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A Tensorial Approach to the Description of Molecular Distortions I. Tetrahedral Molecules

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The inclusion of a tetrahedral XY_4 molecule (or ion) in a crystal is, very often, followed by a lowering of its symmetry. In order to describe the apparent distortions of the tetrahedron, second-rank tensors were constructed. It was shown that the characteristic surface of such a tensor is always an ellipsoid. The relative lengths of the axes of the ellipsoid and their position with respect to the symmetry elements of the XY_4 group can be used to determine the effective symmetry of the molecule, as well as the degree of its distortion. Some of the spectral properties of the studied compounds can also be predicted. 36 SO_4 ions with accurately refined structures were investigated and the results obtained by this method were compared with the results¹ obtained by other²⁻⁴ methods. A correlation of rather high significance ($r^2 = 0.97$) was found between the main components of the tensor and the frequencies of the components of the antisymmetric stretching vibration (ν_3) of the molecule.

INTRODUCTION

In a number of solid state studies of molecules, a lowering of symmetry is observed. In most cases, the local symmetry of such molecules is C_1 — the lowest one possible (see e.g. Baur²). Despite this, it may be important to determine the so-called »effective« symmetry (the term »co-kernel« symmetry is sometimes used in the same sense³), since it often seems that the latter is higher than the local crystallographic one.^{5,6} Unfortunately, it is not altogether clear how the effective symmetry can be exactly determined. One of the possible approaches is based on the use of symmetry coordinates, as shown by Murray-Rust et al.^{3,4,7}

Several methods have so far been used to describe the distortions of tetrahedral molecules in crystals.^{2-4,7,8} Baur² uses distortion indices, Murray-Rust et al.^{3,4} employ displacement vectors and Dollase⁸ defines the degree of distortion as the average distance between corresponding atoms of the

given molecule and the reference one, the latter being chosen as the »... least-squares bestfit polyhedron with optimum location, orientation, size parameters and prescribed symmetry«.⁸

The intention of the present work is to show that the degree of distortion and the effective symmetry of the tetrahedron can be quantitatively expressed by the use of tensors. In addition to this, some spectra-structure correlations are also pointed out.

MATHEMATICAL METHOD

Let us consider a second-rank tensor with components constant with respect to some space-fixed coordinate system. If we denote the components as \mathbf{T}_{ij} ($i, j \in \{1, 2, 3\}$), the tensor will define a second-order surface in the tridimensional space, given by:

$$\begin{aligned} \mathbf{T}_{11} \cdot x^2 + \mathbf{T}_{22} \cdot y^2 + \mathbf{T}_{33} \cdot z^2 + (\mathbf{T}_{12} + \mathbf{T}_{21}) \cdot x \cdot y + (\mathbf{T}_{13} + \mathbf{T}_{31}) \cdot x \cdot z + \\ + (\mathbf{T}_{23} + \mathbf{T}_{32}) \cdot y \cdot z = 1 \end{aligned} \quad (1)$$

or

$$\sum \mathbf{T}_{ij} \cdot x_i \cdot x_j = 1 \quad i, j \in \{1, 2, 3\} \quad x_1 \equiv x \quad x_2 \equiv y \quad x_3 \equiv z \quad (2)$$

In the domain of orthogonal transformations, it can be proved (see Appendix 1) that the surface does not depend on the choice of the coordinate system. This allows us to use only Cartesian orthogonal coordinates in which case the covariant and contravariant vectors and tensors coincide and we decide on writing their indices as subscripts.

Let XY_4 be the molecule of interest. The following notation is used:

$$\vec{\text{XY}}_1 = \mathbf{p} = \{p_1, p_2, p_3\}$$

$$\vec{\text{XY}}_2 = \mathbf{q} = \{q_1, q_2, q_3\}$$

$$\vec{\text{XY}}_3 = \mathbf{r} = \{r_1, r_2, r_3\}$$

$$\vec{\text{XY}}_4 = \mathbf{s} = \{s_1, s_2, s_3\}$$

If we write

$$\mathbf{T}_{ij} = \frac{p_i \cdot p_j}{|\mathbf{p}|^\delta} + \frac{q_i \cdot q_j}{|\mathbf{q}|^\delta} + \frac{r_i \cdot r_j}{|\mathbf{r}|^\delta} + \frac{s_i \cdot s_j}{|\mathbf{s}|^\delta} \quad i, j \in \{1, 2, 3\} \quad (3)$$

it is obvious that the right-hand side of equation (3) is a tensorial quantity and so it is independent of the choice of the coordinate system which can, therefore, be chosen quite arbitrarily. The quantity δ is a constant and will be discussed in more detail later.

Let us now briefly examine some characteristic cases:

a) Let the atoms Y_1, Y_2, Y_3, Y_4 be at the corners and the atom X in the center of a regular tetrahedron. The $X - Y_1$ distance is fixed as a unit of length and the x, y, z axes of the coordinate system are chosen to coincide with the C_2 axes of the molecule. The coordinates of the atoms are:

$$X - (0, 0, 0)$$

$$\begin{aligned}
 Y_1 &= (0, \sqrt{3}/3, \sqrt{2}/3) \\
 Y_2 &= (0, \sqrt{3}/3, -\sqrt{2}/3) \\
 Y_3 &= (\sqrt{2}/3, -\sqrt{3}/3, 0) \\
 Y_4 &= (-\sqrt{2}/3, -\sqrt{3}/3, 0)
 \end{aligned}$$

Substituting these coordinates (since they are, at the same time, the components of the four vectors) into (3), one obtains

$$(\mathbf{T}_{ij}) = \begin{bmatrix} \frac{4}{3} & 0 & 0 \\ 0 & \frac{4}{3} & 0 \\ 0 & 0 & \frac{4}{3} \end{bmatrix} \quad (4)$$

This tensor defines the surface:

$$x^2 + y^2 + z^2 = \frac{3}{4} \quad (4a)$$

and it can, thus, be concluded that the characteristic surface of a tensor adjoint to a regular tetrahedron is a sphere.

b) Let the atoms Y_1, Y_2, Y_3, Y_4 be at the corners of a regular trilateral pyramid with X and Y_4 lying on the C_3 axis. If the coordinate system is chosen in such a way that the z -axis coincides with the C_3 -symmetry axis and Y_1 lies in the yz plane, the coordinates of the atoms would be:

$$\begin{aligned}
 X &= (0, 0, 0) \\
 Y_1 &= (0, \sqrt{8}/3, \mu) \\
 Y_2 &= (\sqrt{6}/3, -\sqrt{2}/3, \mu) \\
 Y_3 &= (-\sqrt{6}/3, -\sqrt{2}/3, \mu) \\
 Y_4 &= (0, 0, \nu)
 \end{aligned}$$

where μ and ν are arbitrary parameters. It follows from (3) that

$$(\mathbf{T}_{ij}) = \begin{bmatrix} \frac{4}{3\omega} & 0 & 0 \\ 0 & \frac{4}{3\omega} & 0 \\ 0 & 0 & \frac{3\mu^2}{\omega} + \nu^{2\delta} \end{bmatrix} \quad (5)$$

with $\omega = (\frac{8}{9} + \mu^2)^{\delta/2}$.

This tensor defines the surface:

$$\frac{4}{3\omega} \cdot x^2 + \left(\frac{4}{3\omega}\right) \cdot y^2 + \left(\frac{3\mu^2}{\omega} + \nu^{2\delta}\right) \cdot z^2 = 1 \quad (5a)$$

Hence, for XY_4 molecules with C_{3v} symmetry the characteristic surface of the tensor is an ellipsoid of revolution, the C_3 -axis being the axis of revolution.

c) Let D_{2d} be the symmetry of the molecule; the y -axis is set to coincide with the S_4 -axis, while the atoms Y_1 and Y_2 are placed in the yz -plane and the atoms Y_3 and Y_4 — in the xy -plane, respectively. If, as earlier, the $X - Y_1$ distance is chosen as a unit of length, the coordinates of the atoms would be:

$$\begin{aligned} X &= (0, 0, 0) \\ Y_1 &= (0, \cos \varphi, \sin \varphi) \\ Y_2 &= (0, \cos \varphi, -\sin \varphi) \\ Y_3 &= (\sin \varphi, -\cos \varphi, 0) \\ Y_4 &= (-\sin \varphi, -\cos \varphi, 0) \end{aligned}$$

(φ is the angle between \vec{XY}_1 and y -axis). The characteristic surface is again ellipsoid of revolution

$$2 \sin^2 \varphi \cdot x^2 + 4 \cos^2 \varphi \cdot y^2 + 2 \sin^2 \varphi \cdot z^2 = 1 \quad (6)$$

the axis of revolution coinciding, in this case, with the $y \equiv S_4$ -axis.

d) Suppose D_2 is the local symmetry of the molecule (for C_{2v} symmetry the discussion is analogous). If the axes of the coordinate system are chosen to pass through the C_2 axes of the molecule and $X - Y_1 = 1$ is taken for convenience, one can write the coordinates of the atoms as

$$\begin{aligned} X &= (0, 0, 0) \\ Y_1 &= (\chi, \nu, \zeta) \\ Y_2 &= (-\chi, \nu, -\zeta) \\ Y_3 &= (-\chi, -\nu, \zeta) \\ Y_4 &= (\chi, -\nu, -\zeta) \end{aligned}$$

where $\chi^2 + \nu^2 + \zeta^2 = 1$. Substituting these coordinates into (3), one obtains a tensor for which the characteristic surface is

$$4\chi^2 \cdot x^2 + 4\nu^2 \cdot y^2 + 4\zeta^2 \cdot z^2 = 1 \quad (7)$$

The axes of the corresponding ellipsoid are: $a = \frac{1}{2\chi}$, $b = \frac{1}{2\nu}$, $c = \frac{1}{2\zeta}$, and thus this ellipsoid is not an ellipsoid of revolution.

e) In fact, it can be proved (see Appendix 2) that the characteristic surface of the tensor is always an ellipsoid, even if the distortion of the tetrahedron is quite arbitrary.

From the arguments given so far, it can be concluded that the symmetry of the XY_4 molecule may be also described by the properties of the adjoined tensor (i. e. the properties of its characteristic surface). Therefore, if the molecule possesses some non-trivial symmetry, at least some of the axes of the

ellipsoid will lie on some symmetry-elements. For C_{3v} and D_{2d} symmetry, the ellipsoid is a solid of revolution, i. e. two of its axes have equal lengths. Hence, the axes a, b, c and their position with respect to the symmetry elements of the tetrahedron may be used to determine (strictly or approximately, depending on the local symmetry) the effective symmetry of the XY_4 group.

Now, we turn back to the value that should be assigned to the constant δ . It is easy to prove that δ has to be greater than 2 — otherwise the ellipsoid would not be »well-behaved«. The crucial assumption was that there should be some interdependence between the components of the tensor and the vibrational energy levels in the molecule (see below). Therefore, it was necessary to assign δ such a value that the components of the tensor should properly reflect the changes in the energy levels (caused by varying the $X-Y_i$ distances). It seemed reasonable to us to suppose that the covalent forces depend on the distance between the atoms in the same way as the overlap forces (except for the sign). From the reasons mentioned above, a value of 12 was assigned to δ — by analogy to the r^{12} term in the Lennard-Jones potential (it is this term that is believed to reflect, the existence of overlap forces).

When the distortion is arbitrary, all the components of the tensor are non-zero. Using an orthogonal-similarity transformation, it is possible⁹ to transform the tensor (\mathbf{T}_{ij}) into another — diagonal tensor (\mathbf{T}'_{ij}):

$$\Gamma \times \begin{bmatrix} \mathbf{T}_{11} & \mathbf{T}_{12} & \mathbf{T}_{13} \\ \mathbf{T}_{21} & \mathbf{T}_{22} & \mathbf{T}_{23} \\ \mathbf{T}_{31} & \mathbf{T}_{32} & \mathbf{T}_{33} \end{bmatrix} \times \Gamma^{-1} = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix} \quad (8)$$

where Γ is some orthogonal matrix.

One can easily calculate the axes of the ellipsoid by use of the components of (\mathbf{T}'_{ij}), which are usually called the main components of (\mathbf{T}_{ij}):

$$a = \frac{1}{\sqrt{\lambda_1}} \quad b = \frac{1}{\sqrt{\lambda_2}} \quad c = \frac{1}{\sqrt{\lambda_3}} \quad (9)$$

In practice, the main components are calculated as solutions of the determinantal equation:

$$\begin{vmatrix} \mathbf{T}_{11} - \lambda & & \mathbf{T}_{12} & & \mathbf{T}_{13} \\ & \mathbf{T}_{21} & & \mathbf{T}_{22} - \lambda & & \mathbf{T}_{23} \\ & & \mathbf{T}_{31} & & \mathbf{T}_{32} & & \mathbf{T}_{33} - \lambda \end{vmatrix} = 0 \quad (10)$$

In the above equations, the λ_i — components were chosen in such a way that $\lambda_1 \leq \lambda_2 \leq \lambda_3$ and hence $a \geq b \geq c$. The excentricities of the ellipsoid — b/a , c/a and c/b — are proportional to the degree of distortion of the molecule. Going one step further, we define the total distortion as:

$$D_t = [(1 - \frac{b}{a})^2 + (1 - \frac{c}{a})^2 + (1 - \frac{c}{b})^2]/3 \quad (11)$$

(as defined above, D_t is scaled between 0 and 1).

* The ellipsoid must collapse into an ellipse, if one of the $X-Y_i$ distances becomes infinitesimal. If, on the other hand, the $X-Y_i$ bond is infinitely stretched, the corresponding axis of the ellipsoid will increase in length and becomes infinitely long as the rest of the molecule becomes complanar.

RESULTS AND DISCUSSION

The distortions of a series of sulfate-ions, taken from compounds with precisely refined structures ($\sigma(s - o) \leq 0.005 \text{ \AA}$)⁺ and calculated by use of the method of Baur², Murray-Rust et al.^{3,4} and our method, are comparatively presented in Table I. Although it can be seen that for the vast majority of compounds there is some correspondence between the measures of distortion obtained by various methods, a direct comparison is not possible since it is not clear which of the quantities $DI(TO)$, $DI(OTO)$, $DI(OO)$ on the one hand, and $D_2(E)$, $D_3(F_2)$, $D_4(F_2)$ on the other, should be compared with D_t . Moreover, the relative differences in the D_t — values are, in some cases, much larger than e. g. the differences in the distortion indices. Because of these differences and the inability to make direct comparisons, it is natural to question the possible advantages of the present method over the existing ones.

We think that our method has indeed some advantages, some of the reasons being outlined below:

a) The tensor adjoined to XY_4 reflects in a simple way the local or effective symmetry of the molecule. Such an information is not obtainable from either the distortion indices, or the $D_3(F_2)$ and $D_4(F_2)$ displacement vectors in molecules with D_{2d} or D_2 symmetry (see e. g. the results for Na_2SO_4 and $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ in Table I).

b) In some cases, such as $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$, two of the ellipsoid axes are almost equal in length (for $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ they are equal by symmetry). This finding is consistent with C_{3v} or D_{2d} approximate (effective) symmetry. On the other hand, in all cases cited above, two components of the ν_3 mode are found in the vibrational spectra, which is in ideal agreement with the $T_d \rightarrow C_{3v}$ and $T_d \rightarrow D_{2d}$ correlation diagrams¹⁰ for descent of symmetry. It should be mentioned again that $DI(TO)$, $D_3(F_2)$ and $D_4(F_2)$ are all equal to zero, for both $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ and Na_2SO_4 . If some of these parameters should be correlated* with the spectroscopic ones, it could only be concluded (incorrectly!) that there is no splitting at all of the ν_3 modes in these compounds, which is in discrepancy with the existing doublet — for $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ and triplet — for Na_2SO_4 , in this spectral region.**

c) The total distortion of the sulfate ions in $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is very small (cf. Table I), two of the axes of the ellipsoid being, in addition, equal

⁺ The convention of crystallographers to use ångström (Å) as a unit of length, rather than picometer (pm) or nanometer (nm) is adopted in this work.

* In fact, we do not see any possibility of correlating the frequencies of the ν_3 -mode bands with some of the distortion indices or displacement vectors. The method of Dollase⁸ has the same shortcoming, although it has the advantage of giving a single parameter as the measure for the distortion of a coordination polyhedron.

** We mention here that in all cases where it was known that there are selenate compounds isostructural with sulfate ones, the spectra were recorded from selenates containing a small amount (~ 1%) of isomorphously isolated SO_4^{2-} ions. As a consequence of the restricted resonant interactions (Davydov-splitting and similar crystal effects) it is believed^{11,12,5,6} that the spectra of such samples reflect the effective SO_4^{2-} symmetry better than the spectra of pure sulfate compounds.

TABLE I
Distortions of Sulfate Ions. Results Obtained by Various Methods.

Compound	$D_1(TO)$	$D_1(OO)$	$D_2(E)^\circ$	$D_3(F_2)/\text{\AA}$	$D_4(F_2)^\circ$	$d/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$D_1 \cdot 10^4$	Ref.
»Free« SO_4^{2-}	0.0000	0.0000	0.0000	0.0000	0.0000	5.990	5.990	5.990	0	4
$\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	0.0020	0.0041	0.0000	0.0007	1.102	6.130	6.130	6.065	7	13
$\text{K}_3\text{Na}(\text{SO}_4)_2$	0.0059	0.0027	0.0000	0.020	0.735	6.042	5.958	5.958	13	14
$3\text{MgSO}_4 \cdot \text{Mg}(\text{OH})_2 \cdot \text{H}_2\text{O}$	0.0000	0.0061	1.732	0.000	0.000	6.032	5.918	5.918	24	15
$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$	0.0000	0.0110	3.118	0.000	0.000	5.983	5.785	5.785	73	16
Na_2SO_4	0.0000	0.0106	3.412	0.000	0.000	6.201	6.076	5.941	88	17
K_2SO_4	0.0034	0.0024	0.520	0.012	0.574	6.023	5.988	5.770	104	18
$\text{Cu}(\text{C}_6\text{H}_6\text{N}_4)\text{SO}_4 \cdot 5\text{H}_2\text{O}$	0.0038	0.0056	0.702	0.013	1.528	6.035	5.915	5.738	124	19
$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	0.0039	0.0051	0.531	0.013	1.482	6.075	6.049	5.766	160	20
LiRbSO_4	0.0055	0.0020	0.426	0.018	0.324	6.033	5.841	5.670	183	21
$(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	0.0051	0.0058	0.624	0.018	1.873	6.134	6.068	5.750	226	22
$\text{C}_3\text{H}_{12}\text{N}_2\text{O}_5\text{SO}_4 \cdot \text{H}_2\text{O}$	0.0049	0.0067	0.902	0.019	1.934	6.341	6.067	5.843	313	23
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	0.0010	0.0195	2.754	0.004	4.800	6.126	6.122	5.773	219	24
$\text{VOSO}_4 \cdot 6\text{H}_2\text{O}$	0.0054	0.0091	0.551	0.019	2.632	6.300	5.920	5.809	335	25
$\text{C}_3\text{H}_{14}\text{N}_4 \cdot \text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$	0.0072	0.0078	0.361	0.024	2.418	6.163	5.811	5.655	359	26
$\text{VOSO}_4 \cdot 5\text{H}_2\text{O} - \beta$	0.0073	0.0073	0.924	0.023	2.078	6.308	6.135	5.743	428	27
$\text{HgSO}_4 \cdot \text{H}_2\text{O}$	0.0076	0.0042	0.808	0.029	1.027	6.424	6.177	5.777	527	28
$\text{Te}(\text{OH})_6 \cdot \text{Na}_2\text{SO}_4$	0.0073	0.0103	1.779	0.027	3.437	6.485	5.986	5.779	632	29
NH_4LiSO_4	0.0089	0.0196	5.590	0.031	2.590	5.651	5.338	4.987	706	30
$\text{C}_5\text{H}_{17}\text{MnNO}_{10}\text{S}$	0.0104	0.0064	1.332	0.038	1.794	6.475	5.863	5.653	878	31

Table I to be continued

Table I continued

Compound	$Dl(TO)$	$Dl(OT)$	$Dl(OO)$	$D_2(E)^\circ$	$D_3(F_2)/\text{Å}$	$D_4(F_3)^\circ$	$d/\text{Å}^3$	$b/\text{Å}^3$	$c/\text{Å}^3$	$D_1 \cdot 10^5$	Ref.
$\text{Te}(\text{OH})_6 \cdot \text{K}_2\text{SO}_4$	0.0100	0.0085	0.0063	2.339	0.037	1.187	6.555	6.347	5.721	897	32
$(\text{NH}_4)_3\text{In}(\text{SO}_4)_3$	0.0127	0.0129	0.0091	3.694	0.038	1.179	6.135	5.806	5.320	918	33
$\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$	0.0104	0.0110	0.0038	1.612	0.035	3.034	6.457	5.727	5.643	963	34
$\text{Na}_3\text{H}(\text{SO}_4)_2$	0.0103	0.0131	0.0030	1.021	0.036	3.673	6.481	5.785	5.579	1072	35
$(\text{NH}_4)_3\text{In}(\text{SO}_4)_3$	0.0142	0.0082	0.0061	1.572	0.045	2.281	6.268	5.802	5.310	1202	33
$(\text{NH}_4)_3\text{In}(\text{SO}_4)_3$	0.0155	0.0094	0.0077	2.663	0.048	1.463	6.359	5.916	5.342	1328	33
$\text{NaHSO}_4 - \alpha$	0.0157	0.0125	0.0045	1.872	0.048	3.974	6.455	5.922	5.290	1693	36
$\text{Na}_3\text{H}(\text{SO}_4)_2$	0.0162	0.0156	0.0039	1.721	0.056	4.355	6.842	5.830	5.506	2103	35
$(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$	0.0171	0.0130	0.0017	0.569	0.058	4.843	6.742	5.553	5.453	2266	37
$\text{Mn}(\text{OH})\text{SO}_4 \cdot 2\text{H}_2\text{O}$	0.0194	0.0164	0.0066	2.400	0.057	5.251	6.645	6.016	5.246	2322	38
$(\text{ND}_4)_3\text{D}(\text{SO}_4)_2$	0.0178	0.0186	0.0001	0.321	0.061	4.989	6.880	5.599	5.526	2452	39
$(\text{As}_2\text{O}_2)\text{SO}_4$	0.0247	0.0262	0.0096	0.635	0.073	8.567	7.181	6.061	5.213	3967	40
CsHSO_4	0.0253	0.0217	0.0082	2.898	0.076	7.802	6.891	6.072	5.002	4011	41
$\text{Y}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	0.0289	0.0322	0.0079	3.118	0.099	8.918	7.755	5.514	5.443	5752	42
KHSO_4	0.0288	0.0348	0.0065	1.637	0.102	9.910	7.821	5.760	5.199	6377	43
KHSO_4	0.0313	0.0306	0.0039	1.758	0.109	8.236	7.849	5.651	5.257	6411	43
$\text{NaHSO}_4 - \alpha$	0.0355	0.0329	0.0073	2.774	0.122	8.947	7.947	5.468	5.118	7623	36
SO_3	1.5000	0.1430	1.0000	0.000	∞	36.740	∞	4.682	4.682	66667	4

(the local symmetry of SO_4^{2-} is C_{3v}). Therefore, a doublet is expected in the ν_3 region, the splitting of which should be considerably smaller than that observed in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (compare the values of D_t , a , b and c in Table I). The appearance of a single peak in the infrared spectrum of $\text{CsAl}(\text{SeO}_4)_2 \cdot 12\text{H}_2\text{O}$ containing isomorphously isolated SO_4^{2-} ions is, in fact, consistent with these expectations (a splitting of about 25 cm^{-1} was found⁵ in the case of SO_4^{2-} -doped $\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$).

We considered the above findings as encouraging enough to search for a correlation between the values of the main components of the tensor (T_{ij}) and the wavenumbers of the ν_3 vibrational bands. Eleven sulfate-ions (from compounds with accurately refined structures, available spectroscopic data and unequivocal assignment) were included in the regression analysis. An ideal SO_4^{2-} tetrahedron and SO_3 (as an example of sulfate-tetrahedron with extremely large distortion) were also included. The data for all these compounds are presented in Table II.

We tested several two-parameter functions. The highest value ($r^2 = 0.97$) for the correlation coefficient was found for the function of the type:

$$Y = k \cdot X^l$$

(see Figure 1). This is, it should be noted, the only function (linear, logarithmic, exponential and $Y = k/X + 1$ — type functions were also tested) that retains its physical significance throughout the whole range of possible X-values, a fact that should not be ignored.

The scatter of the points (see Figure 1) seems to be larger for small distortions, contrary to the expectations. There are several possible reasons for this finding: (i) the uncertainties of the atomic positions are more relevant for small than for large distortions; (ii) the structural data were not corrected for thermal motion; (iii) the effect of the surrounding on the sulfate frequencies is, also, more relevant for small distortions; (iv) the number of pairs (35) of values included in our regression analysis is not too large; (v) finally, it might be possible that there is no simple relation between the value of the constant δ (taken as should be recalled, to be equal to 12) and the

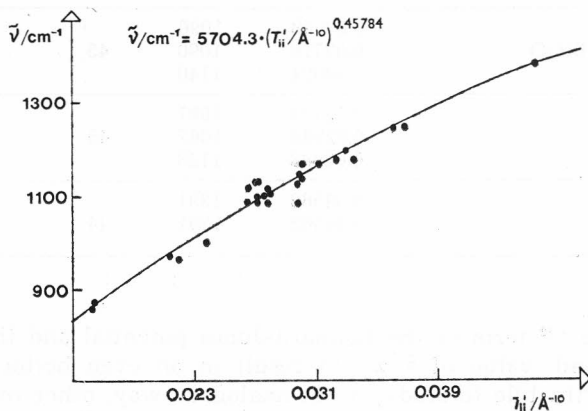


Figure 1. Regression of T_{ii}' vs. ν_3 — best curve fit.

TABLE II

Table II. Pairs of $\mathbf{T}_{ii}' - \nu_3$ data, included in the regression.

Compound	\mathbf{T}_{ii}'/A^{-10}	ν/cm^{-1}	Ref.	Comment
»Free« SO_4^{2-}	0.02787	1105	44	
	0.02787	1105		
	0.02787	1105		
$KHSO_4$	0.01623	860	45	Raman, powder
	0.03132	1170		
	0.03618	1250		
	0.01635	875		
	0.03014	1170		
$(NH_4)_3H(SO_4)_2$	0.03700	1250	46	IR and Raman, powder
	0.02200	966		
	0.03243	1180		
$Na_3H(SO_4)_2$	0.03364	1180	46	Raman, powder * Uncertain assignment
	0.02136	973		
	0.02943	*		
	0.03298	1198		
	0.02381	1004		
K_2SO_4	0.02988	*	45	IR isomorph. isolated
	0.03213	*		
	0.02756	1103		
$CaSO_4 \cdot 2H_2O$	0.02789	1116	5	IR isomorph. isolated
	0.03004	1146		
	0.02665	1121		
$Li_2SO_4 \cdot H_2O$	0.02668	1121	6	IR isomorph. isolated
	0.03000	1146		
	0.02709	1133		
$CsAl(SO_4)_2 \cdot 12H_2O$	0.02733	1133	45	IR isomorph. isolated
	0.03008	1173		
	0.02720	1100		
$Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.02766	1100	45	IR isomorph. isolated
	0.02766	1100		
	0.02658	1090		
$BESO_4 \cdot 4H_2O$	0.02716	1090	45	IR isomorph. isolated
	0.03024	1140		
	0.02793	1087		
SO_3	0.02988	1087	44	IR powder
	0.02988	1128		
	0.04562	1391		
SO_3	0.04562	1391	44	IR gas

exponent of the r^{12} term of the Lennard-Jones potential and that some other, empirically found, value of δ would result in an even better correlation. It thus seems worthwhile to study, in an analogous way, other oxoanions (PO_4^{3-} , AsO_4^{3-} , SeO_4^{2-} etc.) and to compare the results obtained in such studies with the present ones.

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APPENDIX 1

Let x_1, x_2, x_3 and x'_1, x'_2, x'_3 be the axes of two orthogonal Cartesian coordinate systems with a common origin. The primed coordinates may be expressed as

$$x'_i = \sum a_{ij} \cdot x_j \quad i, j \in \{1, 2, 3\}$$

where $[a_{ij}]$ is an orthogonal matrix. Using the equality

$$\mathbf{T}_{ij}' = \sum a_{ik} \cdot a_{jl} \cdot \mathbf{T}_{kl} \quad i, j, k, l, \in \{1, 2, 3\}$$

one obtains

$$\begin{aligned} \sum \mathbf{T}_{ij}' \cdot x'_i \cdot x'_j &= \sum a_{ik} \cdot a_{jl} \cdot \mathbf{T}_{kl} \cdot a_{ir} \cdot x_r \cdot a_{js} \cdot x_s = \\ &= \sum \delta_{kr} \cdot \delta_{ls} \cdot \mathbf{T}_{kl} \cdot x_r \cdot x_s = \sum \mathbf{T}_{kl} \cdot x_k \cdot x_l \quad i, j, k, l, r, s \in \{1, 2, 3\} \end{aligned}$$

which proves that the surface defined by equality (2) does not depend on the choice of the orthogonal Cartesian coordinate system.

APPENDIX 2

To prove that equation (3) always defines an ellipsoid, we consider the vectors $\mathbf{p}', \mathbf{q}', \mathbf{r}', \mathbf{s}'$ ($\mathbf{p}' = \mathbf{p}/|\mathbf{p}|^{\delta/2}$ and similarly for \mathbf{q}', \mathbf{r}' and \mathbf{s}'). Then the tensor is:

$$\mathbf{T}_{ij} = p_i \cdot p_j + q_i \cdot q_j + r_i \cdot r_j + s_i \cdot s_j$$

The surface will be an ellipsoid if and only if the following three conditions are satisfied:

$$\Delta_1 = \mathbf{T}_{11} > 0 \tag{i}$$

$$\Delta_2 = \begin{vmatrix} \mathbf{T}_{11} & \mathbf{T}_{12} \\ \mathbf{T}_{21} & \mathbf{T}_{22} \end{vmatrix} > 0 \tag{ii}$$

$$\Delta_3 = \begin{vmatrix} \mathbf{T}_{11} & \mathbf{T}_{12} & \mathbf{T}_{13} \\ \mathbf{T}_{21} & \mathbf{T}_{22} & \mathbf{T}_{23} \\ \mathbf{T}_{31} & \mathbf{T}_{32} & \mathbf{T}_{33} \end{vmatrix} > 0 \tag{iii}$$

The inequality (i) obviously holds.

To prove the inequality (iii) we consider the tensor (\mathbf{T}_{ij}) as a contravariant one. A coordinate system x'_1, x'_2, x'_3 is chosen so that $\mathbf{p}' = (1, 0, 0)$, $\mathbf{q}' = (0, 1, 0)$ and $\mathbf{r}' = (0, 0, 1)$. In a quite general case, the coordinate system may not be orthogonal. Using the transformation formula

$$\mathbf{T}^{ij} = \sum \frac{\partial x_i}{\partial x'_k} \cdot \frac{\partial x_j}{\partial x'_l} \cdot \mathbf{T}'^{kl} \quad k, l \in \{1, 2, 3\}$$

or

$$\mathbf{T}^{ij} = \sum \frac{\partial x_i}{\partial x'_k} \cdot \mathbf{T}'^{kl} \cdot \left(\frac{\partial x_l}{\partial x'_j} \right)^t \quad k, l \in \{1, 2, 3\}$$

we obtain:

$$\det(\mathbf{T}^{ij}) = [\det(\frac{\partial x_i}{\partial x'_k})]^2 \cdot \det(\mathbf{T}^{'kl})$$

and it is necessary to prove that $\det(\mathbf{T}^{'kl}) > 0$. If the vector \mathbf{s}' has components (a, b, c) in the new coordinate system, then

$$\det(\mathbf{T}^{'kl}) = \begin{vmatrix} 1 + a^2 & ab & ac \\ ab & 1 + b^2 & bc \\ ac & bc & 1 + c^2 \end{vmatrix} = 1 + a^2 + b^2 + c^2 > 0$$

and (iii) is proven.

It may be shown that the proof of inequality (ii) may be treated as a pure two-dimensional problem. Therefore, we identify the vectors p' , q' , r' , s' with their projections on the xy -plane. Similarly as in the previous proof, the components may be chosen as: $p' = (1, 0)$, $q' = (0, 1)$, $r' = (a, b)$, $s' = (c, d)$. In this case, the inequality (ii) takes the form:

$$\Delta_2 = \begin{vmatrix} 1 + a^2 + c^2 & ab + cd \\ ab + cd & 1 + b^2 + d^2 \end{vmatrix} = 1 + a^2 + b^2 + c^2 + d^2 + (ad - bc)^2 > 0$$

This finishes the proof.

APPENDIX 3

The compound $\text{Te}(\text{OH})_6 \text{K}_2\text{SO}_4$ is worked with in the numerical example given below. According to the structural data³² the compound is triclinic, space group $P1$. The unit cell parameters are: $a = 6.243 \text{ \AA}$, $b = 6.647 \text{ \AA}$, $c = 13.405 \text{ \AA}$, $\alpha = 73.14^\circ$, $\beta = 103.05^\circ$, $\gamma = 116.97^\circ$. The fractional coordinates of the five atoms of the SO_4^{2-} ion are:

Atom	x/a	y/b	z/c
S	0.7488	0.2845	0.2516
01	0.6034	0.3692	0.1593
02	0.5835	0.1201	0.3314
03	0.8650	0.1638	0.2179
04	0.9394	0.4777	0.2938

The values of the calculated orthogonal coordinates are:

Atom	$X/\text{\AA}$	$Y/\text{\AA}$	$Z/\text{\AA}$
S	3.810	0.749	3.208
01	3.131	1.365	2.031
02	2.777	0.435	4.225
03	4.504	-0.513	2.778
04	4.810	1.654	3.746

The components of $\vec{\mathbf{p}}(\text{S01})$ are calculated as differences of the X , Y and Z coordinates of the atoms 01 and S:

$$\vec{\mathbf{p}}/\text{\AA} = (-0.679, 0.616, -1.177)$$

And similarly for \vec{q} (S02), \vec{r} (S03) and \vec{s} (S04):

$$\vec{q}/\text{\AA} = (-1.033, -0.314, 1.017)$$

$$\vec{r}/\text{\AA} = (0.694, -1.262, -0.430)$$

$$\vec{s}/\text{\AA} = (1.000, 0.905, 0.538)$$

The lengths of these vectors are:

$$|\vec{p}| = 1.491 \text{ \AA}, |\vec{q}| = 1.484 \text{ \AA}, |\vec{r}| = 1.503 \text{ \AA}, |\vec{s}| = 1.452 \text{ \AA}$$

$$\begin{aligned} \mathbf{T}_{11}/\text{\AA}^{-10} &= \frac{(-0.679) \cdot (-0.679)}{1.491^{12}} + \frac{(-1.033) \cdot (-1.033)}{1.484^{12}} \\ &+ \frac{(0.694) \cdot (0.694)}{1.503^{12}} + \frac{(1.000) \cdot (1.000)}{1.452^{12}} \end{aligned}$$

etc. The results for all components are given below:

$$(\mathbf{T}_{ij}/\text{\AA}^{-10}) = \begin{bmatrix} 0.02817 & 3.113 \cdot 10^{-3} & 1.226 \cdot 10^{-3} \\ 3.113 \cdot 10^{-3} & 0.02525 & 7.947 \cdot 10^{-4} \\ 1.226 \cdot 10^{-3} & 7.947 \cdot 10^{-4} & 0.02522 \end{bmatrix}$$

To calculate the main components of the tensor, the determinantal equation (10) must be solved. The following cubic equation is obtained:

$$\lambda^3 - 7.8647 \cdot 10^{-2} \cdot \lambda^2 + 2.0471 \cdot \lambda - 1.7649 \cdot 10^{-5} = 0$$

The solutions of this equation (the components of the diagonal tensor (\mathbf{T}'_{ij})) can be obtained by using Cardano's method (or numerically) to get:

$$\lambda_1 = 0.02327 \quad \lambda_2 = 0.02482 \quad \lambda_3 = 0.03055$$

The lengths of the axes and the total distortion are, finally, calculated from (9) and (11) to have:

$$a = 6.555 \text{ \AA}^5 \quad b = 6.347 \text{ \AA}^5 \quad c = 5.721 \text{ \AA}^5$$

$$D_t = 0.00897$$

The calculation of the axes (a , b , c) and the total distortion (D_t), in the present work, were performed on a COMMODORE 64 microcomputer with a program written in Basic. The input data were the unit cell parameters and the fractional coordinates of the five atoms forming the XY_4 group. (A listing of the program is available upon request, from the authors. The program was written in standard Basic and, with only minor changes, should work on any microcomputer equipped with a Basic interpreter).

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ИЗВОД

Примена на тензори за опишување на деформациите кај молекулите.

I. Тетраедарски молекули

В. Петрушевски и К. Тренчевски

Вклопувањето на една тетраедарска XY_4 молекула (или јон) во кристал е поврзано, практички во сите случаи, со снижување на нејзината симетрија. За опишување на деформациите на тетраедарот до кои доаѓа при ова, конструирани се тензори од втор ранг. Покажано е дека карактеристичната површина на ваквиот тензор е секогаш елипсоид. Полуоските на елипсоидот и неговата положба во однос на елементите на симетрија на групацијата, може да послужат за определување на ефективната симетрија и степенот на деформираност на тетраедарот. Врз основа на овие податоци, можно е да се претскажат некои од спектралните карактеристики на испитуваните соединенија. За група од 36 SO_4 јони, со прецизно определени структури, споредени се резултатите добиени со примена на оваа метода и резултатите¹ добиени со примена на други методи²⁻⁴. Со доста висок коефициент на корелација ($r^2 = 0,97$) утврдено е постоење на заемна зависност помеѓу главните компоненти на тензорот и фреквенциите на лентите од антисиметричната валентна (ν_3) вибрација.