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Theoretical Study of the Vibrational Structure of the He I Photoelectron Spectrum of H_2Se

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CCSD(T)/6-311G(2d,2p) geometry optimization and harmonic vibrational frequency computation were carried out on the X^1A_1 state of H_2Se and the X^2B_1, A^2A_1, and B^2B_2 states of H_2Se^+. The B3LYP/6-311G**, B3LYP/6-311G(3df,2p), CCSD(T)/LanL2DZ++(2d,2p), and CCSD(T)/LanL2DZ++(3df,2p) calculations were also performed on the ground states of the neutral and cation. Furthermore, vertical and adiabatic ionization energies were computed at the CCSD(T)/6-311G(3df,2pd)//CCSD(T)/6-311G(2d,2p) level for the ionization processes to the three low-lying cationic states. Franck−Condon analyses and spectral simulations were then performed for the first two He I photoelectron bands of H_2Se employing the ab initio data and FC procedures with the use of the harmonic oscillator approximation and the Duschinsky effect. Comparing the observed and simulated spectra as obtained at different cationic geometries, those of the two lowest-lying cationic states of H_2Se^+ that give the best spectral agreement are as follows: the X^2B_1 state: $r_e = 1.471 \pm 0.001$ Å and $\theta_e = 91.5 \pm 0.2°$; the A^2A_1 state: $r_e = 1.475 \pm 0.004$ Å and $\theta_e = 126.3 \pm 0.5°$.

Introduction

Delwiche et al.[1] and Potts and Price[2] reported the He I photoelectron (PE) spectra of H_2Se nearly 25 years ago. Fifteen years later, Borlin et al.[3] reported the same spectrum but with a much higher resolution of 10 meV. The observed spectrum consists mainly of three bands with resolved fine structures corresponding to the ionization processes of H_2Se^+ (X^2B_1, A^2A_1, and B^2B_2) ← H_2Se (X^1A_1). The vibrational structure of the first band is simple, but those of the second and third are rather complex with strong vibronic interactions.[3] Nevertheless, using the Franck−Condon (FC) approximation and the observed difference of the vertical (VIE) and adiabatic (AIE) ionization energies, the bond angle of H_2Se^+ in the A^2A_1 state was deduced by Potts and Price to be 126°.[2]

Highly accurate geometric parameters and harmonic vibrational frequencies for the X^1A_1 state of H_2Se have been reported in recent FTIR studies.[4,5] For previous experimental works, readers may refer to ref 4 and references therein. However, for the cation, very little experimental information is available except those deduced from the He I PE spectra.[1−3] H_2Se has also been investigated in a number of occasions by ab initio calculations[6−13] (for early works, see ref 11). But for the cation, apart from a CASSCF/SOCI[11] and a HF/RSPT[13] study where ionization energies (IEs) were computed, there has been only one HF/ECP investigation on the geometries of the three low-lying cationic states of H_2Se^+.[12] In the study, the calculated energies were fitted to a harmonic potential in the totally symmetric stretching and bending coordinates, and the respective harmonic frequencies ν_1 and ν_2 were obtained for the X^2B_1 and A^2A_1 states. In addition, the FC factors (FCFs) for each of the symmetric vibrational modes for these two cationic states were determined by assuming the ground-state normal coordinates to be parallel to those of the ionic states.

In the present study, B3LYP and CCSD(T) calculations were carried out on H_2Se, and its cation employing different basis sets. FC analyses based on the structural parameters and harmonic frequencies as obtained from the highest-level ab initio calculations on the ground states of H_2Se and the first two lowest-lying states of its cation were performed so as to simulate the He I PE spectrum of the molecule by employing the FC method of Chen.[14] The method makes use of ab initio force constants in the FC analyses with the consideration of the Duschinsky effect.[15] In addition, cationic geometries were varied in the iterative FC analysis (IFCA)[14] to determine accurate structural parameters for the low-lying states of H_2Se^+ by matching the relative peak intensities of the vibrational fine structure of the theoretical spectrum with the observed one. The experimental geometry of the neutral[4] was used throughout. The strategy and computational details of the calculations performed will be given in the next section.

In spectral simulation, IEs of the PE bands of H_2Se were used. Other than those from the He I PE spectroscopic studies,[1−3] the first adiabatic IE (AIE) of H_2Se has also been determined to be 9.886 ± 0.003 eV (79735 ± 25 cm^{-1}) in a photoionization mass spectrometry study.[16] In addition, recent vacuum ultraviolet absorption studies on H_2Se (see ref 17 and references therein) yielded an AIE of 9.8963 ± 0.0003 eV (79824 ± 2 cm^{-1}). This quantity was derived from the extrapolated ionization limit of the observed Rydberg series and agrees very well with that of 9.897(2) eV as determined from the latest and best resolved He I PE spectrum.[3] It should be noted that the threshold PE[3] and (e,2e) momentum[18] spectra of H_2Se have also been reported recently.

Computational Details

B3LYP and CCSD(T) geometry optimization and harmonic vibrational frequency calculations were carried out for the ground states of H_2Se and its cation. The CCSD(T) method was chosen because it is one of the highest level perturbative methods available today. It has been shown recently that the size-extensive CC method was more accurate in predicting IEs than the non-size-extensive CI type methods[19] and converged bond lengths could be obtained at the CCSD/TZ2P+f level.[20] However, for species containing heavy elements, such as Se, density functional theory (DFT) methods are attractive alternatives to ab initio methods on the ground of economy. Among different functionals available nowadays, the B3LYP combination[21,22] has recently been demonstrated to be one of the most

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TABLE 1: Optimized Geometries and Harmonic Vibrational Frequencies (cm^{-1}) of the X^1A_1 State of H_2Se at Different Levels of Calculation

method	r_e/Å	θ_e/deg	ν_1	ν_2	ν_3
B3LYP/6-311G**	1.4713	91.27	2409.1	1080.2	2425.1
B3LYP/6-311G(3df,2p)	1.4693	91.18	2418.9	1073.1	2426.9
CCSD(T)/Lan++(2d,2p)	1.4721	90.72	2421.4	1060.1	2428.9
CCSD(T)/Lan++(3df,2p)	1.4729	91.18	2438.3	1058.5	2445.2
CCSD(T)/6-311G(2d,2p)	1.4667	90.97	2430.2	1051.3	2445.6
HF/ECP-21G(d)[a]	1.490	93			
HF/ECP(6s5p1d)[b]	1.446	93.1	2570	1160	
HF/DZP[c]	1.400	90.53			
CEPA/[12s10p3d][d]	1.461	90.62	2433.5	1099.2	2442.9
HF/[17s13p8d][e]	1.4530	93.14			
DF/[17s13p8d][e]	1.4504	92.87			
MP2/[9s6p2d][f]	1.455	91.6			
CAS/REC(3s3p3d)[g]	1.473	91.6			
CAS/SOCI/REC[g]	1.461	91.5			
FTIR[h]	1.459099 ± 0.000077	90.958 ± 0.011	2437.212 (82)	1059.839 (99)	2453.209 (93)

[a] Reference 6. [b] Reference 12. The contracted basis given is that for Se (the same for the following footnotes) and for H, the [2s1p] contracted basis was used. [c] Reference 7. [d] Reference 8. For H, the contracted basis [4s2p] was used. [e] Reference 10. DF refers to Dirac−Fock relativistic calculations and for H, the [6s1p] contracted basis was used. [f] Reference 9. For H, the [3s1p] contracted basis was used. [g] Reference 11. For H, the [3s1p] contracted basis was used. [h] References 4 and 5. References for earlier less accurate experimental data can be found in ref 4.

successful DFT methods for different types of molecular species in a number of studies (for examples, refs 23−28). Nevertheless, it has been pointed out by Neumann et al.[29] that the three parameters adopted in the B3LYP functional have very little theoretical basis. Therefore it would be of interest to see whether the B3LYP functional would do as well for Se-containing compounds as for those previously reported.[23−28] To our knowledge, neither any CCSD nor DFT calculation has been performed on H_2Se and its cation.

Other than the DFT methods, employing effective core potential (ECP) basis sets to reduce both the numbers of electrons and basis functions to be included in an ab initio calculation is another obvious way to cut cost, particularly for species containing heavy elements. Therefore, both all-electron and ECP basis sets were used for our CCSD(T) calculations in order to assess the reliability of the latters. The LanL2DZ[30] basis set as implemented in the GAUSSIAN 94 suite of programs[31] which is of double-ζ quality for the valence shell and the largest ECP basis available for Se in GAUSSIAN 94 has been selected as the underlying basis. Diffuse sp sets and polarization functions were augmented as extensions to the LanL2DZ basis. The lan++(2d,2p) and lan++(3df,2p) basis sets as listed in Tables 1, 2, and 4 denote the LanL2DZ basis with diffuse sp sets (++) on both Se (exp = 0.0474) and H (exp = 0.0592) as well as polarization functions on both Se (2d: 0.61 and 0.1525; 3df: 0.915, 0.305, and 0.101666; 0.5) and H (2p: 1.407 and 0.388) respectively. The polarization functions invoked in the all-electron bases are available in GAUSSIAN 94.

With regard to the A^2A_1 and B^2B_2 states of H_2Se^+, geometry optimization and vibrational frequency calculations were carried out only at the CCSD(T)/6-311G(2d,2p) level. It should be mentioned that the Hartree−Fock−Kohn−Sham method in the density-functional theory as formulated in GAUSSIAN 94 works only for the ground state (for the difficulties encountered and the possibilities of a workable density-functional theory for excited states, readers may refer to ref 32). Both the AIEs and vertical IES (VIEs) for all the three photoionization processes of H_2Se^+ (X^2B_1, A^2A_1, and B^2B_2) ← H_2Se (X^2A_1) under investigation were also computed at the CCSD(T)/6-311G-(3df,2pd)//CCSD(T)/6-311G(2d,2p) level.

All the CCSD(T) and B3LYP calculations were carried out using the GAUSSIAN 94 suite of program[31] on an IBM and a SGI workstations. Restricted and unrestricted spin wave functions were used for the neutral and cationic states, respectively. The $\langle S^2 \rangle$ values for the latters are less than 0.764, indicating that spin contamination is not serious for the species investigated.

The FCF calculations and spectral simulations of the PE bands of H_2Se were carried out based on the Chen's FC method[14] and have been described elsewhere.[33,34] Briefly, the algorithm for computing the theoretical vibrational intensity distribution upon ionization are formulated in terms of the reduced mass-weighed Cartesian displacements and hence remains valid even for large changes in the equilibrium geometries.[14−15] The harmonic oscillator approximation is adopted in evaluating FCFs. Vibrational components within a PE band were simulated using Gaussians with the respective experimental fwhm (full width at half-maximum). Since the He I spectrum of H_2Se as reported in ref 3 has the best resolution among all the related works, it was utilized in this investigation and will be quoted as the observed spectrum in the following discussion.

Results and Discussion

***A. Ab Initio* Calculations.** *1. Geometry and Vibrational Frequencies.* The optimized geometries and computed vibrational frequencies of the ground state of H_2Se as well as the ground and low-lying excited states of H_2Se^+ as obtained from different levels of ab initio calculation are summarized in Tables 1−3. Experimental and theoretical data from previous studies are also provided. In these tables, quantities enclosed within parentheses are estimated errors and the abbreviation pes stands for PE spectroscopy. For the X^1A_1 state of H_2Se of which the experimental geometry and vibrational frequencies are available for comparison (Table 1), both the CCSD(T) calculations with the ECP bases being utilized and the B3LYP calculations give the magnitudes of r_e too large by at least 0.01 Å. Nevertheless, all the predicted values of the bond angle θ_e as obtained in the present work agree with the experimental value of 90.958 ± 0.011° to within 0.3°. The best overall agreement comes from the CCSD(T)/6-311G(2d,2p) computations as expected, which also give results with reasonably small discrepancies from those of CEPA[8] and CASSCF/SOCI[11] calculations. It is anticipated that inclusion of the relativistic effect would reduce the computed nonrelativistic bond length and angle by ca. 0.003 Å and 0.27°, respectively.[10]

Regarding the theoretical vibrational frequencies obtained in this study for the ground states of H_2Se and its cation, they are rather insensitive to the types of calculation involved. The

TABLE 2: Optimized Geometries and Harmonic Vibrational Frequencies (cm^{-1}) of the X^2B_1 State of H_2Se at Different Levels of Calculation

method	r_e/Å	θ_e/deg	ν_1	ν_2	ν_3
B3LYP/6-311G**	1.4891	91.61	2348.5	1063.9	2355.5
B3LYP/6-311G(3df,2p)	1.4878	91.56	2348.3	1054.4	2349.5
CCSD(T)/Lan++(2d,2p)	1.4865	90.86	2354.6	1055.9	2358.1
CCSD(T)/Lan++(3df,2p)	1.4882	91.56	2365.7	1047.9	2366.4
CCSD(T)/6-311G(2d,2p)	1.4830	91.42	2351.5	1045.7	2361.2
HF/ECP(6s5p1d)[a]	1.459	93.8	2500	1200	
pes[b]			2280	1017	
pes[c]			2260 ± 40		
pes[d]			2266.6	1016.2	

[a] Reference 12. [b] Reference 1. [c] Reference 2. [d] Reference 3. Harmonic frequencies of the ν_1 and ν_2 modes were reported in ref 12 with values of 2339 and 1033 cm^{-1}, respectively.

TABLE 3: Optimized Geometries and Harmonic Vibrational Frequencies (cm^{-1}) of the A^2A_1 and B^2B_2 States of H_2Se^+ at the CCSD(T)/6-311G(2d,2p) Level

	r_e/Å	θ_e/deg	ν_1	ν_2	ν_3
A^2A_1 state					
CCSD(T)	1.4790	124.3	2267.2	894.9	2331.7
HF/ECP(6s5p1d)[a]	1.457	125.2	2410	970	
pes[b]				750	
pes[c]		126		830 ± 20	
pes[d]				863.1	
B^2B_2 state					
CCSD(T)	1.7529	27.7	*e*	*e*	*e*
HF/ECP(6s5p1d)[a]	1.74	28			
pes[b]			1726		
pes[c,f]			2180		
pes[d,g]			1952	581	

[a] Reference 12. [b] Reference 1. [c] From a FC analysis (see ref 2). [d] Reference 3. [e] Scf convergence problems in the numerical second derivatives calculations (see text). [f] The observed band showed strong anharmonicity and the ν_1 frequency is derived from the first vibrational spacing. [g] The observed structure was not fully interpreted and the vibrational assignments were only tentative (see text).

TABLE 4: Computed AIEs and VIEs (in eV) of the First PE Band of H_2Se at Different Levels of Calculation

X^2B_1	AIE	VIE
B3LYP/6-311G**	9.85	
B3LYP/6-311G(3df,2p)	9.87	
CCSD(T)/Lan++(2d,2p)	9.53	
CCSD(T)/Lan++(3df,2p)	9.69	
CCSD(T)/6-311G(2d,2p)	9.58	
CCSD(T)/6-311G(3df,2pd)[a]	9.737	9.743
HF/ECP(6s5pd)-KT[b]		9.66
HF/ECP(6s5pd)-DSCF[b]	8.86	8.86
HF/[8s5p2d]+p+bf-KT[c]		9.72
HF/[8s5p2d]+p+bf-RSPT2[c]		9.55
CASSCF/SOCI/RECP(3s3p3d)[d]		9.34
photoionization mass[e]	9.886 ± 0.003	
pes[f]	9.897(2)	9.897(2)
absorption[g]	9.8963 ± 0.0003	

[a] At the respective CCSD(T)/6-311G(2d,2p) optimized geometries. [b] Reference 12. [c] Reference 13. [d] Reference 11. [e] Reference 16. For earlier experimental data, see references therein. [f] Reference 3. [g] Reference 17.

spread of all the computed values for each individual vibrational mode is less than 30 cm^{-1}. It can be seen that the CCSD(T)/6-311G(2d,2p) and CCSD(T)/lan++(3df,2p) frequencies are very close to each other and also to the experimental data. It seems that the B3LYP frequencies are slightly inferior to the CCSD(T) results. Hence, the CCSD(T)/6-311G(2d,2p) data were utilized in the FC analyses for this electronic state.

As for the X^2B_1 state of H_2Se^+, the spreads of all the computed r_e and θ_e values are less than 0.006 Å and 0.75°, respectively (Table 2). The theoretical vibrational frequencies are even less sensitive to the levels of calculation than those of the X^1A_1 state with a spread of less than 20 cm^{-1} for the individual mode. The discrepancies between these theoretical quantities with the experimental data is reasonably small for the ν_2 bending mode (within 30 cm^{-1}) but is only fair for the ν_1 stretching mode (too large by ca. 80 cm^{-1}). Nevertheless, the experimental harmonic frequency of 2339 cm^{-1} [12] (see footnote *d* of Table 2) agrees very well with the ab initio value. Similar to the X^1A_1 state of the neutral molecule, the magnitude of the HF/ECP r_e is obviously too small, but both the q_e and vibrational frequencies are too large.[12] Therefore, the CCSD(T)/6-311G(2d,2p) data were used in the following FC analyses.

The optimized geometries and harmonic vibrational frequencies for the A^2A_1 and B^2B_2 states of H_2Se^+ are given in Table 3. With regard to the A^2A_1 state, the computed θ_e value (124.3°) agree with that (126°) deduced from the He I PE spectrum by Potts and Price.[2] The theoretical bending frequency also agrees reasonably well with the experimental value. Yet, for the B^2B_2 state, scf convergence problems were encountered in the numerical force constant calculation and we were unable to determine its vibrational frequencies. It is noted that the HF/ECP symmetric bending potential as reported in ref 12 for this electronic state is highly anharmonic and the symmetric stretching potential seems to support a flat and shallow minimum. Computed vibrational frequencies for the B^2B_2 state were also not given in ref 12. Nevertheless, in agreement with the HF/ECP optimized structure provided in ref 12, our CCSD(T)/6-311G(2d,2p) bond length is rather long (1.7529 Å) and the bond angle is very small (27.7°) compared to those of the neutral molecule. A large geometric change upon ionization is hence predicted for this state at both the HF[12] and correlated levels (see next subsection). Moreover, the CCSD(T) H−H distance is short (0.8397 Å; cf. 0.7461 Å in H_2[35]) and the computed charge and spin densities on Se are 0.701 and 0.987, respectively. This structure has been considered as a $Se^+(H_2)$ complex by Muller et al.[12] and our CCSD(T) results confirm it. With the observed vibrational spacings of 200 meV (1613 cm^{-1}) of the He I PE band being assigned to the ν_1 mode, Borlin et al.[3] concluded that the Se−H bonds are much weaker in this state than in the neutral molecule, in line with the HF[12] and our CCSD(T) predictions.

2. AIEs and VIEs. The theoretical AIEs and VIEs of the first three PE bands of H_2Se are summarized in Tables4 and 5. For the first AIE (Table 4), the B3LYP values are the closest to the experimental value. At the same time, the basis size effect seems to be extremely small on the computed relative energies at the B3LYP level. In contrast, this effect is considerably larger at the CCSD(T) level. Nevertheless, the AIEs deduced from the lan++(2d,2p) and 6-311G(2d,2p) basis sets, which are of similar size/quality for the valence shells, have magnitudes very near to each other. This suggests that the ECP basis sets would probably give relative energies which are close to those with all-electron basis sets of similar valence quality. However, when compared with the experimental data, the basis size has certainly not been exhausted at the CCSD(T) level with both the all-electron and ECP bases utilized though the trend in the computed AIEs is pointing to the correct direction of the demand of a basis set with a larger extension in the polarization functions than the (3df,2pd) set invoked.

The second and third AIEs as predicted from the CCSD(T) calculations employing two different basis sets are close in magnitude (Table 5). This indicates that they are not far from the infinite basis limits. For the second PE band, both the CCSD(T) AIEs and VIEs are in reasonably good agreement with the respective experimental values, particularly for the VIE.

TABLE 5: Computed AIEs and VIEs (in eV) of the Second and Third PE Bands of H_2Se at Different Levels of Calculation

	AIE	VIE
A^2A_1 state		
CCSD(T)/6-311G(2d,2p)	12.13	
CCSD(T)/6-311G(3df,2pd)[a]	12.211	12.846
HF/ECP(6s5p1d)/KT[b]		12.87
HF/ECP(6s5p1d)/DSCF[b]	11.40	12.07
HF/[8s5p2d]+p+bf/KT[c]		13.03
HF/[8s5p2d]+p+bf/RSPT2[c]		12.77
pes[d]	12.409(6)	12.825(4)
B^2B_2 state		
CCSD(T)/6-311G(2d,2p)	12.31	
CCSD(T)/6-311G(3df,2pd)[a]	12.390	14.697
HF/ECP(6s5p1d)/KT[b]		15.27
HF/ECP(6s5p1d)/DSCF[b]	11.73	14.47
HF/[8s5p2d]+sp+bf/KT[c]		15.12
HF/[8s5p2d]+sp+bf/RSPT2[c]		14.83
pes[d]	14.118	14.626

[a] At the respective CCSD(T)/6-311G(2d,2p) optimized geometries. [b] Reference 12. [c] Reference 13. The experimental geometries were used with diffuse s and p functions for Se, bond function (bf), and 6-31G for H. [d] Reference 3. For earlier experimental data, see references therein.

With regard to the third VIEs, those obtained from the CCSD(T) calculation are very close to the observation. However, the theoretical AIE values of 12.31 and 12.39 eV at the CCSD(T)/6-311G(2d,2p) and CCSD(T)/6-311(3df,2pd) levels, respectively, are considerably lower than the observed one of 14.118 eV[3]. The predicted AIE−VIE separation is as large as 2.3 eV (cf. the DSCF value of 2.74 eV[12]) in contrast to the experimental one of only ca. 0.5 eV. The large theoretical AIE−VIE separation is essentially due to the large geometric change upon ionization to the B^2B_2 state (see later discussion). The results obtained here indicate that the observed lowest IE onset for the third PE band of H_2Se is not at the adiabatic position. Moreover, the third AIE is predicted to be lower than the second VIE, similar to that arrived at based on the HF/ECP quantities.[12] Hence, one may anticipate that the second and third PE bands of H_2Se would overlap considerably. However, due to the large geometric shift between the X^1A_1 and B^2B_2 states of H_2Se as discussed, it is unlikely that the AIE of the third band of H_2Se would be observed. The above argument and possible vibronic interactions as proposed in ref 12 may explain the experimental observation that the second and third bands seems to overlap only slightly.

B. Simulated Spectra. *1. First Photoelectron Band: H_2Se^+ (X^2B_1) ← H_2Se (X^1A_1).* The simulated spectra of the first PE band of H_2Se with vibrational assignments are shown in Figure 1a. Gaussian peaks with fwhm's of 50 meV were used. The label (v_1', v_2') for the assignment denotes the transition X^2B_1 (v_1', v_2', 0) ← X^1A_1 (0,0,0) or (v_1',v_2',0−0,0,0) with v_i' being the vibrational quantum number of the *i*th mode in the cationic state. Figure 1a was generated by employing the CCSD(T)/6-311G(2d,2p) geometries for both the X^1A_1 and X^2B_1 electronic states. It can be seen that all the observed vibrational structures of the experimental spectrum[3] are well reproduced by the simulated spectrum. The structural parameters used to produce Figure 1b was obtained by using the IFCA method. In matching the simulated fine structure of the first PE band of H_2Se with the experimental one, the observed intensity ratios of the (0,0,0−0,0,0), (1,0,0−0,0,0), and (0,1,0−0,0,0) components were utilized as the basis for comparison because they have relatively high intensities. The IFCA geometry thus deduced for H_2Se^+ in the X^2B_1 state are given as follows: $r_e = 1.471 \pm 0.001$ Å, and $\theta_e = 91.5 \pm 0.2°$. Similar to the X^1A_1 state of H_2Se (Table 1), the bond angle determined from the IFCA procedure agrees very well with our ab initio data (Table 2). Yet, the IFCA bond length is smaller by over 0.01 Å. With the IFCA bond length for the cation and the experimental r_e for the neutral,[4] the change in r_e, Δr_e, upon ionization has a value of 0.012 Å. This quantity compares reasonably well with the predicted one of 0.016 Å at the CCSD(T)/6-311G(2d,2p) level.

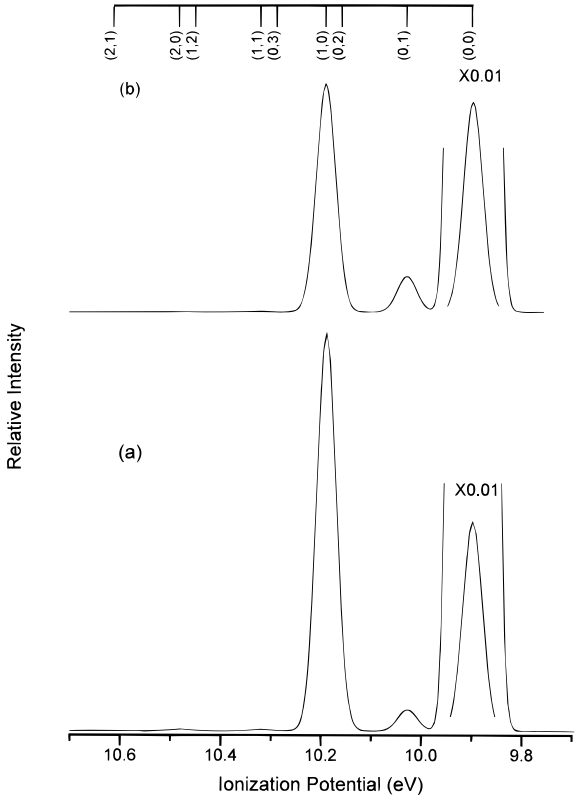

Figure 1. Simulated PE spectrum of the first band of H_2Se using (a) the CCSD(T)/6-311G(2d,2p) geometries for both the X^1A_1 and X^2B_1 states and (b) the IFCA and experimental geometries for the cation and the neutral molecule respectively.

2. Second Photoelectron Band of the H_2Se^+ (A^2A_1) ← H_2Se (X^1A_1). The simulated spectrum of the second PE band of H_2Se with vibrational assignments is shown in Figure 2a. Gaussian peaks with fwhm's of 45 meV were used. The corresponding computed FCFs is also depicted as a stick diagram in Figure 2b. The theoretical spectrum (Figure 2a) was obtained using the IFCA geometry of the A^2A_1 state of H_2Se^+ which is $r_e = 1.475 \pm 0.004$ Å and $\theta_e = 126.3 \pm 0.5°$. The value of IFCA θ_e is almost identical with that given by Potts and Price[2] but is 2° larger than that of 124.3° from the ab initio computation (Table 3). Although the ν_1 progression is weak and unresolved, deviation of the simulated spectrum from the experimental one is discernible when the bond distance of the cation varied outside the given uncertainty. The magnitude of the IFCA r_e as quoted above is very close to our ab initio results.

Comparing the simulated and observed spectra of the second PE band, the agreement is excellent in the region starting from the band onset (12.409 eV) to the band maximum (13.023 eV) or from the (0,0,0−0,0,0) to the (0,6,0−0,0,0) components. From the theoretical FCFs derived here based on the harmonic oscillator model, there should be resolvable and observable fine structures arising from the (1,v_2',0−0,0,0) and (2,v_2',0−0,0,0) transitions in the region beyond the band maximum or the (0,6,0−0,0,0) peak (Figure 2). However, the observed spectrum[3] in this region is rather smooth with very diffuse features. Comparing with the corresponding PE band of H_2S, Borlin et

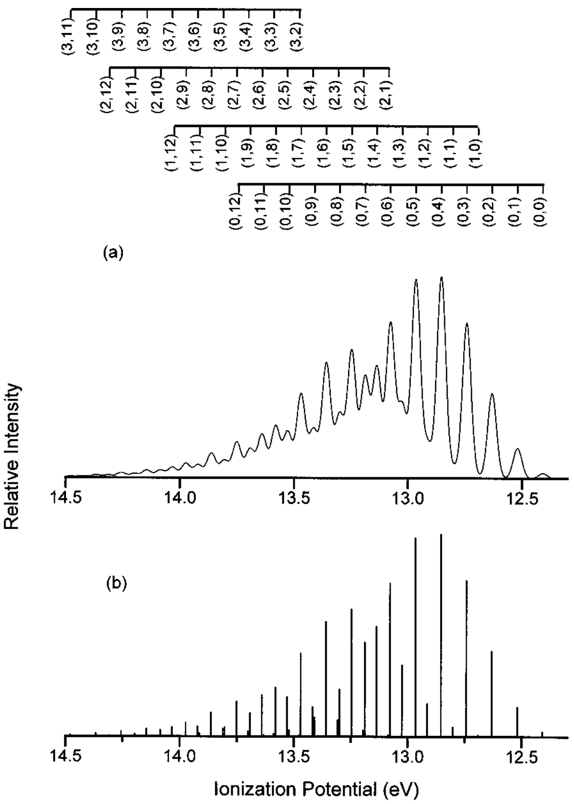

Figure 2. (a) Simulated PE spectrum of the second band of H_2Se using the cationic geometry as obtained from the IFCA treatment with vibrational assignments provided and (b) the associated theoretical FCFs.

al.[3] suggested that both stronger vibronic interaction and faster predissociation in H_2Se^+ than in H_2S^+ were the causes of the broadening of the levels in H_2Se^+. It is of interest to note that the overall vibrational feature of our simulated PE band structure of H_2Se (Figure 2) resembles the corresponding observed one of H_2S (see ref 36 and references therein) over the whole band. This supports the suggestion of Borlin et al.[3]

Concluding Remarks

The first two PE bands of H_2S were simulated by using ab initio calculations and FC analyses. One of the most interesting outcomes from this investigation is the excellent performance of the B3LYP functional in predicting the first AIE of H_2Se. Even with a 6-311G** basis set, the DFT method has outperformed the CCSD(T) method with a basis set as large as 6-311G(3df,2pd) (see Table 4 and also refs 37 and 38). Another advantage of the B3LYP functional as observed in this work is its apparent independence of the computed quantities on the size of the basis sets adopted in determining them (see also refs 37 and 38). This is particularly impressive on the IEs obtained. However, for the theoretical geometries, the CCSD(T) level seems to be slighty more reliable. For instance, the computed first AIEs with the use of the 6-311G** and 6-311G(3df,2p) basis sets differ by only 0.02 eV. As for the ECP basis sets, their performance is similar to the all-electron ones of similar valence quality in the minimum-energy geometries, vibrational frequencies and relative energies at least for the ground states of H_2Se and its cation. Therefore, it may be concluded that the B3LYP functional and/or extended LanL2DZ basis sets could be invoked as alternatives to ab initio methods and/or all-electron basis sets for systems containing heavy elements such as Se.

It has been shown that it is extremely demanding in obtaining a reliable geometry, particularly for bond length, by purely theoretical means for the ground state of H_2Se where highly accurate experimental data are available for comparison. This is also true for the two cationic states under study when comparing the theoretical and IFCA geometries. Nevertheless, the predicted changes in geometry upon ionization seem to be reasonably reliable at the CCSD(T)/6-311G(2d,2p) level. At any rate, from the present study on the He I PE spectrum of H_2Se, reliable IFCA geometries for the two lowest lying cationic states have been obtained for the first time.

Comparison between the simulated and observed spectra of the second PE band of H_2Se supports the previous suggestion from an experimental work on the molecule that fast predissociation for levels over the barrier to linearity in the A^2A_1 state has caused the observed vibrational structure to be diffuse.[3] Although the simulated spectrum for the third PE band of the molecule has not been generated in the present investigation, the computed AIE−VIE separation suggests that the adiabatic position was not observed in the experimental spectrum mainly due to the large geometric change upon ionization. The CCSD(T)/6-311G(2d,2p) geometry obtained here for the B^2B_2 state indicates a structure of a $Se^+(H_2)$ complex with a short HH distance and a long SeH bond length which confirms the previous HF results.

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