

Majorana and the Investigation of Infrared Spectra of Ammonia

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Abstract: An account is given on the first studies on the physics of ammonia, focusing on the infrared spectra of that molecule. Relevant contributions from several authors, in the years until 1932, are pointed out, discussing also an unknown study by E. Majorana on this topic.

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1. Introduction

Because of the intensity and richness of its spectrum, ammonia has played a great role in the development of microwave spectroscopy. It has provided a large number of observable lines on which to try both experimental techniques and the theory. NH_3 provides the simplest and most thoroughly worked out example of a class of spectra which occupied and puzzle microwave spectroscopists for many years. In the paper of 1932 Fermi [1] discusses the influence of the ammonia molecule's rotation on the doubling of its levels. This doubling originates -according Dennis and Hardy [2]- in the oscillation by which the nitrogen atom crosses the plane determined by the three hydrogens, i.e., due to inversion respect the plane of the three atoms of H influenced by the rotation of molecule and he compared the theoretical results with the experimental results and he found accords (inversion problem). This paper on NH_3 , together with other three articles on the accidental degeneracy of the carbon dioxide molecule's frequencies of oscillation on the Raman effect in crystals, constitutes a series of investigations from the period

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1931-33 in which Fermi attempted to explain various molecular phenomena. His interest in these studies is reflected in the book "Molecules and crystals" [3]. Fermi's interest in this type of problem was to give a quantitative explanation to experimental observation at the center of Institutes by Rasetti, which in the period 1929-1930 studied the Raman effect in diatomic gas O_2 , N_2 . In particular the paper on the NH_3 molecule is connected to experiments conducted in Rome during the same period by E. Amaldi on the Raman Effects with theoretical contribute by G. Palczek [4], and theoretical research by G. Placzek and E. Teller [5] on molecular spectra for CO_2 and NH_3 .

In reality W.W. Coblentz [6] in 1905 investigated the positions and fine structure of the infrared bands of polyatomic molecules CO_2 , NH_3 . Coblentz observed two very intense bands at $\lambda = 10.7\mu$, 6.14μ , with a considerable weaker band at $\lambda = 2.97\mu$.

Lately K. Schierklok [7] has re-examined the ammonia infra-red (IR) spectrum and in addition to the bands found by Coblentz, he has found a band at $\lambda = 2.22\mu$. Beyond this he found two bands at $\lambda = 1.94\mu$, 1.49μ whose intensity was about half that of the two previous bands; so Schierklok observed six bands.

Historically the study of systems with several atoms, combining or not to form a molecule, has interested chemists for many years through the rules of valence. But only at the beginning of '900 the physicists interpret these rules in the light of quantum mechanics and the behavior of the constituents of atom with the spectral analysis of radiation emitted by the atom. Heitler and London [8] connected the valence in the formation of homopolar diatomic molecules with symmetry character of wave functions of the outer electrons in each atom. The problem of the vibration groups of atoms possessing geometric symmetry has been considered for the first time by C. J. Brester [9]. A number of models representing particular molecules have been treated making use of various assumptions to obtain the potential energy function. Historically the first example is that of CO_2 [10]. Hund [12] and Kornfeld [13] examined the spectra of H_2O , H_2S , CO_3 ion, NH_3 [14]. Dennison [15] found the normal vibrations for models of NH_3 and CH_4 assuming the forces to be central and Nielsen made a like treatment of the CO_3 ion. In all these investigations, the molecule was assumed to have a certain geometry symmetry in its equilibrium configuration. So another more simple way to analyze these models is to use the theory of vibrations [16]. In particular our interest will be on the NH_3 - molecule which Coblentz in 1905 will start to study. In the present article we will investigate how the NH_3 - molecule, in particular, has been studied qualitatively by character of the vibration of symmetrical polyatomic molecules through the theory of vibrations [12], [15], approximatively using the Wentzel-Kramers-Brillouin method of approximation. And a quantitative analysis with exact solution for a two-minima problem of the ammonia molecule solving secular equation.

We will analyze the historical development of important works in studying molecular spectra by means of the quantum theory, and in obtaining information about the structure of the molecule through an examination of the positions and fine structure of the IR bands. Then we will present briefly the experiments in observations of vibrational and rotational transitions in the cases of gas NH_3 and the comparison of theoretical and experimental

amounts of vibrational frequencies.

Different activities of the Fermi group at the Physics Institute in Rome from 1930 to 1932 was devoted to this subject. In this contest is the contribute of Majorana.

2. Theoretical Analysis of Ammonia Spectra.

2.1 A Brief Introduction to the Theory of Vibrations.

The classical theory of vibrations about an equilibrium configuration has developed from Galileo's study of small oscillations of a pendulum. In the first half of the eighteenth century Brook Taylor, D'Alambert, Euler, Daniel Bernoulli investigated the vibrations of a stretched cord. In 1753 Bernoulli enunciated the principle of the resolution of all compound types of vibration into independent modes. In 1762 – 1765 Lagrange gave the general theory of the vibrations of a dynamical system with a finite number of degrees of freedom. One considers a vibrating system defined by its kinetic energy T and its potential energy V and its position is specified by a set of coordinates (q_1, q_2, \dots, q_n) , giving the displacements from equilibrium. The problem of vibrations around an equilibrium configuration is to solve Lagrangian equations of motion in which the kinetic T (a positive definite form with $|a_{ij}| \neq 0$) and a potential energies V (Taylor expansion in powers of q_1, q_2, \dots, q_n) are homogenous quadratic forms in velocities and coordinates respectively, with constant coefficients:

$$T = \frac{1}{2} (a_{11}\dot{q}_1^2 + \dots a_{22}\dot{q}_2^2 + \dots + a_{nn}\dot{q}_n^2 + 2a_{12}\dot{q}_1\dot{q}_2 + 2a_{13}\dot{q}_1\dot{q}_3 + \dots + 2a_{n-1}\dot{q}_{n-1}\dot{q}_n) \quad (1)$$

$$V = \frac{1}{2} (b_{11}q_1^2 + b_{22}q_2^2 + \dots + b_{nn}q_n^2 + 2b_{12}q_1q_2 + 2b_{13}q_1q_3 + \dots + 2b_{n-1}q_{n-1}q_n) \quad (2)$$

The equation of motion are:

$$\frac{d}{dt} \left(\frac{\partial T}{\partial \dot{q}_r} \right) = - \frac{\partial V}{\partial q_r} \quad (r = 1, 2, \dots, n) \quad (3)$$

If T and V has the form (1), (2) (following the method of Jordan [18]), it is always possible to find a

linear transformation of coordinates $q_i = \sum_{k=1}^n c_{ik}x_k$ such that the kinetic and potential energies, expressed in terms of the new coordinates, called *normal (principal) coordinates*, have the form:

$$T = \frac{1}{2} (\dot{x}_1^2 + \dots \dot{x}_2^2 + \dots + \dot{x}_n^2) \quad (4)$$

$$V = \frac{1}{2} (\lambda_1 x_1^2 + \lambda_2 x_2^2 + \dots + \lambda_n x_n^2) \quad (5)$$

where the constants $\lambda_1, \dots, \lambda_n$, which occur as coefficients of the squares of x_k in V , are the n distinct or multiple roots of the determinant $\det(a_{ik}\lambda - b_{ik}) = 0$, and a_{ik}, b_{ik} are

the coefficients in the original expressions of T and V energies. The Lagrangian equation of motion is therefore:

$$\ddot{x}_r + \lambda_r x_r = 0 \quad r = 1, 2, \dots, n. \quad (6)$$

Thus the classical theory of small oscillations shows that system will vibrate as an aggregation of n independent mode of vibration of the system, provided the corresponding constant λ_r is positive (stable equilibrium configuration), with normal or characteristic frequencies $\nu_i = \lambda_i^{1/2}/2\pi$. Moreover every conceivable vibration of the system may be regarded as the superposition of n independent normal vibrations according Daniel Bernoulli's principle [19]

2.2 Ammonia Molecule Analysis with Theory of Vibrations.

The vibration spectra of polyatomic molecules, in particular of NH_3 , has been investigated in great details both theoretically and experimentally. For this system one has a number $s = 4$ of atomic nuclei which one assumes to have a possible equilibrium position. Dealing with the internal or vibrational degrees of freedom, the whole system has $n = 3s - 6 = 6$ degrees of freedom. The ammonia molecule is like a one-dimensional system of a particle moving in a potential field consisting of two equal minima and was first treated qualitatively by Dennison and Hund [12], [15]. Dennison and Hund assumed that the behavior of the nuclei in the neighborhood of their equilibrium positions may be described by means of central forces acting between them in the case of a polyatomic molecule with certain limitations in regard to the character of the equilibrium of the system.

The assumption for a molecule of the type XY_3 is that in the normal state of the molecule the X -atom is equidistant from each of the Y -atoms which themselves lie at the corners of an equilateral triangle. It is further assumed that the X -atom does only four frequencies, as indeed will any model which posses an axis of symmetry (Hund) and so X is at the apex of a regular pyramid with an equilateral triangle as a base. Experimentally four fundamental ν are found (without axial symmetry are found six fundamental frequencies).

Then they assumed that the four independent active frequencies are four fundamental absorption bands because of their fine structure.

Their study of NH_3 was motivated from IR spectroscopy measures and Raman spectra for polyatomic molecules CO_2 , N_2O , NH_3 , CH_4 , C_2H_4 during the period 1905 – 1935. Dennison and Hund, separately, showed, for molecules H_2O , NH_3 , CH_4 , that the vibrational levels which lie below the potential maximum occur in pairs. To find the normal vibrations they used the wave mechanical treatment of vibration spectrum of NH_3 -molecule and to obtain their properties they investigated the geometric symmetry of NH_3 in its equilibrium configuration. Let there be chosen a set of coordinates q_1, \dots, q_6 giving the displacements from equilibrium. In considering the system either in classical mechanics or in wave mechanics, the first step is to find the Hamiltonian. To the approximation in which the motions of the atoms are small compared with the inter-atomic distances,

the system may absorb or emit radiation with a series of frequencies. These frequencies are the so-called normal frequencies and may be computed with the classical theory of small oscillations (theory of vibrations [16] we have summarized in the above section), for which in first approximation the kinetic and potential energies assume a simple form:

$$T = \frac{1}{2} (a_{11}\dot{q}_1^2 + \dots + a_{66}\dot{q}_6^2 + 2a_{12}\dot{q}_1\dot{q}_2 + \dots) \quad (7)$$

$$V = \frac{1}{2} (b_{11}q_1^2 + \dots + b_{66}q_6^2 + 2b_{12}q_1q_2 + \dots) \quad (8)$$

where the a 's and b 's are constants.

Then a linear transformation to normal-coordinates:

$$q_1 = \sum_{k=1}^n c_{ik}x_k \quad (9)$$

whereby T and V are diagonal. The λ 's are the n roots, distinct or multiple, of the determinant:

$$\det(a_{ik} - b_{ik}) = 0 \quad (10)$$

The Hamiltonian may be then written:

$$H = H_1 + \dots + H_6 \quad (11)$$

where

$$H_i = \frac{1}{2}p_i^2 + \frac{1}{2}\lambda_j x_i^2 \quad (12)$$

So one has an aggregation of 6 independent simple harmonic oscillators, i.e., in the language of wave mechanics, the wave function of the whole system is the product of the wave function for the individual oscillators and characteristic value is the sum of the individual eigenvalues. This method is allowed because the system is separable in 6 normal coordinates.

The properties of 6 normal fundamental vibrations frequencies related to λ can be obtained following the *Hund*'s analysis.

In the investigation, the molecule NH_3 is assumed to have a certain geometric symmetry in its equilibrium configuration. In fact in considering the vibration spectrum of a tetratomic molecule of the general type XY_3 (i.e. NH_3), the assumption is that in the normal state of the molecule the $X(N)$ -atom at

equilibrium position is equidistant, i.e., at the center of gravity, from each of $Y(H)$ -atoms which themselves lie at the corners of an equilateral triangle, not in the same plane in which X -atom is. So a regular pyramid is the normal configuration of NH_3 . The approximation is that the force fields between the X -atoms is strong and those connecting the X and the Y atoms is weak. In this case the potential function energy is assumed to have the same symmetry as the geometric configuration of the molecule. Then will be two frequencies ν_1 and ν_2 corresponding to the mutual vibrations of the $Y_3(H_3)$ group alone which have just the properties of triatomic molecule [17]. In ν_1 the Y atoms remain at the corners of an equilateral triangle throughout the motion. This oscillation

is along the symmetry axis so it is called a \parallel vibration. While ν_2 is a double frequency due to an isotropic vibration of N -atom in a plane perpendicular to the symmetry axis, it is a \perp vibration. The remaining normal vibrations of the system may be determined by considering the motion of the Y_3 group, taken as a rigid triangle, relative to the X atom. The vibration will consist of two sorts, a vibration ν_3 in which the triangle and the point X oscillate with respect to each other, the triangle plane remaining always parallel to itself. Then ν_3 is a single and a \parallel vibration. The last frequencies ν_4 is represented by a typing motion of the triangle relative to the X -point. It is a double \perp vibration frequency. So there are four independent active frequencies, two \parallel and two \perp . Since the latter are double, there are six degrees of internal freedom corresponding to the formula of internal degrees of freedom for four atoms we have seen $n = 3s - 6$ where s is the number of atomic nuclei which one assumes to have a possible equilibrium position. So this qualitative discussion done by Dennison, Hund allowed them to predict the essential features of IR spectrum of the XY_3 molecule. There will be four fundamental absorption bands. The intensity will be different depending upon the force fields, i.e., the configuration of the molecule. The fine structure of the band ν_1 is similar to the fine structure of the band ν_3 since they both correspond to a vibration along the symmetry-axis. The pair of bands ν_2 and ν_4 will have a similar fine structure because \perp to the symmetry axis and will be unlike to the pair ν_1 and ν_3 . Questions with regard to fine structure arise when one discusses experimental spectra by spectrometer analysis.

2.3 Ammonia Molecule Analysis with Theory of Groups

The ammonia infrared spectrum is an example of the application of group theory [11] to physics. Molecules absorb and emit electromagnetic radiation in wide areas of the spectrum. If electrons change state, the radiation may be in the visible region. Molecular ultraviolet spectra are rather rare, since molecules fall apart at these high energies. Changes in vibrational states are associated with infrared wavelengths, and changes in rotational states with the far infrared. There are even finer energy differences that cause spectra even in the radio-frequency region. All of these generally consist of a great number of lines, sometimes not resolved individually, forming bands and such.

Infrared spectra are a valuable tool for determining the structure of molecules. An infrared band is simpler than the band spectra in the visible, but still rather complex, consisting of several series of lines corresponding to transitions between different rotational states. Two methods are generally used, absorption spectra that study the transitions from the ground state to excited states, and Raman spectra that studies the changes in wavelength in scattered radiation. Raman spectroscopy can be done in the visible region with its more convenient experimental conditions, and with the powerful beams of lasers.

Quantum mechanics is necessary for the understanding of molecular spectra, which it perfectly explains. Then there is a relation of group theory to quantum mechanics. Symmetry is a powerful tool in the quantum mechanics of molecules, and the ammonia molecule furnishes a good example. One can consider what infrared and Raman spectra

are to be expected if the molecule is a symmetrical pyramid, which is indeed the case using the character analysis. The symmetrical pyramid has the symmetry group C_{3v} , with its character table¹:

C_{3v}	E	$2C$	3σ	<i>basis functions</i>
A_1	1	1	1	$T_z, x^2 + y^2, z^2$
A_2	1	-1	1	R_z
E	2	-1	0	$(T_x, T_y)(R_x, R_y)(x^2 - y^2, xy)(xz, yz)$

T and R are the representations to which components of the translation and rotation displacements belong; these are vectors and axial vectors, respectively. T also shows the representations of the dipole moment operator which produces the infrared spectrum. Then there are the quadratic functions which transform like the molecular polarizability, the operator which produces the Raman spectrum.

We assign three displacement coordinates to each atom, 12 in all for the four atoms. The first thing to do is to find the characters of this representation. The character for E is 12, since the identity transforms each coordinate into itself. The rotations about the axis leave only the displacements on the nitrogen in the same place, and the character is the same as that of the three T components, or $1 - 1 = 0$. Reflections in a vertical plane leave the nitrogen and one hydrogen unmoved, and the character is easily seen to be $2 - 1 = 1$ for each atom. Therefore, the characters of the reducible representation of the displacements is 12, 0, 2. This must include the representations of the translation and rotation of the molecule as a whole, $A_1 + A_2 + 2E$. Therefore, we subtract the characters 6, 0, 0 to find the character of the vibrations, 6, 0, 2. By character analysis, we find that this gives $2A_1 + 2E$. Ammonia, therefore, should exhibit four fundamentals, all active in both infrared and Raman spectra. This is exactly what is observed. The Raman spectra of the E fundamentals ought to be faint, and they were not observed (or were not until lasers came in). If the ammonia molecule were planar, two more fundamentals would be expected, and they are not observed. Herzfeld gives the four modes as follows. There is a very strong band at 1627.5cm^{-1} (infrared spectroscopists use the reciprocal of the wavelength, since it is proportional to the frequency and the quantum energy), about 6.1μ , and is a so-called perpendicular band, which would be expected from the x and y

¹ This table defines the abstract group C_i , which has many representations, or concrete realizations. Let the symbol σ stands for the transformation $x = -x$. C is either of the rotations. In three dimensions, this would be a reflection in the yz-plane. We can use σ as an operator: $\sigma f(x) = f(-x)$, E is the identity operator, such that $Ef(x) = f(x)$ for any $f(x)$. One calls the elements E and A_i , that all obey the same multiplication table.

components of the dipole moment. This is one of the doubly-degenerate E fundamentals, a symmetric bending of two of the hydrogens to or away from each other. The asymmetric bending is of higher frequency, 3414cm^{-1} , and difficult to observe. These are the two E modes. There is a strong parallel band at 931.58cm^{-1} and 968.08cm^{-1} , about 10.6μ corresponding to an A_1 representation. This band is double, and the reason is curious. The ammonia molecule can turn itself inside-out; that is, the nitrogen can pass through the plane of the hydrogens. This isn't easy, but the nitrogen can tunnel through, and the doubling is the result. The states divide into those symmetrical with respect to this inversion, and those that are antisymmetrical (change sign). The selection rules on the rotational transitions make the band separations the sum of the inversion splitting in the two cases. In the Raman spectrum, the separation is the difference of the splitting. The Raman bands are observed at 934.0cm^{-1} and 964.3cm^{-1} . Finally, there is a strong band at 3335.9cm^{-1} and 3337.5cm^{-1} , and a Raman shift at 3334.2cm^{-1} (about 3.0μ) corresponding to the other A_1 fundamental. In this mode, the bond lengths lengthen and shorten symmetrically. The two A modes can be called bending and stretching, respectively.

ND_3 , with the heavier deuterium substituted for the protons, gives somewhat different (lower) frequencies, and the shifts can be used to nail down the identification of the vibrational frequencies, confirming the conclusion that ammonia is a symmetrical pyramid. The inversion doubling is a very interesting phenomenon. It turns out to be possible to separate molecules in even and odd inversion states, and this led to the ammonia maser, the first of its kind. Although one can form a good picture of ammonia as if it were a macroscopic object, try to picture it with the nitrogen partly on both sides of the hydrogens!

Using the group theory F. Hund (1925) [12] studies the equilibrium of the molecule of ammonia, and he shows that, if the electronic configuration around the nitrogen, originally central, is capable of a polarization induced by the hydrogen nuclei, the molecule in the normal state have just the axial symmetrical form. So he assumed that the molecule NH_3 has a regular pyramid equilibrium configuration. The nitrogen atom at equilibrium position is equidistant, i.e. at the center of gravity, from each of hydrogen atoms, which lie at the corners of an equilateral triangle, not in the same plane of N-atom. In considering the vibrations of such a molecule he erroneously states that there exist only three active characteristic frequencies, whereas, unless the particles all lie in the same plane, there must in general exist four, as shown by Dennison [15]. Hund gives a table of harmonic and combinations bands of NH_3 with three fundamental frequencies $\nu_1 = 970\text{cm}^{-1}$, $\nu_2 = 1700\text{cm}^{-1}$, $\nu_3 = 4500\text{cm}^{-1}$, that may be changed by allowing the band at $\lambda = 97\mu$ i.e. $\nu \sim 3300\text{cm}^{-1}$ to become the fourth fundamental band.

2.4 Approximate Analysis of NH_3 with WKB Method.

Dennison and Uhlenbeck [20] compute the level separation of NH_3 , using the Wentzel-Kramers-Brillouin (WKB) method of approximation for a one-dimensional system of a

particle moving in a potential field, consisting of two equal minima. Then they make an application of the results to the ammonia molecule to determine its form. The WKB method yields an approximate solution of the wave equation whose form depends upon whether the region considered lies within or without the region of classical motion, that is, the region where the kinetic energy is positive. In the first case the solution is oscillatory, in the second or non-classical region the solution consists of a linear combination of an increasing and a decreasing exponential. At each boundary or critical point are valid the so-called Kramers connection formulae [21]. These formulae furnish a method by which one may approximate to any solution of the wave equation.

They show that the infrared spectrum of the ammonia molecule exhibits features which may be directly related to the one dimensional problem of two equal minima. The parallel type vibration bands for example are observed to be composed of two nearly superimposed bands, depending upon the fact that there are two equivalent positions of equilibrium for the nitrogen nucleus. Symmetrical molecules of the NH_3 type which are not coplanar exhibit that all vibrational levels are double, depending upon the fact that there are two exactly equivalent positions of equilibrium for N atom, one above the plane of the H atoms, and the other at an equal distance below. A quantum mechanical treatment reveals that it causes the vibrational level become double. The doublet separation is small compared with the spacing of vibrational levels (inversion problem related to rotational spectrum).

The physical origin and theoretical description of this doubling is presented, followed by a description of the experimental measurement. The inversion doubling of about 35 cm^{-1} represents an excellent coupling of a simple infrared measurement with a quantum mechanical description involving many aspects of the wave nature of vibrations. The normal modes of Ammonia are $\nu_2 = 950cm^{-1}$, (symmetric bend), $\nu_{4a} = 1627cm^{-1}$ (asymmetric bend), $\nu_{4b} = 1627cm^{-1}$ (asymmetric bend), $\nu_1 = 3336cm^{-1}$ (symmetric stretch), $\nu_{3a} = 3414cm^{-1}$ (asymmetric stretch), $\nu_{3b} = 3414cm^{-1}$ (asymmetric stretch); ν_{3a}, ν_{3b} are degenerate modes, as are ν_{4a}, ν_{4b} . All six normal modes are IR active.

2.5 Exact Analysis of NH_3 .

Rosen and Morse [22] give an analysis of the vibration of the nitrogen in the ammonia molecule using an exact solution of the wave equation for a form of one-dimensional potential energy. The potential energy for this molecule has two minima at distance $2x_m$ apart, separated by a "hill" of height H .

They describe another solution, for a form of potential field different from that of Denison [17] and they give an example of its application to the vibrational states of NH_3 . Due to the symmetry of the molecule there are two equivalent positions of equilibrium for the nitrogen, at equal distances above and below the plane of the three hydrogens. This equivalence of the two minima makes every vibrational level a doublet, a result which is found experimentally. To analyze the vibrational behavior one separates off the coordinates of the center of the gravity of the molecule and the Euler angles fixing its

orientation in space, and deal only with the coordinates fixing the relative positions of the atoms.

One of these coordinates is x , the distance of the nitrogen (N) atom from the plane of the hydrogen. The other five coordinates z_1, z_2, z_3, z_4, z_5 , can be chosen that the positions of the two equilibrium configurations are at $z_1 = z_2 = z_3 = z_4 = z_5 = 0, x = \pm x_m$. The potential function $V(x, z_1, z_2, z_3, z_4, z_5)$ therefore has its two minima at these two points. They justify the use of x as a "normal" coordinate (i.e. splitting from the general six-dimensional problem to a one-dimensional problem in x alone) by the following method. From considerations of symmetry all the wave functions are symmetric or antisymmetric about the nodal hypersurface $x = 0$. They give a two minima potential field $V(x)$ which is amenable of exact solution. For each level of the one minimum problem there is a pair of levels for the double minimum case. The separation between the levels in a pair is small compared to the energy difference between different pairs as long as the levels are below the top of the intermediate hill.

Salant and Rosenthal in 1932 [23] derive expressions for the effects of isotopy on the normal frequencies, following Dennison's [17] general, noncentral force treatment of the normal modes of vibration of symmetrical triatomic and tetratomic molecules.

Sanderson and Silverman in 1933 [24], following the procedure of Dennison [17], calculate the positions of the fundamental vibrations of molecule ND_3 .

Rosenthal [25] summarizes briefly the general procedure for obtaining the normal vibration frequencies of a molecule of any type of symmetry, without the use of group theory. He writes the expression for the kinetic energy T in terms of the displacements of the various atoms from their equilibrium positions. The potential energy, V , is written in terms of the mutual displacements of the atoms as the most general quadratic form consistent with geometrical symmetry. As the next step, linear combinations of the original displacements are introduced and both T and V are transformed to them. The normal vibration frequencies, ω , or rather $\lambda = 4\pi^2\omega^2$ are then obtained as the roots of $|\lambda T - V| = 0$. For n degrees of internal freedom, the expansion of this n th order determinant will give rise to an equation in λ of the n th degree. He gives a discussion of the vibration frequencies and isotopic shifts of tetratomic molecules, with a discussion of various intramolecular forces and the physical meaning of the results, for pyramidal and coplanar molecules.

Manning [26] chooses an expression for the potential energy of $NH_3(ND_3)$ which has the correct general characteristics of geometry symmetry of NH_3 and which permits an exact solution of the Schrodinger equation. Making substitutions they obtain the indicial equation from Schrodinger equation and make quantitative calculations of the behavior of the energy levels, those below the top of the center of the hill of V are double according data (Wright, Randall [27]).

3. On the Oscillations Bands of Ammonia by Majorana

Majorana studied the NH_3 spectra [28] and obtained results in agree with the experimental results, i.e., two simple vibrations and two double vibrations. He considered the

symmetry of the NH_3 . The three atoms H occupy the vertices of equilateral triangle; the atom N is on the axes out of the plane. The independent displacements which contribute to elastic forces are six and they obtain from the twelve displacements of the four atoms with the condition that the resultant of applied vectors δP_i at the rest points P'_i is zero.

He defines the displacements $q_1 = 1, q_2 = q_3 = \dots = q_6 = 0$ as those in which the atom H^1 moves in direction NH^1 of $M_N/(M_N + M_H)$ and the atom N in the opposite direction of length $M_H/(M_N + M_H)$. Similarly one defines the displacements $q_i = \delta_{i2}$ e $q_i = \delta_{i3}$. Then we define as displacement $q_i = \delta_{i4}$ that in which the atom H^3 shifts of $1/2$ in the direction H^2H^3 and the atom H^2 of $1/2$ in the opposite direction; for circular permutation he puts the displacements $q_i = \delta_{i5}$ e $q_i = \delta_{i6}$.

Indicating α the angle (in the equilibrium position) $\widehat{NH^1H^2}$ and with β the angle $\widehat{H^1NH^2}$ the kinetic energy is:

$$\begin{aligned}
 T = \frac{1}{2} & \left[\frac{M_H^2 M_N}{(M_N + M_H)^2} (\dot{q}_1^2 + \dot{q}_2^2 + \dot{q}_3^2 + 2\dot{q}_1\dot{q}_2 \cos \beta + 2\dot{q}_2\dot{q}_3 \cos \beta \right. \\
 & + 2\dot{q}_3\dot{q}_1 \cos \beta) + \frac{M_N^2 M_H}{(M_N + M_H)^2} (\dot{q}_1^2 + \dot{q}_2^2 + \dot{q}_3^2) \\
 & + \frac{M_N M_H}{M_N + M_H} \cos \alpha (\dot{q}_1\dot{q}_5 + \dot{q}_1\dot{q}_6 + \dot{q}_2\dot{q}_6 + \dot{q}_2\dot{q}_4 + \dot{q}_3\dot{q}_4 + \dot{q}_3\dot{q}_5) \\
 & \left. + \frac{1}{2} M_H \left(\dot{q}_4 + \dot{q}_5 + \dot{q}_6 + \frac{1}{2} \dot{q}_4\dot{q}_5 + \frac{1}{2} \dot{q}_5\dot{q}_6 + \frac{1}{2} \dot{q}_6\dot{q}_4 \right) \right]. \quad (13)
 \end{aligned}$$

then he defines the potential energy

$$V = \frac{1}{2} \sum_{ik} a_{ik} q_i q_k \quad (14)$$

and he performs a canonical transformation [28]. He obtains a new expression of the kinetic energy in the new coordinates Q_i , similarly for the potential. He obtains then two simple vibrations relative to coordinates Q_1 and Q_2 and two double vibrations relative to coordinates Q_3 and Q_4 with the square of angular velocity:

$$\lambda = 4\pi^2 \nu^2 \quad (15)$$

4. Brief Experimental Investigation until 1932

Now we will give a brief chronology of the experiments on NH_3 .

Fox studies (1928) the IR region of the spectrum of NH_3 using the Prism spectrometer [29]. Sir Robert Robertson and J.J. Fox in 1928 used a small infra red prism spectrometer, filled of ammonia gas. They took a source of energy constant, for calibrating the mechanism for reading wave lengths.

At $\Delta V = (100 \pm 200)V$ and $T \sim 18C$ they used Nernst filaments as source of Radiation, since those gave the most uniform supply having regard to the intensity at different regions of the spectrum. There are source radiation - tubes observation - spectrometer. As the full radiation contains light of short wave length, it may affect chemically the gas

NH_3 under observation. The results is a measure of position of bands of NH_3 and their intensity. He made a preparation of Ammonia generated in the little flask A by warming a mixture of damp solid ammonia and 50% KOH solution was allowed to escape at the two-way top x , until samples were completely absorbed by water.

He confirmed that the view that the NH_3 is a tetrahedron was acceptable.

Rasetti [30] et al. have photographed the Raman spectra in 1929 of gaseous CO_2 , NO_2 , NH_3 , CH_4 , C_2H_4 using the line $\lambda = 2536$ of mercury as the exciting radiation. They have observed vibrational transitions in all the gases, and rotational transitions in the NH_3 and CH_4 .

Berker in 1929 [31] analyzes the NH_3 absorption band extending at 3.0μ and 1.9μ and from 8μ to 24μ interpreting the double character of the 10μ band to be a consequence of the close proximity of the two equilibrium positions for the N atom, one of either side of the plane formed by the H atoms.

Dennison and Hardy in 1932 [2] make an experimental search for the doubling of the 3.0μ band using an IR spectrometer of high resolving power. The experimental results furnishes a strong argument for the theory of the doubling of the ammonia bands. They discuss the form of ammonia molecule with the theory . And then they prove that those states of ammonia existing in nature have vibration-rotation-nuclear spin wave functions which are antisymmetrical for an interchange of two of the hydrogen atoms.

5. Conclusions

In this paper we have depicted the genesis and the first developments of the study of spectra of NH_3 analyzed for the first time by Coblentz. Far from being complete, our account has focused on the results achieved from 1905 to 1932, as given evidence by many articles published in widespread journals. We have also pointed out the practically unknown contribution to spectral analysis Majorana, who was introduced to the subject by studies and experiments in Rome. The result reached by Majorana as early as in the beginning of 1930 is to find the right number of fundamental frequencies of spectrum of NH_3 . Wide room has been made to different approaches to study the spectrum qualitatively and quantitatively and experimentally too. A theoretical analysis of ammonia spectra has been reported in Sect. 2, with a brief account of Theory of Vibrations and Theory of Groups. In the same sections we have showed an approximate analysis of NH_3 with WKB method and an exact analysis with a particular form of potential. Particular attention has been given to the approach of Majorana for the analysis of IR spectra of NH_3 in Sect. 3. Early experiments of ammonia, essentially dealt with atomic spectroscopy, have been discussed above in Sect.4. From what discussed here, it is then evident the interest to study the ammonia spectra by Majorana and its contribute to find the exact solution.

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