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Short Communications

Normal Coordinate Analysis and Molecular Constants of Tetrolyl Chloride

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Recently we made a complete infrared and Raman spectral study [1] of propiolyl chloride (propiolic acid chloride) HC≡CCOCl and tetrolyl chloride (tetrolic acid chloride) CH_3C≡CCOCl and discussed the assignment of the fundamental vibrational modes. Our attention was particularly drawn to the low frequency vibrations of the COCl group and the relatively free internal rotation of the methyl group of tetrolyl chloride, which was evident from the IR spectrum.

Harmonic force fields [2] were recently developed for the four structurally related molecules HC≡CCOCl, ClC≡CCHO, BrC≡CCHO, and IC≡CCHO. Mean amplitudes of vibration and related quantities were calculated.[3] The molecules display very similar magnitudes of mean amplitudes for corresponding distance types. The present normal coordinate analysis of tetrolyl chloride (TC) has been used to evaluate the following molecular constants:[4] (i) mean amplitudes of vibration, (ii) perpendicular amplitude correction coefficients, and (iii) Bastiansen-Morino linear shrinkage effects.

Symmetry coordinates. The molecular model is shown in Fig. 1. The applied values of interatomic distances are estimated from data of structurally related molecules.[5–7] Tetrahedral angles were assumed.

The symmetry of TC is discussed elsewhere.[1] There are in all $3N-7=20$ fundamentals since one internal rotational degree of freedom replaces the torsional motion of the methyl group. The calculations are based on a rigid molecular model having C_s symmetry in its equilibrium position. The additional vibrational degree of freedom is associated with the torsional motion. In order to test numerically the influences of the almost free internal rotation of the CH_3-group the calculations were performed for torsional frequencies of 20 and 50 cm^{-1}.

The vibrational modes are distributed among the irreducible representations of the C_s point group according to:

$$\Gamma_{\mathrm{vib}} = 14\,a' + 7\,a''$$

A suitable set of symmetry coordinates is obtained by combining those for the pyramidal XY_3Z-model [8] and the halopropynal model.[3] In the latter case the valence coordinates are already symmetry coordinates, constituting $S_1(a')$ to $S_9(a')$ and $S_{15}(a'')$ to $S_{17}(a'')$. The remaining nine coordinates are transferred from the C_{3v}-model XY_3Z by correlating the $S(a_1)$ and $S_a(e)$ coordinates to those of the a' type and the $S_b(e)$ coordinates to those of a''. There is one redundant zero-coordinate in species a'. The

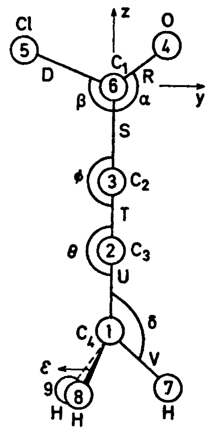

Fig. 1. The $CH_3CCCOCl$ model. The structural parameters are given (capital letters). Stretching valence coordinates are identified by the corresponding small letters. The symbols used for the different types of bending coordinates are indicated. Symmetry coordinates, a'-species: $S_1=\mathrm{r}$, $S_2=\mathrm{d}$, $S_3=\mathrm{s}$, $S_4=\mathrm{t}$, $S_5=\mathrm{u}$, $S_6=(\mathrm{RS})^{\frac{1}{2}}\alpha$, $S_7=(\mathrm{DS})^{\frac{1}{2}}\beta$, $S_8=(\mathrm{ST})^{\frac{1}{2}}\phi_y$, $S_9=(\mathrm{TU})^{\frac{1}{2}}\theta_y$, $S_{10}=3^{-\frac{1}{2}}(\mathrm{v}_1+\mathrm{v}_2+\mathrm{v}_3)$, $S_{11}=6^{-\frac{1}{2}}(2\mathrm{v}_1-\mathrm{v}_2-\mathrm{v}_3)$, $S_{12}=\left\{\frac{\mathrm{V}}{3[\mathrm{V}(4-\sec^2\mathrm{E})+\mathrm{U}]}\right\}^{\frac{1}{2}}[(4-\sec^2\mathrm{E})^{\frac{1}{2}}\mathrm{V}(\varepsilon_1+\varepsilon_2+\varepsilon_3)-\mathrm{U}(\delta_1+\delta_2+\delta_3)]$, $S_{13}=6^{-\frac{1}{2}}\mathrm{V}(2\varepsilon_1-\varepsilon_2-\varepsilon_3)$, $S_{14}=6^{-\frac{1}{2}}(\mathrm{VU})^{\frac{1}{2}}(2\delta_1-\delta_2-\delta_3)$; a''-species: $S_{15}=(\mathrm{ST})^{\frac{1}{2}}\phi_x$, $S_{16}=(\mathrm{TU})^{\frac{1}{2}}\theta_x$, $S_{17}=[(\mathrm{RD})^{\frac{1}{2}}\mathrm{S}]^{\frac{1}{2}}\gamma_{5463}$, $S_{18}=2^{-\frac{1}{2}}(\mathrm{v}_2-\mathrm{v}_3)$, $S_{19}=2^{-\frac{1}{2}}\mathrm{R}(\varepsilon_2-\varepsilon_3)$, $S_{20}=2^{-\frac{1}{2}}(\mathrm{RD})^{\frac{1}{2}}(\delta_2-\delta_3)$, $S_{21}=(\mathrm{VD})^{\frac{1}{2}}\tau_{7165}$. Redundant zero coordinate in species a′:

$$\mathrm{V}\left\{\frac{\mathrm{U}}{3[\mathrm{V}(4-\sec^2\mathrm{E})+\mathrm{U}]}\right\}^{\frac{1}{2}}[\varepsilon_1+\varepsilon_2+\varepsilon_3+(4-\sec^2\mathrm{E})^{\frac{1}{2}}(\delta_1+\delta_2+\delta_3)]=0.$$

torsional coordinate is $S_{21}(a'')=\sqrt{VD}\tau_{7165}$, (see Fig. 1).

Force constants. The standard Wilson *GF* matrix method [9] in terms of symmetry coordinates was applied. The initial force constants were taken from Devarajan and Cyvin [10] and Rogstad and Cyvin.[3] Also nonvanishing off-diagonal elements from the *F*-matrix [3] of HC≡COCl were included in the initial force field (F_0). A final force field was produced by iterative calculations in order to fit exactly the observed vibrational frequencies. The diagonal elements of the initial and refined force constant matrices are given in Table 1. Table 2 shows that the frequencies calculated from the initial set of force constants give good agreement with the observed frequencies. This indicates that most of the force constants are transferable among related molecules.

Table 1. Force constants (mdyn/Å) for tetrolyl chloride, $CH_3CCCOCl$.

	Initial	Final
Species a'		
$F_{11}(C_1=O)$	10.38	10.19
$F_{22}(C_1-Cl)$	3.97	4.11
$F_{33}(C_1-C_2)$	4.20	4.55
$F_{44}(C_2\equiv C_3)$	15.57	15.22
$F_{55}(C_3-C_4)$	3.95	3.92
$F_{66}(C_1C_2O)$	1.21	1.20
$F_{77}(C_1C_2Cl)$	0.660	0.646
$F_{88}(C_1C_2C_3)$	0.197	0.214
$F_{99}(C_2C_3C_4)$	0.133	0.160
$F_{10\,10}(C_4-H)$	4.90	4.91
$F_{11\,11}(C_4-H)$	4.70	4.66
$F_{12\,12}(HC_4H)$	0.415	0.381
$F_{13\,13}(HC_4H)$	0.450	0.433
$F_{14\,14}(HC_3C_4)$	0.430	0.414
Species a''		
$F_{11}(C_1C_2C_3)$	0.126	0.136
$F_{22}(C_2C_3C_4)$	0.181	0.164
$F_{33}(OC_1Cl)$	0.241	0.221
$F_{44}(C_4H)$	4.70	4.66
$F_{55}(HC_4H)$	0.450	0.432
$F_{66}(HC_3C_4)$	0.430	0.407
F_{77}(torsion)	0.0008	0.0004

Potential energy distribution. Calculated potential energy distribution terms,[11,12] $100\,F_{ii}L_{ik}/\lambda_k$, are listed in Table 2. The approximate descriptions of normal modes according to these calculations are fairly well compatible with the assignments [1] of frequencies done *a priori*.

Mean amplitudes of vibration and related quantities. The harmonic force field developed was used to calculate the mean amplitudes of vibration (u), perpendicular amplitude correction coefficients (K) and Bastiansen-Morino shrinkages (δ) for the linear chain. The u- and δ-values are given in Table 3. The interatomic separations (R) are included in the table. Only for two distance types of the totality of twenty-four we may expect the mean amplitudes to depend significantly on the barrier of internal rotation. They are the O···H and Cl···H types. The corresponding mean amplitudes are not quoted. As expected the linear shrinkage effects are unaffected by variations in the torsional frequency, whereas the perpendicular correction coefficients (except those for the linear chain) increase considerably on diminishing the barrier of internal rotation. These values are therefore not reported.

Table 2. Vibrational frequencies (cm^{-1}) and distribution of potential energy for tetrolyl chloride, $CH_3CCCOCl$.

	Obs.	Calc.	PED
Species a'			
ν_1	2961	2974	99 v
ν_2	2921	2918	99 v
ν_3	2225	2259	85 t
ν_4	1758	1772	76 r
ν_5	1431	1459	91 ε
ν_6	1378	1451	90 ε
ν_7	1161	1063	41 s + 28 α + 21 d
ν_8	1016	1041	87 δ
ν_9	842	865	42 u + 27 α
ν_{10}	600	639	23 d
ν_{11}	472	542	47 β + 36 ϕ_y + 30 d + 20 s
ν_{12}	395	406	35 α
ν_{13}	293	271	48 θ_y + 31 β
ν_{14}	104	84	51 ϕ_y + 27 θ_y + 22 β
Species a''			
ν_{15}	2961	2974	99 v
ν_{16}	1431	1459	92 ε
ν_{17}	1016	1043	89 δ
ν_{18}	652	679	83 γ
ν_{19}	365	412	75 θ_x + 32 ϕ_x
ν_{20}	135	123	57 ϕ_x + 23 θ_x
ν_{21}	20[a]	29	100 τ

[a] Unobserved; calc. are also performed for $\nu_{21}=50$ cm^{-1}, giving the following numerical variations in the PED terms: $\nu_{18}-84\gamma, \nu_{20}-58\phi_x+24\theta_x, \nu_{21}-99\tau$.

The calculated mean amplitudes of vibration were compared with those of propiolyl chloride,[3] propiolaldehyde,[3] and methylated acetylenes.[5,10] Reported values [3,5,10] for various bonded and nonbonded distances were found to be very well consistent with those listed in Table 3. Also the listed values of shrinkage effects (Table 3) were found to be compatible with characteristic

Table 3. Mean amplitudes of vibration (u in Å) and linear shrinkage effects (δ in Å) for tetrolyl chloride, $CH_3CCCOCl$.

Distance	(R, Å)	0 K	298 K
$u(C_1=O)$	(1.192)	0.039	0.039
$u(C_1-Cl)$	(1.789)	0.045	0.047
$u(C_1-C_2)$	(1.426)	0.048	0.049
$u(C_2\equiv C_3)$	(1.207)	0.036	0.036
$u(C_3-C_4)$	(1.458)	0.049	0.051
$u(C_4-H)$	(1.110)	0.078	0.078
$u(C_1\cdots C_3)$	(2.633)	0.051	0.053
$u(C_1\cdots C_4)$	(4.091)	0.062	0.066
$u(C_1\cdots H)$	(4.582)	{0.135 {0.134	{0.154 {0.151
$u(C_2\cdots C_4)$	(2.665)	0.053	0.055
$u(C_2\cdots O)$	(2.346)	0.055	0.059
$u(C_2\cdots Cl)$	(2.683)	0.058	0.069
$u(C_2\cdots H)$	(3.210)	{0.125 {0.123	{0.132 {0.129
$u(C_3\cdots O)$	(3.484)	0.059	0.067
$u(C_3\cdots Cl)$	(3.710)	0.068	0.101
$u(C_3\cdots H)$	(2.106)	0.109	0.110
$u(C_4\cdots O)$	(4.903)	0.071	0.092
$u(C_4\cdots Cl)$	(5.057)	0.081	0.143
$u(O\cdots Cl)$	(2.602)	0.053	0.060
$u(O\cdots H)$	(5.181)	0.156	0.207
$u(O\cdots H)$	(5.461)	0.143	–
$u(Cl\cdots H)$	(5.349)	0.181	–
$u(Cl\cdots H)$	(5.814)	0.122	0.143
$u(H\cdots H)$	(1.813)	0.128	0.128
$\delta(C_1\cdots C_3)$	(2.633)	0.007	0.012
$\delta(C_1\cdots C_4)$	(4.091)	0.015	0.030
$\delta(C_2\cdots C_4)$	(2.665)	0.008	0.012

values deduced from structurally related molecules.[3,5,10]

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Aqueous Chemistry of Protactinium(IV). 3. Solvent Extraction of Pa(IV) Perchlorate by Trioctyl Phosphine Oxide

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In studying the aqueous chemistry of Pa(IV)[1,2] it was found that a pH independent extraction method would be of value. An investigation of the extraction of Pa(IV) from perchlorate solutions by neutral adduct forming agents was therefore undertaken. The neutral organophosphorus compounds, which are among the strongest adduct forming molecules,[3] were selected for this investigation. Because the commonly used TBP (tributylphosphate) showed unsatisfactory extraction power, the more basic TOPO (trioctyl phosphine oxide) was chosen for a more detailed study.

Chemicals. Stock solutions of ^{233}Pa (in 7 M $HClO_4$), $(Na,H)ClO_4$, Zn(Hg) and 1.92 M $Cr(ClO_4)_3$ were prepared as described earlier.[1] The isotopes ^{51}Cr and ^{65}Zn were supplied from AB Atomenergi, Studsvik, Sweden, and Institutt for Atomenergi, Kjeller, Norway, respectively. The ^{24}Na was obtained by 1.8 h neutron irradiation (AB Atomenergi, Studsvik, Sweden) of 30 mg Na_2CO_3 at a neutron flux of 2.5×10^{12} n s^{-1} cm^{-2}. Stock solutions of ^{51}Cr (9 mCi/ml) in 0.1 $HClO_4$, ^{65}Zn (0.2 mCi/ml) in 1 M $HClO_4$, and ^{24}Na (0.4 mCi/ml)