

The effect of external electric field on AlH radical

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Abstract. Using the density functional B3P86/cc-PV5Z method, the geometric structure of AlH molecule under different external electric fields are optimized, and the bond lengths, dipole moments, vibration frequencies and other physical properties parameters are obtained. The potential energy curves under different external fields are also obtained by CCSD(T) method with the same basis set. These results show that the properties parameters and potential energy curves may change with different external electric field, especially in the reverse electric fields. The potential energy function without external electric field is fitted by Morse potential, and the potential energy curves under different external fields are fitted using constructed potential model, which adopted the dipole approximation theory. It is found that the fitting parameters are good agreement with experimental values and the critical dissociation electric parameter is consistent with numerical calculation. These results will provide important theoretical and experimental reference for further studying the molecular spectrum, dynamics and molecular cooling with Stark effect.

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Key words: AlH radical, potential function, external electric field

1 Introduction

AlH is the main reaction products of aluminum atoms in the hydrogenation reaction, moreover, is the main component of sun shading too. It widely exists in the upper atmosphere, interstellar space, discharge and the combustion process, which is the intermediates in many chemical reactions. Aluminium hydride is a white to gray powder, they can be attached with plastic, metal, fiber and textile, flammable, explosive and corrosive, is harmful to the human body. Hydride AlH radical as the typical hybrid molecule has been made many studies. In experiment, Huber [1], Kurth [2], Gurvich *et al.* [3], measured the

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formation enthalpy, entropy, heat capacity at constant pressure, vibration frequency, zero point energy, rotational constants and bond length of AlH molecule at 0K and 298.15K; In theory, Cobos [4] further studied the standard heat of formation, structure and optical properties of AlH and its cation using G3, CBS and density functional method [5-7]; Pople *et al.* [8] calculated the electronic affinity energy of AlH molecule by molecular orbital theory; Rice *et al.* [9] measured the Einstein transition probability of AlH molecule $A^1\Pi - X^1\Sigma$ transition; Qian *et al.* [10] observed six emission bands of AlH molecule by Fu Liye optical transform method; Yan *et al.* [11] studied the potential energy function of ground state, the first and third excited states of AlH molecule by SAC/SAC-CI method; Shen *et al.* [12] studied the structure and thermodynamic stability of AlH molecule using density functional theory [13-15] and two configuration interaction method. In these literatures, they are not related to AlH free radical molecular structure and potential energy function under an external electric field.

Due to the effect of external electric field, the molecular Hamiltonian system energy based on no external electric field, increases the interaction Hamiltonian of external electric field and molecular systems, then the problem becomes more complicated, but in the dipole approximation, the energy of molecular system can be divided into zero-field potential energy and the interaction potential of external field with molecule [16-18].

2 Theoretical details

In this letter, we accurately construct the potential model adopting dipole approximation theory. At zero-field, the potential energy function is fitted by Morse potential model. The Morse potential is applied to three-parameter function of stable diatomic molecule [18]

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

where D_e is the dissociation energy, a is the Morse parameter, R is the inter-nuclear distance, and R_e is its equilibrium distance.

Under an external electric field, the Hamiltonian of molecular system energy will increase the interaction between external electric field and molecular system, and H is given as [19, 20]

$$H = H_0 + H_{int}, \quad (2)$$

where H_0 is the Hamiltonian at zero-field, and H_{int} is the interaction Hamiltonian between external electric field and molecular system. Thus the Hamiltonian of external field F and molecular system interaction can be expressed as

$$H_{int} = -\mu \cdot F. \quad (3)$$

Here, μ is the dipole moment and F is the external electric field. Therefore, the molecular potential energy under an external field can be divided into zero-field potential energy

and the interaction potential of external field with molecule, and the scalar expression is

$$V(r) = D_e(1-y)^2 + br, \quad (4)$$

where $y = e^{-a(r-R_e)}$, $b = -E(q + \alpha E)$ is the related quantity to external electric field (equivalent to the electric field force). When no external electric field exists, the potential energy minimum point is at R_e , D_e is the dissociation energy if except zero point vibrational energy, a is the Morse parameter, r is the nuclear space, q is the dipole charge corresponding to intrinsic dipole moment, and is its polarizable parameter, which is the induced dipole moment under external electric field corresponding to molecular polarization.

3 Results and discussion

When different external electric fields, namely positive electric field (0-0.03a.u.) and reverse electric field (-0.03a.u.-0), are applied along the Z axis, the optimum calculating of stable geometrical structures and physical properties parameters of AIH are conducted by B3P86/cc-PV5Z. The calculated results are listed in Table 1, the varied relations of bond length, dipole moment and vibration frequency with external field are plotted in Fig. 1. It can be seen from Table 1 and Fig. 1, the bond lengths, dipole moments and vibration frequencies of AIH molecule change little in the positive electric field, but the bond lengths and dipole moments increase rapidly with reverse electric field increasing, the vibration frequencies decreases sharply. These show that the reverse electric field has greater impact on geometric structure and physical properties of AIH molecule.

Table 1: Bond lengths, vibration frequencies, and dipole moments under different external electric fields.

$F/a.u.$	-0.03	-0.02	-0.01	0	0.01	0.02	0.03
R_e/nm	0.2030	0.1807	0.1714	0.1650	0.1623	0.1560	0.1587
f/cm^{-1}	690.26	1201.53	1485.34	1689.83	1768.54	1854.29	1904.30
$\mu/Debye$	1.6841	0.7521	0.3696	0.0943	0.0065	0.0822	0.1303

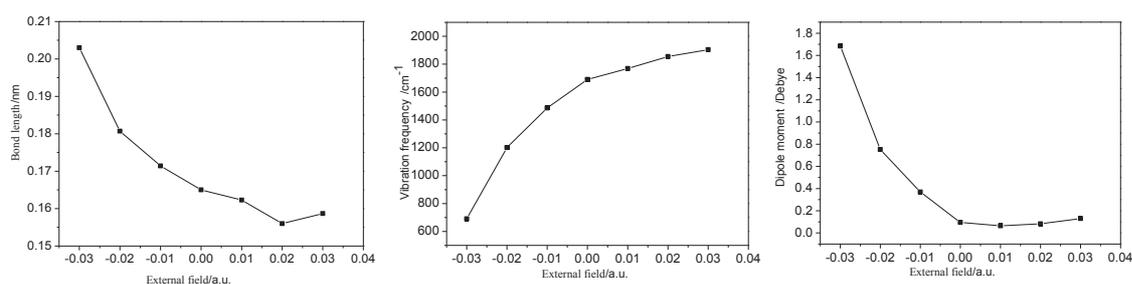


Figure 1: The varied relations of bond length, dipole moment and vibration frequency with external field.

Without external electric field, the single-point energy of AIH molecule is scanned adopting high precision energy calculation of coupled cluster CCSD(T)/cc-PV5Z method,

in which the nucleus distance changes in steps of 0.005nm, and calculated 50 *ab initio* potential energies. Firstly, the potential energy curve without external electric field is fitted to Morse potential function and potential parameters are obtained. The numerical calculation values, fitting parameters, literature datum [9], and experimental datum [18] are all given in Table 2. It can be seen from the table that the numerical calculation and fitting parameters are the closest to experimental data. These results show that the model can be reliably used to fit the potential energy function under external electric field.

Table 2: Potential fitting parameters of AIH without external electric field.

	Cal.	Fit.	Lit. [20]	Lit. [11]	Lit. [12]	Lit. [21]	Exp. [1]
R_e/nm	0.1650	0.1648	0.16496	0.1655	0.1666	0.1647	0.16478
D_e/eV	3.168	3.165	3.29	3.565	3.134	3.146	3.163
f/cm^{-1}	1689.83	-	1693.46	1771.86	1641.77	-	1682.56
a/nm^{-1}	-	14.51	-	-	-	-	-

Applying different external electric fields along the Z axis, the single-point energies are scanned using the same method CCSD(T)/cc-PV5Z. The nucleus distance changes in steps of 0.1nm, and calculated 30 *ab initio* potential energies at positive and reverse electric field, respectively. The potential energy curves under different external electric fields are all shown in Fig. 1, where the insets exhibit the curves of potential energy nearby equilibrium bond length. According to Fig. 1, the dissociation energy declines slowly and the equilibrium internuclear distances almost constant with the gradual increase of positive electric field, but as reverse electric field increases, the dissociation energy decreases sharply and equilibrium nuclear distance increases gently. The potential energy curve has a stable minimum and a unstable maximum point, similar to the volcano state [18], and the barrier will decrease with external electric fields. When a critical electric field is reached, the stable point of potential energy curve disappears, the barrier tends to be 0 and the molecule dissociates, which explains the fact that the dissociation energy decreases as external electric field increases, but decreases obviously in reverse electric field, that is to say, the molecule will more easily dissociate. These analyses are consistent with the variety of physical properties. Therefore the critical dissociation electric parameters should be identified from the reverse electric field.

In order to find the critical dissociation electric field from numerical calculation, the molecular structure of reverse electric field (-0.05a.u. and -0.06a.u.) is optimized. When the reverse electric field arrives at -0.04a.u., the optimization will not be carried out any more, so it must make a new starts of optimization as the reverse electric field decreases slightly. The results show that the optimization will not be carried out any more if the reverse electric field is more than -0.0326a.u. Through scanning the single energies of that reverse electric field, the potential energy curves are obtained as shown in Fig. 2. It can also be seen from the figure that the stable point disappears when the reverse electric field reaches -0.0326a.u., which shows that the molecule dissociates. Consequently,

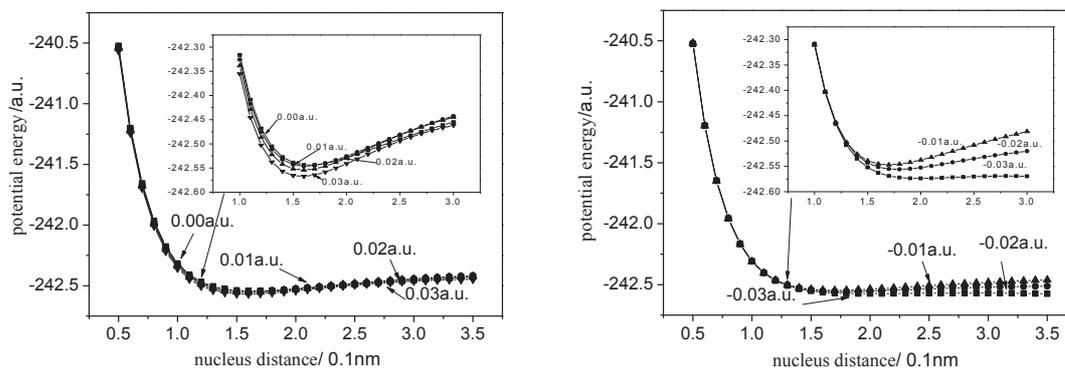


Figure 2: Plots of potential energy versus nucleus distance under different external electric fields.

the critical dissociation field of AlH molecule is -0.0326a.u. , the corresponding dissociation bond length is 0.2258nm , dipole moment is 2.6263Debye and vibration frequency is 193.45cm^{-1} .

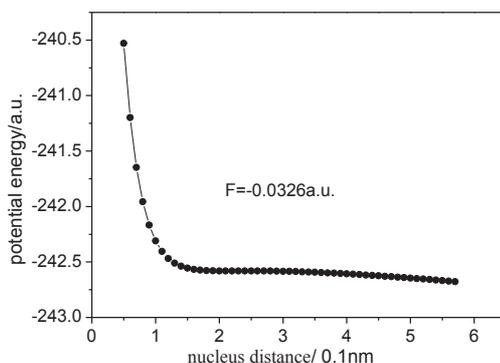


Figure 3: Potential energy curves under critical dissociation fields.

Using the constructed model, the potential energy curve fitting program of critical electric field is compiled, and the parameter of potential energy function analytical expression is obtained, the value is $b = -23.404\text{ eV}\cdot\text{nm}^{-1}$, which is parameter under external field, within D_e and a are the parameters for the case of no external field.

In order to calculate the critical parameters, $z = b/2aD_e$ is introduced. And according to potential energy extremum condition, the critical dissociation bond length can be obtained as

$$R_c = R_e + 1/a1n2 = R_e + 0.6931/a. \quad (5)$$

Due to the fact that AlH molecule is a heteronuclear diatomic molecule, the molecular polarization is ignored in external fields, then $\alpha=0$, the critical dissociation field F_c can be obtained by dissociation conditions as

$$F_c = aD_e/2q. \quad (6)$$

The critical dissociation electric and bond length are calculated by the above two formulas under different external electric fields. The results indicate that when the external electric field is -0.0326a.u. , the critical dissociation electric field F_c and bond length R_c are -0.0320a.u. and 0.2126nm , respectively, which are close to numerical calculations, with the relative errors being only 1.84% and 5.85%. These results show that the constructed model is reasonable and reliable.

4 Conclusions

In summary, we have optimum calculated the geometry structure and physical property parameters of AlH molecule by B3P86/cc-PV5Z method under different external electric fields, at the same time single-point energy is scanned with CCSD(T) method. The results show that the equilibrium bond lengths, dipole moments and vibration frequencies are all changed with external electric field, and the changed amplitudes of reverse electric fields are larger than those of positive electric fields. The potential barrier decreases and equilibrium bond length increases at reverse electric field. The potential energy curves without external electric field are fitted using the Morse model, and potential parameters are obtained which are good agreement with experimental values. The different reverse electric potential energy curves are fitted by the constructed potential model of external electric fields, and the corresponding fitting parameters are obtained. On the basis of the above data, the calculated critical dissociation electric field parameters are compared with numerical calculations, with the relative errors being only 1.84% and 5.85%, which explains the fact that the constructed model is reasonable and reliable. These results will provide important theoretical and experimental reference for further investigating molecular spectrum, dynamics and Stark effect cooling.

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