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

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A variational calculation of the lower-lying vibrational energy levels of the ammonia molecule is performed, in which all six vibrational degrees of freedom are treated simultaneously. A literature potential is assumed for all non-inversion motions; a new inversion barrier potential with a barrier of 1616 cm^{-1} is determined by fitting experimental data.

I. Introduction

The calculation of the lower-lying vibrational energy levels of the ammonia molecule, in particular those associated with the inversion motion, has been the focus of many investigations [1–5]. The inversion motion usually has been separated from the other degrees of freedom; thus the parameters of a double minimum potential have been adjusted so that the resulting energy levels of a one-dimensional calculation fit the observed inversion spectrum. The quantity which has often been referred to as the experimental barrier height (2022 cm^{-1}) for inversion in ammonia was derived by Swalen and Ibers [2] by such calculation for NH_3 and ND_3. Limited treatments of interaction between inversion motion and other vibrational motion and rotation have been previously carried out [4, 5]. This communication reports a variational calculation of the vibrational energy levels of ammonia in which all degrees of freedom are permitted to interact.

II. Method

Variational calculations of the vibrational energy levels of triatomic molecules have been reported [6, 7]. The method of solution used here is based on such work of Whitehead and Handy, extended to tetraatomic molecules. The Watson [8] form of the kinetic energy operator expressed in normal coordinates is combined with a suitable potential energy expression. The representation of the total Hamiltonian operator is constructed in a given finite basis. For $J = 0$ here, the basis functions are products of normal coordinate harmonic oscillator wavefunctions. This basis suggests the numerical evaluation of the vibrational matrix elements by a Gauss-Hermite quadrature technique. The expression used for the potential energy can be quite flexible.

In the application here, one must recognize the double-well character of the potential function. Thus, the normal coordinates, in terms of which the kinetic energy operator as well as the basis functions are expressed, are taken to be those of a planar symmetric ammonia molecule with the N-H distance at the corresponding experimental equilibrium internuclear distance. The details of this procedure will be discussed elsewhere [9]. The six normal coordinates of planar ammonia are designated in terms of principal constituents: 1. symmetric nitrogen-hydrogen stretch, 2. inversion motion, 3. and 5. degenerate asymmetric nitrogen-hydrogen stretches, and 4. and 6. degenerate asymmetric bends.

Because of computational limitations, it is impractical to determine the parameters of a complete potential energy surface for ammonia by fitting the calculated energy levels to spectroscopic data. Consequently, the potential was based on a modification of a potential derived by Morino et al. [10] by fitting perturbation theory formulae to spectroscopic data without taking into account the double minimum problem. The Morino potential contains up to quartic terms in the displacements of N-H stretching coordinates and the H-N-H bond-angle-bending coordinates from their respective experimental equilibrium values. This potential has been modified to eliminate terms involving the symmetrical combination of the bond-angle-bending coordinates so that it no longer contains any restraint to symmetric (umbrella) inversion motion. The form of the "inversion barrier potential", which is added to this potential, is assumed to be the one used by Swalen and Ibers [2], namely the sum of a quadratic parabola and a Gaussian. The three parameters of

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this potential *(vide infra)* are determined by the calculations reported here.

The basis functions are products of six harmonic oscillator wavefunctions corresponding to the six normal coordinates. A maximum of 256 basis functions was used for each symmetry block of the vibrational problem, including all combinations of up to 15 excitations in the inversion motion and up to 7 excitations in the symmetric stretch, as well as selected functions of the other coordinates.

Each matrix element of the variational procedure is a six-dimensional integral; stringent limitations must be imposed on the number of points used in each dimension of the integration procedure. A total of 49152 Gauss-Hermite points is found sufficient for an integration accuracy of 1 cm^{-1} in the five or six lowest states and 2 cm^{-1} in the other states reported: 24 points for the inversion coordinate, 8 points for the symmetric stretch and 4 for each of the asymmetric stretches and bends.

III. Results and Discussion

Table 1 shows results obtained for NH_3 and ND_3 and relevant experimental data. The three parameters of the inversion potential were varied to obtain a fit to the spectroscopic data for NH_3 (not ND_3) for "pure" inversion motion (i. e. O^-, $n\,\nu_2^{\pm}$ in Table 1). While computer time requirements prevented a least squares fitting procedure, the parameters obtained for the inversion potential are expected to be close to "optimum" (given the fixed parameters of the modified Morino potential):

$$V = 0.50762\,\theta^2 + 1.045111\exp(-0.63689\,\theta^2)$$

with

$$\theta = (\alpha_1 + \alpha_2 + \alpha_3)/(3)^{1/2}.$$

V is in 10^{-11} ergs and α_i is the angle between the i'th N-H bond and the H-H-H- plane in radians. The potential enables one to determine the equilibrium geometry of the symmetric pyramidal ammonia molecule; a value of 21.58° is found for the H-N-H angle which compares favorably with the experimental value [10] 22.13°. The barrier height to inversion is found to be 3.21×10^{-13} ergs or 1616 cm^{-1}, about 400 cm^{-1} lower than that reported by Swalen and Ibers [2] from their one-dimensional analysis. The calculations of [4] and [5] both yielded inversion barriers of about 1800 cm^{-1}.

Table 1. Experimental and Calculated Energy Levels of NH_3 and ND_3.

State	NH_3		ND_3	
	Exp [a]	Calc.	Exp [a]	Calc.
O^+	0	0	0	0
O^-	0.8	0.6	0.05	0
ν_2^+	932.5	932	745.7	737
ν_2^-	968.3	968	749.4	741
$2\,\nu_2^+$	1597 [b]/1602 [c]	1588	1359	1327
ν_4^+	1626.1	1644	1191	1213
ν_4^-	1627.4	1644		1213
$2\,\nu_2^-$	1882.2 [c]/1910	1884	1429	1419
$3\,\nu_2^+$	2383.5	2394	1830	1815
$\nu_4+\nu_2^+$	2539	2632		1995
$\nu_4+\nu_2^-$	2585/2586 [b]	2656		1998
$3\,\nu_2^-$	2895.5	2915	2106.6	2128
$2\,\nu_4^+$	3216.4/3217 [b]	3314 E [d]	2359	2452 A_1 [d]
		3325 A_1 [d]		2455 E [d]
$2\,\nu_4^-$	3218.6	3314 E [d]		2453 A_1 [d]
		3326 A_1 [d]		2455 E [d]
ν_1^+	3336.2/3337 [b]	3454	2420.1	2503
ν_1^-	3337.2	3456	2420 [c]	2502
$4\,\nu_2^+$	3442 [c]	3524	2482 [c]	2568
ν_3^+	3443.6	3504	2564.0	2629
ν_3^-	3443.9	3505		2630
$4\,\nu_2^-$		4122	2876 [c]	2994

[a] All data from [11] unless noted otherwise.
[b] Reference [12].
[c] Reference [13].
[d] Symmetry designations.

The assignment in Table 1 of the excitation state of each eigenvalue was made on the basis of the dominating contribution to the wavefunction [9]. A satisfactory fit to experiment is achieved for the pure inversion spectra. Other energy levels, which must depend strongly on the fixed parameters in the modified Morino potential are found to be systematically higher than experimental values. An improved fit of all the spectral data would require variation of these parameters.

The kinetic energy operator is "almost" diagonal in the normal coordinates. The fact that the calculation here gives an inversion barrier different from a one-dimensional calculation must arise from normal coordinate interaction terms in the potential energy. The normal coordinate Q_2 corresponds to pure z motion, perpendicular to the plane of the planar molecule, while the normal coordinate Q_1 corresponds to planar x, y motion. If one considers only symmetric displacements from the planar origin of the normal coordinates (with the N-H distance at the experimental equilibrium internuclear distance), it is clear that neither pure Q_1 nor pure

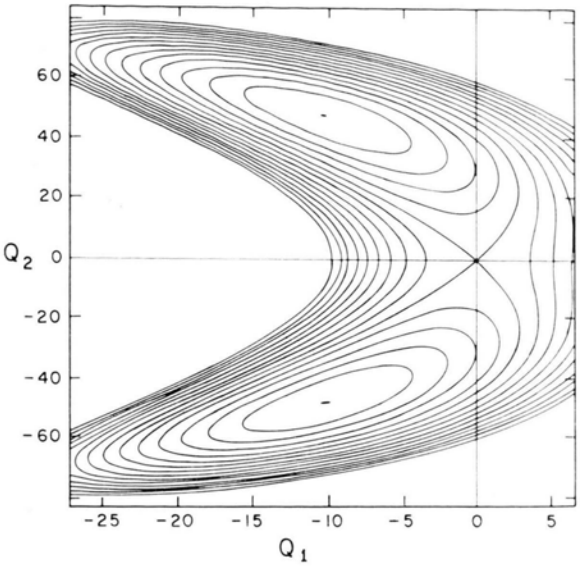

Fig. 1. Potential function in the space of the normal coordinates Q_1 and Q_2, as defined in the text. The minima are denoted by a dash-; the spacing between contours is 323 cm^{-1}.

Q_2 displacements will lead to the C_{3v} minima of the molecule. In Fig. 1, a plot of the potential for symmetrical displacements (i. e. as a function of Q_1 and Q_2) is shown. The interaction between Q_1 and Q_2 in the potential is clear. A limited number of two-dimensional calculations have been carried out with just Q_1 and Q_2 as variables; these have shown that a major portion of the lowering of the potential barrier, from its one-dimensional values, arises from just the introduction of the second dimension.

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