ISSN 0974 - 9373

Vol. 16 No. 2 (2012) **Journal of International Academy of Physical Sciences** pp. 205-209

# Normal Coordinate Analysis and Vibrational Modes of Nitrosylchloride

**Sangeeta Prasher and Priya Sangar**
Department of Physics
Kanya Maha Vidyalaya, Vidyalaya Marg, Jalandhar-144004
Email: priya.sangar@yahoo.com

**Mukesh Kumar**
Department of Physics
Lovely Professional University, Jalandhar-Ludhiana

(Received December 22, 2011)

**Abstract:** The infrared absorption spectrum of nitrosylchloride gas was first observed by Bailey and Cake[1] who assigned the three fundamentals at 1832($\nu_1$), 633($\nu_2$), and 923($\nu_3$) cm$^{-1}$ but Beeson and Yost[2] later showed that these fundamentals could not account for the observed entropy and reinterpreted the spectrum. Mini and Mazzariol[3] determined centrifugal distortion constants from microwave studies and by using these data along with the vibrational frequencies they calculated the force constants for a general quadratic force field. Therefore, in order to obtain additional information of the molecule the Wilson's FG matrix method has been followed to carry out the normal coordinate analysis of NOCl with a systematic set of symmetry coordinates. The molecule exhibits the Cs point group symmetry. Potential energy distribution has also been calculated for the normal modes of vibration to check whether the chosen set of vibrational frequencies contribute maximum to the potential energy associated with the normal coordinates of the molecule.

**Keywords:** Nitrosylchloride, Normal coordinates analysis, PED distribution, Wilson's FG- Matrices.

**PACS Nos:** 34.20.-b; 34.20.Cf; 36.20.Ng

## 1. Introduction

Nitrosylchloride is a yellow gas which liquefies at -5.5°C and has a planar molecular structure and most commonly encountered as a decomposition product of aqua regia[4], a mixture of hydrochloric acid and nitric acid. NOCl is highly toxic and non-flammable gas having an irritating odour. It is used in the diazotization, nitrosation and often employed as a catalyst in organic synthesis. Nitrosylchloride can also be used in plastics and fertilizers. In the present paper, a normal coordinate analysis has been made for nitrosylchloride. From the knowledge of force constants[5], mass of the atoms constituting the molecule, internal parameters and symmetry of the molecule, the secular equation has been solved. Validation of the obtained set of force constants and frequency assignments is done through potential energy distribution(PED) calculations. McDonald et al.[5] have observed the band origins to be at 595.860 and 331.973 cm$^{-1}$ for $\nu_2$ and $\nu_3$ respectively, for ON$^{35}$Cl. However The first IR absorption spectrum of NOCl gas was observed by Bailey and Cassie who assigned the three fundamentals at 1832($\nu_1$), 633($\nu_2$), 923($\nu_3$)cm$^{-1}$.

## 2. Theoretical Considerations

The symmetry of a molecule helps to determine and classify the actual number of fundamental vibrations of the system. The modes of vibrations and the normal coordinates of the molecule have been explained on the basis of Cs point group symmetry[6] as is evident from Figure 1. The three optically active vibrations are distributed as $\Gamma_{vib}$= 3A' (in plane) using the character table of the Cs symmetry.

All the modes are active in both Raman and Infrared spectra. The vibrational assignments are discussed in terms of the potential energy distribution which was obtained from the calculated eigenvector matrix L corresponding to the three eigen values of the product of FG matrix. The molecular parameters for NOCl have been taken from the crystal structure analysis reported in the literatures[7] and are presented in Table 1.

## 3. Potential Energy Distribution

The normal coordinate calculations have been carried out to obtain vibrational frequencies and the potential energy distribution for the various modes. The potential energy distribution plays an important role for the characterisation of the relative contributions from each internal coordinates to the total potential energy associated with particular normal coordinate of the molecule and hence has been calculated using the relation[8]

$$P.E.D. = (F_{ij} L^2_{ij}) / \lambda_j \qquad (1)$$

to check whether the chosen set of assignments contribute maximum to the potential energy associated with normal coordinates of the molecules, where $F_{ij}$ are the force costants defined by damped least square technique, $L_{ij}$ the normalised amplitude of the associated element (i, j) and $\lambda_j$, the Eigenvalue corresponding to the vibrational frequency of the element j. The potential energy distribution contribution corresponding to each of the observed frequencies is alone listed in the present work.

## 4. Normal Coordinate Analysis

The molecule possesses Cs symmetry has been solved using the Wilson's FG matrix Method. The method assumes the foreknowledge of the equilibrium molecular geometry namely, bond angles and bond lengths, vibrational frequencies and atomic masses. The normal coordinate analysis has been carried out on the basis of set of symmetry coordinates which were constructed using the knowledge of projection operator, internal coordinates and the character table pertaining to the Cs symmetry point group and have been reported in Table 1. The knowledge of symmetry coordinates is utilized to solve master secular determinant of Wilson method

$$|FG-\lambda I|=0, \tag{2}$$

where F is the matrix of force constants through which the vibrational potential energies enter the calculation. For nitrosyl chloride the values of force constants have been taken from the literature available[10] G is the inverse kinetic energy matrix and involves the atomic weights and equilibrium geometric relationships. Elements of the inverse kinetic energy matrix have been derived from the relation $G = B\mu B^T$ where $B^T$ is the matrix formulated using the vectors which have been evaluated from the expression of the symmetry coordinates in terms of Cartesian displacement coordinates, $\mu$ is the diagonal matrix of the reciprocal masses of the atoms in the molecule. $\lambda$'s are the eigen values of the product matrix of F and G matrices and is related to the normal frequencies of the molecule by the relation

$$\lambda = (4\pi^2 c^2 \nu^2)/N. \tag{3}$$

Nitrosyl chloride exhibits three fundamental modes of vibration distributed as $\Gamma_{vib} = 3A'$. All the three modes are symmetric. The structure orientation[9] of the principal axes of NOCl is presented by Figure 1.

The basis set of an FG calculation consists of internal coordinates suitably chosen to eliminate rebundancies. The observed frequencies along with the percentage of potential energy distribution for NOCl are presented in Table 2. The calculated frequencies of vibrational modes of the molecule have been correlated with the observed infrared and Raman frequencies[10]. A detailed analysis of the NOCl stretches has been discussed.

**N=O stretching vibrations** The Raman frequency due to symmetric vibration of N=O stretching, labelled $\nu_1$ has been calculated to be occurring at about 1676 cm$^{-1}$ and is of weak intensity. The stretch is sensitive to solvent polarity as has been reported by L. S. Bellamy[11].

**N-Cl stretching/ONCl bending vibrations** The other two calculated frequencies are 594.9 and 217.9 cm$^{-1}$ with their potential energy distributions as given in Table (2). These frequencies refer to the N-Cl stretching/ ONCl bending vibrations. But as the PED% does not differ a lot an accurate assignment has not been made. However the concept of lower frequency for bending mode suggests that the 217.9 cm$^{-1}$ may be attributed to the ONCl bending mode. The same peaks have been noticed by Mc Donald et al.[5] at 495 and 275 cm$^{-1}$ in the Raman spectrum of the molecule, which corroborates our results.

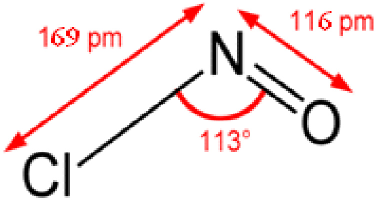

**Fig. 1. Structure and internal parameters of NOCl**

**Table 1.Molecular parameters of NOCl**

| Nature | Symbol | Value (Å)/ deg |
|---|---|---|
| N=O | r | 1.16 |
| N-Cl | s | 1.69 |
| O-N-Cl | θ | 113 |

**Table 2.Observed, Calculated Frequencies (cm$^{-1}$), Potential Energy Distribution of NOCl**

| **Species** | | **Observed (cm$^{-1}$)** | | **Calculated (cm$^{-1}$)** | **P.E.D. (%)** |
|---|---|---|---|---|---|
| | | **Raman** | **IR** | | |
| A’ | $\nu_1$ | 1799.7(vs) | ------- | 1676 | N=O stretch (90) |
| | $\nu_2$ | 595.7(vs) | 597.6 | 594.9 | ONCl bend (95) |
| | $\nu_3$ | 331.8(--) | 329.5 | 217.9 | ONClbend(35),N-Cl stretch (65) |

vs -very strong

## 5. Conclusions

In conclusion, we studied the potential energy distribution obtained in this analysis provides some insight into the nature of many of the normal modes of this molecule and it contribute maximum value. Also the corresponding calculated potential energy distribution is greater than 50 reinforcing the correctness of frequency arrangement. Thus, the close agreement between the observed and calculated frequencies confirms the validity of the present assignment.

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