

Green's function application to chemical perturbation studies

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Abstract. Using Green's function techniques, equations for the force field changes resulting from different chemical perturbations in XY_2 bent molecules have been derived and are shown to predict the changes reasonably well in a number of cases. In perturbations involving negligible change of the interbond angle, the equations generate the changes in a straightforward manner.

Keywords. Green's function; perturbation; interbond angle.

1. Introduction

In continuation of our earlier studies (Lacha Goud *et al* 1978, 1979) we present in this paper some results of perturbation studies on symmetric XY_2 bent molecules. The perturbations are associated with X , Y and all atoms *en bloc*, without changing the symmetry of the molecule. The basic theory employed is the same, with appropriate modifications for the C_{2v} symmetry. The resulting equations involve the perturbed, unperturbed frequencies and the change of the force field due to the perturbation expressed in terms of a few easily calculable parameters. The force field changes due to all types of perturbations mentioned above have been calculated. Advantage of our equations is that they predict the changes in the force field directly without a knowledge of the unperturbed force field, wherever the perturbation does not involve a large change in the value of the interbond angle, as in the case of $ClO_2 \rightarrow O_3$.

2. Theory

Following the theory outlined in earlier papers and using appropriate $G(\omega^2)$ and ΔD in equation (1) there we derive the following equation for the a_1 species vibrations for the perturbation under consideration,

$$(\epsilon_x + 1)(\epsilon_y + 1)^2 \omega^4 - \omega^2 (\epsilon_y + 1) \left[(\epsilon_x + 1) m_x + 2(\epsilon_y + 1) m_y \right] \\ \times \frac{\Delta F_{22}}{2m_x m_y} + \frac{(\epsilon_x + 1)}{m_y} \Delta F_{33} - F_{35} + \frac{2m_y}{d_1^2 C^2} \{ (\epsilon_x + 1)(\omega_1^2 + \omega_2^2 c^2) \}$$

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$$\begin{aligned}
& + (\epsilon_y + 1) (\omega_1^2 c^2 + \omega_2^2) \left. + \frac{(\epsilon_x + 1) m_x (\omega_1^2 + \omega_2^2)}{d_1^2} \right] \\
& + \{m_x (\epsilon_x + 1) + 2m_y (\epsilon_y + 1)\} \left[\frac{\omega_1^2 + \omega_2^2 c^2}{2m_x m_y C^2} \Delta F_{22} + \frac{\omega_1^2 c^2 \omega_2^2}{m_y d_1^2 C^2} \right. \\
& \times \Delta \overline{F_{33} - F_{35}} + \frac{2(m_x c^2 d_1^2)^{1/2} (\omega_1^2 - \omega_2^2)}{m_x m_y d_1^2 C^2} \Delta F_{23} + \frac{\Delta F}{2m_x m_y^2} \\
& \left. + \frac{\omega_1^2 \omega_2^2}{d_1^2} \right] = 0. \tag{1}
\end{aligned}$$

From the above expressions the sum and product of the eigenvalues (squares of frequencies) are obtained as given below :

$$\begin{aligned}
\omega_1^2 + \omega_2^2 & = \left\{ \frac{m_x}{(\epsilon_y + 1)} + \frac{2m_y}{(\epsilon_x + 1)} \right\} \frac{\Delta F_{22}}{2m_x m_y} + \frac{\Delta \overline{F_{33} - F_{35}}}{m_y (\epsilon_y + 1)} + \frac{2m_y}{d_1^2 C^2} \\
& \times \left\{ \frac{\omega_1^2 + \omega_2^2 c^2}{(\epsilon_y + 1)} + \frac{\omega_1^2 c^2 + \omega_2^2}{(\epsilon_x + 1)} \right\} + \frac{m_x (\omega_1^2 + \omega_2^2)}{d_1^2 (\epsilon_y + 1)}, \tag{2}
\end{aligned}$$

$$\begin{aligned}
\omega_1^2 \omega_2^2 & = \frac{1}{(\epsilon_y + 1)} \left\{ \frac{m_x}{(\epsilon_y + 1)} + \frac{2m_y}{(\epsilon_x + 1)} \right\} \left[\frac{\omega_1^2 + \omega_2^2 c^2}{2m_x m_y C^2} \Delta F_{22} \right. \\
& + \frac{\omega_1^2 c^2 + \omega_2^2}{m_y d_1^2 C^2} \Delta \overline{F_{33} - F_{35}} + \frac{2(m_x c^2 d_1^2)^{1/2} (\omega_1^2 - \omega_2^2)}{m_x m_y d_1^2 C^2} \Delta F_{23} \\
& \left. + \frac{\Delta F}{2m_x m_y^2} + \frac{\omega_1^2 \omega_2^2}{d_1^2} \right], \tag{3}
\end{aligned}$$

where $\Delta F = \Delta F_{22} \Delta \overline{F_{33} - F_{35}} - 2\Delta F_{23}^2$,

$$\epsilon_x = \frac{m_x^p - m_x}{m_x}, \quad \epsilon_y = \frac{m_y^p - m_y}{m_y}, \quad d_1^2 = m_x + 2m_y$$

and $C^2 = (1 + c^2)$,

c is the mixing parameter and ω^p 's are the frequencies of perturbed molecule and ΔF_{ij} 's are changes in the following cartesian force constants of the XY_2 system

$$\begin{aligned}
F_{22} & = 2C_\alpha^2 (f_\beta + f_{\beta\beta}) + 4S_\alpha^2 f_\alpha - 4S_{2\alpha} f_{\beta\alpha}, \\
\overline{F_{33} - F_{35}} & = S_\alpha^2 (f_\alpha + f_{\beta\beta}) + 2C_\alpha^2 f_\alpha + 2S_{2\alpha} f_{\beta\alpha}, \\
F_{23} & = -C_\alpha S_\alpha (f_\beta + f_{\beta\beta}) + S_{2\alpha} f_\alpha - 2C_{2\alpha} f_{\beta\alpha}.
\end{aligned} \tag{4}$$

As can be seen (2) involves ΔF_{22} and $\Delta \overline{F_{33} - F_{35}}$ only whereas (3) involves ΔF_{23} also in addition. Thus the force field changes are expressed in terms of just three parameters which can be evaluated without much difficulty. The above equations

refer to the most general perturbation involving all atoms of the XY_2 system en bloc. The equations for the perturbation involving X atom only can be deduced from the above by taking ϵ_y to be zero and for perturbations involving Y atoms only by taking ϵ_x to be zero. The equations for electronic perturbation can be obtained by taking ϵ_e and ϵ_v to be zero, assuming a bent structure in the excited state.

The three parameters ΔF_{22} , $\Delta F_{33} - F_{35}$ and ΔF_{23} can be evaluated as follows. As such these are changes in the cartesian force constants and can be expressed in terms of changes in valence force constants as mentioned above. Generally among the valence force constants f_d changes comparatively by a larger amount than the other constants. A reasonable value for Δf_d due to perturbation can be found from the vibration model suggested by Borkman (1969) for polyatomic molecules, taking initially the other Δf 's to be zero. We start with approximate values of ΔF 's, and vary them in a systematic way so that (2) and (3) are satisfied. This procedure leads to a number of sets of ΔF 's that simultaneously satisfy (2) and (3), revealing the multiplicity character of the cartesian force constants. To decide unambiguously the correct set of ΔF 's, ΔF_{22} and $\Delta F_{33} - F_{35}$ are plotted as a function of ΔF_{23} , since for a given set of ΔF_{22} and $\Delta F_{33} - F_{35}$ we fix the value of ΔF_{23} from (2) and (3). The plots for $\text{ClO}_2 \rightarrow \text{O}_3$ are shown in figure 1 and they intersect corresponding to ΔF_{23} (0.585). The ΔF values used in the plot in the region of intersection are given in table 1. This predicts corresponding values of ΔF_{22} (1.236) and $\Delta F_{33} - F_{35}$ (1.449) and it is most significant that only for this set of ΔF 's, the isotopic frequencies of the perturbed molecules ($^{18}\text{O}_3$, $^{18}\text{O}^{16}\text{O}^{18}\text{O}$ and $^{16}\text{O}^{18}\text{O}^{16}\text{O}$) are reproduced while other sets fail to do so. Thus we conclude the change of force field corresponding to the ΔF 's associated with the intersection point to be most meaningful and the same procedure was adopted for all perturbations. Having thus determined the correct set of ΔF 's, the actual F 's of the perturbed molecule can be found from those of the unperturbed system. This gives immediately the changes in $(f_d + f_{dd})$, f_a and f_{da} . Table 2 presents the perturbed valence f 's based on these changes along with the literature values. Using relations (2) and (3) and the set of ΔF 's obtained from the plots the frequencies of the isotopic species of the perturbed molecules can be calculated and table 3 presents the results in some cases.

Equations (2) and (3) possess another clear advantage in the case of perturbations involving very small changes in the interbond angle values. A look at the expressions for ΔF 's shows that in such a case, S_a^2 , C_a^2 and $C_a S_a$ remain almost

Table 1. ΔF values (m. dyn./Å) used to draw the graph for $\text{ClO}_2 \rightarrow \text{O}_3$ perturbation.

| ΔF_{23} | ΔF_{22} | ΔF_{35} |
|-----------------|-----------------|-----------------|
| 0.44 | 0.80 | 0.10 |
| 0.49 | 1.00 | 1.80 |
| 0.57 | 1.20 | 1.50 |
| 0.66 | 1.40 | 1.20 |
| 0.78 | 1.60 | 0.90 |

Table 2. Changes of cartesian force constants and final values of force constants of perturbed molecule in m. dyn./Å

| Perturbation | ΔF_{22} | $\Delta (F_{33} - F_{33})$ | ΔF_{33} | $f_d + f_{ed}$ | f_a | f_{aa} | Literature values | | | Reference |
|---|-----------------|----------------------------|-----------------|----------------|-------|----------|-------------------|-------|----------|-----------|
| | | | | | | | $f_d + f_{ed}$ | f_a | f_{aa} | |
| $\text{ClO}_2 \rightarrow \text{NO}_2$ | 0.679 | 7.182 | -0.774 | 13.431 | 1.120 | 0.579 | 13.346 | 1.110 | 0.543 | 1 |
| $\text{ClO}_2 \rightarrow \text{O}_2$ | 1.236 | 1.449 | 0.585 | 7.546 | 1.335 | 0.343 | 7.590 | 1.310 | 0.486 | 2 |
| $\text{ClO}_2 \rightarrow \text{SO}_2$ | 1.853 | 2.765 | -1.182 | 10.174 | 0.834 | 0.076 | 10.341 | 0.816 | 0.167 | 1 |
| $\text{ClO}_2 \rightarrow \text{NO}_2^-$ | 3.059 | 2.856 | 0.119 | 9.144 | 1.695 | 0.410 | 9.160 | 1.670 | 0.394 | 3, 7 |
| $\text{H}_2\text{O} \rightarrow \text{H}_2\text{S}$ | 2.376 | 3.597 | 1.498 | 4.190 | 0.359 | 0.013 | 4.248 | 0.448 | 0.219 | 1 |
| $\text{H}_2\text{O} \rightarrow \text{OF}_2$ | -2.662 | -1.599 | 1.325 | 5.254 | 0.695 | 0.355 | 4.955 | 0.738 | 0.152 | 1 |
| $\text{H}_2\text{S} \rightarrow \text{SCl}_2$ | -2.596 | 0.301 | 0.408 | 3.609 | 0.619 | 0.591 | .. | .. | .. | 8 |
| $\text{NO}_2^- \rightarrow \text{NF}_2$ | -1.881 | -3.995 | 0.911 | 5.234 | 1.165 | 0.042 | 5.318 | 1.103 | 0.335 | 4 |
| $\text{NO}_2 \rightarrow \text{H}_2\text{O}$ | 1.406 | -6.449 | -0.001 | 8.478 | 0.718 | 0.066 | 8.353 | 0.761 | 0.229 | 1 |
| $\text{NO}_2^- \rightarrow \text{SF}_2$ | -2.293 | -5.875 | 0.584 | 4.281 | 0.548 | 0.331 | 4.030 | 0.481 | 0.079 | 5 |
| $\text{H}_2\text{O} \rightarrow \text{ClO}_2$ | -2.837 | 0.187 | 0.856 | 7.248 | 0.673 | 0.313 | 6.939 | 0.635 | 0.054 | 1 |
| $\text{NO}_2^- \rightarrow \text{CF}_2$ | -1.159 | -1.574 | 0.168 | 7.608 | 1.369 | 0.427 | 7.929 | 1.336 | 0.771 | 6 |

1. Speirs and Spirko (1975); 2. Barbe *et al* (1974); 3. Kato and Rolfe (1967); 4. Brown *et al* (1974); 5. Kirchoff *et al* (1973);
6. Kirchoff *et al* (1973); 7. Ramaswamy and Shanmugam (1972); 8. Davis and Gerry (1977).

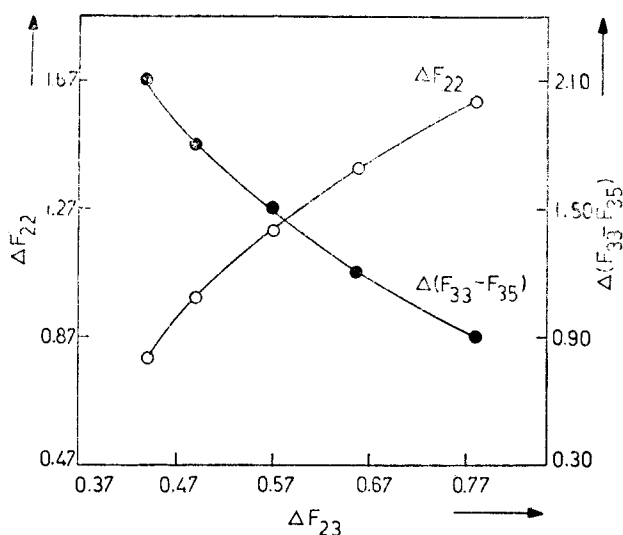


Figure 1. Plot of Δf 's for the perturbation $\text{ClO}_2 \rightarrow \text{O}_3$.

Table 3. Isotopic frequencies of perturbed molecules in cm^{-1} .

| Perturbation | ω_1 | ω_2 | Literature values | | Reference |
|--|------------|------------|-------------------|------------|-----------|
| | | | ω_1 | ω_2 | |
| $\text{ClO}_2 \rightarrow {}^{18}\text{O}_2$ | 1070.39 | 674.38 | 1070.00 | 674.75 | 1 |
| $\text{ClO}_2 \rightarrow {}^{18}\text{O}^{16}\text{O}^{18}\text{O}$ | 1102.70 | 681.35 | 1100.90 | 682.77 | 1 |
| $\text{ClO}_2 \rightarrow {}^{16}\text{O}^{18}\text{O}^{16}\text{O}$ | 1104.85 | 707.26 | 1105.75 | 707.07 | 1 |
| $\text{ClO}_2 \rightarrow {}^{16}\text{NO}_2$ | 1344.71 | 745.08 | 1344.40 | 745.30 | 2 |
| $\text{H}_2\text{O} \rightarrow \text{D}_2\text{S}$ | 1947.89 | 871.79 | 1946.00 | 872.00 | 3 |
| $\text{NO}_2 \rightarrow \text{D}_2\text{O}$ | 2768.46 | 1204.34 | 2763.90 | 1206.10 | 2 |
| $\text{ClO}_2 \rightarrow {}^{16}\text{NO}_2^-$ | 1291.97 | 794.37 | 1294.20 | 793.00 | 4 |
| $\text{ClO}_2 \rightarrow {}^{16}\text{N}^{18}\text{O}_2^-$ | 1257.87 | 755.17 | 1256.10 | 756.60 | 4 |
| $\text{ClO}_2 \rightarrow {}^{14}\text{N}^{16}\text{O}_2^-$ | 1282.91 | 758.81 | 1279.23 | 760.90 | 4 |
| $\text{H}_2\text{O} \rightarrow {}^{37}\text{ClO}_2$ | 959.27 | 448.19 | 957.60 | 448.60 | 2 |

1. Barbe *et al* (1974)
2. Speirs and Spirko (1975)

3. De Wames and Wolfram (1964)
4. Ramaswamy and Shanmugam (1972)

the same for the two systems, the changes $\Delta(f_a + f_{aa})$, Δf_a and Δf_{aa} being directly evaluated without the knowledge of the parent force field. Table 4 presents a few examples.

3. Conclusion

The equations derived by us are useful in calculating the force field changes accompanying different types of perturbations in XY_2 bent molecules. The calcu-

Table 4. Change of valence force constants in m dyn./Å.

| Perturbation | $\Delta (f_a + f_{aa})$ | Δf_a | Δf_{aa} | Literature values | | | |
|---|-------------------------|--------------|-----------------|-------------------------|--------------|-----------------|-------|
| | | | | $\Delta (f_a + f_{aa})$ | Δf_a | Δf_{aa} | |
| ClO ₂ → O ₂ (117° 35') | (116·8°) | 0·861 | 0·625 | 0·543 | 0·826 | 0·665 | 0·347 |
| ClO ₂ → SO ₂ (117° 35') | (119° 20') | 3·327 | 0·183 | 0·111 | 3·402 | 0·181 | 0·112 |
| ClO ₂ → NO ₂ ⁻ (117° 35') | (117°) | 2·377 | 1·005 | 0·324 | 2·221 | 1·035 | 0·339 |

lated values agree well with those published earlier. The changes are computed without much difficulty and give information of chemical importance. Another significant application of our equations will be the prediction of unknown spectra by a reasonable guess of the change of force field from a parent system.

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