possess an even number of lines. A possible explanation could be that the unpaired electron cannot move freely within the whole molecule since it is not planar, but for reasons of steric hindrance at least one phenyl-group must be more or less perpendicular to the rest of the molecule. If the unpaired electron is restricted to two phenyl groups for a time long compared with the reciprocal coupling constants, a spectrum with an even number of lines does not seem impossible.

In the case of the m-terphenyl the resolution obtainable with our spectrometer using 100 Kc. modulation was not sufficient; only about 250 of the 900 theoreticall lines could be partially resolved. It may be mentioned that the even number of lines observed agrees with the symmetry of the molecule. The total extent of the spectrum (25 Gauss) is about 30% larger than for the para- and ortho-terphenyl indicating appreciable negative spin densities at some positions.

Influence of Atomic Masses on the Coriolis Coupling Coefficients in some Symmetrical Molecules. Part II Tetrahedral XY_4 Molecules and Ions

By S. J. Cyvin, J. Brunvoll, B. N. Cyvin, and E. Meisingseth

Institute of Theoretical Chemistry, Technical University of Norway, Trondheim, Norway

(Z. Naturforschg. **19 a**, 780—783 [1964]; eingegangen am 23. März 1964)

An investigation of Coriolis coupling of rotation-vibration in 35 tetrahedral XY_4 ions and 5 molecules of the same type is reported. The theoretical limits for $|\zeta_{24}|$ and ζ_{44} are quoted. The results for ζ_{24} are represented graphically and discussed in relation to the methane-curve for mass dependence of the same quantity.

In the first paper of this series [1] we communicated our studies on Coriolis coupling coefficients (ζ-values) for 36 tetrahedral XY_4 molecules. The main subject of the present work is a corresponding study of tetrahedral XY_4 ions. Also supplementary results are given for 5 molecules, which have not been included in the cited paper [1].

1. Brief Survey of the Theory

The Coriolis coupling of the presently considered molecule model (XY_4 of T_d symmetry) is described in terms of two ζ values, viz. ζ_{24} and ζ_{44}. These are of the types $E \times F_2$ and $F_2 \times F_2$, respectively, where E and F_2 refers to the species of the appropriate symmetry group (T_d). Theoretical limits for $|\zeta_{24}|$ and ζ_{44} have been found when the mass ratio,

$$\varrho = m_Y/m_X ,$$

approaches infinity or zero. The limiting values are as follows:

$$\varrho \to \infty ; \quad |\zeta_{24}| \to \tfrac{1}{2} , \quad \zeta_{44} \to \tfrac{1}{2} \text{ (upper limitis)}.$$

$$\varrho \to 0; \quad |\zeta_{24}| \to 8^{-1/2}(1-\tfrac{1}{3}\varkappa)^{1/2} ,$$

$$\zeta_{44} \to -\tfrac{1}{4}(1+\varkappa) \text{ (lower limits)}.$$

Here $\varkappa$ is a function of the force constants belonging to the triply degenerate species, viz.,

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

For exact explanation of the symbols, and further details, the previous article of this series [1] should be consulted.

2. Five Tetrahedral XY_4 Molecules

The presently considered molecules are specified in Table 1, along with the corresponding mass ratios (ϱ) and values of $\varkappa$. The vibrational frequencies were taken from Nagarajan [2, 3], and an Urey-Brad-

Molecule	$\varrho = m_Y/m_X$	$\varkappa$	Reference
SnH_4	0.008	1.126	2
ZrF_4	0.208	1.187	2
TiF_4	0.397	1.252	2
TiI_4	2.649	2.471	2
SiI_4	4.518	1.491	3

Table 1. Mass ratios and $\varkappa$ of 5 tetrahedral XY_4 molecules.

[1] S. J. Cyvin, J. Brunvoll, B. N. Cyvin, L. A. Kristiansen and E. Meisingseth, J. Chem. Phys. **40**, 96 [1964].
[2] G. Nagarajan (to be published).
[3] G. Nagarajan (to be published).

LEY force field was found, based on the assumption $H'=0$ (cf. Ref. [1, 4]). In Table 2 the computed CORIOLIS coefficients are given, and the ζ_{24} values

Molecule	ζ_{24}	ζ_{44}
SnH_4	0.284	− 0.517
ZrF_4	0.342	− 0.299
TiF_4	0.373	− 0.165
TiI_4	0.484	0.406
SiI_4	0.486	0.416

Table 2. CORIOLIS coupling coefficients of 5 tetrahedral XY_4 molecules.

are also represented graphically in Fig. 1. Except for the SnH_4 molecule the points are seen to fit perfectly the methane isotopic-molecule curve here used as standard reference. The result for SnH_4 may not be much reliable in view of the fact that the frequencies have not been corrected for anharmonicity. The importance of this correction was clearly demonstrated for silanes [1]. It is not possible te perform the corresponding correction in the present case of SnH_4 since the frequencies of SnD_4 are not known.

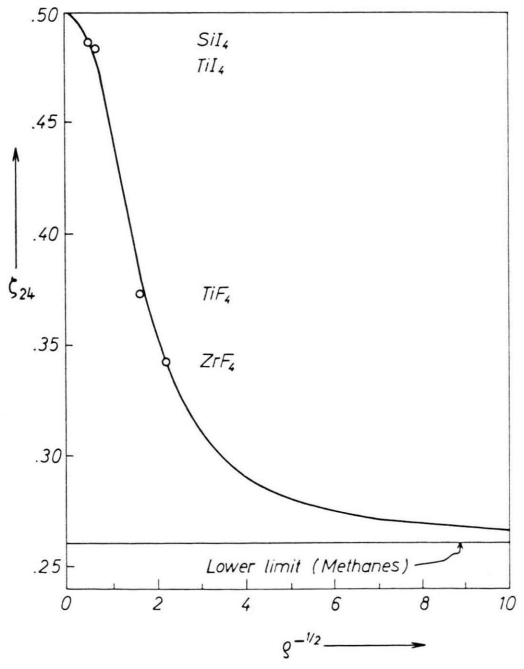

Fig. 1. The CORIOLIS coupling coefficient ζ_{24} as function of the mass ratio for some tetrahedral XY_4 molecules (for SnH_4, see Fig. 2). $\varrho^{-1/2}=(m_X/m_Y)^{1/2}$.

[4] T. SHIMANOUCHI, J. Chem. Phys. **17**, 245 [1949].
[5] S. SUNDARAM, J. Chem. Phys. **33**, 708 [1960].

3. Tetrahedral XY_4 Hydride Ions

Ammonium ions

The fundamental frequencies of NH_4^+ and ND_4^+ taken from SUNDARAM [5] were corrected for anharmonicity using the anharmonicity constants from the same paper [5]. The result of this correction is found in Table 3 for the frequencies of the species F_2 (nos. 3 and 4). Also included are the correspond-

Ion	NH_4^+	ND_4^+
ν_3	3138	2350
ν_4	1403	1066
ω_3	3323.1	2455.8
ω_4	1485.8	1114.0
F_3	6.038 (5.353)	6.087 (5.527)
F_4	0.561 (0.497)	0.557 (0.510)
F_{34}	0.227 (0.096)	0.220 (0.128)

Table 3. Fundamental frequencies, ν (in cm^{-1}), normal frequencies (corrected for anharmonicity), ω (in cm^{-1}), and force constants (in mdyne/Å) of ammonium and ammonium-d_4.

ing UREY-BRADLEY force constants from the corrected and uncorrected frequencies, the latter ones being given in parentheses. The identity of force constants for the two isotopic species was found to be fulfilled with sufficient accuracy in case of the corrected frequencies. Therefore the calculations of CORIOLIS coefficients were based on these force constants without further refinements. The results are found in Table 5.

Borohydride ions

Four isotopic species of borohydride ions have been investigated. Here we used the uncorrected fundamental frequencies [6, 7], which gave approximately the same UREY-BRADLEY force constants, as shown in Table 4. The resulting CORIOLIS coefficients are included in Table 5.

Ion	$^{11}BH_4^-$	$^{11}BD_4^-$	$^{10}BH_4^-$	$^{10}BD_4^-$
F_1	3.043	2.925	3.059	2.928
F_2	0.290	0.289	0.289	0.291
F_3	2.690	2.731	2.679	2.711
F_4	0.285	0.291	0.287	0.292
F_{34}	0.092	0.047	0.096	0.054

Table 4. UREY–BRADLEY force constants (in mdyne/Å) for borohydride ions.

[6] A. R. EMERY and R. C. TAYLOR, J. Chem. Phys. **28**, 1029 [1958].
[7] M. RADHAKRISHNAN, Z. Phys. Chem., N.F. **36**, 227 [1963].

Hydride ions	ζ_{24}	ζ_{44}
NH_4^+	0.297	−0.469
ND_4^+	0.327	−0.358
PH_4^+	0.310	−0.422
$^{11}BH_4^-$	0.310	−0.423
$^{11}BD_4^-$	0.358	−0.232
$^{10}BH_4^-$	0.313	−0.412
$^{10}BD_4^-$	0.362	−0.212
AlH_4^-	0.300	−0.461
Halogen ions	ζ_{24}	ζ_{44}
BF_4^-	0.455	0.240
$AlCl_4^-$	0.456	0.248
$GaCl_4^-$	0.386	−0.104
$GaBr_4^-$	0.436	0.139
GaI_4^-	0.456	0.248
$InCl_4^-$	0.354	−0.247
$InBr_4^-$	0.405	−0.017
InI_4^-	0.426	0.091
$TlCl_4^-$	0.334	−0.332
$TlBr_4^-$	0.366	−0.196
TlI_4^-	0.378	−0.144
ZnI_4^{--}	0.450	0.215
$CdBr_4^{--}$	0.380	−0.134
CdI_4^{--}	0.411	0.012
PCl_4^-	0.448	0.205
$AsCl_4^-$	0.388	−0.095
Hydroxyl ions	ζ_{24}	ζ_{44}
$B(OH_4^-$	0.489	0.433
$Al(OH_4^-$	0.398	−0.051
Oxide ions	ζ_{24}	ζ_{44}
ClO_4^-	0.454	0.235
IO_4^-	0.348	−0.274
SO_4^{--}	0.432	0.120
SeO_4^{--}	0.373	−0.165
TeO_4^{--}	0.347	−0.278
CrO_4^{--}	0.373	−0.163
MoO_4^{--}	0.327	−0.357
PO_4^{---}	0.404	−0.022
AsO_4^{---}	0.354	−0.248

Table 5. CORIOLIS coupling coefficients of tetrahedral XY_4 ions.

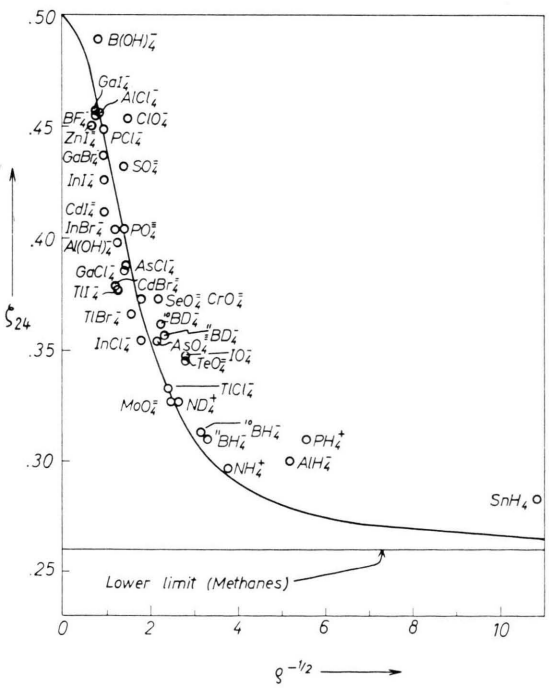

Fig. 2. The CORIOLIS coupling coefficient ζ_{24} as function of the mass ratio for tetrahedral XY_4 ions (and SnH_4). $\varrho^{-1/2}=(m_X/m_Y)^{1/2}$.

Ion	$\varrho=\frac{m_Y}{m_X}$	$\varkappa$	Ref.
PH_4^+	0.033	0.920	8
AlH_4^-	0.037	1.119	9
NH_4^+	0.072	1.357	5
$^{11}BH_4^-$	0.092	1.337	6,7
$^{10}BH_4^-$	0.101	1.355	6,7
TeO_4^{--}	0.125	1.215	10
IO_4^-	0.126	0.913	11
ND_4^+	0.144	1.343	5
MoO_4^{--}	0.167	1.371	11
$TlCl_4^-$	0.173	1.171	7
$^{11}BD_4^-$	0.183	1.173	6,7
$^{10}BD_4^-$	0.201	1.198	6,7
SeO_4^{--}	0.203	1.065	11
AsO_4^{---}	0.214	1.148	7,10
CrO_4^{--}	0.308	1.746	11
$InCl_4^-$	0.309	1.350	7
$TlBr_4^-$	0.391	1.363	7,10
ClO_4^-	0.451	1.120	11
$AsCl_4^-$	0.473	1.481	7
SO_4^{--}	0.499	1.528	11
$GaCl_4^-$	0.509	1.494	10
PO_4^{---}	0.517	1.518	11
TlI_4^-	0.621	1.619	7
$Al(OH)_4^-$	0.630	1.690	9
$InBr_4^-$	0.697	1.416	10
$CdBr_4^{--}$	0.711	1.770	9
InI_4^-	1.106	1.533	10
CdI_4^{--}	1.129	1.748	12
PCl_4^-	1.145	1.527	7
$GaBr_4^-$	1.146	1.622	10
$AlCl_4^-$	1.314	1.166	7
$B(OH)_4^-$	1.572	2.697	10
BF_4^-	1.756	2.330	10
GaI_4^-	1.820	1.671	10
ZnI_4^{--}	1.941	1.983	7,10

Table 6. Mass ratios $\varrho=m_Y/m_X$ and $\varkappa$ of tetrahedral XY_4 ions.

Other hydride ions

In Table 5 also the CORIOLIS coefficients of PH_4^+ and AlH_4^- are given, as calculated from the frequencies quoted by PISTORIUS [8] and VENKATESWARLU et al. [9], respectively.

4. Other Tetrahedral XY_4 Ions

The same calculations were performed for numerous other ions of the considered type: halogen ions, two hydroxides (where OH is regarded as one particle), and several oxide ions. All the ions considered are specified in Table 6, including the mass

[8] C. W. F. T. PISTORIUS, J. Chem. Phys. **27**, 965 [1957].
[9] K. VENKATESWARLU, V. SOMA SUNDARAM, and M. G. PILLAI KRISHNA, Z. Phys. Chem. **212**, 145 [1959].

ratios, $\varkappa$ values and references to the works from which the vibrational frequencies have been taken [5–12]. The resulting values of ζ are included in Table 5. Some additional tetrahedral XY_4 ions have been studied by PISTORIUS [13], who has not quoted the vibrational frequencies in the cited paper [13]. The calculations on SiO_4^{4-} ion using the frequencies according to VENKATESWARLU and SUNDARAM [11] and following our method, resulted in imaginary force constants.

[10] G. NAGARAJAN, Bull. Soc. Chim. Belg. **71**, 119 [1962].
[11] K. VENKATESWARLU and S. SUNDARAM, J. Chem. Phys. **23**, 2365 [1955].

5. Graphical Representation and Discussion

The values of ζ_{24} for all the ions here considered are plotted in a diagram (Fig. 2). The points are found to be grouped fairly close to the methane isotopic-molecule curve, but the deviations are generally greater than those observed for the XY_4 molecules [1]. It seems to be a systematic tendency for the halogen ions to have points below the methane curve, while those of the oxide ions are above the curve.

[12] C. W. F. T. PISTORIUS and P. C. HAARHOFF, Z. Phys. Chem., N.F. **19**, 202 [1959].
[13] C. W. F. T. PISTORIUS, J. Chem. Phys. **28**, 514 [1958].

Doppeldiffraktometrische Transmissions-Topographie?

Von M. RENNINGER

Kristallographisches Institut der Universität Marburg

(Z. Naturforschg. **19 a**, 783—787 [1964]; eingegangen am 25. Februar 1964)

It is examined to what extent double diffractometric methods make sense in transmission topography. The result is that they do, but mainly for essentially different reasons than in reflection topography: They also bring—it is true—improvements for the dissolution of small lattice distortions (dislocations etc.), but their main superiority consists in a remarkable gain of intensity and therefore of time. The contrasts in the pictures of transmission topography are preferably produced by ray bending connected with variation of anomalous absorption (BORRMANN-effect) or by variation of extinction, that is, by variation of the rocking curve in *hight* rather than in *abscissa*.

Das von BERG [1, 2] und später erneut von BARRETT [3] eingeführte Verfahren der röntgenographischen Abbildung von Kristallen im eigenen Interferenzlicht fand in den letzten Jahren zunehmend verbreitete Anwendung und auch Weiterentwicklung nach verschiedenen Richtungen zur Steigerung der Empfindlichkeit für kleinste Kristallbaufehler. Eine davon ist die Einführung doppeldiffraktometrischer Methodik durch BONSE und KAPPLER [4–6], später aufgenommen durch BARTH [7] und – modifiziert in Richtung weiterhin erhöhter Winkel-Auflösung (bis 10^{-7}) – durch den Verfasser [8, 9]. Diese Untersuchungen arbeiteten durchweg im BRAGG-Fall, d. h. mit Oberflächen-Reflexion, und vermitteln sonach Abbildung oberflächennaher Gitterbereiche und ihrer Fehler. Für den LAUE- (d. h. Transmissions-) Fall wurden Zweikristall-Anordnungen erstmals herangezogen durch AUTHIER [10] sowie durch KOHRA, YOSHIMATSU und SHIMIZU [11], und zwar unter Verwendung *beider* Kristalle in Transmission.

Ein vom Verfasser zunächst nur beiläufig unternommener Versuch doppeldiffraktometrischer Transmissions-Topographie in (n, –n)-Stellung, wobei aber im Unterschied zu den zuletzt zitierten Autoren nur der zweite, der Test-Kristall in Transmission verwendet wurde, der erste dagegen in (asymmetrischer) Reflexion derselben Ordnung, lieferte mit Cu-Strahlung bei Siliciumscheiben von 0,3 – 1 mm Dicke so verblüffend kontrastreiche und vor allem räumlich ausgedehnte Bilder der Verzerrungsfelder von

[1] W. F. BERG, Naturwiss. **19**, 391 [1931].
[2] W. F. BERG, Z. Krist. **89**, 286 [1934].
[3] CH. S. BARRETT, Trans. Amer. Inst. Mining Met. Engr. **161**, 15 [1945].
[4] U. BONSE u. E. KAPPLER, Z. Naturforschg. **13 a**, 349 [1958].
[5] U. BONSE, Z. Phys. **153**, 278 [1958].
[6] U. BONSE, Direct Observation of Imperfections in Crystals, Interscience Publ., New York 1962, S. 431.
[7] H. BARTH, Phys. Verh. **1961**, 214.
[8] M. RENNINGER, Phys. Letters **1**, 104, 106 [1962].
[9] M. RENNINGER, Crystallography and Crystal Perfection, Academic Press, New York 1963, S. 145.
[10] A. AUTHIER, Bull. Soc. Franc. Miner. **84**, 51 u. 91 (These) [1961].
[11] K. KOHRA, M. YOSHIMATSU u. J. SHIMIZU, Direct Observation of Imperfections in Crystals, Interscience Publ., New York 1962, S. 461.