Molecular Constants of some Nitrogen-Halogen Compounds by Green’s Function Analysis-Nitrosyl Fluoride

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Green’s function and partitioning techniques have been applied to the case of nitrosyl fluoride to evaluate the molecular constants. The values of the molecular constants evaluated by this procedure are, in general, in very good agreement with those obtained by the conventional normal coordinate analysis.

The determination of an unambiguous set of force constants from the vibrational spectral data alone is not possible because the number of force constants exceeds the number of fundamental vibrational frequencies. Therefore one is forced to turn to other sources for the determination of a unique set of force constants. As a result one has to reduce the number of force constants as in the UBFF 1, HBFF 2 and OVFF 3 or turn to other factors like rotational distortion constants, Coriolis coupling constants and mean amplitudes of vibration which are closely related to the force constants. Such attempts have been made earlier by several workers 4-6. However, it is of interest to find out some method by which the symmetry force constants can be determined without recourse to any assumption regarding the force fields. Green’s function and partitioning technique developed by De Wames and Wolfgram 7-9 is one such attempt in this direction. This method can be applied to the molecules for which isotopic data are available. By the use of this method elegant isotopic rules like Tellier-Redlich product rule 10 can be obtained. Such attempts have been made earlier for XY 2, XY 3, XY 4 and X 2Y type molecules 11-15. In the present paper an attempt is being made to extend this study to XYZ bent type molecules. As a typical example nitrosyl fluoride and its isotopic species are chosen.

Potential Energy Constants

The external symmetry coordinates \( S^F \) for the ONF molecule were constructed from the cartesian displacement coordinates by the method suggested by Wolfram et al. 7-9. The symmetry coordinates thus constructed consist of orthonormalized, mass weighted, translations, rotations and vibrational type of motions which transform according to the irreducible representations of the \( C_2 \) point group for the nitrosyl fluoride molecule.

In the ONF molecule NO is a pure stretching vibration \( (S_1^F) \), NF stretch \( (S_2^F) \) and ONF bend \( (S_3^F) \) are considerably mixed. So \( S_2^F \) and \( S_3^F \) are mixed which give

\[
Q_a = \left( S_2^F + p S_3^F \right) \left( 1 + p^2 \right)^{-1/2};
Q_b = \left( S_2^F - p S_3^F \right) \left( 1 + p^2 \right)^{-1/2}.
\]

The remaining symmetry coordinates \( S_1^E \), \( S_1^T \), \( S_1^Y \) and \( S_1^R \) are also normal coordinates. All the three vibrations are in-plane vibrations and belong to \( A' \)

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species. For them, the following combination was chosen with the normal coordinates \((Q)\) and the mixing parameter \((p)\):

\[
\begin{bmatrix}
Q_1 \\
Q_2 \\
Q_3
\end{bmatrix} = \begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & p \\
0 & -p & 1
\end{bmatrix} \begin{bmatrix}
S_1^E \\
S_2^E \\
S_3^E
\end{bmatrix}
\]

were \(P = \sqrt{1 + p^2}\).

To determine the mixing parameter \(p\) the Green's function matrix and the vibrational frequencies of \(^{18}\text{O}^{14}\text{N}^{19}\text{F}\), the isotope of \(^{16}\text{O}^{14}\text{N}^{19}\text{F}\) were used. The interbond angle, internuclear distances and vibrational frequencies of unperturbed and perturbed molecules are given in Table I.

Table I. Fundamental vibrational frequencies and molecular parameters for nitrosyl fluoride.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(\omega_1)</td>
<td>1876.8</td>
</tr>
<tr>
<td>(\omega_2)</td>
<td>522.9</td>
</tr>
<tr>
<td>(\omega_3)</td>
<td>775.5</td>
</tr>
</tbody>
</table>

Table II. Symmetry F-matrix elements and the valence force constants for nitrosyl fluoride.

<table>
<thead>
<tr>
<th>F-Matrix Elements</th>
<th>Valence Force constants in ([\text{mdyn/Å}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F_{11} = 15.7491)</td>
<td>(f_t = 15.7491)</td>
</tr>
<tr>
<td>(F_{22} = 2.0390)</td>
<td>(f_d = 2.0390)</td>
</tr>
<tr>
<td>(F_{33} = 0.9550)</td>
<td>(f_{rd} = 0.9550)</td>
</tr>
<tr>
<td>(F_{12} = 0.3393)</td>
<td>(f_{ta} = 0.2589)</td>
</tr>
<tr>
<td>(F_{23} = 0.2504)</td>
<td>(f_{da} = 0.1911)</td>
</tr>
</tbody>
</table>

Mean Amplitudes of Vibration

The Wilson L-matrix is given by the equation

\[
L = BA
\]

where \(B\)-matrix is given by eq. (5) and \(A\) is mixing parameter matrix. The symmetrized mean square amplitude matrix \(\Sigma\) is determined from the Cvvin's equation

\[
\Sigma = L^T A L;
\]

where

\[
A_k = \frac{h}{3 \pi^2 v_k c} \coth \frac{h v_k c}{2 K T},
\]

where \(h\) is Planck's constant and \(K\) is Boltzmann's constant. The means square amplitude matrix \(\Sigma\), the mean amplitudes and the mean amplitudes for nonbonded distance which was determined by the method of Ramaswamy et al. are given in Table III.

\[\text{Table III.} \]

\[\text{Mean Amplitudes of Vibration.}\]

\[\text{Table II. Symmetry F-matrix elements and the valence force constants for nitrosyl fluoride. * This number of significant figures is retained to secure internal consistency in the calculation.}\]

\[\text{Table I. Fundamental vibrational frequencies and molecular parameters for nitrosyl fluoride.}\]
Table III. Mean amplitudes of vibration for nitrosyl fluoride at 298.16 °K. * As in Table II.

<table>
<thead>
<tr>
<th></th>
<th>Mean Amplitudes [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N=O</td>
<td>0.034767 *</td>
</tr>
<tr>
<td>N—F</td>
<td>0.059528</td>
</tr>
<tr>
<td>ONF</td>
<td>0.050432</td>
</tr>
<tr>
<td>O...F</td>
<td>0.0618</td>
</tr>
</tbody>
</table>

Table III. Mean amplitudes of vibration for nitrosyl fluoride at 298.16 °K. * As in Table II.

Rotational Distortion Constants

Using the expressions given by Oka and Morino\(^\text{19}\) and Alti et al.\(^\text{20}\) the rotational distortion constants \(D_J, D_K, D_{JK}, R_5, R_6\) and \(\delta_J\) were evaluated. They are given in Table IV.

![Table IV](image)

Table IV. Rotational distortion constants in MHz and Coriolis coupling constants of nitrosyl fluoride.

Coriolis Coupling Constants

Coriolis coupling constants were calculated using Meal and Polo's equation\(^\text{21}\):

\[
\xi^{(i)} = \ell M^{(i)} l, \quad (9)
\]

where \(i = (x, y, z)\) denotes the axis of rotation and \(M^{(i)}\) is the block diagonal supermatrix made up of \(n\) identical \((3 \times 3)\) submatrices, one for each atom. The values obtained are also presented in Table IV.

Discussion

It is seen from Table II that the values of NO stretching, ONF bending and NF stretching force constants \((15.749, 1.0489 \text{ and } 2.039 \text{ mdyn/Å})\) compare very well with those \((15.9, 1.048 \text{ and } 2.3 \text{ mdyn/Å})\) obtained by Jones et al.\(^\text{16}\) by conventional method. This shows the applicability of Green's function analysis to molecular vibrational problems even in asymmetric substitutions.

The vibrational mean amplitude values of \(N=O, N—F\) and \(O...F\) also compare very well with the values of Jones et al.\(^\text{16}\). The rotational distortion constants obtained here compare well with the experimental value of Cook\(^\text{22}\).

The Coriolis coupling constants evaluated here are in good agreement with the values calculated by Jones et al.\(^\text{16}\) and they also satisfy the "sum rule" \((\xi^{(1)}_x)^2 + (\xi^{(1)}_y)^2 + (\xi^{(1)}_z)^2 = 1\). No experimental data are available for comparison.

This shows that the use of Green's function analysis, where there are no assumptions regarding the force fields, greatly simplifies the problem of determination of the molecular constants unambiguously (force constants, mean amplitude of vibration, rotational distortion constants and Coriolis coupling constants). This method requires in the case of molecules for which isotopic data are available the determination of only the mixing parameter matrix which is computed from the observed vibrational frequencies and molecular geometry.


\(^{19}\) T. Oka and Y. Morino, J. molecular Spectroscopy 6, 472 [1961].

