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FORCE FIELD STUDY OF SOME XY_2 TYPE MOLECULES

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The most probable force fields of some of the XY_2 type molecules like SO_2, NO_2, SiF_2 and CF_2 have been fixed using the method of Redington and using the observed molecular parameters such as the Coriolis coupling constant, mean amplitudes of vibration, rotation distortion constants and isotopic shifts.

1. Introduction

It is well known that the unambiguous determination of force fields is possible only with the help of some additional data such as the Coriolis coupling constants [1], mean amplitudes of vibration [2], rotation distortion constants [3], and isotopic shifts [4]. Attempts have been made to obtain mathematically feasible and physically meaningful set of force constants using several methods [1–6]. A critical survey of all these methods in uniquely fixing the force field was made earlier for sulfur trioxide [2]. The present paper is an extension of the above method to fix the unique force fields of some of the XY_2 bent type molecules namely SO_2, NO_2, SiF_2 and CF_2.

2. Spectral data

The necessary vibrational frequencies and molecular parameters used in the present calculations are summarised in Table I along with the references [7–19] from which they are taken. The symmetry coordinates used here are essentially the same as those reported by Cleveland and Meister [20].

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TABLE I

The observed vibrational frequencies (cm^{-1}), bond parameters, Coriolis coupling constants, rotation distortion constants (MHz) and mean amplitudes of vibration (Å) of some XY_2 type molecules

Molecule	Vibrational frequencies			Bond parameters		Coriolis coupling constant	Rotation distortion contants in MHz.		
	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(B_2)$	R_{x-y}	$X\hat{Y}X$	ζ_{13}	τ_{XXXX}	τ_{YYYY}	τ_{XXYY}
$^{32}S\,^{16}O_2$	1156 [7]	522	1366	1.435 [11]	119°21′	0.3066 [14]	−9.9216 [17]	−0.0399	0.4314
$^{34}S\,^{16}O_2$	1147 [7]	518	1349						
$^{14}N\,^{16}O_2$	1357.8 [8]	756.8	1665.5	1.197 [12]	134°15′	—	−299.4 [18]	−0.0414	1.8430
$^{15}N\,^{16}O_2$	1342.5 [8]	747.1	1628						
$^{28}Si\,^{19}F_2$	843 [9]	343	855	1.5946 [11]	100°53′	0.4285 [15]	−1.9807 [19]	−0.0715	0.2613
$^{12}C\,^{19}F_2$	1222 [10]	668	1102	1.3035 [13]	104°47′	—	−11.2778 [13]	−0.0691	—
$^{13}C\,^{19}F_2$	1191 [10]	668	1073						

Note: The electron diffraction values of mean amplitudes of vibration of both bonded and nonbonded atoms are $\sigma_{x-y} = 0.041$ and $\sigma_{y\ldots y} = 0.053$, Ref. [16].

3. *Results and discussion*

The Redington method [5] was successfully applied to the SO_2, NO_2 and SiF_2. "F_{stp}" solutions of 47°15′, 53°15′ and 27°45′ were obtained by this method. But for CF_2, Redington's method could not yield reliable force field. The observed Coriolis coupling constants of SO_2 and SiF_2 were used as additional data and angles of 48°30′ and 28°30′ were determined which reproduced the experimentally observed molecular constants.

Electron diffraction values of the mean amplitudes of vibration were available only for the SO_2 molecule. The use of mean amplitude of vibration of non bonded atoms yields a rather low value for ϕ, and as a result does not reproduce any of the molecular constants. The mean amplitude of vibration of bonded atoms gives only an imaginary solution.

The rotation distortion constants like τ_{XXXX}, τ_{YYYY} and τ_{XXYY} give comparable force fields for NO_2 and SiF_2. In the case of SO_2 the τ_{XXXX} and τ_{YYYY} parameters alone yielded ϕvalues which coincide well with the values determined by other methods. But the τ_{XXYY} experimental value is higher than those calculated for various angle parameters varying from 0° to 180° and hence it could not be used to fix the force field. For CF_2, the τ_{XXXX} and τ_{YYYY} parameters yielded a very reliable set of force constants and other molecular constants.

The isotopic shifts used for the NO_2 and CF_2 furnished force fields comparable with the force fields obtained through the other methods. But for SO_2 since the angle obtained was very low, the molecular constants determined for this parameter were considerably lower than the others.

The various ϕ values obtained through different methods are given in Table II.

TABLE II

The ϕ values obtained through different methods

Method	Parameter ϕ			
	SO_2	NO_2	SiF_2	CF_2
Redington	47°15′	53°15′	27°45′	15°46′
Using ζ	48°30′	—	28°30′	—
Using σ_{YY}	42°10′	—	—	—
Using τ_{XXXX}	51°	53°	29°	27°32′
Using τ_{YYYY}	47°15′	53°15′	29°30′	25°51′
Using τ_{XXYY}	—	53°36′	27°45′	—
Using isotopic shifts	43°41′	51°16′	—	25°15′

Most probable ϕ: The most probable ϕ can be stated as the average of all the ϕ's obtained by different approaches which reproduce all molecular constants within reasonable accuracy. The various molecular constants obtained for the most probable ϕ of SO_2, NO_2, SiF_2 and CF_2 are given in Table III.

TABLE III

Force constants (mdyn/Å), Coriolis coupling constants, mean amplitudes of vibration (Å) and rotation distortion constants (MHz) obtained for the most probable ϕ of some XY_2 type molecules

Molecular constants	Molecule			
	SO_2	NO_2	SiF_2	NF_2
Most probable ϕ	47°40′	52°53′	28°30′	26°13′
F_{11}	10.0793[a] (10.03) [21] (10.05) [22]	13.1265 (12.963) [8] (13 185) [18]	5.1636 (5.329) [15] (5.34) [25]	7.656 (7.756) [13] (7.450) [26]
F_{22}	0.8086 (0.7933) [21] (0.7930) [22]	1.1181 (1.125) [8] (1.109) [18]	0.4356 (0.44) [15] (0.439) [25]	1.383 (1.373) [13] (1.400) [26]
F_{12}	0.2513 (0.267) [21] (0.280) [22]	0.6281 (0.055) [8] (0.0679) [18]	0.1634 (0.174) [15] (0.195) [25]	0.7413 (0.7713) [13] (0.6800) [26]
ζ_{13}	0.3224	0.4755	0.4285	0.7182
σ_{X-Y}	0.0351	0.0381	0.0426	0.0450
$\sigma_{Y...Y}$	0.0507	0.0431	0.0745	0.0505
τ_{XXXX}	−9.3029	−299.035	−1.9492	−10.9343
τ_{YYYY}	−0.0393	−0.0417	−0.0729	−0.0689
τ_{XXYY}	0.3979	1.8488	0.2637	—

[a] This number of significant figures is retained to secure internal consistency in the calculations. mdyn/Å $= 10^2$ N/m. The values in parenthesis are taken from their respective references.

For the SO_2 molecule, as in Redington's method, we observed the Coriolis coupling constant and τ_{XXXX} and τ_{YYYY} parameters furnished comparable force fields. An average value of the three was taken as the most probable ϕ.

The force constants calculated for the most probable ϕ of 47°40′ compare extremely well with those reported by Kivelson [21], Polo and Wilson [22] and Morino et al. [14]. The mean amplitudes of vibration of both bonded and non bonded atoms determined for the most probable ϕ coincide well with those spectroscopically calculated by Clark and Beagley [16], even though their experimental values are higher than these values. But the most probable ϕ could not reproduce the Coriolis coupling constant accurately. This may probably be due to the fact that ζ is a highly sensitive parameter in fixing the force fields. The rotational distortion constants are in good agreement with the reported values.

For the NO_2, the most probable ϕ was determined as the average of the angle parameters obtained through Redington's method, using observed rotation distortion constants and isotopic shifts. The force field furnished by this angle of 52°53′ can be assumed to be unique as it reproduces the diagonal force constants reported by Arkawa et al. [8], Bird et al. [18], the observed rotation distortion constants and Coriolis coupling constants calculated by Cyvin [23], namely $\xi_{13}^2 = 0.249$ and Oka and Morino [24] namely $\xi_{13}^2 = 0.241$. The off diagonal force constants differ considerably from the reported values.

In the case of SiF_2, the force constants reported by Khanna et al. [15] and Shoji and others [25] were accurately reproduced by the most probable force field in addition to the observed Coriolis coupling constants and rotation distortion constants.

The Redington method could not yield a reliable force field for the CF_2 molecule. The experimental isotopic shifts and rotation distortion parameters were utilized in uniquely fixing the force field. This most probable force field yields a good set of force constants in agreement with the values of Milligan et al. [26] and Kirchoff et al. [13].

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REFERENCES

[1] T. R. Ananthakrishnan, G. Aruldhas, *J. Mol. Struct.* **13**, 1636 (1972).
[2] K. Ramaswamy, R. Srinivasan, *Acta Phys. Pol.* **A49**, 763 (1976).
[3] L. H. Jones, R. R. Rayan, L. B. Asprey, *J. Chem. Phys.* **49**, 581 (1968).
[4] B. Jordonov, B. Nickolova, *J. Mol. Struct.* **13**, 21 (1972); **15**, 7 (1973); **15**, 19 (1973).
[5] R. L. Redington, A. L. Khidir Aljibury, *J. Mol. Spectrosc.* **37**, 494 (1971).
[6] E. B. Wilson Jr., J. C. Decius, P. C. Cross, *Molecular Vibrations*, McGraw Hill, New York 1955.
[7] M. Allawena, R. Rysnik, D. White, V. Calder, D. E. Mann, *J. Chem. Phys.* **50**, 3399 (1969).
[8] E. T. Arkawa, A. H. Nielson, *J. Mol. Spectrosc.* **2**, 413 (1958).
[9] D. E. Milligan, M. E. Jacox, *J. Chem. Phys.* **49**, 4269 (1968).
[10] D. E. Milligan, D. E. Mann, M. E. Jacox, R. A. Mitch, *J. Chem. Phys.* **41**, 1199 (1964).
[11] W. H. Kirchoff, *J. Mol. Spectrosc.* **41**, 333 (1972).
[12] G. R. Bird, R. Kato, J. Rolfe, *J. Chem. Phys.* **25**, 1040 (1968); **47**, 1901 (1967).
[13] W. H. Kirchoff, D. R. Lide Jr., F. X. Powell, *J. Mol. Spectrosc.* **47**, 491 (1973).

[14] Y. Morino, Y. Kikuchi, S. Saito, E. Hirota, *J. Mol. Spectrosc.* **13**, 95 (1964).
[15] V. M. Khanna, R. Hauge, R. F. Curl Jr., J. L. Margrave, *J. Chem. Phys.* **47**, 5031 (1967).
[16] A. H. Clark, B. Beagley, *Trans. Faraday Soc.* **67**, part 8 (1971).
[17] H. A. Gebbie, W. B. Stone, E. K. Gora, S. A. Clough, F. X. Kneizys, *J. Mol. Spectrosc.* **19**, 7 (1966).
[18] G. R. Bird, J. C. Baird, A. W. Jache, J. A. Hodgeson, R. F. Curl Jr., A. C. Kunkee, J. W. Bransford, J-Anderson Rastrup, J. Rosenthal, *J. Chem. Phys.* **40**, 3378 (1966).
[19] V. M. Rao, R. R. Curl Jr., *J. Chem. Phys.* **45**, 2032 (1966).
[20] A. G. Meister, F. F. Cleveland, *Am. J. Phys.* **41**, 13 (1946).
[21] D. Kivelson, *J. Chem. Phys.* **22**, 904 (1954).
[22] S. R. Polo, M. K. Wilson, *J. Chem. Phys.* **22**, 900 (1954).
[23] S. J. Cyvin, *J. Mol. Spectrosc.* **11**, 195 (1963).
[24] T. Oka, Y. Morino, *J. Mol. Spectrosc.* **8**. 9 (1962).
[25] H. Shoji, T. Tawaka, E. Hirota, *J. Mol. Spectrosc.* **47**, 268 (1973).
[26] D. E. Milligan, M. E. Jacox, *J. Chem. Phys.* **48**, 2265 (1968).