Vol 17 No 9, September 2008
1674-1056/2008/17(09)/3318-04

Chinese Physics B

© 2008 Chin. Phys. Soc.
and IOP Publishing Ltd

Spin–orbit *ab initio* curves of $^{80}Se_2^+$ ion and the assignment of photoelectron spectra of $^{80}Se_2$ molecule*

Yan Bing(闫 冰), Pan Shou-Fu(潘守甫)†, and Guo Qing-Qun(郭庆群)

Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, *China*

(Received 5 September 2007; revised manuscript received 21 January 2008)

This paper carries out *ab initio* calculations to study the $^{80}Se_2(X^3\Sigma_g^-)$ state and $^{80}Se_2^+(X^2\Pi_g)$, $^{80}Se_2^+(a^4\Pi_g)$ states by using completed active space self-consistent field and multi-reference second order perturbation theory. The electronic curves of these states including spin–orbit coupling are calculated, and then the spectroscopic parameters are obtained. The photoelectron spectra of $^{80}Se_2$ molecule in gas phase are assigned according to Franck–Condon analysis based on calculated potential energy curves. The ionization energies of $^{80}Se_2$ molecule are determined by the present calculation.

Keywords: potential energy curves, spin–orbit coupling, Franck–Condon factor, ionization energy
PACC: 3365C, 3370C, 3510F

1. Introduction

The photoelectron spectra (PES) of the Group VI homonuclear diatomic molecules have been investigated experimentally and theoretically during last several decades.[1−3] The photoionization efficiency (PIE) spectra also measured for S_2, Se_2, and Te_2 molecules in gas phase to explore the properties of molecules.[4,5] Theoretical calculations of PES with *ab initio* and density functional theory are main methods to assign the PES observed in experiments.[6,7] The transition length of PES is expressed[8] (under Born–Oppenheimer approximation) as

$$I = |M_e|^2 \cdot \left| \int \varphi_{v'} \varphi_{v''}^* \mathrm{d}\tau \right|^2, \qquad (1)$$

where M_e is electronic dipole transition moment, and $\int \varphi_{v'} \varphi_{v''}^* \mathrm{d}\tau$ is the overlap integral between the vibrational level of upper and lower electronic states, that is, Franck–Condon factor (FCF). For a pair of specific electronic states, $|M_e|^2$ is nearly constant, and the FCF governs the structure of PES. The PES of heavy atoms containing molecules often exhibit fine structures in high-resolution measurements because of the relativistic effect due to the large number of electrons. Thus, the relativistic effect should be considered in the calculations of electronic structure.

In this paper, firstly, the potential energy curves (PEC) of Se_2 molecule and molecular ion including spin–orbit coupling (SOC) are calculated using *ab initio* methods. The spectroscopic parameters then are fitted. The vibrational equations based on the fitted PECs are resolved and the FCFs are obtained. Finally, the adiabatic ionization energies and the vertical energies are determined, and the comparisons with the PIE experiments are made.

2. Methodology and computational details

The calculations are performed using GAMESS[9] suite of program in D_{2h} symmetry. The PECs of $^{80}Se_2(X^3\Sigma_g^-)$ and $^{80}Se_2^+(X^2\Pi_g)$, $^{80}Se_2^+(a^2\Pi_g)$ are calculated using multireference perturbation theory[10] with the optimized wavefunctions by complete active space self-consistent field (CASSCF) method. The active space includes two σ_g, two σ_u, one π_g and one π_u orbit correlated to 4s and 4p electrons of Se, and one additional π_u orbit is included to describe the polarization effect. The all-electron basis set cc-pvQz[11] is used in above calculations.

The effects of SOC are calculated using spin-obit multiconfigurational quasidegenerate perturbation theory (SO-MCQDPT)[12] (second order), where low-lying states of Se_2^+ were coupled and only one-

*Project supported by the National Natural Science Foundation of China (Grant No 10604022).
†Corresponding author. E-mail: pansfjlu@yahoo.com.cn

electron SOC terms were kept at the second order and full two-electron SOC terms were kept at first order in the Pauli–Breit operator. In SO-MCQDPT calculations, 10 core orbitals are frozen and other orbitals corresponding to $n = 3, 4$ of Se atoms are correlated. The relative small basis set cc-pvDz[10] is used in the calculations of SO-MCQDPT curves.

The one-dimension radial Schrödinger equations are resolved[13] based on the SO-MCQDPT PECs to obtain the vibrational wavefunctions of different electronic states. The FCFs between the $^{80}Se_2(X^3\Sigma_g^-)$ states and $^{80}Se_2^+(X^2\Pi_{1/2g,3/2g})$, $^{80}Se_2^+(a^4\Pi_{5/2g,3/2g,1/2g,1/2g})$ levels then are calculated using the vibrational wavefunctions.

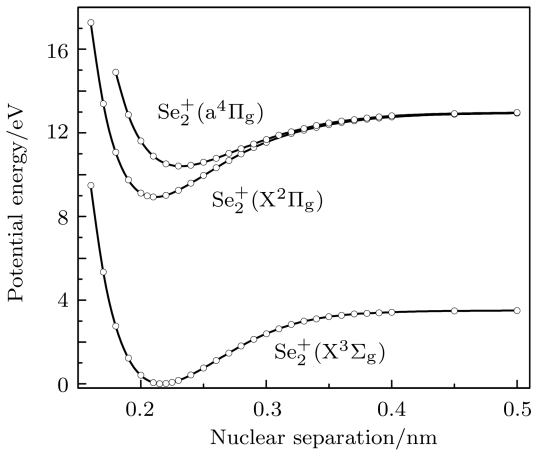


Fig.1. The spin-free PECs of $^{80}Se_2$ and $^{80}Se_2^+$.

3. Results and discussion

3.1. The PECs of Se_2 and Se_2^+

The spin-free PECs of $^{80}Se_2(^3\Sigma_g^-)$ and $^{80}Se_2^+(X^2\Pi_g)$, $^{80}Se_2^+(a^4\Pi_g)$ are shown in Fig.1. The dissociation energies of ground state of Se_2 is 3.50 eV according to present multireference calculation, which is similar to 3.41–3.61 eV with photoionization experiment,[5] 3.163 ± 0.002 eV with spectroscopic experiment,[14] 3.28 ± 0.11 eV, 3.23 ± 0.09 eV and 3.27 ± 0.09 eV with thermochemical experiments.[15,16]

The geometry and spectroscopic parameters of $^{80}Se_2$ are shown in Table 1, together with the values in other references. The equilibrium bond length r_e of $^{80}Se_2$ molecule in ground state is 0.21670 nm according to present calculation, this agrees with Barrow's experimental spectroscopic result (0.21661 nm for 0_g^+),[17] electron diffraction experiment by Maxwell and Mosley (0.219 ± 0.003 nm),[18] and the values collected by Setzer *et al* (0.216620 nm for 0_g^+, 0.216367 nm for 1_g).[19] The present calculated harmonic vibrational frequency ω_e is 389.9 cm^{-1} and anharmonic vibrational frequency $\omega_e x_e$ is 0.97 cm^{-1}, which is in accordance with other references listed in Table 1.

Table 1. The parameters of Se_2 and Se_2^+ levels.

levels	r_e/nm	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}	T_e/cm^{-1}
$^{80}Se_2(X^3\Sigma_g^-)$	0.21670	389.9	0.97	0
	0.21661[a]	385.3[a]	0.96[a]	
	0.216620[b]	385.370[b]	0.9786[b]	
	0.216367[c]	387.129[c]	0.9606[c]	
	0.219±0.003[d]			
$^{80}Se_2^+(X^2\Pi_{1/2g})$	0.21136	412.2	1.38	71221
$Se_2^+(X^2\Pi_{3/2g})$	0.21145	407.1	1.18	73145
$Se_2^+(a^4\Pi_{5/2g})$	0.23120	317.2	1.36	83010
$Se_2^+(a^4\Pi_{3/2g})$	0.23121	317.0	1.37	83607
$Se_2^+(a^4\Pi_{1/2g})$	0.23124	316.8	1.33	84212
$Se_2^+(a^4\Pi_{1/2g})$	0.23125	316.9	1.38	84806

[a] Ref.[17]
[b] values for 0_g^+ collected in Ref.[19]
[c] values for 1_g collected in Ref.[19]
[d] Ref.[18]

The spin-mixed PECs of molecular ion $^{80}Se_2^+$ are calculated using SO-MCQDPT, and shown in Fig.2. The PECs of $^{80}Se_2^+(X^2\Pi_g)$ and $^{80}Se_2^+(a^4\Pi_g)$ states split when considering SOC effect as perturbation. The bond lengths r_e, energies T_e relative to equilibrium $^{80}Se_2(^3\Sigma_g^-)$ and spectroscopic parameters of each level are also listed in Table 1. The bond lengths of split levels, $^{80}Se_2^+(X^2\Pi_{1/2g})$ and $^{80}Se_2^+(X^2\Pi_{3/2g})$,

are 0.21136 nm and 0.21145 nm, respectively. The energy split of $^{80}Se_2^+(X^2\Pi_g)$ is approximately 0.2 eV. It is clearly seen in Fig.2 that the $^{80}Se_2^+(a^4\Pi_g)$ state splits into four more closely packed spin–orbit levels in comparison with $^{80}Se_2^+(X^2\Pi_g)$ state, the energy gap is about 0.07 eV. The equilibrium distance of each level differs little in the magnitude of 10^{-5} nm, and is larger for upper levels. The harmonic frequency ω_e and anharmonic frequency $\omega_e x_e$ of each level are similar with the difference of less than 1 cm^{-1}. This indicates that the curve shapes of the group PECs of $^{80}Se_2^+(a^4\Pi_g)$ state are nearly same. The weak SOC effect in $^{80}Se_2(^3\Sigma_g^-)$ state is neglected, and in fact this SOC calculation cannot be achieved in $^3B_{1g}$ (denotes $^3\Sigma_g^-$ state in D_{2h}) irreducible representation.

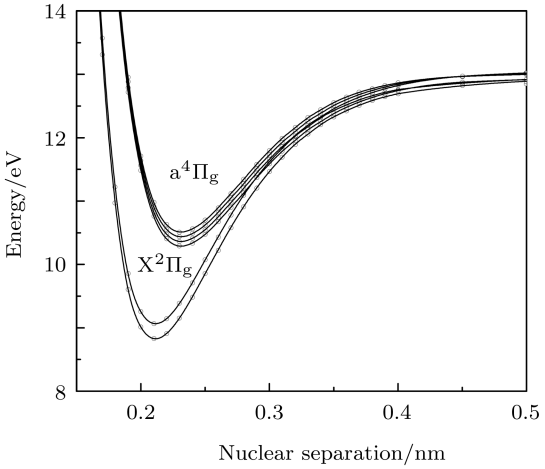


Fig.2. The spin-mixed PECs of Se_2^+.

3.2. Assignment of PES

The relation of ionization energy and FCF for $^{80}Se_2^+(X^2\Pi_g)$ and $^{80}Se_2^+(a^4\Pi_g)$ state are illustrated separately in Fig.3. The 0–0 adiabatic ionization

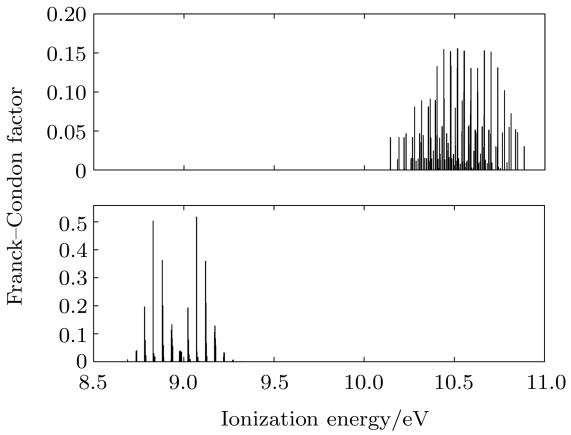


Fig.3. The vibrational resolved ionization progression of $^{80}Se_2$. up: $^{80}Se_2^+(a^4\Pi_g)$, down: $^{80}Se_2^+(X^2\Pi_g)$.

energies and the vertical ionization energies for each sublevel are determined, as shown in Table 2. For comparison with PIE measured at the temperature of 920K in experiment, other transitions $v'' = 1, 2, 3 \rightarrow v'$ are illustrated simultaneously. In order to take into account the internal energy at high temperature, the Boltzmann factors are scaled to the $v'' = 1, 2, 3 \rightarrow v'$ transitions. The Boltzmann factors, determined by formula[20] $e^{-E/0.6952T}$, are approximately 0.6, 0.3, 0.2 for $v'' = 1, 2, 3 \rightarrow v'$ transition at 1000K, respectively. The first adiabatic ionization energy is 8.83 eV according to present *ab initio* calculation, the experimental value[5] is 8.88 ± 0.03 eV, the small deviation is probably caused by the splitting of the triplet ground state of Se_2. Because of the minor difference of the optimized bond length between $^{80}Se_2^+(X^2\Pi_g)$ and $^{80}Se_2(X^3\Sigma_g^-)$ state, the adiabatic and vertical energies of $^{80}Se_2^+(X^2\Pi_g)$ progression coincide, they are 8.83 eV and 9.07 eV, respectively. The adiabatic energies for the sublevels of $^{80}Se_2^+(a^4\Pi_g)$ state are 10.29 eV, 10.36 eV, 10.44 eV, and 10.51 eV, respectively, whose average energy splitting is 0.07 eV.

Table 2. The adiabatic and vertical ionization energies (in eV) of $^{80}Se_2$ molecule at 0K.

levels	$X^2\Pi_{1/2g}$	$X^2\Pi_{3/2g}$	$a^4\Pi_{5/2g}$	$a^4\Pi_{3/2g}$	$a^4\Pi_{1/2g}$	$a^4\Pi_{1/2g}$
adiabatic energies	8.83 8.88± 0.03[a]	9.07	10.29	10.36	10.44	10.51
vertical energies	8.83	9.07	10.44	10.52	10.59	10.66

[a] Ref.[5].

To compare with experiment, the PIE curves of Se_2 molecule in Ref.[5] are quoted as Fig.4. In Fig.4, two maximums are found in the PIE curves of the $^{80}Se_2^+(X^2\Pi_g)$ state, which are corresponding to the

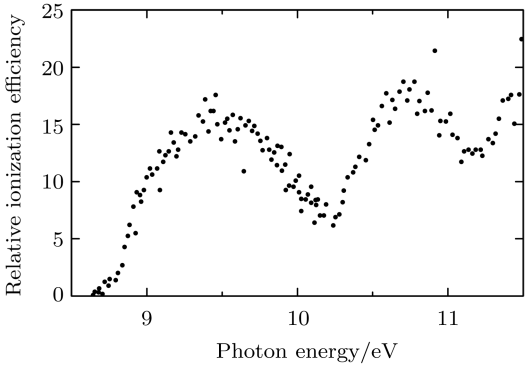


Fig.4. The PIE of Se_2 (quoted from Ref.[5]).

SOC splitting. In Fig.3, $^{80}Se_2^+(X^2\Pi_g)$ progression with similar structure as PIE curves is found. The theoretical SOC splitting is 0.24 eV, and the experimental value is approximately 0.35 eV according to data collected from Ref.[5]. Consider the Boltzmann distribution of the Se_2 populations in various vibrational levels, a plateau with two maximums is formed which is observed in both experimental measurement and theoretical calculations. While for the $^{80}Se_2^+(a^4\Pi_g)$ progression, because the SOC sublevels are closely packed and with same curve shape, the ionization efficiency curves for each level are mixed; the experimental ionization curve is in the range of 10.23–11.11 eV, and the calculated is 10.14–10.89 eV with up to $v'' = 3$ considered.

4. Summary

The $Se_2^+(X^2\Pi_g)$, $Se_2^+(a^4\Pi_g)$ and $Se_2(X^3\Sigma_g^-)$ systems are investigated using spin-obit multiconfigurational quasidegenerate perturbation theory, the spin-mixed electronic curves are calculated. The spectroscopic parameters for above states are fitted. The adiabatic and the vertical ionization energies are determined with the aid of Franck–Condon factors between neutral system and ionic systems. The comparisons between present calculation and experimental PIE curves are made.

References

[1] Berkowitz J 1975 *J. Chem. Phys.* **62** 4074
[2] Wu M and Fehlner T P 1976 *J. Am. Soc.* **98** 7578
[3] Takeshita K, Sadamatu Y and Tanaka K 2005 *J. Chem. Phys.* **112** 044302 and reference therein
[4] Liao C L and Ng C Y 1986 *J. Chem. Phys.* **84** 778
[5] Berkowitz J and Chupka W A 1969 *J. Chem. Phys.* **50** 4245
[6] Wang J Q and Yang Z Z 1988 *Ultraviolet Photoelectron Spectroscopy* (Beijing: Scientific Press) p77
[7] Yuan Y B and Liu Y Z 2006 *Acta Phys. Sin.* **55** 4496 (in Chinese)
[8] Hüfner S 2003 *Photoelectron Spectroscopy: Principle and Application* (New York: Springer) p215
[9] Gordon M S, Jensen J H, Koseki S, Matsunaga N, Nguyen K A, Su S, Windus T L, Dupuis M and Montgomery J A 1993 *J. Comput. Chem.* **14** 1347
[10] Nakano H 1993 *J. Chem. Phys.* **99** 7983
[11] Woon D E and Dunning Jr T H 1993 *J. Chem. Phys.* **98** 1358
[12] Fedorov D G and Finley J P 2001 *Phys. Rev.* A **64** 042502
[13] Le Roy R J 2002 *LEVEL 7.5: A Computer Program for Solving the Radial Schröinger Equation for Bound and Quasibound levels* University of Waterloo, Chemical Physics Research Report CP-655
[14] Barrow R F, Chandler G G and Meyer C B 1996 *Phil. Trans. Roy. Soc. London* A **395** 260
[15] Budininkas P, Edwards R K and Wahlbeck P G 1968 *J. Chem. Phys.* **48** 2859
Budininkas P, Edwards R K and Wahlbeck P G 1968 *J. Chem. Phys.* **48** 2867
Budininkas P, Edwards R K and Wahlbeck P G 1968 *J. Chem. Phys.* **48** 2870
[16] Drowart J and Goldfinger P 1966 *Quart. Rev. Chem. Soc.* (London) **545** 20
[17] Barrow R F, Chandler G G and Meyer C B 1966 *Phil. Trans. Roy. Soc. London.* Series A, *Mathematical and Physical Sciences* **260** 395
[18] Maxwell L R and Mosley V M 1940 *Phys. Rev.* **57** 21
[19] Setzer K D, Dorn A, Lorenz M and Fink E H 2003 *J. Molecular Spectr.* **221** 13
[20] Hertzberg G 1953 *Molecular Spectroscopy and Molecular Structure I. Spectra of Diatomic Molecules* (Toronto: D Van Nostrand) p91