

## Characterizing New Molecular Species: A Systematic Study of Stationary States on the Singlet [H, Se, Br] Potential Energy Surface

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Usando um alto nível de teoria, CCSD(T)/CBS, investigou-se a estrutura, o espectro no infravermelho, a estabilidade relativa, as energias de dissociação e a barreira energética para a interconversão de novas espécies moleculares, HSeBr e HBrSe. Previu-se a molécula HSeBr mais estável por 44,95 kcal mol<sup>-1</sup> que HBrSe, com uma barreira ( $\Delta G^\ddagger$ ) para a isomerização de 52,24 kcal mol<sup>-1</sup>. Pelo fato da barreira para a reação reversa ser bem menor que a do processo direto, espera-se que o isômero menos estável, caso venha a ser formado, seja prontamente convertido em HSeBr, exceto a temperaturas criogênicas. A possibilidade de dissociação em Se e HBr é também provável por um mecanismo de acoplamento spin-órbita. Calores de formação a 298,15 K para SeBr e HSeBr foram estimados como sendo 31,54 e 12,31 kcal mol<sup>-1</sup>, respectivamente. Estimou-se ainda o efeito da inclusão do efeito da correlação caroço-valência nos parâmetros estruturais e nas frequências, como também a contribuição da anarmonicidade nas frequências. Cálculos adicionais realizados com funções de onda explicitamente correlacionadas mostraram resultados bastante promissores de convergência mais rápida para o limite de base completa (CBS) com bases relativamente bem menores.

Structural characterization, infrared spectra, relative stability, dissociation energies and energy barrier for isomerization of new molecular species, HSeBr and HBrSe, were investigated at a high level of theory, CCSD(T)/CBS. HSeBr is predicted to be 44.95 kcal mol<sup>-1</sup> more stable than HBrSe, with a barrier ( $\Delta G^\ddagger$ ) for isomerization of 52.24 kcal mol<sup>-1</sup>. Due to the much smaller barrier for the reverse reaction, if formed, the less stable isomer is expected to be readily converted to HSeBr, except at cryogenic temperatures. The possibility of dissociation into atomic Se and HBr is also a likely one by a spin-orbit coupling mechanism. Heats of formation of SeBr and HSeBr were estimated to be 31.54 and 12.31 kcal mol<sup>-1</sup>, respectively, at 298.15 K. The effect of core-valence correlation on the structural parameters and harmonic frequencies was also evaluated, as well as the contribution of anharmonicity to the frequencies. Additional calculations performed with explicitly correlated wavefunctions showed promising results of fast convergence to the complete basis set (CBS) limit with relatively smaller basis sets.

**Keywords:** [H, Se, Br] potential energy surface, structures, frequencies, heats of formation, isomerization

### Introduction

Halogen-containing species like FO, ClO, BrO, IO, HOCl, HOBr and HOI are known to participate in reaction cycles leading to the catalytic depletion of ozone in the troposphere and stratosphere where they are photodissociated by UV radiation from the Sun thus generating reactive radicals. The role as a temporary reservoir played by these species is a central one to the

understanding of the mechanisms underlying the catalytic cycles and has thus received considerable attention in the literature.<sup>1-9</sup>

Motivated by analogies with the series of oxygenated molecules, our group has investigated a series of sulfur-halogen species with special focus on the manifold of electronic states correlating with the lowest-lying dissociation channels, including potential energy curves and the associated vibrational and rotational spectroscopic constants, radiative transition probabilities and lifetimes of the radicals SCl, SBr and SI. These earlier studies on

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sulfur-halogen diatomics have been extended to include the calculation of heats of formation, relative stability, energy barrier for isomerization, structural characterization, and the prediction of infrared spectra of triatomics like HSCl, HSBr and HSI, which if formed by any process can also be seen to have a potential role in the chemistry of the Earth atmosphere.<sup>10-16</sup> In the case of HSCl, our group showed that the molecule can be formed in the reaction between the HS radical, generated by atmospheric decomposition of H<sub>2</sub>S, and Cl<sub>2</sub> or the Cl radical that are relatively abundant in the stratosphere.<sup>17</sup> Concerning selenium compounds, the prototype selenide, H<sub>2</sub>Se, known to be very toxic like H<sub>2</sub>S, and quite familiar to inorganic chemists, has also been detected in unexpected environments like the liver of male rats.<sup>18</sup> In the soil, microbial action has also been the source of volatile selenium compounds.<sup>19</sup> Many physical and biological processes of natural or anthropogenic origin have led to an increase of selenium species in the atmosphere. Studies by Mosher and Duce<sup>20</sup> estimated that there is an ocean-to-atmosphere vapor phase selenium flux of  $5-8 \times 10^9$  g Se year<sup>-1</sup>. This ubiquitous presence of selenium in nature and the scarcity of data on simple diatomic and triatomic systems has called our attention, and as a natural extension of previous studies on sulfur-halogen compounds, a series of selenium-halogen species, SeF, HSeF, SeCl and HSeCl, was investigated in our group.<sup>21-24</sup>

In this context, as part of ongoing studies on chalcogen-halogen compounds, our previous investigations are further extended on this series by focusing now on the species HSeBr and SeBr. To the best of our knowledge, only calculations of spectroscopic parameters for SeBr and a bond analysis of a series of chalcogen-halogen diatomics have been reported in the literature.<sup>25,26</sup> In this work, using a highly correlated method for the description of the electronic structure, CCSD(T), along with a series of correlation consistent basis sets, this investigation is focused mainly on the prediction of the infrared spectra, structural characterization, energy barrier and relative stability of isomerization, and the determination of heats of formation. Our group hopes that these results can motivate and guide further studies on their isolation and characterization in the laboratory and in their potential role as trace species in the Earth atmosphere.

## Methodology

In this study, the stationary state geometries were computed with the series of correlation consistent basis sets of Dunning and co-workers,<sup>27,28</sup> aug-cc-pVnZ ( $n = D, T, Q$  and 5) for H, and the sets aug-cc-pVnZ-PP (aVnZ) with  $n = D, T, Q$  and 5 for Br and Se, as developed by

Peterson *et al.*<sup>29</sup> The basis sets for the heavier atoms include a small-core (10 electrons) energy consistent relativistic pseudo-potential (PP), namely ECP10MDF, in which the 1s-2p inner-core was replaced by an energy consistent pseudo-potential optimized in a multiconfigurational Dirac-Hartree-Fock calculation. The energetic results were further extrapolated to the complete basis set (CBS) limit using the three- and two-parameter formulas given below, in which the first (second) one usually underestimates (overestimates) the energy. According to Feller *et al.*,<sup>30</sup> the best CBS estimate can be taken as the average of two energy limits, and half the spread as an estimate in the uncertainty of the extrapolation procedure

$$E(n) = E_{\text{CBS}} + B \exp\{-(n-1)\} + C \exp\{-(n-1)^2\} \quad (1)$$

$(n = 3, 4, 5)$

and

$$E(n) = E_{\text{CBS}} + B/n^3 \quad (n = 4, 5) \quad (2)$$

Strictly speaking, equation 2 was intended for the correlation energy component of the energy, but since for large basis sets the truncation error for the correlation energy far exceeds that of the Hartree-Fock contribution, this expression has also been used to extrapolate the total CCSD(T) energy, following a common practice in the literature. Concerning the sources of errors in electronic structure calculations, the reader is referred to the work of Feller *et al.*<sup>30</sup> on the performance of CBS extrapolation approaches in the calculation of atomization energies using CCSD(T).

Aiming at results approaching chemical accuracy, our choice of methods for describing the electronic structure considered essentially the possibility of incorporating in the wave-function as many correlation effects as possible, and the coupled cluster single and double excitations approach with perturbative contribution of connected triples, CCSD(T), was the one employed for the closed shell states. For open shell species, the partially spin restricted approach, RCCSD(T), based on high-spin restricted Hartree-Fock (ROHF) orbitals was used. This approach imposes a restriction on the coupled cluster amplitudes such that the linear part of the wavefunction becomes a spin eigenfunction. Spin contamination thus becomes a negligible effect.<sup>31,32</sup>

Additionally, for the heats of formation and the enthalpies of reaction calculated in this study, core-valence correlation corrections (CV) were also estimated using the cc-pwCVnZ-PP basis set for Se and Br, where  $n = D, T$  and  $Q$ , for both the valence only correlated calculation and

the core-valence correlated one that included all but the inner-core 1s-2p electrons of Se and Br.<sup>33</sup> Scalar relativistic effects (SR) were also estimated. It is important to point out that, for the Se and Br atoms, the major contribution of scalar relativistic effects has already been accounted for by the relativistic pseudo-potential. However, to consider this effect outside of the pseudo-potential region, it was estimated as expectation values of the one-electron Darwin and mass-velocity terms in the Breit-Pauli Hamiltonian from CISD/aV5Z calculations at the optimized CCSD(T)/aV5Z geometries.

Anharmonic vibrational frequencies were determined by the self-consistent field (VSCF)<sup>34,35</sup> and the configuration interaction (VCI)<sup>36-40</sup> approaches based on a grid representation of the potential.<sup>41,42</sup> A 3-mode expansion of the potential energy surface was used in the 1-D, 2-D and 3-D surfaces, which were generated at the CCSD(T) level of theory.

Explicitly correlated coupled-cluster calculations were additionally performed within the CCSC(T)-F12b<sup>43,44</sup> approximation; for such, the diagonal fixed amplitude *Ansatz* 3C(FIX) was selected, and the cc-pVnZ-F12 (VnZ-12) basis sets, where  $n = D, T, \text{ and } Q$ , was employed. As recommended by Peterson *et al.*,<sup>45,46</sup> the geminal exponents  $\gamma$  employed were set equal to 0.9, 1.0, 1.0  $a_0^{-1}$  for VDZ-F12, VTZ-F12 and VQZ-F12, respectively. In the resolution of the identity (RI), the cc-pVnZ-F12/OptRI

basis set was used,<sup>46,47</sup> and in the density fitting of the Fock and exchange matrices, the cc-pVnZ/JKFIT ( $n = T$  for VDZ-F12 and VTZ-F12, and  $n = Q$  for VQZ-F12) for H and the QZVPP/JKFIT basis sets of Weigend for Se and Br was employed.<sup>48,49</sup> The aug-cc-pVnZ/MP2FIT basis set ( $n = T$  for VDZ-F12 and VTZ-F12, and  $n = Q$  for VQZ-F12) for hydrogen and cc-pVnZ-F12/MP2FIT sets for selenium and bromine<sup>46,50</sup> were used for density fitting of the remaining two-electron integrals. In this work, all calculations were performed with the MOLPRO suite of programs.<sup>51</sup>

## Results and Discussion

### Atomization energies and heats of formation of SeBr and HSeBr

The heats of formation were computed in two steps. First, the atomization energies ( $\Sigma D_0$ ) were evaluated using the energies extrapolated to the complete basis set (CBS) limit plus additional corrections accounting for core-valence correlation effects, and both scalar relativistic and spin-orbit effects. Then, the theoretical atomization energies were combined with the experimental heats of formation of the atomic fragments making use of Hess's law. All the energetic contributions to the atomization energies and heats of formations are summarized in Table 1.

**Table 1.** Total CCSD(T) energies for H, Br, Se, SeH, SeBr, HSeBr, HBrSe and the transition state (HSeBr  $\rightarrow$  HBrSe), and various contributions from core-valence correlation effects, scalar relativistic (SR) and spin-orbit (SO) effects, and zero-point energies (ZPE) for the atomization energy of HSeBr

|   | H          | Br          | Se ( <sup>3</sup> P) | HSe         | SeBr        | HSeBr       | HBrSe       | TS          |
|---|------------|-------------|----------------------|-------------|-------------|-------------|-------------|-------------|
| aVDZ / a.u.   | -0.499334  | -415.590276 | -371.939271          | -372.553538 | -787.600613 | -788.218629 | -788.146559 | -788.137648 |
| aVTZ / a.u.   | -0.499821  | -415.652742 | -371.986554          | -372.607144 | -787.721685 | -788.343860 | -788.272703 | -788.263060 |
| aVQZ / a.u.   | -0.499948  | -415.668280 | -371.996284          | -372.618938 | -787.751746 | -788.375284 | -788.303572 | -788.293401 |
| aV5Z / a.u.   | -0.499995  | -415.673316 | -371.999307          | -372.622548 | -787.761555 | -788.385426 | -788.313545 | -788.303186 |
| CBS1 / a.u.   | -0.500022  | -415.676238 | -372.001060          | -372.624641 | -787.767249 | -788.391312 | -788.319334 | -788.308865 |
| CBS2 / a.u.   | -0.500044  | -415.678598 | -372.002479          | -372.626335 | -787.771845 | -788.396066 | -788.324008 | -788.313452 |
| Average / a.u.                                      | -0.500033  | -415.677418 | -372.001770          | -372.625488 | -787.769547 | -788.393689 | -788.321671 | -788.311158 |
| (Spread/2) / (kcal mol <sup>-1</sup> ) <sup>a</sup> | $\pm 0.01$ | $\pm 0.74$  | $\pm 0.44$           | $\pm 0.53$  | $\pm 1.44$  | $\pm 1.47$  | $\pm 1.49$  | $\pm 1.44$  |
| $\Delta E_{el}$ / (kcal mol <sup>-1</sup> )         |            |             |                      | 77.61       | 56.70       | 134.58      |             |             |
| $E_{cv}$ / a.u.                                     |            | -0.907124   | -0.905322            | -0.906105   | -1.813372   | -1.813936   |             |             |
| $\Delta E_{cv}$ / (kcal mol <sup>-1</sup> )         |            |             |                      | 0.49        | 0.58        | 0.94        |             |             |
| $E_{sr}$ / a.u.                                     | -0.000007  | -0.370052   | -0.304170            | -0.304203   | -0.674309   | -0.674342   |             |             |
| $\Delta E_{sr}$ / (kcal mol <sup>-1</sup> )         |            |             |                      | 0.02        | 0.06        | 0.07        |             |             |
| $E_{so}$ / (kcal mol <sup>-1</sup> )                |            | -3.51       | -2.70                | -2.52       | -2.78       | 0.00        |             |             |
| $\Delta E_{so}$ / (kcal mol <sup>-1</sup> )         |            |             |                      | -0.18       | -3.43       | -6.21       |             |             |
| $\Delta E_{zpe}$ / (kcal mol <sup>-1</sup> )        |            |             |                      | -3.45       | -0.47       | -4.97       |             |             |
| $\Sigma D_0$ / (kcal mol <sup>-1</sup> )            |            |             |                      | 74.49       | 53.44       | 124.41      |             |             |
| $\Delta H_f$ (0 K) / (kcal mol <sup>-1</sup> )      |            |             |                      | 35.05       | 32.64       | 13.31       |             |             |
| Exper. <sup>52</sup> / (kcal mol <sup>-1</sup> )    |            |             |                      | 35.25       |             |             |             |             |
| $\Delta H_f$ (298.15 K) / (kcal mol <sup>-1</sup> ) |            |             |                      | 35.38       | 31.54       | 12.31       |             |             |

<sup>a</sup>Measure of uncertainties in the extrapolated energies.

As an assessment of the quality of our results, the atomization energy and the heat of formation of SeH, for which experimental data are reported in the literature, were also evaluated. Our estimate of the atomization energy of SeH, 74.49 kcal mol<sup>-1</sup> is in excellent agreement with that derived experimentally by Gibson *et al.*,<sup>52</sup> 74.27 ± 0.23 kcal mol<sup>-1</sup>. The inclusion of spin orbit effects in the two diatomic molecules was based on the following values of spin-orbit coupling constants: SeH (-1764 cm<sup>-1</sup> = -5.04 kcal mol<sup>-1</sup>) reported by Gibson *et al.*,<sup>52</sup> and SeBr (-1945 cm<sup>-1</sup> = -5.56 kcal mol<sup>-1</sup>) evaluated at the MRCI/aV5Z level of theory in our group. For the atomic species, the corrections were estimated as a weighted average of the corresponding multiplets using the experimental energies of Radzig and Smirnov:<sup>53</sup> Br (-3.51 kcal mol<sup>-1</sup>) and Se (-2.70 kcal mol<sup>-1</sup>). To determine the heats of formation of SeH (g), SeBr (g) and HSeBr (g) at 0 K, the following experimental data for the heats of formation were used: H (51.63 kcal mol<sup>-1</sup>), Br (28.18 kcal mol<sup>-1</sup>) and Se (57.90 kcal mol<sup>-1</sup>).<sup>52,54</sup> Since the larger part of the scalar relativistic effects was accounted for by the relativistic pseudo-potential for the Se and Br atoms, those due to the outer electrons have a very small influence on the atomization energy, increasing it by only 0.07 kcal mol<sup>-1</sup>. Thus, our final estimate

of Δ<sub>f</sub>H (0 K) is 35.05 kcal mol<sup>-1</sup> for SeH, which is in excellent agreement with the experimental evaluation of Gibson *et al.*,<sup>52</sup> 35.25 kcal mol<sup>-1</sup>. For SeBr and HSeBr, our final estimates are 32.64 and 13.31 kcal mol<sup>-1</sup>, respectively. Assuming ideal gas behavior and using standard statistical mechanics expressions to account for the thermal effects and the vibrational frequencies listed in Table 2, Δ<sub>f</sub>H<sub>f</sub> (289.15 K) was predicted to be 35.38 kcal mol<sup>-1</sup> for SeH, 31.54 kcal mol<sup>-1</sup> for SeBr and 12.31 kcal mol<sup>-1</sup> for HSeBr. For the sake of comparison, our previous results of Δ<sub>f</sub>H<sub>f</sub> (289.15 K) for HSeF and HSeCl are -22.81 and 4.97 kcal mol<sup>-1</sup>, respectively.

Concerning the different contributions to the atomization energies, as mentioned above, the scalar relativistic corrections turned out to be very small because they are mainly included in the relativistic pseudopotential. As to the spin-orbit ones, they are significant for the open shell systems containing heavy atoms. This contribution is largest for the species HSeBr due to the energy lowering of the atomic fragments Se (<sup>3</sup>P) and Br (<sup>2</sup>P) only; this result should be contrasted with that for SeH, in which the spin-orbit interactions cause an energy lowering of about the same magnitude for both SeH and Se, and the overall contribution to the atomization energy turns out to be small. For core-valence correlation effects, the correction amounts

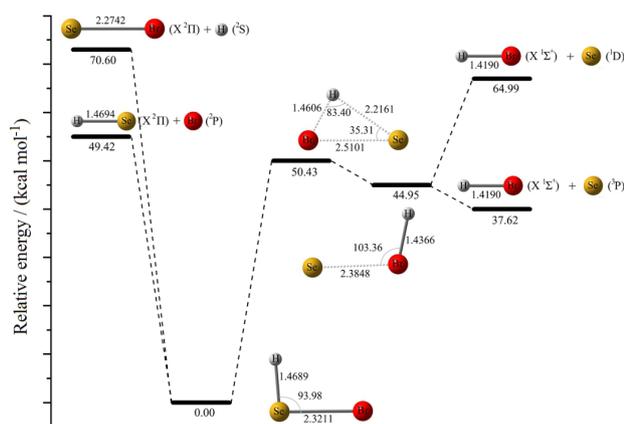
**Table 2.** Structural parameters, harmonic and fundamental frequencies for HSeBr, HBrSe and the associated transition state (TS)

| Basis sets | Geometry / Å, degree |        |        | Frequency / cm <sup>-1</sup> |                 |                 |                 |                 |                 |        |
|------------|----------------------|--------|--------|------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------|
|            | rHSe                 | rSeBr  | aHBr   | ω <sub>e1</sub>              | ν <sub>1</sub>  | ω <sub>e2</sub> | ν <sub>2</sub>  | ω <sub>e3</sub> | ν <sub>3</sub>  |        |
| HSeBr      | aVDZ                 | 1.4784 | 2.3706 | 93.71                        | 286.2           | 283.1           | 740.5           | 726.4           | 2405.1          | 2308.0 |
|            | aVTZ                 | 1.4703 | 2.3390 | 93.84                        | 299.8           | 296.9           | 747.2           | 733.6           | 2404.1          | 2310.1 |
|            | aVQZ                 | 1.4690 | 2.3275 | 93.98                        | 305.7           | 302.9           | 752.4           | 739.2           | 2409.9          | 2316.1 |
|            | aV5Z                 | 1.4689 | 2.3234 | 93.98                        | 307.7           | 304.8           | 753.5           | 740.6           | 2410.4          | 2316.2 |
|            | CBS(1)               | 1.4689 | 2.3211 | 93.98                        | 308.8           | 305.9           | 754.1           | 741.3           | 2410.7          | 2316.2 |
| Basis sets | Geometry / Å, degree |        |        | Frequency / cm <sup>-1</sup> |                 |                 |                 |                 |                 |        |
|            | rHBr                 | rBrSe  | aHSe   | ω <sub>e1</sub>              | ω <sub>e1</sub> | ω <sub>e1</sub> | ω <sub>e1</sub> | ω <sub>e1</sub> | ω <sub>e1</sub> |        |
| HBrSe      | aVDZ                 | 1.4419 | 2.4767 | 102.01                       | 190.1           | 185.5           | 542.4           | 521.5           | 2520.2          | 2387.1 |
|            | aVTZ                 | 1.4350 | 2.4142 | 102.89                       | 216.6           | 212.1           | 570.0           | 549.3           | 2501.6          | 2367.8 |
|            | aVQZ                 | 1.4353 | 2.3955 | 103.23                       | 224.5           | 220.2           | 581.3           | 561.0           | 2494.8          | 2360.6 |
|            | aV5Z                 | 1.4361 | 2.3888 | 103.31                       | 227.5           | 223.1           | 586.7           | 564.9           | 2489.3          | 2354.6 |
|            | CBS(1)               | 1.4366 | 2.3848 | 103.36                       | 229.2           | 224.8           | 589.8           | 567.2           | 2486.1          | 2351.1 |
| Basis sets | Geometry / Å, degree |        |        | Frequency / cm <sup>-1</sup> |                 |                 |                 |                 |                 |        |
|            | rHSe                 | rSeBr  | aHBr   | ω <sub>e1</sub>              | ω <sub>e1</sub> | ω <sub>e1</sub> | ω <sub>e1</sub> | ω <sub>e1</sub> | ω <sub>e1</sub> |        |
| TS         | aVDZ                 | 2.2492 | 2.6064 | 34.18                        | 662.8i          |                 | 174.7           |                 | 2303.0          |        |
|            | aVTZ                 | 2.2312 | 2.5411 | 34.83                        | 695.6i          |                 | 197.5           |                 | 2323.3          |        |
|            | aVQZ                 | 2.2214 | 2.5216 | 35.12                        | 717.7i          |                 | 204.7           |                 | 2315.8          |        |
|            | aV5Z                 | 2.2180 | 2.5143 | 35.24                        | 724.8i          |                 | 207.6           |                 | 2312.5          |        |
|            | CBS(1)               | 2.2161 | 2.5101 | 35.31                        | 729.0i          |                 | 209.3           |                 | 2310.6          |        |

to 0.49, 0.58 and 0.94 kcal mol<sup>-1</sup> for SeH, SeBr, and HSeBr, respectively. These corrections are not expected to change significantly with improvements in either the 1-particle or *n*-particle space. However, it is noticed that the uncertainties in the extrapolated energies are still significant at this level of theory, being larger than the contribution of some of the corrections made, as clearly shown in Table 1. Further improvements to reduce this spread can be made with the aV6Z and aV7Z basis sets, but they are very demanding computationally.

#### Relative stability, barrier to isomerization and dissociation channels

An overall energetic profile of the two triatomic minima, the associated transition state and two possible dissociation channels (H-SeBr and HSe-Br) on the singlet potential energy surface (PES) is presented in Figure 1.



**Figure 1.** Energy (kcal mol<sup>-1</sup>) profile and optimized geometric parameters (Å, degree) calculated at the CCSD(T)/CBS level of theory, including spin-orbit corrections and zero-point energies.

As also seen in Table 1, the global minimum can be clearly identified, for all basis set, with the HSeBr species, which is more stable than HBrSe by 45.19 kcal mol<sup>-1</sup>, considering the difference between the two average CBS energy values; with the inclusion of the zero-point energy, this difference becomes 44.95 kcal mol<sup>-1</sup>. The CCSD(T)/CBS values of the isomerization enthalpy and Gibbs energy at 298 K are 45.06 and 44.84 kcal mol<sup>-1</sup>, respectively. The transition state was located at 51.79 kcal mol<sup>-1</sup> (50.43 kcal mol<sup>-1</sup> including the zero-point energy) relative to the global minimum. In terms of the Gibbs energy ( $\Delta G^\ddagger$ ), a barrier of 52.24 kcal mol<sup>-1</sup> for the direct process HSeBr  $\rightarrow$  TS  $\rightarrow$  HBrSe was predicted, and of 7.40 kcal mol<sup>-1</sup> for the reverse one, at 298.15 K. Here, the harmonic oscillator/rigid rotor model was used to evaluate the Gibbs energy. In this context, it is important to mention that the magnitude of the  $T_1$  diagnostic for the transition state

remained below 0.02, a well-known recommendation in the literature, thus indicating that no multireference description was needed. Additionally, a test calculation at the CASSCF/MRCI level showed that the HF configuration contributed with a coefficient of 0.92, and that the next state of the same symmetry at the same geometry was located 11,478 cm<sup>-1</sup> higher in energy. Overall, no difficulty in the calculations was found that could be ascribed to an avoided crossing.

An estimate of the rate constant for the reverse process, using the conventional transition state theory, results in a value of  $6.05 \times 10^8$  s<sup>-1</sup> ( $\tau_{1/2} = 1.15 \times 10^{-9}$  s) at 298.15 K, which implies that, if formed, HBrSe would be readily converted to the more stable species, unless trapped in a cryogenic matrix. This rate constant estimated at the temperature of the liquid nitrogen, 77 K, is  $4.77 \times 10^{-4}$  s<sup>-1</sup> ( $\tau_{1/2} = 1.45 \times 10^3$  s).

A first estimate of the location of possible dissociation channels on the PES, H (<sup>2</sup>S) + SeBr (X <sup>2</sup>Π) and HSe (X <sup>2</sup>Π) + Br (<sup>2</sup>P), associated with bond breaking in HSeBr, resulted in dissociation energy values ( $D_e$ ) of 77.88 and 56.97 kcal mol<sup>-1</sup>, respectively. Inclusion of spin-orbit coupling contributions of bromine (-3.51 kcal mol<sup>-1</sup>) and of both diatomics, HSe (-2.52 kcal mol<sup>-1</sup>) and SeBr (-2.78 kcal mol<sup>-1</sup>), reduced the values of  $D_e$  to 75.10 and 50.94 kcal mol<sup>-1</sup>, respectively for H-SeBr and HSe-Br; with the inclusion of the zero-point energies, the estimated  $D_0$  values are 70.60 and 49.42 kcal mol<sup>-1</sup>, respectively. The channels that can lead to the formation of atomic selenium via HBrSe (HBr + Se) were also located, but one should notice that the lowest one is associated with a triplet PES. Considering the possibility of a spin-coupling perturbation, the dissociation of HBrSe rather than the isomerization is also a likely event. In Figure 1, the triplet dissociation channel is located at 37.62 kcal mol<sup>-1</sup> relative to HSeBr, and the singlet one at 64.99 kcal mol<sup>-1</sup>. To estimate the location of the triplet dissociation channel, the spin-orbit and zero-point energies contributions of HBr were also included; for the energy of the singlet dissociation channel, the experimental energy difference between the Se (<sup>1</sup>D<sub>2</sub>) and Se (<sup>3</sup>P<sub>3</sub>) states and the theoretical triplet value was added.

#### Structural parameters and vibrational spectra

Geometrical parameters, harmonic and fundamental vibrational frequencies for the two minima and the transition state are collected in Table 2. For the species HSeBr, the equilibrium internuclear distance of 1.4689 Å H-Se is very close to the one in HSeF and HSeCl, of 1.4707 and 1.4693 Å, respectively. In the case of the SeBr internuclear distance, it is about 2.7% longer in HBrSe (2.3848 Å) than the one in

HSeBr (2.3211 Å); this distance in the free SeBr molecule is 2.2742 Å according to our best theoretical estimate (CBS/RCCSD(T)). The HSeBr bond angle of 93.98° is very close to that in HSeF (94.27°) and HSeCl (94.94°), as well as in the sulfur analogues HSCl (95.7°), HSB (95.2°) and HSI (94.94°). In this context, both H and Br atoms can be viewed as covalently bonded to the Se atom. The bond angle in HBrSe (103.36°) is very close to those in the isovalent species HCIS (103.6°), HBrS (104.7°), HIS (104.8°), HFSe (101.83°) and HClSe (102.51°). In these structures, the valence electron pairs can be viewed as oriented in a slightly distorted tetrahedral shape. Our best estimate of the HBr bond length in HBrSe is 1.4366 Å, which is close to the experimental value of the corresponding gas phase diatomic, 1.4144 Å. In the transition state structure (TS), it is possible to notice the migration of the H atom from the Se to the Br moiety. This is evidenced from the analysis of the values of the SeH internuclear distance (2.2180 Å) and the HSeBr angle (35.24°), compared to the values 1.4689 Å and 93.98° of HSeBr.

From the CCSD(T)/CBS values of the harmonic and fundamental frequencies in Table 2, it is possible to verify that both isomers can be easily identified by their vibrational spectra if these species were isolated in a matrix. The SeBr stretching harmonic (fundamental) modes in both HSeBr and HBrSe are 309 (306) and 229 (225) cm<sup>-1</sup>, respectively, the larger one reflecting the stronger Se–Br bond in HSeBr which is also close to the harmonic frequency obtained for the free SeBr species, 324 cm<sup>-1</sup> (CCSD(T)/aV5Z). For the wavenumbers associated with

the harmonic (fundamental) bending modes, 754 (741) and 589 (567) cm<sup>-1</sup> were found for HSeBr and HBrSe, respectively. For HBrSe, the harmonic (fundamental) band at 2486 (2351) cm<sup>-1</sup> can be associated with the H-Br stretching, which in the free HBr molecule is equal to 2646 cm<sup>-1</sup>. In the case of HSeBr, the wavenumber 2411 (2316) cm<sup>-1</sup> corresponds to the HSe stretching frequency, and the corresponding diatomic gas value is 2421 cm<sup>-1</sup>. These values are close to the ones in HSeF (2403 cm<sup>-1</sup>) and HSeCl (2408 cm<sup>-1</sup>). For completeness, the harmonic frequencies of the deuterated species DSeBr and DBrSe were also obtained, which turned out to be (308, 540 and 1721 cm<sup>-1</sup>) and (229, 421 and 1778 cm<sup>-1</sup>), respectively; here, atomic weights of 79.904 and 78.96 were used for Br and Se.

Aiming at further improved estimates of structural parameters and harmonic frequencies, new calculations of anharmonic effects on the vibrational frequencies and structural parameters were also evaluated for both valence-only correlation, and those including core-valence correlation effects. These results are summarized in Table 3, in which one can see that the internuclear distances and bond angles have decreased by about 0.01 Å and 0.06°, respectively, the frequencies were underestimated by 11 cm<sup>-1</sup> for the modes of HSeBr, and for the isomer HBrSe, an increase close to 10 cm<sup>-1</sup> was obtained.

#### Performance of the CCSD-F12 methodology

Besides the CCSD(T)/CBS approach, explicitly correlated calculations were also performed and Table 4

**Table 3.** Structural parameters, harmonic and fundamental frequencies calculated at the CCSD(T)/cc-pwCVnZ (*n* = D, T, Q) level of theory with valence-only and core-valence (in italics) correlation

| Basis sets | Geometry / Å, degree |               |               | Frequency / cm <sup>-1</sup> |              |               |              |               |               |               |
|------------|----------------------|---------------|---------------|------------------------------|--------------|---------------|--------------|---------------|---------------|---------------|
|            | rHSe                 | rSeBr         | aHBr          | $\omega_{e1}$                | $\nu_1$      | $\omega_{e2}$ | $\nu_2$      | $\omega_{e3}$ | $\nu_3$       |               |
| HSeBr      | VDZ                  | 1.4709        | 2.3533        | 94.18                        | 292.1        | 288.7         | 757.2        | 742.1         | 2421.5        | 2325.1        |
|            |                      | <i>1.4667</i> | <i>2.3459</i> | <i>94.17</i>                 | <i>294.1</i> | <i>290.7</i>  | <i>759.5</i> | <i>744.4</i>  | <i>2426.1</i> | <i>2329.8</i> |
|            | VTZ                  | 1.4672        | 2.3326        | 94.16                        | 302.4        | 299.5         | 749.9        | 736.4         | 2411.9        | 2318.2        |
|            |                      | <i>1.4609</i> | <i>2.3216</i> | <i>94.12</i>                 | <i>305.0</i> | <i>302.2</i>  | <i>754.8</i> | <i>740.9</i>  | <i>2420.5</i> | <i>2326.6</i> |
|            | VQZ                  | 1.4679        | 2.3244        | 94.10                        | 306.9        | 304.1         | 752.4        | 739.5         | 2414.1        | 2320.4        |
|            |                      | <i>1.4608</i> | <i>2.3113</i> | <i>94.04</i>                 | <i>309.9</i> | <i>307.0</i>  | <i>758.0</i> | <i>745.0</i>  | <i>2424.8</i> | <i>2330.4</i> |
| Basis sets | Geometry / Å, degree |               |               | Frequency / cm <sup>-1</sup> |              |               |              |               |               |               |
|            | rHBr                 | rBrSe         | aHSe          | $\omega_{e1}$                | $\nu_1$      | $\omega_{e2}$ | $\nu_2$      | $\omega_{e3}$ | $\nu_3$       |               |
| HBrSe      | VDZ                  | 1.4349        | 2.4738        | 103.16                       | 180.5        | 174.3         | 548.1        | 525.1         | 2539.2        | 2401.9        |
|            |                      | <i>1.4320</i> | <i>2.4615</i> | <i>103.11</i>                | <i>185.1</i> | <i>179.3</i>  | <i>552.8</i> | <i>529.7</i>  | <i>2543.5</i> | <i>2404.9</i> |
|            | VTZ                  | 1.4328        | 2.4086        | 103.56                       | 215.4        | 210.7         | 575.3        | 552.7         | 2501.8        | 2366.8        |
|            |                      | <i>1.4284</i> | <i>2.3946</i> | <i>103.50</i>                | <i>219.8</i> | <i>215.3</i>  | <i>579.5</i> | <i>556.8</i>  | <i>2508.6</i> | <i>2374.4</i> |
|            | VQZ                  | 1.4344        | 2.3928        | 103.37                       | 224.7        | 220.2         | 582.0        | 561.6         | 2497.9        | 2365.5        |
|            |                      | <i>1.4292</i> | <i>2.3772</i> | <i>103.28</i>                | <i>228.9</i> | <i>224.6</i>  | <i>584.8</i> | <i>566.1</i>  | <i>2506.9</i> | <i>2375.4</i> |

**Table 4.** Total energies, structural parameters, harmonic and fundamental frequencies calculated at the CCSD(T)-F12/*VnZ*-F12 (*n* = D, T, Q) level of theory

| HSeBr | Basis sets | Geometry / Å, degree |        |        | Frequency / cm <sup>-1</sup> |               |               | Energy / a.u. |
|-------|------------|----------------------|--------|--------|------------------------------|---------------|---------------|---------------|
|       |            | rHSe                 | rSeBr  | aHSeBr | $\omega_{e1}$                | $\omega_{e2}$ | $\omega_{e3}$ |               |
|       | VDZ-F12    | 1.4677               | 2.3219 | 94.01  | 308.9                        | 755.8         | 2414.7        | -788.358624   |
|       | VTZ-F12    | 1.4694               | 2.3226 | 94.05  | 307.7                        | 753.5         | 2408.9        | -788.382729   |
|       | VQZ-F12    | 1.4692               | 2.3209 | 94.07  | 308.9                        | 754.6         | 2409.8        | -788.390362   |
| HBrSe | Basis sets | Geometry / Å, degree |        |        | Frequency / cm <sup>-1</sup> |               |               | Energy / a.u. |
|       |            | rHBr                 | rBrSe  | aHBrSe | $\omega_{e1}$                | $\omega_{e2}$ | $\omega_{e3}$ |               |
|       | VDZ-F12    | 1.4350               | 2.3841 | 103.65 | 229.6                        | 593.6         | 2488.6        | -788.285472   |
|       | VTZ-F12    | 1.4366               | 2.3870 | 103.40 | 227.5                        | 587.1         | 2486.0        | -788.310579   |
|       | VQZ-F12    | 1.4363               | 2.3856 | 103.34 | 228.5                        | 587.5         | 2488.4        | -788.318225   |
| TS    | Basis sets | Geometry / Å, degree |        |        | Frequency / cm <sup>-1</sup> |               |               | Energy / a.u. |
|       |            | rHSe                 | rSeBr  | aHSeBr | $\omega_{e1}$                | $\omega_{e2}$ | $\omega_{e3}$ |               |
|       | VDZ-F12    | 2.2315               | 2.5111 | 35.13  | 208.7                        | 2335.1        | 721.4         | -788.274573   |
|       | VTZ-F12    | 2.2231               | 2.5129 | 35.24  | 207.4                        | 2317.6        | 724.6         | -788.300245   |
|       | VQZ-F12    | 2.2171               | 2.5106 | 35.31  | 208.8                        | 2310.4        | 728.4         | -788.307751   |

lists the resulting total energies, structural parameters and harmonic frequencies at the CCSD(T)-F12b/*VnZ*-F12, where *n* = D, T and Q, levels of calculation. One interesting point to notice is the convergence of some results already at the VTZ-F12 level, which are close to those of the usual CCSD(T)/aV5Z data. An analysis of the data at the VTZ-F12 level shows that in general the discrepancies relative to the aV5Z results can be as large as about 0.005 Å for the bond distances, 0.1° for the bond angle, 5 cm<sup>-1</sup> for the harmonic frequencies and 0.2 kcal mol<sup>-1</sup> for the relative energy. For the VQZ-F12 results, one can notice that they approached the convergence reached at the CBS limit. Here, the discrepancies decrease to 0.001 Å in the bond length, 0.01° in the angle, 2.5 cm<sup>-1</sup> in the harmonic frequencies and 0.08 kcal mol<sup>-1</sup> in the relative energy. These results clearly point us to the possibility of using smaller basis sets and obtaining results close to the CBS limit.

## Conclusions

In this study, energetic, structural and vibrational data for species on the singlet potential energy surface [H, Se, Br] were obtained at a high level of theory, CCSD(T). Extrapolation to the complete basis set limit, inclusion of both valence and core-valence electron correlation, of spin-orbit interactions, and the incorporation of anharmonicity effects in the calculated frequencies make our results very reliable. An explicit correlation method was also explored showing a faster convergence of properties with basis sets than conventional CCSD(T); it is very promising to obtain accurate results for larger systems but

using not so extended basis sets. The present investigation complements previous studies on other chalcogen-halogen triatomics, thus allowing an overall view on the structural, energetic, spectroscopic and bonding properties of these systems. Being the first study in the literature about this surface, the present results are expected to be an important source of data and a guide to the experimentalist in search for these yet unknown species.

## Acknowledgement

We are grateful to the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) of Brazil for research support.

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Submitted: January 23, 2013

Published online: June 5, 2013

FAPESP has sponsored the publication of this article.