

文章编号:2095-6134(2018)06-0839-06

Brief Report

Dissociation and physical properties of methyl iodide in external electric field*

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(Received 20 July 2017; Revised 12 September 2017)

Zhang X Y, Liu Y Z, Ma X Y, et al. Dissociation and physical properties of methyl iodide in external electric field [J]. Journal of University of Chinese Academy of Sciences, 2018, 35(6):839-844.

Abstract As a kind of toxic methylation reagent and disinfectant, methyl iodide (CH_3I) is widely used. It is important to study the basic physical properties of methyl iodide and to use effective measures to degrade it. The ground states of methyl iodide in different electric fields from 0 to 0.04 a. u. (atomic unit) are optimized using the B3LYP calculation with the LANL2DZ basis set. Optimized parameters, total energies, bond lengths, dipole moments, the highest occupied molecular orbital energies, the lowest unoccupied molecular orbital energies, energy gaps, infrared spectra, and dissociation potential energy surface (PES) are obtained. The obtained results show that when the external electric field gradually increases from 0 to 0.04 a. u. along the molecular axis Z (the C-I bond direction), the total energy decreases while the dipole moment increases. The C-I and C-H bond lengths increase gradually. The energy gap first increases and then decreases with the external electric field. Further studies show that when the external electric field increases from 0 to 0.04 a. u., the dissociation PES along the C-I bond becomes unbound with the potential energy barrier disappearing. The external electric field of 0.04 a. u. is sufficient to induce the degradation of methyl iodide with the C-I bond breaking. This work provides an important support for the degradation of methyl iodide in the external electric field.

Keywords methyl iodide; external electric field; degradation; infrared spectrum

CLC number: O561; O433 **Document code:** A **doi:**10.7523/j.issn.2095-6134.2018.06.016

碘甲烷在外电场下的光谱和解离特性

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* Supported by Natural Science Foundation of the Higher Education Institutions of Jiangsu Province(18KJA140002), Six Talent Peaks Project in Jiangsu Province(2015-JNHB-011), College Students Practice Innovative Training Program of Nuist(201710300058Y), and Undergraduate Training Program for Innovation and Entrepreneurship(201710762008, 201710762055)

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摘要 碘甲烷是一种有毒的甲基化试剂和土壤消毒剂, 应用十分广泛, 研究其基本的物理性质和使其降解的有效措施很有必要。使用密度泛函理论(density functional theory, DFT), 在 B3LYP/LANL2DZ 水平上研究在外电场(0 ~ 0.04 a. u.) 作用下碘甲烷分子的解离特性以及多种物理性质。计算结果表明, 在 C—I 键连线 Z 方向上, 外电场从 0 逐渐增加到 0.04 a. u. 时, 分子体系能量逐渐减小, 偶极矩单调增大。HOMO-LUMO 能隙 E_G 却呈现先增大后减小的变化趋势, C—I 和 C—H 键键长逐渐增大, 更加易于裂解。在外电场逐渐增强时, 解离特性表现为: CH_3I 分子的 C—I 键方向扫描得到的势能曲线的束缚状态逐渐消失, 势垒逐渐变小最后消失。计算发现, 强度为 0.04 a. u. 的外电场足以使 CH_3I 分子发生 C—I 键断裂而降解。该结果为保护环境和对碘甲烷进行电场降解提供理论依据。

关键词 碘甲烷; 外电场; 降解; 红外光谱

Methyl iodide is used primarily in the production of pharmaceutical intermediates and the organic synthesis for methylation reagents. It was considered as an alternative to soil disinfectants in the 1998 and 2002 Methyl Bromide Technical Options Committees Assessment. Methyl iodide is also widely used as a soil disinfectant to replace methyl bromide that severely destroyed the environment (prohibited by the Montreal Protocol Copenhagen Amendment). Methanol is toxic, corrosive, and carcinogenic, and methyl iodide naturally decomposes more slowly. At the same time, methyl iodide is widely used as a soil disinfectant but the possibility of entering the groundwater is very high. Inhalation of a large amount of methyl iodide inhibits the central nervous system and exerts strong stimulating effects on the skin and mucous membranes. Methyl iodine is easily decomposed by heat and produces toxic iodide fumes. It can be absorbed through the respiratory tract, skin, and digestive tract and causes poisoning. Domestic and foreign reports described how CH_3I harmed people and animals and some poisoning incidents caused by CH_3I ^[1,2].

In recent years, the degradation kinetics of halogenated compounds containing CH_3I has received unprecedented attention^[3-7]. Molecules in the external electric field will have a series of physical and chemical changes. The characteristic of molecules in external electric field has become an important method for studying molecular properties. This method has been successfully applied to a

number of fields to study the properties of molecules^[8-12]. Applying a strong electric field to a molecule to break off the chemical bond is an effective method for the degradation of the molecule. However, there is no reported study on the dissociation of the CH_3I molecule in the external electric field.

The molecular total energy, molecular dipole moment, molecular energy gap, molecular spectrum, and dissociation properties of the CH_3I molecule in external electric field (0 ~ 0.04 a. u. (atomic unit)) were studied using density functional theory at the B3LYP/LANL2DZ level. The Gaussian 09^[13] software was used. The result provides important theoretical support for the degradation of CH_3I .

1 Theoretical method

The Hamiltonian of the radiation process is given as

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

Where H_0 is the complete molecular Hamiltonian, H_{int} is the interaction Hamiltonian between the electron field and the molecule. Under the dipole approximation, H_{int} is given in a. u. as

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

where \boldsymbol{F} is the radiation field, $\boldsymbol{\mu}$ is the dipole moment, and 1 a. u. (atomic unit) = $5.142\ 25 \times 10^{11}$ V/m.

Based on the model proposed by Grozema et al.^[14-15], excitation energy under the action of field E_{exc} , electric field strength F with the variation

amounts $\Delta\mu$, $\Delta\alpha$ of the electric dipole moment and the polarization rate satisfies the relational expression

$$E_{\text{exc}}(F) = E_{\text{exc}}(0) - \Delta\mu \cdot F - 1/2 \cdot \Delta\alpha \cdot F^2. \quad (3)$$

Based on the geometric structure of the CH_3I molecule without electric field, we use the B3LYP/LANL2DZ method of density functional theory to optimize the ground state structure and study the molecular total energy, molecular dipole moment, molecular energy gap, molecular spectrum, and dissociation properties of the CH_3I molecule.

2 Results and discussion

2.1 Molecular stable structure without external electric field

Theoretical calculations show that the CH_3I molecule has the C_{3v} symmetry. In the present work, we optimize the structure of CH_3I with different methods. The experimental data^[16] and optimization data are listed in Table 1. By comparing the calculated data with the experimental data, we can see that the structure parameters (the bond lengths and the bond angle) calculated at the B3LYP/LANL2DZ level are the closest to the experimental data. Therefore, the dissociation and spectral characteristics of CH_3I in the external electric field are calculated at the B3LYP/LANL2DZ level. The calculated stable structure is shown in Fig. 1. The X -axis, Y -axis, and Z -axis are defined according to the Dicker coordinate system, and the Z -axis is along the the C-I bond.

Table 1 Optimized parameters of the structure of CH_3I at different levels, together with the experimental data

Method	$R_{\text{C-I}}/\text{nm}$	$R_{\text{C-H}}/\text{nm}$	$\angle\text{H-C-H}/(^{\circ})$
BPV86/LANL2MB	0.225 2	0.110 4	112.575
BPV86/LANL2DZ	0.220 0	0.109 8	111.480
B3LYP/LANL2MB	0.224 0	0.109 7	112.304
B3LYP/LANL2DZ	0.219 3	0.109 0	111.403
exp. ^[16]	0.213 9	0.111 0	111.400

2.2 Effect of external electric fields on bond length and total energy

The CH_3I molecule was optimized and calculated at the B3LYP/LANL2DZ level when

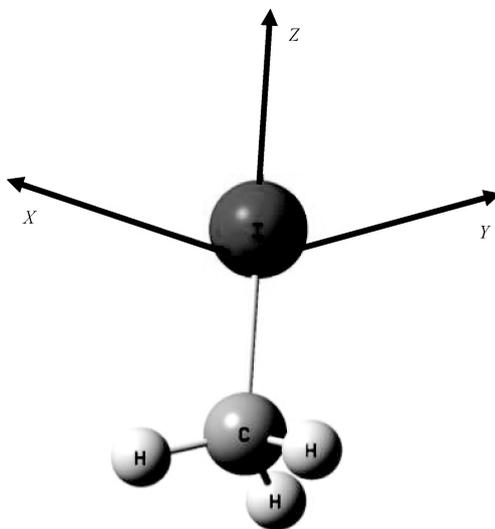


Fig. 1 Optimized geometry of the ground-state CH_3I

different electric fields ($0 \sim 0.04$ a. u.) were applied in the Z -axis (along the C—I bond). The stable structures of methyl iodide at different field strengths were obtained. The calculated bond length, and dipole moments of the CH_3I molecule are given in Table 2. It can be seen in Table 2 that the total energy decreases gradually with the increase of the external electric field ($0 \sim 0.04$ a. u.). The C—I and C—H bond lengths increase gradually with the increase of the electric field ($0 \sim 0.04$ a. u.) in the Z -axis. The results show that the chemical bond length increases gradually with the external electric field and the molecule becomes more and more prone to dissociation. With the increase of the external field from 0 to 0.04 a. u. along the Z -axis, the dipole moment increases.

2.3 Effect of external electric fields on the molecular orbital energies

It is well known that many properties of a molecule are determined by the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The HOMO and LUMO energies of the CH_3I molecule are obtained at the B3LYP /LANL2DZ level. The HOMO energy E_H , the LUMO energy E_L , and the energy gap E_G are shown in Table 3. E_G is given as

$$E_G = (E_L - E_H) \times 27.2 \text{ eV}. \quad (4)$$

Table 2 Calculated molecular total energies, bond distances (C—I and C—H), and dipole moments of CH₃I in different external electric fields

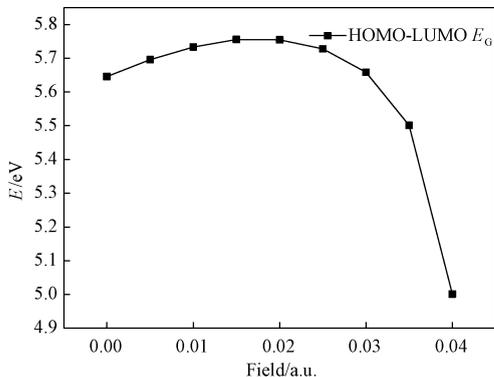
<i>F</i> /a. u.	0	0.005	0.010	0.015	0.020	0.025	0.030	0.035	0.040
<i>E</i> /Hartree	-49.29	-49.294	-49.3	-49.306	-49.314	-49.323	-49.334	-49.347	-49.363
Re(C—I)/nm	0.219 3	0.220 1	0.221 4	0.223 0	0.225 4	0.228 8	0.233 7	0.241 9	0.262 3
Re(C—H)/nm	0.109 0	0.108 9	0.108 8	0.108 8	0.108 7	0.108 7	0.108 8	0.108 8	0.108 9
μ /Debye	1.856 2	2.490 0	3.138 5	3.810 8	4.528 0	5.310 4	6.209 4	7.349 4	9.359 4

It can be seen in Fig. 2 that with the increase of electric field the HOMO-LUMO energy gap E_G gradually increases first and then decreases sharply. It is shown that at the beginning the methyl iodide molecule is hard to be excited to the excited state.

When the electric field strength is greater than 0.02 a. u., molecule are getting more and more easily excited. It is also shown that the ability of methyl iodide to participate in chemical reactions weakens and then becomes strong.

Table 3 Calculated LUMO energy E_L , HOMO energy E_H , and HOMO-LUMO energy gap E_G for CH₃I in different external fields

<i>F</i> /a. u.	0	0.005	0.010	0.015	0.020	0.025	0.030	0.035	0.040
E_L /Hartree	-0.040 7	-0.037 7	-0.035 5	-0.033 8	-0.033 1	-0.033 5	-0.035 5	-0.040 7	-0.058 0
E_H /Hartree	-0.248 2	-0.247 1	-0.246 2	-0.245 4	-0.244 6	-0.244 0	-0.243 5	-0.243 0	-0.241 9
E_G /Hartree	0.207 5	0.209 4	0.210 7	0.211 5	0.211 5	0.210 5	0.208 0	0.202 2	0.183 8
E_G /eV	5.645 80	5.695 99	5.733 11	5.755 32	5.754 28	5.727 88	5.658 35	5.500 99	5.000 95

**Fig. 2** Variations in the HOMO-LUMO energy gap of CH₃I in external fields

2.4 Effect of external electric fields on IR spectra

The IR spectra of CH₃I were calculated at the B3LYP/LANL 2DZ level. The calculated IR spectra mainly correspond to six kinds of vibration peaks, as shown in Table 4. Frequency of 481.67 cm⁻¹ is attributed to the CI str vibration, frequency of 890.77 cm⁻¹ is attributed to the CH₃ rock vibration, frequency of 1 282.34 cm⁻¹ is attributed to the CH₃ s-deform vibration, frequency of 1 431.46 cm⁻¹ is attributed to the CH₃ s-str vibration, frequency of

2 981.21 cm⁻¹ is attributed to the CH₃ s-str vibration, and frequency of 3 110.33 cm⁻¹ is attributed to the CH₃ d-str vibration. As shown in Table 4, the calculated symmetries and vibration frequencies are in agreement with the experimental results^[17], with errors of no more than 10%.

Table 4 Calculated IR parameters for CH₃I including vibrational frequencies and symmetries, together with the experimental data

vibration mode	symmetry	vibration frequency/cm ⁻¹	
		calculated values	exp. ^[17]
CI str	a ₁	481.67	533
CH ₃ rock	e	890.77	882
CH ₃ s-deform	a ₁	1 282.33	1 252
CH ₃ d-deform	e	1 431.45	1 436
CH ₃ s-str	a ₁	2 981.21	2 933
CH ₃ d-str	e	3 110.33	3 060

In Table 4, str denotes the stretching vibration, and deform denotes the bending vibration. The IR spectra of the CH₃I molecule under different external electric fields were calculated by applying different intensity of electric fields (0 ~ 0.04 a. u.) in the direction of the C—I bond. The external electric

field has significant influences on the IR spectra of the CH_3I molecule.

2.5 Effect of external electric field on molecular potential energy curve

Without external electric field, we carried out energy scanning for CH_3I along the C—I bond direction at the B3LYP /LANL2DZ level to obtain the potential energy curve. The same method was used to calculate the potential energy curves along the C—I bond direction with different electric fields along the Z-axis (the C—I bond direction). The potential energy curves without and with the field are plotted in Fig. 3. It is shown that the potential energy curves of the CH_3I molecule are gradually repulsive in the external electric fields ($0 \sim 0.04$ a. u.). When the external electric field is 0.04 a. u., the potential energy curve of CH_3I changes from “bound” to “repulsive”. The CH_3I molecule will be degraded at the strength of 0.04 a. u.. The electrochemical degradation of the CH_3I molecule will be important for the protection of the environment.

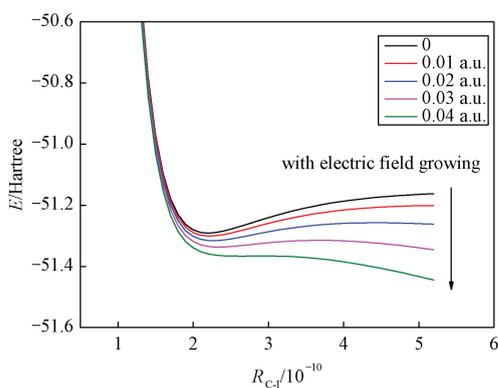


Fig. 3 Variation of the potential energy curve along the C—I bond of CH_3I in external field

3 Conclusions

In the present work, the dissociation characteristics and spectral characteristics of CH_3I in external electric field were calculated using the principle of density functional theory. It is found that the results obtained at the B3LYP/LANL2DZ level are the closest to the experimental data. Therefore, the B3LYP/LANL2DZ method was used

to calculate the configuration, IR spectrum, and dissociation potential energy curve of CH_3I in different electric fields. When a series of external electric fields are applied along the Z-axis (the C—I bond), the energy of the molecular system gradually decreases. The dipole moment decreases, indicating that the polarity is constantly increasing. HOMO -LUMO energy gap E_G increases first and then decreases sharply, indicating that at the beginning, the methyl iodide molecule is hard to be excited into the excited state. When the electric field strength is greater than 0.02 a. u., the excitation of the molecule to the excited state will become more and more simple. It is also shown that the ability of methyl iodide to participate in chemical reactions weakens and then becomes strong. The C—I and C—H bond lengths monotonously increase. The external electric field also has effects on the positions and intensities of the IR spectra of the CH_3I molecule. The potential energy curve of the CH_3I molecule along the C—I bond changes gradually from “bound” to “repulsive”. It is found that the electric field of 0.04 a. u. is sufficient to cause the C—I bond breakage of CH_3I , which provides an important scientific basis for the degradation of CH_3I .

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