Quantum Mechanical Studies of Atomic, Bond, and Molecular Polarizabilities, Spectroscopic Studies of Root-Mean-Square Amplitudes, and Statistical Thermodynamics: Isotopic Species of Nitrogen Trichloride

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The infrared absorption and Raman spectra, evaluation of potential energy constants with various potential functions, and other spectroscopic studies have been briefly analyzed for the isotopic species of nitrogen trichloride molecule possessing a trigonal pyramidal symmetry. Among the various quantum mechanical models, the delta-function potential model based on the variational method and the delta-function electronic wave functions has been employed here to evaluate the atomic polarizabilities, the contributions by the bonding and nonbonding electrons to the bond parallel component of the polarizability, the bond perpendicular component of the polarizability, and the mean molecular polarizability of nitrogen trichloride. On the basis of group theoretical considerations, the symmetrized mean- square amplitudes, mean-square amplitudes, and root-mean-sqare amplitudes for both bonded and nonbonded atom pairs have been computed at the temperatures 298 °K and 500 °K. On the basis of a rigid rotator and harmonic oscillator approximation, enthalpy function, free enthalpy function, entropy, and heat capacity have been computed for the temperatures from 200 °K to 2000° K for both isotopic species of nitrogen trichloride. A discussion of the results follows.

Introduction

Among the various trihalides of group VA elements, the most interesting compound, nitrogen trichloride, the next higher member of nitrogen trifluoride, has twenty valence electrons with very many unusual properties. For a molecule of the present study with a single lone pair of electrons around nitrogen atom for which supplementary data on vibration-rotation interactions (Coriolis coupling constants) and centrifugal distortion constants are not available, the computation of either potential energy constants or root-mean-square amplitudes seems to be highly complicated. The reason is that there are more number of molecular constants than the available number of vibrational frequencies. A general valence force field, Urey-Bradley force field, a valence force field with a lone pair model, and a modified Urey-Bradley field were applied to many molecular systems of the present type by several investigators [1–7], and the vibrational data were satisfactorily reproduced. CARTER and his associates [8] studied the infrared absorption and Raman spectra of nitrogen trichloride and assigned the fundamental frequencies on the basis of a pyramidal symmetry. Spectral studies on nitrogen trichloride were also later reported by HENDRA and MCKENZIE [9] and DELHAYE and his coworkers [10]. Recently, BAYERSDORFER and his coworkers [11, 12] studied the infrared absorption and Raman spectra for the isotopic species of nitrogen trichloride, and assigned the fundamentals on the basis of a three-fold symmetry. CARTER and his coworkers [13] recently carried out a normal coordinate analysis and force constant calculations by using these vibrational data and structural data ($N-Cl=1.76$ Å and $Cl-\hat{N}-Cl=106°$)

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[1] M. K. WILSON and S. R. POLO, J. Chem. Phys. **20**, 1716 [1952].

[2] P. N. SCHATZ, J. Chem. Phys. **29**, 481 [1958].

[3] A. ALLAN, J. L. DUNCAN, J. H. HOLLOWAY, and D. C. MCKEAN, J. Mol. Spectroscopy **31**, 368 [1969].

[4] J. L. DUNCAN, J. Mol. Spectroscopy **18**, 62 [1965].

[5] M. PARISEAU, E. WU, and J. OVEREND, J. Chem. Phys. **39**, 217 [1963].

[6] E. C. CURTIS and J. S. MUIRHEAD, J. Phys. Chem. **70**, 3330 [1966].

[7] T. SHIMANOUCHI, I. NAKAGAWA, J. HIRAISHI, and M. ISHII, J. Mol. Spectroscopy **19**, 78 [1966].

[8] J. C. CARTER, R. F. BRATTON, and J. F. JACKOVITZ, J. Chem. Phys. **49**, 3751 [1968].

[9] P. J. HENDRA and J. R. MCKENZIE, Chem. Commun. 760 [1968].

[10] M. DELHAYE, N. DURRIEU-MERCIER, and M. MIGEON, C. R. Acad. Sci. Paris **267 B**, 135 [1968].

[11] L. BAYERSDORFER, U. ENGELHARDT, K. HOHNE, J. FISHER, and J. JANDER, Z. Naturforsch. **23 b**, 1602 [1968].

[12] L. BAYERSDORFER, U. ENGELHARDT, K. HOHNE, J. FISHER, and J. JANDER, Z. Anorg. Allg. Chem. **366**, 169 [1969].

[13] J. C. CARTER, J. F. JACKOVITZ, J. E. DEVIA, and R. F. BRATTON, J. Chem. Phys. **53**, 3827 [1970].

[14] G. E. MOORE and R. M, BADGER, J. Amer. Chem. Soc. **74**, 6076 [1952].

from the related molecular systems [14]. On the basis of these spectroscopic data, it is aimed here to compute the atomic, bond, and molecular polarizabilities from the delta-function potential model and the delta-function electronic wave functions, root-mean-square amplitudes by the group theoretical method, and statistical thermodynamics by the rigid rotator and harmonic oscillator approximation. The importance of studying such investigations is that the results of the present study would be very useful in future for (a) testing the utility of the delta-function potential model in other complex systems, (b) the interpretation of the experimental refractive indices and molar refractions, (c) the evaluation of normal frequencies in other related molecular systems having similar chemical bonds, (d) the interpretation of the results of electron diffraction studies, and (e) the interpretation of the results of experimental entropes and heat capacities at a pressure of one atmosphere for the ideal gaseous state.

Atomic, Bond, and Molecular Polarizabilities

Many intestigators computed the polarizabilities for several atoms, ions, and simple diatomic molecules by making use of different quantum mechanical models in order to test how far the polarizability could be a useful criterion for testing the utility of the wave functions adopted. Of the various quantum mechanical models so far developed, the most recent one is the delta-function potential model. The first use of a delta-function potential model was made by RÜDENBERG and his associates [15, 16] in studying the properties of chemical bonds. Later, FROST [17] applied a delta-function model of chemical binding to the calculation of energies of hydrogen-like atoms and diatomic systems, and to the calculation of energies of conjugated hydrocarbons by introducing a branching condition [18]. Then LIPPINCOTT [19] explained with a semi-empirical delta-function potential model that the delta-function spacing, *a*, is less than the internuclear distance, *R*, when the bond is stretched; the delta-function spacing is greater than the internuclear distance, when the bond is compressed; and the delta-function spacing is equal to the internuclear distance, when the bond is neither compressed nor stretched (equilibrium condition). On the basis of this semi-empirical delta-function potential model, LIPPINCOTT and DAYHOFF [20] predicted the bond dissociation energies, vibrational frequencies, anharmonicities, and equilibrium internuclear distances for various diatomic molecules and bonds of polyatomic systems, and their calculated values were in good agreement with the available experimental results. LIPPINCOTT and STUTMAN [21] very recently applied the same semi-empirical delta-function potential model and computed the bond and molecular polarizabilities of various diatomic and polyatomic molecules. The same method has been employed here except the nitrogen atom is considered as if it is involved in a bond of polyatomic system, since there is a greater distribution of polarizability along the bonds from nitrogen to chlorine.

In the present investigation two kinds of delta-function strengths have been considered. The delta-function strength for an atom having a bonding with another is different from that of the same atom having two or more bondings with other atoms, and this is due to the difference in the electronic distributions. As an example, the delta-function strength for the sulfur atom in SO molecule is different from that of the same in SO_2 and SO_3 molecules, whereas the delta-function strength for the oxygen atom is considered to be the same in all these molecules. The delta-function strength of an atom in a bond of diatomic molecule and that of an atom in a bond of polyatomic molecule have been, in line with earlier studies [20], obtained from the following:

$$A = [x/(2.6\,n - 1.7\,p - 0.8\,D + 3.0\,F)]^{1/2}, \quad (1)$$

$$A^* = A[(n-3)/(n-1)]^{1/2} \quad (2)$$

where x is the electronegativity on the Pauling's scale [22]; *n*, the principal quantum number; *p* is 1 for an atom with *p* electrons in the valence shell and 0 for an atom with no *p* electrons in the valence shell; *D*, the total number of completed p and d

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[15] K. RÜDENBERG and R. G. PARR, J. Chem. Phys. **19**, 1268 [1951].

[16] K. RÜDENBERG and C. W. SCHERR, J. Chem. Phys. **21**, 1565 [1953].

[17] A. A. FROST, J. Chem. Phys. **22**, 1613 [1954]; **23**, 985 [1955]; **25**, 1150 [1956]

[18] A. A. FROST and F. A. LELAND, J. Chem. Phys. **25**, 1154 [1956].

[19] E. R. LIPPINCOTT, J. Chem. Phys. **23**, 603 [1955]; **26**, 1678 [1957].

[20] E. R. LIPPINCOTT and M. O. DAYHOFF, Spectrochim. Acta **16**, 807 [1960].

[21] E. R. LIPPINCOTT and J. M. STUTMAN, J. Phys. Chem. **68**, 2926 [1964].

[22] L. PAULING, The Nature of the Chemical Bond, Cornell University Press, Ithaca, New York 1960.

shells in an atom; F, the total number of completed f shells in an atom; A, the delta-function strength for an atom in a bond of a diatomic molecule; and A^*, the delta-function strength for an atom in a bond of a polyatomic molecule. The calculated values of the delta-function strengths A's in atomic units for nitrogen atom and chlorine atom of nitrogen trichloride are 0.829, and 0.753, respectively.

The potential energy for the n-electron problem is considered to be the sum of the single delta-function potentials each having the form for a diatomic system as

$$V = -[A_1 g\,\delta(x-\tfrac{1}{2}a) + A_2 g\,\delta(x+\tfrac{1}{2}a)] \qquad (3)$$

where x is the coordinate of motion along the internuclear axis; a, the delta-function spacing; A_1 and A_2, the delta-function strengths or reduced electronegativities for the nuclei 1, and 2, respectively; g, the delta-function strength (the value for the hydrogen atom); and $\delta(x)$, a delta-function whose properties are described by the following:

$$\begin{aligned} \delta(x) &= 0\,, && \text{when} \quad x \neq 0\,, \\ \delta(x) &= \infty\,, && \text{when} \quad x = 0\,, \qquad (4) \\ \int_{-\infty}^{\infty} \delta(x)\,\mathrm{d}x &= 1\,. \end{aligned}$$

Thus, the potential is zero everywhere except at the delta-function positions, i. e., $x = a/2$ and $x = -a/2$. The delta-function strength obtainable from separated atom energies E_1 is defined as $A = (-2\,E_i)^{1/2}$.

The solution of Schrödinger equation for the molecular problem yields to separate wave functions for the chemical bonds. The delta-function branching condition outlined by FROST[17] can then be applied to obtain the following expression for the homonuclear case:

$$c_i = A\,g[1 \pm \exp\{-c_i\,a\}] \qquad (5)$$

where the plus and minus signs correspond to the attractive and repulsive states, respectively. By combining the above equation with $A = (-2\,E_i)^{1/2}$, one may have the following:

$$\lim_{a\to\infty} c_i = A\,g = (-2\,E_i)^{1/2}_{a=\infty}\,. \qquad (6)$$

On the basis of the above equation, a resultant c written as c_R may be obtained and assumed to account for all the electrons in the system. One may then have the following:

$$c_R = A(n\,N)^{1/2} \text{ for the homonuclear case} \qquad (7)$$

$$c_{R12} = (c_{R1}\,c_{R2})^{1/2} = n_1\,n_2\,N_1\,N_2(A_1\,A_2)^{1/2} \qquad (8)$$
for the heteronuclear case

where A is the one-electron delta-function strength for the atom; n, the principal quantum number of the valence shell; and N, the number of electrons making the contributions to the bonding or two times the column number in the periodic table. The calculated "c" values in atomic units for nitrogen atom and chlorine atom of nitrogen trichloride are 3.707, and 4.88, respectively.

On the basis of the variational treatment[23] first introduced by HYLLERAAS[24] and HASSE[25], one may generate the polarizability component α_{xx} in the following form:

$$\alpha_{xx} = \frac{4\,n\,A}{a_0}\,[\langle(x_1-\langle x\rangle)^2\rangle - (n-1)\langle(x_1-\langle x\rangle)\;(x_2-\langle x\rangle)\rangle]^2 \qquad (9)$$

where x_1 is the coordinate of any one of n equivalence classes of electrons which falls in the first equivalence class; $\langle x\rangle$, the average coordinate of any of these electrons; and a_0, the radius of the first Bohr orbit of the atomic hydrogen. If the delta-function potentials are symmetrically placed, no electron correlation is allowed, and bonding electrons are considered to be perfectly equivalent, then the above equation may be reduced to

$$\alpha_{xx} = \frac{4\,A}{a_0}\sum(\langle x_i\rangle)^2. \qquad (10)$$

If the atom is assumed to be perfectly isotropic, one then may have the following:

$$\langle x^2\rangle = \langle y^2\rangle = \langle z^2\rangle = \langle r^2\rangle/3\,. \qquad (11)$$

If the delta-function is located at the nucleus, and the wave function is normalized, one then may have the following:

$$\langle r^2\rangle = 3/A^2 \quad \text{and hence,} \quad \langle x^2\rangle = 1/A^2. \qquad (12)$$

Solution of the Hamiltonian for the negative value of E yields to $A = (-2\,E_i)^{1/2}$. Finally, the polarizability along the x axis of an atom is given by

$$\alpha_{xx} = 4/a_0{}^3\,A^3. \qquad (13)$$

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[23] J. O. HIRSCHFELDER, C. F. CURTISS, and R. B. BIRD, Molecular Theory of Gases and Liquids, John Wiley & Sons, Inc., New York 1954.

[24] E. A. HYLLERAAS, Z. Physik **65**, 209 [1930].

[25] H. R. HASSE, Proc. Camb. Phil. Soc. **26**, 542 [1930]; **27**, 66 [1931].

On the basis of these theoretical considerations, the atomic polarizabilities for the nitrogen atom and chlorine atom of nitrogen trichloride were calculated, and their values are 10.43×10^{-25} cm^3, and 13.88×10^{-25} cm^3, respectively.

The bond parallel component can be obtained from the contributions of two sources, namely, the bond region electrons, and the nonbond region electrons. The contributions to the parallel component of the polarizability by the bond region electrons is calculated by using a linear combination of atomic delta-function wave functions representing the two nuclei involved in the bond, i. e., the expectation value of the electronic position squared $\langle x^2 \rangle$ along the bond axis is calculated, and this is used to obtain the bond parallel component of the polarizability $\alpha_{\parallel \mathrm{b}}$ from the following:

$$\alpha_{\parallel \mathrm{b}} = \frac{4\, n\, A_{12}}{a_0} \, (\langle x^2 \rangle)^2 \tag{14}$$

where n is the bond order; A_{12}, the root-mean-square delta-function strength of the two nuclei involved; and $\langle x^2 \rangle$, the mean-square position of the bonding electron which is expressed as

$$\langle x^2 \rangle = \frac{R^2}{4} + \frac{1}{2\,(c_{R_{12}})^2} \tag{15}$$

where R is the internuclear distance at the equilibrium configuration which is here allowed to equal the delta-function spacing, a. In case the bond is of the heteronuclear type, a polarity correction is necessary to produce the ionic character believed to exist in reality. Thus, after the polarity correction, one may have the following:

$$\alpha_{\parallel \mathrm{p}} = \sigma\, \alpha_{\parallel \mathrm{b}} \tag{16}$$

where $\sigma = \exp\{-(1/4)(x_1 - x_2)^2\}$. Here, x_1 and x_2 are the electronegativities of the atoms 1, and 2, respectively on the PAULING's scale[22].

The contribution by the nonbond region electrons to the bond parallel component of the polarizability $\Sigma\, \alpha_{\parallel \mathrm{n}}$ is calculated from the remaining valence electrons not involved in the bonding, and the general expression for this is given as

$$\sum \alpha_{\parallel \mathrm{n}} = \sum f_i\, \alpha_i \tag{17}$$

where f_i is the fraction of the valence electrons in the i-th atom not involved in the bonding, and α_i, the atomic polarizability of the i-th atom obtainable from the delta-function strength, A_i.

The bond perpendicular component of a diatomic molecule is, on the basis of a semi-empirical delta-function potential model, simply the sum of the two atomic polarizabilities. If the electronic shape of an atom is assumed to be viewed from a point on a line perpendicular to the internuclear axis, and passing through the nucleus approximate that of the nonbonded atom, then the bond perpendicular component of the polarizability can be written as

$$\alpha_{\perp} = 2\, \alpha_{\mathrm{A}} \quad \text{for a nonpolar } \mathrm{A_2} \text{ molecule} \tag{18}$$

and $\alpha_{\perp} = \alpha_{\mathrm{A}} + \alpha_{\mathrm{B}}$ for a polar AB molecule (19)

where α_{A} and α_{B} are the atomic polarizabilities of the atoms A, and B, respectively. If the atom A is less electronegative than the atom B, the atomic cotnributions would be considered here according to the square of their respective electronegativities; and the bond perpendicular component of the polarizability can be written as

$$\alpha_{\perp} = 2\,(x_{\mathrm{A}}^2\, \alpha_{\mathrm{A}} + x_{\mathrm{B}}^2\, \alpha_{\mathrm{B}}) \,/\, (x_{\mathrm{A}}^2 + x_{\mathrm{B}}^2). \tag{20}$$

This shows that a greater contribution to the bond perpendicular component is due to that of the atom which has in its vicinity the larger charge distribution. In this manner, extending this principle to a polyatomic molecule, the analytical expression for the sum of all the perpendicular components is given by

$$\sum 2\, \alpha_{\perp \mathrm{i}} = n_{\mathrm{df}} \left(\sum x_i^2\, \alpha_i / \sum x_i^2 \right) \tag{21}$$

where n_{df} is the number of remaining (residual) atomic polarizability degrees of freedom. This can directly be obtained from a consideration of the symmetry of the molecular system and the assumption that every isolated atom is allowed to possess three degrees of polarizability freedom and every bond which is formed between two atoms removes two of these polarizability degrees of freedom with the exception that if two bonds are formed from the same atom (carbon in carbon dioxide) and exist in a linear configuration, then only three atomic polarizability degrees of freedom are lost, and if three bonds are formed from the same atom (sulfur in sulfur trioxide) and exist in a planar configuration, then only five atomic polarizability degrees of freedom are lost. Thus, the number of residual atomic polarizability degrees of freedom is five for water (see Fig. 1), six for hydrogen cyanide (see Fig. 2), seven for sulfur trioxide (see Fig. 3), and six for nitrogen trichloride (see Fig. 4). Hence, the analytical expression for the average molecular polariza-

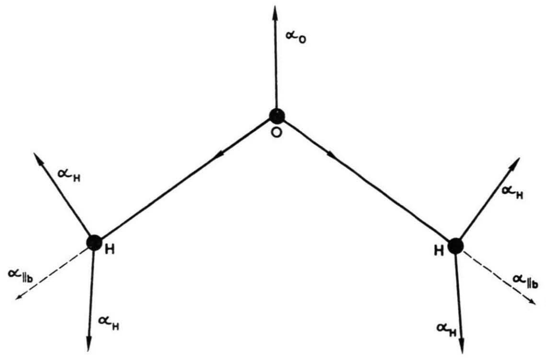

Fig. 1. Residual atomic polarizability degrees of freedom for water.

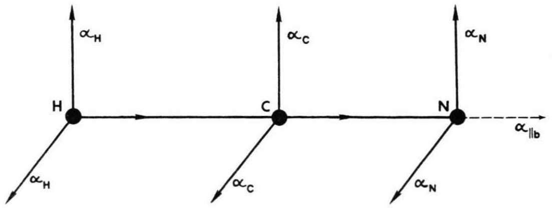

Fig. 2. Residual atomic polarizability degrees of freedom for hydrogen cyanide.

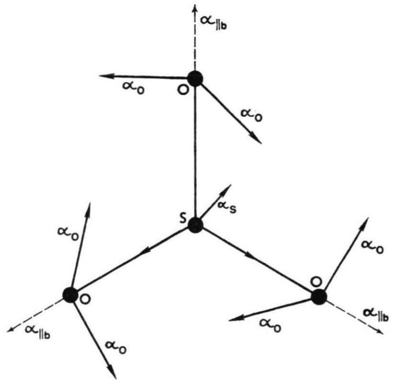

Fig. 3. Residual atomic polarizability degrees of freedom for sulphur trioxide.

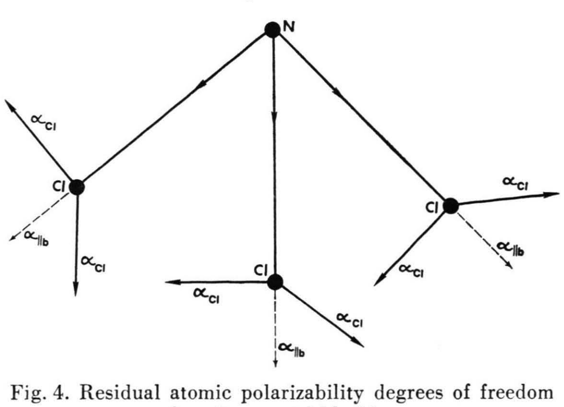

Fig. 4. Residual atomic polarizability degrees of freedom for nitrogen trichloride.

bility for a polyatomic molecule is given by

$$\bar{a}_M = (1/3)\left[\sum a_{\|b} + \sum f_i\, a_i + n_{df}\left(\sum x_i^2\, a_i / \sum x_i^2\right)\right], \quad (22)$$

$$\bar{a}_M = (1/3)\left[\sum a_{\|n} + \sum a_{\|p} + \sum 2\, a_{\perp i}\right]. \quad (23)$$

The computed values of the bond parallel components, contribution by the nonbond region electrons, bond perpendicular components, and the average molecular polarizability for nitrogen trichloride are given as follows:

$$\begin{aligned} a_{\|b} = a_{\|p} &= 36.5463 \times 10^{-25}\,\mathrm{cm}^3, \\ \sum a_{\|p} &= 109.6389 \times 10^{-25}\,\mathrm{cm}^3, \\ \sum a_{\|n} &= 39.8634 \times 10^{-25}\,\mathrm{cm}^3, \\ \sum 2\, a_{\perp i} &= 78.1050 \times 10^{-25}\,\mathrm{cm}^3, \\ \bar{a}_M &= 75.8691 \times 10^{-25}\,\mathrm{cm}^3. \end{aligned}$$

The molecular structural data used for the present computation are from the earlier studies of related molecules [14]. Since there are three lone pairs of electrons around the chlorine atom and one lone pair of electrons around the nitrogen atom of nitrogen trichloride, the LEWIS-LANGMUIR octet rule [26, 27] modified by LINNETT [28] as a double quartet of electrons has been satisfied here. In viewing these results, the smallest contribution is the one that made by the nonbond region electrons to the bond parallel components of the polarizability. Though the number of nonbond region electrons is greater than that of the bond region electrons, the contribution made by the bond region electrons is greater than that of the nonbond region electrons. Since the nitrogen and chlorine atoms have the same value of electronegativity [22], no polarity correction has been introduced here. The sum of all the bond perpendicular components is, as obtained above, the greatest of all other components.

The bond parallel components as well as the bond perpendicular components were experimentally obtained by DENBIGH [29], and VICKERY and DENBIGH [30], and their perpendicular components were qualitatively equal to the sum of the respective atomic polarizabilities calculated from the delta-function potential model. As an example, the values of atomic polarizabilities in 10^{-25} cm^3 derived from the experimental values of the perpendicular compo-

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[26] G. N. LEWIS, J. Amer. Chem. Soc. **38**, 762 [1916].

[27] I. LANGMUIR, J. Amer. Chem. Soc. **38**, 2221 [1916].

[28] J. W. LINNETT, J. Amer. Chem. Soc. **83**, 2643 [1961].

[29] K. G. DENBIGH, Trans. Faraday Soc. **36**, 936 [1940].

[30] B. C. VICKERY and K. G. DENBIGH, Trans. Faraday Soc. **45**, 61 [1940].

nents[29,30] for oxygen, nitrogen, and carbon atoms are 5.94, 7.24, and 10.22, while the delta-function potential model yields to 5.92, 7.43, and 9.78, respectively, for the same atoms. Thus, the delta-function potenital model is able to give explicit expressions for the bond parallel components, bond perpendicular components, contribution by the nonbond region electrons, and mean molecular polarizability. All these are in line with the investigations of DENBIGH[29] in which the molar refraction of a molecule is assumed to be the sum of the refractions of all the bonds in the molecule, and similarly, the molecular polarizability is assumed here to be the sum of the bond polarizabilities. The contributions by the bond region electrons and the nonbond region electrons are clearly distinguished. The bond perpendicular component is a linear combination of atomic polarizabilities, and independent of the internuclear distance. The bond parallel components can easily be transfered from one molecular system to another irespective of the configurations of the two molecular systems, provided the internuclear distances in the two different molecular systems are nearly identical. Thus, it is clear from this investigation that the delta-function potential model is very useful in predicting the atomic, bond, and molecular polarizabilities for any molecular system in the ground electronic state.

Root-Mean-Square Amplitudes

Molecules of the XY_3 type possessing a pyramidal structure with a symmetry point group C_{3v} give rise, according to the relevant symmetry considerations and selection rules[31], to six vibrational degrees of freedom constituting only four fundamental frequencies which are distributed under the various irreducible representations as follows:

$$2\,A_1(R, p; I, \|) + 2\,E(R, dp; I, \perp)$$

where R, I, p, dp, $\|$ and $\perp$ stand for Raman active, infrared active, polarized, depolarized, parallel, and perpendicular, respectively. The frequencies ν_1 and ν_2 correspond to a totally symmetrical stretching vibration and a bending vibration under the symmetry species A_1, while ν_3 and ν_4 correspond to an asymmetrical stretching vibration and a bending vibration under the species E. A schematic representation of the normal modes of oscillation for a molecule of the present study have been given by HERZBERG[31].

On the basis of the group theoretical method, the mean-square amplitudes and root-mean-square amplitudes for both bonded and nonbonded atom pairs for many molecules and ions of the present type were determined by many workers[32–35]. The same method has been adopted here. In order to construct the secular equations, the basic equation $|\Sigma\, G^{-1} - E\,\Delta| = 0$ postulated by CYVIN[35] has been considered here. In the above equation Δ has been related to the normal frequency ν in the equation given as $\Delta_i = (h/8\,\pi^2\,\nu_i)\,\coth(h\,\nu_i/2\,k\,T)$, where h is the Planck's constant, k the Boltzman constant, and T the absolute temperature. The secular equations giving the normal frequencies in terms of the mean-square amplitudes (σ) were constructed at the temperatures 298 °K and 500 °K with help of the symmetrized mean-square amplitude matrices (Σ), inverse kinetic energy matrices, fundamental frequencies in cm^{-1} given in Vable 1, and the molecular structural data used for the above calculation of polarizabilities. The mean-square amplitude (σ) is obtainable in terms of the internal coordinates, while the symmetrized mean-square amplitude (Σ) is obtainable in terms of the symmetry coordinates. There are only two equations with three symmetrized mean-square amplitudes under each symmetry species, and it is not possible to solve them uniquely unless some restricting approximations are adopted. When the off-diagonal elements were neglected, the equations under both symmetry species resulted in imaginary values to the diagonal elements. Hence, it was deemed necessary to introduce the off-diagonal elements, and the equations under each symmetry species were then solved by the elliptical method of TORKINGTON[36,37]. The values of the symmetrized mean-square amplitudes were evaluated from the frequencies of both isotopic molecules of nitrogen trichloride, and their values in Å^2 are

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[31] G. HERZBERG, Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand Company, Inc., New York 1960.

[32] S. SUNDARAM, J. Mol. Spectroscopy **7**, 53 [1961].

[33] S. SUNDARAM, Z. Physik. Chem. N.F. **34**, 233 [1962].

[34] G. NAGARAJAN, Indian J. Pure Appl. Phys. **2**, 237 [1964]; **4**, 456 [1966].

[35] S. J. CYVIN, Molecular Vibrations and Mean Square Amplitudes, Elsevier Publishing Co., Amsterdam 1968.

[36] P. TORKINGTON, J. Chem. Phys. **17**, 357 [1949].

[37] P. TORKINGTON, Proc. Roy. Soc. London A **64**, 32 [1951].

Table 1. Observed fundamental frequencies in cm^{-1} for the isotopic species of nitrogen trichloride.

Symmetry species	Number	Description of mode	Fundamental frequency $^{14}NCl_3$	$^{11}NCl_3$
A_1	ν_1	N-Cl symmetrical stretching	540.5	528
A_1	ν_2	Cl-$\hat{\mathrm{N}}$-Cl symmetrical bending	349	348
E	ν_3	N-Cl asymmetrical stretching	643	628
E	ν_4	Cl-$\hat{\mathrm{N}}$-Cl asymmetrical bending	257	257

Table 2. Symmetrized mean-square amplitudes in Å^2 for nitrogen trichloride molecule.

Element	Symmetrized mean-square amplitude $T = 298$°K	$T = 500$°K
Σ_{11}	0.0026512	0.0034022
Σ_{22}	0.0095496	0.0144918
Σ_{12}	−0.0020124	−0.0027023
Σ_{33}	0.0032988	0.0043108
Σ_{44}	0.0143527	0.0219983
Σ_{34}	−0.0034243	−0.0034233

Table 3. Mean-square amplitudes in Å^2 for nitrogen trichloride molecule.

Symbol	Mean-square amplitude $T = 298$°K	$T = 500$°K
σ_r	0.0030829	0.0040079
σ_{rr}	−0.0002159	−0.0003028
σ_θ	0.0127516	0.0194961
$\sigma_{\theta\theta}$	−0.0016010	−0.0025021
$\sigma_{r\theta}$	−0.0014455	−0.0020418
$\sigma_{r\theta}'$	0.0008787	0.0013814
σ_d	0.0048016	0.0078586
σ_{dd}	−0.0012761	−0.0020114
σ_{rd}	0.0014195	0.0017298
σ_{rd}'	0.0001841	0.0003476

given in Table 2 for the temperatures 298 °K and 500 °K, respectively. From the computed numerical values of the symetrized mean-square amplitude matrices, the mean-square amplitudes at the temperatures 298 °K and 500 °K were evaluated, and their values in Å^2 are given in Table 3, where σ_r is the mean-square amplitude quantity due to the bonded atom pair $\mathrm{N-Cl}$, σ_{rr} the quantity due to the interaction of two bonded atom pairs, σ_Θ the quantity due to the angle $\mathrm{Cl}-\hat{\mathrm{N}}-\mathrm{Cl}$, $\sigma_{\Theta\Theta}$ the quantity due to the interaction of two $\mathrm{Cl}-\hat{\mathrm{N}}-\mathrm{Cl}$ angles, σ_d the quantity due to the nonbonded atom pair $\mathrm{Cl-Cl}$, σ_{dd} the quantity due to the interaction of two nonbonded atom pairs, $\sigma_{r\Theta}$ the quantity due to the interaction of a bonded atom pair and an adjacent $\mathrm{Cl}-\hat{\mathrm{N}}-\mathrm{Cl}$ angle, $\sigma_{r\Theta}'$ the quantity due to the interaction of a bonded atom pair and a non-adjacent $\mathrm{Cl}-\hat{\mathrm{N}}-\mathrm{Cl}$ angle, σ_{rd} the quantity due to the interaction of a nonbonded atom pair and an adjacent bonded atom pair, and σ_{rd}' the quantity due to the interaction of a nonbonded atom pair and a non-adjacent bonded atom pair. The corresponding calculated values of the root-mean-square amplitudes in Å are 0.0555 at 298 °K and 0.0633 at 500 °K, respectively, for the bonded atom pair, and 0.0693 at 298 °K and 0.0887 at 500 °K, respectively, for the nonbonded atom pair.

The values of the mean-square amplitude quantity due to the bending of the molecule σ_Θ is very greater than those of the bonded as well as the nonbonded atom pairs, and this situation is exactly reversed in the case of the corresponding force constants [13]. The quantities due to the interaction of the bonded atom pairs σ_{rr} and the nonbonded atom pairs σ_{rd}' are very smaller in magnitude than all other mean-square amplitude quantities. As it is expected, the quantity due to the nonbonded atom pair σ_d is very greater than that of the bonded atom pair σ_r. The quantity due to the interaction of angles is similar in magnitude to those of the other interaction quantities. The negative values of the quantities due to the interaction of bonded atom pairs as well as the angles are exactly opposite to those of the corresponding force constants [13]. Though the quantities due to the interaction of bonded atom pairs and angles are smaller in magnitude, they are the deciding factors in solving the secular equations. The interaction quantities $\sigma_{\Theta\Theta}$, $\sigma_{r\Theta}$, σ_{dd}, and σ_{rd} are of the same magnitude except the signs. The values obtained here for the mean-square amplitudes for both bonded and nonbonded atom pairs at 500 °K are in general greater than those of the same quantities obtained at 298 °K. The results of the present investigation would be very useful in future for the interpretation of the results of electron diffraction studies, and for the evaluation of normal frequencies in other related molecules having similar chemical bonds. Further, the values presented here at different temperatures would be made use of for the interpretation of the shrinkages of the intermolecular distances.

Statistical Thermodynamics

In the domain of molecular spectra and molecular structure, the infrared absorption and Raman spectroscopy provides valuable information on the accurate assignments of the fundamental frequencies of molecules and ions in the ground as well as the excited states, and on the other vibrational constants. In a similar manner, the microwave, electron difraction, neutron diffraction, and X-ray diffraction studies determine the structure of molecules and crystals, whatever complicated, and yield to very reliable values of molecular constants. One of the best applications of the study of infrared absorption and Raman spectra of polyatomic molecules and other molecular structural determinations enables us to statistically compute the thermodynamics functions, namely, enthalpy function $(H^0-H_0^0)/T$, free enthalpy function $(F^0-H_0^0)/T$, entropy S^0, and heat capacity C_p^0. A rigid rotator and harmonic oscillator were assumed, and all the four thermodynamic quantities were computed for a gas in the thermodynamic standard gaseous state of unit fugacity (one atmosphere) for the temperature range from 200 °K to 2000 °K. The vibrational, translational, and rotational contributions to the total thermodynamic quantities would be computed in the following manner:

The internal thermal energy, $u_i = h\,c\,\omega_i/T$, is calculated for each normal mode, where h is the Planck's constant, c is the velocity of light in vacuum, ω_i is the i-th normal mode in cm^{-1}, and T is the absolute temperature. For each normal mode, the harmonic oscillator contributions to the four thermodynamic quantities, namely, C/R, $(H-H_0)/RT$, $-(F-H_0)/RT$, and S/R, were entered in a tabular form from the standard tables of thermodynamic functions given by PITZER[38] for the corresponding values of the internal thermal energies. After summing up all these values under each column, each value was multiplied by the gas constant R in order to obtain the four quantities, namely, C, $(H-H_0)/T$, $-(F-H_0)/T$, and S. The value under each column of C was added to $4\,R$ in order to get the heat capacity at constant pressure, C_p^0, for the harmonic oscillator approximation at a pressure of one atmosphere. Similarly, the value under the column of $(H-H_0)/T$ was added to $4\,R$ in order to get the enthalpy function, $(H^0-H_0^0)/T$, for the harmonic oscillator approximation at a pressure of one atmosphere. The values under the columns of S and $-(F-H_0)/T$ represent the vibrational contributions to the entropy and the free energy function.

From the molecular structural data the rotational and translational contributions to the entropy, heat capacity, and free energy function for one mole of a perfect gas at a pressure of one atmosphere were obtained from the following:

$$S_{\text{tr}}{}^0 + S_{\text{r}}{}^0 = 2.2868\,(8\log T + 3\log M + \log I_{xx} I_{yy} I_{zz} - 2\log\sigma) - 7.6965\,, \qquad (24)$$

$$-(F_{\text{tr}}{}^0 + F_{\text{r}}{}^0 - H_0{}^0)/T = S_{\text{tr}}{}^0 + S_{\text{r}}{}^0 - 4\,R\,, \qquad (25)$$

$$(C_p{}^0)_{\text{tr}} + (C_p{}^0)_{\text{r}} = (H_{\text{tr}}{}^0 + H_{\text{r}}{}^0 - H_0{}^0)/T = 4\,R\,, \qquad (26)$$

where S, F, C_p, H, tr, r, T, M, and σ stand for entropy, free energy, heat capacity, at constant pressure, enthalpy, translational part, rotational part, temperature in degrees Kelvin, total mass of the molecule, and symmetry number of the point group to which the molecule belongs. I_{xx}, I_{yy}, and I_{zz} are the principal moments of inertia in atomic mass units times Å^2 along the x-axis, y-axis, and z-axis, respectively. The value of the gas constant, R, is 1.9872 cal./degree mole. These contributions due to translation and rotation were added to the contributions due to vibration in order to obtain the total contributions to the free energy function, $-(F^0-H_0^0)/T$, and the entropy, S^0, at a pressure of one atmosphere.

The principal moments of inertia were calculated for nitrogen trichloride from the molecular structural data [14], and their values for both isotopic species are given as follows:

For the $^{14}\text{NCl}_3$ molecule:

$$I_{xx} = I_{yy} = 145.8985\ \text{AMU Å}^2\ (242.3564 \times 10^{-40}\ \text{g cm}^2)\,,$$
$$I_{zz} = 280.3293\ \text{AMU Å}^2\ (465.6634 \times 10^{-40}\ \text{g cm}^2)\,.$$

For the $^{15}\text{NCl}_3$ molecule:

$$I_{xx} = I_{yy} = 146.2575\ \text{AMU Å}^2\ (242.9527 \times 10^{-40}\ \text{g cm}^2)\,,$$
$$I_{zz} = 280.3293\ \text{AMU Å}^2\ (465.6634 \times 10^{-40}\ \text{g cm}^2)\,.$$

The fundamental frequencies in cm^{-1} given in Table 1 were made use of for the present computa-

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[38] K. S. PITZER, Quantum Chemistry, Prentice-Hall, Inc., New York 1953.

tions for both isotopic species. Assumed in the calculations were a symmetry number of 3, a singlet ground electronic state, and chemical atomic weights. Neglected in the computations were the contributions due to the centrifugal distortion, nuclear spins, isotopic mixing, and interaction between vibration and rotation, since the contributions of these are negligibly small compared to the total thermodynamic quantities due to vibration, rotation, and translation. The computed values of all the four thermodynamic quantities in calories per degree mole for both isotopic species of nitrogen trichloride are given in Tables 4 and 5 at the temperatures from 200 °K to 2000 °K. Since these molecular species have been recently synthesized, elaborate investigations of experimental thermodynamic quantities have not yet been undertaken, so that the spectroscopic values of the present study could be compared and discussed. The values presented here for all the temperatures are the most reliable ones, and would be very useful in future for the evaluation of normal frequencies in other related molecules having similar chemical bonds, and for the interpretation of the results of experimental entropies and heat capacities at a pressure of one atmosphere for the ideal gaseous state.

Table 4. Enthalpy function, free enthalpy function, entropy, and heat capacity of $^{14}NCl_3$ for the ideal gaseous state at a pressure of one atmosphere (all the quantities are in cal./degree mole).

T(°K)	$(H^\circ - H^\circ)/T$	$-(F^\circ - H^\circ)/T$	S°	C_p^0
200	10.1117	54.9751	65.0868	13.6643
273.16	11.3313	58.3080	69.6393	15.5787
298.16	11.7351	59.3373	71.0724	16.0904
300	11.7417	59.3908	71.1325	16.1107
400	13.0186	62.9540	75.9726	17.4558
500	13.9826	65.9569	79.9395	18.2138
600	14.7205	68.5515	83.2720	18.6734
700	15.3132	70.8777	86.1909	18.9715
800	15.7848	72.9721	88.7569	19.1704
900	16.1664	74.8501	91.0165	19.3113
1000	16.4829	76.5571	93.0400	19.4109
1100	16.7486	78.1009	94.8495	19.4895
1200	16.9847	79.5951	96.5798	19.5489
1300	17.1939	81.0294	98.2233	19.5967
1400	17.3652	82.3096	99.6748	19.6334
1500	17.5053	83.4284	100.9337	19.6616
1600	17.6484	84.6239	102.2723	19.6867
1700	17.7656	85.6279	103.3935	19.7087
1800	17.8769	86.6464	104.5233	19.7258
1900	17.9821	87.7620	105.7441	19.7397
2000	18.0588	88.5143	106.5731	19.7534

Table 5. Enthalpy function, free enthalpy function, entropy, and heat capacity of $^{15}NCl_3$ for the ideal gaseous state at a pressure of one atmosphere (all the quantities are in cal./degree mole).

T(°K)	$(H^\circ - H^\circ)/T$	$-(F^\circ - H^\circ)/T$	S°	C_p^0
200	10.1398	59.3710	69.5108	13.7410
273.16	11.3802	62.7257	74.1059	15.6783
298.16	11.7581	63.7310	75.4891	16.1610
300	11.7949	63.8133	75.6082	16.2023
400	13.0838	76.3969	80.4807	17.5326
500	14.0446	70.4048	84.4530	18.2688
600	14.7773	73.0166	87.7939	18.7108
700	15.3611	75.3359	90.6970	18.9997
800	15.8363	77.4464	93.2827	19.1964
900	16.2248	79.3416	95.5664	19.3347
1000	16.5395	81.0650	97.6045	19.4327
1100	16.7929	82.5956	99.3885	19.5093
1200	17.302	84.1034	101.1336	19.5627
1300	17.2251	85.5115	102.7366	19.6052
1400	17.3974	86.8007	104.1981	19.6089
1500	17.5455	87.9463	105.4918	19.6708
1600	17.6973	89.1856	106.8829	19.6974
1700	17.7992	89.7880	107.5872	19.7143
1800	17.9022	91.1388	109.0410	19.7306
1900	17.9803	91.8222	109.8025	19.7415
2000	18.1029	93.2152	111.3181	19.7578

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