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Green's function application to chemical perturbation studies

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Abstract. Green's function technique has been applied to the calculation of force field changes when all the atoms in a linear XY_2 symmetric molecule undergo perturbation. The formulae for the valence force constant changes have been derived and verified in about 13 different perturbations.

Keywords. Green's function; chemical perturbation; force field changes.

1. Introduction

In an earlier paper the present authors (Lacha Goud *et al* 1978) showed the applicability of Green's function technique to calculate the force field changes resulting from a chemical perturbation in linear symmetric triatomic molecules. The perturbation considered involved only the central or the end atoms. Now the results for perturbations involving all the atoms are presented.

2. Theory

The basic theory and other details are the same as in Lacha Goud *et al* (1978). The equations involving the force constant changes associated with the perturbations $XY_2 \rightarrow ZT_2$ are given below

$$\triangle (f_d - f_{dd}) = \left\{ \epsilon_y \omega^2 + \frac{1}{(G_{44} - G_{47})} \right\} m_y, \tag{1}$$

$$\triangle (f_{dd} + f_{dd}) \left\{ \left(\frac{\epsilon_x}{m_y} + \frac{2\epsilon_y}{m_y} \right) [G_{11} (G_{44} + G_{47}) - 2G_{14}^2] + \frac{2G_{11}}{m_x} \right.$$

$$\left. + \frac{(G_{44} + G_{47})}{m_y} - \frac{4G_{14}}{\sqrt{m_x m_y}} \right\} = \{ \epsilon_x \epsilon_y \omega^4 [G_{11} + (G_{44} + G_{47}) - 2G_{14}^2]$$

$$+ \epsilon_x \omega^2 G_{11} + \epsilon_y \omega^2 (G_{44} + G_{47}) + 1 \} \tag{2}$$

$$\Delta f_\alpha \left\{\left(\frac{\epsilon_x}{m_y} + \frac{2\epsilon_y}{m_x}\right)\omega^2 [G_{22}(G_{55} + G_{58}) - 2G_{25}^2] + \frac{2G_{22}}{m_x} + \frac{(G_{55} + G_{58})}{m_y} - \frac{4G_{25}}{\sqrt{m_x m_y}}\right\} = \{\epsilon_x \epsilon_y \omega^4 [G_{22}(G_{55} + G_{58}) - 2G_{25}^2] + \epsilon_x \omega^2 G_{22} + \epsilon_y \omega^2 (G_{55} + G_{58}) + 1\}. \quad (3)$$

where f_d, f_{dd} and f_α refer to the valence force constants, ω^2, to the perturbed frequency, the various G_{ij}s are the Green's function elements given in our earlier work.

$$\epsilon_x = \frac{m_z - m_x}{m_x} \quad \text{and} \quad \epsilon_y = \frac{m_T - m_y}{m_y}.$$

The equations for the central and end atoms perturbations derived in our earlier work can be obtained from the above more general equations by equating ϵ_y and ϵ_x to zero respectively.

Tables 1 and 2 presents the results obtained from the above equations along with experimental values.

Table 1. Vibrational frequencies of linear molecules.

Molecule	Frequencies*		
	w_1	w_2	w_3
$^{12}CO_2$	1354·91 (*R*)	673·0 (*R*)	2396·49 (*R*)
$^{11}BO_2$	1070·00 (*S*)	464·0 (*S*)	1322·00 (*S*)
CS_2	657·98 (*H*)	396·7 (*H*)	1532·50 (*H*)
C_3	1230·00 (*H*)	63·1 (*H*)	2040·00 (*H*)
CN_2	1197·00 (*H*)	423·0 (*H*)	1475·00 (*H*)
$HgCl_2$	363·00 (*H*)(*M*)	75·00 (*H*)(*M*)	413·00 (*H*) (*M*)
$HgBr_2$	221·00 (*G*)	53·0 (*G*)	295·00 (*G*)

* Frequencies are given in the units of cm^{-1}.

(*R*) Robert *et al* (1962) ; (*S*) Somer *et al* (1963)
(*H*) Herzberg (1966) ; (*M*) Milligan and Jaco x (1966)
(*G*) Gedanken *et al* (1969)

3. Conclusions

The results convincingly demonstrate the absolute success of the application of Green's function technique to the study of all possible perturbations in linear triatomic molecules.

Table 2. XY_2 (linear) → ZT_2 (linear) perturbation.

Perturbation	Calculated from eqs. (1—3)			Calculated directly		
	$\triangle f_d$	$\triangle f_{dd}$	$\triangle f_\alpha$	$\triangle f_d$	$\triangle f_{dd}$	$\triangle f_\alpha$
$CN_2 \rightarrow BO_2$	−1·131	0·095	0·035	−1·131	0·095	0·035
$CN_2 \rightarrow HgBr_2$	− 6·324	−3·216	−0·185	− 6·324	−3·216	−0·185
$CN_2 \rightarrow HgCl_2$	− 5·922	−3·165	−0·178	− 5·922	−3·165	−0·178
$CO_2 \rightarrow HgCl_2$	−13·360	−1·212	−0·540	−13·361	−1·212	−0·540
$CO_2 \rightarrow HgBr_2$	−13·764	−1·262	−0·546	−13·764	−1·262	−0·546
$BO_2 \rightarrow HgBr_2$	− 5·193	−3·311	−2·197	− 5·193	−3·311	−2·197
$BO_2 \rightarrow HgCl_2$	− 4·791	−3·261	−0·213	− 4·791	−3·261	−0·213
$C_3 \rightarrow HgBr_2$	− 7·973	−0·435	0·032	− 7·973	−0·435	0·032
$C_3 \rightarrow HgCl_2$	− 7·570	−0·385	0·039	− 7·570	−0·385	0·039
$C_3 \rightarrow BO_2$	− 2·779	2·876	0·252	− 2·779	2·876	0·252
$CS_2 \rightarrow BO_2$	− 2·728	0·109	0·022	− 2·728	0·109	0·022
$CS_2 \rightarrow HgCl_2$	− 4·900	−0·533	−0·191	− 4·900	−0·533	−0·191
$CS_2 \rightarrow HgBr_2$	− 5·302	−0·583	−0·198	− 5·302	−0·583	−0·198

Change in the force constants are given in the units of *m*, *dy*, /A.

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