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RELATION BETWEEN FORCE FIELD
PARAMETER AND MASS RATIO

THE fundamental problem of intra-molecular mechanics is the determination of the normal coordinate transformation matrix L which may be written as $L = TA$, normalised to the inverse kinetic energy matrix G in the sense $T\tilde{T} = G$. A is an orthogonal matrix. For a two-dimensional vibrational species, the A matrix can be generated by a single parameter c . From studies conducted on isotopic species¹ it is clear that the parameter c is mass-dependent, but the true functional form of this dependence cannot be determined from the theory of molecular vibrations. Müller and collaborators² have investigated the variation of the ratio L_{12}/L_{21} with the mass coupling parameter defined as $T = G_{12}/|G|^{1/2}$ which turns out to be a function of masses and geometry of the molecule and have

noted certain regularities. In the present note we have, however, studied the variation of the parameter c with the mass-ratio m_y/m_x in a number of molecules of the XY_2 and XY_4 types.

TABLE I
Values of mass-ratio and parameter

Molecular Type	Molecule	Mass ratio m_y/m_x	Parameter c	Reference for exact force fields
XY ₂	SeO ₂	0.203	0.046	3
	ClO ₂	0.451	0.082	4
	SO ₂	0.499	0.084	5
	OF ₂	1.188	1.156	6
	OCl ₂	2.216	0.256	7
XY ₄	GeF ₄	0.262	-0.048	8
	GeCl ₄	0.469	-0.013	8
	VCl ₄	0.696	0.02	8
	TiCl ₄	0.740	0.022	8
	CF ₄	1.582	0.15	8

TABLE II
Force fields* and coriolis constants for XY₂ and XY₄ type molecules

Molecule	XY ₂			Molecule	XY ₄			Coriolis constants ζ_4		
	Force fields (A ₁)				Force fields (F ₂)			Coriolis constants ζ_4		
	Present Work	Previous Result	Reference		Present Work	Previous Result	Reference	Present Work	Previous Result	Reference
NO ₂	12.375 0.390 1.188	12.309 0.592 1.100	9	SiF ₄	6.592 0.345 0.435	6.406 ± 0.37 0.291 ± 0.15 0.438 ± 0.01	8	0.506	0.56	14
Cl ₂ S	2.586 -0.021 0.295	2.58 0 0.294	10	SiCl ₄	2.744 0.109 0.242	2.96 ± 0.09 0.14 ± 0.03 0.236 ± 0.005	8	-0.361	-0.23 ± 0.05	15
MgF ₂	2.236 -0.02 0.1465	2.321 0.03 0.141	11	SnCl ₄	2.530 0.121 0.122	2.688 ± 0.08 0.22 ± 0.1 0.118 ± 0.01	8	0.284	0.27 ± 0.05	16
SiF ₂	5.0398 -0.063 0.362	5.329 0.174 0.44	12	RuO ₄	6.699 0.369 0.390	6.49 ± 0.05 0.07 ± 0.05 0.381 ± 0.05	8	0.420	0.32	17
CaF ₂	2.364 0.014 0.085	2.48 0.05 0.08	13	CsO ₄	7.903 0.358 0.441	8.11 ± 0.08 0.1 ± 0.1 0.47 ± 0.01	8	0.507	0.407	17

* The three values of the force constants reported correspond to F_{11} , F_{12} , and F_{22} in the case of XY₂ type molecules and F_{33} , F_{31} and F_{32} in the case of XY₄ type molecules.

The parameter c has been evaluated for XY_2 type molecules like SeO_2 , ClO_2 , SO_2 , OF_2 and OCl_2 and for XY_4 type molecules like GeF_4 , $GeCl_4$, VCl_4 , $TiCl_4$ and CF_4 using published force fields based on vibrational frequencies and other experimental data. Plots of c versus m_y/m_x have been drawn and are found to be linear (Fig. 1). Values of c as well as m_y/m_x are collected in Table I.

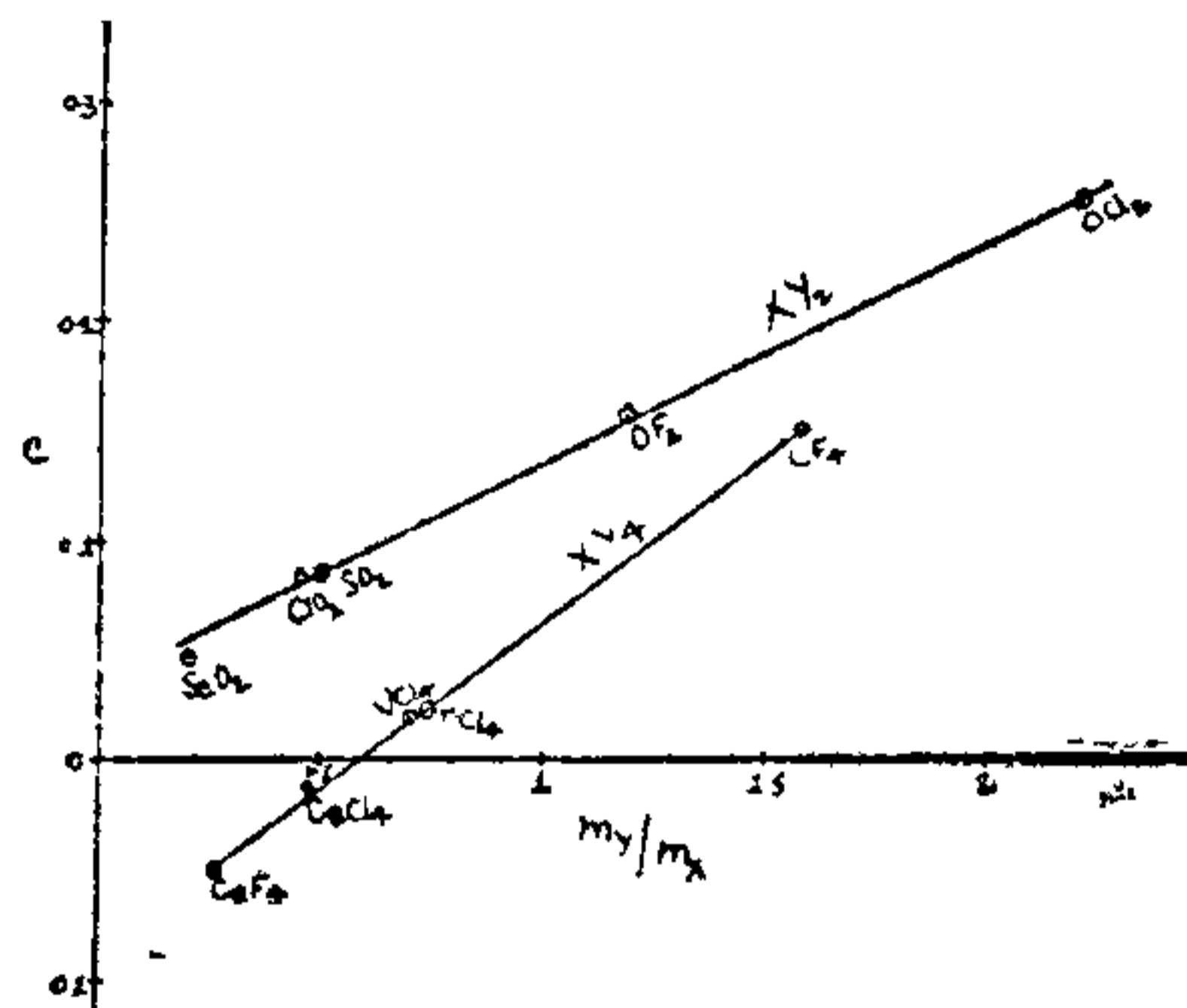


FIG. 1. Plots of parameter c vs. mass-ratio m_y/m_x .

With the help of the parameter-mass-ratio graphs an attempt has been made to determine the force fields and Coriolis constants of several XY_2 and XY_4 type molecules. The results of the investigation (Table II) are seen to be in good agreement with force fields and experimental Coriolis constants reported in the literature. In the light of the results reported here, it is highly plausible that smooth relationships may exist between the parameter and mass-ratio in other XY_n systems also. Such relationships will be of value in the elimination of spurious force fields and the correct assignment of frequencies. These aspects of the problem are being looked into.

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ON THE Z-DEPENDENCE OF TOTAL TO K-SHELL PHOTOELECTRIC CROSS SECTION RATIOS AT K-THRESHOLD

THERE have been very few studies on the total to K-shell photoelectric cross section ratios (T/K) at the K-edges. In the absence of reliable theoretical predictions, till recently, some empirical thumb rule of '5/4' law was used¹. Later, Davisson² deduced the values of the total to K-shell ratios from the data of Kirchner for the first time systematically. From such deduced data Z-dependence of the ratio is found. The value is found to vary from 1.09 for aluminum to 1.235 for uranium. Based on the measurements of such ratios, empirical expressions were proposed by Allen³ and Hubbell⁴ to express the Z-dependence. However, recent theoretical^{5,6} as well as experimental^{7,8} data at higher energies show that deduced values at K-threshold are under estimated specially in high Z-elements. Hence, it is of interest to measure and study the Z-dependence of these ratios at K-threshold. In the recent investigations in these laboratories, the total photon attenuation coefficients above and below the K-edges are measured in the elements Cu, Zr, Ag, Sn, Ta, Pb, Th and U using proportional counters and Ge (Li) systems on a good geometry set-up^{9,10}. Using these attenuation coefficients the photoelectric cross sections are deduced by subtracting the coherent and incoherent scattering contributions. The deduced photoelectric cross sections are fitted to log-log curves using IBM 1130