

An ab initio global potential-energy surface for $\text{NH}_2(\text{A}2\text{A}')$ and vibrational spectrum of the Renner–Teller $\text{A}2\text{A}'\text{-X}2\text{A}''$ system

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Citation: *J. Chem. Phys.* **130**, 184307 (2009); doi: 10.1063/1.3125511

View online: <http://dx.doi.org/10.1063/1.3125511>

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An *ab initio* global potential-energy surface for $\text{NH}_2(A^2A')$ and vibrational spectrum of the Renner–Teller $A^2A'-X^2A''$ system

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(Received 12 March 2009; accepted 7 April 2009; published online 8 May 2009)

A global potential-energy surface for the first excited electronic state of $\text{NH}_2(A^2A')$ has been constructed by three-dimensional cubic spline interpolation of more than 20 000 *ab initio* points, which were calculated at the multireference configuration-interaction level with the Davidson correction using the augmented correlation-consistent polarized valence quadruple-zeta basis set. The ($J=0$) vibrational energy levels for the ground (X^2A'') and excited (A^2A') electronic states of NH_2 were calculated on our potential-energy surfaces with the diagonal Renner–Teller terms. The results show a good agreement with the experimental vibrational frequencies of NH_2 and its isotopomers. © 2009 American Institute of Physics. [DOI: 10.1063/1.3125511]

I. INTRODUCTION

The NH_2 system has served as a prototype in understanding vibronic interactions in polyatomic systems. The first spectroscopic detection of this molecule was reported by Herzberg and Ramsay,¹ and a comprehensive analysis of the spectrum in the range between 390 and 830 nm was later presented by Dressler and Ramsay.^{2,3} The spectrum originates from transitions from the ground (X^2A'') electronic state of NH_2 to its first excited (A^2A') electronic state. The former is known to be strongly bent, while the latter has a quasilinear equilibrium H–N–H angle. Interestingly, the two electronic states become degenerate at linearity as the two components of a $^2\Pi_u$ state. As pointed out by Renner,⁴ the energy levels on these two electronic states are affected by the so-called Renner–Teller (RT) coupling, which is a nonadiabatic effect due to coupling of the electronic and rotational angular momenta. Since the initial work, many experimental studies on both the absorption and emission spectra of NH_2 have revealed that some of the vibrational levels are strongly affected by the RT coupling.^{5–8} Theoretical studies using both reduced dimensional^{9–12} and full dimensional models^{13–15} have resulted in a deeper understanding of the phenomenon.

Recently, the NH_2 system has also attracted much attention as prototype for insertion reactions. The reaction $\text{N}(^2D) + \text{H}_2(X^1\Sigma_g^+) \rightarrow \text{NH}(X^3\Sigma^-) + \text{H}(^2S)$ plays an important role in combustion of nitrogen-containing fuels and in atmospheric chemistry.¹⁶ At low energies, it occurs largely on the ground (X^2A'') electronic state of NH_2 , following an insertion pathway. The excited A^2A' state correlates with the same reactants as the ground X^2A'' state, but it leads adiabatically to the excited products $\text{NH}(a^1\Delta) + \text{H}(^2S)$, which ~ 1.6 eV higher than the ground state products $\text{NH}(X^3\Sigma^-) + \text{H}(^2S)$. As

discussed above, the RT coupling between the two electronic states will inevitably make the reaction dynamics nonadiabatic, especially giving the fact that the insertion nature the reaction necessities multiple passes over the linearity. Although most previous dynamical studies were performed within the single-surface approximation,^{17–31} several recent investigations have started to address the nonadiabatic effects and their impact on reaction dynamics.^{32–36} These calculations have indicated that nonadiabatic transitions due the RT coupling play an important role in the reaction. However, its impact on final state resolved scattering attributes is still unknown.

Given the small number of electrons and two hydrogen atoms, it should now be possible to treat both the spectroscopy and reaction dynamics with uniform accuracy. This requires globally accurate potential-energy surfaces (PESs) for both electronic states and their couplings. So far, spectroscopic calculations were typically performed on semiglobal PESs constructed either empirically or based on a small number of *ab initio* points near the potential minimum.^{13,14} On the other hand, dynamical studies have relied on global PESs that are often not spectroscopically accurate.^{17,21,32,37,38}

In this work, we report a new global PES of the excited A^2A' state for the NH_2 system based on more than 20 000 high-level *ab initio* points distributed in the three-dimensional configuration space, including the dissociation channels. As in our recent work on the ground X^2A'' state PES,³¹ the *ab initio* calculations were performed at the multireference configuration-interaction (MRCI) level with the Davidson correction (MRCI+Q) using a large correlation-consistent basis set. In order to investigate the influence of RT effect on the vibrational states of the NH_2 system and the reaction dynamics, matrix elements of the electronic angular momentum $\hat{L}_z$, and $\hat{L}_z^2$ were calculated at the state-averaged complete active space self-consistent field (CASSCF) level. To illustrate the accuracy of the PESs, low-lying vibrational

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frequencies in both the X^2A'' and A^2A' states were calculated for NH_2 and its isotopomers and compared to available experimental band origins. The good agreement with experimental data confirms the accuracy of the PESs. This paper is organized as follow. Section II describes the *ab initio* calculations and the analytical representation of the PES and electronic matrix elements, as well as the quantum mechanical method to calculate the vibrational spectra. Section III presents the main features of the new PES and discusses the vibrational spectra obtained on the PESs. Finally, a brief summary is given in Sec. IV.

II. THEORY

A. *Ab initio* calculations and surface fitting

Following our earlier work on the ground (X^2A'') state NH_2 PES,³¹ the *ab initio* energies of the excited A^2A' state were calculated using the internally contracted MRCI (Refs. 39 and 40) method with the augmented correlation-consistent polarized valence quadruple-zeta (aug-pVQZ) basis set.⁴¹ The effects of higher excitations were included using the Davidson correction.⁴² The MRCI calculations were based on optimized state-averaged CASSCF (Refs. 43 and 44) wave functions for equally weighted $1^2A'$, $2^2A'$, $1^2A''$, $2^2A''$, and $3^2A''$ states. Seven active electrons and seven active orbitals, including two for the two hydrogen atoms and five for the nitrogen atom, were used. The $1s$ orbital for nitrogen was fully optimized while constrained to be doubly occupied during the CASSCF calculations. In the MRCI calculations, the correlation energy was generated for all electrons and the total number of contracted configurations was about 7.9×10^5 . The electronic angular momentum elements $\langle X^2A'' | \hat{L}_z^2 | X^2A'' \rangle$, $\langle A^2A' | \hat{L}_z^2 | A^2A' \rangle$, and $\langle X^2A'' | \hat{L}_z | A^2A' \rangle$ were calculated at the CASSCF level. Here, $\hat{L}_z$ is the electronic angular momentum operator along the body-fixed (BF) z axis, which was defined as the axis parallel to the H–H bond. All calculations were performed in the C_s symmetry using the MOLPRO suite of *ab initio* programs.⁴⁵

A nonuniform and truncated direct product grid in the internal coordinates ($r_{\text{NH}_1}, r_{\text{H}_1\text{H}_2}, \xi_{\text{NH}_1\text{H}_2}$) was selected to construct a global PES of the A^2A' state. To correctly account for the dissociation channels of NH_2 , we have chosen relatively dense grids in both radial coordinates. 33 points from $1.1a_0$ to $15.0a_0$ were used in the N– H_1 radical coordinate and 31–63 points from $0.7a_0$ to $14.0a_0$ were selected in the H_1 – H_2 radial coordinate. For the angular coordinate, 20 points were employed ranged from 0° to 180° . This gives a total of more than 20 000 symmetry-unique points. Finally, a three-dimensional cubic spline interpolation provides the global potential-energy function. The symmetry of the PES with respect to the exchange of the two H atoms is retained by selecting the shorter NH bond as the NH_1 coordinate in interpolation.

To construct the surfaces for matrix elements of $\hat{L}_z$ and $\hat{L}_z^2$, a nonuniform direct product grid in the internal coordinates ($R_{\text{NH}_1}, R_{\text{NH}_2}, \chi_{\text{HNH}}$) was employed. For N– H_1 and N– H_2 radial coordinates, we have used 33 and 33–66 points, respectively, covering $1.1a_0$ to $15a_0$. And 13 points from 60°

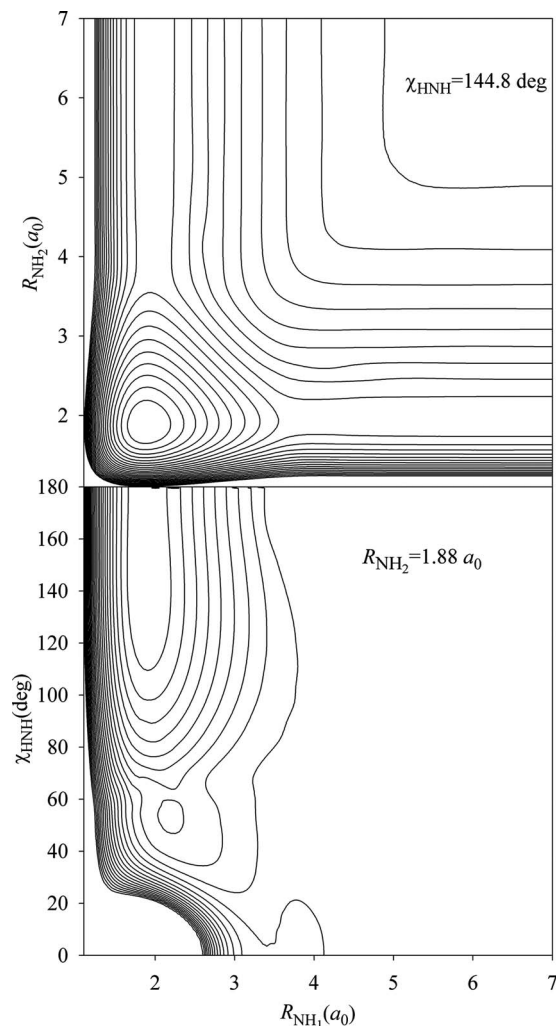


FIG. 1. Contour plots of the $\text{NH}_2(A^2A')$ PES in internal coordinates ($R_{\text{NH}_1}, R_{\text{NH}_2}, \chi_{\text{HNH}}$). Upper panel: PES with $\chi_{\text{HNH}} = 144.8^\circ$. Lower panel: PES with $R_{\text{NH}_2} = 1.88a_0$. The energy zero is defined at the $\text{N}(^2D) + \text{H}_2$ asymptote and the spacing between the contours is 0.5 eV.

to 180° were selected for the enclosed angle. Finally, global surfaces of these matrix elements were generated using the same three-dimensional cubic spline interpolation method.

We note that there are several conical intersections among the lowest-lying electronic states of NH_2 . It is possible to construct *ab initio* diabatic PESs and their couplings, including the RT terms, by treating the electronic nonadiabatic couplings as topological effects.^{46–48} In this work, however, we will only focus on the RT coupling and ignore other nonadiabatic terms.

B. Calculations of vibrational energy levels

The rovibrational Hamiltonian in the reactant (N– H_2) Jacobi coordinates (R, r, γ), within a BF frame has the following form ($\hbar = 1$ hereafter):^{49,50}

$$\hat{H} = -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} + \hat{T}_{\text{rot}} + V(R, r, \gamma), \quad (1)$$

where the rotational kinetic energy operator is given in the following form:⁵⁰

TABLE I. Comparison of geometries and energies of stationary points between the present and previous global PESs of NH₂(A²A'). Energies are given in kcal/mol relative to N(²D)+H₂, and bond lengths and bond angles are given in a₀ and deg, respectively.

Configuration	Property	This work	Pederson <i>et al.</i> ^a	Qu <i>et al.</i> ^b	Expt. ^a	Expt. ^b
N(² D)+H ₂	d(H-H)	1.402	1.40	1.402	1.40	1.401
	Energy	0	0	0	0	0
NH ₂	d(N-H)	1.88	1.8763	1.884	1.8871	1.897
	∠HNN	144.84	142.7	145.14	144.2	144.0
	Energy	-97.81	-93.5	-94.71	-92.30	-97.48
NH(a ¹ Δ)+H	d(N-H)	1.952	1.96	1.977	1.97	1.954
	Energy	7.88	8.3	9.51	7	5.9
C _{2v} barrier N-H ₂	d(H-H)	1.421	1.42	1.421	...	...
	d(N-H ₂)	3.76	3.79	3.74	...	...
	Energy	2.79	3.39	3.08	...	...
Linear barrier N-HH	d(N-H)	2.215		...	...	...
	d(H-H)	2.07		...	...	...
	Energy	16.86	16.3	...	...	...

^aReference 32.

^bReference 37.

$$\begin{aligned} \hat{T}_{\text{rot}} = & \left(\frac{1}{2\mu_R R^2} + \frac{1}{2\mu_r r^2} \right) \left(-\frac{1}{\sin \gamma} \frac{\partial}{\partial \gamma} \sin \gamma \frac{\partial}{\partial \gamma} + \frac{\hat{N}_z^2}{\sin^2 \gamma} \right) \\ & + \frac{1}{2\mu_r r^2} \left[\hat{N}^2 - 2\hat{N}_z^2 + \hat{N}_+ \left(\cot \gamma \hat{N}_z + \frac{\partial}{\partial \gamma} \right) \right. \\ & \left. + \hat{N}_- \left(\cot \gamma \hat{N}_z - \frac{\partial}{\partial \gamma} \right) \right]. \end{aligned} \quad (2)$$

In the above equation, the nuclear angular momentum $\hat{N}$ is the difference between total angular momentum ($\hat{J}$) and electronic angular momentum ($\hat{L}$) and $\mu_R = m_N(m_H + m_H)/(m_N + m_H + m_H)$, $\mu_r = m_H m_H/(m_H + m_H)$, here m_N and m_H are masses of N and H atoms, respectively. To simplify the calculation, the electronic orbital angular momentum ($\hat{L}$) is assumed to be aligned with the BF z -axis for the average effect of its x and y components is negligible.⁵⁰ In our model, the r -embedding scheme^{51,52} was used. The alternative R -embedding is formally equivalent, but small differences exist in real calculations. Furthermore, we ignored the spin-orbit coupling.

In this publication, we only consider the $J=0$ case, in which the rotational kinetic energy operator becomes

$$\begin{aligned} \hat{T}_{\text{rot}} = & \left(\frac{1}{2\mu_R R^2} + \frac{1}{2\mu_r r^2} \right) \left(-\frac{1}{\sin \gamma} \frac{\partial}{\partial \gamma} \sin \gamma \frac{\partial}{\partial \gamma} + \frac{\hat{L}_z^2}{\sin^2 \gamma} \right) \\ & - \frac{\hat{L}_z^2}{2\mu_r r^2}. \end{aligned} \quad (3)$$

Note that the Hamiltonian is diagonal in the Born-Oppenheimer basis. In other words, there is no RT coupling between the two Born-Oppenheimer states for $J=0$. However, the rotational kinetic energy operator is affected by the projection of the electronic angular momentum operator on

the BF z -axis ($\hat{L}_z^2$), which is diagonal in the electronic basis and they will be called the diagonal RT terms. These terms will affect the vibrational states, particularly those with significant amplitudes near linearity due to the $\sin^{-2} \gamma$ factor. However, their effects amount to additional potential terms in the Hamiltonian and the vibrational energy levels for the X^2A'' and A^2A' states can be treated separately. In future studies, the off-diagonal RT coupling will be taken into consideration for $J>0$ cases.

The vibrational energy levels for both electronic states were calculated using the Lanczos method.⁵³ In particular, a direct product discrete variable representation⁵⁴ (DVR) grid was used. The R coordinates were represented by a 130 sine-DVR point grid in the range of $(0.001, 4)a_0$. 80 sine-DVR points were used to cover the r range of $(0.9, 6)a_0$. For the angular variable, 100/120 Gauss-Legendre grid points were used in the interval $(0, \pi)$ for the X^2A''/A^2A' state. The converged vibrational energy levels were generated by carrying out about 65 000 Lanczos recursion steps with cutoffs of 8 and 12 eV for the X^2A'' and A^2A' PESs, respectively. Spurious eigenvalues were removed using the method detailed in Ref. 55. When the eigenfunctions were required, the Lanczos recursion was repeated to assemble the wave functions of interest.

III. RESULTS AND DISCUSSION

A. Potential-energy surface and surfaces of electronic elements

Figure 1 displays the contour plots of the A^2A' PES of NH₂ in the internal coordinates ($R_{\text{NH}_1}, R_{\text{NH}_2}, \chi_{\text{HNN}}$). The upper panel shows the dependence of the PES on the two bond lengths with the bond angle fixed at its equilibrium value of 144.8°, while the lower panel displays the variation in the R_{NH_1} and χ_{HNN} coordinates with the other bond length (R_{NH_2})

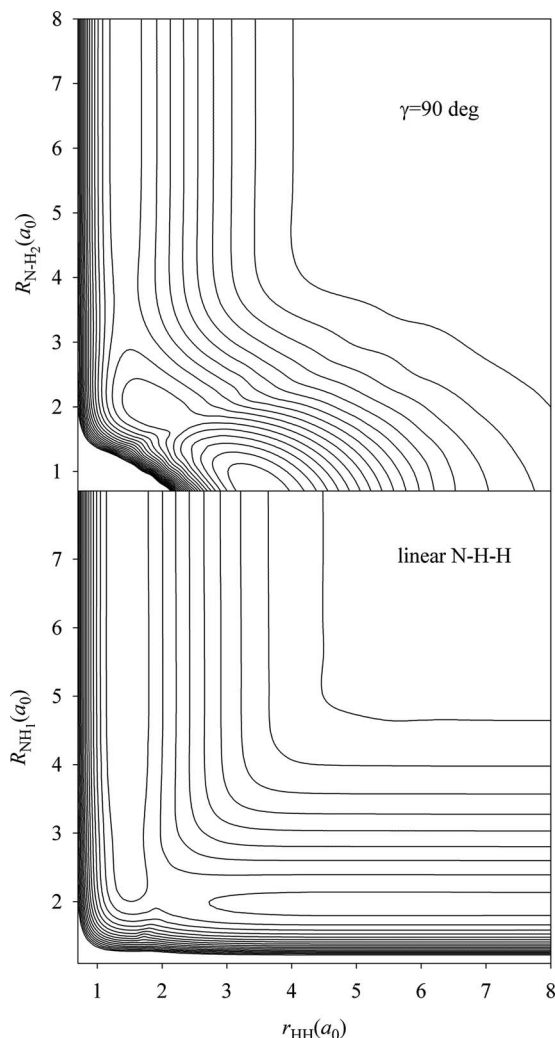


FIG. 2. Contour plots of the $\text{NH}_2(A^2A')$ PES. Upper panel: PES for the C_{2v} insertion of the N atom into H_2 in the Jacobi coordinates $(R_{\text{N-H}_2}, r_{\text{HH}}, \gamma)$. Lower panel: PES in collinear N-H-H configurations in the internal coordinates $(R_{\text{NH}_1}, r_{\text{HH}}, \xi_{\text{NH}_1\text{H}_2} = 180^\circ)$. The energy zero is defined at the $\text{N}(^2D) + \text{H}_2$ asymptote and the spacing between the contours is 0.5eV .

fixed at its equilibrium value of $1.88a_0$. The global minimum for A^2A' PES is located at $R_{\text{NH}_1} = R_{\text{NH}_2} = 1.88a_0$ and $\chi_{\text{HNN}} = 144.8^\circ$. Table I compares the results with experimental and previous theoretical values. The calculated equilibrium geometry is in good agreement with the experimental values.^{32,37} The calculated dissociation energy ($D_e(\text{N-H}_2)$) is -97.81 kcal/mol , which is in a much better agreement with experimental values³⁷ than that obtained on the earlier PESs.^{32,37} The endoergicity associated with the formation of $\text{NH}(a^1\Delta)$ also shows a good agreement with experimental and theoretical results.^{32,37} Moreover, at $R_{\text{NH}_1} = R_{\text{NH}_2} = 2.195a_0$ and $\chi_{\text{HNN}} = 48.7^\circ$, we find a shallow minimum (-26.21 kcal/mol) due to the conical intersection between the lowest two states with $^2A'$ symmetry. The local minimum was also found in the earlier PES of Qu *et al.*³⁷

Figure 2 shows the contour plots of A^2A' PES at perpendicular and linear approaches of N to H_2 . The upper panel displays the contour plot of the A^2A' PES along an insertion pathway perpendicular to the H-H bond, using the $\text{N} + \text{H}_2$ Jacobi coordinates $(R_{\text{N-H}_2}, r_{\text{HH}}, \gamma)$. A C_{2v} ($\gamma = 90^\circ$) barrier is

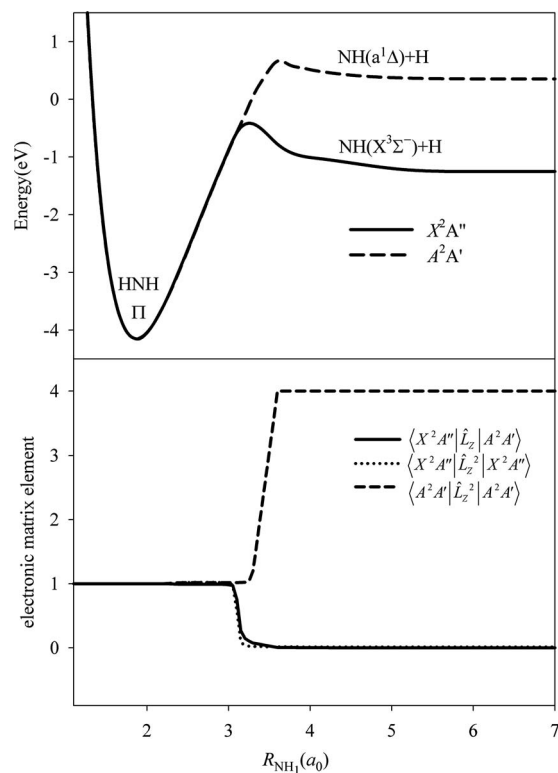


FIG. 3. PESs of the X^2A'' and A^2A' states of NH_2 (upper panel) and electronic matrix elements $\langle X^2A'' | \hat{L}_z | A^2A' \rangle$, $\langle X^2A'' | \hat{L}_z^2 | X^2A'' \rangle$ and $\langle A^2A' | \hat{L}_z^2 | A^2A' \rangle$ (lower panel) as a function of bond length R_{NH_1} with $R_{\text{NH}_2} = 1.9a_0$ and $\chi_{\text{HNN}} = 180^\circ$. The energy zero is defined at the $\text{N}(^2D) + \text{H}_2$ asymptote.

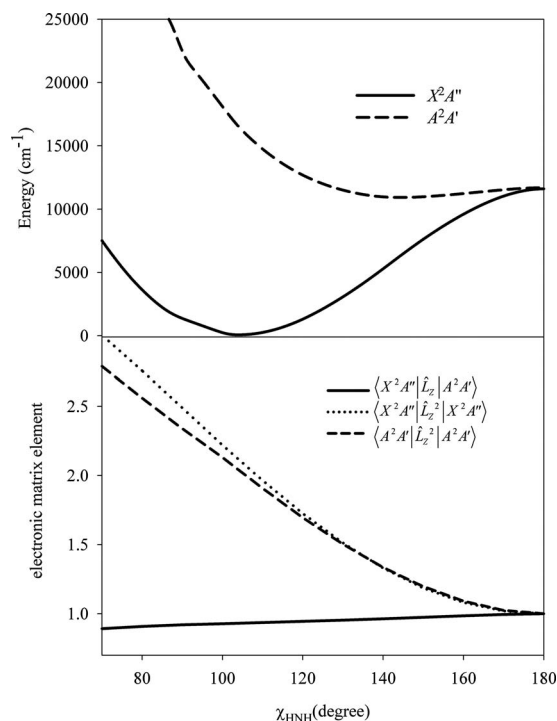


FIG. 4. PESs of the X^2A'' and A^2A' states of NH_2 (upper panel) and electronic matrix elements $\langle X^2A'' | \hat{L}_z | A^2A' \rangle$, $\langle X^2A'' | \hat{L}_z^2 | X^2A'' \rangle$ and $\langle A^2A' | \hat{L}_z^2 | A^2A' \rangle$ (lower panel) as a function of bond angle with the bond lengths fixed at $1.9a_0$. The energy zero is defined at the global minimum of the X^2A'' ground state.

TABLE II. Calculated vibrational energy levels (in cm⁻¹) of NH₂(X²A'') with and without the diagonal RT terms and comparison with known experimental band origins.

(<i>n</i> ₁ , <i>n</i> ₂ , <i>n</i> ₃)	Expt. ^a	Calc. without RT ^b	Calc.-Expt.	Calc. with RT(this work)	Calc.-Expt.
(0,0,0)	0.00	0.00	0.00	0.00	0.00
(0,1,0)	1497.32	1504.69	7.37	1506.96	9.64
(0,2,0)	2961.24	2959.67	1.57	2964.93	3.69
(1,0,0)	3219.37	3228.36	8.99	3227.66	8.29
(0,0,1)	3300.10	3319.99	19.89	3319.33	19.23
(0,3,0)	4391.35	4392.50	1.15	4402.08	10.73
(1,1,0)		4720.39		4722.00	
(0,1,1)		4806.66		4808.06	
(0,4,0)	5785.55	5781.68	3.87	5797.27	11.72
(1,2,0)	6151.95	6165.75	13.80	6170.30	18.35
(0,2,1)		6247.84		6251.78	
(2,0,0)	6335.15	6362.03	26.88	6360.99	25.84
(1,0,1)		6401.38		6400.31	
(0,0,2)		6586.50		6585.41	
(0,5,0)	7140.35	7125.05	15.30	7150.80	10.45
(1,3,0)	7564.63	7579.68	15.05	7588.27	23.64
(0,3,1)		7664.86		7672.32	
(2,1,0)	7804.54	7836.83	32.39	7838.08	33.54
(1,1,1)		7873.95		7875.05	
(0,1,2)	8000.40	8047.75	47.35	8048.59	48.19
(0,6,0)	8451.45	8416.09	35.36	8462.03	10.58
(1,4,0)	8942.59	8952.99	10.40	8967.92	25.33
(0,4,1)		9046.42		9058.76	
(2,2,0)	9227.14	9260.29	33.15	9263.87	36.73
(1,2,1)		9293.47		9296.28	
(3,0,0)		9363.80		9362.95	
(2,0,1)		9370.78		9370.14	
(0,2,2)	9421.50	9473.22	51.72	9476.27	54.77
(1,0,2)		9601.61		9600.22	
(0,7,0)	9716.90	9630.02	86.88	9724.97	8.07
(0,0,3)		9754.29		9752.85	
(1,5,0)	10 286.30	10 280.25	6.05	10 307.89	21.59
(0,5,1)		10 384.51		10 404.49	
(2,3,0)	10 609.00	10 653.68	44.68	10 661.87	52.87
(1,3,1)		10 688.72		10 694.87	
(3,1,0)		10 816.45		10 817.66	
(2,1,1)		10 825.79		10 827.18	
(0,3,2)		10 873.72		10 879.14	
(0,8,0)	10 948.00	10 749.34	198.66	10 956.88	8.88
(1,1,2)		11 056.73		11 057.40	
(0,1,3)		11 193.00		11 193.13	
(1,6,0)		11 549.16		11 608.43	
(0,6,1)		11 680.44		11 713.69	
(0,9,0)		11 832.80		12 194.01	
(0,10,0)	13 448.6	13 002.34	446.26	13 469.34	20.74

^aReferences 11 and 13.^bReference 31.

located at $R_{\text{N-H}_2}=3.760a_0$ and $r_{\text{HH}}=1.421a_0$. The calculated barrier height (2.790 kcal/mol) on the A²A' PES is about 0.842 kcal/mol higher than that obtained on our ground state PES (Ref. 31) and lower than those obtained on the previous A²A' PESs.^{32,37} In this panel, the global and local minima are also visible. The lower panel shows the contour plot of the A²A' PES in collinear N-H-H configurations. The collinear barrier lies at $r_{\text{HH}}=2.07a_0$ and $R_{\text{NH}_1}=2.215a_0$, with a barrier height of 16.86 kcal/mol which is in good agreement with the PES of Pederson *et al.*³² (The barrier height on the PES

of Pederson *et al.* was found in Fig. 3 in Ref. 32 because the value listed in Table 1 of Ref. 32 seems to be the linear barrier height of the ground state PES with the Davidson correction). Since the collinear barrier is much higher than the C_{2v} barrier, the N+H₂ reaction on the A²A' PES favors the perpendicular insertion pathway.

The upper panel of Fig. 3 shows the cuts through the PESs of the X²A'' and A²A' states of NH₂ at HNH linear geometries. At linearity, both states correlate with the degenerate Π state for small N-H bond distances. Due to the

TABLE III. Calculated ($J=0$) vibrational energy levels (in cm^{-1}) for $\text{NH}_2(A^2A')$ with and without the RT terms and comparison with experimental band origins and results on the PES of Pederson *et al.* (Ref. 32).

(n_1, n_2, n_3)	Expt. ^a	Calc. without RT	Calc. with RT	Calc.-Expt.	Calc. with RT (PES of ^b)	Calc.-Expt.
		(this work)	(this work)			
(0,0,0)	0.00	0.00	0.00	0.00	0.00	0.00
(0,1,0)	1157.9	895.96	1158.23	0.33	1187.43	29.53
(0,2,0)	2496.3	2057.78	2485.88	10.42	2572.47	76.17
(1,0,0)		3510.89	3498.51		3476.68	
(0,0,1)		3824.29	3799.12		3761.59	
(0,3,0)	3997.5	3453.95	3981.74	15.76	4140.95	143.45
(1,1,0)		4397.44	4644.10		4659.29	
(0,1,1)		4704.35	4928.68		4936.02	
(0,4,0)	5619.0	5011.84	5600.73	18.27	5814.26	195.26
(1,2,0)	5950.7	5536.86	5956.39	5.69	6039.18	88.48
(0,2,1)		5814.05	6216.38		6282.67	
(2,0,0)	6892.6	6946.97	6918.75	26.15	6873.52	19.08
(1,0,1)		7203.01	7165.74		7104.98	
(0,5,0)	7307.6	6677.40	7293.66	13.94	7654.60	347.00
(1,3,0)	7461.3	6917.54	7463.19	1.89	7496.90	35.60
(0,0,2)		7566.83	7520.40		7445.88	
(0,3,1)		7163.52	7668.28		7804.90	
(2,1,0)		7819.14	8051.31		8053.47	
(1,1,1)		8073.21	8283.16		8277.37	
(0,1,2)		8436.68	8625.62		8612.06	
(1,4,0)	8966.0	8365.77	8958.92	7.08	9155.23	189.23
(0,6,0)	9189.1	8538.55	9192.23	3.13	9456.24	267.14
(0,4,1)		8675.62	9240.06			
(2,2,0)		8935.49	9349.88			
(1,2,1)		9160.35	9555.23			
(0,2,2)		9498.23	9874.40			
(3,0,0)		10 274.92	10 257.40			
(2,0,1)			10,445.92			
(1,5,0)		10 025.08	10 619.88			
(1,0,2)		10 830.79	10 771.57			
(2,3,0)		10 304.2	10 834.19			
(0,5,1)		10 291.02	10 875.44			
(1,3,1)		10 512.28	11 024.87			
(0,7,0)		10 372.88	11 063.00			
(0,0,3)		11 224.51	11 159.93			
(0,3,2)		10 798.64	11 282.62			
(3,1,0)		11 162.11	11 376.88			
(2,1,1)		10 481.94	11 551.32			
(1,1,2)		11 690.96	11 866.75			
(0,1,3)			12 243.84			
(2,4,0)		11 674.50	12 252.23			
(1,4,1)		11 910.91	12 471.77			
(1,6,0)		11 900.87	12 530.17			
(3,2,0)			12 663.71			

^aReference 13.^bReference 32.

$\Pi/{}^3\Sigma^-$ and $\Pi/a^1\Delta$ intersections at large N–H bond distances, however, the X^2A'' state correlates to the $\text{NH}(X^3\Sigma^-)+\text{H}$ and the A^2A' state correlates to $\text{NH}(a^1\Delta)+\text{H}$. This feature is consistent with the PES of Qu *et al.*³⁷

The lower panel of Fig. 3 shows the dependence of the electronic matrix elements $\langle X^2A''|\hat{L}_z|A^2A'\rangle$, $\langle X^2A''|\hat{L}_z^2|A^2A''\rangle$, and $\langle A^2A'|\hat{L}_z^2|A^2A'\rangle$ on the N–H bond length in linearity with the other N–H fixed at $1.9a_0$ (note that $\langle X^2A''|\hat{L}_z|A^2A'\rangle$ is imaginary and its absolute value is thus used.) The values of these elements are almost a constant (~ 1) for $R_{\text{NH}_1} < 3.1a_0$

due to quantization of the electronic angular momentum ($L_z=1$ for the Π state), however they change rapidly at about $R_{\text{NH}_1}=3.1a_0$ ($R_{\text{NH}_1}=3.3a_0$ for $\langle A^2A'|\hat{L}_z^2|A^2A'\rangle$) due apparently to the $\Pi/{}^3\Sigma^-$ and $\Pi/a^1\Delta$ intersections. At large N–H bond lengths, they reflect the quantized electronic angular momenta ($L_z=0, 2$).

The upper panel of Fig. 4 displays the bending potentials for NH_2 in the X^2A'' and A^2A' states as functions of bond angle χ_{HNNH} with the bond lengths fixed at $1.9a_0$. It can be seen that these two states are properly degenerate at linearity.

TABLE IV. Calculated ($J=0$) vibrational energy levels (in cm⁻¹) for ND₂(X^2A'') and comparison with available experimental band origins.

(n_1, n_2, n_3)	This work	Expt. ^a	(n_1, n_2, n_3)	This work
(0,0,0)	0.00		(0,6,0)	6381.27
(0,1,0)	1122.25	1108(1110)	(1,4,0)	6672.24
(0,2,0)	2202.24		(0,4,1)	6774.26
(1,0,0)	2362.55		(2,2,0)	6869.67
(0,0,1)	2469.88		(1,2,1)	6933.61
(0,3,0)	3278.44		(3,0,0)	6960.68
(1,1,0)	3477.46		(2,0,1)	6999.01
(0,1,1)	3582.90		(0,2,2)	7071.92
(0,4,0)	4333.93		(1,0,2)	7142.29
(1,2,0)	4559.26		(0,0,3)	7301.38
(0,2,1)	4658.61		(0,7,0)	7371.05
(2,0,0)	4685.49		(1,5,0)	7695.51
(1,0,1)	4758.38		(0,5,1)	7801.88
(0,0,2)	4911.14		(2,3,0)	7924.38
(0,5,0)	5366.90		(1,3,1)	7988.69
(1,3,0)	5625.63		(3,1,0)	8065.88
(0,3,1)	5724.01		(2,1,1)	8100.71
(2,1,0)	5795.84		(0,1,3)	8127.34
(1,1,1)	5865.45		(1,1,2)	8235.72
(0,1,2)	6004.97		(0,8,0)	8334.96

^aReferences 57 and 58.

The calculated barrier to linearity in the X^2A'' state PES is 11 773 cm⁻¹, which is lower than that calculated by Gabriel *et al.*¹³ (11914 cm⁻¹). However, it is in excellent agreement with a recent empirical estimated value 11774 cm⁻¹.¹¹ On the other hand, the well in the A^2A' state PES toward the linear H–N–H geometry is very shallow, making it a quasi-linear molecule. Its barrier height to linearity is only 719 cm⁻¹ which is 26 cm⁻¹ higher than that calculated on the PES of Qu *et al.*³⁷ and 49 cm⁻¹ lower than that calcu-

TABLE V. Calculated ($J=0$) vibrational energy levels (in cm⁻¹) for NHD(X^2A'') and comparison with available experimental band origins.

(n_1, n_2, n_3)	This work	Expt. ^a	(n_1, n_2, n_3)	This work
(0,0,0)	0.00	0	(2,2,0)	7335.83
(0,1,0)	1329.65	1321	(0,6,0)	7481.60
(1,0,0)	2413.97		(1,4,0)	7586.67
(0,2,0)	2616.40		(0,1,2)	7688.58
(0,0,1)	3272.77		(2,0,1)	8010.55
(1,1,0)	3732.10		(1,2,1)	8235.63
(0,3,0)	3895.72		(3,1,0)	8315.48
(0,1,1)	4583.28		(0,4,1)	8355.80
(2,0,0)	4754.18		(2,3,0)	8583.22
(1,2,0)	5012.19		(0,7,0)	8647.10
(0,4,0)	5146.03		(1,5,0)	8787.39
(1,0,1)	5681.65		(1,0,2)	8799.49
(0,2,1)	5857.87		(0,2,2)	8945.38
(2,1,0)	6062.57		(4,0,0)	9194.20
(1,3,0)	6269.27		(2,1,1)	9292.23
(0,5,0)	6371.51		(0,0,3)	9381.55
(0,0,2)	6402.83		(1,3,1)	9470.10
(1,1,1)	6973.54		(0,5,1)	9566.81
(3,0,0)	7017.10		(3,2,0)	9582.47
(0,3,1)	7119.14		(0,8,0)	9737.39

^aReference 58.TABLE VI. Calculated ($J=0$) vibrational energy levels (in cm⁻¹) for N ¹⁵H₂(X^2A'') and comparison with available experimental band origins.

(n_1, n_2, n_3)	This work	Expt. ^a	(n_1, n_2, n_3)	This work
(0,0,0)	0.00	0.00	(0,6,0)	8440.96
(0,1,0)	1502.89	1495.50	(1,4,0)	8949.41
(0,2,0)	2957.04		(0,4,1)	9035.90
(1,0,0)	3223.25	3215.00	(2,2,0)	9246.90
(0,0,1)	3310.91		(1,2,1)	9277.05
(0,3,0)	4390.64		(3,0,0)	9347.33
(1,1,0)	4713.35		(2,0,1)	9352.59
(0,1,1)	4795.63		(0,2,2)	9453.70
(0,4,0)	5782.49		(1,0,2)	9582.78
(1,2,0)	6158.02		(0,7,0)	9700.74
(0,2,1)	6235.73		(0,0,3)	9730.32
(2,0,0)	6351.70		(1,5,0)	10 286.49
(1,0,1)	6387.86		(0,5,1)	10 378.33
(0,0,2)	6569.95		(2,3,0)	10 641.98
(0,5,0)	7132.77		(1,3,1)	10 672.38
(1,3,0)	7572.81		(3,1,0)	10 797.15
(0,3,1)	7652.77		(2,1,1)	10 805.29
(2,1,0)	7824.22		(0,3,2)	10 853.26
(1,1,1)	7858.37		(0,8,0)	10 928.83
(0,1,2)	8029.29		(1,1,2)	11 035.83

^aReference 58.

lated on the PES of Pederson *et al.* As a result, the diagonal RT coupling is important to the vibrational energy levels of A^2A' NH₂, while they only affect highly excited bending states on its ground electronic state.

The lower panel of Fig. 4 presents the variation of the electronic matrix elements $\langle X^2A'' | \hat{L}_z | A^2A' \rangle$, $\langle X^2A'' | \hat{L}_z^2 | X^2A'' \rangle$, and $\langle A^2A' | \hat{L}_z^2 | A^2A' \rangle$ as a function of the bond angle. The element $\langle X^2A'' | \hat{L}_z | A^2A' \rangle$ is found to deviate slightly from

TABLE VII. Calculated ($J=0$) vibrational energy levels (in cm⁻¹) for ND₂(A^2A') and comparison with available experimental band origins.

(n_1, n_2, n_3)	This work	Expt. ^a	(n_1, n_2, n_3)	This work
(0,0,0)	0.00	0	(1,4,0)	6309.39
(0,1,0)	791.38		(0,1,2)	6466.77
(0,2,0)	1679.56		(0,4,1)	6561.76
(1,0,0)	2518.78	2520	(2,2,0)	6667.24
(0,3,0)	2683.43		(1,2,1)	6959.61
(0,0,1)	2872.81		(0,2,2)	7307.20
(1,1,0)	3308.23		(1,5,0)	7369.30
(0,1,1)	3652.09		(3,0,0)	7442.32
(0,4,0)	3779.91		(0,7,0)	7535.90
(1,2,0)	4192.78		(2,3,0)	7674.63
(0,2,1)	4515.04		(0,5,1)	7700.65
(0,5,0)	4947.26		(2,0,1)	7733.01
(2,0,0)	4999.78		(1,3,1)	7936.84
(1,3,0)	5196.28		(1,0,2)	8081.85
(1,0,1)	5323.20		(3,1,0)	8226.93
(0,3,1)	5492.72		(0,3,2)	8257.90
(0,0,2)	5697.08		(0,0,3)	8470.99
(2,1,0)	5786.97		(2,1,1)	8508.94
(1,1,1)	6100.43		(1,6,0)	8575.63
(0,6,0)	6158.19		(2,4,0)	8758.69

^aReference 56.

TABLE VIII. Calculated ($J=0$) vibrational energy levels (in cm^{-1}) for $\text{NHD}(A^2A')$.

(n_1, n_2, n_3)	This work
(0,0,0)	0.00
(0,1,0)	982.43
(0,2,0)	2100.17
(1,0,0)	2668.47
(0,3,0)	3360.79
(1,1,0)	3637.66
(0,0,1)	3684.98
(0,1,1)	4635.04
(0,4,0)	4704.57
(1,2,0)	4783.29
(2,0,0)	5268.77
(0,2,1)	5723.24
(1,3,0)	5978.36
(0,5,0)	6211.97
(2,1,0)	6235.35
(1,0,1)	6332.22
(0,3,1)	6950.51
(0,0,2)	7215.45
(2,2,0)	7263.21
(1,1,1)	7300.27
(1,4,0)	7392.16
(0,6,0)	7750.55
(3,0,0)	7800.31
(0,1,2)	8162.23
(0,4,1)	8271.87
(1,2,1)	8371.73
(2,3,0)	8531.54
(3,1,0)	8756.09
(1,5,0)	8812.63
(2,0,1)	8912.83
(0,2,2)	9217.06
(0,7,0)	9342.40
(1,3,1)	9544.31
(0,5,1)	9738.79
(3,2,0)	9776.77
(2,1,1)	9825.87
(2,2,1)	9879.08
(2,4,0)	9935.10
(4,0,0)	10 264.19
(1,6,0)	10 326.86

TABLE IX. Calculated ($J=0$) vibrational energy levels (in cm^{-1}) for $^{15}\text{NH}_2(A^2A')$.

(n_1, n_2, n_3)	This work
(0,0,0)	0.00
(0,1,0)	1152.34
(0,2,0)	2473.29
(1,0,0)	3497.32
(0,0,1)	3785.36
(0,3,0)	3962.11
(1,1,0)	4636.68
(0,1,1)	4909.53
(0,4,0)	5574.37
(1,2,0)	5941.35
(0,2,1)	6191.19
(2,0,0)	6916.21
(1,0,1)	7151.12
(0,5,0)	7263.84
(1,3,0)	7437.04
(0,0,2)	7494.03
(0,3,1)	7636.78
(2,1,0)	8042.26
(1,1,1)	8262.85
(0,1,2)	8594.28
(1,4,0)	8929.33
(0,6,0)	9153.01
(0,4,1)	9202.58
(2,2,0)	9331.59
(1,2,1)	9527.94
(0,2,2)	9837.63
(3,0,0)	10 253.36
(2,0,1)	10 430.16
(1,5,0)	10 588.62
(1,0,2)	10 745.38
(2,3,0)	10 804.28
(0,5,1)	10 836.11
(1,3,1)	10 986.28
(0,7,0)	11 015.28
(0,0,3)	11 121.87
(0,3,2)	11 240.22
(3,1,0)	11 366.58
(2,1,1)	11 529.71
(1,1,2)	11 835.38
(0,1,3)	12 201.11

unity as the molecule bends. However, the variation of the elements $\langle X^2A'' | \hat{L}_z^2 | X^2A'' \rangle$ and $\langle A^2A' | \hat{L}_z^2 | A^2A' \rangle$ is much more significant. At $R_{\text{NH}_1} = R_{\text{NH}_2} = 1.9a_0$ and $\chi_{\text{HNH}} = 70^\circ$, the values of $\langle X^2A'' | \hat{L}_z^2 | X^2A'' \rangle$ and $\langle A^2A' | \hat{L}_z^2 | A^2A' \rangle$ are 3.01 and 2.79, respectively.

B. Vibrational states of NH_2 and its isotopomers

In this work, we have calculated the ($J=0$) vibrational energy levels with the diagonal RT terms for the X^2A'' and A^2A' states of NH_2 . Table II presents low-lying vibrational energy levels with and without the diagonal RT terms in the X^2A'' electronic state of NH_2 , along with the available experimental band origins. The energy levels are labeled with three vibrational quantum numbers (n_1 , n_2 , and n_3), representing the symmetric stretching, bending, and antisymmetric

stretching modes, respectively. The PES reproduces the fundamental frequencies within a few cm^{-1} , with the largest error of $\sim 20 \text{ cm}^{-1}$ for the antisymmetric stretching mode. The addition of the diagonal RT terms slightly increase the errors for low-lying bending levels, but for high [say, above (0,6,0)] bending energy levels the calculated energies are in a much better agreement with the experimental data.¹³ For instance, the calculated energy for the (0,8,0) level overestimates the experimental value by $\sim 9 \text{ cm}^{-1}$ with the diagonal RT terms, which represents a substantial improvement over the error of 199 cm^{-1} obtained on the same PES without the RT terms. As pointed out by previous authors,^{31,37} the RT effect becomes important for high bending states on the X^2A'' state because their wave functions approach linearity.

The level of agreement with experimental data is not as satisfactory as that reported by Gabriel *et al.*,¹³ whose semi-

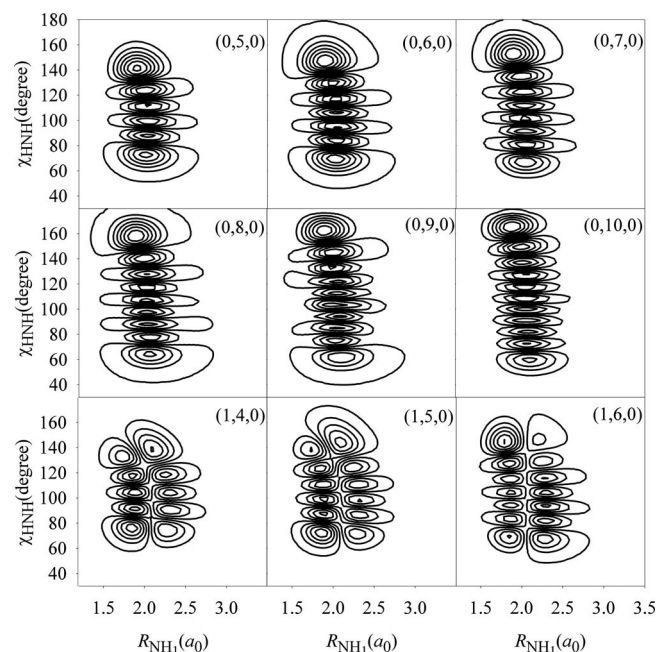


FIG. 5. Contour plots of nine vibrational eigenfunctions of NH₂(A²A'') in internal coordinates (R_{NH_1} , R_{NH_2} , χ_{NNH}).

global PES was also based on MRCI calculations. The excellent agreement in that work is presumably due to the adjustments made in the PES to improve the agreement with experiment.¹⁴ The vibrational energies reported by Jensen *et al.*¹⁴ are less accurate than those reported by Gabriel *et al.*,¹³ but no adjustment was made in their PES. Our errors are also larger than those reported by Jensen *et al.*,¹⁴ which can presumably be attributed to the higher quality *ab initio* method, namely, CCSD(T), used to construct their semiglobal PES. However, the errors are much smaller than those on the global PES of Pederson *et al.*,³² as shown in Table III.

Since the excited A²A' state is quasilinear, it can be expected that its vibrational levels, even the lowest-lying ones, are strongly influenced by the RT terms. In Table III, the calculated ($J=0$) vibrational energies with and without the diagonal RT terms are compared to available experimental band origins,¹³ and the differences are quite dramatic. Even for the lowest-lying levels, ignoring the RT terms will lead to errors on the order of a few hundreds of wave numbers. These large errors, underscoring the importance of the diagonal RT terms, sometimes result in changes in the energy order of the levels. Overall, the errors between the theoretical values and the experimental data are on the order of few to tens of wave numbers, comparable to those on the ground X²A'' state of NH₂ (Table II).

Vibrational energy levels for the fully deuterated ND₂, monodeuterated NHD, and ¹⁵NH₂ were also calculated with the RT terms on our X²A'' and A²A' PESs. The results are listed in Tables IV–IX, respectively, along with available experimental data. The theory-experiment agreement is typically very good. For example, the calculated fundamental symmetric stretching frequency for ND₂(A²A') of 2518.78 cm⁻¹ is only about 1 cm⁻¹ lower than the experimental value of 2520 cm⁻¹.⁵⁶

The assignment of all the vibrational energy levels was

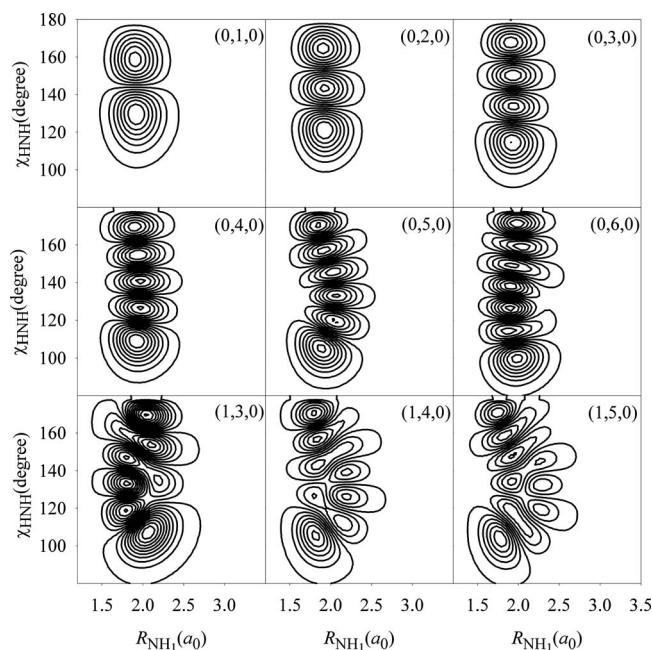


FIG. 6. Contour plots of nine vibrational eigenfunctions of NH₂(A²A') in internal coordinates (R_{NH_1} , R_{NH_2} , χ_{NNH}).

determined by inspecting the nodal structures of their eigenfunctions in internal coordinates (R_{NH_1} , R_{NH_2} , R_{HNNH}). Figures 5 and 6 present the wave functions of NH₂ on the X²A'' and A²A' states in the (0, n_2 , 0) and (1, n_2 , 0) series, respectively. The X²A''-state wave functions shown in Fig. 5 are regular and can be easily assigned. For the A²A' state (Fig. 6), the bending overtones are also assignable, but the combinations are clearly influenced by Fermi resonances. Such Fermi resonances, which have been noted in earlier studies,¹³ signify the complexity in the excited state vibrational spectrum.

IV. CONCLUSIONS

In this publication, we reported a new *ab initio* PES for the first excited electronic state of NH₂ based on Davidson corrected MRCI calculations with a large (aug-cc-PVQZ) basis set. A three-dimensional spline interpolation of more than 20 000 *ab initio* points yielded a globally accurate PES. In addition, elements of the electronic angular momentum operators were also calculated, albeit at a lower level of theory. Besides an excellent prediction of the NH₂ minimal energy structure, the dissociation energy and endoergicity associated with the formation of NH($a^1\Delta$)+H products are in good agreement with experimental data.

To verify the accuracy of the PES, we carried out quantum calculations of the vibrational energy levels ($J=0$) of NH₂ and its isotopomers on both the X²A'' and A²A' states with the diagonal RT terms. The calculated vibrational energy levels are in a reasonably good agreement with experimental band origins, underscoring the importance of diagonal RT terms in the Hamiltonian. The new PESs and their couplings will be used for studying the nonadiabatic RT effects in the state-to-state dynamics of the N(²D)+H₂ insertion reaction.

ACKNOWLEDGMENTS

S.Z., Z.L., and D.X. were supported by the National Natural Science Foundation of China (Grant Nos. 20725312 and 20533060) and the Ministry of Science and Technology (Grant Nos. 2007CB815201). S.Y.L. and H.G. were supported by the U.S. Department of Energy (Grant No. DE-FG02-05ER15694). We would like to thank George Schatz for sending us the potential routines reported in Refs. 17 and 32, and Michael Baer and Gabor Halasz for discussions on the diabaticization of the NH_2 PESs.

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