

Brief Report

Dissociation characteristics of bromoethane
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Abstract Bromoethane dissociates and generates the bromine radical under the radiation from the sun, which destroys the atmospheric ozone layer. So, it is necessary to take effective measures to degrade bromoethane. We use the density function theory (DFT) and calculate the dissociation properties and spectral characteristics of bromoethane under the external electric fields (0–0.028 5 a.u.) at the B3LYP/6-31G+(d,p) level. It is showed that the total energy of the molecule decreases as the external field increases from 0 a.u. to 0.028 5 a.u. along the *Z*-axis. Meanwhile, the energy gap decreases monotonically and the dipole moment increases. It is shown in the potential energy curves that the electric field of 0.030 a.u. is strong enough to break the C—Br bond. The results provide important information for the degradation of bromoethane under external electric fields.

Keywords bromoethane; DFT; degradation; external electric field

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溴乙烷在外电场下的光谱和解离特性

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摘 要 溴乙烷在太阳辐射下解离生成溴自由基, 破坏大气臭氧层, 因此有必要采取措施对其

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进行降解。采用密度泛函理论(DFT)方法,在 B3LYP/6-31G+(d,p) 水平上计算外电场(0~0.028 5 a.u.)下溴乙烷的解离特性和光谱特征。计算结果表明,随着 Z 轴方向的电场强度从 0 a.u. 增加到 0.028 5 a.u., 分子体系总能量逐渐减小。同时在这一过程中,能隙单调变小,偶极矩逐渐增大。计算的溴乙烷解离势能曲线显示,强度为 0.030 a.u. 的外电场将使 C—Br 键断裂。以上这些结果为溴乙烷进行电场降解提供了重要信息。

关键词 溴乙烷;密度泛函理论;降解;外电场;红外光谱

The large family of VOCs contains mainly hydrocarbons, aldehydes, ketones, etc. These compounds have different contribution rates in emission source and have different reactivities in the atmosphere^[1]. While the halogenated hydrocarbon compounds enter the atmosphere, the photochemical reactions take place under the irradiation of sunlight. The halogen atoms produced by photolysis catalyze the decomposition of ozone, posing a great threat to the life on the earth^[2]. Therefore, the degradation of halogenated hydrocarbon compounds has attracted widespread attention. As a kind of halogenated hydrocarbons, bromoethane dissociates under the radiation of sunlight and generates the bromine radical, which severely damages the atmospheric ozone layer.

Several methods have been applied to dissociate the bromoethane, including microbial degradation, photocatalytic degradation, ultrasonic degradation, and electrochemical degradation, and they have different advantages and disadvantages in their applications. The degradation of pollutants under external electric fields is a promising new method^[3-4] and a hot spot in current researches^[5-7]. The physical properties and dissociation characteristics of bromoethane under external electric fields have not yet been studied.

In this paper, the structure and the spectral and dissociation properties of bromoethane under external field have been calculated by using the density functional theory. The geometric structure, bond lengths, dipole moments, vibration frequencies, and other physical parameters are obtained. Meanwhile the potential energy curves under different external electric fields are obtained by scanning the single point energy along the C—Br bond.

1 Theory and computational method

The Hamiltonian of the molecule under external

electric field is

$$H = H_0 + H_{\text{int}}, \quad (1)$$

where H_0 is the Hamiltonian of the molecule without the external field, and H_{int} is the interaction Hamiltonian between the external electric field and the molecular system.

Using the dipole approximation, the interaction Hamiltonian can be expressed as

$$H_{\text{int}} = -\boldsymbol{\mu} \cdot \boldsymbol{F}, \quad (2)$$

where $\boldsymbol{\mu}$ is the dipole moment and \boldsymbol{F} represents the external electric field^[8] (a. u. stands for atomic units, 1 a.u. = $5.142\,25 \times 10^{11} \text{ V} \cdot \text{m}^{-1}$).

Gaussian 09^[9] is used to carry out the theoretical calculations. First, the structure of bromoethane as shown in Fig.1, has been optimized with different methods. By comparing the calculated data in Table 1 with the experimental values, we find that the calculation results at the B3LYP/6-31G+(d,p) level are in the best agreement with the experimental values. So, the B3LYP/6-31G+(d,p) level is used in further calculations for the total energy, dipole moment, frontier orbital levels, IR spectra, and potential energy curves.

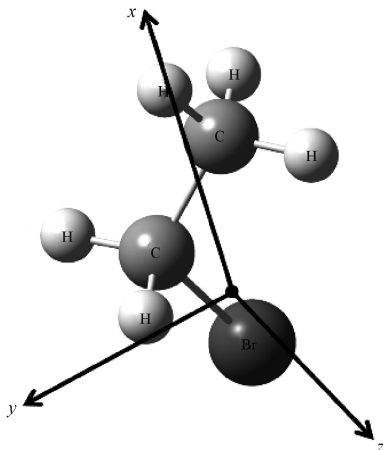


Fig.1 The optimized geometry of the ground-state bromoethane

Table 1 The ground-state structure parameters of bromoethane obtained using different optimization methods

Method	$R_{\text{C-Br}}/\text{\AA}$	$\angle \text{HCH}/(^{\circ})$	$\angle \text{HCB}/(^{\circ})$
B3LYP/6-31G	2.033	110.5	104.4
B3LYP/STO-3 * G	1.944	107.9	108.1
B3LYP/3-21G	2.014	110.1	105.3
B3LYP/6-311G+(d,p)	1.988	109.5	104.9
B3LYP/6-31G+(d,p)	1.984	109.5	104.9
HF/6-31G	2.015	110.6	104.4
BPV86/6-31G	2.038	110.4	104.3
HF/3-21G	2.006	110.2	105.2
experimental value ^[10-11]	1.980	109.9	105.4

2 Results and discussions

2.1 Effect of external electric fields on bond length, total energy and dipole moment

When different electric fields are applied in the x -axis or y -axis direction, the degradation effect is less important than in the z -axis direction. Thus, in this study, bromoethane is exposed under different external electric fields along the z -axis.

The calculated results for the bond length (C—Br), total energy, and electric dipole moment under different external electric fields (0–0.028 5 a.u.) are shown in Fig. 2.

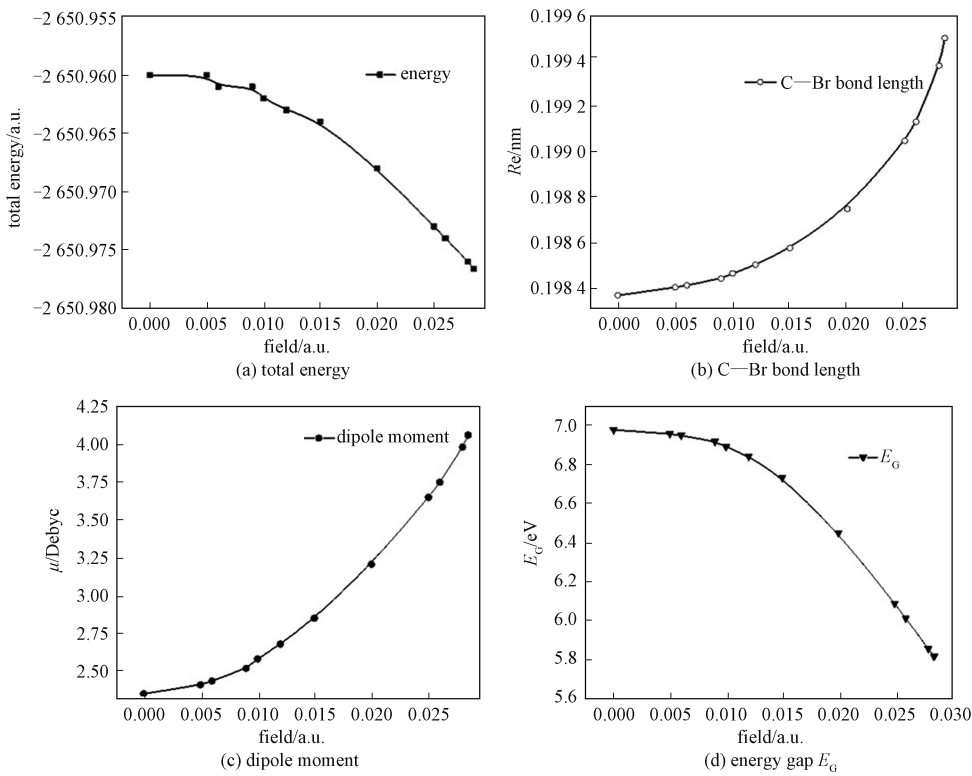


Fig.2 Calculated physical characteristics of bromoethane under different electric fields

As shown in Fig.2, the total energy decreases when the external electric field gradually increases, and the C—Br bond becomes longer in this process, which indicates that the C—Br bond is apt to break. At the same time, the dipole moment increases sharply, which means the molecule is splitting up.

2.2 Effects of external electric fields on molecular orbital energy level distribution

The total energies, the lowest unoccupied molecule orbital (LUMO) energy E_L , the highest

occupied molecule orbital (HOMO) energy E_H , and the energy gap E_H of bromoethane under different external fields were also obtained. The energy gap E_G is given as

$$E_G = (E_L - E_H) \times 27.2 \text{ eV}. \tag{3}$$

It shows that the energy gap decreases monotonously while the external field increases from 0 to 0.028 5 a.u., as shown in Fig. 2 (d). This result indicates that the bromoethane molecule is more easily excited to a higher state.

2.3 Effects of external electric fields on IR spectrum

The infrared spectra of bromoethane under different external electric fields are also obtained. Bromoethane has eighteen different vibration modes. The calculated spectrum of the C—Br str (the calculated frequency of the C—Br str is 551 cm^{-1} under zero external fields, which is in good agreement with the experimental values^[12-13]) under different external fields is shown in Fig. 3. It is seen that the frequency of the C—Br str shows red shift while the external field increases.

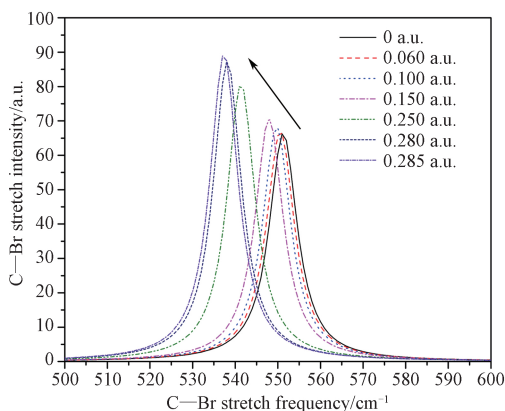


Fig.3 The change of the C—Br stretch spectrum with the increase of external electric field

2.4 Effects of external electric fields on molecular dissociation

By scanning single point energies along the C—Br distance, the potential energy curves under different external electric fields are obtained at the B3LYP/6-31+G(d,p) level (see Fig. 4). To smooth the curves, the results are fitted by the Morse potential model^[15]

$$V(\gamma) = D_e [1 - e^{-a(\gamma - R_e)}]^2, \quad (4)$$

where D_e is the dissociation energy, a is the Morse parameter, γ is the internuclear distance, and R_e is the equilibrium distance.

It is seen that the molecule stays in a stable point without external fields. However, the barrier of the dissociation of bromoethane drops significantly while the external field increases. When the external electric field reaches to 0.030 a.u. , the barrier of the dissociation of bromoethane disappears completely, which demonstrates that the C—Br bond

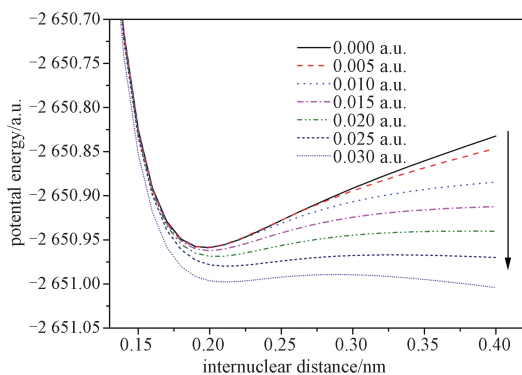


Fig.4 The dissociation PESS (potential energy surfaces) along the C—Br bond of bromoethane under external electric fields

breaks and bromoethane is degraded under 0.030 a.u. . The results provide important information for studying the degradation mechanism of bromoethane under different external electric fields.

3 Conclusions

In the present work, the spectral and dissociation properties of bromoethane under external electric fields ($0-0.0285\text{ a.u.}$) are calculated. The density functional theory at the B3LYP/6-31G+(d,p) level is employed.

It is seen that the structure properties and the spectral and dissociation characteristics of bromoethane are quite interesting under different external electric fields.

The results show that the total energy decreases as the external electric field gradually increases. The C—Br bond becomes longer in this process, which implies that the C—Br bond is apt to break. At the same time, the dipole moment increases sharply, which means the molecule is splitting up. Meanwhile, the energy gap decreases monotonously and the C—Br str frequency shows red shift while the external field increases.

It is shown that the dissociation barrier of bromoethane drops significantly while the external field increases. When the external electric field reaches to 0.030 a.u. , the dissociation barrier of bromoethane disappears completely, which demonstrates that the C—Br bond breaks and bromoethane is degraded under 0.030 a.u. . The results provide important information for studying the degradation of

bromoethane under different external electric fields.

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