Energy Levels of a Symmetrical Double Minima Problem with Applications to the NH3 and ND3 Molecules

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The resulting gas was active. The experiment was repeated but without passing over hot CuO. The result was the same. These results excluded H_2, and N as NO or NO_2, for hydrogen would burn to water and be mixed with the water in the permanganate solution; NO or NO_2 would be oxidized completely to HNO_3 by the acidified permanganate.[9] Fluorine, if present as BF_3, would be completely hydrolyzed and absorbed by the aqueous solution. Boron, if present as volatile hydrides, would be oxidized and decomposed by the heated CuO or hydrolyzed by the solution.

The results of the chemical experiments eliminate all elements in the first row of the periodic system except carbon. The gas driven from

the boric oxide target has the properties of a mixture of carbon dioxide and carbon monoxide. Just why the newly formed carbon atoms should be oxidized partly to monoxide and partly to dioxide is not evident. It was not determined whether the two compounds were always formed in the same proportions.

Measurements on the half-life of the radioactive gas both before and after chemical treatment yielded the value 20.5 minutes in all cases, indicating that the activity is due to a single substance. Since C^{12} is stable, on the physical grounds outlined above, this substance is probably C^{11}.

We wish to express here our thanks to the Seeley W. Mudd fund for the financial support which made this work possible.

[9] Klemenc and Bunzl, Zeits. f. anorg. Chemie 122, 315 (1922).

Energy Levels of a Symmetrical Double Minima Problem with Applications to the NH₃ and ND₃ Molecules[1]

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The energy levels for a potential energy $V = -C \operatorname{sech}^2 r/2\rho + D \operatorname{sech}^4 r/2\rho$ have been obtained by numerical solution of continued fractions. Values of the constants have been found such that the computed energy levels agree satisfactorily with the experimental values for the NH_3 and ND_3 molecules. The height of the ammonia pyramid is found to be 0.37A, the height of the potential hill is found to be 2076 cm^{-1}, and the dissociation energy is about five volts.

IT has been found possible to obtain a satisfactory interpretation of the infrared spectrum of ammonia by assuming that the molecule is shaped like a symmetrical pyramid. The potential energy as a function of the distance of the nitrogen atom from the plane of the hydrogens has the general shape indicated in Fig. 1. Whenever there are symmetrical double minima in the potential energy, the energy levels below the top of the center of the hill will be double, and above the top of the hill the levels for which

the wave functions are symmetric will be shifted upward with respect to the levels for which the wave functions are antisymmetric.

Quantitative calculations of the behavior of the energy levels of a symmetrical double minima problem have been carried out by several authors.[2] The assumed forms of potential energy have been somewhat artificial, and except for the paper of Morse and Stueckelberg the methods used have been approximate. For these

[1] A preliminary report of these results is given in an abstract, Phys. Rev. 46, 335 (1934).

[2] Morse and Stueckelberg, Helv. Phys. Acta 4, 337 (1931); Dennison and Uhlenbeck, Phys. Rev. 41, 313 (1932); Rosen and Morse, Phys. Rev. 42, 210 (1932).
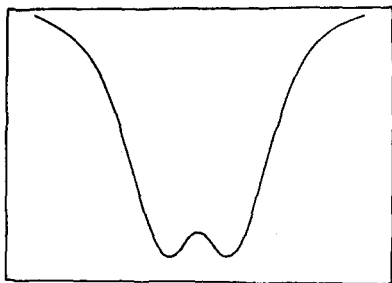
FIG. 1. Approximate form of the potential energy of the ammonia molecule as a function of the distance from the nitrogen atom to the plane of the hydrogen atoms.

reasons and because there are now available further data on the spectra of the NH₃ and ND₃ molecules further study of the problem has been considered worth while.

An expression for the potential energy which has the correct general characteristics and which permits an exact solution of the Schroedinger equation is:

$$V = \frac{1}{k\rho^2} \left[-\frac{\beta}{2}\left(\frac{\beta}{2}+\frac{1}{2}\right) \operatorname{sech}^2 \frac{r}{2\rho} \right.$$
$$\left. -D\left(\operatorname{sech}^2 \frac{r}{2\rho} - \operatorname{sech}^4 \frac{r}{2\rho} \right) \right], \quad (1)$$

where k equals $8\pi^2 c/h$ times the reduced mass of the molecule for the type of vibration considered; r is the distance from the nitrogen atom to the plane of the hydrogens; and ρ, β and D are arbitrary constants.

The potential energy is:

$$-\frac{1}{k\rho^2}\frac{\beta}{2}\left(\frac{\beta}{2}+\frac{1}{2}\right) \quad (2)$$

at $r=0$, and zero at $r=\pm\infty$. There is a minimum at $\pm r_0$, where

$$\operatorname{sech}^2 \frac{r_0}{2\rho} = \frac{(\beta/2)(\beta/2+\frac{1}{2})+D}{2D}. \quad (3)$$

The height of the central hill above the minima is

$$\frac{1}{k\rho^2}\frac{[D-(\beta/2)(\beta/2+\frac{1}{2})]^2}{4D}. \quad (4)$$

The Schroedinger equation for the vibration is:[3]

$$\frac{d^2R}{dr^2} + k\left[E + \frac{(\beta/2)(\beta/2+\frac{1}{2})+D}{k\rho^2} \operatorname{sech}^2 \frac{r}{2\rho} \right.$$
$$\left. -\frac{D}{k\rho^2} \operatorname{sech}^4 \frac{r}{2\rho} \right]R = 0, \quad (5)$$

where E is the energy in cm⁻¹.

Making the substitutions $x = \tanh^2 (r/2\rho)$ and $R = (1-x)^{\beta/2-\lambda}F$, it is found that F must satisfy the differential equation:

$$(x-x)^2 F'' + [\tfrac{1}{2} - (\beta - 2\lambda + \tfrac{3}{2})x]F'$$
$$+ [\lambda(\beta - \lambda - \tfrac{1}{2}) + Dx]F = 0, \quad (6)$$

where $$E = -(1/k\rho^2)(\beta/2-\lambda)^2. \quad (7)$$

If $F = \Sigma a_n x^{m+n}$, the recursion relation between successive coefficients is:

$$(m+n)(m+n+\tfrac{1}{2})a_{n+1}$$
$$- (m+n-\lambda)(m+n+\beta+\tfrac{1}{2}-\lambda)a_n + Da_{n-1} = 0. \quad (8)$$

The roots of the indicial equation are $m=0$ and $m=\frac{1}{2}$. The first corresponds to solutions which are symmetric about the plane of the hydrogens and the second to solutions which are antisymmetric. When $\beta/2-\lambda$ is positive, the boundary conditions are satisfied if there are no terms containing negative powers of x, and if the series converges at $x=1$. The values of λ for which these two conditions are fulfilled are the roots of the continued fraction

$$0 = 1 - \frac{Q_0}{1 - \dfrac{Q_1}{1 - \dfrac{Q_2}{1 - \cdots}}}, \quad (9)$$

where $$Q_n = \frac{(m+n+1)(m+n+\tfrac{1}{2})}{P_n P_{n+1}}D$$

$$P_n = (m+n-\lambda)(m+n+\beta+\tfrac{1}{2}-\lambda). \quad (10)$$

As n is increased Q_n becomes smaller and after some reasonable number of terms can be neglected in comparison with unity. For given values

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[3] See Rosen and Morse for a justification of the method of normal coordinates as applied to polyatomic molecules.

of β and D, the values of λ for which Eq. (9) is satisfied can be found numerically by a process of successive approximations. By this method it was found that $\beta=70$, $D=1920$, $k\rho^2=2.885 \times 10^{-2}$, give energy levels which are in good agreement with those found experimentally for the parallel type vibrations of ammonia. The results are given in Table I.

TABLE I.

| | NH$_3$ | | ND$_3$ | |
	calc.	obs.	calc.	obs.
0_s	0	0	0	0
0_a	0.83	0.67	<0.2	
1_s	935	932± 0.5	746.0	746± 2
1_a	961	964± 0.5	748.5	755±10
2_s	1610	1600±15	1379	1363± 2
2_a	1870	1910±15	1434	1437±10
3_s	2360	2380±15	1852	1831± 2
3_a	2840		2140	

In order to find r_0 from Eq. (3) and the value of $k\rho^2$ it is necessary to know the reduced mass for the vibrations considered. The reduced mass cannot be found unless some further assumptions about the motion are made. If the binding between hydrogen and hydrogen is much stronger than the binding between nitrogen and hydrogen, the hydrogens will move as a rigid triangle, the reduced mass will be independent of amplitude, and k will be equal to 1.47×10^{15}. If, as is probably true, the binding between hydrogen and nitrogen is much stronger than the binding between hydrogen and hydrogen, the motion will consist of a bending of the nitrogen — hydrogen bond. For this sort of motion the reduced mass for finite amplitudes of vibration can be determined only as an average and will depend upon the amplitude of vibration. For given dimensions of the pyramid, the reduced mass for infinitesimal vibrations can be calculated and k is equal to 1.66×10^{15}. Even for finite amplitudes of oscillation this value is probably a good approximation. These two values of k are probably upper and lower limits. The corresponding values of the height of the pyramid are 0.40A and 0.37A.

In accordance with the general theory of isotope effects, the force constants should be the same for the ND$_3$ molecule as for the NH$_3$ molecule. For the ND$_3$ molecule the constants $(\beta/2)(\beta/2+1/2)$ and D should be increased by the same ratio as the reduced mass is increased. It turns out that this ratio is practically the same whichever assumption is made about the reduced mass for the NH$_3$ molecule. The constants used for the ND$_3$ molecule were $\beta=91.40$, $D=3261$, $k\rho^2=4.899 \times 10^{-2}$. The energy levels are given in Table I.

The lowest four levels of NH$_3$ are from data given by Wright and Randall.[4] The rest of the data were very kindly supplied by Dr. W. S. Benedict in a private communication.

The agreement is as good as can be expected considering the approximations that have been made, and considering that only three constants were used to fit eleven experimental values. A better estimate of the form of the potential curve can be made when accurate data on the separation of the doublets of the ND$_3$ spectrum are available.

[4] Wright and Randall, Phys. Rev. **44**, 391 (1933).