Resolution of K-Splitting in the Rotation-Inversion Raman Spectrum of Ammonia NH_3

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The rotation-inversion Raman spectrum of the NH_3 molecule has been photoelectrically recorded. The K-splitting in the R- and S-branch could be partly resolved. The intensity contour has been simulated by use of a computer program.

Introduction

Because of its relatively small moment of inertia the ammonia molecule is well suited for the investigation of the structure of rotational Raman spectra of symmetric top molecules. The splitting of the rotational lines due to the quantum number K of the component of the angular momentum along the molecular symmetry axis has not been observed before in a pure rotational Raman spectrum of any other molecule [1]. The unresolved K-splitting leads to a displacement of the rotational Raman lines which is different for the S- and R-branches and therefore causes difficulties in the determination of rotational constants B_0 and centrifugal distortion constants D^J which were overcome theoretically by introducing estimated values for the centrifugal distortion constant D^{JK} in the analysis [2–4]. Our photoelectrically recording Raman spectrometer [5] allows to achieve a resolution of 0.3 cm^{-1}. This is sufficient to resolve the expected K-splitting for NH_3 at least partly and therefore we decided to use this molecule to study experimentally the influence of this effect on the profile of the rotational Raman lines of a symmetric top molecule.

Since the early paper by Amaldi and Placzek [6] no investigation of the rotational Raman spectrum of gaseous ammonia has been published. This may be due to the fact that the molecular constants of this very polar molecule could be determined with high accuracy from infrared and microwave spectra [7–16]. Therefore the purpose of this investigation can only be to discuss the principal problems of the structure of the pure rotational Raman spectrum of a symmetric top molecule, to check the agreement of theory and experiment, and to draw conclusions for the evaluation of Raman spectra of other molecules of this type with higher moments of inertia. Part of this work has been reported earlier [17].

Experiment

The Raman spectrum was excited with 7 W of argon ion laser power at 514.5 nm and recorded with a Jarrell-Ash 1 m double monochromator equipped with holographic gratings (2400 grooves/mm) and a computing photon counting system. A more detailed description of the spectrometer can be found elsewhere [5].

Theory

The rotational term levels of an oblate symmetric top molecule are represented in good approximation by [13]

$$\begin{aligned} F_v^{\pm}(J,K) = {} & B_v^{\pm}\, J(J+1) + (C_v^{\pm} - B_v^{\pm})\, K^2 \\ & - D_v^{J\pm}\, J^2 (J+1)^2 \\ & - D_v^{JK\pm}\, J(J+1)\, K^2 - D_v^{K\pm}\, K^4 \, . \end{aligned} \tag{1}$$

B_v and C_v are the rotational constants for the vibrational state v and D_v^J, D_v^{JK}, and D_v^K are the corresponding centrifugal distortion constants. The indices + and − denote the symmetric and antisymmetric levels with respect to inversion, respectively, J is the quantum number of the total angular momentum, and K that of its component along the molecular symmetry axis.

For rotation-inversion Raman transitions the selection rules are $\Delta J = \pm 1, \pm 2$; $\Delta K = 0$; $+ \leftrightarrow +$ and $- \leftrightarrow -$.

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The relative intensity of a rotational Raman transition can be calculated with the formula [18]

$$I^{\pm vJ'K}_{vJK} \sim (\nu_0 + \nu^{vJ'K}_{vJK})^4 \cdot g^{\pm}_{JK} \, (L^{(2)})^{vJ'K}_{vJK} \cdot \exp(-E^{\pm}_{v}(J,K)/kT)\,, \tag{2}$$

where $\boldsymbol{\nu}_0$ denotes the wavenumber of the exciting radiation and $\nu^{vJ'K}_{vJK}$ that of the Raman transition, $g^{\pm}_{JK}$ the statistical weight of the initial state due to nuclear spin degeneracy, $E^{\pm}_{v}(J,K)$ the energy of the initial state, k Boltzmann's constant, and T the temperature. Altmann and Strey [18] have shown that the line strength $(L^{(t)})$ can be expressed in closed form for a symmetric top molecule. Only anisotropic scattering with $t=2$ must be considered in our case, namely

$$(L^{(2)})^{vJ'K}_{vJK} = (2J+1)(2J'+1) \cdot \begin{pmatrix} J' & 2 & J \\ -K & 0 & K \end{pmatrix}^2 \left| (\bar{f}_0{}^{(2)})^v_v \right|^2 , \tag{3}$$

where $(\bar{f}_0{}^{(2)})$ is the anisotropic component of the polarizability tensor in spherical coordinates (in the molecular system). Wigner's 3-j symbol depends on the quantum number K in a different way for the S-branch $(\Delta J = 2)$

$$\begin{pmatrix} J+2 & 2 & J \\ -K & 0 & K \end{pmatrix}^2 = \frac{6[(J+2)^2-K^2][(J+1)^2-K^2]}{(2J+5)(2J+4)(2J+3)(2J+2)(2J+1)} \tag{4}$$

and for the R-branch $(\Delta J = 1)$

$$\begin{pmatrix} J+1 & 2 & J \\ -K & 0 & K \end{pmatrix}^2 = \frac{24K^2[(J+1)^2-K^2]}{(2J+4)(2J+3)(2J+2)(2J+1)\,2J} \tag{5}$$

which leads to a different intensity distribution (see also [1]).

Results and Discussion

The line positions and line strengths for the rotational transitions from $J=0$ to $J=12$ were calculated using Eqs. (1) and (2). A consistent set of molecular constants derived from the literature [7–15] was used. The more refined sets of constants including higher order terms [16, 19] were not required in view of the limited accuracy of our Raman measurement. The resulting line spectrum was convoluted with the instrument profile which was obtained by recording the profile of the

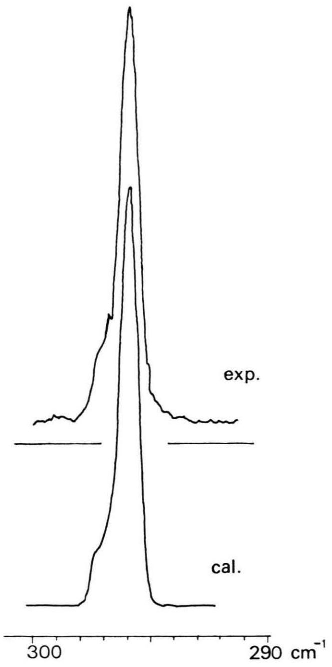

Fig. 1. Rotational Raman transition $S(6, K)$ of NH_3. Pressure $p=0.4$ bar, laser power 7 W at 514.5 nm, slit width $s=0.33$ cm^{-1}, scanning speed $v=3 \cdot 10^{-3}$ cm^{-1}/s, time constant $\tau=16$ s.

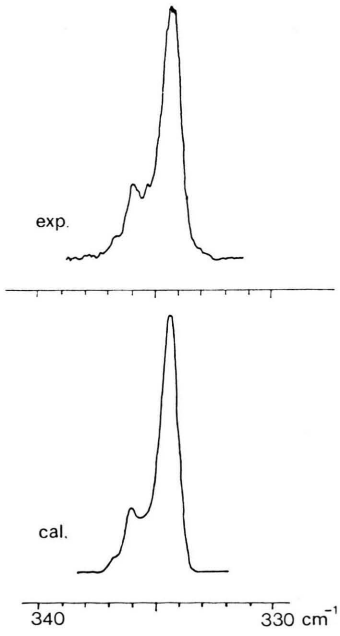

Fig. 2. Rotational Raman transition $S(7, K)$.

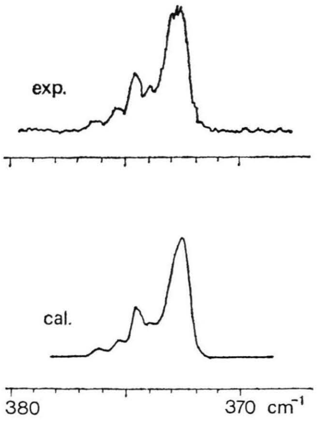

Fig. 3. Rotational Raman transition $S(8, K)$.

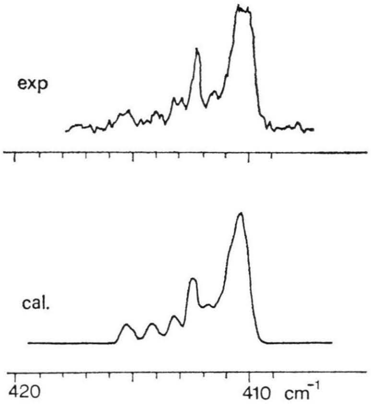

Fig. 4. Rotational Raman transition $S(9, K)$.

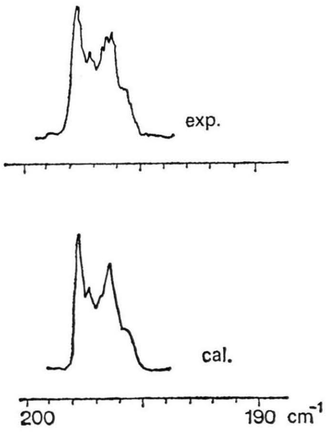

Fig. 5. Rotational Raman transition $R(9, K)$.

Rayleigh line; the half band width was measured to be 0.5 cm^{-1} for the scanning conditions used for the Raman spectrum.

Figures 1 to 5 show the experimental and calculated intensity distributions of the rotational Raman transitions for $J=6$ to $J=9$ in the S-branch and $J=9$ in the R-branch. The K-structure is clearly resolved from $J=7$ on. The intensity distribution is determined by three K-dependent factors: the statistical weight g_{JK}, the line strength through Eqs. (4) and (5), and the K-dependent part of the exponential in Eq. (2), namely

$$\exp\alpha = \exp(-[(C_0 - B_0)K^2 - D_0{}^{JK} J(J+1)K^2 - D_0{}^K K^4]/kT).$$

A numerical example for the relative contributions of the three factors is given in Table 1 for $J=9$. The exponential increases monotonically with K (for a prolate symmetric top with $(A_0 - B_0) > 0$ on the contrary it decreases with K and therefore it would be more difficult to observe the K-structure in such a case). The statistical weight is 12 for K=multiples of 3 and 6 for the other K. For $K=0$ the average has to be taken of $g_{JK}^{+}=12$ for the symmetric inversion state and $g_{JK}^{-}=0$ for the anti-symmetric one. The line strength attains its maximum for an intermediate, but relatively high K — in this example for $K=7$ — in the R-branch and for $K=1$ in the S-branch. Together with the other factors this results in a shift of the intensity maximum of an R-branch transition to high K-values (and to high wavenumbers, when D_0^{JK} is negative as for NH_3). For an unresolved K-structure the center of an R-branch line is shifted from the $K=0$ position to a greater extent than the center of an S-branch line.

Conclusion

The results of our investigation of the K-structure in the pure rotational Raman spectrum of NH_3 demonstrate quantitatively the validity of the theoretical expressions for rotational energies and Raman intensities of symmetrical tops within our experimental accuracy. As long as modern high resolution methods of nonlinear Raman spectroscopy [20] are not applicable to pure rotational Raman spectra, the approximations used in the analysis of unresolved symmetric top spectra [2—4] can be used with confidence.

Table 1. Relative values of K-dependent factors determining the intensity profile for $J = 9$.

			S-branch		R-branch	
K	$\exp\alpha$	$g_{JK}\exp\alpha$	$\begin{pmatrix} J+2 & 2 & J \\ -K & 0 & K \end{pmatrix}^2$	$(\ldots)^2\, g_{JK}\exp\alpha$	$\begin{pmatrix} J+1 & 2 & 2 \\ -K & 0 & K \end{pmatrix}^2$	$(\ldots)^2\, g_{JK}\exp\alpha$
0	1	2	0	0	0	0
1	1.02	2.04	$1.77 \cdot 10^{-2}$	$3.6 \cdot 10^{-2}$	$7.52 \cdot 10^{-4}$	$1.53 \cdot 10^{-3}$
2	1.07	2.15	$1.67 \cdot 10^{-2}$	$3.59 \cdot 10^{-2}$	$2.92 \cdot 10^{-3}$	$6.27 \cdot 10^{-3}$
3	1.17	4.7	$1.51 \cdot 10^{-2}$	$7.12 \cdot 10^{-2}$	$6.22 \cdot 10^{-3}$	$2.92 \cdot 10^{-2}$
4	1.33	2.66	$1.31 \cdot 10^{-2}$	$3.49 \cdot 10^{-2}$	$1.02 \cdot 10^{-2}$	$2.72 \cdot 10^{-2}$
5	1.56	3.13	$1.07 \cdot 10^{-2}$	$3.35 \cdot 10^{-2}$	$1.42 \cdot 10^{-2}$	$4.46 \cdot 10^{-2}$
6	1.91	7.63	$8.08 \cdot 10^{-3}$	$6.17 \cdot 10^{-2}$	$1.75 \cdot 10^{-2}$	$1.34 \cdot 10^{-1}$
7	2.41	4.83	$5.46 \cdot 10^{-3}$	$2.64 \cdot 10^{-2}$	$1.9 \cdot 10^{-2}$	$9.17 \cdot 10^{-2}$
8	3.17	6.35	$3.05 \cdot 10^{-3}$	$1.94 \cdot 10^{-2}$	$1.75 \cdot 10^{-2}$	$1.11 \cdot 10^{-1}$
9	4.34	17.35	$1.13 \cdot 10^{-3}$	$1.96 \cdot 10^{-2}$	$1.17 \cdot 10^{-2}$	$2.03 \cdot 10^{-1}$

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