CORIOLIS COUPLING CONSTANTS AND CENTRIFUGAL DISTORTION CONSTANTS OF SOME XY_2 BENT SYMMETRICAL MOLECULES

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(Received April 18, 1979; revised version received June 7, 1979)

With the help of kinetic constants, the molecular constants viz., Coriolis coupling constants and the centrifugal distortion constants of sixteen bent symmetrical XY_2 molecules have been evaluated. The values of these constants are in the expected range and they are also in good agreement with the observed values, indicating the significance of kinetic constants method.

1. Introduction

The attention of molecular spectroscopists has been recently drawn to the concept of kinetic constants. The utilisation of kinetic constants in evaluating the molecular constants cannot be overemphasised. The kinetic constants not only bring the reasonable and acceptable results with respect to the force constants but also with respect to other molecular constants [1–7]. Thus the validity of the force field is easily tested by evaluating the other molecular constants namely, the mean amplitudes of vibration, Coriolis coupling constants and the centrifugal distortion constants. Recently, the kinetic constants, the force constants and the mean amplitudes of vibration of XY_2 bent symmetrical molecules have been discussed in detail by Thirugnanasambandam and Mohan [1]. The purpose of the present paper is to calculate the Coriolis coupling constants and the centrifugal distortion constants of some XY_2 bent symmetrical molecules on the basis of kinetic constants.

2. Coriolis coupling constants

The Coriolis coupling constants which may be determined experimentally can however be evaluated from a reliable set of force constants and the values can be used for a detailed interpretation of vibrational spectra. The Coriolis coupling constants ζ^{α} ($\alpha = x, y, z$) in the bent symmetrical XY_2 type of molecules arise from the coupling $A_1 \times B_2$. The Coriolis

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TABLE I

Coriolis coupling constants

Molecule	$-\zeta^c_{13}$	ζ^c_{23}	$(\zeta^c_{13})^2$	Reference
H_2O	0.0574	0.9984	0.0033	PW
	—	1.0000	0.000 ± 0.003	[10]
D_2O	0.1084	0.9941	0.0118	PW
	0.06325	0.99800	0.004 ± 0.003	[10]
T_2O	0.1540	0.9881	0.0237	PW
H_2S	0.0304	0.9995	0.0009	PW
	0.02646	0.9997	0.0007	[11]
D_2S	0.0591	0.9983	0.0035	PW
	0.06245	0.99805	0.0039	[11]
H_2Se	0.0126	0.9999	0.0002	PW
	—	1.0000	0.000 ± 0.008	[10]
D_2Se	0.0249	0.9997	0.0006	PW
	0.03163	0.9995	0.001 ± 0.007	[10]
	0.03317	0.9995	0.0011	[12]
$^{14}NO_2$	0.4114	0.9115	0.1692	PW
	0.49092	0.87121	0.241 ± 0.009	[10]
$^{15}NO_2$	0.3962	0.9181	0.1570	PW
SO_2	0.2936	0.9559	0.0862	PW
	0.31781	0.94816	0.101 ± 0.012	[10]
ClO_2	0.2763	0.9611	0.0764	PW
	0.28282	0.95917	0.08 ± 0.17	[10]
O_3	0.4581	0.8889	0.2099	PW
SeO_2	0.1669	0.9860	0.0279	PW
F_2O	0.5311	0.8473	0.2821	PW
Cl_2O	0.6644	0.7474	0.4414	PW
	0.64031	0.7671	0.41 ± 0.18	[10]
SCl_2	0.5181	0.8554	0.2684	PW

TABLE II

Centrifugal distortion constants (MHz)

Molecule	$-\tau_{xxxx}$	$-\tau_{zzzz}$	τ_{xxzz}	$-\tau_{xzxz}$	Reference
H_2O	2409.008	279.613	556.360	117.259	PW
	2613.955	256.767	548.837	120.541	[13]
D_2O	751.929	68.337	152.638	31.485	PW
	809.009	64.372	152.870	32.426	[13]
T_2O	408.936	29.755	73.902	14.828	PW
H_2S	255.581	147.617	121.868	29.981	PW
	241.8 ± 3.9	145 ± 1.2	137 ± 3.0	39 ± 1.8	[14]*
	247.56 ± 0.16	151.25 ± 0.16	—	—	[15]
	235.13365	141.69416	121.73994	30.17117	[13]
D_2S	63.742	36.488	32.186	7.894	PW
	67.936 ± 0.012	36.647 ± 0.012	—	—	[15]
	66.05039	35.49549	32.28171	7.96250	[13]
H_2Se	133.509	110.745	82.781	19.347	PW
	141.80 ± 9.0	125.61 ± 4.2	95.93 ± 4.2	26.38 ± 2.7	[16]*
	145.797	121.977	90.036	21.395	[17]
D_2Se	35.218	27.595	21.226	4.902	PW
	33.68	35.92	23.67	5.06	[12]
$^{14}NO_2$	319.394	0.038	1.794	0.245	PW
	299.4	0.04144	1.843	0.245	[18]*
	279.6387	0.044679	1.859044	0.24564	[19]
$^{15}NO_2$	287.207	0.039	1.706	0.245	PW
O_3	28.825	0.061	0.563	0.273	PW
	23.00731	0.07501	0.47778	0.27587	[20]
	23.437531	0.076280	0.459224	0.301097	[24]*
SO_2	10.042	0.038	0.407	0.053	PW
	9.44918	0.03918	0.40103	0.05219	[20]
	9.9216	0.0399	0.4314	0.0532	[21]*
	9.8098	0.039696	0.41170	0.053203	[25]*
ClO_2	8.569	0.043	0.381	0.058	PW
	8.529	0.04557	0.3924	0.060	[22]*
SeO_2	2.813	0.045	0.076	0.013	PW
F_2O	6.637	0.085	0.527	0.167	PW
	6.6134019	0.09495587	0.39961106	0.16248562	[23]
Cl_2O	5.418	0.007	0.113	0.010	PW
SCl_2	0.511	0.008	0.045	0.007	PW

PW — present work, * — observed values.

matrix elements C_{ij}^{α} ($\alpha = x, y, z$) are obtained according to the vector method of Meal and Polo [8]. The Coriolis coupling constants are evaluated from the relation

$$\zeta^{\alpha} = L^{-1} C^{\alpha} (L')^{-1}$$

making use of kinetic constants.

The evaluated Coriolis coupling constants are given in Table I. It may be seen from the Table that the value of ζ_{13} are negative in all cases. The zeta values in Table I may seem to obey the sum rule

$$\zeta_{13}^2 + \zeta_{23}^2 = 1.$$

The Coriolis coupling constants are compared with the observed and the other calculated values in the same table. The good agreement between the present values and the observed values points out the significance of the method of kinetic constants.

3. Centrifugal distortion constants

Kivelson and Wilson [9] gave the general methods for deriving expressions for the centrifugal distortion constants as functions of atomic masses, inernuclear distances, interbond angles and the elements of the compliance matrix (F^{-1}). Following this method the centrifugal distortion constants of some XY_2 bent symmetrical molecules have been calculated, using the force constants obtained by Thirugnanasambandam and Mohan [1].

The calculated values of the centrifugal distortion constants are listed in Table II. The centrifugal distortion constants obtained here are compared with the observed and the calculated values of earlier workers in the same table. It may be seen from Table II that the calculated τ-values compare closely with those determined experimentally, lending further support to the fact that the present values are in the expected range.

4. Conclusion

Using the new approach developed in this laboratory, the molecular constants namely the Coriolis coupling constants and the centrifugal distortion constants have been evaluated in the present investigation. The molecular constants obtained here are in the expected range and compare favourably with the observed values. Thus the extremely satisfactory results obtained here show the significance of kinetic constants and its utility in the evaluation of molecular constants.

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