Force constant calculation of nitrogen trichloride and ammonia adduct

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The paper deals with a brief review on the F.G. matrix analysis of the vibrational spectra of polyatomic molecules. A discussion on the results of such calculations made for nitrogen trichloride explaining its relative instability and for ammonia in ammonia sulphur dioxide adduct is given.

1 INTRODUCTION

The importance of analysis of infrared and Raman spectra has since long been emphasized in studying the structure, symmetry and force fields of the complex polyatomic molecules. In order to explain the Raman and Infrared spectra usually a model for the molecule is assumed which involves parameters like the geometry, stiffness of the valence bonds etc. The qualitative features of the spectra is uniquely determined by the geometry of the molecule. So when the geometry of the molecule is not known earlier, the nature of the vibrational spectra is sufficient to fix the correct configuration from several plausible structures of the molecule.

To calculate the vibrational frequencies a very simple dynamical model is used. The potential and kinetic energy of the molecule are first set up as quadratic functions of coordinate and velocity of the atoms treated as particles with point mass using mass weighted coordinate system.

Thus,

$$2T = \Sigma \dot{q_i}^2, \quad 2V = \Sigma f_{ij} \cdot \dot{q_i} \, q_i \tag{1}$$

Now, using Newton's equation of motion

$$\frac{d}{dt} \left(\frac{\delta T}{\delta \dot{q_j}} \right) + \frac{\delta V}{\delta q_j} = 0, \quad j = 1, 2, \ldots\ldots, 3N \tag{2}$$

a set of 3 N simultaneous second order linear differential equations

$$\ddot{q}_{ij} + \sum_{j} f_{ij} \, q_i = 0 \tag{3}$$

is obtained. Assuming harmonic solutions

$$q_i = A_i \cos (\lambda^{1/2} \, t + \varTheta_i) \tag{4}$$

Where $\lambda = 4\pi^2\nu^2$ the secular equation

$$| f - \lambda I | = 0 \tag{5}$$

results. It is equivalent to an alegebraic equation of 3 N degree. Roots of the equation give vibrational frequencies.

But these equations still involve the rotational and translational degrees of freedom. To circumvent this difficulty one prefers the internal coordinates to ordinary cartesian coordinates. The advantage of this method is still more enhanced by the fact that the potential energy expression can be easily set up and the force constants appearing in the expression can be readily inter-pretted. But the real difficulty is contained in constructing the kinetic energy in matrix. Now if $\{ S_t \}$ represents the set of internal coordinates

$$S_t = \sum_{i=1}^{3N} B_{ti} \, q_i \, , \, t = 1, 2, \ldots\ldots, 3\,N\text{-}6 \tag{6}$$

Then the kinetic energy and potential energy can be written respectively as

$$2 \, T = \sum_{tt'} (\, G^{-1})_{tt'} \, S_t \, S_t' \tag{7}$$

$$2 \, V = \sum_{tt'} F_{tt'} \, S_t \, S_t' $$

where $G_{tt'} = \sum B_{ti} \, B_{t'i} \; ; \, t, \, t' = 1, 2, \ldots\ldots, 3\,N\text{--}6$

The secular equation then assumes the form

$$| F - \lambda \, G^{-1} | = 0$$

or $\quad | GF - \lambda I | = 0 \tag{8}$

Obviously the matrix G is the key element in the calculation. Most of the common elements of G matrix were calculated by Decius (1928).

The difficulty of solving higher order secular equations which results in case of most of the polyatomic molecules can be minimised by taking into

consideration the symmetry of the molecule It is then possible to factorise the secular equation. To achieve this, linear combinations of internal coordinates are choosen such that each combination belongs to particular symmetry species. These are called symmetry coordinates The potential energy and kinetic energy expressions do not involve cross terms between the symmetry coordinates of different species. This partitions the matrix into several blocks, each block corresponding to vibration of a particular symmetry species.

So far it has been assumed that potential energy matrix is known. But except for very simple molecules they are not known a priori. In fact the entire formalism is used to evaluate these force constants utilising the observed frequencies. Since the number of force constants involved in calculation is usually more than the number of observed frequencies some of the force constants are first calculated using a certain number of these frequencies and the reproduction of the rest of the frequencies is used as a check on the validity of the model used. Several models like central force field, valnce force field, Urcy-Bradley force field etc. are prescribed in literatue. There is still another way to overcome this difficulty of inadequate number of observed frequencies compared to the necessary force constants of a given force field. Isotopic substitution of the molecule yields few more frequencies which can be used to calculate the force constants, with the assumption that force constants do not change considerably with isotopic substitution

In the present work we have employed Wilson's F-G. matrix method to evaluate the force constants of the free NCl_3 molecule and the NH_3 molecule in $(NH_3)_2 SO_2$ adduct (1955)

NCl_3

NCl_3 is highly unstable at room temperature and is a very sensitive detonator (1928). Because of he experimental hazards no vibrational study of the molecule was reported for a long time Only in analogy to other Gr. V trihalides its structure was thought to be pyramidal. But later aue to its inability to react with the Lewis acid Boron trifluoride, a planar structure was thought to be more plausible in analogy with nitrogen silamine (1958). Carter, Bratton and Jackovitz made Raman and infrared studies of the molecule at 0°C and proposed that C_{3v} symmetry is compatible with observed frequencies (1968). It was therefore thought worthwhile to calculate the force constants of the molecule using C_{3v} symmetry in an attempt to explain relative instability of the molecule.

2. CALCULATION

The six normal modes of vibration of NCl_3 with C_{3v} symmetry can be classified as $2A + 2E$ of which all the vibrations are Raman and infrared active.

The six internal coordinates used for calculation are changes in bond length and bond angles. The symmetry coordinates are :

A type :

$$S_t^A = \frac{1}{\sqrt{3}} (t_1 + t_2 + t_3)$$

$$S_\alpha^A = \frac{1}{\sqrt{3}} (\alpha_1 + \alpha_2 + \alpha_3)$$

E type

$$S_{t_1}^E = \frac{1}{\sqrt{6}} (2t_1 - t_2 - t_3)$$

$$S_{\alpha_1}^E = \frac{1}{\sqrt{6}} (2\alpha_1 - \alpha_2 - \alpha_3)$$

$$S_{t_2}^E = \frac{1}{\sqrt{2}} (t_2 - t_3)$$

$$S_{\alpha_2}^E = \frac{1}{\sqrt{2}} (\alpha_2 - \alpha_3)$$

Again the valence angle being an undetermined parameter the equation for angle (β) made by the symmetry axis with the valence bond

$$\cos^2\beta = \frac{1}{4 \dfrac{\nu_3^2 \nu_4^2}{\nu_2^2 \nu_1^2} + \dfrac{3 MCl - M_N}{3 MCl + M_N}}$$

obtained on the basis of valence force field was used to estimate α (1964).

α was thus obtained to be $96° 28'$. Using this value of α the G-matrix was set in terms of the bond length d. Since the isotopic data are not available for this molecule and six force constants are involved where as four observed frequencies are available, first the secular equation corresponding to E-vibration was solved, setting $F_{12}' = 0$. The values obtained for F_{11}^r and the observed and calculated frequencies was noted. Further, calculations F_{22}^r were used to predict A vibrations. But large discrepancy between based on general valence force did not yield real force constants. Hence, the high frequency part was decoupled an F_{11}^A was approximated as suggested

by Wilson *et al* (1955). Then F_{22}^A and F_{12}^A were fixed by calculation to to match the observed frequencies. The frequencies and force constants are tabulated in table-1.

Table 1. Vibrational frequencies and force constants of NCl_3

Vibrational frequencies in cm^{-1}		Force constants in 10^5 dynes/cm	
Obs.	Calc.	$f_1 \quad = \quad 1.8630$	
Avib		$f_{11} \quad .0888$	
538	533	$\dfrac{f_\alpha}{d^2} \quad = \quad .6485$	
350	387	$\dfrac{f_{\alpha\alpha}}{d^2} \quad .0788$	
Evib.			
642	642	$\dfrac{f_{1\alpha}}{d} = \dfrac{f_{1\alpha}}{d} \quad - \quad .2571$	
257	257		

NH_3 in $(NH_3)_2 SO_2$ adduct

The infrared spectroscopic study of NH_3-SO_2-H_2O solid state system was reported by I. C. Hiastsune and Julian Heicklen (1975). It was observed that at $-90°C$ an adduct $(NH_3)_2 SO_2$ is formed due to solid state reaction of low temperature matrix of SO_2 with excess of NH_3. They made infrared analysis of the NH_3 present in the molecule. We used these frequencies to evaluate the effective force field using Wilson's matrix method in this changed environment.

CALCULATION

The elaculation was carried out in an analogous manner. The angle β was observed to be $51°22'$ where as for free ammonia it is known to be $72°$. Even the valence force field was found to be quite satisfactory. However, here the force constants have been evaluated in GVF field. The results are given in table 2.

4. DISCUSSION

In case of NCl_3 six force constants were calculated assuming C_{3v} symmetry. The calculated and observed frequencies are in good agreement. The relatively low stretching force constants may be due to internal strain induced by chlorine atoms as suggested by Friedburg to account for the high explosiveness of the molecule.

Table 2. Vibrational frequencies and force constants of NH_3

	Frequencies in cm^{-1}		Force constants in 10^6 dynes/cm	
	Obs.	Calc		
		A vibration	$f_{t.}$	$=$ 5.3466
Valence force field	3045	3130	$\dfrac{f_\alpha}{d^2} =$	0.731
	1700	1721		
		Evibration		
	3140	3140		
	1477	1477		
G.V.F. field		*A vibration*	f_t	$=$ 5.2503
			f_{tt}	$=$ -0.0963
	3045	3045	$\dfrac{f_\alpha}{d^2}$	$=$ 1.0220
	1700	1700	$\dfrac{f_{\alpha\alpha}}{d^2}$	$=$ 0.2910
		Evibration		
	3140	3140		
	1477	2477		

The ammonia molecule was observed to show some novel features. It is generally observed that in the case of Gr.V trihydrides ν_1 and ν_2 are less than ν_3 and ν_4 respectively, whereas opposite trend is marked for Gr V. trihalides (1963). But in this case it was found that even though the modes follow this bending modes do not show the corresponding trend. On the other hand ν_2 in this case was observed to be almost double of ν_2 of the gaseous ammonia (950 c.m.$^{-1}$) The present calculations indicated that the stretching force constants has decreased where as bending force constant has increased relatively with respect to the gaseous phase. This is perhaps due to the fact that the change in angle β brings about a change of H-H distance from 1.670 Å to 1.372 Å. This distance is closer to the equilibrium distance between two hydrogen atoms in the hydrogen molecule. This leads to a higher binding energy which is responsible for the higher of bending force constants.

RFFLRFNCES

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