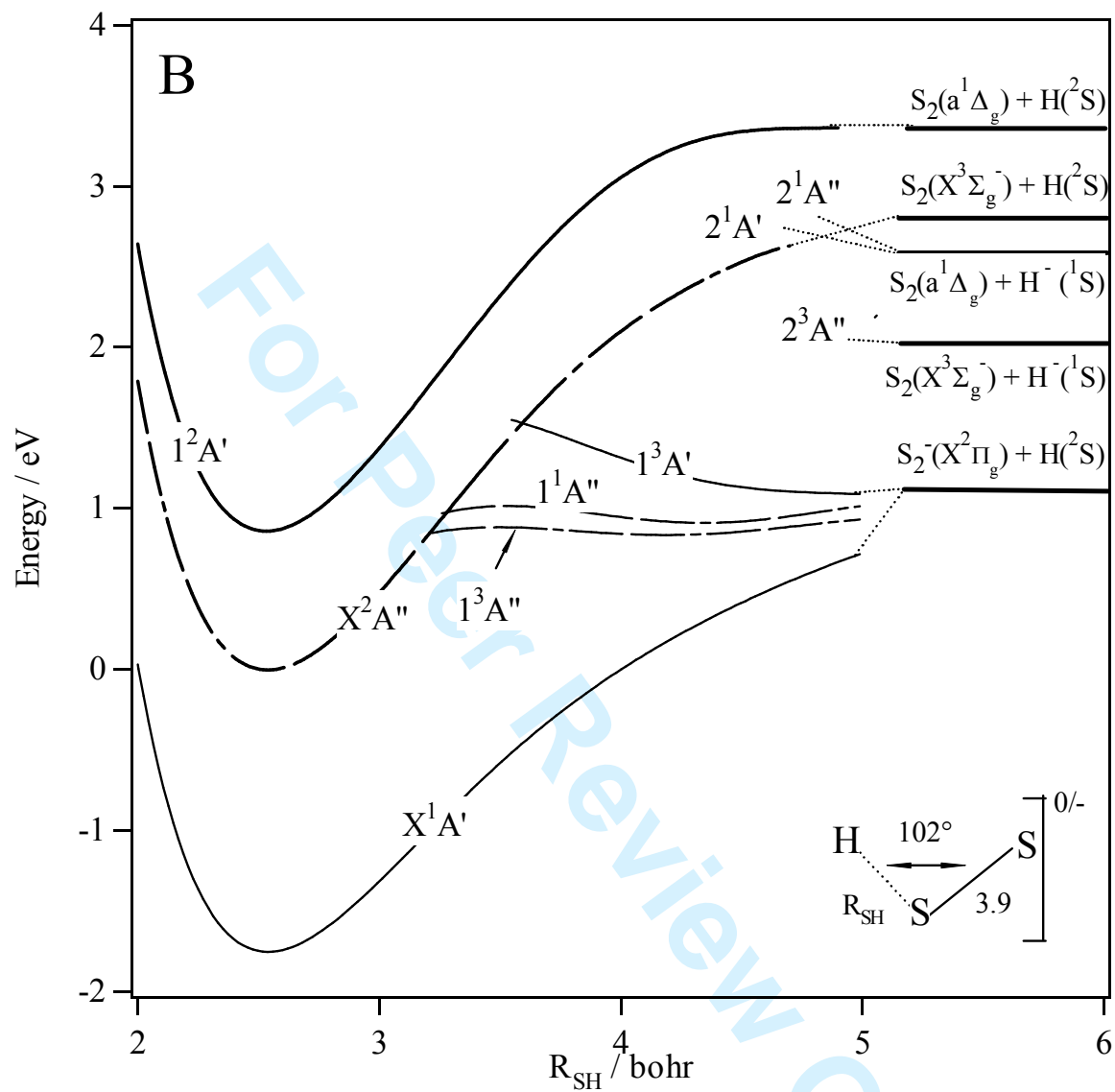


Figure II

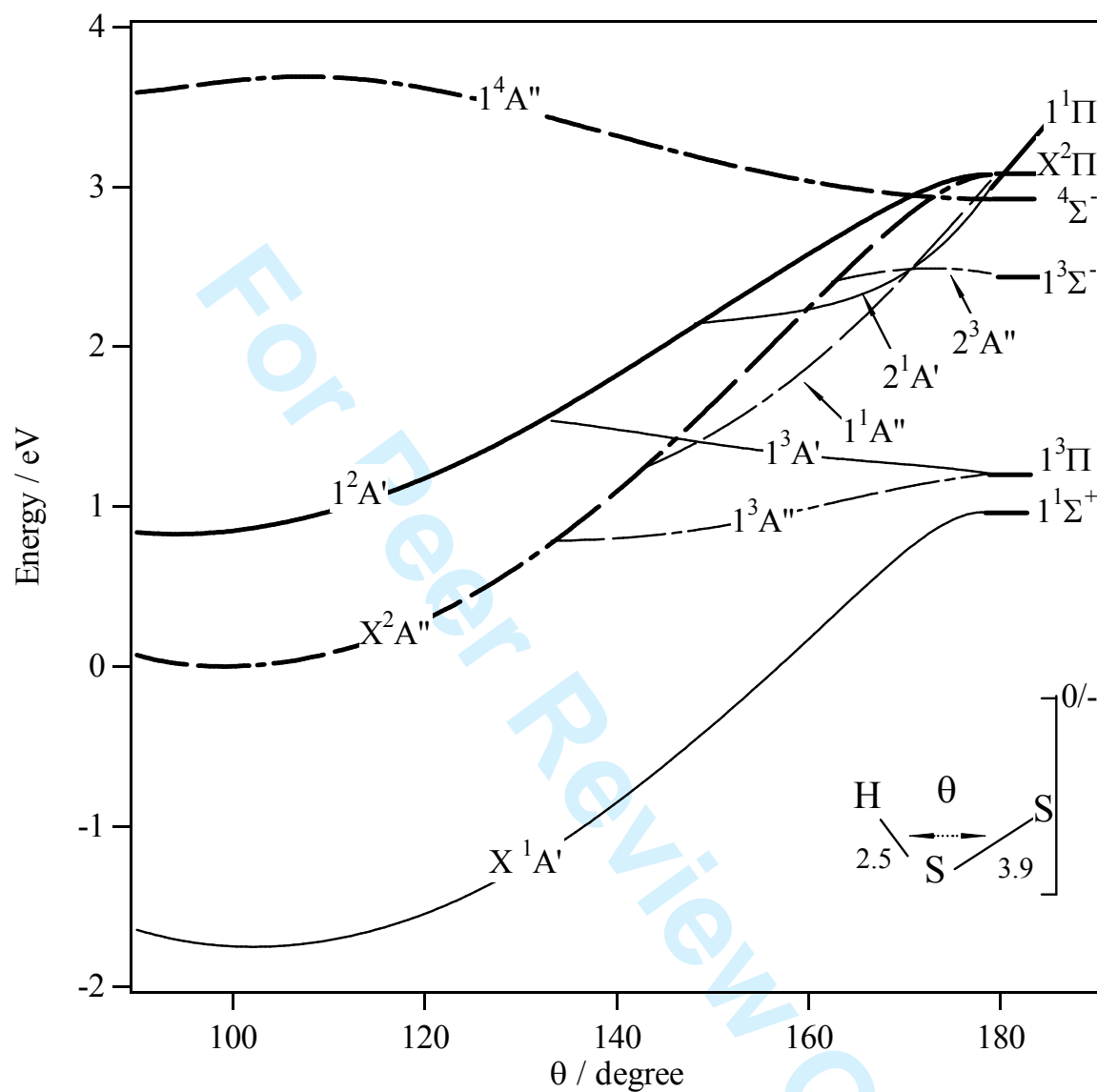


Figure III A

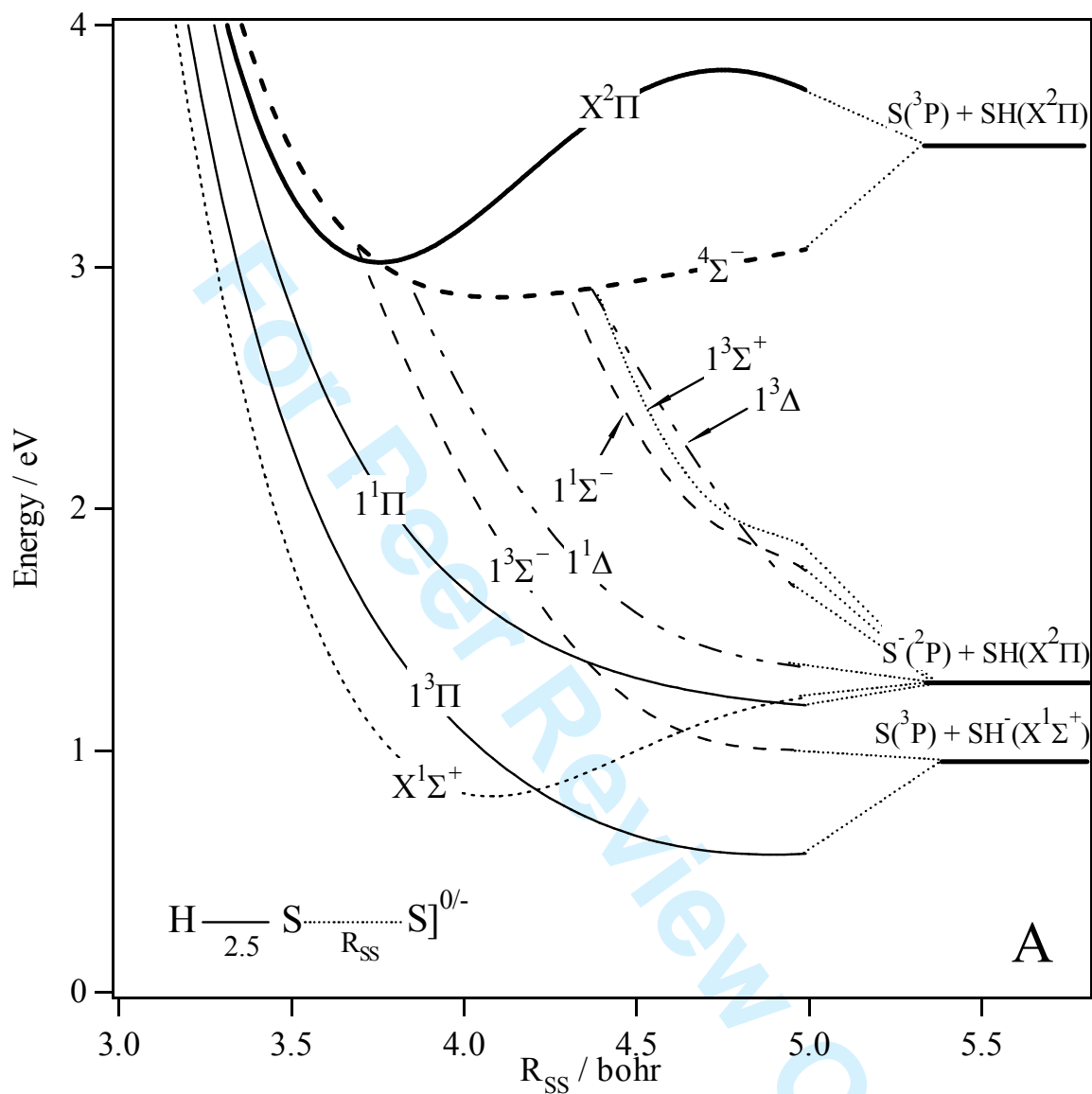


Figure III B

