oxygen atoms, in order to determine if the addition of the oxygen contributions was found to produce a smooth curve. For the $hk0$ reflections, an improvement in the calculated intensities was indeed found. The oxygen contributions were always of the correct sign, although small. On the other hand, the z parameter could only be given an approximate value. The observed $00l$ intensities were always considerably greater than the calculated values, indicating, possibly, the existence of preferred orientation of the crystallites. This may account for some of the uncertainty in evaluating z. However, the value $z = 0{\cdot}1$ appears to be compatible with observations. The addition of the oxygen atoms with the coordinates given above produces a general improvement in the calculated intensities. The extent of the agreement is shown in Table 1, where the calculated intensities I_c include the oxygen contributions. The calculated intensities also contain heavy temperature and absorption corrections. The observed intensities I_o were taken from microphotometer tracings. At the large angles, the overlapping of the α_1 and α_2 maxima is generally so extensive that serious errors are introduced in the evaluation of the intensities and $\sin^2\theta$ values. As indicated in Table 1, a number of reflections could not be resolved in intensity.

Thus, with the assumption that the oxygen positions are assigned correctly, the space group becomes $P\bar{3}$–C_{3i}^1, with atoms in the following positions:

1 U_I in $(0, 0, 0)$;
2 U_{II} in $(\frac{1}{3}, \frac{2}{3}, z_1)$, $(\frac{2}{3}, \frac{1}{3}, \bar{z}_1)$, with $z_1 = 0$;
6 O_I in (x, y, z), $(\bar{x}, \bar{y}, \bar{z})$, $(\bar{y}, x-y, z)$, $(y, y-x, \bar{z})$, $(y-x, \bar{x}, z)$, and $(x-y, x, \bar{z})$ with $x = \frac{1}{3}$, $y = 0$, and $z = 0{\cdot}1$;
2 O_{II} in $(\frac{1}{3}, \frac{2}{3}, z_2)$, $(\frac{2}{3}, \frac{1}{3}, \bar{z}_2)$ with $z_2 = \frac{1}{2}$.

Each U_I is bonded to 6 O_I with O_I–6 O_I = 2·31 Å. Each U_{II} is bonded to 6 O_I with U_{II}–6 O_I = 2·31 Å and in addition to 2 O_{II} with U_{II}–2 O_{II} = 2·06 Å. The latter bonding produces endless U_{II}–O_{II}–U_{II}–O_{II}... chains along the c direction.

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A Method for Calculating Thermal Vibration Amplitudes from Spectroscopic Data

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It is shown how $(\overline{u_i^2})_{\text{int.}}$, the contribution from internal molecular vibrations to the mean square amplitude of thermal motion of an atom in a molecular crystal, may be calculated from the vibrational spectrum of the molecule itself and that of a molecule which differs from it only by the occurrence of a different isotope at position i.

In two previous papers (Higgs, 1953, 1955), which will be referred to as I, II respectively, the effect of thermal motion on the electron distribution in molecular crystals was discussed. The motion of an individual atom i was characterized by its mean square amplitude $\overline{u_i^2}$, a quantity identical apart from a numerical factor with the temperature parameter B_i commonly used by X-ray crystallographers (see II, equation (28)). It was stated in II that the calculation of $(\overline{u_i^2})_{\text{int.}}$, the contribution to $\overline{u_i^2}$ from internal vibrations of a molecule, is hampered by the unreliability (so far) of purely theoretical data on molecular force fields. In view of this fact it is perhaps worth while to point out that $(\overline{u_i^2})_{\text{int.}}$ may be calculated from spectroscopic data. The quantities involved in the formula which is to be derived are the fundamental vibration frequencies of the molecule itself and those of molecules differing from it only by their isotopic composition. Thus the necessary data consist of certain infra-red and Raman spectra or of the vibrational structure of certain ultraviolet spectra.

First, using the notation of II, we write down some properties of normal coordinates. The vibrational kinetic and potential energies of a molecule,

$$T = \tfrac{1}{2}\dot{\mathbf{y}}'\mathbf{G}^{-1}\dot{\mathbf{y}} \quad \text{and} \quad V = \tfrac{1}{2}\mathbf{y}'\mathbf{F}\mathbf{y}\,,$$

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where $\mathbf{y}$ is a set of internal coordinates, are transformed by the normal coordinate transformation

$$\mathbf{y} = \mathbf{Nq}$$

into the simpler sum-of-squares forms

$$T = \tfrac{1}{2}\dot{\mathbf{q}}'\dot{\mathbf{q}} \quad \text{and} \quad V = \tfrac{1}{2}\mathbf{q}'\Lambda\mathbf{q}\,,$$

in which

$$\begin{aligned}\Lambda &= \operatorname{diag}(\lambda_\alpha)\\ &= \operatorname{diag}(4\pi^2\nu_\alpha^2)\,,\end{aligned} \tag{1}$$

where ν_α is a fundamental vibration frequency. Thus the matrix $\mathbf{N}$ has the properties

$$\left.\begin{aligned}\mathbf{N}'\mathbf{G}^{-1}\mathbf{N} &= \mathbf{I}\,,\\ \mathbf{N}'\mathbf{F}\mathbf{N} &= \Lambda\,,\end{aligned}\right\} \tag{2}$$

from which we obtain by induction

$$\mathbf{N}f(\Lambda)\mathbf{N}' = f(\mathbf{GF})\mathbf{G}\,, \tag{3}$$

for any function f which can be defined by a power series expansion. $\mathbf{N}_\alpha$, the αth column of $\mathbf{N}$, is an eigenvector of $\mathbf{GF}$ belonging to the eigenvalue λ_α, that is

$$\mathbf{GFN}_\alpha = \lambda_\alpha\mathbf{N}_\alpha\,. \tag{4}$$

We next consider the effect on the vibration frequencies of a small change in the matrix $\mathbf{G}$ only, i.e. of a small change in the atomic masses and perhaps also in the equilibrium configuration, the force field $\mathbf{F}$ remaining constant.*

Equation (4) becomes

$$(\mathbf{G}+\Delta\mathbf{G})\mathbf{F}(\mathbf{N}_\alpha+\Delta\mathbf{N}_\alpha) = (\lambda_\alpha+\Delta\lambda_\alpha)(\mathbf{N}_\alpha+\Delta\mathbf{N}_\alpha)\,.$$

The zeroth order term of this equation is already satisfied, by (4); the first order term is

$$(\Delta\mathbf{G})\mathbf{FN}_\alpha+\mathbf{GF}(\Delta\mathbf{N}_\alpha) = (\Delta\lambda_\alpha)\mathbf{N}_\alpha+\lambda_\alpha(\Delta\mathbf{N}_\alpha)\,.$$

Premultiplying by $\mathbf{N}_\alpha'\mathbf{G}^{-1}$ and using equations (2) and (4), we obtain

$$\Delta\lambda_\alpha/\lambda_\alpha = \mathbf{N}_\alpha'\mathbf{G}^{-1}(\Delta\mathbf{G})\mathbf{G}^{-1}\mathbf{N}_\alpha\,. \tag{5}$$

Now $\mathbf{G}$ is defined by the equation (see also II, equation (6))

$$\mathbf{G} = \mathbf{bM}^{-1}\mathbf{b}',$$

where $\mathbf{M}$ is the diagonal matrix of the atomic masses (each m_i occurs three times, corresponding to the three Cartesian components of the displacement $\mathbf{u}_i$) and $\mathbf{b}$ is the transformation matrix defining the internal coordinates $\mathbf{y}$ in terms of the Cartesian coordinates $\mathbf{x}$. So if we change only the masses, leaving the equilibrium configuration (characterized by $\mathbf{b}$) unaltered, the change in $\mathbf{G}$ is given by

$$\Delta\mathbf{G} = -\mathbf{bM}^{-1}(\Delta\mathbf{M})\mathbf{M}^{-1}\mathbf{b}'.$$

* Changes of this type have been treated by perturbation methods by Bernstein (1951) and others.

Substituting this expression into (5), we get finally

$$-\Delta\lambda_\alpha/\lambda_\alpha = \mathbf{N}_\alpha'\mathbf{G}^{-1}\mathbf{bM}^{-1}(\Delta\mathbf{M})\mathbf{M}^{-1}\mathbf{b}'\mathbf{G}^{-1}\mathbf{N}_\alpha\,. \tag{6}$$

We now employ equation (6) to evaluate an expression of the form

$$-\sum_\alpha f(\lambda_\alpha).\Delta\lambda_\alpha/\lambda_\alpha\,,$$

where $f(\lambda)$ is a general power series and the summation is over all normal modes α. Using successively the relation

$$\operatorname{trace}\mathbf{AB} = \operatorname{trace}\mathbf{BA}$$

and equation (3), we obtain from (6)

$$\begin{aligned}&-\sum_\alpha f(\lambda_\alpha).\Delta\lambda_\alpha/\lambda_\alpha\\ &\quad= \operatorname{trace}\{f(\Lambda)\mathbf{N}'\mathbf{G}^{-1}\mathbf{bM}^{-1}(\Delta\mathbf{M})\mathbf{M}^{-1}\mathbf{b}'\mathbf{G}^{-1}\mathbf{N}\}\\ &\quad= \operatorname{trace}\{\mathbf{M}^{-1}\mathbf{b}'\mathbf{G}^{-1}\mathbf{N}f(\Lambda)\mathbf{N}'\mathbf{G}^{-1}\mathbf{bM}^{-1}(\Delta\mathbf{M})\}\\ &\quad= \operatorname{trace}\{\mathbf{M}^{-1}\mathbf{b}'\mathbf{G}^{-1}f(\mathbf{GF})\mathbf{bM}^{-1}(\Delta\mathbf{M})\}\,.\end{aligned} \tag{7}$$

If $\Delta\mathbf{M}$ consists merely of a change Δm_i in the mass of the ith atom and the function f is particularized by the definition

$$f(\lambda) = \tfrac{1}{2}\hbar\lambda^{-\frac{1}{2}}\coth(\hbar\lambda^{\frac{1}{2}}/2kT)\,, \tag{8}$$

then the right-hand side of (7) is seen by comparison with equation (25) of II to be just $(\overline{u_i^2})_{\text{int.}}\Delta m_i$. Thus we obtain finally, by substituting into (7) the definitions (1) and (8),

$$(\overline{u_i^2})_{\text{int.}} = (h/4\pi^2)\sum_\alpha(-\partial\nu_\alpha/\partial m_i)\nu_\alpha^{-2}\coth(h\nu_\alpha/2kT)\,. \tag{9}$$

Inspection of equation (9) shows that the quantities which we require, ideally, in order to determine $(\overline{u_i^2})_{\text{int.}}$ are the complete vibrational spectrum of the molecule (ν_α) together with the change induced in this spectrum by an infinitesimal change in the mass of atom i ($\partial\nu_\alpha/\partial m_i$). The nearest practical possibility to the latter is the change induced by substituting for atom i its neighbouring isotope: using the ratios $\Delta\nu_\alpha/\Delta m_i$ in (9) will lead to a reasonably accurate estimate of $(\overline{u_i^2})_{\text{int.}}$ provided that $\Delta m_i/m_i$ is small. Obviously it is absurd to apply this method to a very light atom such as hydrogen, where $\Delta m_i/m_i \sim 1$; but when we reach carbon, the thermal motion of which is of considerable interest, then already $\Delta m_i/m_i < 0{\cdot}1$ for the isotopes C^{12} and C^{13}. Thus the method seems to be quite promising as a way of determining thermal amplitudes for a large class of organic molecules.

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