



## Research paper

# Electronic states and spectroscopic parameters of selenium monoiodide, SeI: A theoretical contribution

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## ABSTRACT

A new species, selenium monoiodide (SeI), was investigated for the first time at a high level of theoretical approach, SA-CASSCF/MRCI. The overall picture of all doublet and quartet ( $\Lambda + S$ ) states correlating with the three lowest dissociation channels and the associated  $\Omega$  states provide reliable results to help understand the lack of experimental data on its transitions and to plan the investigation and determination of spectroscopic parameters. Transition probabilities were computed for the transitions  $X_2 - X_1$ ,  $A_1 - X_1$ ,  $A_2 - X_1$ , and  $A_2 - X_2$ , originated from the spin-forbidden  $1^4\Sigma^- - X^2\Pi$  system, and the corresponding radiative lifetimes evaluated.

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## 1. Introduction

Diatomic radicals containing both a chalcogen and a halogen atom, XY, with X = O, S, Se, Te and Y = F, Cl, Br, and I, have received varying degrees of attention in the literature. In fact, one can find out that as the atomic number of the chalcogen atom increases, the number of systems investigated both experimentally and theoretically significantly decreases. This contrast is especially true for the case of the extensively studied OY species for their role in stratospheric chemistry as temporary reservoirs of halogen radicals in reaction cycles leading to the catalytic destruction of ozone [1–3]. For the sulfur series, experimental results are scarce for SF and SCl, and unknown for SBr and SI, to the best of our knowledge. Theoretical investigations were reported for SF and SCl by Yang and Boggs [4,5], and for SCl and SBr by our group [6,7]. In analogy with species on the surface [H, O, Y], Y = halogen, we have also explored triatomics of the type [H, S, Y], with Y = Cl, Br, I [8,9]. For HSCl, in particular, we have shown that in regions of strong volcanic eruptions, it is very likely that this species is formed and play a role in atmospheric chemistry similar to that of its isoelectronic analogue HOCl [8]. For the heavier chalcogen atoms, results are more abundant for TeX than for SeX. Experimental studies on TeX (X = Cl, Br, I) were reported by Oldershaw and Robinson [10,11], and by Fink and coworkers [12,13]. Theoretical results on electronic states and transitions were presented for TeF [14], and for TeCl, TeBr, and TeI [15] by Rai et al. Finally, for the selenium monohalides, the formation of SeF was investigated in a chemilu-

minescent reaction of selenium with fluorine [16], whereas in a photolysis experiment of SeCl<sub>2</sub> in the presence of argon the observed spectra was assigned to the radical SeCl [17]; absorption spectra were also reported for SeBr [10]. As far as we know, the only theoretical works on SeBr report on spectroscopic parameters for the ground state, and a bond analysis of a series of chalcogen-halogen diatomics [18], and on the heat of formation of SeBr [19]. For SeF and SeCl, detailed investigations on their electronic states were carried out by our group [20,21].

Existing theoretical studies on the TeX and SX series (X = F, Cl, Br, I) show that excited electronic states that were found to be bound for these radicals with the lighter halogens tend to become more weakly bound and even repulsive with the heavier ones. Considering the limited experimental data obtained in the investigation of these species, one can ask whether the lack of any information on SeI could not be similarly explained. In this context, the major goal of this Letter is to provide a high-level theoretical description of a manifold of  $\Lambda + S$  states of SeI correlating with the three lowest-lying dissociation channels and the associated  $\Omega$  electronic states that can aid in the elucidation of this problem. By characterizing the electronic structure of the lowest-lying states, their potential energy curves, and possible electronic transitions, this study will certainly provide reliable data that will help and guide the experimental search and identification of this radical.

## 2. Theoretical approach

The description of potential energy curves of a manifold of electronic states necessarily implies accounting for both static and

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dynamic electron correlation into the construction of the electronic wavefunction. In this investigation, the state-averaged complete active space self-consistent field (CASSCF) approach was used to recover static correlation effects as well documented in the literature [22,23]. Next, on top of a CASSCF reference space, all single and double electron excitations were generated according to the configuration interaction (CI) method, thus incorporating dynamic correlation effects. The internally contracted (icMRCI) version of the CI method, as developed by Knowles and Werner [24,25] and implemented in the Molpro-10 suite of programs [26], was used throughout the calculations. To maintain the overall calculation within manageable computing time, the icMRCI calculations used subsets of the original CASSCF spaces that contained all configuration state functions with coefficients greater than 0.025 in magnitude.

Concerning the electronic states, a direct application of the Wigner-Witmer rules [27] showed that there are 23 ( $\Lambda + S$ ) molecular states correlating with the three lowest dissociation channels of SeI. For the first channel, associated with the fragments Se ( $^3P_g$ ) + I ( $^2P_u$ ), one finds 12 molecular states, namely,  $^2,4\Sigma^+$ ,  $^2,4\Sigma^-(2)$ ,  $^2,4\Pi(2)$ ,  $^2,4\Delta$ . Higher in energy by 8631  $\text{cm}^{-1}$ , the second channel (Se ( $^1D_g$ ) + I ( $^2P_u$ )) leads to nine molecular states,  $^2\Sigma^+(2)$ ,  $^2\Sigma^-$ ,  $^2\Pi(3)$ ,  $^2\Delta(2)$ ,  $^2\Phi$ . For the third channel, Se ( $^1S_g$ ) + I ( $^2P_u$ ), located at 21,501  $\text{cm}^{-1}$ , only two molecular states can be formed,  $^2\Sigma^+$  and  $^2\Pi$ . We note that the above energy values were obtained as averages of the corresponding atomic multiplets [28].

Working in the  $C_{2v}$  point group representation, a restriction due to computer code design, a total of 36 states were mixed in state averaged CASSCF calculations:  $A_1(7)$ ,  $B_1(7)$ ,  $B_2(7)$ ,  $A_2(6)$  doublets and  $A_1(2)$ ,  $B_1(2)$ ,  $B_2(2)$ ,  $A_2(3)$  quartets. This choice accounts for all the 23 states listed above, besides maintaining the symmetry equivalence of the  $b_1(\pi_x)$  and  $b_2(\pi_y)$  molecular orbitals. As well known,  $\Sigma^+$  and  $\Delta$  states transform according to the representation  $A_1, \Pi_x(\Pi_y)$  according to  $B_1(B_2)$ , and  $\Sigma^-$  and  $\Delta$  according to  $A_2$ . In this step, eleven electrons ( $4s^2 4p^4$  of Se and  $5p^5$  of I) were distributed in all possible ways in the active space (4, 3, 3, 0) for both for doublet and quartet states. This active space includes the  $4s$ ,  $4p_x$ ,  $4p_y$ , and  $4p_z$  orbitals of Se and the  $5p_x$ ,  $5p_y$ , and  $5p_z$  orbitals of I; here, the innermost orbital of  $A_1$  symmetry, corresponding essentially to  $5s$  of I, was excluded from the active space in the CASSCF step, but correlated in the MRCI treatment. In addition, we included three orbitals of symmetries  $\sigma$ ,  $\pi_x$ , and  $\pi_y$  for correlation purpose, with a consequent increase in the dimension and flexibility of the reference space. The final CASSCF/MRCI function was expanded in terms of an  $N$ -particle space based on averaged natural orbitals calculated in the CASSCF step. The dimensions of the MRCI spaces ranged from 3.6 to 9.1 million configuration state functions depending on the spatial and spin symmetries. The basis set for iodine contains a large-core (28 electrons) energy consistent relativistic pseudopotential (PP) optimized in a multi-configurational Dirac-Hartree-Fock calculation, namely ECP28MDF, replacing the  $1s$ - $3d$  inner core; for selenium, it contains a small-core pseudopotential (ECP10MDF) that replaces the  $1s$ - $2p$  electrons. In combination with the energy consistent pseudopotential, correlation consistent basis sets of quintuple-zeta quality were employed thus resulting in the aug-cc-pV5Z-PP set, as usually referred in the literature. They are derived from extensive sets of spherical gaussians comprised of (17s, 14p, 14d, 4f, 3g, 2h) primitive functions contracted to [8s, 8p, 6d, 4f, 3g, 2h] for iodine, and [8s, 7p, 6d, 4f, 3g, 2h] for selenium [29]. To account for extra flexibility in the basis sets, especially for treating the high-lying states, sets of diffuse functions were added to the above sets following the recommendation given by van Mourik et al. [30]. For selenium, we added two  $s$ -type (0.013244 and 0.005315) and two  $p$ -type (0.009457 and 0.003940) functions; for iodine, we also added two  $s$ -type (0.012329 and 0.004984) and two  $p$ -type (0.009847 and 0.004197) functions.

For the evaluation of vibrational energies and wavefunctions, and transition probabilities the LEVEL 8.0 program [31] was used. For such, numerically generated potential energy functions were constructed from single point energies calculated at 40 internuclear distances, the largest one being 50.0  $a_0$ . These energies were corrected by an estimate of the contribution of the missing higher excitations needed to reach the full configuration interaction limit known as the Davidson correction (+Q) [32,33]. Spectroscopic parameters were also determined by standard fitting procedures as described in the literature [34–36].

Spin-orbit couplings were computed with a mixed SA-CASSCF/MRCI approach. First, the spin-orbit matrix elements were evaluated at the CASSCF level with the quintuple-zeta quality basis sets described above in a model space comprising all the 36 states mixed in the SA-CASSCF step. Next, the diagonal elements of the spin-orbit matrix were replaced by the highly correlated MRCI + Q energy values of all the ( $\Lambda + S$ ) states. The final  $\Omega$  energies resulted from the diagonalization of a matrix of the electronic and spin-orbit operators ( $H_{el} + H_{SO}$ ) in the basis of ( $\Lambda + S$ ) eigenstates of  $H_{el}$  using the one- and two-electron Breit-Pauli operator [37] as implemented in the Molpro-2010 suite of programs.

### 3. Results and discussion

An overview of the manifold of 23 ( $\Lambda + S$ ) electronic states correlating with the three lowest dissociation channels of the SeI species described in the previous section is illustrated in Fig. 1. In Fig. 2 we show the potential energy curves of the lowest-lying  $\Omega$  states that result from the inclusion of spin-orbit coupling interactions in the characterization of this system. In Table 1, we summarize the associated spectroscopic parameters of these two

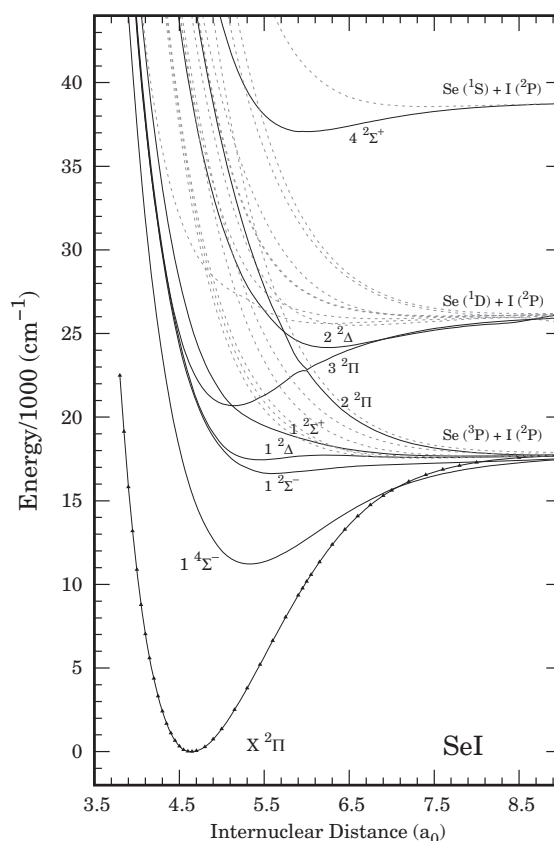


Fig. 1. Potential energy curves for the lowest-lying doublet and quartet ( $\Lambda + S$ ) states of the molecule SeI.

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