Mean Amplitudes of Vibration, Force Constants and Coriolis Coupling Constants of $ZXY_2(C_{2v})$ and $ZXY_3(C_{3v})$ Type Molecules and Ions

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For a large number of $ZXY_3(C_{3v})$ and $ZXY_2(C_{2v})$ molecules and ions symmetry force constants, mean amplitudes of vibration for bonded and nonbonded distances and Coriolis coupling constants have been calculated.

In the last years several papers have appeared dealing with the calculation of mean amplitudes of vibration. They were almost exclusively obtained by solving the secular equation

$$|\boldsymbol{\Sigma} \boldsymbol{G}^{-1} - \Delta \boldsymbol{E}| = 0 \qquad (1)$$

given by CYVIN[1] with drastic approximations of neglecting off-diagonal elements. This procedure has inappropriately frequently been referred to as CYVIN's method. Already MÜLLER[2] has pointed out that the calculation of the $\boldsymbol{\Sigma}$ matrix is better when using the equation

$$\boldsymbol{\Sigma} = \boldsymbol{L} \boldsymbol{\Delta} \boldsymbol{L}' \qquad (2)$$

given by CYVIN. The physical basis for this has been discussed[2]. In this paper mean amplitudes of vibration for several molecules and ions shall be calculated according to (2), i.e. after initial calculation of force constants. In the cases of the molecules the values obtained can be useful for electron diffraction studies.

I. Frequencies of the Normal Vibrations, Molecular Data and Symmetry Coordinates

References for the data on which the calculations for the $ZXY_3(C_{3v})$ compounds are based are given in Table 1. The frequencies are taken from the most recent papers. In some cases the assignment of $\delta_{as}(XY_3) = \nu_5(E)$ and $\delta(ZXY) = \varrho(XY_3) = \nu_6(E)$ is not completely clear[8,10] but this has almost no effect on the results except on the values for the mean amplitudes for the nonbonded distances and the ζ_{55} and ζ_{66} values as shown for $BrSiCl_3$ and $ISiBr_3$, where the calculations have been done with the assignments of ν_5 and ν_6 interchanged. References for the corresponding data of the $ZXY_2(C_{2v})$ type compounds are summarized in Table 2.

For the four-atomic molecular models (C_{2v} symmetry) the applied symmetry coordinates are specified elsewhere[3]. Those for the XY_3Z model of symmetry C_{3v} are also to be published[4]. But since this latter paper probably will not appear before the present article we reproduce the appropriate coordinates in the following for the sake of convenience. R and D are used to designate the X–Y and X–Z distances, respectively, and the equilibrium YXY angle is $2A$. The three angle bendings α_i are opposite to the corresponding X–Y stretchings r_i (for $i = 1, 2, 3$). The three bendings γ_i have atoms in common with the corresponding r_i's.

$$S_1(A_1) = 3^{-1/2}(r_1 + r_2 + r_3),$$
$$S_2(A_1) = d,$$
$$S_3(A_1) = \left\{\frac{R}{3[R(4 - \sec^2 A) + D]}\right\}^{1/2} \cdot [(4 - \sec^2 A)^{1/2} R(\alpha_1 + \alpha_2 + \alpha_3) - D(\gamma_1 + \gamma_2 + \gamma_3)].$$
$$S_{1a}(E) = 6^{-1/2}(2r_1 - r_2 - r_3),$$
$$S_{2a}(E) = 6^{-1/2} R(2\alpha_1 - \alpha_2 - \alpha_3),$$
$$S_{3a}(E) = 6^{-1/2}(RD)^{1/2}(2\gamma_1 - \gamma_2 - \gamma_3).$$
$$S_{1b}(E) = 2^{-1/2}(r_2 - r_3),$$
$$S_{2b}(E) = 2^{-1/2} R(\alpha_2 - \alpha_3),$$
$$S_{3b}(E) = 2^{-1/2}(RD)^{1/2}(\gamma_2 - \gamma_3).$$

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[1] S. J. CYVIN, Molecular Vibrations and Mean Square Amplitudes, Universitetsforlaget, Oslo, and Elsevier, Amsterdam 1968.

[2] A. MÜLLER, Z. Phys. Chem. Leipzig **238** 116 [1968].

[3] S. J. CYVIN, J. BRUNVOLL, B. N. CYVIN, I. ELVEBREDD, and G. HAGEN, Mol. Phys. **14**, 13 [1968].

[4] S. J. CYVIN, B. N. CYVIN, I. ELVEBREDD, G. HAGEN and J. BRUNVOLL, to be published.

ZXY_3	$F_{11}(A_1)$	$F_{12}(A_1)$	$F_{13}(A_1)$	$F_{22}(A_1)$	$F_{23}(A_1)$	$F_{33}(A_1)$	References fre-quencies	References structural data
OPF_3	7.4210	0.2709	0.0875	11.8329	− 0.1335	0.6240	7	11, 12
$OPCl_3$	3.5053	0.0522	0.1073	10.0661	− 0.0658	0.3153	8	11, 13
$OPBr_3$	3,3046	0.0173	0.1510	9.7296	− 0.0482	0.2229	8	11
OVF_3	5.4011	0.0767	0.0098	7.8041	− 0.0185	0.2381	7	1,56 Å; 1,86 Å; 109°[a]
$OVCl_3$	3.0422	0.0106	0.0152	7.6040	− 0.0133	0.1572	8	11
$OVBr_3$	2.6214	0.0012	0.0392	7.4828	− 0,0147	0.1350	8	1,56 Å; 2,36 Å; 112°[a]
$ClReO_3$	9.1352	0.0025	− 0.0012	1.5902	− 0.0104	0.5992	9	11
$BrReO_3$	9.0941	0.0033	− 0.0010	1.3635	− 0.0104	0.3838	9	2,42 Å; 1,70 Å; 109°[a]
SPO_3^{3-}	6.9025	0.1072	0.0156	2.8149	− 0.3043	0.7129	8	14b
HPO_3^{2-}	7.6252	− 0.0075	0.0727	3.0970	− 0.0045	0.7529	8	14
FPO_3^{2-}	7.4087	0.3157	0.1452	4.7818	− 0.2158	0.7743	8	14
$HOPO_3^{2-}$	7.2691	0.9808	0.1891	5.5507	− 0.1915	0.7657	8	14
SSO_3^{2-}	7.5571	0.1370	0.0463	2.9498	− 0.2705	0.8578	8	14
HSO_3^-	8.5723	0.0496	0.0960	3.9345	− 0.0223	0.9526	8	14
FSO_3^-	8.7284	0.0914	0.1332	4.6595	− 0.2983	0.8977	8	14
$ClSO_3^-$	8.5101	0.0398	− 0.0286	2.7528	− 0.3561	0.5418	8	14
$HOSO_3^-$	8.2066	0.5346	0.2077	5.5977	− 0.2495	0.9742	8	14
$HOSeO_3^-$	6.4072	0.0850	0.0171	4.6411	− 0.0184	0.5118	8	14
$SReO_3^-$	8.0423	− 0.0031	0.0016	4.0378	− 0.0110	0.4014	8	14
$FCrO_3^-$	6.9060	0.0329	0.0194	3.3730	− 0.0354	0.3579	8	1.53 Å; 1.53 Å; 109.5°[a]
$ClCrO_3^-$	6.9102	− 0.0311	0.0097	2.3727	− 0.0903	0.2509	8	14
$NOSO_3^-$	7.4245	0.0403	0.0007	7.9661	− 0.0068	0.3935	8	1.58 Å; 1.75 Å; 109,5°[a]
$FClO_3$	8.6437	− 0.0376	0.0875	3.9221	− 0.3038	0.8491	8	14
$HOClO_3$	8.1621	− 0.0020	0.1109	3.9372	− 0.2953	0.9162	8	14
$FSiH_3$	2.8525	0.0021	− 0.0019	5.5564	− 0.0903	0.2444	10	10
$ClSiH_3$	2.8411	0.0033	− 0.0004	3.0233	− 0.0112	0.2003	10	10
$BrSiH_3$	2.8387	0.0032	− 0.0003	2.4723	− 0,0081	0.1854	10	10
$ISiH_3$	2.8183	0.0027	− 0.0002	1.9480	− 0.0059	0.1652	10	10
$HSiF_3$	6.5981	− 0.0050	0.0566	3.0666	− 0.0036	0.4434	10	10
$HSiCl_3$	3.4043	− 0.0015	0.0835	2.9205	− 0.0028	0.2397	10	10
$HSiBr_3$	3.1643	− 0.0055	0.1445	2.8644	− 0.0025	0.1691	10	10
$FSiCl_3$	3.6585	0.1275	0.0536	5.3458	− 0.0583	0.2072	10	10
$BrSiCl_3$	4.0313	0.4028	0.0883	2.3638	− 0.1835	0.2211	10	10
$ClSiBr_3$	2.9537	0.2461	0.1190	2.9452	− 0.1070	0.1895	10	10
$ISiCl_3$	3.6506	0.3485	0.0649	2.2625	− 0.1964	0.1864	10	10
$ClSiI_3$	2.3158	0.1663	0.1147	2.7594	− 0.0679	0.1307	10	10
$ISiBr_3$	4.5306	0.3209	0.1011	1.3487	− 0.1666	0.1574	10	10
$FGeH_3$	2,6591	0,0003	− 0,0001	4.2990	− 0.0043	0.1953	10	10
$ClGeH_3$	2.6567	− 0.0016	− 0,0004	2,5420	− 0.0011	0.1701	10	10
$BrGeH_3$	2.6435	− 0.0164	− 0.0080	2.3600	− 0.1941	0.1613	10	10
$IGeH_3$	2.6317	− 0.0012	− 0.0011	1.7208	− 0.0018	0.1394	10	10
$HGeCl_3$	2.9613	0.0206	0.0108	2.7304	− 0.0009	0.1935	10	10
$HGeBr_3$	2.4848	− 0.0014	0.0395	2.6225	− 0.0006	0.1547	10	10
$ClGeBr_3$	2.5719	0.0793	0.0340	2.4380	− 0.0321	0.1445	10	10
$BrSnCl_3$	2.5697	0.0396	0.0064	2.1475	− 0.0159	0.1007	10	10
$ClSnBr_3$	2.2475	0.0275	0.0142	2.2453	− 0.0132	0.1251	10	10
$BrTiCl_3$	2.9991	0.2891	0.0279	2.2677	− 0.0479	0.1035	10	10
$ClTiBr_3$	2.5824	0.1455	0.0362	2.5194	− 0.0359	0.1020	10	10

Table 1a. Symmetry force constants for species A_1 (in mydne/Å).[a] Estimated values, in the order d_{X-Z}, d_{X-Y}, angle Y−X−Y. [b] Angles assumed to be tetrahedral for all the following ions and molecules (the frequencies of Ref.[10] have not been corrected for anharmonicities. This has been done by NAGARAJAN in a physically unreasonable way (see[10,14]).

[5] A. FADINI, Z. Angew. Math. Mech. **44**, 506 [1964].
[6] W. SAWODNY, A. FADINI and K. BALLEIN, Spectrochim. Acta **21**, 995 [1965].
[7] H. SELIG and H. H. CLAASEN, J. Chem. Phys. **44**, 1404 [1952].
[8] H. SIEBERT, Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie, Springer, Berlin 1966.
[9] A. MÜLLER, B. KREBS and C. J. PEACOCK, Spectrochim. Acta, in press.
[10] A. MÜLLER, R. KEBABCIOGLU, B. KREBS and O. GLEMSER, Z. Phys. Chem. Leipzig, in press.
[11] L. E. SUTTON (Ed.), Tables of Interatomic Distances and Configuration in Molecules and Ions, The Chemical Society, London 1959 and 1965.
[12] N. J. HAWKINS, V. W. COHEN and W. S. KOSKI, J. Chem. Phys. **20**, 528 [1952].
[13] G. R. BADGLEY and R. L. LIVINGSTON, J. Amer. Chem. Soc. **76**, 261 [1954].

ZXY_3	F_{44}(E)	F_{45}(E)	F_{46}(E)	F_{55}(E)	F_{56}(E)	F_{66}(E)
OPF_3	5.8924	— 0.0492	0.1181	0.4113	0.0017	0.7121
$OPCl_3$	2.7457	— 0.0630	0.1498	0.2518	0.0063	0.3643
$OPBr_3$	2.4832	— 0.0915	0.1472	0.1759	0.0106	0.2650
OVF_3	4.7718	— 0.0070	0.0153	0.1510	0.0002	0.2903
$OVCl_3$	2.6042	— 0.0164	0.0322	0.1029	0.0017	0.2111
$OVBr_3$	2,2656	— 0.0327	0.0519	0.0821	0.0033	0.1643
$ClReO_3$	7,8090	— 0.0002	0.0014	0.4154	— 0.0019	0.1879
$BrReO_3$	7.8325	0,0001	0.0011	0.3813	— 0.0014	0.1553
SPO_3^{3-}	5.6993	— 0.1038	0.0537	0.7944	0.0035	0.4984
HPO_3^{2-}	6.2890	— 0.0711	0.1498	0.6232	0.0073	0.3801
FPO_3^{2-}	6.8917	— 0.0918	— 0.0490	0.7896	0.0033	0.4536
$HOPO_3^{2-}$	6.2168	— 0.1033	0.0507	0.8182	0.0030	0.4577
SSO_3^{2-}	6.6138	— 0.1009	0.0397	0.8552	0.0023	0.4237
HSO_3^-	7.7792	— 0.0831	0.1694	0.7624	0.0081	0.4552
FSO_3^-	8.9817	— 0.1141	0.0513	1.0294	0.0026	0.5347
$ClSO_3^-$	7.7783	— 0.1164	0.0143	1.0119	0.0008	0.1778
$HOSO_3^-$	7.7501	— 0.1272	0.0578	1.0416	0.0030	0.5621
$HOSeO_3^-$	6.1997	— 0.0077	0.0056	0.5026	— 0.0001	0.3516
$SReO_3^-$	6.7006	— 0.0001	0.0028	0.3262	— 0.0053	0.2843
$FCrO_3^-$	5.9542	— 0.0155	0.0075	0.4236	0.0002	0.2203
$ClCrO_3^-$	5.9932	— 0.0145	0.0052	0.4119	0.0001	0.1729
$NOSO_3^-$	6.4109	0.0000	0.0019	0.4752	— 0.0032	0.3071
$FClO_3$	9,8175	— 0.0936	0.0403	1.0380	0.0016	0.5321
$HOClO_3$	8,5458	— 0.0950	0.0456	0.9918	0.0017	0.5769
$FSiH_3$	2,7306	0.0013	0.0032	0.1940	— 0.0138	0.2834
$ClSiH_3$	2.7286	0.0001	0.0016	0.1998	— 0.0083	0.1956
$BrSiH_3$	2.7312	0.0001	0.0013	0.1988	— 0.0067	0.1681
$ISiH_3$	2.7563	0.0001	0.0010	0.1959	— 0.0050	0.1343
$HSiF_3$	5.5612	— 0.0454	0.0544	0.3074	0.0021	0.2573
$HSiCl_3$	2.8061	— 0.0498	0.0100	0.1835	0.0013	0.1667
$HSiBr_3$	2.3122	— 0.0896	0.0036	0.1561	0.0011	0.1475
$FSiCl_3$	4.4170	— 0.0493	0.0799	0.1686	0.0060	0.2811
$BrSiCl_3$	2.8078	— 0.0368	0.1058	0.1107	0.0010	0.3038
	2.7982	— 0.0717	0.0456	0.2383	0.0071	0.1413
$ClSiBr_3$	2.4154	— 0.0700	0.1246	0.1260	0.0097	0.2360
$ISiCl_3$	2.7226	— 0.0300	0.1042	0.0908	— 0.0000	0.3032
$ClSiI_3$	1.8249	— 0.0688	0.0940	0.1002	0.0096	0.1531
$ISiBr_3$	2,3543	— 0.0485	0.1286	0.0808	0.0033	0.2176
	2,3410	— 0.1060	0.0532	0.1874	0.0070	0.0941
$FGeH_3$	2.6502	— 0.0001	0.0009	0.1696	— 0.0134	0.2274
$ClGeH_3$	2,6427	— 0.0000	0.0007	0.1703	— 0.0095	0.1679
$BrGeH_3$	2.6378	0.0000	0.0006	0.1697	— 0.0079	0.1465
$IGeH_3$	2.6230	0.0000	0.0005	0.1633	— 0.0068	0.1238
$HGeCl_3$	2.4235	— 0.0105	— 0.0000	0.1433	0.0001	0.1320
$HGeBr_3$	2.0101	— 0.0292	— 0.0005	0.1179	0.0002	0.1156
$ClGeBr_3$	1.9836	— 0.0283	0.0368	0.1084	0.0035	0.1579
$BrSnCl_3$	2.3135	— 0.0016	0.0055	0.0566	— 0.0001	0.1470
$ClSnBr_3$	1.9199	— 0.0093	0.0149	0.0706	0.0008	0.1264
$BrTiCl_3$	2,5578	— 0.0113	0.0233	0.0701	0.0005	0.1439
$ClTiBr_3$	2.1902	— 0.0316	0.0379	0.0864	0.0046	0.1227

Table 1b. Symmetry force constants for species E (in mdyne/Å).

II. Force Constants

The symmetry force constants calculated according to the "Kopplungsstufenverfahren" of FADINI[5,6,8] are given in Tables 1 and 2. The force constants with respect to internal coordinates are not listed, because they are not necessary for the calculation of the amplitudes of vibration. The values obtained from the "Kopplungsstufenverfahren" are the better, the more characteristic the vibrations are. But, in any case, the accuracy of the F values is good enough for the calculation of reliable amplitudes of vibration.

III. Mean Amplitudes of Vibration

The mean amplitudes of vibration have been calculated from the force constants as usual[1], employing a suitable computer program. The values for

$ZXY_2(C_{2v})$	$F_{11}(A_1)$	$F_{12}(A_1)$	$F_{13}(A_1)$	$F_{22}(A_1)$	$F_{23}(A_1)$	$F_{33}(A_1)$	$F_{44}(B_1)$	$F_{45}(B_1)$	$F_{55}(B_1)$	References: frequencies	References: structural data
OCH_2	4.3205	— 0.0417	0.0130	12.0516	0.4241	1.1712	4.2122	0.0038	0.5925	8	15
OCD_2	4.4022	0.3015	— 0.0366	12.2027	0.1716	1.1976	4.3025	0.0200	0.6188	8	15
HCO_2^-	11.2122	— 0.0501	— 0.6557	4.3265	0.0425	3.0090	7.3388	0.3362	0.4814	8	15
DCO_2^-	11,3447	0,0272	— 0.5958	4.4160	0.1127	3.0376	7.0965	0.1849	0.4782	8	15
OCO_2^{2-} (unident.)	10.4421	1.8784	— 1.1286	6.4575	0.9791	3.4030	6.7457	0.5469	0.9522	14	15
OCO_2^{2-} (bident.)	8.4774	1.3315	— 0.6645	9.8812	1.1004	3.5395	5.1096	0.5663	0.8928	14	15
OCF_2	7.7108	1.1301	— 0.4343	14.1936	0.6749	2.7086	5.5169	0.5602	0.7753	8	15
$OCCl_2$	3.7659	0.4611	— 0.3141	13.1326	0.2746	1.3427	3.2149	0.4191	0.4062	8	15
$OCBr_2$	3.0868	0.4141	— 0.5016	13.3390	0.2112	1.2558	2.9865	0.3394	0.2677	8	15
SCF_2	5.9638	1.6175	— 0.3206	9.5236	0.8296	1.7696	4.9530	0.2892	0.4523	8	15
$SCCl_2$	3.8469	0.9837	— 0.1012	6.5812	0.2035	0.4880	2.7859	0.2698	0.2954	8	1,63 Å; 1,32 Å; 112°[a]
$FClF_2$	2.4001	0.3222	— 0.0308	3.8007	0.1029	1.0568	3.4472	0.1266	0.4322	8	15
$FBrF_2$	2.6928	0.1455	— 0.0058	3.7600	0.0245	0.9561	3.2074	0.0284	0.4005	14	15
$HONO_2$	10.7291	0.5967	— 0.4200	4.7530	0.5920	1.8923	8.7011	0.4305	1.0717	8	1,40 Å; 1,22 Å; 135°[16]
$DONO_2$	10.7138	0.5074	— 0.4873	4.9876	0.8741	2.3315	8.4546	0.3101	0.8066	14	1,40 Å; 1,22 Å; 135°[16]
$(CH_3)NO_2$	11.1841	0.5762	— 0.5073	4.6008	0.6051	2.1205	7.9930	0.1820	0.4915	8	15
FNO_2	10.5872	0.5158	— 0.2354	4.0241	0.2834	1.1037	10.3615	0.2966	0.7612	8	15
$ClNO_2$	10.2986	0.0703	— 0.1787	4.9349	0.3181	0.7662	9.2358	0.1307	0.3638	8	15

Table 2. Symmetry force constants (in mdyne/Å). [a] Estimated, in the order d_{X-Z}, d_{X-Y}, angle Y—X—Y.

0° and 298,2 °K are given in Tables 3 and 4. For the reason given above they are believed to be more reliable than previously published ones, for instance the calculations of NAGARAJAN et. al.[14,15a] (see also[1] where other incorrect values for Ge and Si compounds are cited).

IV. Coriolis Coupling Constants

The band contours in the infrared spectra of gaseous compounds are essentially dependent on the Coriolis coupling constants. In the case of symmetrical top molecules and especially for spherical top compounds the ζ values can be obtained from the contours.

We have calculated type E × E ζ values for the molecules ZXY_3 according to the method of MEAL and POLO[17]:

$$\boldsymbol{\zeta}^{\alpha} = \boldsymbol{L}^{-1} \cdot \boldsymbol{C}^{\alpha} \cdot (\boldsymbol{L}^{-1})' . \qquad (3)$$

However, only the physically interpretative diagonal elements of the $\boldsymbol{\zeta}$ matrices are given (Table 4). They effect the band contours of the corresponding vibrations. In the present case the sum rule is

$$\zeta_4 + \zeta_5 + \zeta_6 = I_A / 2\, I_B .$$

It should be realized that reliable ζ values can only be calculated from force constants or eigenvectors $\boldsymbol{L}$ if the latter are accurate enough, because Coriolis coupling constants are strongly dependent on the force constants, contrary to the mean amplitudes of vibration.

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[14] G. NAGARAJAN and A. MÜLLER, Z. Anorg. Allg. Chem. **349**, 87 [1967]; Monatsh. Chem. **98**, 68 [1967]. — G. NAGARAJAN, Z. Phys. Chem. Leipzig, **237**, 297 (1968)
[15] A. MÜLLER and G. NAGARAJAN, Z. Phys. Chem. Leipzig **235**, 113 [1967].
[15a] There are also some mistakes in the general expressions
[16] P. A. AKISHIN, L. V. VILKOV and V. YA. ROSOLOVSKII, Zhur. Strukt. Khim. **1**, 1 [1960].
[17] J. H. MEAL and S. R. POLO, J. Chem. Phys. **24**, 1119 [1956].

				$T = 0$				$T = 298.2$ °K			
ZXY_3	ζ_{44}	ζ_{55}	ζ_{66}	u_{X-Y}	u_{X-Z}	$u_{Y\ldots Y}$	$u_{Y\ldots Z}$	u_{X-Y}	u_{X-Z}	$u_{Y\ldots Y}$	$u_{Y\ldots Z}$
OPF_3	0.57	− 0.61	0.55	0.0385	0.0339	0.060	0.054	0.0390	0.0340	0.069	0.058
$OPCl_3$	0.75	− 0.71	0.64	0.0428	0.0353	0.060	0.058	0.0464	0.0354	0.085	0.068
$OPBr_3$	0.86	− 0.80	0.78	0.0407	0.0357	0.051	0.059	0.0464	0.0359	0.090	0.077
OVF_3	0.39	− 0.48	0.68	0.0394	0.0364	0.072	0.065	0.0404	0.0366	0.098	0.079
$OVCl_3$	0.58	− 0.57	0.74	0.0411	0.0366	0.068	0.067	0.0459	0.0369	0.112	0.090
$OVBr_3$	0.76	− 0.71	0.82	0.0384	0.0368	0.058	0.067	0.0465	0.0371	0.119	0.097
$ClReO_3$	0.13	− 0.34	0.46	0.0343	0.0432	0.060	0.067	0.0346	0.0550	0.068	0.091
$BrReO_3$	0.13	− 0.32	0.33	0.0343	0.0382	0.061	0.066	0.0346	0.0571	0.070	0.099
SPO_3^{3-}	0.61	− 0.67	0.35	0.0401	0.0439	0.057	0.059	0.0405	0.0479	0.061	0.067
HPO_3^{2-}	0.72	− 0.62	0.77	0.0392	0.0862	0.058	0.109	0.0395	0.0862	0.063	0.109
HPO_3^{2-}	0.57	− 0.64	0.53	0.0386	0.0414	0.056	0.060	0.0389	0.0423	0.060	0.067
$HOPO_3^{2-}$	0.60	− 0.66	0.54	0.0394	0.0409	0.056	0.060	0.0398	0.0415	0.059	0.067
SSO_3^{2-}	0.58	− 0.66	0.35	0.0387	0.0429	0.056	0.059	0.0390	0.0467	0.059	0.069
HSO_3^-	0.71	− 0.61	0.77	0.0373	0.0812	0.055	0.103	0.0375	0.0812	0.059	0.104
FSO_3^-	0.56	− 0.63	0.50	0.0363	0.0416	0.053	0.058	0.0364	0.0426	0.055	0.064
$ClSO_3^-$	0.57	− 0.66	0.33	0.0373	0.0440	0.055	0.066	0.0375	0.0485	0.058	0.087
$HOSO_3^-$	0.59	− 0.66	0.53	0.0374	0.0405	0.053	0.058	0.0377	0.0411	0.056	0.063
$HOSeO_3^-$	0.30	−0.43	0.60	0.0376	0.0400	0.061	0.064	0.0381	0.0411	0.068	0.074
$SReO_3^-$	0.13	−0.33	0.51	0.0357	0.0351	0.063	0.062	0.0360	0.0384	0.074	0.077
$FCrO_3^-$	0.38	−0.48	0.57	0.0384	0.0433	0.063	0.069	0.0389	0.0454	0.071	0.086
$ClCrO_3^-$	0.37	− 0.49	0.35	0.0384	0.0426	0.063	0.069	0.0388	0.0485	0.072	0.093
$NOSO_3^-$	0.14	− 0.31	0.73	0.0360	0.0356	0.061	0.065	0.0366	0.0359	0.069	0.076
$FClO_3$	0.52	−0.60	0.49	0.0354	0.0431	0.053	0.053	0.0356	0.0446	0.056	0.065
$HOClO_3$	0.54	− 0.62	0.51	0.0365	0.0439	0.054	0.059	0.0367	0.0452	0.056	0.065
$FSiH_3$	0.06	− 0.33	0.35	0.0888	0.0404	0.150	0.117	0.0888	0.0409	0.151	0.119
$ClSiH_3$	0.06	− 0.32	0.30	0.0888	0.0431	0.150	0.125	0.0888	0.0461	0.151	0.128
$BrSiH_3$	0.06	− 0.32	0.28	0.0888	0.0422	0.150	0.127	0.0888	0.0476	0.151	0.132
$ISiH_3$	0.06	− 0.31	0.27	0.0887	0.0435	0.151	0.132	0.0887	0.0516	0.152	0.139
$HSiF_3$	0.63	− 0.62	0.86	0.0397	0.0865	0.063	0.115	0.0402	0.0865	0.075	0.117
$HSiCl_3$	0.98	− 0.74	0.70	0.0432	0.0876	0.062	0.125	0.0464	0.0876	0.090	0.129
$HSiBr_3$	0.99	− 0.85	0.82	0.0421	0.0880	0.053	0.127	0.0476	0.0880	0.094	0.134
$FSiCl_3$	0.70	—	—	0.0395	0.0407	0.062	0.062	0.0416	0.0413	0.092	0.078
$BrSiCl_3$	0.70	—	—	0.0429	0.0433	0.066	0.053	0.0460	0.0502	0.106	0.077
	0.73	—	—	0.0430	0.0433	0.059	0.059	0.0460	0.0502	0.082	0.097
$ClSiBr_3$	0.85	—	—	0.0419	0.0437	0.054	0.056	0.0477	0.0471	0.100	0.084
$ISiCl_3$	0.70	—	—	0.0435	0.0429	0.069	0.052	0.0467	0.0510	0.115	0.078
$ClSiI_3$	0.89	—	—	0.0437	0.0443	0.051	0.059	0.0528	0.0480	0.112	0.099
$ISiBr_3$	0.83	—	—	0.0414	0.0487	0.057	0.049	0.0463	0.0648	0.118	0.087
	0.84	—	—	0.0414	0.0487	0.050	0.055	0.0463	0.0648	0.087	0.114
$FGeH_3$	0.02	− 0.31	0.35	0.0893	0.0401	0.154	0.122	0.0893	0.0415	0.156	0.125
$ClGeH_3$	0.02	− 0.30	0.31	0.0893	0.0407	0.154	0.128	0.0893	0.0464	0.156	0.134
$BrGeH_3$	0.02	− 0.30	0.29	0.0894	0.0379	0.155	0.128	0.0894	0.0477	0.156	0.134
$IGeH_3$	0.02	− 0.30	0.28	0.0895	0.0380	0.155	0.134	0.0895	0.0517	0.157	0.143
$HGeCl_3$	0.46	− 0.56	0.99	0.0405	0.0886	0.066	0.130	0.0461	0.0886	0.102	0.137
$HGeBr_3$	0.66	− 0.71	0.99	0.0376	0.0895	0.056	0.132	0.0476	0.0895	0.109	0.142
$ClGeBr_3$	0.69	—	—	0.0376	0.0411	0.057	0.060	0.0477	0.0472	0.111	0.099
$BrSnCl_3$	0.32	—	—	0.0400	0.0356	0.076	0.062	0.0468	0.0468	0.146	0.107
$ClSnBr_3$	0.55	—	—	0.0361	0.0406	0.061	0.063	0.0481	0.0480	0.132	0.104
$BrTiCl_3$	0.55	—	—	0.0417	0.0395	0.073	0.062	0.0464	0.0478	0.133	0.104
$ClTiBr_3$	0.75	—	—	0.0391	0.0424	0.059	0.063	0.0472	0.0476	0.122	0.109

Table 3. Coriolis coupling constants of the type E × E and mean amplitudes of vibration (in Å); where the ζ_{55} and ζ_{66} values are not given these cannot be calculated with enough accuracy. In these cases the $u_{Y\ldots Y}$ and $u_{Y\ldots Z}$ are also not very accurate (see text).

	$T = 0$				$T = 298.2°$			
ZXY_2	u_{X-Y}	u_{X-Z}	$u_{Y\ldots Y}$	$u_{Y\ldots Z}$	u_{X-Y}	u_{X-Z}	$u_{Y\ldots Y}$	$u_{Y\ldots Z}$
OCH_2	0.0805	0.0377	0.121	0.096	0.0805	0.0377	0.121	0.096
OCD_2	0.0686	0.0375	0.100	0.082	0.0686	0.0375	0.100	0.083
HCO_2^-	0.0408	0.0802	0.048	0.096	0.0409	0.0802	0.049	0.096
DCO_2^-	0.0407	0.0683	0.048	0.083	0.0408	0.0683	0.049	0.083
OCO_2^{2-} (unident.)	0.0421	0.0451	0.047	0.050	0.0422	0.0454	0.048	0.051
OCO_2^{2-} (bident.)	0.0446	0.0400	0.049	0.050	0.0448	0.0401	0.050	0.051
OCF_2	0.0434	0.0362	0.051	0.048	0.0436	0.0362	0.053	0.050
$OCCl_2$	0.0480	0.0368	0.054	0.052	0.0498	0.0369	0.068	0.058
$OCBr_2$	0.0474	0.0367	0.046	0.052	0.0506	0.0368	0.071	0.062
SCF_2	0.0453	0.0383	0.053	0.049	0.0457	0.0385	0.056	0.053
$SCCl_2$	0.0491	0.0416	0.059	0.052	0.0509	0.0420	0.083	0.065
$FClF_2$	0.0466	0.0435	0.070	0.059	0.0493	0.0450	0.085	0.064
$FBrF_2$	0.0438	0.0412	0.071	0.059	0.0468	0.0432	0.088	0.066
$HONO_2$	0.0389	0.0463	0.048	0.052	0.0390	0.0469	0.049	0.054
$DONO_2$	0.0391	0.0458	0.047	0.053	0.0391	0.0463	0.048	0.055
$(CH_3)NO_2$	0.0393	0.0473	0.048	0.057	0.0394	0.0478	0.049	0.060
FNO_2	0.0379	0.0472	0.052	0.055	0.0380	0.0481	0.055	0.059
$ClNO_2$	0.0387	0.0425	0.053	0.055	0.0388	0.0434	0.056	0.063

Table 4. Mean amplitudes of vibration (in Å).