Study on The Physical Properties of The Cis and Trans Isomers of Methyl Nitrite under The External Electric Field

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Abstract. This article uses the optimization method of B3LYP and 6-31G (d, p) basis set to calculate the stable ground state configurations of two isomers of methyl nitrite, cis and trans, respectively.With external electric fields of -0.03 ~ 0.03 a.u. applied, the structures, Raman spectra, and potential energy curves of cis and trans subjected to varying external electric fields were obtained. Computational results demonstrate that subjected to an external electric field, the bond length, dipole moment, total energy, and charge of the cis and trans forms all change, and the changes in both are the same; When the external electric field increases to 0.015 a.u., HOMO-LUMO gap of the cis significantly decrease,,making it easier for it to participate in chemical reactions. The Raman spectra of cis and trans are significantly different, but the chemical bonds and vibrational modes corresponding to each Raman peak remain unchanged; The potential energy curve indicates that the external electric field increases along the O atom pointing towards the N atom, which can promote degradation of methyl nitrite in water.

Keywords: Methyl Nitrite, Isomer, DFT, External Electric Field, Raman Spectroscopy.

1. Introduction

Methyl nitrite is an important photochemical research model compound with many unique chemical and physical properties. Methyl nitrite has an easy-to-distinguish resonance peak in the near ultraviolet band, and the ultraviolet photolysis of this substance can be used to study the solvent effect [1-2]. Methyl nitrite is also widely used in the field of chemical synthesis, such as preparing industrial raw materials such as dimethyl oxalate and dimethyl carbonate, synthesizing explosives and preparing vasodilators [3-4]. Methyl nitrite is also an excellent fuel additive and stabilizer of unsaturated organic compounds [5]. Concurrently, the chemical and physical characteristics of methyl nitrite have recently attracted the attention of photochemical physicists and industrial production departments.

For a long time, the properties of methyl nitrite have been concerned by all walks of life, but the research focuses on photolysis, pyrolysis and other processes, and the research methods rarely involve the application of external electric field [6]. This paper attempts to further broaden the understanding of the material structure of methyl nitrite by studying the characteristics of methyl nitrite in the external electric field. According to the data, there are two different isomers of methyl nitrite: cis and trans [7-8]. By comparing the optimization results of cis- and trans-isomers obtained from different computational methods with experimental values, the B3LYP/6-31G(d,p) basis set method, which exhibited the smallest relative error, was selected as the optimal approach. Ground-state stable configurations, energies, molecular dipole moments, and orbital energy level distributions were calculated both in the absence of external electric fields and under various applied electric fields. Subsequently, the Raman spectrum was derived, and a detailed analysis was performed to identify the vibrational modes corresponding to each Raman peak [9-10]. This systematic investigation employed density functional theory to elucidate structure-property relationships under electrostatic modulation. In addition, the potential energy curve is drawn, which shows that the degradation of methyl nitrite can be promoted by applying an external electric field in a specific direction.

2. Calculation method

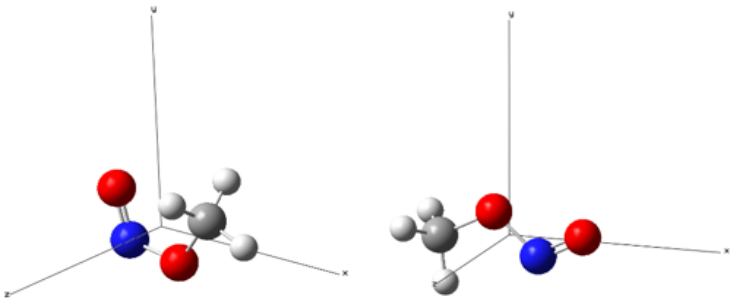

Figure 1. Molecular structures of cis (left) and trans (right).

The research shows that there are two isomers methyl nitrite: cis and trans, and the optimization results of their ground state structures are shown in Figure 1. In the following, the positive direction of the external electric field is cis and trans respectively, wherein the cis positive direction of the X axis points to the O atom along the N-O bond, and the trans positive direction of the X axis points to the N atom along the O atom, so the positive directions of the external electric field applied by the two are actually opposite.

In this paper, B3LYP/6-31G(d,p) basis set is used, in which B3LYP is one of the most widely used exchange-correlation functionals. The theoretical basis of DFT is Hohenberg-Kohn theorem and Kohn-Sham equation.

Hohenberg-Kohn theorem can be expressed as follows: the ground state energy of the identical Fermi subsystem without spin is the only functional of the particle number density function $\rho(r)$, and the energy functional $E[\rho]$ takes the minimum value of the particle number density $\rho(r)$ and is equal to the ground state energy on the premise of the same particle number.

Kohn-Sham equation is expressed as:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\mathbf{r})\right)\psi_i(\mathbf{r}) = E_i\psi_i(\mathbf{r}) \tag{1}$$

Effective potential decomposition:

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{XC}}(\mathbf{r}) \tag{2}$$

Here, $V_{\text{ext}}(\mathbf{r})$ is the potential energy of electrons under the applied external electric field, $V_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$ is the interaction energy between electrons, and the related potential energy term is expressed as $V_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})}$.

3. Results and discussion

3.1. Stable configuration of methyl nitrite in the ground state without external electric field

In this paper, different calculation methods and basis sets are used to calculate the equilibrium spacing R_e and ground state energy E of cis-N-O bonds, and the obtained equilibrium spacing R_e is compared with the experimental value. The method B3LYP with 6-31G(d,p) basis sets, which has the smallest deviation from the experimental value, is selected as the calculation method of subsequent parameters. The calculation results are shown in Table 1(+stands for (d, p): D polarization function is added to heavy atoms, and P polarization function is added to hydrogen atoms.) Similarly, the equilibrium spacing R_e and ground state energy E of trans-N-O bond are calculated, and the obtained equilibrium spacing R_e is compared with the experimental value, and the method B3LYP with the smallest deviation from the experimental value plus 6-31G(d,p) basis set is selected as the

calculation method of subsequent parameters, and the calculation results are shown in Table 2(+stands for (d,p): D polarization function is added to heavy atoms and P polarization function is added to hydrogen atoms.)

Table 1. Ground state of cis obtained by different calculation methods.

	B3PW91/6-311+	B3PW91/6-31+	B3LYP/6-311+	B3LYP/6-31+	Exp.
R_e / $\mathring{A}$	1.38539	1.38247	1.40091	1.39653	1.394
E / hartree	-244.986209	-244.927010	-245.085233	-245.023738	

Table 2. Ground state of trans obtained by different calculation methods.

	B3PW91/6-311+	B3PW91/6-31+	B3LYP/6-311+	B3LYP/6-31+	Exp.
R_e / $\mathring{A}$	1.40874	1.40329	1.42503	1.41759	1.415
E / hartree	-244.985727	-244.925750	-245.085110	-245.022844	

3.2. Stable configuration of methyl nitrite in the ground state driven by the electric field

3.2.1. Changes of N-O bond length, energy and molecular dipole moment of ground state with external electric field.

The external electric fields of ± 0.030, ± 0.025, ± 0.020, ± 0.015, ± 0.010 and ± 0.005 a.u. were applied along the positive X-axis of cis and trans respectively, and the N-O bond length R_e, molecular dipole moment μ and energy E of cis and trans were obtained. Figure 2-4 shows the relationship between N-O bond length R_e, molecular dipole moment μ and energy E with external electric field for cis and trans respectively.

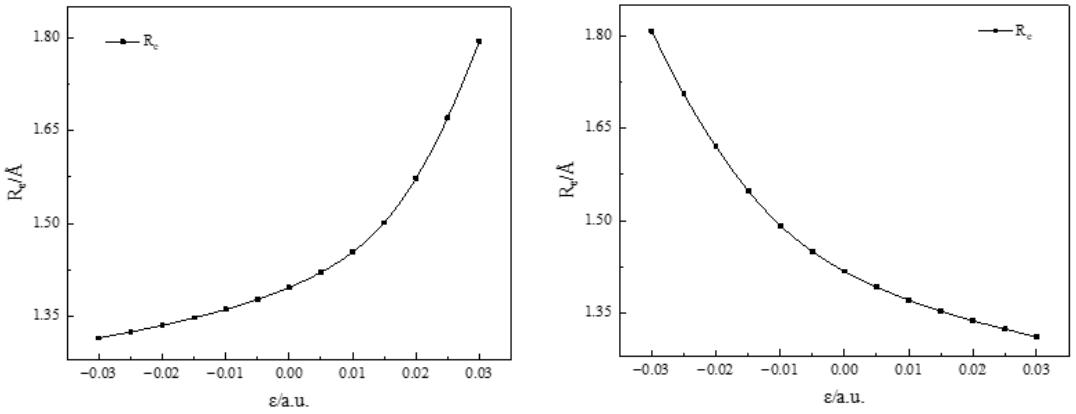

Figure 2. The dependence of the N-O bond lengths in cis (left) and trans (right) configurations under the external electric field.

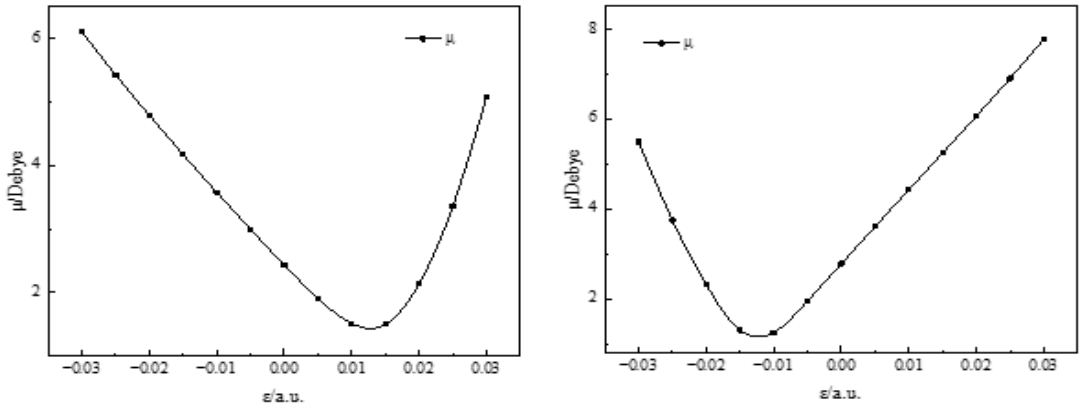

Figure 3. The dependence of molecular dipole moment in cis (left) and trans (right) configurations under the external electric field.

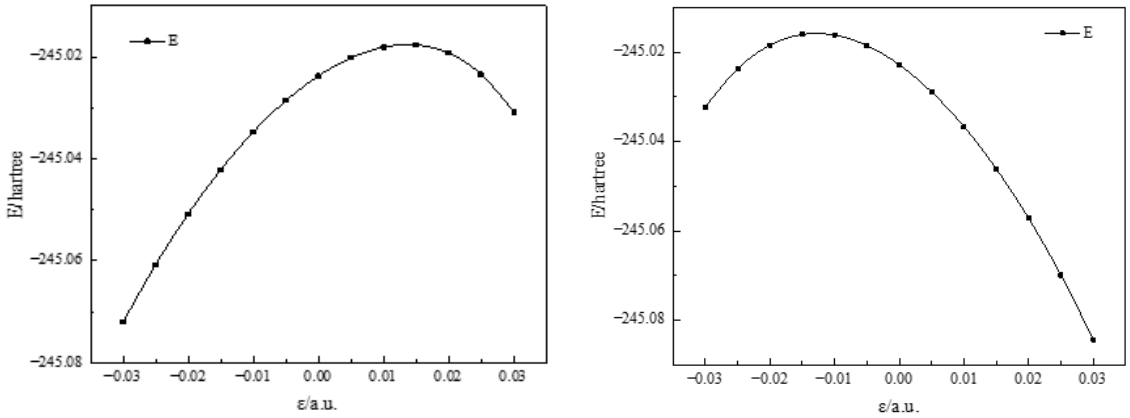

Figure 4. The dependence of energy in cis (left) and trans (right) configurations under the external electric field.

Considering that the positive directions of external electric fields applied to cis and trans in this paper are opposite, when the external electric field increases in the same direction, the changes of N-O bond length, electric dipole moment and energy with the external electric field are just the same. Take cis as an example to analyze the influence of external electric field on various parameters.

Investigate the effects of external electric field on the length of N-O bond (Figure 2): With progressive augmentation of the applied field, the electron cloud of N-O bond is further biased towards O, weakening the strength of N-O bond, leading to the increase of bond length, and the degree of this deviation is gradually accelerated, so the tangent slope of each point is gradually increased.

Investigate the effects of external electric field on electric dipole moment (Figure 3): The total electric dipole moment is the result of superposition of permanent dipole moment and induced dipole moment. Since the electronegativity of O is higher than that of N, the direction of permanent dipole moment points to N atom along O atom, which is the same as the positive direction of external electric field. When the external electric field is -0.03□ 0 a.u., the induced dipole moment is in the same direction as the external electric field, that is, in the same direction as the permanent dipole moment, so the induced dipole moment decreases gradually, and the total polar moment decreases gradually. When the external electric field is 0□ 0.015a.u., the induced dipole moment is opposite to the external electric field, and the induced dipole moment gradually increases and the total polar moment gradually decreases. When the external electric field is 0. 015□ 0.03a.u., the induced dipole moment is in the same direction as the external electric field, and the induced dipole moment gradually increases, and the total polar moment gradually increases.

Investigate the effects of external electric field on energy (Figure 4): With the enhancement of the applied field, the electric dipole moment of N-O bond first decreases and then increases, so the energy first increases and then decreases [11].

3.2.2. Variation of orbital energy level distribution of methyl nitrite in ground state with applied electric field

Similarly, the external electric fields of ± 0.030, ± 0.025, ± 0.020, ± 0.015, ± 0.010, ± 0.005 and 0 a.u were applied along the positive direction of the X axis of cis and trans respectively, and cis and trans were obtained. The bandgap energy is computed employing the expression:

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

Herein, E_L , E_H and E_G represent the energy of the lowest unoccupied molecular orbital (LUMO), the highest occupied molecular orbital (HOMO), and the energy gap, respectively. Electrons will occupy the orbit with lower energy first. The lower E_L is, the easier it is for electrons to enter the empty orbit, and the stronger the ability of molecules to get electrons. The higher E_H is, the easier it is for electrons to be excited to empty orbits, and the stronger the ability of molecules to lose electrons; The larger E_G is, the more energy is needed for the transition from E_H to E_L , and the more stable the

molecule is [12]. Draw the curves of the relationship between E_H and E_L of cis-and trans-methyl nitrite and the external electric field as shown in Figure 5, and the curves of the relationship between E_G and the external electric field as shown in Figure 6.

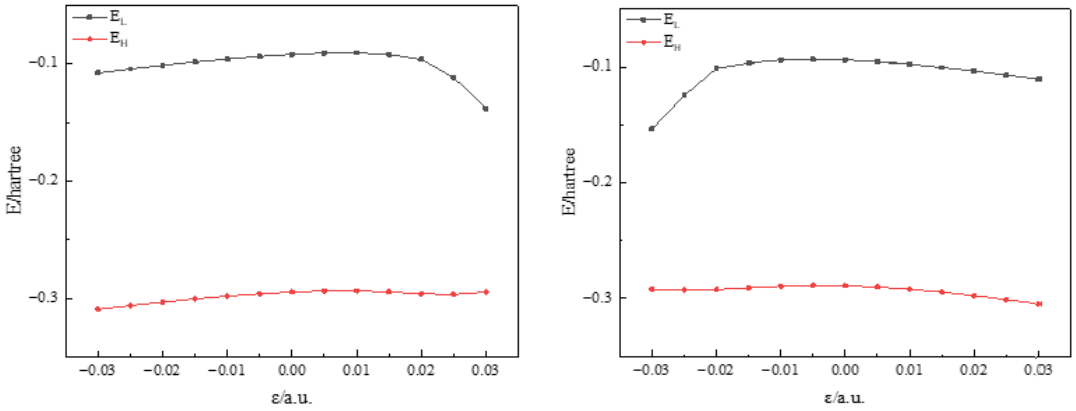

Figure 5. The dependence of E_H and E_L in cis (left) and trans (right) configurations under the external electric field.

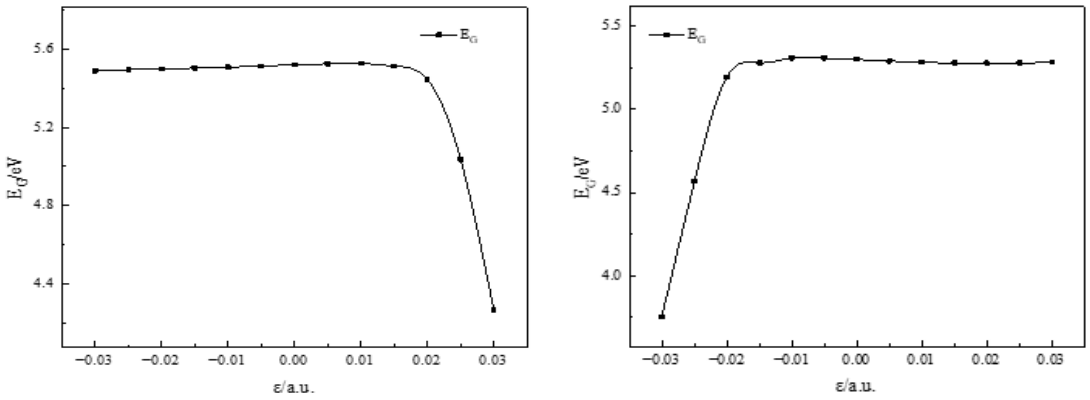

Figure 6. The dependence of E_G in cis (left) and trans (right) configurations under the external electric field.

Under co-directional enhancement of the applied field, the field-dependent behaviors of E_L , E_H and E_G exhibit no significant difference between cis and trans isomers. Take cis as an example to analyze the influence of external electric field on various parameters.

As illustrated in Figure 5, when the electric field increases, E_L exhibits an initial slow increase, followed by a sharp decrease within the range of 0.015 to 0.030 a.u. which may be related to the rearrangement of electron clouds or the change of molecular geometry caused by the strong electric field; When the electric field increases, E_H first increases slowly and then remains basically unchanged. As can be seen from Figure 6, with the increase of the external field, E_G initially increases slowly with the applied electric field, subsequently decreases gradually within the range of 0.010 to 0.015 a.u., and finally undergoes a sharp drop in the 0.015 to 0.030 a.u.interval, which shows that the enhancement of the external electric field effectively reduces the energy gap of cis molecules, which reduces the stability of molecules.

3.2.3. Variation of Raman spectra of methyl nitrite in ground state with external electric field

According to the above method, different external electric fields are added, and the Raman spectra of cis subjected to varying applied fields are obtained by frequency analysis, as illustrated in Figure7.

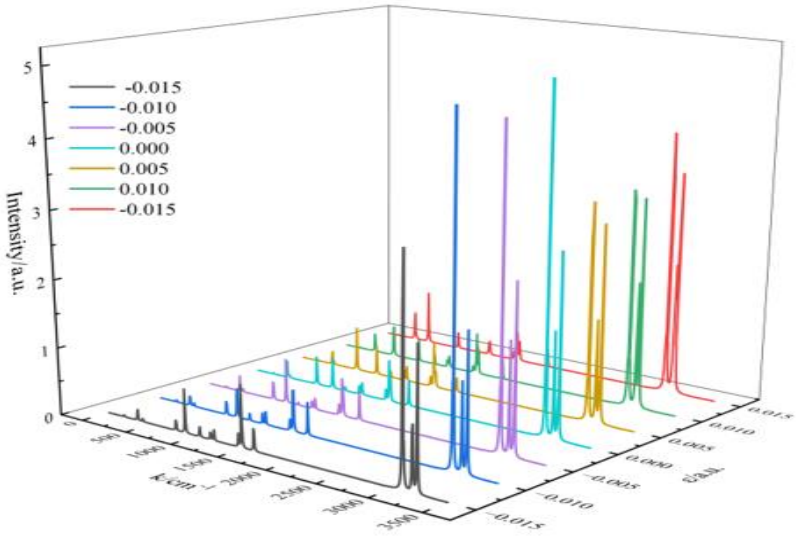

Figure 7. Raman spectra of cis subjected to various applied fields.

In the above figure, the x-axis coordinate k represents the wave number, the y-axis coordinate ε represents the applied field Intensity, and the z-axis coordinate Intensity represents the Raman scattering intensity. There are 15 peaks in total, indicating that there are 15 different vibration modes. The 15 peaks with wave numbers from small to large are numbered from 1 to 15 in turn, and the curve of Raman scattering intensity of each peak with external electric field is drawn as shown in Figure 8.

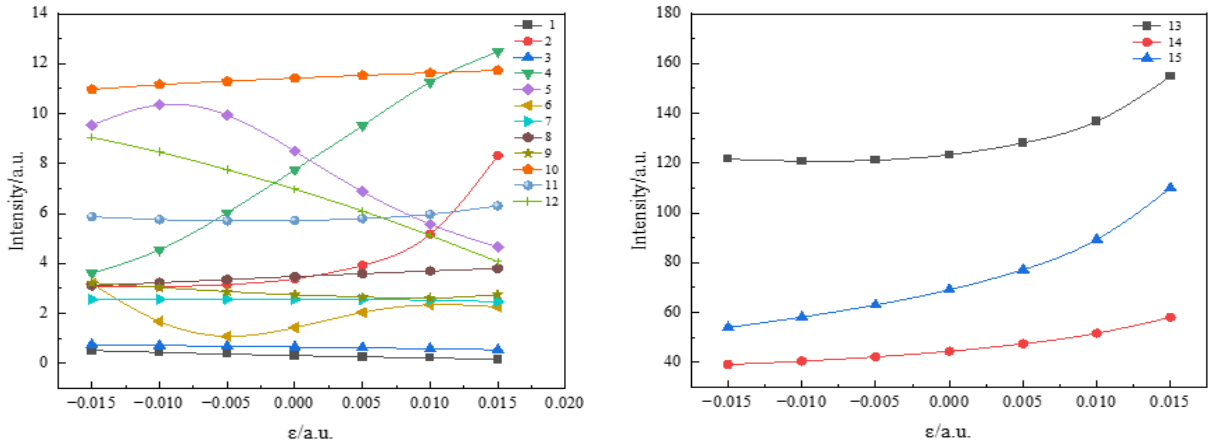

Figure 8. Variation curve of Raman scattering intensity of each peak in cis Raman spectrum with external electric field.

As shown in Figure 8, peak 1 corresponds to the torsional vibration of C-O bond, and its peak intensity decreases with the increase of external electric field, indicating that its vibration may be suppressed by external field; Peak 2 corresponds to the torsional vibration of N-O bond, and its peak intensity increases with the increase of external electric field, indicating that its vibration may be enhanced by external field. Peak 3 corresponds to the bending vibration of N-O-C, and its peak intensity decreases with the increase of external electric field; Peak 4 corresponds to the stretching vibration of N-O bond, and its peak intensity increases with the increase of external electric field. The changes of peaks 5, 6, 7, 9 and 11 are nonlinear, corresponding to the bending vibration of O=N-O, the stretching vibration of C-O bond, the swinging vibration of C-H bond and the bending vibration of C-H bond respectively. The peak intensities of peaks 8 and 10 increase gradually, corresponding to the rocking vibration of C-H bond and the bending vibration of C-H bond respectively. The peak intensity of peak 12 decreases gradually, corresponding to the telescopic vibration of N=O bond; Peaks 13-15 correspond to the stretching vibration of C-H bond, and their peak intensity increases with the enhancement of external electric field [6]. Among them, the peak intensities of peaks 4, 5, 6,

6, 12, 13, 14 and 15 change significantly with the external electric field, which may be related to the electric field enhancing the polarization of the corresponding chemical bonds. The intensity of other peaks changes little with the external electric field, which shows that these vibration modes have weak response to the external electric field. Because the direction of applying the external electric field is along the N-O bond, the change degree of peak 4 is the largest.

The Raman spectra of trans under different electric field intensities are obtained by frequency analysis, as shown in Figure 9.

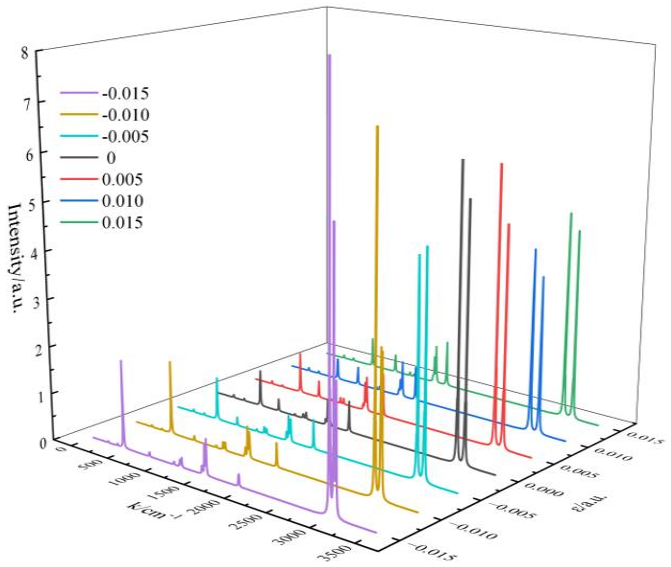

Figure 9. Raman spectra of trans subjected to various applied fields.

The spectrum contains 15 characteristic peaks, indicating that there are 15 different vibration modes. Compared with cis-Raman spectra, it can be found that the peak intensity of peaks 13-15 in trans-Raman spectra is greater than that in cis-Raman spectra. The 15 peaks with wave numbers from small to large are numbered from 1 to 15 in turn, and the curve of Raman scattering intensity of each peak with external electric field is drawn as shown in Figure 10.

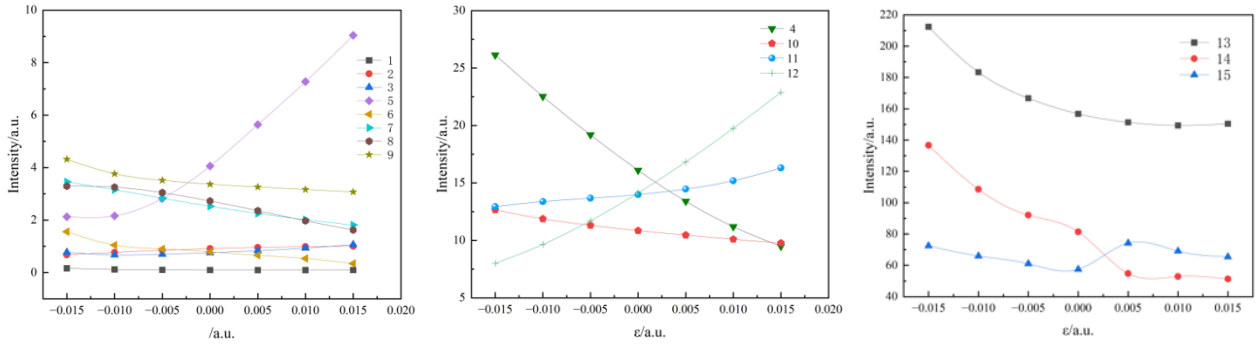

Figure 10. Variation curve of Raman scattering intensity of each peak in trans Raman spectrum with external electric field.

In Figure 10, the chemical bonds corresponding to peaks 1-15 and their vibration modes are the same as those in cis. When the external electric field increases along the trans N atom and points to the O atom (that is, it increases in the negative direction of the ε axis in Figure 10), unlike cis, the peak intensities of peaks 2, 5 and 11 gradually decrease, while those of peaks 6, 7 and 9 gradually increase, while the peak intensity of peak 15 decreases from 0 to 0.005 a.u..It shows that the molecular structure of trans is slightly different from that of cis, and its response to external electric field is different.

3.2.4. Variation of dissociation energy of methyl nitrite with external electric field

When an external electric field of ± 0.03, ± 0.02 and ± 0.01 a.u. is applied and no external electric field is applied along the positive direction of X axis of cis and trans respectively, energy scanning is carried out for cis and trans respectively, and corresponding potential energy curves are obtained as shown in Figure 11.

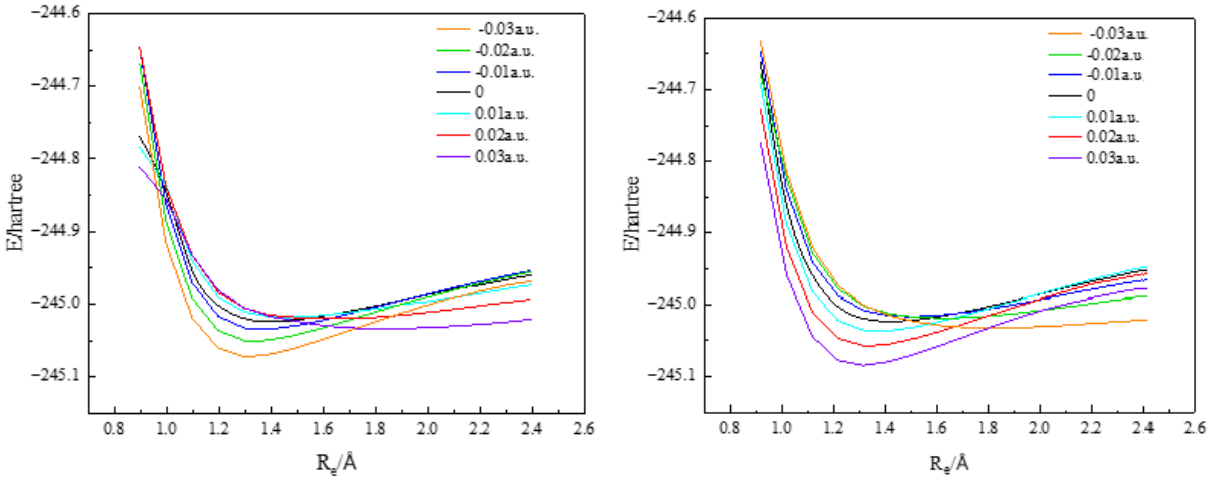

Figure 11. Potential energy curves of cis (left) and trans (right).

When the external electric field increases along the N atom of methyl nitrite to the O atom, the e quilibrium distance of molecules increases, the dissociation energy increases and the potential energ y curve increases. Therefore, when the external electric field increases along the O atom of methyl n itrite to the N atom, it can promote the degradation of methyl nitrite in water.

4. Conclusion

There are two isomers of methyl nitrite, cis and trans. For the two isomers, the calculation method of B3LYP/6-31G(d,p) basis set can get the optimized results which are in good agreement with the experimental values. Then, using the above calculation method, the cis-form and trans-form are optimized respectively when there is no external field and external electric fields of ± 0.03, ± 0.025, ± 0.02, ± 0.015, ± 0.01 and ± 0.005 a.u. are added. The results indicate that as the external electric field (applied along the same direction) increases, N-O bond lengths of both configurations gradually increase, molecular dipole moment first decreases and then increases, ground-state energy shows an initial rise followed by a decline, E_H exhibits a slow initial increase before stabilizing, E_L and E_G demonstrate a gradual increase followed by a sharp decrease. In addition, the Raman spectra of cis and trans ground States are drawn. The intensity and variation trend of each Raman peak in the Raman spectra of the two are quite different, but the vibration mode corresponding to each Raman peak remains unchanged. Finally, the potential energy curves of cis and trans are drawn, and it is concluded that the degradation in water can be promoted when the applied field increases along the O atom pointing to the N atom.

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