

The inversion potential for NH₃ and its isotopic species

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Abstract. Using *ab initio* data of the potential surface for the ground state of NH₃ a function is obtained to represent, with a very high precision, the potential along the inversion coordinate. The inversion spectra of NH₃, ND₃, NH₂D and NHD₂ are found by numerically solving the Schrödinger equation for this potential. Comparison is made of the calculated inversion frequencies and the experimental values, and the molecular constants of NH₃ are also compared to those found in the literature.

Keywords. Vibrational spectrum of NH₃; quartic anharmonic oscillator; double-well potential; molecular constants of NH₃.

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1. Introduction

The inversion of the NH₃ molecule, in which a nitrogen atom oscillates between both sides of the plane defined by the hydrogen atoms (figure 1) is an old problem that has been extensively studied by means of experimental and empirical methods [1–12] while the *ab initio* approaches have been rather scarce [13–15].

Several types of double-well potentials have been used [3, 8, 9, 12–14] to simulate the inversion barrier of NH₃, but perhaps the simplest analytical way to represent this potential is by means of a quartic anharmonic oscillator with a symmetrical double-well [15]:

$$V(x) = -\frac{1}{2}x^2 + \lambda x^4, \quad \lambda > 0$$

with an energy spectrum consisting of doublets, one member of each doublet belonging to a symmetrical state and the other to the antisymmetrical state. It is known [16] that the Schrödinger equation for this potential is not solvable by perturbation theory, since the perturbative series in powers of the parameter λ is divergent for any value of $\lambda > 0$. Some years ago, Bunker *et al* [13] calculated the energy surface for NH₃ and showed that the inversion barrier can be predicted from the first principles. Palma *et al* [14] chose some points from the energy surface calculated by Bunker [13] and used the method of least squares to find an eighth degree polynomial to represent the inversion potential. In the present work a fourth degree polynomial $V(x) = c_0 + c_1x^2 + c_2x^4$ (which satisfactorily reproduces the points of the surface chosen by Palma [14]) is

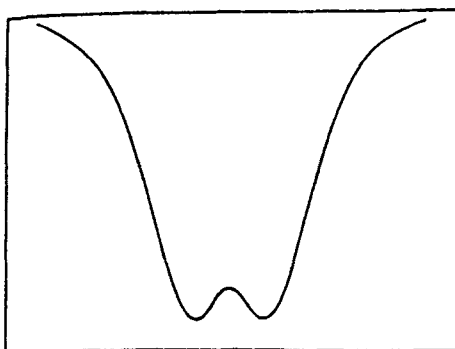


Figure 1. The double-well potential for the inversion of the NH_3 molecule.

proposed, from which the quartic anharmonic oscillator potential with double-well is found and the molecular constants and the inversion frequencies for NH_3 are determined.

2. The quartic anharmonic potential

If we assume that the inversion potential $V(x)$ can be represented by a fourth degree polynomial then the corresponding Hamiltonian can be written as:

$$H' = \frac{\hbar p^2}{2\mu} - \frac{1}{2}ax^2 + \frac{1}{2}bx^4 \quad (1)$$

where μ is reduced mass.

This Hamiltonian can be reduced to that of a quartic anharmonic oscillator with double-well

$$H = \frac{1}{2}P^2 - \frac{1}{2}Q^2 + \lambda Q^4 \quad (2)$$

by means of the transformations:

$$P = \left(\frac{\hbar^2}{\mu a}\right)^{1/4} p \quad \text{and} \quad Q = \left(\frac{\mu a}{\hbar^2}\right)^{1/4} x.$$

The energy unit ε and the anharmonic constant of (2) are expressed as:

$$\varepsilon = \hbar v_0 = \left(\frac{a\hbar^2}{\mu}\right)^{1/2}, \quad (3a)$$

$$\lambda = \frac{b\varepsilon}{2a}. \quad (3b)$$

3. The inversion frequencies for NH_3

The inversion of NH_3 may be treated, to a good approximation, as a problem of one particle in a one-dimensional potential $V(x)$, where x represents the inversion coordinate,

Inversion potential for NH₃

i.e., it measures the distance of the N atom to the plane of the hydrogen atoms. Both quantities, x and $V(x)$, are given in atomic units. If R stands for the distance of the N atoms to one of the H atoms and α is the angle between the H–N–H bonds, then the inversion coordinate will be given by:

$$x = [1 - \frac{4}{3}\sin^2(\alpha/2)]^{1/2} R = R \sin \beta.$$

where β is the angle between the N–H bond and the plane of the H atoms. If m and M are the masses of the H and N atoms, respectively, the reduced mass may be expressed as $\mu = 3m(M + 3m \sin^2 \beta)/(M + 3m)$. Unlike other works [14, 15], in the present one the angle β is not taken as 21°49', corresponding to the experimental equilibrium configuration [11], but it is calculated by interpolation from the data in table 1 of ref. [14], which determine an angle of 22°44' for the theoretical equilibrium configuration.

As already mentioned, there exists a number of suggestions for the analytical form of $V(x)$, and in this work we propose the use of a fourth degree polynomial which satisfactorily reproduces the points of the potential surface. This is achieved by taking the same six points (table 1, ref. [14]) chosen by Palma *et al* [14] from the 54 point calculated by Bunker *et al* [13] using *ab initio* methods.

The fourth degree polynomial $V(x) = c_0 + c_1 x^2 + c_2 x^4$ which best reproduces the mentioned data has $c_0 = -56.4064$, $c_1 = -3.034493 \times 10^{-2}$ and $c_2 = 2.666604 \times 10^{-2}$. With these values the energy unit ϵ , eq. (3a), the anharmonic constant λ , eq. (3b), and the other molecular constants are readily determined for NH₃. Some of these constants are summarized in table 1. Reference [10] is the best empirical calculation ever made, where a potential of the form $V(x) = aq^2/2 + bq^4/2 + d \exp(-cq^2)$ was used; the parameters β , a , b , c and d were varied until the value of the energy closest to the experimental value was obtained. The experimental values for the barrier height and the equilibrium distance [5] are $2020 \pm 12 \text{ cm}^{-1}$ and $0.382 \pm 0.004 \text{ \AA}$, respectively.

As shown in §2, the Hamiltonian associated with the fourth-degree polynomial potential, eq. (1) reduces to that of a double-well anharmonic oscillator, eq. (2). The corresponding Schrödinger equation was numerically solved for the NH₃ and its isotopic species. Two numerical methods were employed, the first being described in ref. [14, 19], while the second is mentioned in ref. [15, 17], and the results found were

Table 1. Values of the molecular constants for NH₃.

Molecular constant	This work	Ref. [10]
$\mu(\text{g})$	4.263×10^{-24}	4.263×10^{-24}
$a(\text{dynes/cm})$	9.45×10^{-4}	9.42×10^4
$b(\text{dynes/cm}^3)$	2.96×10^{21}	0.47×10^{21}
$c(\text{cm}^{-2})$	0.00	4.269×10^{16}
$d(\text{ergs})$	0.00	2.452×10^{-12}
$\nu_0(\text{cm}^{-1})$	790.3	789.9
$H(\text{Barrier height, cm}^{-1})$	1894.5	2018
$X_e(\text{Equilibrium dist., \AA})$	0.399	0.382
$\beta(\text{Equilibrium angle})$	22°44'	22°12'

Table 2. Vibrational spectrum for NH_3 ($\lambda = 0.02607$) along the inversion coordinate in cm^{-1} . (*s* = symmetrical, *a* = antisymmetrical).

State	Ref. [13]	Ref. [14]	Present work	Experiment [5]
O^s	0.0	0.0	0.0	0.0
O^a	1.02	0.995	0.969	0.793
1^s	986.7	924.12	928.92	932.51
1^a	1032.3	981.04	981.46	986.70
2^s	1682.0	1559.57	1561.41	1597.60
2^a	2011.6	1931.34	1913.56	1910.00
3^s		2473.40	2435.88	2383.46
3^a		3065.91	2998.67	2895.48

Table 3. Vibrational spectrum for ND_3 ($\lambda = 0.01970$) along the inversion coordinate in cm^{-1} . (*s* = symmetrical, *a* = antisymmetrical).

State	Ref. [14]	Present work	Experiment [5]
O^s	0.0	0.0	0.0
O^a	0.048	0.047	0.053
1^s	756.01	757.55	745.7
1^a	760.84	761.91	749.4
2^s	1338.91	1344.31	1359
2^a	1442.98	1438.90	1429
3^s	1818.64	1811.33	1830
3^a	2151.52	2127.62	2106.6

identical. In table 2 we present the values of the vibrational spectrum of NH_3 predicted by this model, the experimental values [5], and the results obtained by Palma *et al* [14] and by Bunker *et al* [13].

Although we have taken only six points of the surface potential calculated by Bunker to determine $V(x)$ through a least squares fitting, from tables 2 and 3 it may be seen that the obtained results are very accurate.

4. Isotopic species of NH_3

From the Born–Oppenheimer approximation, the same potential curve for NH_3 may be used for the isotopic species ND_3 , NH_2D and NHD_2 and the results must also be satisfactory since the deuterium nucleus is heavier than that of hydrogen. From table 3 it can be seen that our results are very similar to those obtained using an eight degree polynomial [14] as the inversion potential for ND_3 .

The results obtained for the isotopic species NH_2D and NHD_2 are shown in table 4. In these cases, the motion is more complex but we will still assume that the potential surface is the same as for NH_3 . In table 5, our results are compared to some experimental values, for example the ground state splitting $\Delta_0 = |O^a - O^s|$ and the first excited state splitting $\Delta_1 = |1^a - 1^s|$. Further, also in that table we show the value of k ,

Inversion potential for NH_3

Table 4. Vibrational spectrum for NH_2D ($\lambda = 0.02354$) and NHD_2 ($\lambda = 0.02152$) along the inversion coordinate in cm^{-1} . (*s* = symmetrical, *a* = antisymmetrical)

State	NH_2D	NHD_2
0^s	0.0	0.0
0^a	0.342	0.133
1^s	854.16	799.17
1^a	877.32	809.58
2^s	1443.16	1379.14
2^a	1681.40	1536.35
3^s	2122	1930.49
3^a	2580.77	2313.36

Table 5. Splitting energies for NH_3 , ND_3 , NH_2D and NHD_2 in cm^{-1} . (*s* = symmetrical, *a* = antisymmetrical)

	Experiment	Calculated	Ref. [14]	Ref. [13]
NH_3				
Δ_0	0.793	0.969	0.995	1.02
Δ_1	35.81	52.54	56.92	45.6
1^s	932.51	928.92	924.12	986.7
1^a	968.32	981.46	981.04	1032.3
<i>k</i>		1.0		
ND_3				
Δ_0	0.053	0.047	0.048	
Δ_1	3.7	4.36	4.83	
1^s	745.7	757.55	756.01	
1^a	749.4	762.91	760.84	
<i>k</i>		1.323		
NH_2D				
Δ_0	0.406	0.342		
Δ_1	19.7	23.16		
1^s	874	854.16		
1^a	894	877.32		
<i>k</i>		1.128		
NHD_2				
Δ_0	0.1705	0.133		
Δ_1	9.84	10.41		
1^s	808	799.17		
1^a	818	809.58		
<i>k</i>		1.233		

the square root of the ratio of the reduced mass of a given species to the reduced mass of NH_3 .

The experimental values of Δ_0 and Δ_1 for NH_2D and NHD_2 have been taken from refs. [10, 18]. From table 5 it can also be observed that the fourth degree potential

used in this work produces, in general, better results than the eight degree potentials [13,14].

5. Conclusions

The energy levels for ND_3 are not particularly sensitive to the type of potential used to model the inversion, and this may be seen from table 4 where the results obtained using a fourth degree polynomial and those from ref. [14], where an eighth degree polynomial are practically the same; we believe that the NH_2D and NHD_2 molecules must behave similarly, whereas for the case of NH_3 a difference is indeed observed between our results and those of ref. [14], ours being closer to the experimental values.

The discrepancy between our calculated values (especially the higher energy levels) and the experimental values may be produced by the fact that the fourth degree polynomial increases indefinitely as the inversion coordinate x increases, while the true potential has a limit before molecular dissociation takes place (figure 1).

The points of the potential surface completely determine the observables of the problem (spectrum and molecular constants), so that in the present work it has not been necessary to rely on experimental values of the geometry or to use adjustable parameters, i.e., everything is determined from first principles.

The molecular constants found with this model are very similar to those obtained by Swalen and Ibers [10] with a totally empirical method, where five adjustable parameters were present. Finally, it must be pointed out that only experimental data for NH_2D and NHD_2 are available in the literature, whereas no theoretical data calculated from first principles can be found.

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