

CCA-1693

YU ISSN 0011-1643

UDC 541

Original Scientific Paper

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

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Received March 5, 1986

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 results<sup>1</sup> obtained by other<sup>2-4</sup> 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 ( $\nu_3$ ) 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. Baur<sup>2</sup>). Despite this, it may be important to determine the so-called »effective« symmetry (the term »co-kernel« symmetry is sometimes used in the same sense<sup>3</sup>), since it often seems that the latter is higher than the local crystallographic one.<sup>5,6</sup> 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.<sup>3,4,7</sup>

Several methods have so far been used to describe the distortions of tetrahedral molecules in crystals.<sup>2-4,7,8</sup> Baur<sup>2</sup> uses distortion indices, Murray-Rust et al.<sup>3,4</sup> employ displacement vectors and Dollase<sup>8</sup> 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«.<sup>8</sup>

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  $\text{XY}_4$  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  $\delta$  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  $\mu$  and  $\nu$  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:

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

( $\varphi$  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  $\delta$ . It is easy to prove that  $\delta$  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  $\delta$  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  $\delta$  — 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 possible<sup>9</sup> 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  $\Gamma$  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  $\lambda_i$  — 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 ( $\sigma(s - o) \leq 0.005 \text{ \AA}$ )<sup>+</sup> and calculated by use of the method of Baur<sup>2</sup>, Murray-Rust et al.<sup>3,4</sup> 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  $\text{Na}_2\text{SO}_4$  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  $\nu_3$  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 diagrams<sup>10</sup> 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  $\text{Na}_2\text{SO}_4$ . 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  $\nu_3$  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  $\text{Na}_2\text{SO}_4$ , 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

<sup>+</sup> 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  $\nu_3$ -mode bands with some of the distortion indices or displacement vectors. The method of Dollase<sup>8</sup> 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  $\text{SO}_4^{2-}$  ions. As a consequence of the restricted resonant interactions (Davydov-splitting and similar crystal effects) it is believed<sup>11,12,5,6</sup> that the spectra of such samples reflect the effective  $\text{SO}_4^{2-}$  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.
$\gg$ Free $\ll$ $\text{SO}_4^{2-}$	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
$\text{Na}_2\text{SO}_4$	0.0000	0.0106	3.412	0.000	0.000	6.201	6.076	5.941	88	17
$\text{K}_2\text{SO}_4$	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
$\text{LiRbSO}_4$	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
$\text{NH}_4\text{LiSO}_4$	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
$\text{CsHSO}_4$	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
$\text{KHSO}_4$	0.0288	0.0348	0.0065	1.637	0.102	9.910	7.821	5.760	5.199	6377	43
$\text{KHSO}_4$	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
$\text{SO}_3$	1.5000	0.1430	1.0000	0.000	$\infty$	36.740	$\infty$	4.682	4.682	66667	4

(the local symmetry of  $\text{SO}_4^{2-}$  is  $C_{3v}$ ). Therefore, a doublet is expected in the  $\nu_3$  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  $\text{SO}_4^{2-}$  ions is, in fact, consistent with these expectations (a splitting of about  $25 \text{ cm}^{-1}$  was found<sup>5</sup> in the case of  $\text{SO}_4^{2-}$ -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  $\nu_3$  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  $\text{SO}_4^{2-}$  tetrahedron and  $\text{SO}_3$  (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  $\delta$  (taken as should be recalled, to be equal to 12) and the

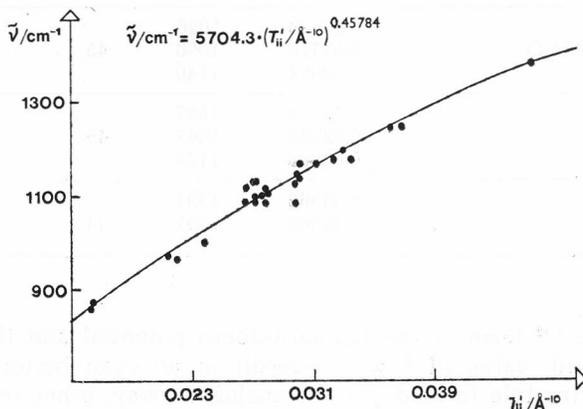


Figure 1. Regression of  $T_{ii}'$  vs.  $\nu_3$  — best curve fit.

TABLE II

Table II. Pairs of  $T_{ii}' - \nu_3$  data, included in the regression.

Compound	$T_{ii}'/A^{-10}$	$\nu/cm^{-1}$	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		
$(NH_4)_3H(SO_4)_2$	0.02200	966	46	IR and Raman, powder
	0.03243	1180		
	0.03364	1180		
$Na_3H(SO_4)_2$	0.02136	973	46	Raman, powder  * Uncertain assignment
	0.02943	*		
	0.03298	1198		
	0.02381	1004		
	0.02988	*		
$K_2SO_4$	0.02756	1103	45	IR isomorph. isolated
	0.02789	1116		
	0.03004	1146		
$CaSO_4 \cdot 2H_2O$	0.02665	1121	5	IR isomorph. isolated
	0.02668	1121		
	0.03000	1146		
$Li_2SO_4 \cdot H_2O$	0.02709	1133	6	IR isomorph. isolated
	0.02733	1133		
	0.03008	1173		
$CsAl(SO_4)_2 \cdot 12H_2O$	0.02720	1100	45	IR isomorph. isolated
	0.02766	1100		
	0.02766	1100		
$Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.02658	1090	45	IR isomorph. isolated
	0.02716	1090		
	0.03024	1140		
$BESO_4 \cdot 4H_2O$	0.02793	1087	45	IR powder
	0.02988	1087		
	0.02988	1128		
$SO_3$	0.04562	1391	44	IR gas
	0.04562	1391		

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

*Acknowledgement.* — The authors are indebted to Prof. Dr B. Šoptrajanov for the valuable discussions and critical reading of the manuscript. Thanks are also due to Doc. Dr B. Minčeva-Šukarova, Prof. Dr G. Čupona and Doc. Dr G. Jovanovski for their helpful suggestions. The financial support of the Community for Scientific Activities of the Socialist Republic of Macedonia is gratefully acknowledged.

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:

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

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 data<sup>32</sup> 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  $\text{SO}_4^{2-}$  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  $XU_4$  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 резултатите<sup>1</sup> добиени со примена на други методи<sup>2-4</sup>. 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 ( $\nu_3$ ) вибрација.