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反式和顺式 HOOOH 的电子光谱的理论研究

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摘要 用密度泛函方法(DFT)和全活化空间自洽场方法(CASSCF)以及耦合簇理论(CCS)优化了反式和顺式 HOOOH 的平衡几何构型, 用 DFT 计算了 HOOOH 顺反异构化反应的势能曲线和谐振动频率. 用含时密度泛函理论(TD-DFT)和二阶全活化空间微扰理论(CASPT2)计算了反式和顺式 HOOOH 垂直激发能. 计算结果表明: (1) 反式异构体比顺式异构体稳定; (2) 两种稳定构型的异构化反应有两种路径; (3) 对于垂直跃迁能最低的单态和叁态, 反式的垂直跃迁能比顺式的低; (4) 在单激发态中, CASPT2 方法预测的顺式 HOOOH 寿命最长的激发态为 2¹A, 其跃迁能是 167.43 nm, 寿命为 1.44 × 10⁻⁵ s; 反式 HOOOH 寿命最长的激发态为 2¹A, 其跃迁能是 165.52 nm, 寿命为 2.07 × 10⁻⁵ s.

关键词: DFT, CASPT2, HOOOH, 过渡态, 电子光谱

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Theoretical Study on the Electronic Spectra of cis-HOOOH and trans-HOOOH

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Abstract Equilibrium geometries of cis-HOOOH and trans-HOOOH have been investigated using the density functional theory (DFT), complete active space self-consistent-field (CASSCF), and coupled cluster with single and double replacement (CCSD) approaches. The harmonic vibrational frequencies on the optimized geometries were calculated using the DFT theory. The potential energy curve of the isomerization between the trans-HOOOH and cis-HOOOH was obtained by DFT calculations. Time-dependent density functional theory (TD-DFT) and complete active space perturbation theory of second order (CASPT2) calculations have been performed to obtain the vertical excitation energies of selected low-lying singlet and triplet excited states. Computed results show that: (1) trans-isomer is more stable than cis-isomer; (2) there are two pathways of the conversion between the trans-HOOOH and cis-HOOOH; (3) the vertical excitation energies of the lowest singlet and triplet excited states in trans-HOOOH are lower than those in cis-isomer; (4) in the singlet excited states, 2¹A state in trans-HOOOH and 2¹A state in cis-HOOOH have the longest lifetimes of 2.07 × 10⁻⁵ s and 1.44 × 10⁻⁵ s with the excitation energies of 165.52 and 167.43 nm, respectively.

Keywords: DFT, CASPT2, HOOOH, Transition state, Electronic spectra

In recent years, dihydrogen trioxide (HOOOH) and relevant analogs have drawn considerable attention in atmospheric, envi-

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ronmental^[1-3], and biological chemistry^[4-7]. Most studies mainly concentrated on the formation, characterization, decomposition, and reaction mechanism of dihydrogen trioxide and analogs^[6-12]. The chemistry of alkyl hydrotrioxides (ROOOH) and dialkyl trioxides (ROOOR) has also been well investigated in the past years^[13-17].

In the year 1880, Berthelot^[18] reported the possibility of transient existence of dihydrogen trioxide as an intermediate in the decomposition of hydrogen peroxide. However, there were no methods available to confirm his report at that time. Until 1917, Rothmund and Burgstaller^[19] investigated the kinetics of the reaction between ozone and hydrogen peroxide for the first time. Subsequently, the formation of dihydrogen trioxide was experimentally reported by Czapski and Bielski^[20]. Nekrasov et al.^[21-23] attempted to detect hydrogen polyoxides by IR. Giguère et al.^[24-27] reported fundamental skeletal vibrations of H₂O₃ and H₂O₄. Bielski and Schwarz^[28] reported the electronic absorption spectrum of dihydrogen trioxide in air-saturated perchloric acid solution, with the regions obtained below 280 nm. According to the experiment, the most intensive absorption wavelength was measured at about 210 nm, or at a probably shorter wavelength.

According to a recent report by Engdahl and Nelander^[5], all fundamental vibrations of HOOOH were observed through experiments. They suggested that the O—O antisymmetric stretch at 776 cm⁻¹ could be used to detect HOOOH even in the presence of high concentrations of H₂O. Certain theoretical calculations were performed by ab initio method for resolving its structure, infrared spectrum, and stability^[5, 29-33]. Plesničar^[6] reviewed these studies of dihydrogen trioxide in detail.

More recently, Suma et al.^[34] reported the rotational spectrum and structure of HOOOH using Fourier transform microwave (FTMW) spectroscopy and TMW-mm-wave double resonance and triple resonance spectroscopy. In their experiment, they could not observe the transitions of the *cis*-HOOOH under similar experimental conditions in sufficiently wide frequency regions.

However, among these studies, few theoretical and even experimental studies on the excited states of dihydrogen trioxide have been reported. It is obvious that detailed knowledge about the excited states is of utmost importance. Therefore, in this study, the equilibrium geometry, harmonic frequency, the energies of the ground states and the partial excited states, and their lifetimes have been investigated. This article reports for the first time, the vertical transition energies of HOOOH. Moreover, an attempt is made to explain the puzzle in Suma's experiment by the isomerization between the *trans*-HOOOH and *cis*-HOOOH.

1 Computational details

Density functional theory (DFT) calculations using the mixed hybrid functional-B3LYP approach were used to determine the equilibrium geometries and harmonic vibrational frequencies of the molecules in their ground states. For comparison, geometrical optimizations have also been performed by complete active space self-consistent-field (CASSCF) and restricted coupled cluster with single and double replacement (RCCSD)^[35-37] calculations. All geometries and vibrational frequency calculations used the standard split-valence 6-31G^{**} basis set, which includes a single d-polarization on oxygen atom and p-polarization on hydrogen atom. In the CASSCF calculations, the active space consists of eight electrons and eight orbitals, whereas the lowest nine orbitals are always double occupied.

For a given torsion angle, the potential curve of the isomerization between the *trans*-HOOOH and *cis*-HOOOH was obtained using the B3LYP approach with the 6-31G^{**} and the triplet-zeta^[38] basis sets while the other geometrical parameters were optimized. The two different transition states were optimized at the B3LYP/6-31G^{**} level. Time-dependent density functional theory (TD-B3LYP) was used to calculate the electronic transition energies with the triplet-zeta basis set as well as the complete active space perturbation theory of second order (CASPT2)^[39-40] with the double-zeta basis set. In the CASPT2 calculations, the active reference space contains 14 valence electrons and 11 valence orbitals, whereas the core and the lowest six orbitals of the tri-oxygen unit are always double occupied. The B3LYP/6-31G^{**}-optimized geometries are used in all the feature computations. These calculations were carried out using Gaussian 98^[41] and MOLPRO 2002^[42] program packages.

The oscillator strengths (*f*) are calculated with the following formula:

$$f = \frac{2}{3} \Delta E |\text{TM}|^2$$

where *E* (a.u.) denotes the transition energy between the ground state and the excited state, and TM denotes the transition moment in a.u..

The corresponding lifetime (in second) is defined by the following equation:

$$\tau = \frac{3}{2f\bar{\nu}^2}$$

where $\bar{\nu}$ is the transition energy in cm⁻¹, and *f* is the oscillator strength. For spin-allowed singlet-singlet transition, CASPT2 transition energies and corresponding oscillator strengths are used in the estimation of lifetimes.

2 Results and discussion

2.1 Geometries and vibrational frequencies

The optimized geometrical parameters and computed rota-

Table 1 Optimized geometrical parameters of trans-HOOOH and cis-HOOOH at various levels

	B3LYP/6-31G**		RCCSD/6-31G**		CASSCF/6-31G**		Ref. ^a
	trans	cis	trans	cis	trans	cis	trans
H(1)—O(2)	0.0974	0.0974	0.0970	0.0970	0.0949	0.0949	0.0996
O(2)—O(3)	0.1431	0.1431	0.1438	0.1438	0.1459	0.1459	0.1428
A(1-2-3)	101.4	101.8	100.7	101.2	100.4	100.9	101.1
A(2-3-4)	107.5	107.8	106.3	106.6	106.2	106.6	107.0
D(4-3-2-1)	80.1	93.6	79.5	94.3	81.6	95.9	81.8
D(5-4-3-2)	80.1	-93.6	79.5	-94.3	81.6	-95.9	81.8

a) computed values from Ref.[34]; bond lengths in nm and angles in degree

Table 2 The predicted rotational constants (MHz) of trans-HOOOH and cis-HOOOH using different methods

	B3LYP/6-31G**		RCCSD/6-31G**		CASSCF/6-31G**		Ref. ^a		Exp. ^a
	trans	cis	trans	cis	trans	cis	trans	cis	
A ₀	51365	49816	52823	51358	49154	50658	51152	52437	51149
B ₀	10675	10762	10494	10555	10463	10270	10719	10558	10688
C ₀	9384	9394	9297	9297	9127	9031	9380	9297	9355

a) Computed and experimental values from Ref.[34]

tional constants of trans-HOOOH and cis-HOOOH at several levels of theory are displayed in Table 1 and Table 2.

For trans-HOOOH, as shown in Table 1, the predicted results by B3LYP and RCCSD calculations are very close, with the difference being less than 0.001 nm for bond length and 1° for angle. A comparison of B3LYP-optimized bond lengths using sophisticated CASSCF and RCCSD treatments shows that B3LYP calculations predict excellent geometries. In Table 2, the calculated rotational constants using B3LYP/6-31G** method are 51365, 10675, and 9384 MHz for trans-HOOOH, respectively, which are in reasonable agreement with the corresponding experimental values of 51149, 10688, and 9355 MHz^[34]. At

the B3LYP/6-31G** level, for trans-HOOOH, the optimized H—O and O—O bond lengths are 0.0974 and 0.1431 nm, the optimized H-O-O and O-O-O bond angles are 101.4° and 107.5°; and the optimized dihedral angles are 80.1°. The O—O bond length is shorter than that in H₂O₂ (0.1463 nm), whereas the H—O bond length is longer than that in H₂O₂ (0.0965 nm)^[43]. The distances between the atoms suggest a dominant singlet bonding character in the two isomers. The bond lengths and bond angles in trans-HOOOH and cis-HOOOH remain unchanged whereas the dihedral angles have notable change, suggesting that the dihedral is the key factor that is responsible for their difference.

Harmonic vibrational frequencies of trans-HOOOH and cis-HOOOH in their ground states by B3LYP calculations are shown in Table 3.

As shown in Table 3, the two isomers have no imaginary vibrational frequencies, indicating that they are minima on the corresponding potential energy surface (PES). Both of them are stable, the energy of ground state trans-HOOOH is -226.68787 a.u., lower than that of cis-isomer, which is -226.68321 a.u. at the B3LYP/6-31G** level, with the difference 0.00466 a.u. . After being scaled by 0.95, B3LYP predicted vibrational frequencies (Table 3) show good agreement with available experimental fundamentals^[5]. For example, in trans-HOOOH, the OOO bend vibrational frequency is 506.3 cm⁻¹, close to the observed value of 509.1 cm⁻¹^[5]. However, the difference of symmetric OO stretch is a little larger.

2.2 Isomerization between the trans-HOOH and cis-HOOH

Suma and coworkers^[34] observed five rotational transitions

Table 3 The computed harmonic vibrational frequencies (cm⁻¹) for trans-HOOOH and cis-HOOOH at the B3LYP/6-31G** level

Vibronic mode	trans		cis		Ref. ^b		Exp. ^c
	cal.	cal. ^a	cal.	cal. ^a	trans	cis	
symmetric OH stretch	3713.8	3528.1	3701.4	3516.3	3529.6	3533.1	3529.6
antisymmetric OH stretch	3708.7	3523.3	3697.9	3513.0	3529.6	3528.4	3529.6
antisymmetric HOO bend	1395.8	1326.0	1403.2	1333.0	1359.2	1353.6	1359.1
symmetric HOO bend	1391.1	1321.5	1371.1	1302.5	1347.6	1349.6	1347.4
symmetric OO stretch	942.9	895.8	946.4	899.1	820.4	899.5	821.0
antisymmetric OO stretch	807.9	767.5	806.6	766.3	776.1	770.2	776.3
OOO bend	532.9	506.3	513.1	487.4	509.2	506.5	509.1
antisymmetric torsion	432.0	410.4	450.7	428.2	387.0	410.4	387.0
antisymmetric torsion	373.3	354.6	260.5	247.5	345.9	346.9	346.4

a) scaled by 0.95; b) computed values from Ref.[33]; c) observed value from Ref.[5]

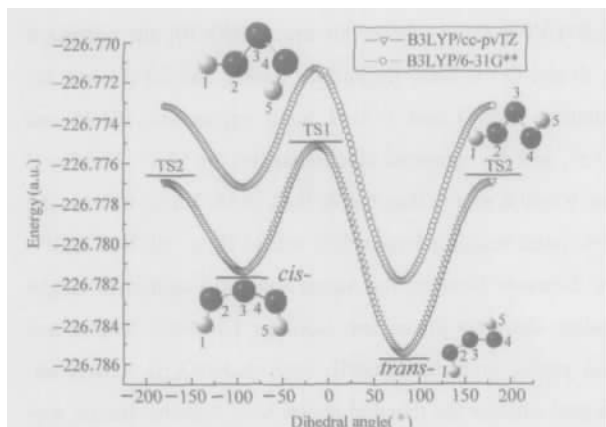


Fig.1 Potential energy curves of HOOOH by scanning dihedral angle

for trans-HOOOH through experiments, but under the same conditions the transitions of cis- isomer could not be observed. For exploring this problem, B3LYP/6-31G^{**} calculations were performed to yield the potential curve of the isomerization between the trans-HOOOH and cis-HOOOH by scanning the HOOO dihedral angles as shown in Fig.1. To obtain reliable results, the B3LYP/cc-pvTZ calculations were also performed for comparison. The two different transition states (TS) were located. The analytical frequencies show only one imaginary frequency -278.5 cm^{-1} for TS1 and -420.1 cm^{-1} for TS2 at the B3LYP/6-31G^{**} level. The results testify that they are first-order saddle point on the PES. Fig.1 shows that the trans-HOOOH is the most stable geometric structure. The optimized geometrical parameters of the two transition states using the B3LYP/6-31G^{**} method are shown in Table 4. The results indicate that there are two pathways with regard to the transition between the two stable isomers: one is cis- TS1 trans- and the other is cis- TS2 trans-. The single-point energies of trans-, cis-, and two transition structures are -226.78536 , -226.78132 , -226.77504

Table 4 Optimized geometrical parameters (bond lengths in nm and angles in degree) and obtained total energies (a.u.) of transition states

	TS1	TS2
H(1)-O(2)	0.0975	0.0976
O(2)-O(3)	0.1422	0.1396
O(3)-O(4)	0.1465	0.1483
O(4)-H(5)	0.0974	0.0974
H(1)-O(2)-O(3)	101.2	102.2
O(2)-O(3)-O(4)	106.8	104.2
O(3)-O(4)-H(5)	100.5	97.9
H(1)-O(2)-O(3)-O(4)	102.5	80.7
O(2)-O(3)-O(4)-H(5)	-13.4	179.8
Total energies ^a	-226.67732	-226.67916
Total energies ^b	-226.77504	-226.77683

a) B3LYP/6-31G^{**}; b) B3LYP/cc-pvTZ

and -226.77683 a.u., respectively. The energy barriers of the trans- to cis- are 27.1 and $22.4\text{ kJ}\cdot\text{mol}^{-1}$, whereas those of cis- to trans- are 16.5 and $11.8\text{ kJ}\cdot\text{mol}^{-1}$, respectively. The conversion energy barrier of cis- to trans- is so little that the existence of cis- may be instantaneous, which leads to its unobservable rotational transitions.

2.3 Singlet and triplet excited states

The selected vertical transition energies (λ) and oscillator strengths (f) of trans-HOOOH and cis-HOOOH predicted by CASPT2/cc-pvDZ and TD-B3LYP/cc-pvTZ methods are shown in Table 5 and Table 6.

The trans-HOOOH isomer has the ground state X¹A, with electronic configuration $[\text{core}]^6(3a)^2(2b)^2(4a)^2(3b)^2(5a)^2(4b)^2(6a)^2(7a)^2(5b)^2(6b)^2(8a)^0(7b)^0(9a)^0$. The electronic excitations of b \rightarrow a or a \rightarrow b give rise to ¹B and ³B states, whereas a \rightarrow a or b \rightarrow b electronic excitations produce ¹A and ³A states. According to the spin and dipole rules, the ¹A \rightarrow X¹A and ¹B \rightarrow X¹A electronic excitations are allowed among these electronic excitations. For trans-HOOOH, Table 5 shows the selected 11 low-lying excited states, including 5 singlet states and 6 triplet states. By CASPT2 computations the vertical transition energies of selected singlet states were predicted between 194.44 and 152.29 nm, whereas the triplet states were between 209.75 and 162.34 nm. The computations using the TD-B3LYP method showed that the regions of corresponding transitions are from 200.08 to 162.79 nm for singlet states and 261.28 to 173.05 nm for triplet states. Considering the results of CASPT2 calculations as an example, the lowest energy of vertical transition among these allowed transitions derived from ¹B \rightarrow X¹A transition is 194.44 nm with $f=1$.

Table 5 Selected vertical excitation energies (λ) and oscillator strengths (f) of trans-HOOOH

Electronic state	Transition	CASPT2/cc-pvDZ		TD-B3LYP/cc-pvTZ	
		λ/nm	f	λ/nm	f
X ¹ A	$\dots(7a)^2(5b)^2(6b)^2(8a)^0(7b)^0(9a)^0$				
¹ A	7a \rightarrow 8a	169.08	7.44×10^{-4}	170.93	0.0097
² A	6b \rightarrow 7b	165.52	1.99×10^{-5}	177.31	0.0000
¹ B	6b \rightarrow 8a	194.44	1.32×10^{-4}	200.08	0.0014
² B	5b \rightarrow 8a	172.10	6.18×10^{-3}	175.85	0.0147
³ B	6b \rightarrow 9a	152.29	4.93×10^{-2}	162.79	0.0400
¹ A	7a \rightarrow 8a	209.75		219.43	
² A	6b \rightarrow 7b	191.83		203.22	
³ A	5b \rightarrow 7b	162.34		173.05	
¹ B	6b \rightarrow 8a	238.56		261.28	
² B	5b \rightarrow 8a	204.18		220.34	
³ B	7a \rightarrow 7b	167.06		175.20	

Table 6 Selected vertical excitation energies (λ) and oscillator strengths (f) of cis-HOOOH

Electronic state	Transition	CASPT2/cc-pvDZ		TD-B3LYP/cc-pvTZ	
		λ /nm	f	λ /nm	f
X ¹ A	... $(7a)^2(5a)^2(8a)^2$ $(9a)^0(10a)^0(6a)^0$				
1 ¹ A	8a 9a	188.11	1.80×10^{-4}	201.57	0.0013
2 ¹ A	7a 9a	166.96	7.13×10^{-4}	174.94	0.0098
1 ¹ A	5a 9a	176.85	5.55×10^{-3}	179.44	0.0145
2 ¹ A	8a 6a	167.43	2.92×10^{-5}	175.32	0.0023
3 ¹ A	5a 10a	151.00	7.55×10^{-3}	159.05	0.0091
4 ¹ A	7a 6a	128.91	1.80×10^{-4}	139.53	0.0524
1 ³ A	8a 9a	234.10		262.01	
2 ³ A	7a 9a	198.46		215.03	
3 ³ A	5a 6a	159.09		171.63	
4 ³ A	8a 10a	165.00		175.41	
1 ³ A	5a 9a	209.61		223.16	
2 ³ A	8a 6a	193.96		208.80	
3 ³ A	7a 6a	163.30		175.78	
4 ³ A	5a 10a	159.06		167.11	

32×10^{-4} , due to the 6b 8a orbital electronic promotion, whereas the energy of the most intensive transition arising from 3¹B X¹A transition is 152.29 nm with $f=4.93 \times 10^{-2}$, due to the 6b 9a orbital electronic promotion. According to Bielski's experiment^[28], in the region of 210 to 280 nm, the molar extinction coefficient increases with the decrease of absorption wavelength. Based on this trend, it is expected that the most intensive absorption may occur below 210 nm. Hence, the result is reasonable. The triplet state of the lowest excitation energy is 1³B, with the absorption wavelength 238.56 nm. It can be seen from Table 5 that the energies of the singlet states are higher than those of triplet states derived from the same electronic excitation.

The cis-HOOOH isomer has the ground state X¹A with electronic configuration $[\text{core}]^6(3a)^2(2a)^2(4a)^2(3a)^2(5a)^2(6a)^2(4a)^2(7a)^2(5a)^2(8a)^2(9a)^0(10a)^0(6a)^0$. The electronic excitations of a a or a a give rise to the ¹A and ³A states, and the a a or a a electronic excitations produce ¹A and ³A states. Among these electronic excitations, the ¹A X¹A and ¹A X¹A electronic excitations are allowed by the spin and dipole rules. For cis-HOOOH, Table 6 shows the selected 14 low-lying excited states, including 6 singlet states and 8 triplet states. At the CASPT2 level the vertical transition energies of the selected singlet states were predicted to have values between 188.11 and 128.91 nm, whereas the triplet states ranged from 234.10 to 159.06 nm. The computations using the TD-B3LYP

Table 7 Calculated lifetimes (τ) of spin-allowed excited states for trans-HOOOH and cis-HOOOH

trans-	τ /s	cis-	τ /s
1 ¹ A	5.76×10^{-7}	1 ¹ A	2.95×10^{-6}
2 ¹ A	2.07×10^{-5}	2 ¹ A	5.86×10^{-7}
1 ¹ B	4.29×10^{-6}	1 ¹ A	8.46×10^{-8}
2 ¹ B	7.19×10^{-6}	2 ¹ A	1.44×10^{-5}
3 ¹ B	7.06×10^{-9}	3 ¹ A	4.53×10^{-8}
		4 ¹ A	2.95×10^{-6}

method proposed that the regions of corresponding transitions are from 201.57 to 139.53 nm for the singlet states and 262.01 to 167.11 nm for the triplet states, respectively. In the CASPT2 calculations, among the allowed transitions the energy of 1¹A X¹A transition is the lowest, due to the 8a 9a electronic promotion, which is 188.11 nm with $f=1.80 \times 10^{-4}$, whereas 3¹A X¹A transition is the most intensive transition with the vertical transition energy 151.00 nm and $f=7.55 \times 10^{-3}$, due to the 5a 10a electronic promotion. The triplet state of the lowest excitation energy is 1³A, with the absorption wavelength of 234.10 nm. Table 6 shows that, for the singlet and triplet states derived from the same electron excitation, the energy of the former is higher than that of the latter, which is the same as trans-HOOOH. It is noticeable that the vertical transition energies of 3³A X¹A and 4³A X¹A are 159.09 and 159.06 nm, respectively, almost the same, suggesting that the electronic states 3³A and 4³A are nearly degenerated.

2.4 Lifetimes of spin-allowed excited states

The calculated lifetimes (τ) of singlet excited states for cis-HOOOH and trans-HOOOH are shown in Table 7. From Table 7, it can be observed that the predicted lifetimes are in the magnitude of 10^{-5} to 10^{-9} s. Among the selected excited states, 2¹A state in trans-HOOOH and 2¹A state in cis-HOOOH have the longest lifetimes, 2.07×10^{-5} s and 1.44×10^{-5} s, respectively. Photochemical reaction may occur at such excited states and result in different photochemistry products.

3 Conclusions

The equilibrium geometric structures of the trans-HOOOH and cis-HOOOH have been investigated using the DFT, CAS-SCF, and RCCSD theories. The results indicate that the DFT method could describe the geometric structures for the species commonly, economically, and convincingly. The potential energy curve of the isomerization between the trans-HOOOH and cis-HOOOH scanned using the DFT method shows that there are two pathways with regard to the conversion between the two stable isomers. The conversion energy barrier of cis- to trans- is so little that the existence of cis- may be instantaneous, which is

used to explain the puzzle of Suma's experiment. The vertical excitation energies of singlet and triplet states of HOOOH show that the lowest excitation energies in trans-HOOOH are lower than those in cis-isomer; the energies of singlet states are higher than those of triplet states derived from the same electronic excitation. In these allowed excitation states, the state of the longest lifetime is 2^1A with 2.07×10^{-5} s for trans-isomer whereas it is 2^1A with 1.44×10^{-5} s for cis-isomer. Their excitation energies are 165.52 and 167.43 nm, respectively.

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