Table 2. *Interpolated values (Rydbergs) for the absorption edges not listed by Sandström or by Cromer*

The values for potassium were obtained by linear interpolation, the others by four-point interpolation.

	$1s\frac{1}{2}$	$2s\frac{1}{2}$	$2p\frac{1}{2}$	$2p\frac{3}{2}$	$3s\frac{1}{2}$	$3p\frac{1}{2}$	$3p\frac{3}{2}$	$3d\frac{3}{2}$	$3d\frac{5}{2}$	$4s\frac{1}{2}$	$4p\frac{1}{2}$	$4p\frac{3}{2}$	$4d\frac{3}{2}$	$4d\frac{5}{2}$	$4f\frac{5}{2}$	$4f\frac{7}{2}$
K	—	—	—	—	—	1·5	1·5									
Kr	1055	141	127	123	21	16	16	6·9	6·7							
Ra	7676	—	—	—	—	329	—	—	—	—	—	—	—	44	22	21

sities of the α and β radiations to obtain the scale factor between the two sets of data.

The anomalous scattering corrections have therefore been calculated for elements $Z=10$ (Ne) to $Z=98$ (Cf) for the $K\beta_1$ radiations of Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Rh, Pd, and Ag.

Calculations

The values of $\Delta f'$ and $\Delta f''$ were calculated by the method of Parratt & Hempstead (1954) and are listed in Table 1; values are printed to only one decimal place if the wavelengths of the incident radiation and one of the absorption edges differ by less than 0·1 %; this is not intended as an absolute measure of the accuracy but to indicate which values are most likely to be in error. The oscillator strengths used were those calculated by Cromer (1965); the frequencies of the absorption edges were those of Sandström (1957) or the eigenvalues calculated by Cromer (1965) where Sandström (1957) gave no values. These two sources gave values for all but a few edges for which the frequencies were obtained by interpolation (Table 2). The wavelengths of the β_1 incident radiations are those listed in *International Tables for X-ray Crystallography* (1962).

For elements Ne to and including Cl four edges were considered; Ar to Ni, seven edges; Cu to Xe, nine edges; Cs to Lu, fourteen edges; Hf to Cf, sixteen edges. For all elements the values of n used were: 11/4 for the $1s\frac{1}{2}$ edge, 7/3 for the $2s\frac{1}{2}$ edge, and 5/2 for the remaining edges. These are the values of n used by Dauben & Templeton (1955) and by Cromer (1965) in their calculations of anomalous scattering corrections for α radiations. Neither damping effects nor the change of Δf with $\sin(\theta/\lambda)$ have been considered.

The calculations were carried out with a program written in GIER-Algol on the Aarhus University GIER computer. The program was checked by calculating some values for α radiations and comparing them with those of Cromer (1965).

References

CATICHA-ELLIS, S. (1962). *Acta Cryst.* **15**, 863.

CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.

DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.

HAZELL, A. C. (1964). *Acta Cryst.* **17**, 155.

HAZELL, A. C. (1966). *Acta Chem. Scand.* **20**, 170.

International Tables for X-ray Crystallography (1962). Vol. III, p. 60. Birmingham: Kynoch Press.

PARRATT, L. G. & HEMPSTEAD, C. F. (1954). *Phys. Rev.* **94**, 1593.

RAMASESHAN, S., VENKATESAN, K. & MANI, N. V. (1957). *Proc. Indian Acad. Sci.* **A46**, 95.

SANDSTRÖM, A. E. (1957). *Handbuch der Physik*, **30**, 78. Berlin: Springer.

Acta Cryst. (1967). **23**, 1098

The rigid-body motion of molecules referred to triclinic coordinates.

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(*Received* 21 *April* 1967 *and in revised form* 3 *July* 1967)

The rigid body analysis of the anisotropic temperature parameters, including the translation–libration correlation term introduced by Schomaker & Trueblood, is presented in triclinic coordinates. It is shown that the equations relating U^{ij} to **T**, **S** and $\boldsymbol{\omega}$ have the same form as in orthogonal coordinates provided that reduced covariant coordinates defined by $x_i g^{-\frac{1}{2}}$ are used.

The analysis of the anisotropic thermal vibrations in molecular crystals in terms of rigid-body motions of the molecules was first suggested by Cruickshank (1956). In the original work the librations were taken to be about the mass-centre of the molecule as origin, but this procedure was criticized by Pawley (1963) who found improved agreement in the case of azulene by moving the origin 0·53 Å from the mass centre. A survey of the whole problem by Schomaker & Trueblood (1966) showed that the choice of origin is in fact arbitrary provided that correlations between translations and librations are properly taken into account. In order, however, to ensure that results published by different workers should be directly comparable, they suggested a procedure for specifying a unique coordinate system, a procedure that involves reducing the complex 20-parameter rigid-body motion to three principal mean-square translations and three screw motions about and along non-intersecting orthogonal axes. The object of the present note is to suggest that compatibility between different workers can more easily be achieved by referring everything to the crystal axes. A secondary object is to show how the use of the full notation of tensor algebra helps materially to avoid such errors as have been pointed out by Scheringer (1966).

When a rigid body is rotated through a small angle $\boldsymbol{\lambda}$ and simultaneously undergoes a translation **t**, a point of

Table 1. *The coefficients* $G^{ij,\,mr}$

mr	11	22	33	23	31	12	32	13	21
ij									
11	0	$(y_3)^2$	$(y_2)^2$	$-y_2y_3$	0	0	$-y_3y_2$	0	0
22	$(y_3)^2$	0	$(y_1)^2$	0	$-y_3y_1$	0	0	$-y_1y_3$	0
33	$(y_2)^2$	$(y_1)^2$	0	0	0	$-y_1y_2$	0	0	$-y_2y_1$
23	$-y_2y_3$	0	0	0	y_1y_2	y_3y_1	$-(y_1)^2$	0	0
31	0	$-y_3y_1$	0	y_1y_2	0	y_2y_3	0	$-(y_2)^2$	0
12	0	0	$-y_1y_2$	y_3y_1	y_2y_3	0	0	0	$-(y_3)^2$

Table 2. *The coefficients* $H^{ij,m}_r$

mr	11	22	33	23	31	12	32	13	21
ij									
11	0	0	0	0	$-2y_2$	0	0	0	$2y_3$
22	0	0	0	0	0	$-2y_3$	$2y_1$	0	0
33	0	0	0	$-2y_1$	0	0	0	$2y_2$	0
23	0	$-y_1$	y_1	0	0	y_2	0	$-y_3$	0
31	y_2	0	$-y_2$	y_3	0	0	0	0	$-y_1$
12	$-y_3$	y_3	0	0	y_1	0	$-y_2$	0	0

the body at position vector **x** undergoes (to first order) a displacement $\mathbf{u}=\boldsymbol{\lambda}\times\mathbf{x}+\mathbf{t}$. In components referred to the crystal axes this is

$$u^i=\varepsilon^{imn}\lambda_m x_n+t^i, \tag{1}$$

where we specify the contravariant components of **u** and **t** which are simply the usual fractional coordinates of X-ray crystallography, and this requires that λ_m and x_n be covariant. The skew-symmetric tensor ε^{imn} has the value zero when any two of its indices are equal, and has the values $\pm g^{-\frac{1}{2}}$ when (imn) is an $\binom{\text{even}}{\text{odd}}$ permutation of (123), where g is the determinant of the metric tensor g_{ij} (McConnell, 1957).

The temperature factor has the form $\exp(-M)$ with $M=2\pi^2\,\overline{(\mathbf{u}\,.\,\mathbf{h})^2}$, where **h** is the reciprocal-lattice vector for the reflexion (James, 1948). In tensor notation, $\mathbf{u}\,.\,\mathbf{h}=u^ih_i=u_ih^i$. In such expressions an index that appears once as a superscript and once as a subscript is to be summed from 1 to 3. The second of these expressions is not acceptable, since customary usage always makes the Miller indices of a plane covariant quantities. Hence the exponent in the temperature factor becomes

$$M=2\pi^2\,(\overline{u^iu^jh_ih_j})=2\pi^2\,U^{ij}h_ih_j. \tag{2}$$

If the values of the U^{ij} are desired in units of Å², then the doubly contravariant nature of this tensor requires that they be multiplied by a_ia_j, where a_i is the length of the direct-cell edge (Scheringer, 1966). To effect the conversion to Å², as originally suggested by Cruickshank, by dividing by a^ia^j, where a^i is the length of the reciprocal-cell edge, is like converting fractional coordinates to Å by dividing by a^i: it is a type of error that could hardly have occurred if the full subscript-superscript notation had been used.

From equations (1) and (2) we readily obtain

$$\begin{aligned}U^{ij}&=\overline{(\varepsilon^{imn}\lambda_mx_n+t^i)\,(\varepsilon^{jrs}\lambda_rx_s+t^j)}\\&=(\varepsilon^{imn}\varepsilon^{jrs}x_nx_s)\overline{\lambda_m\lambda_r}+(\varepsilon^{imn}x_n\overline{\lambda_mt^j}+\varepsilon^{jrs}x_s\overline{\lambda_rt^i})\\&\quad+\overline{t^it^j}\,.\end{aligned} \tag{3}$$

The quadratic averages in equation (3) may be written, $\overline{\lambda_i\lambda_j}=\omega_{ij}$, $\overline{t^it^j}=T^{ij}$ and $\overline{\lambda_it^j}=S_i{}^j$. The mixed tensor $S_i{}^j$ is the correlation tensor introduced by Schomaker & Trueblood, and unlike ω_{ij} and T^{ij} it is not symmetric. Equation (3) may now be written in the form

$$U^{ij}=G^{ij,\,mr}\omega_{mr}+H^{ij,m}_rS_r{}^m+T^{ij}\,. \tag{4}$$

The coefficients $G^{ij,\,mr}$ and $H^{ij,m}_r$ are given (Tables 1 and 2) in terms, not of the covariant components of the position vector x_i, but of reduced covariant components defined by the equation $y_i=x_ig^{-\frac{1}{2}}$. These tables have precisely the same form as those derived by Schomaker and Trueblood. This invariance of form occurs only if the covariant components of **x** and **λ** are used. If the usual crystallographic practice of using contravariant components is followed, equation (1) becomes $u^i=\varepsilon^{ijk}g_{jm}g_{kn}\lambda^mx^n+t^i$ and the resulting analysis becomes very cumbersome. Patterson (1959) has also pointed out the simplification that results from the use of covariant components in the computation of bond lengths and angles in oblique cells.

For a molecule with N atoms, there are $6N$ equations of condition for the determination of the 21 components of ω_{ij}, $S_i{}^j$ and T^{ij}. Inspection of Table 2 shows that only the differences $S_3{}^3-S_2{}^2$, $S_1{}^1-S_3{}^3$, and $S_2{}^2-S_1{}^1$ are determined, and the sum of these is necessarily zero. This constraint must be written into the least-squares program, giving a 22 × 22 normal-equations matrix to be inverted for the 20 independent variables. The program JMTFAC (Burns, Ferrier & McMullan, 1967) was modified to perform this analysis. It is written in Fortran IID for the IBM 1620 computer with 60,000 digits of direct-access storage operating under two-disk monitor control.

We gratefully acknowledge the cooperation of Professor K. N. Trueblood in letting us see a pre-publication draft of the Schomaker–Trueblood paper.

References

Burns, D. M., Ferrier, W. G. & McMullan, J. T. (1967). *Acta Cryst.* **22**, 623.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 754.

James, R. W. (1948). *The Optical Principles of the Diffraction of X-Rays*. p. 23. London: Bell.

McConnell, A. J. (1957). *Applications of Tensor Analysis*, p. 42. New York: Dover Publications.

Patterson, A. L. (1959). In *International Tables for X-Ray Crystallography*. p. 60. Birmingham: Kynoch Press.

Pawley, G. S. (1963). *Acta Cryst.* **16**, 1204.

Scheringer, C. (1966). *Acta Cryst.* **20**, 316.

Schomaker, V. & Trueblood, K. N. (1966). *Acta Cryst.* **21**, A247.