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The structure and the analytical potential energy function of NH_2 (X^2B_1)*

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This paper reports that the equilibrium structure of NH_2 has been optimized at the QCISD/6-311++G (3df, 3pd) level. The ground-state NH_2 has a bent (C_{2v}, X^2B_1) structure with an angle of 103.0582°. The geometrical structure is in good agreement with the other calculational and experimental results. The harmonic frequencies and the force constants have also been calculated. Based on the group theory and the principle of microscopic reversibility, the dissociation limits of NH_2(C_{2v}, X^2B_1) have been derived. The potential energy surface of NH_2(X^2B_1) is reasonable. The contour lines are constructed, the structure and energy of NH_2 reappear on the potential energy surface.

Keywords: molecular structure, analytical potential energy function, dissociation limits
PACC: 3420, 3520G

1. Introduction

NH_2 is one of the main compositions of the substance and the primeval air that exists extensively in interstellar space. It plays an important role in the origin of life. So the study on NH_2 radical has certain significance to explore the nature of space and the process of burning. It has attracted the attentions of spectroscopists and chemists.[1] NH_2 radical was firstly found by Herzberg and Ramsay in 1952 when they conducted a photochemical decompose to NH_3.[2] After that, Dressler and Ramsay analysed the absorbing spectrum in the range of 390–830 nm.[2] From then on, many technologies and methods of spectroscopy has been applied to experimental research of NH_2.[3−7] To our knowledge, the potential energy curves of the ground state molecule NH_2 still have not been given. In order to explore NH_2 intensively, we calculate the equilibrium geometries, dissociation energies and force constants for NH_2(X^2B_1) at the QCISD/6-311++G(3df, 3pd) level in this work. Based on the results, the analytical potential energy function (APEF) and the potential energy curves of NH_2 have been obtained according to the many-body expansion theory. These results can be used for their dynamic studies directly.

2. *Ab initio* calculation of $NH_2(X^2B_1)$

The equilibrium geometry, force constants and harmonic frequencies of NH_2 have been calculated by using QCISD/6-311++G(3df, 3pd) method. The ground symmetry of NH_2 belongs to point group C_{2v} with $^2B_1$, the bond length of NH_2 is 0.10249 nm and the bond angle is 103.0582° with the dissociation energy 4.16574 eV(which is the dissociation energy of the channel $NH_2(X^2B_1)$ →$NH(^3\Sigma^-)$+$H(^2S_g)$). The results is listed in the Table 1. In addition, the harmonic force constants are determined and listed in the Table 1. It can be seen clearly that our calculation of NH_2 is in good agreement with experiment.

Table 1. Equilibrium geometry and property of $NH_2(X^2B_1)$.

Equilibrium structure $R_{HN} = R_{NH}$/nm	0.10249	0.1024[8]
∠ HNH/(°)	103.0582	103.38[8]

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Table 1 (*Continued*)

Harmonic frequency $\omega_1(a_1)/\mathrm{cm}^{-1}$	1542.7245	
$\omega_2(a_1)/\mathrm{cm}^{-1}$	3411.2652	
$\omega_3(b_2)/\mathrm{cm}^{-1}$	3500.1542	
Dissociation energy D_e /eV	4.16574	3.95±0.02[9]
		3.96[10]
Force constants $f_{R_1R_1}$/a.u.	0.42578	
$f_{R_1R_2}$/a.u.	−0.00360	
$f_{R_1\alpha}$/a.u.	0.02937	
$f_{\alpha\alpha}$/a.u.	0.16055	

3. Potential energy function of two-body terms

The Murrell–Sorbie (M–S) function is one of the best functional forms among a number of functions which have been proposed to fit the APEF of diatomic molecule:

$$V = -D_\mathrm{e}(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho), \quad (1)$$

where $\rho = R - R_\mathrm{e}$, R is the distance of two atoms and R_e is the equilibrium distance. Based on a series of calculated energies, the dissociation energy D_e and the parameters a_1, a_2, a_3 can be obtained by the nonlinear least square fitting method.

The relations between the parameters in Eq.(1) and the force constants are

$$f_2 = D_\mathrm{e}(a_1^2 - 2a_2), \quad (2)$$

$$f_3 = -6D_\mathrm{e}\left(a_3 - a_1a_2 + \frac{1}{3}a_1^3\right), \quad (3)$$

$$f_4 = D_\mathrm{e}(3a_1^4 - 12a_1^2a_2 + 24a_1a_3), \quad (4)$$

where f_2, f_3, f_4 are quadratic, cubic and quartic force parameters, respectively. Then the spectroscopic parameters are

$$B_\mathrm{e} = \frac{h}{8\pi c\mu R_\mathrm{e}^2}, \quad (5)$$

$$\alpha_\mathrm{e} = -\frac{6B_\mathrm{e}^2}{\omega_\mathrm{e}}\left(1 + \frac{f_3R_\mathrm{e}}{3f_2}\right), \quad (6)$$

$$\omega_\mathrm{e}\chi_\mathrm{e} = \frac{B_\mathrm{e}}{8}\left[-\frac{f_4R_\mathrm{e}^2}{f_2} + 15\left(1 + \frac{\omega_\mathrm{e}\alpha_\mathrm{e}}{6B_\mathrm{e}^2}\right)^2\right]. \quad (7)$$

The molecular structures of NH and H_2 have been calculated at the level of QCISD/6-311++G(3df, 3pd), QCISD(T)/6-311++G(3df, 3pd), QCISD(T)/6-311++G(3df, 2pd), QCISD(T)/aug-cc-pvtz, respectively. The results are listed in Tables 2 and 3.

Table 2. Parameters of M–S potential energy function for NH($X^3\Sigma^-$).

	R_e/nm	D_e/eV	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}
QCISD/6-311++G(3df, 3pd)	0.1034	4.8707	38.008	341.41	3052.9
QCISD(T)/6-311++G(3df, 3pd)	0.1036	3.9881	49.526	690.67	4286.9
QCISD(T)/6-311++G(3df, 2pd)	0.1039	3.5700	48.598	631.50	3909.5
QCISD(T)/aug-cc-pvtz	0.1037	3.9748	49.173	675.21	4193.0
Ref.[11]	0.1036	3.671	44.82	497.1	3397

Table 3. Parameters of M–S potential energy function for $H_2(X^1\Sigma_\mathrm{g}^+)$.

	R_e/nm	D_e/eV	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}
QCISD/6-311++G(3df, 3pd)	0.07423	4.6962	41.589	493.50	4752.5
QCISD(T)/6-311++G(3df, 3pd)	0.07425	4.6962	41.589	493.50	4752.5
QCISD(T)/6-311++G(3df, 2pd)	0.07428	4.6912	41.835	503.06	4888.1
QCISD(T)/aug-cc-pvtz	0.07432	4.6997	41.233	477.10	4651.9
Ref.[12]	0.07415	4.7105	41.730	452.44	5125.8

We obtain optimized results of NH and H_2 by comparing the calculated results at the four levels. It has been found that the results of NH at QCISD(T)/6-311++G(3df, 2pd) level and the results of H_2 at QCISD(T)/aug-cc-pvtz level are in excellent agreement with the experimental data and other theoretical data. So, the potential energy curves of NH at QCISD(T)/6-311++G(3df, 2pd) and H_2 at QCISD(T)/aug-cc-pvtz level are shown in Figs.1 and 2. Based on the fitted APEF and Eqs.(2)–(7), the spectroscopic parameters of them have been calculated. All the calculated results are shown in Table 4. We can see that the spectroscopic parameters of NH and H_2 are in good agreement with the experimental values.

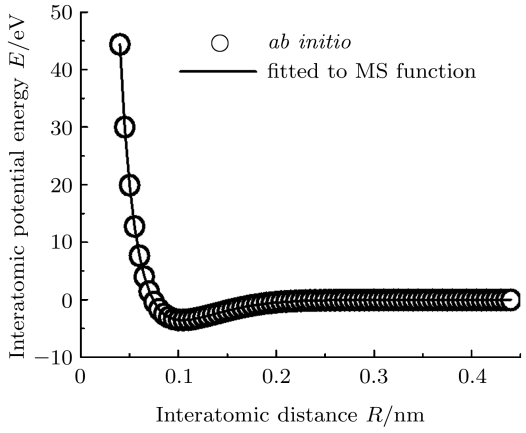


Fig.1. Potential energy curves of the ground state for NH.

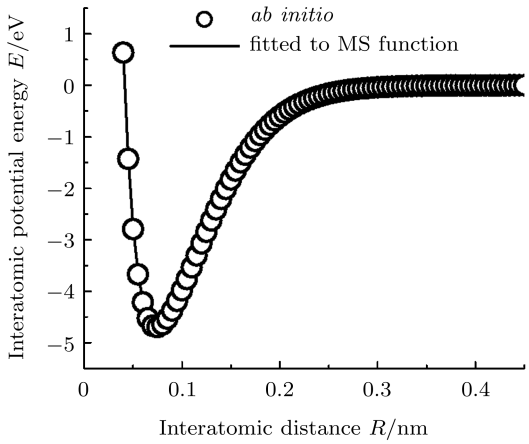


Fig.2. Potential curves of the ground state for H_2.

Table 4. The spectroscopic parameters of NH and H_2.

	R_e/nm	D_e/eV	B_e/cm^{-1}	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	α_e/cm^{-1}
NH	0.1039	3.5700	8.7477	3298.15	40.791	0.1629
Ref.[13]	0.1036		8.7913	2398	42	0.2531
experiment	0.1037[14,15]	3.5997[16]		3282.58[17]		
H_2	0.07432	4.6997	60.548	4398.72	115.604	3.31667
Ref.[12]	0.07415	4.7105	60.826	4195.49	87.76	3.167
Ref.[13]	0.07416	4.476	60.809	4395.2	117.99	2.993

4. Analytical potential function of NH_2 (C_{2v}, X^2B_1)

Based on group theory and the principle of microscopic reversibility, the dissociation limits of $NH_2(C_{2v}, X^2B_1)$ have been derived:

$$NH_2(C_{2v}, X^2B_1) \longrightarrow \begin{cases} N(^4S_u) + H_2(X^1\Sigma_g^+), \\ NH(^3\Sigma^-) + H(^2S_g), \\ N(^4S_g) + H(^2S_g) + H(^2S_g). \end{cases} \quad (8)$$

According to the many-body expansion theory,[18−20] the potential energy function of $NH_2(X^2B_1)$ is

$$V = V_{HN}^{(2)}(R_1) + V_{NH}^{(2)}(R_2) + V_{H_2}^{(2)}(R_3) + V_{NH_2}^{(3)}(R_1, R_2, R_3). \quad (9)$$

Where $R_1 = R_2 = R_{NH}$, $R_3 = R_{H_2}$, $V_{HN}^{(2)}(R_1)$, $V_{NH}^{(2)}(R_2)$, $V_{H_2}^{(2)}(R_3)$ are the two-body terms represented by the potential functions of $HN(X^3\Sigma^-)$, $NH(X^3\Sigma^-)$ and $H_2(X^1\Sigma_g^+)$, respectively. $V_{NH_2}^{(3)}(R_1, R_2, R_3)$ is the three-body term, which will be zero if any one of the atoms is removed to infinity. The form of potential energy function of two-body terms is Eq.(1). The parameters of two-body terms are listed in Table 2 and Table 3.

Here, we mainly derive the three-body terms. It is convenient that three-body terms are shown as the functions of symmetrical internal coordinates. We choose C_{2v} symmetry ($R_1^0 = R_2^0 = 0.10249$ nm, $R_3^0 = 0.16048$ nm) as the reference structure, then the

internal coordinates are

$$\rho_i = R_i - R_i^0, \quad (i = 1, 2, 3). \tag{10}$$

The corresponding symmetrical internal coordinates are

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{bmatrix}. \tag{11}$$

Three-body term is

$$V^{(3)}(R_1, R_2, R_3) = PT, \tag{12}$$

where P is a polynomial

$$P = C_0 + C_1 S_1 + C_2 S_2^2 + C_3 S_3 + C_4 S_3^2 + C_5 S_1 S_3 + C_6 S_1^2, \tag{13}$$

and T is a range function

$$T = [1 - \tanh(\gamma_1 S_1/2)][1 - \tanh(\gamma_3 S_3/2)]. \tag{14}$$

S_2 is asymmetrical when R_1 and R_2 interchange, but the molecule is the same after the interchange. So, S_2 has the even powers. The seven linear parameters $C_0 - C_6$ can be determined by using the equilibrium structure and the force constants (in Table 1) and the nonlinear ones γ_1 and γ_3 in the range function, T can be determined by optimizing the potential energy surface. By using the program which is compiled by Fortran, the parameters of the three-body term of $NH_2(X^2B_1)$ are calculated and listed in Table 5.

Table 5. Parameters of three-body term of $NH_2(X^2B_1)$.

$C_0 = 4.45699263$	$C_1 = 25.8262777$	$C_2 = -50.6053805$
$C_3 = -8.60577524$	$C_4 = 836.943054$	$C_5 = -1157.44572$
$C_6 = 511.876154$	$\gamma_1 = 0.8$	$\gamma_3 = 1.0$

Figures 3 and 4 are the contour graphs of the $NH_2(X^2B_1)$ potential. These figures reproduce the equilibrium geometry of $NH_2(X^2B_1)$. Figure 3 is the N–H bond stretching contours for a fixed angle $\angle$HNH = 103.0582°. From this figure, we can see that there is a potential well (−4.17 eV) at $R_{HN} = R_{NH} = 0.10249$ nm and two symmetrical saddle points at (0.216 nm, 0.104 nm) and (0.104 nm, 0.216 nm), the barrier height which is approximately 1.15086 eV can be seen. It shows that NH_2 could difficultly form if H atom attacks NH from N–H bond near H atom direction at the two equivalent channels. The potential energy surface reproduces C_{2v} symmetry of NH_2. It is in agreement with the result of Table 1. Figure 4 is the contours for H atom moving around the fixed N–H bond ($R_{N-H} = 0.10249$ nm), the N–H bond is fixed at the X axis, and then Y axis is established at the zero by the central point of the N–H bond. The dissociation energy of NH_2 is the lowest energy (−4.17 eV) when H atom is moving to $\angle$HNH = 103.0582°. It is of great interest to find that there is barrier between −1.0 eV and −1.8 eV contour lines on the reaction channel H+NH→NH_2 from the Fig.4. The barrier at $x = 0.05366$ nm and $y = 0.21599$ nm ($R_{NH1} = 0.104$ nm, $R_{NH2} = 0.216$ nm) is approximately 1.15086 eV. It is in agreement with the result of the Fig.3. These are in good agreement with the *ab initio* calculated results.

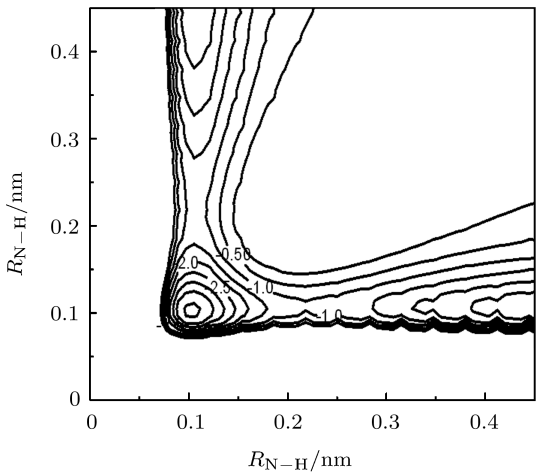


Fig.3. Stretched vibrational contour of moving potential energy function for NH_2.

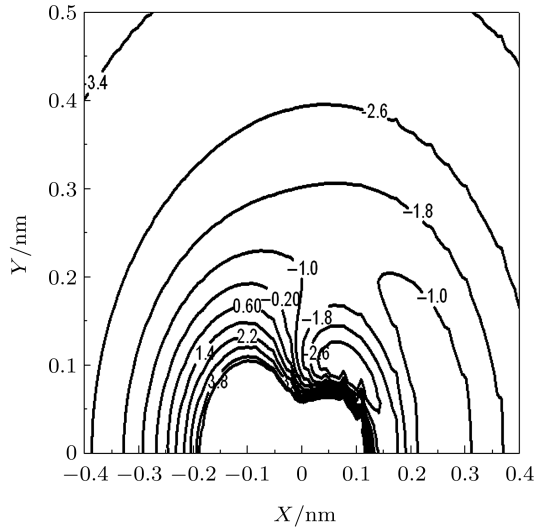


Fig.4. Contour lines of NH_2 for H atom around the fixed N–H bond 0.10249 nm.

5. Conclusions

The equilibrium geometry, force constants and harmonic frequencies of NH_2 have been calculated by QCISD/6-311++G(3df, 3pd) method. The geometries and harmonic frequencies of them are in good agreement with those in the literature. Based on group theory and the principle of microscopic reversibility, the dissociation limits of $NH_2(X^2B_1)$ are determined, we extend the many-body expansion theory to NH_2, and get satisfactory results. These results are helpful for the dynamic study of NH_2.

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