An Improved Variational Calculation of the Lower Vibrational Energy Levels of the Ammonia Molecule

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A new variational calculation of the inversion spectrum of ammonia is reported in which all six vibrational degrees of ammonia are employed. By fitting spectroscopic data, an inversion barrier of 1810 cm^{-1} is obtained.

I. Introduction

A full variational calculation of the lower vibrational energy levels ($J = 0$) of ammonia has been recently reported [1]. All six internal degrees of freedom of the molecule were employed. The main interest of the calculation was in the so-called inversion spectrum. In earlier calculations of the inversion spectrum, the inversion motion had either been considered completely separable from the other motions [2] or the interaction between inversion motion and other motions had only been considered in a limited manner [3, 4].

In the previously reported full variational calculation, the ammonia potential was taken to be the sum of two terms, $V_{r,\alpha}$ and V_θ. $V_{r,\alpha}$ is a potential involving the displacements of N–H stretching coordinates and H–N–H bending coordinates from their respective equilibrium values which was derived from a potential obtained by Morino et al. [5] by fitting perturbation theory formulae to spectroscopic data without taking into account the double minimum problem of the inversion. V_θ is an inversion barrier double minimum potential which is of a form used by Swalen and Ibers [2 b] and which contains three parameters. The Morino potential $V_{r,\alpha}$ was considered to be fixed while the three parameters of the inversion potential V_θ were varied in such a way as to give agreement with the observed inversion spectrum of ammonia. The previously reported calculation, which was based on the full Watson [6] Hamiltonian and on the work of Whitehead and Handy [7] extended to tetraatomic molecules, involved the numerical evaluation of matrix elements with use of 49 152 Gauss-Hermite points for each integral. This latter procedure is very expensive in computer time and placed severe limits on the calculation. However, symmetry considerations lead to the realization that many of the integration points in the integration procedure for a symmetric molecule are equivalent. This finding (which has also been employed in recent calculations on formaldehyde [8]) permits one to reduce the number of integration points in ammonia to one quarter of the number previously used. It was consequently decided to reinvestigate the ammonia inversion problem within the framework of the faster computational procedure.

II. Method

The Whitehead-Handy procedure as applied to ammonia has already been described in the previous publication [1]. The basis functions are products of six harmonic oscillator wavefunctions corresponding to the six normal frequencies of a "planar ammonia" molecule. The frequency parameters of the harmonic oscillator wavefunctions may be considered as variational parameters. In the previous calculations, these parameters were chosen 2500, 725, 2500, and 1500 cm^{-1} for the six normal frequencies respectively (the last two listed of which are doubly degenerate). In the new more extensive calculations here better (variationally) values are found to be 2500, 725, 3580, and 1690 cm^{-1} respectively. Extensive calculations were carried out here on integration point number and on basis set size with respect to accuracy and convergence of the calculation. The final new calculations here correspond to the use of 448 basis functions in each symmetry block, whereas the previously reported calculations corresponded to a maximum of 252 basis functions in each symmetry block. The number of integration points corresponds to 12 points for the symmetrical stretching coordinate, 16 points for the inversion coordinate, and 4 points for each of the four degenerate asymmetrical coordinates. The basis function set for the final calculations reported here includes all excitations of symmetric stretch up to and including seven excitations, all excitations of inversion motion up to and including 15 excitations, and excitations of asymmetric motions up to and including two excitations. Only the A_1 and A_2 symmetry states are determined as similar criteria for E states would require the use of 640 basis functions.

The testing of accuracy of these calculations, which was similar (but not as extensive) to that carried out for H_2CO in [8 b] leads us to report here only the results for: a) the ground state 0^+, b) the states of the lower inversion spectrum 0^-, $n\nu_2^{\pm}$ ($n \leqq 3$); and c) the singly excited "stretching" states $\nu_1^{\pm}$. For the ground state, absolute energies are reported while for the other states spectral energies (differencing from ground state) are reported. For a given potential, we judge the accuracy of the calculation of spectral energies to be ~ 0.1 cm^{-1} for 0^-, ~ 1 cm^{-1} for $\nu_2^{\pm}$, ~ 2 cm^{-1} for $2\nu_2^{+}$, ~ 5 cm^{-1} for $2\nu_2^{-}$ and $\nu_1^{\pm}$.

III. Results and Discussion

As in [1], the inversion potential has the form

$$V_\theta = A\theta^2 + B\exp(-C\theta^2)$$

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Table 1. Observed and calculated energy levels (cm^{-1}) of NH_3.

State	$\nu_{\mathrm{obs}}^{\mathrm{a}}$	$\nu_{\mathrm{calc}}^{\mathrm{b}}$ (I)	$\nu_{\mathrm{calc}}^{\mathrm{c}}$ (II)
0^+	0	58 449.86 [d]	63 068.70
0^-	0.8	1.33	0.74
ν_2^+	932.5	891.35	941.69
ν_2^-	968.3	946.65	977.04
$2\nu_2^+$	1597 [e]/1602 [f]	1518.54	1604.32
$2\nu_2^-$	1882.2 [c]/1910	1846.40	1890.22
$3\nu_2^+$	2383.5	2351.95	2382.39
$3\nu_2^-$	2895.5	2868.12	2884.15
ν_1^+	3336.2/3337 [f]	3366.10	3367.65
ν_1^-	3337.2	3367.80	3368.69

[a] Energy levels with respect to ground state (0^+) as zero of energy. All data from [9] unless noted otherwise.

[b] Absolute energy of ground state; other energies relative to ground state. Potential function of reference [1], the inversion parameters of which (A, B, C) are labelled I in text.

[c] Energies as in footnote b. New potential function with inversion potential parameters labelled II in text.

[d] In reference [1], an energy of 58 557 cm^{-1} was obtained with the same potential function.

[e] Reference [10].

[f] Reference [11].

with

$$\theta = (\alpha_1 + \alpha_2 + \alpha_3)/\sqrt{3}\,.$$

V_θ is in atomic units and α_i is the angle between the i'th N−H bond and the H−H−H plane in radians. With the fixed parameters of the Morino potential $V_{r,\alpha}$ a parameter set A, B, C was found in [1] which gave reasonable agreement with the observed inversion spectrum:

$$A = 0.1164 \text{ au rad}^{-2}\,,\quad B = 0.2397 \text{ au}\,,\quad C = 0.6369 \text{ rad}^{-2}\,. \tag{I}$$

This parameter set corresponds to an H−N−H equilibrium angle of 21.58° and a barrier height to inversion of 1616 cm^{-1}. It has now been found that the previous calculations are not variationally "converged". The "converged" calculations for this potential are presented as ν_{calc} (I) in Table 1; it is seen that the agreement of the observed and calculated inversion spectrum is not very good and that, indeed, the present calculations do lead to lower energies (see footnote d, Table 1). The inversion splittings (splittings between corresponding + and − states) tend to be too large, indicating that the barrier to inversion is too low.

Consequently it was decided to search for a new A, B, C parameter set to yield better agreement with the inversion spectrum while keeping $V_{r,\alpha}$ as in [1]. This new parameter set was found,

$$A = 0.1220 \text{ au rad}^{-2}\,,\quad B = 0.26161 \text{ au}\,,\quad C = 0.6140 \text{ rad}^{-2}\,. \tag{II}$$

This set corresponds to a barrier height of 1810 cm^{-1}. The parameters were chosen to yield an equilibrium H−N−H bond angle of 22.13° in agreement with the experimental value [9]. The results of the calculations are shown in Table 1 as ν_{calc} (II).

It is to be noted that the inversion barrier of 1810 cm^{-1} of the new calculation is close to that found in [4] and [5], where only limited interaction between inversion motion and other motions was permitted. Further details of the present calculations will be presented in another publication.

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