is not true anymore if the multiplicity of the states due to spin and isospin is taken into account.

3. By straightforward extrapolation of the PSE one obtains for the far transactinides a new electron shell which has a maximum angular momentum $\hat{l} = 4$ and is started with the element $Z = 121$.

4. Modern algebraic approach to elementary particle physics has brought out some parallels between the properties of hadrons and the H-atom. It has been shown[6] that not only the H-atom but also the hadron spectrum can be described by the group $0(4,2)$. It seems to be of interest to use the transformation from the hydrogen spectrum to the PSE-spectrum as an experimentally well accessible model for similar problems in the physics of strong interaction. In this connection it would be desirable to obtain more experimental values on the properties of highly ionized atoms than are currently available.

We thank K. HARDENBERG, H. LÜBBIG and J. MIMKES for stimulating discussions.

Vibrational Potential Energy Distributions and Coriolis Coefficients for Extremal Force Constants in Bent XY_2, Pyramidal XY_3, and Tetrahedral XY_4 Molecules

D. E. FREEMAN

Air Force Cambridge Research Laboratories, L. G. Hanscom Field, Bedford, Massachusetts, USA

(Z. Naturforsch. **25 a**, 217—221 [1970]; received 17 May 1969)

For 27 molecules with approximately extremal force fields, an empirical distinction between hydrides and non-hydrides is linked, via the comparison of calculated and observed Coriolis coefficients, to a difference, based ultimately on the relative lightness of the hydrogen atom, in the potential energy distributions of hydrides and non-hydrides. The potential energy criteria of Becher and Ballein are compared to those corresponding to extremal diagonal force constants. Coriolis coefficients for the model of progressive rigidity are mostly in rough agreement with those observed.

Introduction

Recently, papers have appeared[1, 2] dealing with the extremal properties of the vibrational force constants in the second order secular equation, the general solution of which is the subject of a rather thorough earlier treatment[3]. Only in the case of a secular equation of the second order does an extremum of either diagonal force constant procure a unique solution for the force field and normal coordinate transformation. From the results of STREY and KLAUSS[1] and of BECHER and BALLEIN[2] on the extremal force constants of a variety of molecules, the following two empirical statements may be made:

(a) One of the two extremal solutions (corresponding either to the maximal stretching force constant or to the minimal bending force constant) is often a fairly good approximation to the accurately determined force field.

(b) In such cases, a distinction exists between hydride and non-hydride molecules, in that for *all* of the latter the extremal solutions with maximal stretching force constants are never close to the accurately determined force fields.

The main point of the present note is to supplement the recent work on extremal force constants[1, 2] by correlating the above remark (b) to properties of the potential energy distributions and Coriolis coefficients for 27 molecules for which the remark (a) is true.

Discussion

(1) Vibrational potential energy distributions

The two distributions of potential energy among the symmetry force constants, corresponding to the force fields with maximal $F_{\sigma\sigma}$ (stretching) and mini-

Reprint requests to Dr. D. E. FREEMAN, Department of the Air Force, Headquarters Air Force Cambridge Research Laboratories (OAR), Laurence G. Hanscom Field, *Bedford*, Massachusetts 01730.

---

[1] G. STREY, J. Mol. Spectry. **24**, 87 [1967]. — G. STREY and K. KLAUSS, Z. Naturforsch. **23 a**, 1667, 1717 [1968].

[2] H. J. BECHER and K. BALLEIN, Z. physik. Chem. Frankfurt **54**, 302 [1967].

[3] P. TORKINGTON, J. Chem. Phys. **17**, 357 [1949].

Criterion	Potential energy distribution (P.E.D.) [a]	Normal coordinate transformation [b]
$F_{\sigma\sigma}=(F_{\sigma\sigma})_{\max}$ [c]	$V_{\sigma\sigma}^{(\sigma)}=1\,,\ V_{\beta\beta}^{(\sigma)}=-2\,V_{\sigma\beta}^{(\sigma)}=0$	$S_\sigma=G_{\beta\beta}^{-\frac{1}{2}}\lvert\boldsymbol{G}\rvert^{\frac{1}{2}}(Q_\sigma+G_{\sigma\beta}\lvert\boldsymbol{G}\rvert^{-\frac{1}{2}}Q_\beta)$
	$V_{\sigma\sigma}^{(\beta)}=-V_{\sigma\beta}^{(\beta)}=(G_{\sigma\beta}^2\lvert\boldsymbol{G}\rvert^{-1})(\omega_\sigma^2/\omega_\beta^2)\,,\ V_{\beta\beta}^{(\beta)}=1+V_{\sigma\sigma}^{(\beta)}$	$S_\beta=G_{\beta\beta}^{\frac{1}{2}}Q_\beta$
$F_{\beta\beta}=(F_{\beta\beta})_{\min}$ [d]	$V_{\beta\beta}^{(\sigma)}=-V_{\sigma\beta}^{(\sigma)}=(G_{\sigma\beta}^2\lvert\boldsymbol{G}\rvert^{-1})(\omega_\beta^2/\omega_\sigma^2)\,,\ V_{\sigma\sigma}^{(\sigma)}=1+V_{\beta\beta}^{(\sigma)}$	$S_\sigma=G_{\sigma\sigma}^{\frac{1}{2}}Q_\sigma$
	$V_{\beta\beta}^{(\beta)}=1\,,\ V_{\sigma\sigma}^{(\beta)}=-2\,V_{\sigma\beta}^{(\beta)}=0$	$S_\beta=G_{\sigma\sigma}^{-\frac{1}{2}}\lvert\boldsymbol{G}\rvert^{\frac{1}{2}}(Q_\beta+G_{\sigma\beta}\lvert\boldsymbol{G}\rvert^{-\frac{1}{2}}Q_\sigma)$
BECHER and BALLEIN	$V_{\sigma\sigma}^{(\sigma)}=1\,,\ V_{\beta\beta}^{(\sigma)}=-2\,V_{\sigma\beta}^{(\sigma)}\neq 0$	

[a] For the general n-th order secular equation, the P.E.D. in the k-th mode among the force constants F_{st} is given by the n^2 quantities $V_{st}^{(k)}=L_{sk}\,L_{tk}\,F_{st}\,\Lambda_k^{-1}$, in which L_{sk} and L_{tk} are elements of the matrix $\boldsymbol{L}$ transforming normal coordinates $\boldsymbol{Q}$ to symmetry coordinates $\boldsymbol{S}=\boldsymbol{LQ}$, and Λ_k is related to the vibrational wavenumbers ω_k via $\Lambda_k=5.8909\times10^{-7}\,\omega_k^2$. The frequencies involved in the second order secular equation are ordered so that $\omega_\sigma>\omega_\beta$.

[b] $\boldsymbol{G}$ is Wilson's symmetric inverse kinetic energy matrix [12].

[c] The force field implied is: $F_{\sigma\sigma}=G_{\beta\beta}\lvert\boldsymbol{G}\rvert^{-1}\Lambda_\sigma$, $F_{\sigma\beta}=-G_{\sigma\beta}\lvert\boldsymbol{G}\rvert^{-1}\Lambda_\sigma$, $F_{\beta\beta}=G_{\beta\beta}^{-1}(G_{\sigma\beta}^2\lvert\boldsymbol{G}\rvert^{-1}\Lambda_\sigma+\Lambda_\beta)$.

[d] The force field implied is: $F_{\beta\beta}=G_{\sigma\sigma}\lvert\boldsymbol{G}\rvert^{-1}\Lambda_\beta$, $F_{\sigma\beta}=-G_{\sigma\beta}\lvert\boldsymbol{G}\rvert^{-1}\Lambda_\beta$, $F_{\sigma\sigma}=G_{\sigma\sigma}^{-1}(G_{\sigma\beta}^2\lvert\boldsymbol{G}\rvert^{-1}\Lambda_\beta+\Lambda_\sigma)$.

For the second order secular equation, the model of progressive rigidity [13] is equivalent to the condition for minimal $F_{\beta\beta}$.

Table 1. Potential energy distribution and normal coordinate transformations for various criteria applied to the second order secular equation.

mal $F_{\beta\beta}$ (bending), are compared in Table 1 to the related potential energy distribution suggested by BECHER and BALLEIN [2]. The force field with maximal $F_{\sigma\sigma}$ requires that an increasingly heavy potential energy contribution $V_{\sigma\beta}^{(\beta)}$ be associated with the interaction constant $F_{\sigma\beta}$ as the frequencies become further separated, and $V_{\sigma\beta}^{(\beta)}$ may become numerically large for large values of $\omega_\sigma^2/\omega_\beta^2$. The magnitude of the interaction constant is also larger, by the factor $\omega_\sigma^2/\omega_\beta^2$, in the force field with maximal $F_{\sigma\sigma}$ compared to its value in the force field with minimal $F_{\beta\beta}$. The value of $\omega_\sigma^2/\omega_\beta^2$ is typically quite large, being in the range $3-10$ for the molecules studied. Consequently, unless $G_{\sigma\beta}^2\lvert\boldsymbol{G}\rvert^{-1}$ is small, large potential energy contributions $V_{\sigma\beta}$ result in mode β when $F_{\sigma\sigma}$ is maximal but not in mode σ when $F_{\beta\beta}$ is minimal (Table 1). Since the quantity $G_{\sigma\beta}^2\lvert\boldsymbol{G}\rvert^{-1}$ is given by

$$\frac{m^2\sin^2\Phi}{1+2\,m}\quad\text{for } XY_2\ (C_{2v},\ a_1\text{ modes}),\tag{1}$$

$$\frac{2\,m^2(1-\cos\Phi)(1+2\cos\Phi)}{1+3\,m}\quad\text{for } XY_3\ (C_{3v},\ a_1\text{ modes}),\tag{2}$$

$$\frac{m^2(1-\cos\Phi)^3}{2+\cos\Phi+3\,m(1-\cos\Phi)}\quad\text{for } XY_3\ (C_{3v},\ e\text{ modes}),\tag{3}$$

and

$$\frac{32\,m^2}{9(1+4\,m)}\quad\text{for } XY_4\ (T_d,\ f_2\text{ modes}),\tag{4}$$

in which Φ and m denote, respectively, the bond angle YXY and the mass ratio of atom Y to atom X, it follows that $G_{\sigma\beta}^2\lvert\boldsymbol{G}\rvert^{-1}$ is much smaller for hydrides (and possibly deuterides) than for most other molecules.

Accordingly, heavy "fractional" potential energy contributions will be associated with the interaction constant if $F_{\sigma\sigma}$ is maximal in the non-hydrides XY_2, XY_3, or XY_4. Instances of this are shown in Table 2 for molecules such as the Group IV and V halides, for which it is seen that the force fields with maximal $F_{\sigma\sigma}$ lead to serious disagreement between calculated and observed Coriolis coefficients, whereas, in contrast, the force fields with minimal $F_{\beta\beta}$ lead to much better agreement between calculated and observed Coriolis coefficients. For the non-hydrides in Table 2 the serious disagreements between calculated and observed Coriolis coefficients are correlated empirically with potential energy distributions that are heavy, compared to those for which the agreement between calculated and observed Coriolis coefficients is much better. This marked disparity in the abilities of force fields with $F_{\sigma\sigma}$ maximal and $F_{\beta\beta}$ minimal [4] to account for the observed Coriolis coefficients of non-hydrides is not found for hydrides. Coriolis coefficients corresponding to $F_{\sigma\sigma}$ maximal and to $F_{\beta\beta}$ minimal are much closer to each

---

[4] Simultaneous extrema of both diagonal force constants cannot occur unless $\boldsymbol{L}$ (and hence $\boldsymbol{G}$) is diagonal. It may be shown that, when the sum of the (positive) deviations of the two diagonal force constants from their respective extremal values is minimal, the normal coordinate transformation $\boldsymbol{L}^{-1}$ is most diagonal, in the sense that the sum of the squares of its off-diagonal elements is then minimal; the condition for this is given by replacing Γ by Γ^{-1} in Eq. (33) of Ref. [22]. This property is not invariant to a scaling change in the symmetry coordinates.

[12] E. B. WILSON, J. C. DECIUS, and P. C. CROSS, Molecular Vibrations, McGraw-Hill, New York 1955.

[13] P. TORKINGTON, J. Chem. Phys. **17**, 1026 [1949]. — M. LARNAUDIE, J. Phys. Rad. **15**, 365 [1954].

	$G_{\sigma\beta}^2 \lvert \boldsymbol{G} \rvert^{-1}$	$\omega_\sigma^2/\omega_\beta^2$	B & B[b]	$F_{\sigma\sigma} = (F_{\sigma\sigma})_{\max}$		$F_{\beta\beta} = (F_{\beta\beta})_{\min}$		ζ_σ obs
			$-V_{\sigma\beta}^{(\sigma)}$	$-V_{\sigma\beta}^{(\beta)}$	ζ_σ[c]	$-V_{\sigma\beta}^{(\sigma)}$	ζ_σ[c]	
CH_4	0.019[d]	5.416[e]		0.103	− 0.091	0.004	0.101	0.056[e]
CD_4	0.059	5.188[e]		0.306	− 0.155	0.011	0.183	0.167[e]
CT_4	0.112	5.134[e]		0.575	− 0.201	0.022	0.251	0.252[e]
$^{28}SiH_4$	0.004	6.050[e]		0.024	− 0.044	0.001	0.046	0.046[e]
$^{28}SiD_4$	0.014	5.879[e]		0.082	− 0.081	0.002	0.088	0.10[e]
GeH_4	0.001	6.732[e]		0.007	− 0.018	0.000	0.018	− 0.042[e]
GeD_4	0.002	6.574[e]		0.013	− 0.034	0.000	0.036	− 0.025[e]
$^{12}CF_4$	1.215	4.318[f]	0.21[g]	5.246	− 0.404	0.281	0.679	0.80[f], 0.84[h]
$^{28}SiF_4$	0.441	7.023[f]	0.04[i]	3.097	− 0.332	0.059	0.475	0.53[j]
GeF_4	0.119	9.191[f]		1.094	− 0.206	0.013	0.259	0.19[f], 0.20[j]
CCl_4	2.421	6.108[k]	0.27	14.787	− 0.444	0.396	0.798	—
					ζ_β[l]		ζ_β[l]	ζ_β obs
$^{14}NH_3$	0.006	4.475[e]		0.027	− 0.167	0.001	− 0.298	− 0.255[e]
$^{14}ND_3$	0.019	4.687[e]		0.089	− 0.096	0.004	− 0.344	− 0.321[m]
PH_3	0.001	4.533[e]		0.003	− 0.426	0.000	− 0.463	− 0.441[e]
PD_3	0.002	4.616[e]		0.011	− 0.400	0.001	− 0.474	− 0.463[n]
AsH_3	0.000	4.838[e]		0.001	− 0.468	0.000	− 0.483	− 0.366[e]
AsD_3	0.000	4.841[e]		0.002	− 0.458	0.000	− 0.486	− 0.402[n]
SbH_3	0.000	5.463[e]		0.000	− 0.474	0.000	− 0.482	− 0.43[e]
SbD_3	0.000	5.476[e]		0.001	− 0.467	0.000	− 0.485	− 0.465[e]
NF_3	0.665	3.398[j, o, p]		2.260	0.373	0.196	− 0.708	− 0.965[j, o, p]
PF_3	0.141	6.250[j, o, p]		0.878	0.028	0.022	− 0.594	− 0.64[j, o, p]
AsF_3	0.035	7.179[j, o, p]		0.250	− 0.179	0.005	− 0.489	− 0.435[j, o, p]
PCl_3	0.363	7.351[q]		2.668	0.274	0.049	− 0.684	− 0.82[q]
					$(\zeta_{13}^{(c)})^2$		$(\zeta_{13}^{(c)})^2$	$(\zeta_{13}^{(c)})^2$
H_2O	0.003	5.404[r]		0.018	0	0.001	0.003	0.000[s], 0.001[t]
D_2O	0.012	5.249[r]		0.062	0	0.002	0.012	0.004[s], 0.005[t]
SO_2	0.095	4.922[r]	0.02	0.466	0	0.019	0.087	0.089[u], 0.094[v] 0.101[s], 0.105[w]
NO_2	0.205	3.219[r]	0.05	0.660	0	0.064	0.170	0.219[u], 0.240[w] 0.241[s]

[a] The frequencies are ordered so that $\omega_\sigma > \omega_\beta$. The quantities listed, viz. $V_{\sigma\beta}^{(\beta)}$ for $(F_{\sigma\sigma})_{\max}$ and $V_{\sigma\beta}^{(\sigma)}$ for $(F_{\beta\beta})_{\min}$, are, together with the relations given in Table 1, sufficient to determine the complete P.E.D. for extremal force constants. Notice also from Table 1 that $V_{\sigma\sigma}^{(\sigma)}=1$ for $(F_{\sigma\sigma})_{\max}$ and for the solution of BECHER and BALLEIN [2].

[b] The P.E.D. contributions $-V_{\sigma\beta}^{(\sigma)}$ for the force field of BECHER and BALLEIN are estimated from Figs. 2−9 of Ref. [2] (in which Fig. 3 b seems to be somewhat in error in that the three points $V_{11}^{(2)}=0$, $V_{12}^{(2)}=0$, and $V_{22}^{(2)}=1$ do not have exactly equal abscissae).

[c] Usually denoted ζ_3.

[d] Quantities in this column are calculated from Eqs. (1) − (4).

[e] Cited by DUNCAN and MILLS [6].

[f] Ref. [14].

[g] The value $\zeta_3=0.85$ is calculated for $^{12}CF_4$ from the force field of BECHER and BALLEIN [2].

[h] Ref. [15].

[i] The value $\zeta_3=0.55$ is calculated for $^{28}SiF_4$ from the force field of BECHER and BALLEIN [2].

[j] Ref. [16].

[k] Ref. [2].

[l] Usually denoted ζ_4.

[m] Obtained from ζ_3 obs[6]$=0.133$ and the zeta sum rule.

[n] Calculated by DUNCAN and MILLS [6] from their general harmonic force field for the hydride and the deuteride.

[o] Ref. [17].

[p] Ref. [18].

[q] Ref. [19].

[r] Ref. [1].

[s] Calculated by OKA and MORINO [11].

[t] Calculated from the general harmonic force field of SHIMANOUCHI and SUZUKI [20] for H_2O, D_2O, and HDO.

[u] Calculated from the refined force field cited by STREY [1].

[v] Obtained from inertial defect data [21].

[w] Calculated from the force field, frequencies, and geometry of BECHER and BALLEIN [2].

Table 2. Potential energy distributions and Coriolis coefficients for XY_4 (T_d, f_2 modes), XY_3 (C_{3v}, e modes), and XY_2 (C_{2v}, a_1 modes) molecules [a].

---

[14] A. RUOFF, Spectrochim. Acta **23 A**, 2421 [1967].

[15] J. L. DUNCAN and I. M. MILLS, Spectrochim. Acta **20**, 1089 [1964].

[16] I. W. LEVIN and S. ABRAMOWITZ, J. Chem. Phys. **44**, 2562 [1966]; J. Res. Nat. Bur. Stand. (U. S.) **72 A**, 247 [1968].

[17] L. C. HOSKINS, J. Chem. Phys. **45**, 4594 [1966].

[18] A. M. MIRRI, J. Chem. Phys. **47**, 2823 [1967].

[19] I. W. LEVIN, J. Chem. Phys. **47**, 4685 [1967].

[20] T. SHIMANOUCHI and I. SUZUKI, J. Chem. Phys. **42**, 296 [1965]; **43**, 1854 [1965].

[21] Y. MORINO, Y. KIKUCHI, S. SAITO, and E. HIROTA, J. Mol. Spectry. **13**, 95 [1964].

other for small m values (hydrides) than for large m values (non-hydrides), and in Table 2 the observed and calculated Coriolis coefficients for hydrides are sometimes (e. g., for PH_3, AsH_3, SbH_3) in slightly better agreement for $F_{\sigma\sigma}$ maximal and sometimes (e. g., for CH_4, SiH_4) for $F_{\beta\beta}$ minimal.

For the molecules possessing force fields which are approximately extremal, the above discussion elucidates the distinction, stated as (b) in the introduction, between hydrides and non-hydrides by linking it empirically to potential energy distribution differences which stem ultimately from the relative lightness of the hydrogen atom. The underlying fact, stated as (a) in the introduction, that molecules apparently often possess accurately determined force fields that are approximately extremal, remains surprising. It is noted that, for the second order secular equation, an extremal diagonal force constant is accompanied (Table 1) by identity of form between one normal coordinate and the corresponding symmetry coordinate[5]. The *a priori* expectation is that this situation should obtain most probably for a pair of frequencies which are widely separated, as is the case for those listed in Table 2; on the other hand, however, the widely spaced a_1 frequencies of XH_3 (X = N, P, As, Sb)[6] and the not so widely spaced σ^+ frequencies of HCN and DCN[7] are not characterized by an "unmixed" normal coordinate and concomitant extremal force constant[8]. In general, no purely mechanical preference exists for an "unmixed" normal coordinate, and it is difficult to conjecture, in electronic terms, a plausible explanation for "unmixed" normal coordinates which is applicable only to the requisite variety of molecular vibrations.

(2) Potential energy criteria of Becher and Ballein

BECHER and BALLEIN[2] have demonstrated that a special assumption, shown in Table 1, about the potential energy distribution is useful in establishing good values for the symmetry strteching force constants for the a_1 vibrations of SO_2, NO_2, and ClO_2, the e' vibrations of BF_3 and NO_3^-, and the f_2 vibrations of CF_4, CCl_4, and SiF_4. They studied non-hydrides only, and it is remarkable that the values of $F_{\beta\beta}$ for their suggested potential energy distribution (Table 2 of Ref. [2]) are often quite close to the minimal values of $F_{\beta\beta}$, whereas the analogous values of $F_{\sigma\sigma}$ are not ever close to the maximal values of $F_{\sigma\sigma}$ (Table 1 of Ref. [2]) even though $V_{\sigma\sigma}^{(\sigma)} = 1$ for both the potential energy distribution of Becher and Ballein and for maximal $F_{\sigma\sigma}$. This possibility can arise because the value of $V_{\sigma\sigma}^{(\sigma)}$ when $F_{\beta\beta}$ is minimal may, provided that $(G_{\sigma\beta}^2 |\mathbf{G}|^{-1})\ (\omega_\beta^2/\omega_\sigma^2)$ is small, approach close to unity, which is the value of $V_{\sigma\sigma}^{(\sigma)}$ for the potential energy distribution of Becher and Ballein. Examples (SO_2, NO_2, SiF_4) and counterexamples (CF_4, CCl_4) of this situation are among those shown in Table 2, which compares the results of applying the potential energy criterion of Becher and Ballein and the potential energy criteria appropriate to minimal $F_{\beta\beta}$ and maximal $F_{\sigma\sigma}$.

(3) Coriolis Coefficients

For extremal values of either diagonal symmetry force constant, the usual formulae[9–11] involving frequencies, force constants, masses, and geometry become especially simple for certain Coriolis coefficients, and are expressible solely in terms of the bond angle Φ and mass ratio m of atom Y to atom X.

The Coriolis coefficient $\zeta_{13}^{(c)}$ coupling the ω_1 and ω_3 stretching modes of bent XY_2 molecules is given by

$$(\zeta_{13}^{(c)})^2 = 0 \qquad \text{for } F_{11} = (F_{11})_{\max} \tag{5 a}$$

and by

$$(\zeta_{13}^{(c)})^2 = \frac{m^2 \sin^2 \Phi}{1 + 2m + m^2 \sin^2 \Phi} \text{ for } F_{22} = (F_{22})_{\min} . \tag{5 b}$$

The Coriolis coefficient ζ_4 for the degenerate e species containing ω_3 and ω_4 of pyramidal XY_3 molecules is given by

$$\zeta_4 = \frac{1 - 4\cos^2 \frac{1}{2}\Phi + 4m \sin^4 \frac{1}{2}\Phi}{1 + 2\cos^2 \frac{1}{2}\Phi + 4m \sin^4 \frac{1}{2}\Phi} \text{ for } F_{33} = (F_{33})_{\max} \tag{6 a}$$

---

[5] A stationary diagonal force constant in the general n-th order secular equation is always accompanied by identity of form between a normal coordinate and a symmetry coordinate; see D. E. FREEMAN, J. Mol. Structure **4**, 145 [1969].

[6] J. L. DUNCAN and I. M. MILLS, Spectrochim. Acta **20**, 523 [1964].

[7] D. E. FREEMAN, J. Chem. Phys. **49**, 4250 [1968].

[8] For example, the normal modes for HCN[7] are given by $Q_\sigma = 0.921\, S_\sigma - 0.409\, S_\beta$ and $Q_\beta = 0.351\, S_\sigma + 2.564\, S_\beta$, in which S_σ and S_β denote, respectively, CH stretching and CN stretching coordinates. The corresponding force field is not well approximated by either extremal solution.

[9] J. H. MEAL and S. R. POLO, J. Chem. Phys. **24**, 1126 [1956].

[10] T. SHIMANOUCHI, I. NAKAGAWA, J. HIRAISHI, and M. ISHII, J. Mol. Spectry. **19**, 78 [1966].

[11] T. OKA and Y. MORINO, J. Mol. Spectry. **8**, 9 [1962].

and by

$$\zeta_4 = \frac{1-4\cos^2\tfrac{1}{2}\Phi - 12\,m\sin^2\tfrac{1}{2}\Phi\cos^2\tfrac{1}{2}\Phi - 12\,m^2\sin^4\tfrac{1}{2}\Phi}{1+2\cos^2\tfrac{1}{2}\Phi + 4\,m\sin^2\tfrac{1}{2}\Phi(\cos^2\tfrac{1}{2}\Phi+2) + 12\,m^2\sin^4\tfrac{1}{2}\Phi} \quad \text{for } F_{44} = (F_{44})_{\min}\,. \qquad (6\,\text{b})$$

The Coriolis coefficient ζ_3 for the degenerate f_2 species containing ω_3 and ω_4 of tetrahedral XY_4 molecules is given by

$$\zeta_3 = \frac{-4\,m}{8\,m+3} \quad \text{for } F_{33} = (F_{33})_{\max} \quad \text{and by} \quad \zeta_3 = \frac{4\,m}{4\,m+3} \quad \text{for } F_{44} = (F_{44})_{\min}\,. \qquad (7\,\text{a, b})$$

It is noteworthy that, in each case, as the mass ratio m decreases, both Coriolis coefficients, corresponding to maximal stretching and minimal bending force constants, converge to a common limiting value characteristic of a pair of pure valence vibrations.

Coriolis coefficients calculated from Eqs. (5) to (7) are compared in Table 2 to experimental values. The single assumption of a force field with minimal bending force constant, i. e., the model of progressive rigidity, accounts roughly for the observed Coriolis coefficients (excepting those involving the a_1 modes of the XH_3 molecules), so that this model often gives tolerable approximations to the true harmonic force fields [6, 10] for these molecules. This conclusion is in general accord with recent work [22] in which advantages of the model of progressive rigidity over other kinematically determined model force fields were noted.

Note added in proof:

Approximate formulae for the force constants corresponding to the potential energy criteria of Becher and Ballein have recently been given by PFEIFFER [23], who shows that $(F_{\beta\beta})_{\min}$ is then a fair approximation to $F_{\beta\beta}$, provided that $G^2_{\sigma\beta}|\mathbf{G}|^{-1}G^{-1}_{\sigma\sigma}\Lambda_\beta$ is small. This proviso, coupled with Pfeiffer's Eq. (12), entails that $(G^2_{\sigma\beta}|\mathbf{G}|^{-1})$ $(\omega^2_\beta/\omega^2_\sigma)$ be small. This result is comparable to that obtained in the present discussion.

Recent articles by PEACOCK and MÜLLER [24] and by SAWODNY [25] refer to the distinction between hydrides and non-hydrides. Other recent papers discuss the mass dependence of Coriolis coefficients for various molecular models [26]. The approximate calculation of ζ-constants using the condition $L_{12}=0$ equivalent to $(F_{22})_{\min}$ was first used in the papers cited above and especially in Ref. [27].

---

[22] D. E. FREEMAN, J. Mol. Spectry. **27,** 27 [1968].

[23] M. PFEIFFER, Z. physik. Chem. Frankfurt **61,** 253 [1968].

[24] C. J. PEACOCK and A. MÜLLER, Z. Naturforsch. **23 a,** 1029 [1968].

[25] W. SAWODNY, J. Mol. Spectry **30,** 56 [1969].

[26] A. MÜLLER, Z. physik. Chem. Leipzig **238,** 116 [1968]. — A. MÜLLER, B. KREBS, and S. J. CYVIN, Mol. Phys. **14,** 491 [1968]. — A. MÜLLER and C. J. PEACOCK, J. Mol. Spectry. **30,** 345 [1969].

[27] R. KEBABCIOGLU and A. MÜLLER, Z. Naturforsch. **23 a,** 1310 [1968].