Influence of Atomic Masses on the Coriolis Coupling Coefficients in some Symmetrical Molecules. Part III. Planar Symmetrical XY_3 Molecules and Ions

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CORIOLIS coupling coefficients for the planar symmetrical XY_3 molecular model are studied. One has found the upper limits $|\zeta_{23}| \to \frac{1}{2}$ and $\zeta_3 \to 1$ with increasing atomic mass ratio m_Y/m_X. Lower limits are also given, and appear to be functions of the force constants.

Calculated ζ_{23} and ζ_3 values for sixteen molecules (and radicals), and five ions of the considered type are reported. Curves are given for the mass-ratio dependence.

1. The Coriolis Coefficients

The CORIOLIS coupling in the planar symmetrical XY_3 molecular model has been treated previously [1] by the method of MEAL and POLO [2]. We shall adhere to the conventions and notation of the previous paper [1]. It has been stated that two types of the coefficients (ζ-values) exist for the presently considered model, namely those belonging to (i) $E' \times E'$ and (ii) $A_2'' \times E'$ in terms of the symmetry species classification.

(i) $E' \times E'$ type. In accord with the previous notation [1] one has

$$\zeta_3 = \zeta^z_{3a,3b} = -\zeta^z_{4a,4b},$$

$$\zeta^z_{3a,4b} = \zeta^z_{4a,3b}, \text{ where } |\zeta^z_{3a,4b}| = (1-\zeta_3^2)^{1/2}.$$

If $\zeta_3 \to 1$, then obviously $\zeta^z_{4a,4b} \to -1$ and $\zeta^z_{3a,4b} \to 0$.

As stated below, this limit is approached when $m_Y/m_X \to \infty$. The limit of -1 for $\zeta^z_{4a,4b}$ may be identified with the value of ζ for a three-particle regular trigonal system. This point has been discussed in the introduction of the first article of this series [3].

(ii) $A_2'' \times E'$ type. We introduce the notation $\zeta_{23} = \zeta^x_{2,3a} = \zeta^y_{2,3b}$.

Hence in accord with the notation and relations previously given [1] one has

$$\zeta^x_{2,3b} = -\zeta^y_{2,3a} = 3^{1/2}\zeta_{23},$$

$$\zeta^x_{2,4a} = \zeta^y_{2,4b}, \text{ where } |\zeta^x_{2,4a}| = (\tfrac{1}{4} - \zeta^2_{23})^{1/2},$$

$$\zeta^x_{2,4b} = -\zeta^y_{2,4a}, \text{ where } |\zeta^x_{2,4b}| = (\tfrac{3}{4} - 3\zeta^2_{23})^{1/2}.$$

If $|\zeta_{23}| \to 1/2$, as actually is the case for $m_Y/m_X \to \infty$ (see below), then $|\zeta^x_{2,3b}| \to (1/2)\,3^{1/2}$, $\zeta^x_{2,4a} \to 0$ and $\zeta^x_{2,4b} \to 0$.

In the following we shall only consider the two independent CORIOLIS coefficients: ζ_3 and ζ_{23}. They are given in terms of the force constants by

$$\zeta_3 = -\frac{\mu_Y}{\lambda_3 - \lambda_4}(F_3 + 3F_4 - 12^{1/2}F_{34}) + \frac{\lambda_3 + \lambda_4}{\lambda_3 - \lambda_4}$$

$$\zeta_{23}^2 = \frac{\frac{1}{4}(3\mu_X + \mu_Y)}{\lambda_3 - \lambda_4}(\tfrac{1}{2}F_3 + \tfrac{3}{2}F_4 + 3^{1/2}F_{34}) - \frac{\frac{1}{4}\lambda_4}{\lambda_3 - \lambda_4}$$

as has been found from the previously evaluated relations [1]. Here μ_X and μ_Y denote the inverse masses of the X and Y atoms, respectively. Also the λ's have their usual meaning as proportional to the squared frequencies. The force constants (F) refer to a previously defined set of symmetry coordinates (l. c. [1, 4]).

2. Upper Limits

Let $$\varrho = m_Y/m_X = \mu_X/\mu_Y$$

and consider the case $$\varrho \to \infty$$

while the force constants are assumed to remain finite. By the same methods as used for the tetrahedral XY_4 model [3, 5], one has found

$$\zeta_3 \to 1, \quad |\zeta_{23}| \to \tfrac{1}{2}.$$

These limiting values are independent of the force constants.

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3. Lower Limits

Now consider the case

$$\varrho \to 0 .$$

The limiting values in question are no longer independent of the force constants, but may be expressed in terms of the only quantity

$$\varkappa = 3^{1/2} F_{34} [\tfrac{1}{4} (F_3 + 3 F_4)^2 - 3 (F_3 F_4 - F_{34}^2)]^{-1/2} .$$

It has been found

$$\zeta_3 \to \varkappa , \qquad |\zeta_{23}| \to 8^{-1/2} (1 + \varkappa)^{1/2} .$$

4. Computations and Results

The considered molecules, radicals and ions are given in Table 1 in the sequence of increasing mass ratio ϱ. In the same table are given the values of $\varkappa$ (as defined in the preceding section), and references to the experimental vibrational frequencies [5–12]. Most of them have been quoted by PISTORIUS [13] and NAGARAJAN [14, 15]. All the compounds have been subjected to a unique treatment, applying UREY–BRADLEY force field [16–18]. One additional assumption had to be introduced, and we put $F' = -F/10$ in all of the cases. The reliability of this assumption has been demonstrated by MEISINGSETH [18]. The resulting values of CORIOLIS coefficients are reported in Table 2. For SO_3 two sets of values were calculated, using the frequencies from LANDOLT-BÖRNSTEIN, and those from a recent investigation by KHACHKURUZOV [9]. The former set is given in parentheses in Table 2.

Compound	$\varrho = m_Y/m_X$	$-\varkappa$	References
UO_3	0.067	0.0120	5, 15
CH_3	0.084	0.0024	6, 7, 15
WO_3	0.087	0.0653	5,6, 15
MoO_3	0.167	0.1043	5, 15
SO_3	0.499	0.0651 0.0796	8, 13 9, 14
PO_3^{---}	0.517	0.2967	8, 13
AlF_3	0.704	0.1438	6, 15
NO_3^-	1.142	0.5211	8, 13
$AlCl_3$	1.314	− 0.0034	6, 15
CO_3^{--}	1.332	0.5120	8, 13
$^{11}BO_3^{---}$	1.453	0.5223	10, 13
CF_3	1.582	0.2470	11, 15
$^{10}BO_3^{---}$	1.597	0.5243	10, 13
$^{11}BF_3$	1.725	0.2434	12(Table VII)
$^{10}BF_3$	1.897	0.2453	12(VII)
$^{11}BCl_3$	3.220	0.2573	12(VII)
$^{10}BCl_3$	3.540	0.2583	12(VII)
$^{11}BBr_3$	7.257	0.2547	12(VII)
$^{10}BBr_3$	7.979	0.2558	12(VII)
$^{11}BI_3$	11.52	0.2313	12(VII)
$^{10}BI_3$	12.67	0.2305	12(VII)

Table 1. The considered compounds with their mass ratios and values of $\varkappa$.

Compound	ζ_{23}	ζ_3	Compound	ζ_{23}	ζ_3
Halides			Oxides		
$^{11}BF_3$	0.474	0.794	SO_3	0.429 (0.451)	0.469 (0.625)
$^{10}BF_3$	0.476	0.812			
$^{11}BCl_3$	0.483	0.869	MoO_3	0.384	0.180
$^{10}BCl_3$	0.485	0.881	WO_3	0.370	0.094
$^{11}BBr_3$	0.493	0.945	UO_3	0.372	0.107
$^{10}BBr_3$	0.494	0.949	Ions		
$^{11}BI_3$	0.495	0.963	NO_3^-	0.478	0.832
$^{10}BI_3$	0.496	0.967	CO_3^{--}	0.474	0.800
AlF_3	0.438	0.537	PO_3^{---}	0.415	0.376
$AlCl_3$	0.465	0.734	$^{11}BO_3^{---}$	0.477	0.817
Radicals			$^{10}BO_3^{---}$	0.479	0.837
CH_3	0.384	0.183			
CF_3	0.471	0.777			

Table 2. CORIOLIS coupling coefficients of planar symmetrical XY_3 compounds.

The mass dependence of the CORIOLIS coefficients was investigated for all the presently studied compounds. The values of ζ_{23} are represented graphically as functions of $\varrho^{-1/2}$ (see Fig. 1) and ζ_3 as functions of ϱ^{-1} (Fig. 2). During the mass ratio variation the force constants are held unchanged on each curve.

The numerical computations have been performed on a GIER electronic computer, using programmes coded in GIER–ALGOL [19]. The same system was suc-

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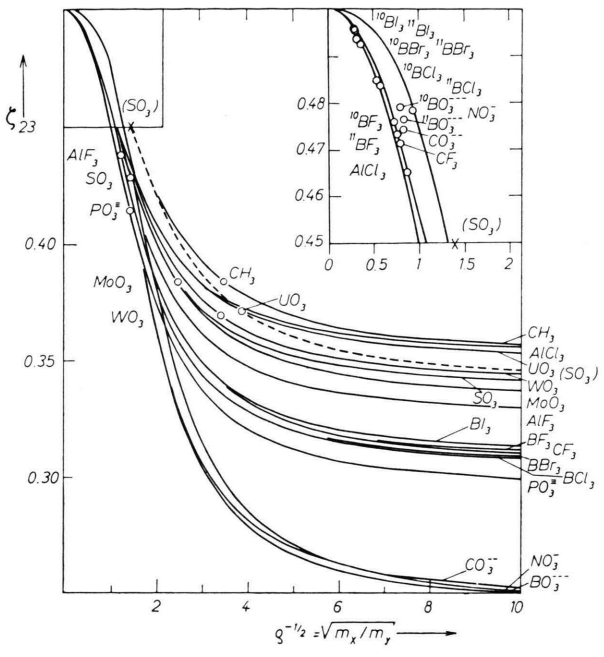

Fig. 1. Values of ζ_{23} for planar symmetrical XY_3 compounds.

cessfully applied for the previous calculations of the same kind [3, 20].

5. Discussion and Conclusion

The curves of mass dependence (Figs. 1 and 2) are seen to possess approximately to same form for all of the compounds considered. The SO_3 curve with the new frequencies from KHACHKURUZOV fit better the general forms than those with frequencies from LANDOLT–BÖRNSTEIN. It seems likely that the frequencies really have been improved.

The considered curves separate over a larger range than was the case with corresponding curves for tetrahedral XY_4 compounds [3, 20]. As a consequence it will hardly be possible to estimate values of ζ from the mass ratio only in the present case. Nevertheless there seem to be some regularities as to the location of the curves: The halides of boron all lay on curves close together. Another group of curves is formed by all the considered ions except PO_3^{---}. Also the oxides of S, Mo, W and U have similar curves.

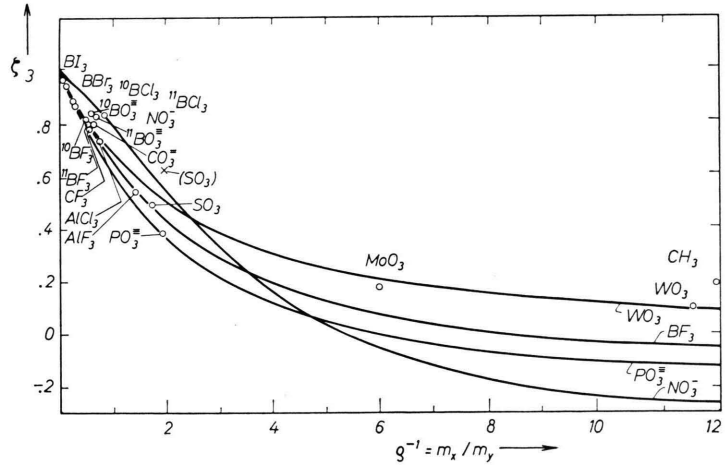

Fig. 2. Values of ζ_3 for planar symmetrical XY_3 compounds.

[20] S. J. CYVIN, J. BRUNVOLL, B. N. CYVIN, and E. MEISINGSETH, to be published.