

Ab initio calculation of the vibronically averaged values for the hyperfine coupling constants in NH₂, NHD, and ND₂

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Vibronically averaged values for $K=0$ and $K=1$ bending levels in the energy range between 0 and 25 000 cm⁻¹ are computed for the ¹⁴N, H, and D atoms in NH₂, NHD, and ND₂. The pure *ab initio* electronic potentials, as well as those derived by fitting of experimentally observed band positions are employed. Effects of vibronic coupling and local perturbations of close-lying levels belonging to different electronic states are discussed.

I. INTRODUCTION

In a previous paper¹ (hereafter referred to as Paper I) we published the results of an *ab initio* calculation of the hyperfine coupling constants (hfcc) for the two lowest-lying electronic states X^2B_1 and A^2A_1 of the NH₂ radical at various molecular geometries (particularly bond angle values). Mean values of the hfcc's in the ($K=0$ and 1) vibronic states of NH₂ lying in the energy range from 0–20 000 cm⁻¹ were also computed. Because one of the aims of Paper I was to investigate with which accuracy the hfcc's can be calculated for a molecule exhibiting the Renner–Teller effect,² we employed in computations of the vibronically averaged values for hfcc's the potential curves obtained by Jungen *et al.*³ (JHM) by fitting the experimentally observed band positions instead of employing the original *ab initio* potentials. In this way we attempted to eliminate the possible error in the description of local interactions of close-lying states by the *ab initio* method (the usual calculation error being of roughly 0.1 eV for electronic transition energy, for example).⁴ In the present study we extend our *ab initio* investigation of the hyperfine structure of the NH₂ spectrum in three directions (i) the results for the mean values of the hfcc's for ND₂ and NHD are presented (ii) the calculations are performed using both the JHM and *ab initio* computed⁵ potential curves (iii) an effort is made to extract those quantities which can be compared directly with the data derived from experimental observations, and furthermore predictions are made for several quantities which can be useful for experimentalists.

II. COMPUTATION OF VIBRONICALLY AVERAGED VALUES FOR HFCC'S

The two sets of the bending potential curves (points refer to purely *ab initio* data, the solid line denotes the experimentally derived curves³) for the X^2B_1 and A^2A_1 states of NH₂, correlating at the linear geometry with the

$1^2\Pi_u$ electronic species are presented in Fig. 1. The energy scale is chosen such that the minima of both the 2B_1 curves correspond to the zero in energy. The bending curves shown in Fig. 1 correspond to the optimized N–H distances and in this way the stretch–bend interaction is effectively incorporated in them. Although the overall agreement between the pure *ab initio* curves and those derived by fitting the experimental data is quite satisfactory, two significant discrepancies can be noted (i) the *ab initio* calculated barrier to linearity in the 2A_1 state (980 cm⁻¹) is by 250 cm⁻¹ higher than that derived from the fitting of measured band positions (730 cm⁻¹), (ii) at strongly bent geometries the *ab initio* bending curves become steeper than their experimentally derived counterparts. Consequences of these differences are discussed in Sec. III of the present paper.

The electronic mean values of the isotropic hfcc and the Cartesian components of the anisotropic hf tensor are published in Paper I to which the reader is referred to for technical details. Figures 2–5 of the present paper show the bond-angle dependence of the components of the anisotropic tensor along the main inertia tensor axes for both the symmetric (NH₂, ND₂) and asymmetric (NHD) isotopomers. The molecule is assumed to lie in the yz plane with the z axis ($\equiv b$) coinciding with the symmetry axis in the C_{2v} point group and y axis ($\equiv a$) becoming the molecular axis at the linear nuclear arrangement. The sign of the A_{ab} component for the hydrogen (deuterium) atom corresponds to its location in the first quadrant of the yz plane. Note a strong geometry dependence of most of the quantities presented in Figs. 2–5 (as discussed in detail in Paper I), the exception representing the hfcc's for the nitrogen atom in the 2B_1 state.

The vibronic energy levels, the corresponding wave functions and the matrix elements of the hfcc's are calculated employing the approach described in detail elsewhere.^{4,6,7} The Hamiltonian of Bunker and Landsberg,^{8,9} allowing for a treatment of the large amplitude bending vibrations and incorporating the leading part of the bend–stretch interaction is adjusted to the problem of two electronic states interacting strongly via the Renner–Teller effect. Thereby it is assumed that the stretching vibrations,

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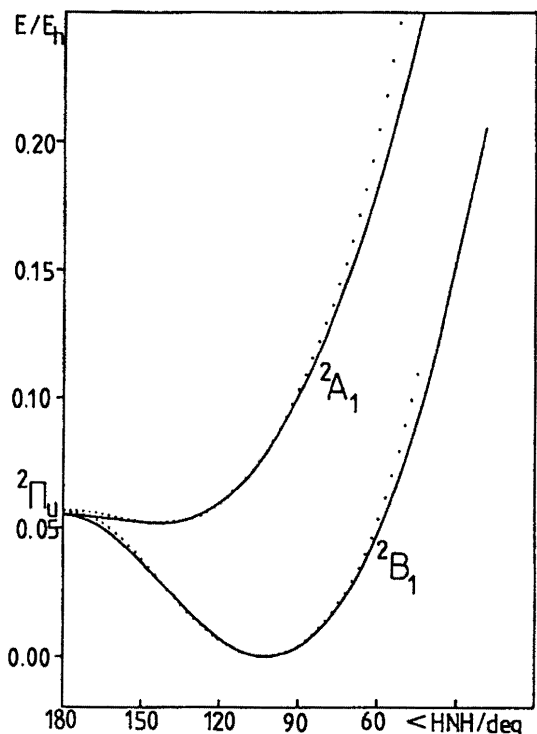


FIG. 1. Two sets of the bending potential curves employed in the present work. Full lines: potentials derived by Jungen *et al.* (Ref. 3) by fitting experimentally observed bond positions; dotted lines: *ab initio* potentials (Ref. 5).

as well as the rotations around the axes orthogonal to the axis a ($\equiv y$ axis in the present case) can be separated. The remaining degrees of freedom (electronic, bending, and a axis rotations) are treated simultaneously. The corre-

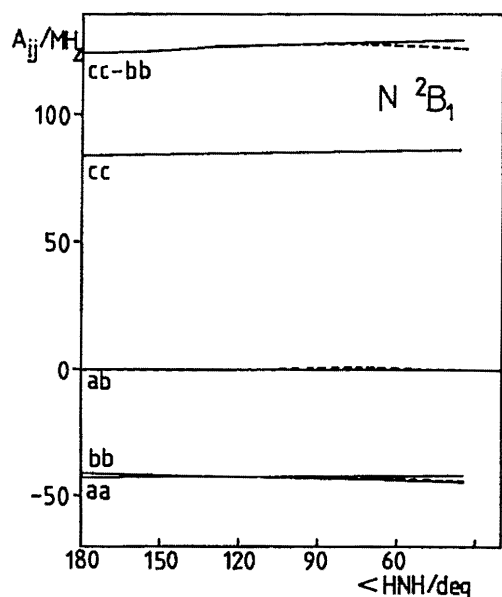


FIG. 2. Bond angle dependence of the components of the hyperfine tensor for the nitrogen atom in the 2B_1 electronic state of NH₂. Full lines: along the principle inertia axes (pia) of NH₂; dashed lines: along pia of NHD.

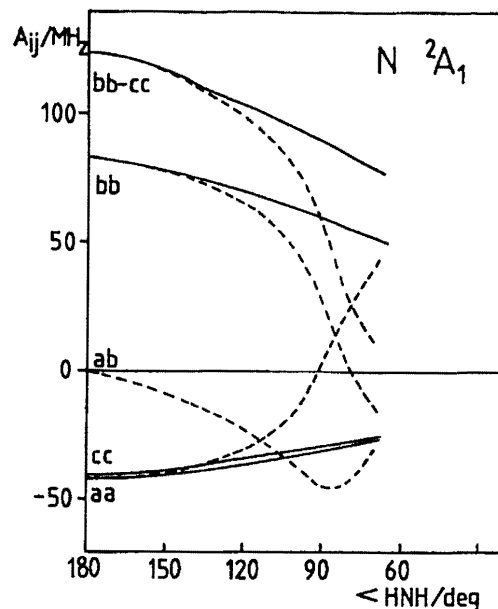


FIG. 3. Bond angle dependence of the anisotropic coupling constants for ¹⁴N atom in the 2A_1 electronic state. Full lines: in pia system of NH₂; dashed lines: in pia system of NHD.

sponding part of the Hamiltonian can be written in the form

$$H = H_e - \frac{1}{2} \left[T_1(\rho) \frac{\partial^2}{\partial \rho^2} + T_2(\rho) \frac{\partial}{\partial \rho} + T_3(\rho) \frac{\partial^2}{\partial \phi^2} + T_4(\rho) \right], \quad (1)$$

where H_e represents the electronic part of the Hamiltonian, ρ is the bending coordinate ($\rho = \pi - \text{bond angle}$), and ϕ is

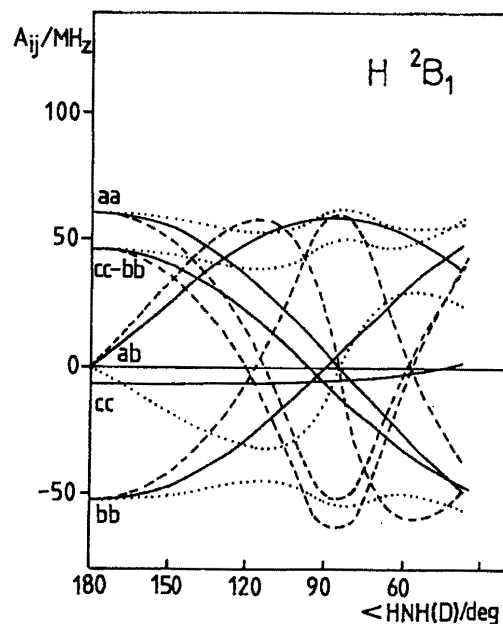


FIG. 4. Anisotropic hfcc's for the hydrogen atom in the 2B_1 electronic state of NH₂, along the pia of NH₂ (full lines) and NHD (dashed and dotted lines). Dashed lines correspond to the ¹H isotope, dotted line functions (multiplied by the factor 0.153 506) to deuterium.

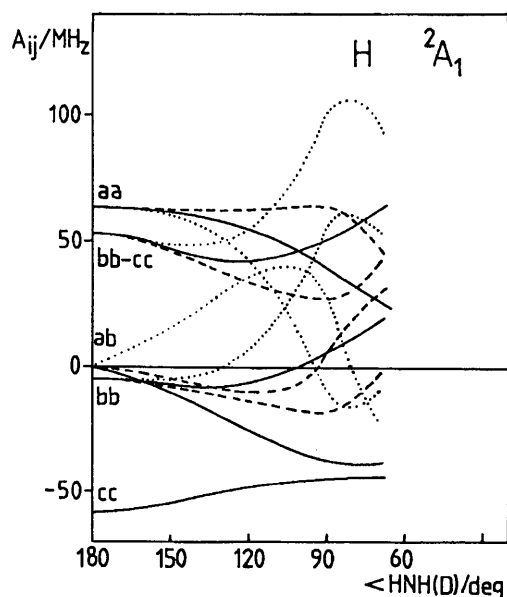


FIG. 5. Anisotropic hfcc's for the hydrogen atom in the 2A_1 electronic state along the *a* axis of NH₂ (full lines) and NHD (dashed and dotted lines). For key to notation see also Fig. 4.

the angle between the molecular plane and a space fixed plane and defines rotations around the *a* axis. The T_i functions, whose form depends on the choice of the moving coordinate system bound to the molecule and on the internal coordinates employed, are assumed to be dependent on ρ in order to enable a treatment of the large-amplitude vibrations, and in the case when the stretch-bend interaction is taken into account they also vary with the stretching coordinate. The actual form of the coefficients T_1 – T_4 employed in the present paper are given in Refs. 8 and 9. Other terms as, e.g., those describing the spin-orbit coupling, are neglected in the present study.

The eigenfunctions of the Hamiltonian (1) for the two electronic state problem in question are assumed to be expanded in a suitable basis

$$\Psi = \psi^\alpha \sum_i c_i^\alpha \Phi_i^\alpha(\rho, \phi) + \psi^\beta \sum_i c_i^\beta \Phi_i^\beta(\rho, \phi), \quad (2)$$

where ψ^α , ψ^β are the electronic basis functions and $\Phi_i^\alpha(\rho, \phi)$ suitable rovibronic functions describing the bending vibrations and the rotations around the *a* axis. We assume the latter functions to have the form

$$\Phi_i(\rho, \phi) = e^{iK\phi} \chi_i(\rho), \quad (3)$$

where K is the quantum number corresponding to the projection of the total angular momentum (excluding spin) onto the *a* axis. Thus, like in most studies in which the Renner-Teller effect has been treated (see e.g., Ref. 10), the assumption is made that K is a good quantum number in spite of the fact that the NH₂ molecule has (at bent nuclear arrangements) significantly pronounced asymmetric-top characteristics. This approximation has been discussed, e.g., by Carter and Handy.¹¹ (Thus we

identify in the present study K with the asymmetric-top quantum number K_a .)

The expansion coefficients $c_i^{\alpha/\beta}$ in Eq. (2) are determined by applying the variation principle. After integrating over the electronic coordinates and ϕ , and neglecting the derivatives of the electronic wave functions with respect to ρ , the matrix elements of the Hamiltonian (1) appearing in the secular equation become

$$H_{ij}^{\alpha\beta} = \langle \chi_i^\alpha | H^{\alpha\beta} | \chi_j^\beta \rangle, \quad (4)$$

where $H^{\alpha\beta}$ is the effective operator acting still only on the bending basis functions. It has the form

$$H^{\alpha\beta} = \left[V^{\alpha\beta} - \frac{1}{2} \left(T_1^{\alpha\beta} \frac{\partial^2}{\partial \rho^2} + T_2^{\alpha\beta} \frac{\partial}{\partial \rho} - K^2 T_3^{\alpha\beta} + T_4^{\alpha\beta} \right) \right] \delta_{\alpha\beta} - (iK_\phi B^{\alpha\beta} + \frac{1}{2} \phi C^{\alpha\beta}) T_3^{\alpha\beta} \quad (5)$$

where

$$V^{\alpha\beta} = \langle \psi^\alpha | H | \psi^\beta \rangle,$$

$$B^{\alpha\beta} = \langle \psi^\alpha | \partial \psi^\beta / \partial \phi \rangle, \quad (6)$$

$$C^{\alpha\beta} = \langle \psi^\alpha | \partial^2 \psi^\beta / \partial \phi^2 \rangle,$$

and the coefficients T_i are generally different for α and β .

The actual form of expression (5) depends on the choice of the electronic basis functions. Two sets of the electronic functions are used most frequently.

(i) The electronic wave functions for the component electronic states calculated in the Born-Oppenheimer approximation, $\psi^+({}^2A_1)$, and $\psi^-({}^2B_1)$. In the linear limit ($\rho \rightarrow 0$) the angular parts of these functions have the form $\psi^+ \sim \cos \Lambda(\Theta - \phi)$, $\psi^- \sim i \sin \Lambda(\Theta - \psi)^2$, where Θ represents the coordinate conjugate to the projection of the electronic angular momentum onto the *a* axis and Λ ($=1$ in the present case) is the corresponding quantum number. From symmetry reasons B^{++} , B^{--} , C^{+-} , and C^{-+} then vanish and the remaining B and C terms defined by Eqs. (6) can in a good approximation (because they appear in the secular equation weighted by the factor T_3 being proportional to $1/\rho^2$ as $\rho \rightarrow 0$) be replaced by their $\rho \rightarrow 0$ asymptotic values, $B^{-+} = \Lambda = -B^{+-}$, $C^{-+} = C^{+-} = \Lambda$ (see, e.g., Ref. 6). (Note that in contrast to the Refs. 4 and 6, we define now the function ψ^- to be imaginary in order to obtain the secular equation with only real elements.) Expression (5) reduces then to

$$H^{\alpha\beta} = \left[V^{\alpha\beta} - \frac{1}{2} \left[T_1^{\alpha/\beta} \frac{\partial^2}{\partial \rho^2} + T_2^{\alpha/\beta} \frac{\partial}{\partial \rho} - (K^2 + \Lambda^2) T_3^{\alpha/\beta} + T_4^{\alpha/\beta} \right] \right] \delta_{\alpha\beta} + K\Lambda T_3^{\alpha\beta} (1 - \delta_{\alpha\beta}) \quad (7)$$

[$\alpha, \beta = +$ or $-$; α/β means α or β ; $T_3^{\alpha\beta} = (T_3^\alpha + T_3^\beta)/2$], i.e., to the usual form employed by most authors [see Eq. (13) of Ref. 10].

(ii) A new electronic basis ψ_1 , ψ_2 can be derived by a unitary transformation

$$\psi_1 = 1/\sqrt{2}(\psi^+ + \psi^-), \quad \psi_2 = 1/\sqrt{2}(\psi^+ - \psi^-). \quad (8)$$

In the linear limit ψ_1 and ψ_2 become eigenfunctions of the Π electronic state, $\lim_{\rho \rightarrow 0} \psi_1 \sim \exp[i\Lambda(\theta - \phi)]$, $\lim_{\rho \rightarrow 0} \psi_2 \sim \exp[-i\Lambda(\theta - \phi)]$. Replacing again the corresponding B and C elements with their $\rho \rightarrow 0$ asymptotic values we obtain for the effective Hamiltonian (5) the expression

$$H^{\alpha\beta} = \left[\frac{V^+ + V^-}{2} - \frac{1}{2} \left[\frac{T_1^+ + T_1^-}{2} \frac{\partial^2}{\partial \rho^2} + \frac{T_2^+ + T_2^-}{2} \frac{\partial}{\partial \rho} - (K \mp \Lambda)^2 \frac{T_3^+ + T_3^-}{2} + \frac{T_4^+ + T_4^-}{2} \right] \right] \delta_{\alpha\beta} + \left[\frac{V^+ - V^-}{2} - \frac{1}{2} \left[\frac{T_1^+ - T_1^-}{2} \frac{\partial^2}{\partial \rho^2} + \frac{T_2^+ - T_2^-}{2} \frac{\partial}{\partial \rho} - (K^2 + \Lambda^2) \frac{T_3^+ - T_3^-}{2} + \frac{T_4^+ - T_4^-}{2} \right] \right] (1 - \delta_{\alpha\beta}). \quad (9)$$

$\alpha, \beta = 1$ or 2 , $(K - \Lambda)^2$ and $(K + \Lambda)^2$ in the first expression on the right-hand side corresponds to H^{11} and H^{22} , respectively. Expression (9) is essentially equal to Eq. (15) or Ref. 10 (in the last one the terms $T_i^+ - T_i^-$ vanishing at $\rho \rightarrow 0$ are omitted). The convenience of using this electronic basis consists in the fact that the off-diagonal element of Eq. (7) becoming singular in the linear limit ($\lim_{\rho \rightarrow 0} T_3 \sim 1/\rho^2$) is now absorbed in the diagonal elements where it is exactly canceled by other singular terms when $\rho \rightarrow 0$.

As the basis functions for representing the bending motion we employ in the present study (i) the eigenfunctions of a two-dimensional harmonic oscillator⁶ or (ii) the trigonometric series in ρ .⁷ The bending potentials as well as the coefficients T_i in the kinetic energy expression are fitted by polynomials or trigonometric series in ρ .

Note that the secular equation in the basis (i) has off-diagonal elements being proportional to K . That means that for $K=0$ there is no coupling between the vibronic states belonging to different electronic states. Furthermore, the levels differing only in the sign of K have the same energy and their wave functions are of the form

$$\Psi_{(+K)} = e^{i|K|\phi} \left[\psi^+ \sum_i c_{iK}^+ \chi_{iK}(\rho) + \psi^- \sum_i c_{iK}^- \chi_{iK}(\rho) \right] \equiv e^{i|K|\phi} (\psi^+ f_K^+ + \psi^- f_K^-), \quad (10a)$$

$$\Psi_{(-K)} = e^{-i|K|\phi} \left[\psi^+ \sum_i c_{iK}^+ \chi_{iK}(\rho) - \psi^- \sum_i c_{iK}^- \chi_{iK}(\rho) \right] \equiv e^{-i|K|\phi} (\psi^+ f_K^+ - \psi^- f_K^-). \quad (10b)$$

In Paper I we published the mean values for the Cartesian components of the hyperfine tensor (in its phenomenological form) in the $K=0$ and 1 vibronic states of NH₂. While some of them ($A_{yy} \equiv A_{aa}$, as well as $A_{xx} \equiv A_{cc}$ and $A_{zz} \equiv A_{bb}$ for $K=1$, calculated from $\langle K=1 | A_{aa} | K=1 \rangle = -\langle K=1 | A_{bb} + A_{cc} | K=1 \rangle$ and $\langle K=-1 | A_{bb} - A_{cc} | K=+1 \rangle$ are directly correlated to the corresponding parts of the effective hf Hamiltonians used in the experimental studies, the other ($\langle K=0 | A_{bb} | K=0 \rangle$, $\langle K=0 | A_{cc} | K=0 \rangle$ and $\langle K=0, 1 | A_{ab} | K=0, 1 \rangle$ see Tables II and III of Paper

I) are hypothetical and serve only to give a picture of variation of the hfcc's from one vibronic level to another as consequence of the geometry dependence of the electronically averaged hfcc's and the change in the composition of the vibronic wave function. In the present paper we are dealing instead with the irreducible components of the anisotropic hf tensor and we present the vibronic matrix elements between the states connected by proper selection rules giving rise to the allowed transitions between the components of the hyperfine manifolds

$$\langle K | A_{iso} | K \rangle, \quad (11a)$$

$$\langle K | A_{aa} | K \rangle = -\langle K | A_{bb} + A_{cc} | K \rangle, \quad (11b)$$

$$\langle K | A_{ac} \pm iA_{ab} | K \pm 1 \rangle, \quad (11c)$$

$$\langle K | A_{cc} - A_{bb} \pm 2iA_{bc} | K \pm 2 \rangle. \quad (11d)$$

Relation (11b) holds because the anisotropic part of the hf Hamiltonian is represented by a traceless tensor. In the present study we employ the electronic matrix elements for the hfcc's reported in Paper I which are diagonal with respect to two species in question (${}^2B_1, {}^2A_1$), i.e., we neglect the term A_{bc} (ϵB_1) having nonvanishing value between 2B_1 and 2A_1 electronic wave functions for both N and H atoms, as well as A_{ac} ($\epsilon A''$) for H atom, connecting the states ${}^2A''$ and ${}^2A'$ which correlate in the lower C_s point group to 2B_1 and 2A_1 of C_{2v} , respectively. These neglected terms connecting vibronic states with energy differences of generally at least some hundreds wave numbers are expected to have nonsignificant effects on the hyperfine structure of spectra. The terms A_{ac} (ϵA_2) and A_{ab} (ϵB_2) for the nitrogen atom vanish by symmetry reasons.

The results of computation of the vibronic matrix elements for the hfcc are presented in Tables I–VI. The data given in Tables I–IV for NH₂, NHD, and ND₂ are generated in calculations in which the potential curves and the dependence on the equilibrium N–H bond lengths published by JHK³ are employed. In Table V are presented pure *ab initio* results for NH₂, obtained by employing the bending potential curves and the bond lengths values published in Ref. 5. In Tables I and II are given the results for the isotropic hfcc and the irreducible components of the anisotropic hf tensor in NH₂. In Tables III–V are presented only the results for A_{iso} . The other values are placed in the Physics Auxiliary Publication Service (PAPS).¹² Finally, the results of both sets of calculations are compared in Table VI with available experimental findings.

III. DISCUSSION

Two sets of the vibronic energies for NH₂ are presented in Table I. The first one consists of the experimentally derived values (Refs. 13–18) employed by JHM for constructing the effective bending potential curves shown in Fig. 1; the second set represents the results calculations in which these curves have been employed. As already shown in a previous study,⁶ if the same input parameters (potentials, N–H bond lengths) are used, with our vibronic treatment, briefly described in Sec. II, we are able to reproduce all the vibronic levels published by JHK with

TABLE I. Vibronically averaged values for the hfcc's in the ${}^2\Pi_u$ electronic state of NH₂, computed by employing JHM potential curves (Ref. 3). (a) $K=0$ vibronic levels. (b) $K=1$ vibronic levels. (The values hfcc's are given in Tables I, III, IV, V, and VI with two decimals places to show their variation from one vibronic level to another (and for the sake of uniformity); actually, only two or three digits are significant.)

(a)			N		H	
	E_{expt}^a (cm ⁻¹)	E (cm ⁻¹)	A_{iso} (MHz)	A_{aa} (MHz)	A_{iso} (MHz)	A_{aa} (MHz)
ν_2						
0 ⁻	0	0	22.40	-42.43	-62.23	19.65
1 ⁻	1 497	1 495	22.85	-42.40	-62.18	19.68
2 ⁻	2 961	2 959	23.38	-42.38	-62.24	19.87
3 ⁻	4 391	4 389	23.98	-42.35	-62.42	20.23
4 ⁻		5 785	24.66	-42.33	-62.72	20.79
5 ⁻		7 141	25.43	-42.32	-63.13	21.56
6 ⁻		8 453	26.28	-42.30	-63.65	22.57
7 ⁻		9 717	27.15	-42.29	-64.22	23.60
8 ⁻		10 946	27.74	-42.28	-64.61	23.98
0 ⁺ (1)	11 123	11 126	103.77	-39.46	11.51	60.53
9 ⁻		12 175	27.75	-42.26	-64.58	22.96
1 ⁺ (3)	12 281	12 279	110.39	-39.22	14.48	59.83
10 ⁻		13 448	27.29	-42.23	-64.16	20.80
2 ⁺ (5)	13 619	13 615	123.10	-38.70	26.56	58.72
11 ⁻		14 782	26.70	-42.21	-63.61	18.31
3 ⁺ (7)	15 120	15 120	135.79	-38.18	38.30	57.52
12 ⁻		16 176	26.14	-42.19	-63.03	15.86
4 ⁺ (9)	16 742	16 753	147.98	-37.70	48.30	56.29
13 ⁻		17 621	25.63	-42.17	-62.44	13.34
5 ⁺ (11)	18 480	18 484	159.87	-37.24	56.80	55.04
14 ⁻		19 109	25.18	-42.15	-61.83	11.32
6 ⁺ (13)	20 285	20 293	171.48	-36.80	64.20	53.76
15 ⁻		20 631	24.76	-42.14	-61.17	9.18
7 ⁺ (15)	22 176	22 164	182.65	-36.37	70.93	52.48
16 ⁻		22 181	24.39	-42.12	-60.45	7.10
17 ⁻		23 754	24.05	-42.11	-59.64	5.06
8 ⁺ (17)	24 087	24 086	193.20	-35.94	77.37	51.19
18 ⁻		25 343	23.77	-42.10	-58.72	3.04
9 ⁺ (19)		26 050	203.12	-35.51	83.72	49.91
19 ⁻		26 943	23.54	-42.09	-57.67	1.03

(b)			N			H		
	E_{expt}^a (cm ⁻¹)	E (cm ⁻¹)	A_{iso} (MHz)	A_{aa} (MHz)	$A_{bb}-A_{cc}$ (MHz)	A_{iso} (MHz)	A_{aa} (MHz)	$A_{bb}-A_{cc}$ (MHz)
ν_2								
0 ⁻	24	24	22.38	-42.43	128.31	-62.22	19.59	6.25
1 ⁻	1 523	1 521	22.83	-42.40	128.19	-62.16	19.61	6.49
2 ⁻	2 990	2 987	23.35	-42.37	128.08	-62.22	19.78	6.88
3 ⁻	4 424	4 422	23.95	-42.35	127.95	-62.39	20.11	7.41
4 ⁻		5 822	24.62	-42.33	127.83	-62.66	20.61	8.11
5 ⁻		7 185	25.40	-42.31	127.69	-63.01	21.34	9.00
6 ⁻		8 504	26.36	-42.29	127.51	-63.42	22.41	10.21
7 ⁻		9 761	28.08	-42.26	127.21	-63.66	24.58	12.48
8 ⁻		10 859	37.95	-41.97	125.49	-57.70	33.71	21.47
0 ⁺ (2)	11 318	11 320	97.54	-39.64	115.94	6.79	53.41	38.90
9 ⁻		11 845	48.90	-41.57	123.79	-48.26	37.82	25.58
1 ⁺ (4)	12 637	12 649	82.09	-40.20	118.67	-10.36	43.23	30.32
10 ⁻		12 987	66.88	-40.82	121.08	-28.30	39.67	27.34
11 ⁻		14 044	53.80	-41.21	123.24	-37.83	29.26	17.76
2 ⁺ (6)	14 358	14 343	104.67	-39.36	115.37	9.29	48.65	36.35
12 ⁻		15 449	34.91	-41.87	126.23	-55.20	20.04	9.28
3 ⁺ (8)	15 890	15 894	134.28	-38.22	111.10	36.85	53.87	42.53
13 ⁻		16 884	29.67	-42.03	127.07	-59.20	16.01	5.66
4 ⁺ (10)	17 580	17 577	150.35	-37.60	109.03	49.87	54.15	44.32
14 ⁻		18 358	28.17	-42.05	127.33	-59.63	13.39	3.40
5 ⁺ (12)	19 343	19 350	161.98	-37.16	107.69	57.70	52.96	44.83
15 ⁻		19 868	28.53	-42.01	127.31	-58.40	11.48	1.84
6 ⁺ (14)	21 205	21 184	163.92	-37.07	107.75	56.78	49.00	42.48
16 ⁻		21 417	37.78	-41.64	126.01	-49.71	12.11	3.13
17 ⁻		22 941	42.36	-41.45	125.42	-45.10	11.12	2.75
7 ⁺ (16)		23 125	169.88	-36.81	107.16	59.44	46.67	41.87
18 ⁻		24 539	26.24	-42.01	127.77	-57.29	4.71	-3.67
8 ⁺ (18)	25 050	25 054	195.83	-35.81	103.67	78.78	49.78	47.35
19 ⁻		26 139	24.83	-42.05	128.01	-57.26	2.39	-5.62
9 ⁺ (20)	27 025	27 034	206.39	-35.35	102.32	85.74	48.75	48.33

^aExperimentally derived values (Refs. 13-18 employed by JHM) (Ref. 3). Notation for ν_2 : $\nu_2^{+/-\text{bent}}$ (ν_2^{in}).

TABLE II. Vibronic matrix elements for the $A_{bb}-A_{cc}$ irreducible component of the anisotropic hf tensor between the $K=0$ vibronic states $v_2' = 0^-$ and $v_2' = 2^+(5)$ and individual $K=2$ states of NH₂ calculated by formula (15).

v_2	$K=2$		$\langle K=0, v_2' A_{bb} - A_{cc} K=2, v_2 \rangle$ (MHz)			
	E_{expt}^a (cm ⁻¹)	E_{JHM} (cm ⁻¹)	$v_2' = 0^-$		$v_2' = 2^+(5)$	
			N	H	N	H
0 ⁻	94.43	94.10	-128.2	-6.00	-0.30	-0.13
1 ⁻	1 600.59	1 597.71	1.24	8.26	0.49	0.20
2 ⁻	3 075.39	3 072.20	0.25	0.00	0.38	0.15
3 ⁻	4 519.57	4 517.39	-0.15	0.11	0.13	0.05
4 ⁻		5 932.20	-0.01	-0.01	-0.92	-0.35
5 ⁻		7 314.46	-0.04	-0.01	-1.41	-0.52
6 ⁻		8 659.72	-0.00	-0.00	-0.58	0.13
7 ⁻		9 955.68	0.00	0.00	0.31	1.44
8 ⁻		11 154.85	-0.04	-0.01	9.37	4.28
0 ⁺ (3)	11 673.9	11 671.92	-0.23	-0.05	-4.91	-1.58
9 ⁻		12 335.48	0.12	0.02	15.28	6.77
1 ⁺ (5)	13 156.5	13 134.40	-0.32	-0.05	42.85	16.79
10 ⁻	13 624.4	13 608.70	0.22	0.03	-66.57	-27.40
11 ⁻	14 641.3	14 636.49	0.28	0.03	-59.98	-24.84
2 ⁺ (7)	15 029.5	15 032.45	0.32	0.04	-14.83	-5.75
12 ⁻		16 116.97	-0.16	-0.01	-29.24	-12.15
3 ⁺ (9)	16 619.4	16 635.41	0.33	0.02	20.07	7.03
13 ⁻		17 597.81	-0.09	-0.00	17.39	7.93
4 ⁺ (11)	18 269.7 ^b	18 367.60	0.25	0.00	-16.11	-6.89
14 ⁻		19 104.87	-0.06	0.00	-12.08	-5.50
5 ⁺ (13)	20 191.9	20 176.64	-0.16	0.01	-13.27	-5.74
15 ⁻		20 647.28	0.05	-0.00	-8.48	-3.92
6 ⁺ (15)	22 018.6	22 007.41	-0.07	0.01	12.63	5.60
16 ⁻		22 253.63	-0.05	-0.00	3.08	1.51
17 ⁻		23 706.73	-0.02	0.00	-10.52	-4.76
7 ⁺ (17)		24 062.13	0.04	-0.01	3.82	1.63

^aExperimentally observed values (Refs. 13–18) employed by JHM (Ref. 3).

^bObserved level not included in the fitting because of strong anharmonic resonance effects.

the maximal discrepancies not exceeding 1–2 cm⁻¹ in the energy range as large as up to 30 000 cm⁻¹ in spite of quite different computation techniques. While the discrepancies between the calculated term values and their experimental counterparts in NH₂ are within maximally 20 cm⁻¹, the agreement is significantly worse for NHD and ND₂ (Tables III and IV). This is not surprising because the bending potentials derived by fitting the Bunker–Landsberg Hamiltonian are not quite isotopically invariant⁸ as a consequence of the fact that, e.g., the equilibrium bond lengths involved in the kinetic energy expression represent averages over the stretching vibrational states. On the other hand, the relatively large discrepancies could be an indication that the effectively one-dimensional treatment of the bending motion in the framework of the semirigid bender model of Bunker and Landsberg cannot account satisfactorily for the existing bend–stretch coupling.

If the pure *ab initio* potential curves are employed instead of those derived by JHM the discrepancies between computed vibronic energies and the corresponding experimental data become significantly worse with the differences

TABLE III. Vibronically averaged values for the isotropic hfcc in the ²Π_u electronic states of NHD computed by employing JHM potential curves. (a) $K=0$ vibronic states. (b) $K=1$ vibronic states.

v_2	E_{expt}^a (cm ⁻¹)	E (cm ⁻¹)	A_{iso} (MHz)		
			N	H	D
0 ⁻		0	22.37	-62.24	-9.55
1 ⁻		1 312	22.75	-62.17	-9.54
2 ⁻		2 601	23.19	-62.20	-9.55
3 ⁻		3 865	23.69	-62.32	-9.57
4 ⁻		5 103	24.25	-62.53	-9.60
5 ⁻		6 313	24.87	-62.83	-9.64
6 ⁻		7 491	25.57	-63.21	-9.70
7 ⁻		8 632	26.35	-63.70	-9.78
8 ⁻		9 735	27.17	-64.24	-9.86
9 ⁻		10 803	27.81	-64.68	-9.93
0 ⁺ (1)		11 131	102.27	9.96	1.53
10 ⁻		11 861	27.96	-64.76	-9.94
1 ⁺ (3)		12 105	106.85	10.74	1.65
11 ⁻		12 947	27.61	-64.45	-9.89
2 ⁺ (5)		13 225	118.24	21.63	3.32
12 ⁻		14 081	27.06	-63.95	-9.82
3 ⁺ (7)		14 492	129.87	32.88	5.05
13 ⁻		15 266	26.51	-63.42	-9.74
4 ⁺ (9)	15 868	15 872	140.93	42.65	6.55
14 ⁻		16 496	26.01	-62.90	-9.66
5 ⁺ (11)	17 313	17 341	151.64	51.03	7.83
15 ⁻		17 764	25.56	-62.38	-9.58
6 ⁺ (13)		18 881	162.12	58.30	8.95
16 ⁻		19 065	25.16	-61.84	-9.49
17 ⁻		20 392	24.79	-61.27	-9.41
7 ⁺ (15)		20 478	172.36	64.76	9.94
18 ⁻		21 742	24.45	-60.65	-9.31
8 ⁺ (17)		22 122	182.23	70.72	10.86
19 ⁻		23 110	24.14	-59.97	-9.21
9 ⁺ (19)		23 805	191.61	76.44	11.73

v_2	E_{expt}^b (cm ⁻¹)	E (cm ⁻¹)	A_{iso} (MHz)		
			N	H	D
0 ⁻		19	22.36	-62.23	-9.55
1 ⁻		1 333	22.74	-62.16	-9.54
2 ⁻		2 624	23.18	-62.19	-9.55
3 ⁻		3 890	23.67	-62.30	-9.56
4 ⁻		5 131	24.22	-62.49	-9.59
5 ⁻		6 345	24.84	-62.77	-9.64
6 ⁻		7 528	25.54	-63.12	-9.69
7 ⁻		8 676	26.38	-63.51	-9.75
8 ⁻		9 777	27.69	-63.86	-9.80
9 ⁻		10 779	33.19	-61.66	-9.47
0 ⁺ (2)		11 258	97.06	5.74	0.88
10 ⁻		11 661	48.61	-48.75	-7.48
1 ⁺ (4)		12 336	70.02	-23.04	-3.54
11 ⁻		12 642	76.80	-18.95	-2.91
12 ⁻		13 478	44.70	-47.37	-7.27
2 ⁺ (6)		13 813	109.35	13.80	2.12
13 ⁻		14 656	33.59	-57.18	-8.78
3 ⁺ (8)		15 137	129.67	33.04	5.07
14 ⁻		15 872	30.03	-59.63	-9.15
4 ⁺ (10)	16 546	16 566	142.56	44.00	6.75
15 ⁻		17 127	29.09	-59.63	-9.15
5 ⁺ (12)		18 037	151.43	50.28	7.72
16 ⁻		18 418	30.78	-57.31	-8.80
6 ⁺ (14)		19 624	131.47	30.93	4.75
17 ⁻		19 755	60.80	-30.58	-4.69
18 ⁻		21 052	32.43	-54.31	-8.34
7 ⁺ (16)		21 292	169.55	61.37	9.42
19 ⁻		22 420	26.15	-58.76	-9.02
8 ⁺ (18)		22 951	185.03	72.15	11.08
20 ⁻		23 799	25.18	-58.63	-9.00

^aReference 19, $N_{KaKc}=0_{00}$.

^bReference 19, $N_{KaKc}=1_{10}$.

TABLE IV. Vibronically averaged values for the isotropic hfcc in the $^2\Pi_u$ electronic state of ND₂ computed by employing JHM potential curves. (a) $K=0$ vibronic levels. (b) $K=1$ vibronic states.

(a)	ν_2	E_{expt}^a (cm ⁻¹)	E (cm ⁻¹)	A_{iso} (MHz)	
				N	D
0 ⁻			0	22.30	-9.55
1 ⁻			1 098	22.64	-9.54
2 ⁻			2 181	22.98	-9.54
3 ⁻			3 246	23.36	-9.55
4 ⁻			4 294	23.79	-9.57
5 ⁻			5 324	24.26	-9.60
6 ⁻			6 334	24.77	-9.64
7 ⁻			7 321	25.35	-9.68
8 ⁻			8 284	25.98	-9.74
9 ⁻			9 219	26.69	-9.81
10 ⁻			10 123	27.42	-9.89
11 ⁻			11 000	27.99	-9.95
0 ⁺ (1)			11 146	100.81	1.31
12 ⁻			11 870	28.13	-9.96
1 ⁺ (3)			11 926	102.75	0.98
13 ⁻			12 758	27.81	-9.92
2 ⁺ (5)			12 809	112.33	2.37
14 ⁻			13 684	27.29	-9.85
3 ⁺ (7)			13 811	122.76	3.99
15 ⁻			14 648	26.77	-9.78
4 ⁺ (9)	14 844	14 910	132.59	5.42	
16 ⁻		15 648	26.30	-9.71	
5 ⁺ (11)	16 014	16 085	141.97	6.68	
17 ⁻		16 679	25.88	-9.64	
6 ⁺ (13)	17 224	17 321	151.09	7.78	
18 ⁻		17 736	25.50	-9.57	
7 ⁺ (15)	18 588	18 606	160.03	8.75	
19 ⁻		18 815	25.15	-9.50	
20 ⁻		19 914	24.83	-9.43	
8 ⁺ (17)	19 925	19 934	168.81	9.62	

(b)	ν_2	E_{expt}^a (cm ⁻¹)	E (cm ⁻¹)	A_{iso} (MHz)	
				N	D
0 ⁻			13	22.33	-9.55
1 ⁻			1 112	22.63	-9.54
2 ⁻			2 195	22.97	-9.54
3 ⁻			3 262	23.35	-9.55
4 ⁻			4 312	23.77	-9.57
5 ⁻			5 343	24.23	-9.59
6 ⁻			6 356	24.74	-9.63
7 ⁻			7 347	25.31	-9.67
8 ⁻			8 314	25.94	-9.73
9 ⁻			9 254	26.71	-9.79
10 ⁻			10 156	27.94	-9.84
11 ⁻			10 975	34.95	-9.25
0 ⁺ (2)			11 249	97.96	1.05
12 ⁻			11 680	45.20	-8.10
1 ⁺ (4)			12 154	86.76	-0.99
13 ⁻			12 441	54.32	-6.42
2 ⁺ (6)			13 128	72.86	-3.10
14 ⁻			13 329	74.62	-3.13
15 ⁻			14 127	45.42	-7.09
3 ⁺ (8)			14 342	110.41	2.26
16 ⁻			15 130	32.55	-8.86
4 ⁺ (10)	15 399	15 470	131.77	5.33	
17 ⁻		16 154	29.06	-9.25	
5 ⁺ (12)	16 600	16 676	143.55	6.88	
18 ⁻		17 202	28.08	-9.27	
6 ⁺ (14)	17 944	17 937	151.98	7.83	
19 ⁻		18 275	28.78	-9.07	
7 ⁺ (16)		19 237	147.74	7.00	
20 ⁻		19 374	41.67	-7.24	
21 ⁻		20 455	35.70	-7.94	

^aReference 20.

TABLE V. Vibronically averaged values for the isotropic hfcc in the $^2\Pi_u$ electronic state of NH₂ computed by employing the *ab initio* potential curves. (a) $K=0$ vibronic levels. (b) $K=1$ vibronic states.

(a)	ν_2	E (cm ⁻¹)	A_{iso} (MHz)	
			N	H
0 ⁻		0	22.53	-62.30
1 ⁻		1 552	23.13	-62.34
2 ⁻		3 059	23.69	-62.44
3 ⁻		4 539	24.27	-62.63
4 ⁻		5 998	24.96	-62.94
5 ⁻		7 432	25.77	-63.40
6 ⁻		8 835	26.73	-64.01
7 ⁻		10 196	27.72	-64.69
0 ⁺ (1)		11 196	106.73	14.99
8 ⁻		11 528	28.38	-65.16
1 ⁺ (3)		12 405	111.68	16.02
9 ⁻		12 877	28.36	-65.13
2 ⁺ (5)		13 778	123.49	26.85
10 ⁻		14 300	27.89	-64.74
3 ⁺ (7)		15 324	135.83	38.14
11 ⁻		15 812	27.34	-64.26
4 ⁺ (9)		17 010	147.60	47.75
12 ⁻		17 409	26.83	-63.78
5 ⁺ (11)		18 810	158.93	55.83
13 ⁻		19 079	26.38	-63.32
6 ⁺ (13)		20 703	169.86	62.81
14 ⁻		20 813	25.95	-62.80
15 ⁻		22 589	25.45	-62.13
7 ⁺ (15)		22 675	180.30	69.13
16 ⁻		24 368	24.58	-60.26
8 ⁺ (17)		24 712	190.12	75.14
17 ⁻		25 862	22.01	-52.04

(b)	ν_2	E (cm ⁻¹)	A_{iso} (MHz)	
			N	H
0 ⁻		25	22.52	-62.29
1 ⁻		1 580	23.12	-62.33
2 ⁻		3 090	23.66	-62.41
3 ⁻		4 574	24.24	-62.59
4 ⁻		6 038	24.92	-62.88
5 ⁻		7 480	25.76	-63.27
6 ⁻		8 890	26.89	-63.73
7 ⁻		10 231	29.44	-63.68
8 ⁻		11 238	75.05	-19.24
0 ⁺ (2)		11 539	71.92	-21.78
9 ⁻		12 331	51.44	-45.10
1 ⁺ (4)		12 924	103.86	9.36
10 ⁻		13 614	40.29	-53.93
2 ⁺ (6)		14 439	122.13	26.46
11 ⁻		15 060	35.42	-57.21
3 ⁺ (8)		16 084	135.47	37.97
12 ⁻		16 612	33.73	-57.86
4 ⁺ (10)		17 842	145.83	45.66
13 ⁻		18 249	34.38	-56.50
5 ⁺ (12)		19 693	150.39	47.39
14 ⁻		19 959	40.45	-50.43
6 ⁺ (14)		21 601	120.06	18.93
15 ⁻		21 746	81.02	-14.96
16 ⁻		23 469	40.63	-48.67
7 ⁺ (16)		23 686	169.96	59.49
17 ⁻		25 264	27.59	-57.90
8 ⁺ (18)		25 742	191.80	75.81

TABLE VI. Comparison of the results of the present study for vibronically averaged hfcc's with the corresponding experimental data. theor. I: Theoretical results obtained by using the JHK potentials (Ref. 3). theor. II: Pure *ab initio* results. * Denotes the values obtained from the published data using the relation $A_{bb} + A_{cc} = -A_{ac}$. + Obtained indirectly by comparing the values for A_{aa} and A_{bb} in NH₂ and NHD. Values in parentheses denote three standard deviations and apply to the last digits of the constants. Exceptions are data from f (1 standard deviation) and c (95% confidence limit).

X^2B_1 (000)		NH ₂		NHD			ND ₂	
		N	H	N	H	D	N	D
	theor. I	22.4	-62.2	22.4	-62.2	-9.55	22.3	-9.55
	theor. II	22.5	-62.3					
A_{iso} (MHz)	expt.	27.9(0.6) ^a		28.0 ^c	-67.2 ^c	-10.3 ^c		-10.1(3) ^f
		28.2±0.4 ^b	-67.2±0.4 ^b				28.055(33) ^g	-10.241(28) ^g
		27.88(20) ^d	-67.59(28) ^d					
		28.11(34) ^d	-67.22(43) ^d					
A_{aa} (MHz)	theor. I	-42.4	19.6	-42.5	-23.7	8.45	-42.4	3.01
	theor. II	-42.4	20.2					
	expt.	-43.3(1.5) ^a		-43.0 ^c	-25.5 ^c	8.2 ^c		3.3(7) ^f
		-42.8±1.3 ^b	18.6±1.3 ^b				-43.136(48) ^g	2.874(45) ^g
A_{bb} (MHz)	theor. I	-42.9	-12.9	-42.8	30.3	-7.43	-42.9	-1.99
	theor. II	-42.9	-13.4					
	expt.	-44.2(1.6) ^a		-44.4 ^c	30.5 ^c	-7.4 ^c		-2.3 ^{h*}
		-44.7±1.0 ^b	-13.4±0.9 ^b				-44.272(63) ^g	-2.108(69) ^g
A_{cc} (MHz)	theor. I	85.4	-6.67	85.3	-6.63	-1.02	85.4	-1.03
	theor. II	85.4	-6.68					
	expt.	87.4(0.9) ^a		87.5 ^c	-5.2 ^c	-0.8 ^c		-1.0(4) ^f
		87.5±0.5 ^b	-5.2±0.6 ^b				87.413 ^{g*}	-0.766 ^{g*}
A_{ab} (MHz)	theor. I		55.3					
	expt.		58.5(2.5) ^{c+}					
		$A^2A_1(090)$		$A^2A_1(0 0 0)$				
		N	H	N	H			
A_{iso} (MHz)	theor. I	148.0	48.3	150.4	49.9			
	theor. II	147.6	47.8	145.8	45.7			
	expt. ^e	154.6(26)	49.4(55)	153.0(13)	52.2(14)			
A_{aa} (MHz)	theor. I	-37.7	56.3	-37.6	54.2			
	theor. II	-37.7	56.3	-37.8	53.1			
	expt. ^e	-48.7(49)	48.5(109)	-39.5(33)	59.5(34)			
A_{bb} (MHz)	theor. I			73.3	-4.92			
	theor. II			73.7	-4.97			
	expt. ^e			76.9(14)	-9.5(16)			
A_{iso} (MHz)	theor. I			-35.7	-49.2			
	theor. II			-36.0	-48.1			
	expt. ^e			-37.4(19)	-50.0(20)			

^aReference 21.^eReference 25.^bReference 22.^fReference 26.^cReference 23.^gReference 27.^dReference 24.

increasing systematically with increasing bending quantum numbers. Although it cannot be excluded that the *ab initio* bending potentials are simply somewhat too steep at strongly bent geometries, this might be caused by the above

mentioned smaller reliability of the one-dimensional bending model at large amplitude vibrations. The situation with the potentials derived by fitting the observed bond positions is quite different because these are *defined* so that

they match optimally the experimental data. A good fitting can also be a consequence of cancellation of errors in models for the potentials and the kinetic energy operator.

Variation of the values for the vibronically averaged hfcc's from one level to another reflects generally three effects, connected more or less with each other: (i) geometry dependence of the electronic mean values of the hfcc's; (ii) composition of the vibronic wave functions, particularly the amount of the ${}^2B_1/{}^2A_1$ electronic wave function in them; (iii) strong local coupling between (accidentally) close-lying vibronic levels belonging (predominantly) to different Born–Oppenheimer potential curves. The last two effects are obviously intimately interacting with one another because a near degeneracy of the levels with $K \neq 0$ has dramatic consequences for the composition of the corresponding wave functions.

As well known^{2,10} $K=0$ vibronic levels are unambiguously attributed to one particular of the two electronic states in question and in this case the variation of the vibronically averaged hfcc's is caused predominantly by the geometry variation of the corresponding electronic mean values. As a consequence of that the agreement between the results obtained by employing the JHM and *ab initio* potential curves (Tables I and V) is quite satisfactory, the small differences being caused by systematic overestimation of the vibrational energy values in the pure *ab initio* calculations. The same holds for the $K \neq 0$ (particularly $K=1$) vibronic levels below the barrier to linearity. The agreement between two sets of results is significantly worse in the vicinity of the barrier in which the vibronic coupling is very strong. (The off-diagonal matrix elements in the vibronic secular equation coupling two Born–Oppenheimer electronic states with one another are weighted with the factor $\sim 1/\rho^2$ at $\rho \rightarrow 0$.) So, e.g., the mean values of the isotropic hfcc in the $\nu_2=8$ level belonging predominantly to the 2B_1 electronic state (denoted in tables by 8^-) and the lowest $K=1$ vibronic level of the 2A_1 electronic species corresponding to the quantum number $\nu_2=0$ in the “bent,” i.e., $\nu_2=2$ in the “linear” notation ($\nu_2^{\text{lin}}=2 \times \nu_2^{\text{bent}} + \Lambda + K^{10}$) and denoted by $0^+(2)$ are calculated to be 75 and 72 MHz, respectively, when the *ab initio* potentials are employed [Table V(b)], and 38 and 97 MHz by using the JHM potentials [Table I(b)]. This can be explained by the fact that these levels are computed to lie much closer to one another (300 cm^{-1}) in the pure *ab initio* calculation than in the case when the JHM potentials are used (420 cm^{-1}), with the consequence that the mixing of the electronic character is much stronger in the former case. $K \neq 0$ levels lying far enough above the barrier to linearity have predominantly 2B_1 or 2A_1 electronic character and the agreement between the results for vibronically averaged mean values of the hfcc's generated by employing the two sets of potential curves is again satisfactory. The only exception represent the cases of the above mentioned local interactions which cannot be described quite reliably by pure *ab initio* calculations (see, e.g., discussion in Refs. 28 and 29). So, e.g., the mean values of the isotropic hfcc for nitrogen (JHM potentials) in the $K=1$ levels 16^- and 17^- , 38 and 42 MHz, respec-

tively, [Table I(b)] are significantly larger than for the $K=0$ levels lying in the same energy region [≈ 24 MHz, Table I(a)] because of the presence of relatively close-lying levels ($\Delta E \approx 200 \text{ cm}^{-1}$) belonging predominantly to the 2A_1 electronic state, $6^+(14)$ and $7^+(16)$, respectively. In the calculation with the *ab initio* potentials [Table V(b)], the $K=1$ level 16^- lies close ($\approx 220 \text{ cm}^{-1}$) to the 7^+ level of predominantly 2A_1 electronic character and the mean value for A_{iso} of the nitrogen is computed to be 41 MHz; on the other hand, the energy difference between the level 17^- and the next level of the 2A_1 character $8^+(18)$ is significantly larger ($\approx 480 \text{ cm}^{-1}$) and this is reflected in rather “normal” value for the A_{iso} in 17^- (28 MHz). Because of the above mentioned lack of exact isotopical invariance of the JHM potentials (and/or of the bending dependence of the optimized bond lengths) we cannot expect that the local perturbations are described reliably in NHD and ND₂ even if the calculations in which the empirical potentials are employed instead of their *ab initio* counterparts.

The results for the mean values of the combination $A_{bb} - A_{cc}$ presented in Table I(b), deserve some additional comment. They appear with the same sign for both the component electronic states (except in a few very high levels in NH₂ for the hydrogen atom) in spite of the fact that the electronic mean values for $A_{bb} - A_{cc}$ have different signs in 2B_1 and 2A_1 species in large range of the bond angle values, particularly at the linear geometry at which $A_{bb}^{B_1} = A_{cc}^{A_1}$ and $A_{bb}^{A_1} = A_{cc}^{B_1}$ and thus $(A_{bb} - A_{cc})^{B_1} = -(A_{bb} - A_{cc})^{A_1} = (A_{cc} - A_{bb})^{A_1}$. This is a consequence of the fact that the values given in the tables while corresponding to the same vibronic energy level [in the framework of the calculation model (no K doubling)] represent actually off-diagonal matrix elements between the vibronic wave functions for the $K=+1$ and $K=-1$ component states corresponding to the proper selection rule ($\Delta K = \pm 2$). These functions have the respective forms (10)

$$\Psi_{(K=+1)} = (f^{A_1}\psi^{A_1} + f^{B_1}\psi^{B_1})e^{i\phi}, \quad (12a)$$

$$\Psi_{(K=-1)} = (f^{A_1}\psi^{A_1} - f^{B_1}\psi^{B_1})e^{-i\phi}, \quad (12b)$$

where ψ^{A_1} and ψ^{B_1} are the electronic basis functions calculated in the Born–Oppenheimer approximation, and the coefficients f^{A_1} and f^{B_1} represent actually linear combinations of the bending basis functions determined by solving of the vibronic secular equation. Thus the matrix elements

$$\langle \Psi(K=-1) | A_{bb} - A_{cc} | \Psi(K=+1) \rangle \quad (13)$$

reduce due to orthogonality of ψ^{A_1} and ψ^{B_1} to

$$\langle f^{A_1} | \langle \psi^{A_1} | A_{bb} - A_{cc} | \psi^{A_1} \rangle | f^{A_1} \rangle - \langle f^{B_1} | \langle \psi^{B_1} | A_{bb} - A_{cc} | \psi^{B_1} \rangle | f^{B_1} \rangle. \quad (14)$$

Thus the computation of the $\langle K=-1 || K=+1 \rangle$ matrix elements is equivalent to that for the diagonal elements $\langle K=+1 || K=+1 \rangle$ (or $\langle K=-1 || K=-1 \rangle$) in which the sign of the electronic mean values for $A_{bb} - A_{cc}$ in the 2B_1 state is changed.

A consequence of the fact that the magnitude of the electronically averaged quantities $A_{bb} - A_{cc}$ in 2A_1 and A_{cc}

$-A_{bb}$ in 2B_1 state is similar in the large range of the bond angle values is that the variation of the values for the matrix elements $\langle K=-1|A_{bb}-A_{cc}|K=+1\rangle$ with the bending quantum number is rather regular, even if the vibronic states are of appreciably mixed B_1/A_1 electronic character. If a particular vibronic level is of predominantly 2B_1 electronic character, i.e., if $f^{A_1} = 0$, expression (14) reduces to $-\langle f^{B_1}|\langle\psi^{B_1}|A_{bb}-A_{cc}|\psi^{B_1}\rangle|f^{B_1}\rangle$ and thus represents the vibrationally averaged mean value of the $A_{cc}-A_{bb}$ combination; for the levels belonging predominantly to the 2A_1 electronic state (14) reduces to the mean value of $A_{bb}-A_{cc}$. In both cases it is possible in a good approximation to obtain the mean values of the individual A_{bb} and A_{cc} elements by adding and subtracting from one another the values for $\langle K=1|A_{aa}|K=1\rangle = -\langle K=1|A_{bb}+A_{cc}|K=1\rangle$ and $\langle K=1|A_{bb}-A_{cc}|K=-1\rangle$ derived from experiment. The situation is more complicated in the case of vibronic levels strongly shared between two electronic species. Correct vibronic mean values for A_{bb} and A_{cc} would be obtained if it were possible to measure the diagonal matrix elements $\langle K=+1|A_{bb}-A_{cc}|K=+1\rangle$ and then combine them with $\langle K=+1|A_{aa}|K=+1\rangle$. In the case of a 50%/50% mixture and for $(A_{bb}-A_{cc})_{B_1} = (A_{cc}-A_{bb})_{A_1}$ (this happens approximately, e.g., in "unique" level¹⁰ of a molecule which both component electronic states have linear equilibrium geometry) the vibrationally averaged value for $\langle K=+1|A_{bb}-A_{cc}|K=+1\rangle$ would be close to zero with the consequence that $\langle A_{bb}\rangle \simeq \langle A_{cc}\rangle \simeq -\langle A_{aa}\rangle/2$. Instead the matrix element $\langle K=-1|A_{bb}-A_{cc}|K=+1\rangle$ is under the same conditions close to the electronically mean value of $(A_{bb}-A_{cc})_{A_1} \simeq (A_{cc}-A_{bb})_{B_1}$ so that the combination of the elements $\langle K=-1|A_{bb}-A_{cc}|K=+1\rangle$ with $\langle K=1|A_{aa}|K=1\rangle$ reproduces roughly the electronic rather than vibronic mean values for A_{bb} and A_{cc} .

The remaining (irreducible) components of the isotropic hf tensor, connecting the vibronic levels differing in K by ± 1 and ± 2 can generally not be measured with the current experimental methods except in some convenient cases, indirectly. So, e.g., the A_{ab} hfcc in the ground vibrational state of NH₂ has been determined by comparing the actually measured values for A_{aa} and A_{bb} [more precisely for A_{aa} ($=-A_{bb}-A_{cc}$) and $A_{bb}-A_{cc}$] in NH₂ and NHD along their respective principal inertial axes.²³ (In this case the Born-Oppenheimer approximation is valid and reliable *ab initio* computation of the same quantities is possible without taking into account the vibronic interaction.³⁰) The reason is that the energy differences between the vibronic levels differing in K are generally too large [in NH₂, e.g., between ~ 25 cm⁻¹ ($K=1-K=0$ in the ground vibrational state) and as much as 1000 cm⁻¹ for the levels above the barrier to linearity]. This matter of fact is illustrated in Table I in PAPS. In it we present hypothetical mean values of the quantities $A_{bb}-A_{cc}$ and A_{ab} in $K=0$ and $K=1$ vibronic levels of NH₂ (JHM potentials employed) and an estimation of the effect of interaction of all the vibronic states with the proper symmetry on (i.e., connected by proper ΔK selection rules) with particular $K=0$ and $K=1$ states, according to the perturbative-type formula

$$\langle A_{bb}-A_{cc}\rangle_{v,K=0} = \sum_{v'} \frac{|\langle \Psi_{vK=0}|A_{bb}-A_{cc}|\Psi_{v'K=2}\rangle|^2}{E_{vK=0}-E_{v'K=2}} \quad (15)$$

and analogously for other quantities. [Numerical constants consisting of combinations of quantum numbers are omitted in expression (15).] These quantities, denoted in Table I in PAPS¹² by $\langle 0||\Sigma 2\rangle$, etc., are of magnitude order between Hz and kHz. In the energy region above the barrier to linearity the dependence on the bending quantum number is irregular with particularly large values where the $K=0$ levels of the 2B_1 potential curve are accidentally nearly degenerate with $K=2$ levels belonging predominantly to the 2A_1 state (and vice versa, $K=0$ of 2A_1 with $K=2$ of 2B_1). Such a situation is illustrated by Table II where the matrix elements of $A_{bb}-A_{cc}$ between the $K=0$ vibronic state $v_2' = 2^+(5)$ and individual $K=2$ states are presented. It can be noted that the largest matrix element connects the $K=0$, $v_2=2^+(5)$ state with its nearly degenerate (energy difference 6-7 cm⁻¹) $K=2$ counterpart ($v_2=10^-$), but that there are several other matrix elements of comparable magnitude; the contribution of the latter to the quantity defined by Eq. (15) is, however, due to unfavorable energy nominators negligible. In Table II are presented also the matrix elements between the lowest vibronic $K=0$ level with individual $K=2$ states. In this case the matrix element diagonal in $v_2 (=0^-)$ is clearly dominating all others.

The results obtained in the present study are compared in Table VI with the corresponding experimental findings. The values denoted by th. I represent the results of calculations in which the JHM potentials are employed, those denoted by th. II are obtained by using the *ab initio* potential curves. The theoretical results for A_{bb} and A_{cc} are derived from the values for A_{ag} and $A_{bb}-A_{cc}$ given in Table I and Tables II-IV in PAPS,¹² i.e., via the same procedure as their experimental counterparts. The theoretical results, particularly for the isotropic hfcc, generally underestimate slightly their experimental counterparts, in accordance with our experience with similar systems.^{31,32} Relatively large difference in A_{bb} for the hydrogen atom in the (0 10 0) level of A^2A_1 reflects the sensitivity of the computation of this quantity in that energy region where the magnitude of the corresponding electronic matrix elements in both 2B_1 and 2A_1 states is small and their bending dependence is very strong. However, we find the overall agreement quite satisfactory, especially by taking into account relatively large experimental uncertainties.

IV. CONCLUSION

In the present study we demonstrate the ability of the *ab initio* method to reproduce, explain, and predict the experimental findings concerning the hyperfine structure of the spectrum of a molecule (NH₂) with the two electronic states strongly coupled via the Renner-Teller effect. The influence of various parameters (particularly the reliability of the potential surfaces, the effects of local perturbations between the close-lying vibronic states belonging predominantly to different electronic species) is discussed.

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