Molecular structure and analytical potential energy function of SeCO

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The density functional method (B3P86/6-311G) is used for calculating the possible structures of SeC, SeO, and SeCO molecules. The result shows that the ground state of the SeC molecule is $^1\Sigma$, the equilibrium nuclear distance is $R_{SeC} = 0.1699$ nm, and the dissociation energy is $D_e = 8.7246$ eV. The ground state of the SeO molecule is $^3\Sigma$, with equilibrium nuclear distance $R_{SeO} = 0.1707$ nm and dissociation energy $D_e = 7.0917$ eV. There are two structures for the ground state of the SeCO molecule: Se=C=O and Se=O=C. The linear Se=C=O is $^1\Sigma$. Its equilibrium nuclear distances and dissociation energy are $R_{SeC} = 0.1715$ nm, $R_{CO} = 0.1176$ nm and 18.8492 eV, respectively. The other structure Se=O=C is $^1\Sigma$. Its equilibrium nuclear distances and dissociation energy are $R_{CO} = 0.1168$ nm, $R_{SeO} = 0.1963$ nm and 15.5275 eV, respectively. The possible dissociative limit of the SeCO molecule is analyzed. The potential energy function for the SeCO molecule has been obtained from the many-body expansion theory. The contour of the potential energy curve describes the structure characters of the SeCO molecule. Furthermore, contours of the molecular stretching vibration based on this potential energy function are discussed.

Keywords: SeCO, molecular structure, potential energy

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1. Introduction

The molecular structure and the potential energy function of atoms and molecules are two important fields of research.[1] The potential energy function in the Born–Oppenheimer approximation fully describes the nature of a molecule.[2–5] It not only describes the molecular's energy, geometry, mechanics and spectroscopic properties, but also its potential energy function of nuclear movement. Therefore, it is the foundation for the studies of molecular collisions and reaction dynamics.

In recent years, CO has been widely used in organic synthesis as a reducing agent. There are a large number of researches on the Se activity. For example, Pisani and Clementi obtained the splitting energy and the dissociation energy of H_2Se by means of HF and RECP; Seminario obtained the atomic separation energy and the equilibrium structure of HSe dimer systems; Donacd and others studied the volumes of SeH, SeO_4-, and Se_3Y_2; Lounila and others studied the CSe_2 rotational spectra; and Bach studied the dissociation energies of CSe, NSe, HSe, and OS.[6] Sonoda proposed that the reaction of H_2Se is between a carbonyl diselenide and its hydrolysis[7]

$$\mathrm{Se} + \mathrm{CO} = \mathrm{SeCO}. \quad (1)$$

However, the mechanism of this reaction is still unclear,[8] and there is no article specifying the calculation of the product of the reaction with quantum mechanics theory.

2. Computational method

The density functional method (B3P86/6-311G) with the 6-311G basis set[9–11] is used for optimizing and analyzing C, O, and Se atoms. In the meantime, the structures and features of the molecules (SeC, SeO, and SeCO) are calculated. The potential energy function of SeCO has been obtained from a many-body expansion theory.[12] All calculations reported in this work are performed with the Gaussian 03 package.[13]

3. Results and discussion

3.1. Molecular structure and dissociation limit of SeC and SeO

The ground state of molecule SeC is $^1\Sigma$ with an equilibrium nuclear distance R_e of 0.1699 nm and a dissociation energy of 8.7246 eV. Using the same method, we find that the electronic state of SeO is $^3\Sigma$, with an equilibrium nuclear distance of 0.1707 nm and a dissociation energy of 7.0917 eV. The SeCO linear molecule has two stable configurations, Se=C=O ($^1\Sigma^+$) and Se=O=C ($^1\Sigma^+$).

According to the atomic and molecular reaction statics,[12] SeC in the ground state dissociates into ground state Se and C atoms, and SeO dissociates into Se and O atoms. As SeC and SeO have the same symmetry, the products are in the ground states. The ground states of Se, C, and O are ^3D_g, ^3P_g, and ^3P_g, respectively. Thus, the dissociation limit of SeCO can

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be shown as follows:

$$\mathrm{SeCO}(\mathrm{X}^1\Sigma_\mathrm{g}) \rightarrow \begin{cases} \mathrm{SeO}(\mathrm{X}^3\Sigma)+\mathrm{C}(^3\mathrm{P}_\mathrm{g}), \\ \mathrm{SeC}(\mathrm{X}^1\Sigma)+\mathrm{O}(^3\mathrm{P}_\mathrm{g}), \\ \mathrm{Se}(^3\mathrm{P}_\mathrm{g})+\mathrm{CO}(\mathrm{X}^1\Sigma), \\ \mathrm{Se}(^3\mathrm{P}_\mathrm{g})+\mathrm{C}(^3\mathrm{P}_\mathrm{g})+\mathrm{O}(^3\mathrm{P}_\mathrm{g}). \end{cases} \quad (2)$$

3.2. Energies of SeCO, $SeCO^+$, and SeCO

The molecular energies of SeCO, $SeCO^+$, and SeCO have been calculated at different levels. In order to obtain the low potential energy, these three molecules are optimized.[14] From Table 1, we know that the different methods we chose have a great influence on the results.

Table 1. Potential energies of SeCO, $SeCO^+$, and SeCO at different levels.

	HF	UHF	LSDA	BLYP	B3LYP	BP86	B3P86
SeCO	–2512.4808	–2512.4808	–2511.5422	–2514.8597	–2514.8544	–2515.1073	–2515.8756
$SeCO^+$	–2512.4562	–2512.1389	–2508.7428	–2514.4788	–2514.4666	–2514.7161	–2515.4650
SeCO	–2512.1389	–2512.4562	–2511.5245	–2514.8224	–2514.8292	–2515.0783	–2515.8708

3.3. Potential energy function of two-body terms

The potential energy of SeO is obtained by means of B3LYP-DFT. The potential energy is obtained via the Murrell–Sorbie potential energy function[12]

$$V = -D_\mathrm{e}(1+a_1\rho+a_2\rho^2+a_3\rho^3)\exp(-a_1\rho), \quad (3)$$

where $\rho = r - r_\mathrm{e}$, r and r_e are the inter distance and the equilibrium bond length, respectively, D_e is the dissociation energy, and a_i $(i = 1,2,3)$ are the fitting coefficients. Based on the calculation at the B3P86/6-311++G level, the parameters are obtained and listed in Table 2.

Table 2. Murrell–Sorbie potential energy function parameters for SeCO molecule.

Molecule	D_e/eV	R_e/nm	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}
SeC	8.7246	0.16997	30.152	255.83	1954.23
		0.16885[6]			
CO	14.4675	0.11458	33.203	185.28	2691.31
	11.226[15]	0.11283[16]			
OSe	7.0917	0.17067	30.588	232.54	1587.8
		0.16173[6]			

The data of the two-atom molecules and the potential energy function are used to find the force constants

$$f_2 = D_\mathrm{e}(a_1^2 - 2a_2), \quad (4)$$

$$f_3 = 6D_\mathrm{e}(a_1a_2 - a_2 - a_1^3/3), \quad (5)$$

$$f_4 = D_\mathrm{e}a_1^4 - 6f_2a_2^2 - 4f_3a_1, \quad (6)$$

where f_2, f_3, and f_4 are quadratic, cubic, and quartic force constants, respectively. The relationship between the spectroscopic constants and f_i $(i = 2,3,4)$ can be shown as follows:

$$\omega_\mathrm{e} = \sqrt{\frac{f_2}{4m\pi^2c^2}}, \quad (7)$$

$$\alpha_\mathrm{e} = -\frac{6B_\mathrm{e}^2}{\omega_\mathrm{e}}\left(\frac{f_3R_\mathrm{e}}{3f_2}+1\right), \quad (8)$$

$$\omega_\mathrm{e}\chi_\mathrm{e} = \frac{B_\mathrm{e}}{8}\left[-\frac{f_4R_\mathrm{e}^2}{f_2}+15\left(1+\frac{\omega_\mathrm{e}\alpha_\mathrm{e}}{6B_\mathrm{e}^2}\right)^2\right], \quad (9)$$

$$B_\mathrm{e} = \frac{h}{8\pi c\mu R_\mathrm{e}^2}. \quad (10)$$

Using Eqs. (4)–(10) and the parameters in Table 2, we calculate the spectroscopic constants of the two-atom molecules and listed them in Table 3.

Table 3. Force constants and spectroscopic constants of SeC, CO, and SeO.

Molecule	f_2/aJ·nm^3	f_3/aJ·nm^3	f_4/aJ·nm^4	ω_e/cm^{-1}	$\omega_\mathrm{e}\chi_\mathrm{e}$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}
SeC	5.7116	–29.2136	159.07553	946.3426	3.1839	0.5598	0.003699
CO	16.9725	–121.5992	773.6490	2049.6383	12.2880	0.1873	0.001782
SeO	5.3465	–27.3690	134.1899	825.8784	2.94215	0.4350	0.002691

3.4. Potential energy functions of SeCO and SeOC

The three-body terms are calculated and shown in Table 4. The potential energy of the SeCO molecule is 1.626 eV lower than that of the SeOC molecule. So we know that the configuration of SeCO is the most stable.

According to the many-body expansion theory,[12] the SeCO potential energy function can be written as

$$V(R_1,R_2,R_3) = V_\mathrm{SeC}^{(2)}(R_1)+V_\mathrm{CO}^{(2)}(R_2)+V_\mathrm{SeO}^{(2)}(R_3) + V_\mathrm{SeCO}^{(3)}(R_1,R_2,R_3), \quad (11)$$

where the two-body terms (V_SeC, V_CO, and V_SeO) are gained via the Murrell–Sorbie potential energy function. The three-body term $V_\mathrm{SeCO}^{(3)}(R_1,R_2,R_3)$ is given by

$$V_\mathrm{SeCO}^{(3)}(R_1,R_2,R_3) = P\cdot T, \quad (12)$$

where

$$P = C_0 + C_1S_1 + C_2S_2 + C_3S_3 + C_4S_1^2 + C_5S_2^2$$

$$+C_6S_3^2+C_7S_1S_2+C_8S_2S_3+C_9S_1S_3+C_{10}S_2^3$$
$$+C_{11}S_1^2S_2+C_{12}S_3^2S_2+C_{13}S_1S_2S_3, \quad (13)$$
$$T = (1-\tanh(\gamma_1 S_1/2))(1-\tanh(\gamma_2 S_2/2))$$
$$\times(1-\tanh(\gamma_3 S_3/2)). \quad (14)$$

There are 14 linear coefficients in formula (13) and three linear coefficients in formula (14). The three nonlinear coefficients (γ_1, γ_2, γ_3) can be determined by the potential energy curve; while the 14 linear parameters C_i can be determined by the equilibrium structure and the force constants. The P is a polynomial of S_i, which are the symmetrical internal coordinates. The parameters are shown as follows: $C = 16.2728$, $C_1 = 24.3782$, $C_2 = 12.1407$, $C_3 = 7.9488$, $C_4 = 17.5633$, $C_5 = -10.5902$, $C_6 = 2.2151$, $C_7 = 19.2443$, $C_8 = 5.8768$, $C_9 = 11.1889$, $C_{10} = -10.5517$, $C_{11} = 9.7792$, $C_{12} = 7.3338$, $C_{13} = 1.6859$, $\gamma_1 = 2$, $\gamma_2 = 1$, $\gamma_3 = 1$.

To obtain the symmetrical internal coordinates S_i, we select the appropriate coordinates $C_{\infty v}$ as the reference coordinates. Then the internal coordinates are

$$\rho_i = R_i - R_i^0, \quad (i = 1,2,3), \quad (15)$$

where $R_1^0 = 0.2423$ nm, $R_2^0 = 0.1172$ nm, and $R_3^0 = 0.2427$ nm. The corresponding internal coordinates are

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \end{bmatrix} = \begin{bmatrix} 0.33701957565344 & 0.577308109906153 & -0.743729219449499 \\ -0.909279822660775 & 0.00529869773707297 & 0.416151568427034 \\ 0.244188471735184 & 0.816509197767469 & 0.52314885093323 \end{bmatrix} \begin{bmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{bmatrix}. \quad (16)$$

Table 4. Parameters of SeCO and SeOC molecules.

	SeCO ($X^1\Sigma^+$)	SeOC ($X^1\Sigma^+$)
Equilibrium structure constant	$R_1 = 0.17153$ nm	$R_1 = 0.31315$ nm
	$R_2 = 0.11756$ nm	$R_2 = 0.11684$ nm
	$R_3 = 0.28909$ nm	$R_3 = 0.19631$ nm
Dissociation energy/eV	18.8492	15.5275
Force constants/a.u.	$f_{11} = 0.359694$, $f_{22} = 0.952745$	$f_{33} = 0.0795792$, $f_{22} = 0.915090$
	$f_{12} = 0.044838$, $f_{\alpha\alpha} = 0.117703$	$f_{32} = 0.0513761$, $f_{\beta\beta} = 0.0503657$

$R_1 = R_{\mathrm{SeC}}$, $R_2 = R_{\mathrm{CO}}$, $R_3 = R_{\mathrm{SeO}}$, $\angle_{\alpha\alpha} = \angle$SeCO, $\angle_{\beta\beta} = \angle$SeOC.

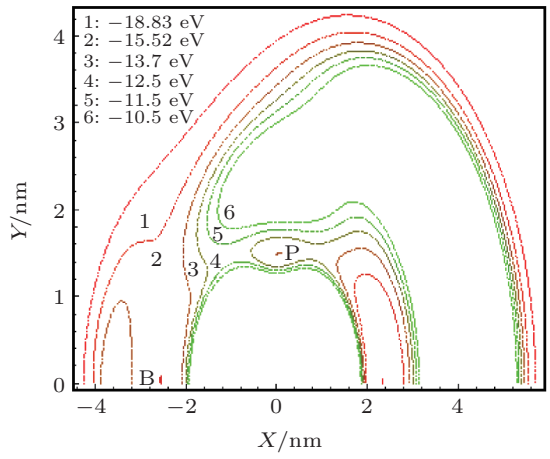


Fig. 1. (color online) Potential energy contours of Se moving around the C–O bond.

Based on the analytical potential energy function of SeCO at the B3P86/6-311G level, we draw the contours of the potential (Fig. 1). The potential energy contours of Se moving around the C–O bond are shown in Fig. 3, and R_{CO} is fixed at 0.11756 nm on the X axis, (C is fixed at $X = 0.05878$ nm, $Y = 0$ nm; O is fixed at $X = -0.05878$ nm, $Y = 0$ nm). When the Se atom approaches molecules C and O in the X direction, there is a potential well at point A (−18.8492 eV) with $X = 0.23031$ nm; when the Se atom approaches the CO molecule from the opposite direction, there is a potential well (15.5275 eV) at $X = -0.25509$ nm. So we know that SeCO is more stable than SeOC. The energy of the saddle point p is −13.7240 eV, CO rotates around Se, and the Se island needs to overcome the 1.8035 eV energy barrier to form a stable Se=C=O molecule.

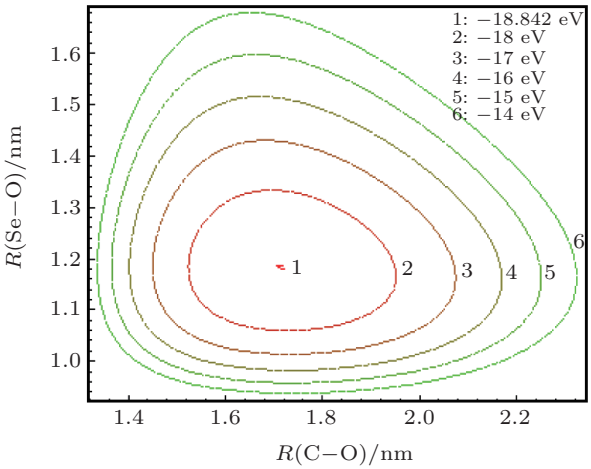


Fig. 2. (color online) Contours of the stretching vibration potential energy for SeCO.

Figure 2 is the Se–C and C–O bond stretching contours for a fixed angle ∠SeCO =180°. From the figure,

we can find the equilibrium structure of the SeCO molecule ($R_{SeC} = 0.17153$ nm, $R_{CO} = 0.11756$ nm) and the potential well (−18.8492 eV). Because there is no saddle point in the reactive paths of Se+CO and SeC+O, the reactions occur easily without a threshold energy.

Figure 3 is the Se–O and O–C bond stretching contours for a fixed ∠SeOC = 180°. From the figure, we can find the equilibrium structure ($R_{SeO} = 0.19631$ nm and $R_{CO} = 0.11684$ nm) and the potential well (−15.5275 eV). Since there is no saddle point in the channels Se+C and SeO+C, the reactions can occur easily without a threshold energy.

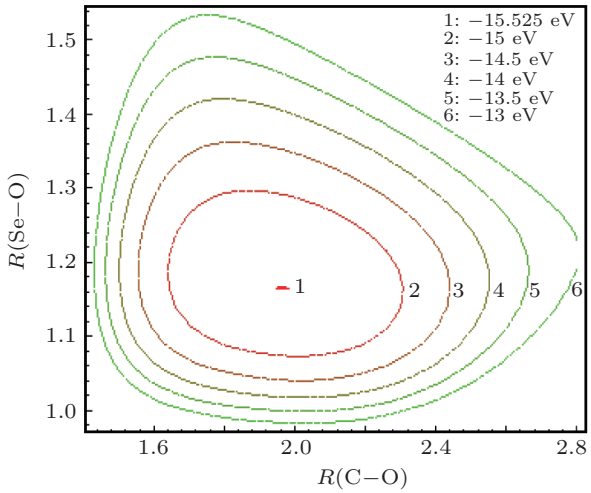


Fig. 3. (color online) Contours of the stretching vibration potential energy for SeOC.

4. Conclusion

The theoretical results of SeC, SeO, and SeCO have been obtained by means of B3LYP/6-311. By optimizing SeCO, we gained the most stable structure and the force constants. According to the many-body expansion theory, we obtained the potential energy function of SeCO. The potential energy curves reproduce the relationship between the structure and the energy in an accurate manner. With the principles of atomic and molecular reaction statics, we discussed the dissociation limits of Se+CO and SeC+O, and found that the reactions do not have a threshold energy.

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