

Determination of the Force Constants of Non-linear XY_2 Molecules in the Gas-Phase by the GF Matrix Method

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The force constants of the internal coordinates of non-linear XY_2 molecules in the gas-phase were calculated by using the GF matrix method. The matrix solution was carried out by means a computer program built relative to the Newton-Raphson method and the calculations were listed in a table. The force constants of some molecules in the liquid- and solid- phase were also found and compared with these ones, and it was seen that the force constants for more condensed phase are lower as in an agreement with having its lower frequency.

Key words: GF Matrix Method; Force Constants;
 XY_2 Molecules.

1. Introduction

The theory of normal vibrations of molecules by the GF matrix method has been given by many authors [1–4], and some authors have calculated the force constants of octahedral MX_6 molecules by this method [5–6].

In the present work, the force constants of non-linear XY_2 molecules in the gas-phase were calculated by the GF matrix method. The matrix solutions were obtained by means a computer program based on the Newton-Raphson method, and the force constants of some molecules in the liquid and solid-phase were also found and compared with those in the gas-phase.

2. Theory and Calculation

Non-linear XY_2 molecules have three fundamental modes of vibration. These are the symmetric (ν_1), bending (ν_2), and antisymmetric (ν_3) stretch mode. All of them are both infrared (IR) and Raman (R) ac-

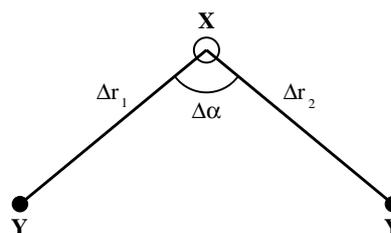


Fig. 1. Structure of a non-linear XY_2 molecule ($\angle YXY = \Delta\alpha$).

tive. These molecules have the symmetry C_{2v} , and the modes of the symmetric stretch and bending are in the A_1 species, and the antisymmetric stretch is in the B_2 species [7].

Bent triatomic molecules have been described in terms of four force constants in the internal coordinates. f_r is the bond stretch force constant, f_{rr} the interaction force constant between two Δr , $f_{r\alpha}$ the interaction force constant between Δr and $\Delta\alpha$, and f_α the bending force constant. The changes of Δr_1 , Δr_2 , and $\Delta\alpha$ can be seen in Figure 1.

The elements of the G and F matrix for the symmetric stretch and bending modes in species A_1 are

$$G_{11} = \mu_y + \mu_x(1 + \cos \alpha), \quad (1a)$$

$$G_{12} = -\frac{\sqrt{2}r}{\mu_x} \sin \alpha = -\frac{\sqrt{2}}{r} \mu_x \sin \alpha, \quad (1b)$$

$$G_{22} = \frac{2}{r^2} [\mu_y + \mu_x(1 - \cos \alpha)], \quad (1c)$$

$$F_{11} = f_r + f_{rr}, \quad (2a)$$

$$F_{12} = (\sqrt{2})r f_{r\alpha}, \quad (2b)$$

$$F_{22} = r^2 f_\alpha, \quad (2c)$$

and for the antisymmetric stretch mode in species B_2 are

$$G = \mu_y + \mu_x(1 - \cos \alpha), \quad (3a)$$

$$F = f_r - f_{rr} \quad (3b)$$

[3–4], where μ_x and μ_y are the reciprocals of the masses of the X and Y atoms. The secular equation of the GF matrix is given by

$$|GF - E\lambda| = 0, \quad (4)$$

Table 1. Bond angles [9], bond lengths [9], and force constants of non-linear XY_2 molecules in the gas-phase. Force constants are in units of $\text{mdyn}/\text{\AA}$.

Molecule	α ($^\circ$)	r (\AA)	f_r	f_{rr}	$f_{r\alpha}$	f_α
NO ₂	134.10	1.1930	11.518410	3.118664	2.040223	1.471169
SO ₂	119.33	1.4308	10.459770	0.432776	1.356724	1.063155
H ₂ O	104.51	0.9575	7.686604	-0.078458	0.218371	0.712676
ClO ₂	117.38	1.4700	7.174260	0.162343	0.884287	0.775637
SeO ₂	113.83	1.6076	6.996035	0.136261	0.511118	0.660133
O ₃	117.47	1.2716	6.780723	2.624146	1.691529	1.549071
NF ₂	103.18	1.3528	6.505670	2.780092	2.297398	1.826044
NH ₂	103.30	1.0240	5.899524	-0.044664	0.191875	0.623822
SiF ₂	100.80	1.5900	5.483900	0.786124	1.152872	0.793329
SF ₂	98.20	1.5921	5.221514	0.810521	1.050825	0.791391
Cl ₂ O	110.89	1.6959	4.371037	1.918162	1.623806	1.066839
GeF ₂	97.17	1.7321	4.177064	0.376420	0.453166	0.389228
H ₂ S	92.12	1.3356	3.955169	-0.010314	0.063053	0.404406
SCl ₂	103.00	2.0060	3.379609	0.840660	0.963780	0.632082
GeCl ₂	100.30	2.1830	2.252106	0.398178	0.401552	0.289220

where E is the diagonal-unit matrix and the λ 's are eigenvalues of the matrix. The values of λ_i depend on the vibration frequencies by

$$\lambda_i = 4\pi^2 c^2 \bar{\nu}_i^2. \quad (5)$$

After forming the GF matrix in (4), the solution of the matrix was carried out using a computer program basing on the Newton-Raphson method [8], taking the vibration frequencies, the bonding distances, and the bond angles into account. For H₂O we calculated the force constants as $f_r = 8.422960$, $f_{rr} = -0.097888$, $f_{r\alpha} = 0.236981$, and $f_\alpha = 0.766369$. These values are very close to the values given in [3] for H₂O. After

Table 2. Force constants in units of $\text{mdyn}/\text{\AA}$, of non-linear XY_2 molecules in the liquid- and solid-phase.

Molecule	f_r	f_{rr}	$f_{r\alpha}$	f_α
SO ₂ (solid)	10.033900	0.784603	1.347134	1.069155
H ₂ O (liquid)	6.213603	-0.318788	0.170778	0.733049
H ₂ O (solid)	6.141674	0.434708	0.187366	0.732937
Cl ₂ O (liquid)	4.239737	1.892958	1.582007	1.044538
H ₂ S (solid)	3.696929	-0.02476	0.059030	0.396166
SCl ₂ (liquid)	3.292140	0.753145	0.923722	0.613745

this agreement, we found the force constants for non-linear XY_2 molecules in the gas-phase. The results of these calculations are given in Table 1. These values are suitable in the error limits, also depend on the values taken from [9], and this suitability can be confirmed by comparing the values of f_r and f_α of some molecules with the ones obtained by neglecting the interaction constants in [4] for the same molecule.

3. Discussion

The calculated force constants of some molecules in the liquid- and solid-phase, using their vibration frequencies taken from [3], are given in Table 2. These values are lower than those of the same molecules in the gas-phase, see Table 1. In general, the more condensed is the phase, the lower is the frequency: $\nu_{\text{gas}} > \nu_{\text{liquid}} > \nu_{\text{solution}} > \nu_{\text{solid}}$ [10]. Because of this, the more condensed phases have the lower force constants.

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