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**Ab initio STUDY OF THE ANHARMONIC PROPERTIES OF DIPOLE MOMENT FUNCTIONS OF AMMONIA AND THE OXONIUM ION**Petr PRACNA<sup>a</sup> and Zdeněk HAVLAS<sup>b</sup><sup>a</sup> *The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 182 23 Prague 8 and*<sup>b</sup> *Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague 6*

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*Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.*

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*Ab initio* SCF electric dipole moment functions of the electronic ground states of ammonia and the oxonium ion are determined over a wide range of vibrational coordinates. The dipole moment functions are used within the framework of the nonrigid inverter Hamiltonian to evaluate transition moments for various types of vibrational bands. Reasonable agreement with experimental data for ammonia is achieved by scaling the dipole moment function. Several new transition moments for combination and hot bands are predicted.

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During the last few years several *ab initio* calculations of dipole moment properties of quasiplanar XY<sub>3</sub> molecules, namely ammonia and the oxonium ion, have been reported<sup>1-7</sup>. These calculations were mainly concerned with the determination of dipole moment derivatives in the vicinity of the equilibrium configuration, from which the integrated intensities of fundamental vibrational bands were determined using the standard theory of molecular vibrations<sup>8</sup>. In these molecules the large amplitude inversion vibration is characterized by a strong anharmonicity of both the potential and the dipole moment functions. There are therefore many interesting features in their spectra which cannot be theoretically treated within the framework of standard theory. For a general description of their spectroscopic behavior it is necessary to use a model taking into account nonrigidity. In particular this has been done for the  $\mu_z$  component of the dipole moment of NH<sub>3</sub> and H<sub>3</sub>O<sup>+</sup> (refs<sup>6,7</sup>). This component determines transition moments between nondegenerate vibrational states. In these two studies the dipole moment was determined over a wide range of vibrational coordinates and the transition moments were calculated using a two-dimensional Hamiltonian for the two nondegenerate vibrational modes. This model neglected the coupling of the large amplitude inversion vibration with the two remaining degenerate vibrations. This coupling, however, is of significant importance<sup>9</sup>. The purpose of the present work is to investigate the full dipole moment

function of ammonia and the oxonium ion by *ab initio* calculations. These dipole moment functions are then used to calculate vibrational transition moments using the anharmonic nonrigid inverter Hamiltonian<sup>10</sup> along with a newly developed model of the anharmonic dipole moment function of quasiplanar XY<sub>3</sub> molecules<sup>11</sup>. These calculations provide various kinds of transition moments in the inversion vibrational mode, e.g. pure inversion, fundamental, higher overtone, and hot band transition moments. The nonrigid inverter approach also allows calculations of combination and hot band transition moments arising from mixing of the inversion vibration and the "small amplitude" vibrations.

### THEORETICAL

The electric dipole moment of a molecule is generally a function of the vibrational coordinates. This dependence is usually expressed as a Taylor expansion of the molecule fixed Cartesian components of the dipole moment  $\mu$  in the vibrational coordinates  $S_i$

$$\begin{aligned} \mu_\alpha &= \mu_\alpha^0 + \sum_i (\partial \mu_\alpha / \partial S_i)_e S_i + 1/2 \sum_{i,j} (\partial^2 \mu_\alpha / \partial S_i \partial S_j)_e S_i S_j + \dots = \\ &= \mu_\alpha^0 + \sum_i \mu_\alpha(S_i) S_i + \sum_{i \leq j} \mu_\alpha(S_i, S_j) S_i S_j + \dots, \quad \alpha = x, y, z. \end{aligned} \quad (1)$$

For molecules with no large amplitude motion such an expansion converges rapidly. This means, for example, that in the interpretation of intensities of fundamental vibrational bands we can limit ourselves to linear terms only. This approximation is referred to as the electric harmonic approximation.

If the molecule under study has a vibrational coordinate for which the higher order derivatives and/or the vibrational displacements are large, the series (1) need not converge rapidly. If the harmonic approximation of the molecular dipole moment and potential function is used in the interpretation of intensities of fundamental bands, the resulting dipole moment can fail to describe anomalous behaviour of transition moments in the large amplitude mode. It is therefore necessary to study the dipole moment surface of nonrigid molecules over a wide range of vibrational displacements in order to determine the higher order terms of the dipole moment expansion. In this work we follow the treatment of ref.<sup>10</sup> for mechanical anharmonicity in quasiplanar XY<sub>3</sub> molecules and use the same set of vibrational coordinates to expand the dipole moment functions. The reference configuration from which the vibrational displacements are measured is the planar configuration with three equal X—Y bonds ( $r_p$ ) and three equal Y—X—Y valence angles ( $\alpha_p = 2\pi/3$ ). The following set of curvilinear symmetry coordinates is used

$$S_1(A'_1) = (\Delta r_1 + \Delta r_2 + \Delta r_3)/3^{1/2}$$

$$\begin{aligned}
 S_2 &\equiv S_{3a}(E') = (2\Delta r_1 - \Delta r_2 - \Delta r_3)/6^{1/2} \\
 S_3 &\equiv S_{4a}(E') = (2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)/6^{1/2} \\
 S_4 &\equiv S_{3b}(E') = (\Delta r_2 - \Delta r_3)/2^{1/2} \\
 S_5 &\equiv S_{4b}(E') = (\Delta\alpha_2 - \Delta\alpha_3)/2^{1/2} \\
 S_6(A_2'') &= h,
 \end{aligned} \tag{2}$$

where  $\Delta r_i$ ,  $\Delta\alpha_i$  are defined as follows

$$\begin{aligned}
 \Delta r_i &= r_{i4} - r_p, \quad i = 1, 2, 3 \\
 \Delta\alpha_i &= \arccos(\mathbf{r}_{j4} \cdot \mathbf{r}_{k4}/r_{j4}r_{k4}) - \alpha_p, \quad i \neq j \neq k.
 \end{aligned} \tag{3}$$

The out-of-plane coordinate  $h$  is the distance between the X atom and the plane of Y atoms (cf. Fig. 1). Respecting the relations between the expansion coefficients of the dipole moment<sup>12</sup> we may write series (1) in the form given in Table I. This expansion is used to fit the *ab initio* points on the dipole moment surface. As the symmetry coordinates (2) are defined with respect to the molecule fixed coordinate system, the derivatives in Table I need not be generally isotopically invariant. This is a consequence of the mass dependence of the Eckart conditions. The asymmetric vibrational displacements ( $E$  symmetry) cause an isotopic mass dependent tilt of the molecule relative to the molecule fixed axes. This means that the  $\mu_x$  and  $\mu_y$  components of the dipole moment are always isotopically dependent. We have taken into account these rotational corrections using the procedure described in ref.<sup>13</sup>. The effect of deuteration on the dipole moment derivatives is stronger than that of the isotopic substitution of the nitrogen and oxygen atoms.

The  $A$  symmetry vibrations, on the other hand, are connected with a translation of the molecule relative to the Eckart axis system and make the dipole moment isotope dependent only in charged molecules. Thus, the  $\mu_z$  component of the dipole moment function in ammonia is isotopically invariant within the framework of the electric harmonic approximation with respect to small amplitude vibrations. If we take into account higher order terms of its expansion, such as  ${}^2\mu_z$ , then the  $\mu_z$  component also becomes isotopically dependent.

In order to calculate the dipole moment matrix elements (transition moments) the dipole moment function (Table I) is expressed in terms of internal coordinates which correspond to normal coordinates for the small amplitude vibrations and the large amplitude coordinate  $\varrho$ . We refer to these coordinates as the *HBJ* (Hougen, Bunker, Johns<sup>14</sup>) coordinates. In the present paper transition moments based on *ab initio* SCF dipole moment function are presented, while the theory used for the calculations is described elsewhere<sup>11</sup>.

TABLE I

Expansion of the dipole moment function ( $\mu_\alpha = {}^0\mu_\alpha + {}^1\mu_\alpha + {}^2\mu_\alpha$ ,  $\alpha = x, y, z$ )<sup>a</sup>

$${}^0\mu_x = {}^0\mu_y = 0$$

$${}^1\mu_x = \sum_k [\mu_x(S_{3a}, h^{2k}) S_{3a} + \mu_x(S_{4a}, h^{2k}) S_{4a}] h^{2k}$$

$${}^2\mu_x = \sum_k [\mu_x^*(S_1, S_{3a}, h^{2k}) S_1 S_{3a} + \mu_x^*(S_1, S_{4a}, h^{2k}) S_1 S_{4a} + \mu_x(S_{3a}^2, h^{2k}) \times \\ \times (S_{3a}^2 - S_{3b}^2) + \mu_x(S_{4a}^2, h^{2k}) (S_{4a}^2 - S_{4b}^2) + \mu_x^*(S_{3a}, S_{4a}, h^{2k}) (S_{3a} S_{4a} - \\ - S_{3b} S_{4b})] h^{2k}$$

$${}^1\mu_y = \sum_k [\mu_x(S_{3a}, h^{2k}) S_{3b} + \mu_x(S_{4a}, h^{2k}) S_{4b}] h^{2k}$$

$${}^2\mu_y = \sum_k [\mu_x^*(S_1, S_{3a}, h^{2k}) S_1 S_{3b} + \mu_x^*(S_1, S_{4a}, h^{2k}) S_1 S_{4b} + \mu_x(S_{3a}^2, h^{2k}) S_{3a} S_{3b} + \\ + \mu_x(S_{4a}^2, h^{2k}) S_{4a} S_{4b} + \mu_x^*(S_{3a}, S_{4a}, h^{2k}) (S_{3a} S_{4b} - S_{3b} S_{4a})] h^{2k}$$

$${}^0\mu_z = \sum_k \mu_z(h^{2k+1}) h^{2k+1}$$

$${}^1\mu_z = \sum_k \mu_z(S_1, h^{2k+1}) S_1 h^{2k+1}$$

$${}^2\mu_z = \sum_k [\mu_z(S_1^2, h^{2k+1}) S_1^2 + \mu_z(S_{3a}^2, h^{2k+1}) (S_{3a}^2 + S_{3b}^2) + \mu_z(S_{4a}^2, h^{2k+1}) \times \\ \times (S_{4a}^2 + S_{4b}^2) + \mu_z^*(S_{3a}, S_{4a}, h^{2k+1}) (S_{3a} S_{4a} + S_{3b} S_{4b})] h^{2k+1}$$

<sup>a</sup> The  ${}^0\mu_\alpha$  terms are functions of the inversion coordinate  $h$  only. These terms should not be confused with the permanent dipole moment  $\mu_\alpha^0$  in Eq. (1) which is zero in the reference configuration. The  ${}^1\mu_\alpha$  terms are linear functions of the small amplitude vibrational coordinates. The  ${}^2\mu_\alpha$  terms are quadratic functions of the small amplitude vibrational coordinates. The starred terms give contributions to transition moments of combination bands which were not studied in the present work. The values of the corresponding coefficients were thus fixed to zero in our fittings.

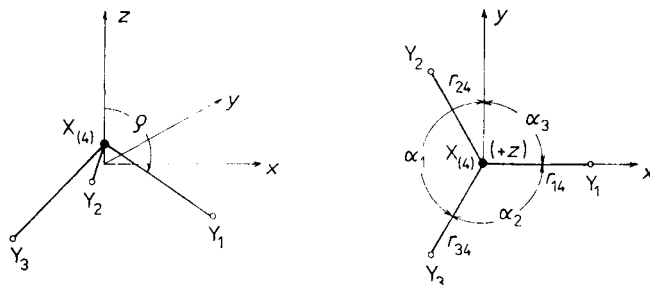


FIG. 1

Definition of the molecule fixed Cartesian coordinate system and internal coordinates for the  $XY_3$  quasiplanar molecules

## RESULTS AND DISCUSSION

In the investigation of the dipole moment function of ammonia and the oxonium ion we used configurations with energies\* up to  $8\,000\text{ cm}^{-1}$  above equilibrium with respect to inversional displacements. The effect of  $S_1$  displacements on the  $\mu_z$  component was studied in the energy range up to  $6\,000\text{ cm}^{-1}$ . Vibrational displacements corresponding to degenerate vibrations in the energy range up to  $4\,000\text{ cm}^{-1}$  were taken into account in the investigation of both  $\mu_x$  and  $\mu_z$  components of the dipole moment. The dipole moments of the specified configurations were calculated at the HF-SCF level with 6-311G\*\* basis set<sup>15</sup> with slightly modified HONDO5 program package<sup>16</sup>.

The coefficients of the dipole moment expansion (Table I) were determined from the *ab initio* points on the dipole moment surface by using a standard least squares fitting procedure. The results are given in Table II. In the fittings of the  $\mu_z$  dipole moment component it was necessary to include the first four terms of  ${}^0\mu_z$  (Table I). In the calculations of inversion transition moments the higher order terms  $\mu_z(h^7)$  are important as they contribute by as much as  $10^{-2}\text{ D}$  ( $1\text{ D} = 3.33563 \cdot 10^{-30}\text{ C m}$ ) and represent a significant fraction of the transition moments for transitions from the ground state to higher inversional levels  $2v_2$  and  $3v_2$ . Finally the first two terms of  ${}^1\mu_z$  were included into our fittings giving the standard deviation of the order  $10^{-3}\text{ D}$ .

Transition moments in the symmetric stretching vibrational mode have contributions from both the  ${}^0\mu_z$  and  ${}^1\mu_z$  terms of the expansion. The magnitude of the contributions from the  ${}^0\mu_z$  terms is comparable to those from the  ${}^1\mu_z$  terms ( $\sim 10^{-1}\text{ D}$ ) due a strong coupling of the nondegenerate vibrational modes. The contributions are, however, of opposite signs which results in transition moments of the order  $10^{-2}\text{ D}$  for the fundamental band. This makes the  $\nu_1$  transition moment extremely sensitive to the description of mechanical coupling of the nondegenerate vibrations. This can be seen from predictions of transition moments from the  $\mu_z$  component of ammonia collected in Table III. Two sets of potential constants (see Table IV) were used for the calculation of the wavefunctions for the determination of transition moments. Each of these sets was determined from the analysis of vibrational-rotational energy levels<sup>17</sup> and provides a similar reproduction of the data. They also give similar values for transition moments in the inversional mode. If, however, they are used to predict transition moments in the symmetric stretching mode, they give significantly different values for the  $\nu_1$  fundamental and the  $\nu_1 + \nu_2$  combination bands as well as for their dependence on isotopical substitution. Compared with experimental results, potential I gives a reasonable decrease of the  $\nu_1$  transition moment caused by deuteration, but the  $\nu_1 + \nu_2$  transition moment is overestimated.

\* The wavenumber unit  $1\text{ cm}^{-1}$  used in molecular spectroscopy also as a unit of energy corresponds to  $1.196256 \cdot 10^{-2}\text{ kJ mol}^{-1}$ .

TABLE II  
Expansion coefficients of the  $\mu_z$  dipole moment function of ammonia and the oxonium ion determined from *ab initio* calculations

Parameters (units)	NH <sub>3</sub> , ND <sub>3</sub>				H <sub>3</sub> O <sup>+</sup>	D <sub>3</sub> O <sup>+</sup>
	Set A	Set B	Set C	Set D		
$\mu_z(h)$ (D Å <sup>-1</sup> ) <sup>a</sup>	-5.3825 (115) <sup>b</sup>	-5.3812 (87)	-5.3774 (65)	-5.1479 (35)	-6.6421 (72)	-6.0887 (73)
$\mu_z(h^3)$ (D Å <sup>-3</sup> )	5.250 (199)	5.394 (153)	5.392 (116)	6.243 (68)	3.766 (139)	3.765 (140)
$\mu_z(h^5)$ (D Å <sup>-5</sup> )	-6.76 (102)	-7.57 (78)	-7.98 (62)	-10.63 (42)	-4.83 (77)	-4.82 (77)
$\mu_z(h^7)$ (D Å <sup>-7</sup> )	5.1 (16)	6.3 (13)	7.5 (10)	9.83 (77)	5.6 (12)	6.6 (13)
$\mu_z(S_1, h)$ (D Å <sup>-2</sup> )	2.326 (50)	2.320 (38)	2.371 (36)	2.886 (11)	-0.524 (28)	-0.524 (28)
$\mu_z(S_1, h^3)$ (D Å <sup>-4</sup> )	-1.81 (22)	-1.48 (19)	-1.85 (16)	-2.440 (68)	-2.42 (15)	-2.41 (15)
$\mu_z(S_1^2, h)$ (D Å <sup>-3</sup> )	0.0 <sup>c</sup>	-0.61 (11)	-0.54 (11)	-1.265 (58)	0.0 <sup>c</sup>	0.0 <sup>c</sup>
$\mu_z(S_1^2, h^3)$ (D Å <sup>-5</sup> )	0.0 <sup>c</sup>	0.0 <sup>c</sup>	0.0 <sup>c</sup>	3.41 (30)	0.0 <sup>c</sup>	0.0 <sup>c</sup>
$\mu_z(S_{3a}^2, h)$ (D Å <sup>-3</sup> )	0.0 <sup>c</sup>	0.0 <sup>c</sup>	-0.83 (14)	0.0 <sup>c</sup>	0.0 <sup>c</sup>	0.0 <sup>c</sup>
$\mu_z(S_{4a}^2, h)$ (D Å <sup>-1</sup> )	0.0 <sup>c</sup>	0.0 <sup>c</sup>	-0.365 (36)	0.0 <sup>c</sup>	0.0 <sup>c</sup>	0.0 <sup>c</sup>
No. of <i>ab initio</i> points	43 <sup>d</sup>	43 <sup>d</sup>	97 <sup>e</sup>	36 <sup>f</sup>	44 <sup>d</sup>	44 <sup>d</sup>
St. deviation (10 <sup>-2</sup> D)	0.45	0.34	0.34	0.09	0.26	0.26
$r_p$ (Å)	0.9860	0.9860	0.9860	1.00079	0.9571	0.9571

<sup>a</sup> 1 D = 3.33564 · 10<sup>-30</sup> C m, 1 Å = 10<sup>-10</sup> m; <sup>b</sup> numbers in parentheses are standard deviations in units of the last digit; <sup>c</sup> fixed value; <sup>d</sup> *ab initio* points corresponding to configurations with  $S_1$  and  $h$  vibrational displacements; <sup>e</sup> *ab initio* points corresponding to configurations with  $S_1$ ,  $S_{3a}$ ,  $S_{4a}$ , and  $h$  vibrational displacements; <sup>f</sup> CASSCF dipole moment points from ref.<sup>5</sup> restricted to the energy range used in our calculations.

TABLE III

Predictions of transition moments (in D) from the *ab initio*  $\mu_z$  dipole moment component of ammonia. Individual sets of dipole moment expansion coefficients correspond to Table II; potential functions correspond to Table IV

Vibrational states	Set A		Set B		Set C		Set D <sup>a</sup>		Ref. <sup>5</sup>
	Pot I	Pot II	Pot I	Pot II	Pot I	Pot II	Pot I	Pot II	
$v_2''-v_2'$									
0 <sup>+</sup> -0 <sup>-</sup>	1.7496	1.7272	1.7336	1.7120	1.7439	1.7220	1.6316	1.6187	1.453
1 <sup>+</sup> -1 <sup>-</sup>	1.4885	1.4649	1.4754	1.4524	1.4840	1.4609	1.3913	1.3749	1.241
2 <sup>+</sup> -2 <sup>-</sup>	1.1373	1.1130	1.1274	1.1038	1.1339	1.1101	1.0615	1.0429	0.932
3 <sup>+</sup> -3 <sup>-</sup>	1.1793	1.1559	1.1690	1.1463	1.1754	1.1526	1.0941	1.1765	0.944
4 <sup>+</sup> -4 <sup>-</sup>	1.2528	1.2285	1.2417	1.2182	1.2475	1.2243	1.1582	1.1402	—
0 <sup>+</sup> -1 <sup>-</sup>	0.2898	0.2869	0.2873	0.2847	0.2896	0.2869	0.2604	0.2591	0.234
0 <sup>-</sup> -1 <sup>+</sup>	0.3028	0.2985	0.3002	0.2961	0.3026	0.2983	0.2730	0.2704	0.242
0 <sup>+</sup> -2 <sup>-</sup>	0.0017	0.0056	0.0021	0.0060	0.0022	0.0063	-0.0081	0.0020	0.002
0 <sup>-</sup> -2 <sup>+</sup>	0.0249	0.0283	0.0250	0.0284	0.0254	0.0288	0.0194	0.0221	0.006
0 <sup>+</sup> -3 <sup>-</sup>	-0.0056	-0.0050	-0.0053	-0.0048	-0.0057	-0.0050	-0.0045	-0.0046	—
0 <sup>-</sup> -3 <sup>+</sup>	-0.0088	-0.0067	-0.0083	-0.0063	-0.0085	-0.0081	-0.0071	-0.0046	—
1 <sup>+</sup> -2 <sup>-</sup>	0.3475	0.3469	0.3444	0.3440	0.3469	0.3463	0.3125	0.3136	0.294
1 <sup>-</sup> -2 <sup>+</sup>	0.6359	0.6223	0.6303	0.6171	0.6341	0.6209	0.5856	0.5759	0.491
1 <sup>+</sup> -3 <sup>-</sup>	-0.0039	0.0015	-0.0034	0.0020	-0.0035	0.0020	-0.0069	-0.0029	—
1 <sup>-</sup> -3 <sup>+</sup>	0.0903	0.0961	0.0898	0.0956	0.0905	0.0964	0.0747	0.0801	—
2 <sup>+</sup> -3 <sup>-</sup>	0.1356	0.1389	0.1345	0.1379	0.1353	0.1389	0.1153	0.1189	—
2 <sup>-</sup> -3 <sup>+</sup>	1.0834	1.0631	1.0739	1.0542	1.0800	1.0602	1.0048	0.9900	0.863

TABLE III  
(Continued)

Vibrational states	Set A		Set B		Set C		Set D <sup>a</sup>		Ref. <sup>5</sup>
	Pot I	Pot II	Pot I	Pot II	Pot I	Pot II	Pot I	Pot II	
$r_2'' - r_2'$									
0 <sup>+</sup> - 0 <sup>-</sup>	1.7600	1.7337	1.7473	1.7217	1.7550	1.7292	1.6459	1.6290	
1 <sup>+</sup> - 1 <sup>-</sup>	1.5956	1.5677	1.5846	1.5573	1.5915	1.5640	1.4949	1.4749	
2 <sup>+</sup> - 2 <sup>-</sup>	1.2784	1.2515	1.2698	1.2435	1.2753	1.2489	1.1991	1.1783	
3 <sup>+</sup> - 3 <sup>-</sup>	1.0950	1.0704	1.0877	1.0636	1.0923	1.0681	1.0232	1.0040	
4 <sup>+</sup> - 4 <sup>-</sup>	1.1698	1.1435	1.1619	1.1382	1.1666	1.1428	1.0885	1.0699	
0 <sup>+</sup> - 1 <sup>-</sup>	0.2517	0.2491	0.2500	0.2476	0.2517	0.2491	0.2266	0.2253	
0 <sup>-</sup> - 1 <sup>+</sup>	0.2530	0.2503	0.2513	0.2487	0.2530	0.2503	0.2279	0.2265	
0 <sup>+</sup> - 2 <sup>-</sup>	0.0010	0.0045	0.0013	0.0048	0.0015	0.0050	-0.0007	0.0018	
0 <sup>-</sup> - 2 <sup>+</sup>	0.0056	0.0088	0.0059	0.0090	0.0061	0.0092	0.0033	0.0057	
0 <sup>+</sup> - 3 <sup>-</sup>	-0.0047	-0.0039	-0.0045	-0.0037	-0.0046	-0.0038	-0.0038	-0.0036	
0 <sup>-</sup> - 3 <sup>+</sup>	-0.0059	-0.0043	-0.0057	-0.0040	-0.0057	-0.0041	-0.0053	-0.0045	
1 <sup>+</sup> - 2 <sup>-</sup>	0.3727	0.3690	0.3700	0.3666	0.3722	0.3686	0.3379	0.3363	
1 <sup>-</sup> - 2 <sup>+</sup>	0.4234	0.4158	0.4204	0.4131	0.4226	0.4152	0.3870	0.3815	
1 <sup>+</sup> - 3 <sup>-</sup>	0.0081	0.0137	0.0084	0.0140	0.0086	0.0142	0.0038	0.0083	
1 <sup>-</sup> - 3 <sup>+</sup>	0.0672	0.0719	0.0669	0.0716	0.0675	0.0722	0.0562	0.0604	
2 <sup>+</sup> - 3 <sup>-</sup>	0.2922	0.2912	0.2901	0.2893	0.2916	0.2908	0.2626	0.2632	
2 <sup>-</sup> - 3 <sup>+</sup>	0.8261	0.8094	0.8204	0.8041	0.8241	0.8077	0.7674	0.7551	
					ND <sub>3</sub>				



$v_1', v_2'' \rightarrow v_1', v_2'$	$v_1', v_2'' \rightarrow v_1', v_2'$	$v_1', v_2'' \rightarrow v_1', v_2'$	$v_1', v_2'' \rightarrow v_1', v_2'$	$v_1', v_2'' \rightarrow v_1', v_2'$	$v_1', v_2'' \rightarrow v_1', v_2'$	$v_1', v_2'' \rightarrow v_1', v_2'$	$v_1', v_2'' \rightarrow v_1', v_2'$	$v_1', v_2'' \rightarrow v_1', v_2'$	$v_1', v_2'' \rightarrow v_1', v_2'$	$v_1', v_2'' \rightarrow v_1', v_2'$
$1,0^+ \rightarrow 1,0^-$	1-7806	1-7786	1-7722	1-7701	1-7729	1-7707	1-6702	1-6717	1-6702	1-6717
$0,0^+ \rightarrow 1,0^-$	0-0414	0-0256	0-0379	0-0237	0-0370	0-0234	0-0187	0-0053	0-0187	0-0053
$0,0^- \rightarrow 1,0^+$	0-0414	0-0256	0-0380	0-0237	0-0371	0-0235	0-0187	0-0053	0-0187	0-0053
$0,0^+ \rightarrow 1,1^-$	0-0300	0-0075	0-0287	0-0067	0-0277	0-0066	0-0245	0-0056	0-0245	0-0056
$0,0^- \rightarrow 1,1^+$	0-0290	0-0074	0-0277	0-0066	0-0267	0-0066	0-0234	0-0054	0-0234	0-0054
$0,1^+ \rightarrow 1,0^-$	0-0320	0-0113	0-0304	0-0102	0-0294	0-0101	0-0242	0-0059	0-0242	0-0059
$0,1^- \rightarrow 1,0^+$	0-0339	0-0117	0-0322	0-0105	0-0312	0-0105	0-0260	0-0064	0-0260	0-0064
$0,1^+ \rightarrow 1,1^-$	0-0555	0-0245	0-0522	0-0227	0-0503	0-0223	0-0339	0-0075	0-0339	0-0075
$0,1^- \rightarrow 1,1^+$	0-0568	0-0252	0-0535	0-0234	0-0515	0-0229	0-0347	0-0076	0-0347	0-0076
<b>NH<sub>3</sub></b>										
$1,0^+ \rightarrow 1,0^-$	1-7684	1-7616	1-7603	1-7534	1-7609	1-7540	1-6610	1-6577	1-6610	1-6577
$0,0^+ \rightarrow 1,0^-$	0-0368	0-0317	0-0339	0-0301	0-0334	0-0298	0-0135	0-0174	0-0135	0-0174
$0,0^- \rightarrow 1,0^+$	0-0368	0-0317	0-0339	0-0301	0-0334	0-0299	0-0135	0-0174	0-0135	0-0174
$0,0^+ \rightarrow 1,1^-$	0-0174	0-0102	0-0165	0-0094	0-0160	0-0093	0-0136	0-0082	0-0136	0-0082
$0,0^- \rightarrow 1,1^+$	0-0173	0-0101	0-0164	0-0094	0-0160	0-0093	0-0135	0-0080	0-0135	0-0080
$0,1^+ \rightarrow 1,0^-$	0-0188	0-0133	0-0178	0-0125	0-0173	0-0123	0-0141	0-0093	0-0141	0-0093
$0,1^- \rightarrow 1,0^+$	0-0190	0-0134	0-0179	0-0126	0-0175	0-0124	0-0143	0-0094	0-0143	0-0094
$0,1^+ \rightarrow 1,1^-$	0-0455	0-0353	0-0427	0-0336	0-0416	0-0330	0-0266	0-0185	0-0266	0-0185
$0,1^- \rightarrow 1,1^+$	0-0456	0-0354	0-0428	0-0337	0-0417	0-0331	0-0266	0-0186	0-0266	0-0186
<b>ND<sub>3</sub></b>										

<sup>a</sup> Calculated using the dipole moment function from ref.<sup>5</sup> and our nonrigid inverter model.

Potential II, on the other hand, gives an incorrect dependence of the  $\nu_1$  transition moment on deuteration, but a more reasonable value for the  $\nu_1 + \nu_2$  transition moment. These discrepancies should be further investigated and may be helpful in the determination of better potential function parameters describing the interaction of  $\nu_1$  and  $\nu_2$  vibrations.

We have also studied the role of those expansion terms of the  $\mu_z$  component which are quadratic in the small amplitude vibrational coordinates. For ammonia, we were able to determine the  $\mu_z(S_1^2, h)$ ,  $\mu_z(S_{3a}^2, h)$ , and  $\mu_z(S_{4a}^2, h)$  derivatives. Their inclusion

TABLE IV  
Potential function parameters of ammonia and the oxonium ion used in calculations of transition moments

Parameters (units)	NH <sub>3</sub> <sup>a</sup>		H <sub>3</sub> O <sup>+</sup> <sup>b</sup>
	I	II	
$f_{rr}$ (mdyn Å <sup>-1</sup> ) <sup>c</sup>	7.45173	7.40802	7.6964
$f_{rr}'$ (mdyn Å <sup>-1</sup> )	0.045	0.07199	0.0
$f_{aa}$ (mdyn Å)	0.40586	0.49648	0.47161
$f_{aa}'$ (mdyn Å)	-0.05673	-0.00149	0.0
$f_{ra}$ (mdyn)	0.1543	0.17770	0.0
$f_{ra}'$ (mdyn)	0.45626	0.51836	0.0823
$a$	0.32067	-0.36134	0.46
$b$	-0.91201	-1.27130	0.0
$\kappa$	-0.12875	-0.24976	0.374
$\gamma$	0.09835	0.0	0.0
$\gamma_m$	0.74357	0.55023	0.0
$r_p$ (Å)	0.99187	1.01425	0.96090
$K_1$ (mdyn Å <sup>-1</sup> )	-0.52225	-0.52619	-0.3208
$K_2$ (mdyn Å <sup>-3</sup> )	2.11933	1.95806	2.329
$K_3$ (mdyn Å <sup>-5</sup> )	-1.31946	-0.85197	-0.771
$K_4$ (mdyn Å <sup>-7</sup> )	1.69064	1.64483	0.0
$k_1^1$ (mdyn Å <sup>-2</sup> )	-1.26557	1.39466	-1.983
$k_2^1$ (mdyn Å <sup>-4</sup> )	0.50995	-9.49802	-3.72
$k_3^1$ (mdyn Å <sup>-6</sup> )	-8.29491	0.0	0.0
$k_1^{11}$ (mdyn Å <sup>-3</sup> )	-1.32878	-5.44821	0.0
$k_2^{11}$ (mdyn Å <sup>-5</sup> )	2.43163	9.08002	0.0
$k_1^{22}$ (mdyn Å <sup>-3</sup> )	-1.07447	-3.56797	0.0
$k_2^{22}$ (mdyn Å <sup>-5</sup> )	1.01752	0.0	0.0
$k_1^{33}$ (mdyn Å <sup>-1</sup> )	1.58682	0.79369	0.0
$k_2^{33}$ (mdyn Å <sup>-3</sup> )	0.10581	3.06432	0.0
$k_1^{23}$ (mdyn Å <sup>-2</sup> )	3.70304	4.85161	0.0

<sup>a</sup> Ref.<sup>17</sup>; <sup>b</sup> ref.<sup>18</sup>; <sup>c</sup> 1 mdyn = 10<sup>-8</sup> N.

lead to a significant improvement of the fittings (see Set C of Table II). We have found no significant difference between the  $\text{NH}_3$  and  $\text{ND}_3$  species for these derivatives. For the oxonium ion, on the contrary, the  ${}^2\mu_z$  terms could not be determined from fits of *ab initio* dipole moment points and were thus neglected in further calculations.

In calculations of transition moments the  ${}^2\mu_z$  terms contribute (e.g. to purely inversional transition moments) by the same order of magnitude as higher order terms of  ${}^0\mu_z$ . Taking into account these  ${}^2\mu_z$  terms also requires the inclusion of terms which arise from  ${}^0\mu_z$  and  ${}^1\mu_z$  and the nonlinear part of the transformation of the dipole moment function to *HBJ* coordinates. Opposite signs of these contributions cause their mutual cancellation to  $10^{-3}$  D or less, which is insignificant from the point of view of purely inversional transition moments. On the other hand, the  ${}^2\mu_z$  terms are important for the estimation of other transition moments, e.g. the  $2\nu_4(A)$  transition moment. Again there is a considerable difference between predictions using different sets of potential function constants. Set II gives a realistic value 0.0023 D while calculations with Set I yield as much as 0.105 D. This can be explained by the

TABLE V

Predictions of transition moments (in D) from the *ab initio*  $\mu_z$  dipole moment component of the oxonium ion

Vibrational states	$\text{H}_3\text{O}^+/\text{D}_3\text{O}^+$	Vibrational states	$\text{H}_3\text{O}^+/\text{D}_3\text{O}^+$
$\nu_2'' - \nu_2'$		$\nu_1'', \nu_2'' - \nu_1', \nu_2'$	
$0^+ - 0^-$	1.6171/1.5423	$1,0^+ - 1,0^-$	1.6099/1.5202
$1^+ - 1^-$	1.2637/1.1134	$0,0^+ - 1,0^-$	0.1057/0.1036
$2^+ - 2^-$	1.4256/1.1946	$0,0^- - 1,0^+$	0.1057/0.1034
$3^+ - 3^-$	1.5613/1.3102	$0,0^+ - 1,1^-$	0.0304/0.0298
$4^+ - 4^-$	1.6697/1.4006	$0,0^- - 1,1^+$	0.0603/0.0426
$0^+ - 1^-$	0.3247/0.3412	$0,1^+ - 1,0^-$	0.0603/0.0405
$0^- - 1^+$	0.8284/0.5530	$0,1^- - 1,0^+$	0.0301/0.0272
$0^+ - 2^-$	0.0118/0.0206	$0,1^+ - 1,1^-$	0.0878/0.0754
$0^- - 2^+$	0.1159/0.1113	$0,1^- - 1,1^+$	0.0877/0.0745
$0^+ - 3^-$	-0.0029/-0.0029		
$0^- - 3^+$	-0.0033/-0.0005		
$1^+ - 2^-$	0.1203/0.1557		
$1^- - 2^+$	1.3283/1.0864		
$1^+ - 3^-$	-0.0054/-0.0010		
$1^- - 3^+$	0.0832/0.0971		
$2^+ - 3^-$	0.0649/0.0802		
$2^- - 3^+$	1.4976/1.2557		

overestimation of the coupling of nondegenerate vibrational modes in potential I and subsequent intensity borrowing from the  $\nu_1$  fundamental band.

Predictions of transition moments from the  $\mu_z$  *ab initio* dipole moment component were collected in Table III for ammonia and Table V for the oxonium ion. Our calculations of transition moments for ammonia are about 20% above the experimental values in case of the inversional mode. However, the ratio of purely inversional, fundamental, and higher overtone transition moments is described very well.

TABLE VI

Transition moments calculated from the scaled  $\mu_z$  dipole moment component of ammonia (Potential II) and the oxonium ion

Vibrational states	Scaled $\mu_z$ component		Experiment		Scaled $\mu_z$ component		Ref. <sup>6</sup> H <sub>3</sub> O <sup>+</sup>
	NH <sub>3</sub>	ND <sub>3</sub>	NH <sub>3</sub>	ref.	H <sub>3</sub> O <sup>+</sup>	D <sub>3</sub> O <sup>+</sup>	
$\nu_2'' - \nu_2'$							
0 <sup>+</sup> - 0 <sup>-</sup>	1.4715	1.4770	1.4715	20	1.3770	1.3140	1.4384
1 <sup>+</sup> - 1 <sup>-</sup>	1.2480	1.3356	1.2480	20	1.0751	0.9486	1.0965
2 <sup>+</sup> - 2 <sup>-</sup>	0.9482	1.0662	1.02	21	1.2127	1.0178	1.2284
3 <sup>+</sup> - 3 <sup>-</sup>	0.9848	0.9120	—	—	1.3284	1.1163	1.3476
4 <sup>+</sup> - 4 <sup>-</sup>	1.0466	0.9759	—	—	1.4208	1.1933	1.4361
0 <sup>+</sup> - 1 <sup>-</sup>	0.2445	0.2122	0.236	22	0.2775	0.2907	0.3025
0 <sup>-</sup> - 1 <sup>+</sup>	0.2543	0.2132	0.248	22	0.7029	0.4711	0.6728
0 <sup>+</sup> - 2 <sup>-</sup>	0.0048	0.0038	—	—	0.0102	0.0176	0.0150
0 <sup>-</sup> - 2 <sup>+</sup>	0.0241	0.0075	0.0226	23	0.0990	0.0948	0.1062
0 <sup>+</sup> - 3 <sup>-</sup>	-0.0043	-0.0033	0.0037	24	-0.0025	-0.0025	0.0028
0 <sup>-</sup> - 3 <sup>+</sup>	-0.0057	-0.0037	0.0060	24	-0.0027	-0.0004	0.0003
1 <sup>+</sup> - 2 <sup>-</sup>	0.2955	0.3144	0.288	25	0.1032	0.1327	0.1127
1 <sup>-</sup> - 2 <sup>+</sup>	0.5302	0.3543	—	—	1.1296	0.9256	1.1382
1 <sup>+</sup> - 3 <sup>-</sup>	0.0013	0.0117	—	—	-0.0046	-0.0009	0.0023
1 <sup>-</sup> - 3 <sup>+</sup>	0.0819	0.0612	—	—	0.0714	0.0828	0.0841
2 <sup>+</sup> - 3 <sup>-</sup>	0.1183	0.2481	—	—	0.0559	0.0683	0.0696
2 <sup>-</sup> - 3 <sup>+</sup>	0.9057	0.6896	1.05	21	1.2740	1.0698	1.2916
$\nu_1'', \nu_2'' - \nu_1', \nu_2'$							
1,0 <sup>+</sup> - 1,0 <sup>-</sup>	1.5153	1.5008	—	—	1.3519	1.2951	1.4943
0,0 <sup>+</sup> - 1,0 <sup>-</sup>	0.0218	0.0270	0.031	19	0.0888	0.0883	0.0559
0,0 <sup>-</sup> - 1,0 <sup>+</sup>	0.0218	0.0270	0.031	19	0.0882	0.0881	0.0597
0,0 <sup>+</sup> - 1,1 <sup>-</sup>	0.0064	0.0087	—	—	0.0267	0.0254	0.0043
0,0 <sup>-</sup> - 1,1 <sup>+</sup>	0.0063	0.0086	—	—	0.0521	0.0362	0.0160
0,1 <sup>+</sup> - 1,0 <sup>-</sup>	0.0096	0.0114	—	—	0.0498	0.0345	0.0376
0,1 <sup>-</sup> - 1,0 <sup>+</sup>	0.0099	0.0114	—	—	0.0240	0.0233	0.0247
0,1 <sup>+</sup> - 1,1 <sup>-</sup>	0.0209	0.0300	—	—	0.0745	0.0642	0.0346
0,1 <sup>-</sup> - 1,1 <sup>+</sup>	0.0215	0.0301	—	—	0.0733	0.0635	0.0529

This can be seen even more clearly if we perform a scaling of our *ab initio* dipole moment function by fitting the leading term of  ${}^0\mu_z$  to the first two experimental transition moments in Table VI. The remaining coefficients of the expansion were fixed in the ratio given by the *ab initio* dipole moment function (Set A). In this way we were able to obtain a very close agreement with the experimental data for all

TABLE VII

Expansion coefficients of the  $\mu_x$  dipole moment function of ammonia and the oxonium ion determined from *ab initio* calculations. The value of  $r_p$  is 0.9860 Å for ammonia and 0.9571 Å for the oxonium ion. Numbers in parentheses are standard deviations in units of the last digit

Parameters (units)	NH <sub>3</sub>	ND <sub>3</sub>	H <sub>3</sub> O <sup>+</sup>	D <sub>3</sub> O <sup>+</sup>
$\mu_x(S_{3a})$ (D Å <sup>-1</sup> )	0.8317 (49)	0.8315 (50)	3.6794 (20)	3.4535 (25)
$\mu_x(S_{3a}, h^2)$ (D Å <sup>-3</sup> )	-5.994 (82)	-5.520 (83)	-4.301 (43)	-3.778 (57)
$\mu_x(S_{3a}, h^4)$ (D Å <sup>-5</sup> )	6.85 (25)	6.43 (25)	2.79 (14)	2.55 (19)
$\mu_x(S_{3a}^2)$ (D Å <sup>-2</sup> )	-0.307 (30)	-0.313 (30)	1.081 (12)	1.079 (15)
$\mu_x(S_{3a}^2, h^2)$ (D Å <sup>-4</sup> )	-1.18 (18)	-1.32 (18)	-0.94 (9)	-1.15 (11)
No. of <i>ab initio</i> points	36	36	36	36
St. deviation (10 <sup>-2</sup> D)	0.14	0.14	0.07	0.09
$\mu_x(S_{4a})$ (D)	0.5337 (22)	0.5335 (22)	1.0507 (15)	0.9261 (15)
$\mu_x(S_{4a}, h^2)$ (D Å <sup>-2</sup> )	0.230 (39)	0.464 (39)	0.134 (41)	0.338 (39)
$\mu_x(S_{4a}, h^4)$ (D Å <sup>-2</sup> )	-1.93 (13)	-2.16 (13)	-3.01 (15)	-2.90 (14)
$\mu_x(S_{4a}^2)$ (D)	0.1451 (52)	0.1452 (52)	0.1957 (36)	0.1808 (35)
$\mu_x(S_{4a}^2, h^2)$ (D Å <sup>-2</sup> )	0.608 (47)	0.644 (47)	0.764 (49)	0.737 (48)
No. of <i>ab initio</i> points	36	36	36	36
St. deviation (10 <sup>-2</sup> D)	0.16	0.16	0.15	0.15

TABLE VIII

Equilibrium dipole moment derivatives  $\mu_x(S_{3a})_e$  and  $\mu_x(S_{4a})_e$  and transition moments of the  $\nu_3$  and  $\nu_4$  fundamental bands of ammonia calculated *ab initio* compared with experimental values

$\mu_x(S_{3a})_e$ D Å <sup>-1</sup>	$\mu_x(S_{4a})_e$ D	Transition moment, D		Reference
		$\nu_3$	$\nu_4$	
0.208	0.480	0.0127	0.0541	1
0.229	0.363	0.0130	0.0425	3
0.078	0.525	0.0103	0.0584	this work
0.195	0.336	0.0112	0.0418	experiment <sup>19</sup>

TABLE IX  
Predictions of transition moments (D) from the  $\mu_x$  *ab initio* dipole moment component of ammonia and the oxonium ion

Vibrational band	Potential I		Potential II		$D_3O^+$
	$NH_3$	$ND_3$	$NH_3$	$ND_3$	
$\nu_3$	<i>s-s</i>	0.0085	0.0089	0.0103	0.1608
$\nu_3$	<i>a-a</i>	0.0085	0.0089	0.0103	0.1342
$\nu_2 + \nu_3$	<i>s-s</i>	-0.0106	-0.0091	-0.0104	-0.0286
$\nu_2 + \nu_3$	<i>a-a</i>	-0.0106	-0.0091	-0.0104	-0.0189
$\nu_3 - \nu_2$	<i>s-s</i>	-0.0094	-0.0082	-0.0085	-0.0049
$\nu_3 - \nu_2$	<i>a-a</i>	-0.0095	-0.0082	-0.0087	-0.0027
$(\nu_2 + \nu_3) - \nu_2$	<i>s-s</i>	0.0163	0.0129	0.0180	0.1634
$(\nu_2 + \nu_3) - \nu_2$	<i>a-a</i>	0.0136	0.0125	0.0158	0.1525
$\nu_4$	<i>s-s</i>	0.0565	0.0503	0.0584	0.1241
$\nu_4$	<i>a-a</i>	0.0565	0.0503	0.0584	0.0886
$\nu_2 + \nu_4$	<i>s-s</i>	-0.0058	-0.0037	-0.0053	-0.0024
$\nu_2 + \nu_4$	<i>a-a</i>	-0.0059	-0.0037	-0.0054	-0.0042
$\nu_4 - \nu_2$	<i>s-s</i>	-0.0057	-0.0034	-0.0050	-0.0094
$\nu_4 - \nu_2$	<i>a-a</i>	-0.0057	-0.0034	-0.0050	-0.0082
$(\nu_2 + \nu_4) - \nu_2$	<i>s-s</i>	0.0603	0.0517	0.0616	0.1253
$(\nu_2 + \nu_4) - \nu_2$	<i>a-a</i>	0.0586	0.0515	0.0602	0.1190
$2\nu_4(E)$	<i>s-s</i>	0.0016	0.0010	0.0038	—
$2\nu_4(E)$	<i>a-a</i>	0.0016	0.0010	0.0038	—

types of transition moments in the inversional mode. Scaling of the  $\mu_z$  dipole moment component of the oxonium ion by the factor 0.8250 determined for ammonia resulted in a good agreement with high quality *ab initio* predictions<sup>6</sup>. The results of scaling of the  $\mu_z$  component are collected in Table VI.

For the description of the  $\mu_x$  dipole moment component we have used three terms of the  $^1\mu_x$  expansion and two terms of the  $^2\mu_x$  expansion in order to reproduce the *ab initio* data with a standard deviation about  $10^{-3}$  D. The resulting values of dipole moment expansion coefficients are summarized in Table VII. From this table it is evident that the  $\mu_x$  dipole moment component is strongly influenced by the inversional motion. In particular, for the asymmetric stretching vibration the dipole moment is a rapidly varying function of the inversion coordinate  $h$ . It is important to respect this fact in calculations of transition moments. We do this by integrating the matrix elements of the  $\mu_x$  component over the wide range of the inversion coordinate explored by the nonrigid inverter wavefunctions. In this way we calculate the  $\nu_3$  fundamental transition moment to be 0.0103 D, which is in excellent agreement with the experimental value of 0.0112 D (ref.<sup>18</sup>). If we replace the dipole moment function by the constant  $\mu_x(S_{3a})_e$  (see Table VIII) and use the standard theory to evaluate the same transition moment we get a significantly lower value of 0.0048 D. This obviously shows that the nonrigid inverter approach is more adequate when dealing with rapidly varying functions of the large amplitude coordinate  $h$ .

The nonrigid inverter model also allows the calculation of combination and hot band transition moments which arise from the combination of degenerate vibrations and inversion. Transition moments calculated from the  $\mu_x$  component of both molecules are reported in Table IX. It can be seen that there is a significant effect of deuteration on transition moments in both molecules and that infrared absorption in degenerate fundamental bands is generally stronger for the oxonium ion.

As a conclusion we can summarize the most important findings.

1) Although the SCF calculations with a modest set of basis functions overestimate the molecular dipole moment and transition moments, they describe very well the anharmonic properties of the dipole moment functions of nonrigid molecules under investigation. The calculated transition moments can be brought into close agreement with experimental data by simple scaling of the dipole moment functions.

2) The effect of the large amplitude molecular inversion on transition moments in the small amplitude vibrational modes is found to be significant. This means that the nonrigid inverter model should be used for calculations of these transition moments rather than the standard approach.

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## REFERENCES

1. Smit W. M. A., van Dam T.: *J. Chem. Phys.* **72**, 3658 (1980).
2. Figeys H. P., Berckmans D., Geerlings P.: *J. Chem. Soc., Faraday Trans. 2*, **77**, 2091 (1981).
3. Swanton D. J., Backsay G. B., Hush N. S.: *J. Chem. Phys.* **107**, 9 (1986).
4. Špirko V., Čársky P.: *J. Mol. Spectrosc.* **87**, 584 (1981).
5. Rosmus P., Botschwina P., Werner H. J., Vaida V., Engelking P. C., McCarthy M. I.: *J. Chem. Phys.* **86**, 6669 (1987).
6. Botschwina P., Rosmus P., Reinsch E. A.: *Chem. Phys. Lett.* **102**, 299 (1983).
7. Colvin M. E., Raine G. P., Schaefer III M. F., Dupuis M.: *J. Chem. Phys.* **79**, 1551 (1983).
8. Person W. P., Zerbi G. (Eds): *Vibrational Intensities in Infrared and Raman Spectroscopy*, Chaps 1—4. Elsevier Scientific Publishing Company, New York 1982.
9. Špirko V., Stone J. M. R., Papoušek D.: *J. Mol. Spectrosc.* **60**, 159 (1976).
10. Špirko V.: *J. Mol. Spectrosc.* **101**, 30 (1983).
11. Pracna P., Špirko V., Kraemer W. P.: *J. Mol. Spectrosc.*, submitted.
12. Papoušek D., Sarka K.: *J. Mol. Spectrosc.* **28**, 125 (1968).
13. Pulay P., Fogarasi G., Pang F., Boggs J. E.: *J. Am. Chem. Soc.* **101**, 2550 (1979).
14. Hougen J. T., Bunker P. R., Johns J. W. C.: *J. Mol. Spectrosc.* **34**, 136 (1970).
15. Krishnan R., Binkley J. S., Seeger R., Pople J. A.: *J. Chem. Phys.* **72**, 650 (1980).
16. King H., Dupuis M., Rys J.: *Natl. Res. Comput. Chem. 1*, Software Cat., Prog. No. QHO2 (HONDO), (1980).
17. Špirko V., Kraemer W. P.: *J. Mol. Spectrosc.*, in press.
18. Sears T. J., Bunker P. R., Davies P. B., Johnson S. A., Špirko V.: *J. Chem. Phys.* **83**, 2676 (1985).
19. Koops T., Visser T., Smit W. M. A.: *J. Mol. Struct.* **96**, 203 (1983).
20. Shimoda K., Ueda Y., Iwahori J.: *Appl. Phys.* **21**, 181 (1980).
21. Takami M., Jones H., Oka T.: *J. Chem. Phys.* **70**, 3557 (1979).
22. Nakanaga T., Kondo S., Saěki S.: *J. Mol. Spectrosc.* **112**, 39 (1985).
23. Urban Š., Papoušek D., Malathi Devi V., Fridovich B., D'Cunha R., Narahari Rao K.: *J. Mol. Spectrosc.* **106**, 38 (1984).
24. Benedict W. S., Plyler E. K., Tidwell E. D.: *J. Chem. Phys.* **29**, 829 (1958).
25. Beckwith P. M., Danagher D. J., Reid J.: *J. Mol. Spectrosc.* **121**, 209 (1987).

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