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The Structure Factor for a Harmonic Quasi-Torsional Oscillator

BY M. I. KAY* AND D. R. BEHRENDT

Lewis Research Center, National Aeronautics and Space Administration, Cleveland, Ohio, U.S.A.

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The scattering function for a harmonic librator has been calculated for small angles of oscillation. The results are compared with the usual form of the structure factor. To calculate the probability density function for an atom constrained to move on the surface of a sphere while oscillating as part of a rigid body, the harmonic potential function for an oscillator was derived as a function of angular displacements on the surface of the sphere.

1. Introduction

For the past several years, vibrations of polyatomic ions and molecules have been analyzed in terms of rigid body motion. This rigid body treatment (e.g., Cruickshank, 1956) consists of separating the molecular motion into two parts: a translational vibration and a torsional oscillation or libration. While translational vibrations can be satisfactorily described by the Debye–Waller theory (James, 1954), the torsional oscillations cannot since they definitely do not satisfy the assumption that the vibration consists of normal linear displacements. In view of this fact, the effect of librations on the refinement of crystal structures using the usual structure factor equations is rather obscure, and a treatment that explicitly takes the librations into account is desirable.

In this paper, an expression will be derived that is valid for small oscillations, and the result will be compared with the usual form of the structure factor.

2. Theory

The model considered below consists of a set of atoms oscillating about a point. No translational motion will be included since the Debye–Waller theory accounts for this motion quite adequately.

If the position vector of the nth atom in the structure factor expression is written as $\mathbf{r}_n^c+\mathbf{r}_n$, where $\mathbf{r}_n^c$ is the vector to the center of oscillation and $\mathbf{r}_n$ is the vector from the center of oscillation to the instantaneous atomic position, then the structure factor,

$$F(H)=\sum_{n=1}^{N} f_n \exp\left[2\pi i\mathbf{H}.\mathbf{r}_n^c\right]\exp\left[\overline{2\pi i\mathbf{H}.\mathbf{r}_n}\right], \quad (1)$$

where H is the reciprocal lattice vector, N is the number of atoms in the unit cell, and f_n is the scattering factor for the nth atom. Bars over a quantity indicate an average over the quantity.

The function g_n, defined by

$$g_n=\exp\left[\overline{2\pi i\mathbf{H}.\mathbf{r}_n}\right]=\int \exp\left[2\pi i\mathbf{H}.\mathbf{r}_n\right].DdA \Big/ \int DdA\,, \quad (2)$$

contains the scattering by the torsional oscillator. Since the atomic position vectors are taken relative to centers of libration, $|\mathbf{r}_n|$ is a constant for a given n. The average in (2) is computed by integrating over the surface of a sphere of radius $|\mathbf{r}_n|$ by using an appropriate distribution function D which is proportional to the probability that $\mathbf{r}_n$ lies in dA.

In order to reduce the complexity of the notation, the subscript n will be omitted in the remainder of the paper. Cartesian coordinate systems will be used in real and reciprocal spaces; thus $\mathbf{r}=x\mathbf{i}+y\mathbf{j}+z\mathbf{k}$, and $\mathbf{H}=h^*\mathbf{i}+k^*\mathbf{j}+l^*\mathbf{k}$. Here $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are orthogonal unit vectors; i.e. x, y, and z have units of length and h^*, k^*, and l^* are not integers but the components of the reciprocal lattice vector. The sum $h^*x+k^*y+l^*z$ will reduce to $h(x/a)+k(y/b)+l(z/c)$ in the crystallographic system since dot products are invariant under the transformations used.

To simplify the integrations in (4), the following transformations were made. If $\mathbf{r}_0$, the vector from the center of libration to the equilibrium position of an atom, has the polar coordinate angles θ_0 and φ_0, the transformation

$$\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}\cos\theta_0\cos\varphi_0 & -\sin\varphi_0 & \sin\theta_0\cos\varphi_0\\ \cos\theta_0\sin\varphi_0 & \cos\varphi_0 & \sin\theta_0\sin\varphi_0\\ -\sin\theta_0 & 0 & \cos\theta_0\end{pmatrix}\begin{pmatrix}x'\\y'\\z'\end{pmatrix} \quad (3)$$

relates the primed and unprimed systems such that the z' axis is parallel to $\mathbf{r}_0$, and the x' axis is in a plane containing both z and z' (Figs. 1(*a*) and (*b*)). The transformation

$$\begin{pmatrix}x'\\y'\\z'\end{pmatrix}=\begin{pmatrix}\cos\psi & -\sin\psi & 0\\ \sin\psi & \cos\psi & 0\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}x''\\y''\\z''\end{pmatrix} \quad (4)$$

relates the double-primed and primed systems such that the principal axes of libration on the surface of the sphere as defined in Appendix A are parallel to x'' and y'' (Fig. 1(*b*)). The instantaneous position of

* Present address: Georgia Institute of Technology, Atlanta, Georgia, U.S.A.

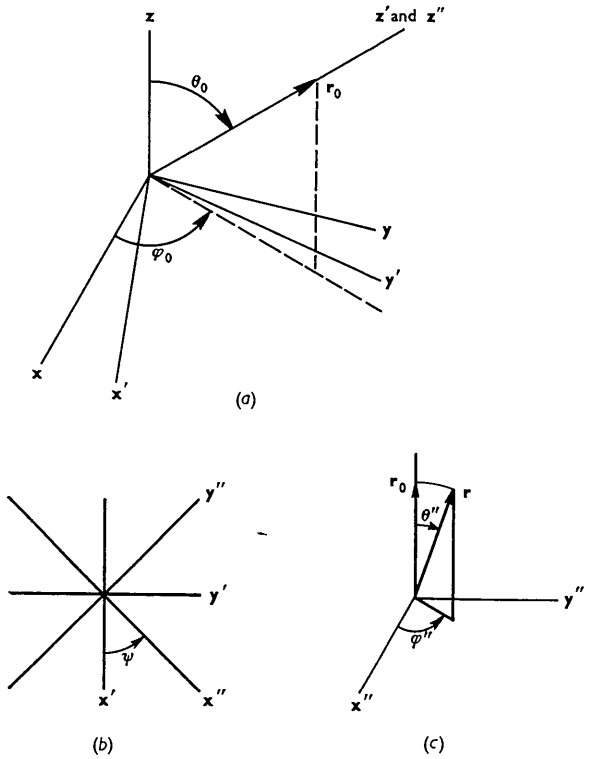

Fig. 1. Coordinate transformations. (*a*) x' is in the plane of z, z'. The vector $\mathbf{r}$ (parallel to z') is the vector from the center of oscillation to the equilibrium position of a librating atom. (*b*) x'' and y'' are the principal axes of libration. (*c*) Polar coordinate system used to express position of $\mathbf{r}$.

the vector $\mathbf{r}$ oscillating about the vector $\mathbf{r}_0$ is thus expressed in the spherical coordinates r, θ'', φ'' (Fig. 1(*c*)), where r is a constant equal to $|\mathbf{r}_0|$.

From these transformations, one obtains:

$$\begin{aligned}
x &= r_0[\cos\theta_0\cos\varphi_0(\cos\psi\sin\theta''\cos\varphi''-\sin\psi\sin\theta''\sin\varphi'')\\
&\quad -\sin\varphi_0(\sin\psi\sin\theta''\cos\varphi''+\cos\psi\sin\theta''\sin\varphi'')\\
&\quad +\cos\varphi_0\sin\theta_0\cos\theta'']\\
y &= r_0[\cos\theta_0\sin\varphi_0(\cos\psi\sin\theta''\cos\varphi''-\sin\psi\sin\theta''\sin\varphi'')\\
&\quad +\cos\varphi_0(\sin\psi\sin\theta''\cos\varphi''+\cos\psi\sin\theta''\sin\varphi'')\\
&\quad +\sin\theta_0\sin\varphi_0\cos\theta'']\\
z &= r_0[-\sin\theta_0(\cos\psi\sin\theta''\cos\varphi''-\sin\psi\sin\theta''\sin\varphi'')\\
&\quad +\cos\theta_0\cos\theta'']\,. \qquad (5)
\end{aligned}$$

The probability density function was chosen as

$$D = \exp[-(a^2\alpha^2+b^2\beta^2)]\,, \qquad (6)$$

where

$$\begin{aligned}
\alpha &= \theta''\cos\varphi''\\
\beta &= \theta''\sin\varphi''. \qquad (7)
\end{aligned}$$

The assumptions and derivation that lead to this function are given in Appendix A.

In (6) a^2 and b^2 are equal to $\frac{1}{2}\omega_{yy}''^2$ and $\frac{1}{2}\omega_{xx}''^2$, respectively, where $\omega_{yy}''^2$ and $\omega_{xx}''^2$ are the respective mean square angular displacements parallel to x'' and y'' of the atom oscillating about $\mathbf{r}_0$.

For small angles,

$$\begin{aligned}
\sin\theta'' &= \theta''\\
\cos\theta'' &= 1-\theta''^2/2\,. \qquad (8)
\end{aligned}$$

Then the scattering function averaged over the surface of a sphere is

$$g = \frac{\int_{-\infty}^{\infty}d\alpha\int_{-\infty}^{\infty}d\beta\,\exp 2\pi i\mathbf{H}.\mathbf{r}\,\exp-(a^2\alpha^2+b^2\beta^2)}{\int_{-\infty}^{\infty}d\alpha\int_{-\infty}^{\infty}d\beta\,\exp-(a^2\alpha^2+b^2\beta^2)} \qquad (9)$$

Because of the exponential damping factor the difference between integration over a sphere and over all of the α, β space is small.

By substituting (5) and (8) into (9) and integrating, (9) becomes

$$\begin{aligned}
g &= \frac{1}{(1+S^2/a^4)^{1/4}}\exp\left\{\left[\frac{-t_\alpha^2a^2}{4(a^4+S^2)}\right]\right.\\
&\quad \left.+\left[i\left(2S-\frac{\tan^{-1}S/a^2}{2}+\frac{t_\alpha^2S}{4(a^4+S^2)}\right)\right]\right\}\\
&\quad\times\frac{1}{(1+S^2/b^4)^{1/4}}\exp\left\{\left[\frac{-t_\beta^2b^2}{4(b^4+S^2)}\right]\right.\\
&\quad \left.+\left[i\left(\frac{-\tan^{-1}S/b^2}{2}+\frac{t_\beta^2S}{4(b^4+S^2)}\right)\right]\right\}, \qquad (10)
\end{aligned}$$

where

$$S = \pi(h^*x_0+k^*y_0+l^*z_0)\,,$$

$$\begin{aligned}
t_\alpha &= 2\pi\left\{h^*\left[\frac{z_0x_0}{(x_0^2+y_0^2)^{1/2}}\cos\psi-\frac{r_0y_0}{(x_0^2+y_0^2)^{1/2}}\sin\psi\right]\right.\\
&\quad +k^*\left[\frac{z_0y_0}{(x_0^2+y_0^2)^{1/2}}\cos\psi+\frac{x_0r_0}{(x_0^2+y_0^2)^{1/2}}\sin\psi\right]\\
&\quad \left.-l^*[(x_0^2+y_0^2)^{1/2}\cos\psi]\right\},\\
t_\beta &= 2\pi\left\{h^*\left[-\frac{z_0x_0}{(x_0^2+y_0^2)^{1/2}}\sin\psi-\frac{y_0r_0}{(x_0^2+y_0^2)^{1/2}}\cos\psi\right]\right.\\
&\quad +k^*\left[\frac{-z_0y_0}{(x_0^2+y_0^2)^{1/2}}\sin\psi+\frac{x_0r_0}{(x_0^2+y_0^2)^{1/2}}\cos\psi\right]\\
&\quad \left.+l^*[(x_0^2+y_0^2)^{1/2}\sin\psi]\right\}. \qquad (11)
\end{aligned}$$

3. Interpretation

Equation (10) accurately describes the scattering to the degree that the approximation (8) is valid. It would now be interesting to establish relationships between (10) and the usual form of the structure factor expression.

Defining the quantities $\bar{r}$ and $\overline{r^2}$ as the average and mean-square projections of $\mathbf{r}$ on $\mathbf{r}_0$ gives

$$\bar{r} = \frac{\int_0^{\pi}\int_0^{2\pi} r\cos\theta''\sin\theta''\exp[-(a^2\cos^2\varphi''+b^2\sin^2\varphi'')\theta''^2]d\varphi''d\theta''}{\int_0^{\pi}\int_0^{2\pi}\sin\theta''\exp[-(a^2\cos^2\varphi''+b^2\sin^2\varphi'')\theta''^2]d\varphi''d\theta''}, \tag{12}$$

$$\overline{r^2} = \frac{\int_0^{\pi}\int_0^{2\pi} r^2\cos^2\theta''\sin\theta''\exp[-(a^2\cos^2\varphi''+b^2\sin^2\varphi'')\theta''^2]d\varphi''d\theta''}{\int_0^{\pi}\int_0^{2\pi}\sin\theta''\exp[-(a^2\cos^2\varphi''+b^2\sin^2\varphi'')\theta''^2]d\varphi''d\theta''}. \tag{13}$$

It may be shown that (see Appendix B)

$$\bar{r} = r_0\left[1-\frac{1}{4a^2}-\frac{1}{4b^2}+\frac{1}{48a^2b^2}+\frac{7}{96a^4}+\frac{7}{96b^4}+\dots\right], \tag{14}$$

and

$$\overline{(\bar{r}-r)^2} = \overline{r^2}-\bar{r}^2 = \frac{r_0^2}{8}\left(\frac{1}{a^4}+\frac{1}{b^4}+\dots\right). \tag{15}$$

If

$$a^2 \gg \frac{S^2}{a^2} \quad \text{and} \quad b^2 \gg \frac{S^2}{b^2}, \tag{16}$$

then

$$\left(1+\frac{S^2}{a^4}\right)^{-1/4}\cdot\left(1+\frac{S^2}{b^4}\right)^{-1/4} \approx \left(1-\frac{1}{4}\frac{S^2}{a^4}\right)\left(1-\frac{1}{4}\frac{S^2}{b^4}\right) \approx \exp\left[-\left(\frac{S^2}{4a^4}+\frac{S^2}{4b^4}\right)\right]$$

$$= \exp\left[-2\pi^2(h^*x_0+k^*y_0+l^*z_0)^2\cdot\left(\frac{1}{8a^4}+\frac{1}{8b^4}\right)\right], \tag{17}$$

and

$$\exp-\left[\frac{t_\alpha^2a^2}{4(a^4+S^2)}+\frac{t_\beta^2b^2}{4(b^4+S^2)}\right] \approx \exp\left[-\left(\frac{t_\alpha^2}{4a^2}+\frac{t_\beta^2}{4b^2}\right)\right]. \tag{18}$$

The terms in the exponents of (17) and (18) are of the form

$$2\pi(h^{*2}\mu_{11}+l^{*2}\mu_{22}\dots+2h^*k^*\mu_{12}+\dots).$$

It is possible to prove that the terms μ_{11} etc. are the tensor components of a displacement matrix; i.e., they correspond to the usual components of an anisotropic temperature factor. In the x'', y'', z'' space, the principal mean-square displacements perpendicular to $\mathbf{r}_0$ are $r_0^2\omega_{yy}''^2$ and $r_0^2\omega_{xx}''^2$ or $r_0^2/2a^2$ and $r_0^2/2b^2$.

The mean-square displacement from the average value of the projection of $\mathbf{r}$ on $\mathbf{r}_0$ was given in (15). The mean-square displacement matrix in the double-primed space is then

$$U'' = \begin{pmatrix} r_0^2/2a^2 & 0 & 0 \\ 0 & r_0^2/2b^2 & 0 \\ 0 & 0 & r_0^2[1/8a^4+1/8b^4] \end{pmatrix}. \tag{19}$$

To find the matrix in x, y, z space, multiply U'' on the left and right by the two transformation matrices defined in (3) and (4) and their inverses (transposes), respectively. The components of the resulting matrix are identical with the coefficients of h^{*2}, k^{*2}, h^*k^*, etc. in (17) and (18). In other words, to the extent that the approximations in (17) and (18) are valid, the exponential damping factor in g may be interpreted as an anisotropic Debye–Waller factor.

The effect of libration on the apparent coordinates may be partially determined by using the approximation

$$\tfrac{1}{2}\left(\tan^{-1}\frac{S}{a^2}+\tan^{-1}\frac{S}{b^2}\right) \approx \frac{2\pi}{4}(h^*x_0+k^*y_0+l^*z_0)\cdot\left(\frac{1}{a^2}+\frac{1}{b^2}\right). \tag{20}$$

From the preceding paragraph and equations (10), (14), and (20)

$$g \approx \exp\left\{2\pi i(h^*\bar{x}+k^*\bar{y}+l^*\bar{z})+i\times\left[\frac{t_\alpha^2S}{4(a^4+S^2)}+\frac{t_\beta^2S}{4(b^4+S^2)}\right]\right\} \times\exp 2\pi^2(h^{*2}\mu_{11}+k^{*2}\mu_{22}+l^{*2}\mu_{33} +2h^*k^*\mu_{12}+2h^*l^*\mu_{13}+2k^*l^*\mu_{23}). \tag{21}$$

Then

$$F(H) \approx \sum_{n=1}^{N} f_n \exp 2\pi i\mathbf{H}.\overline{\mathbf{r}_n'} \times\exp\left\{iS\left[\frac{t_\alpha^2}{4(a^4+S^2)}+\frac{t_\beta^2}{4(b^4+S^2)}\right]\right\}\exp 2\pi^2(h^{*2}\mu_{11}\dots), \tag{22}$$

where μ_{ij} are the elements of displacement tensor, and $\overline{\mathbf{r}_n'}$ is the average value of a vector from the origin of the unit cell to an atom.

One rather simple special case may be noted. Consider an atom in the crystallographic **b**, **c** plane librating about an axis parallel to that plane and examine the expression for g for the $0kl$ reflections. Then

$$\cos\psi = 0,\ b\to\infty,\ h=0,$$

and

$$x_0 = 0,$$

then

$$t_\alpha = 0$$

$$g \approx \exp\left\{-2\pi^2\left[\frac{(k^{*2}y_0^2+l^{*2}z_0^2+2k^*l^*y_0z_0)}{8a^4}\right]\right\} \times\exp 2\pi i(k^*\bar{y}+l^*\bar{z}). \tag{23}$$

In other words, if one projects onto a plane containing the axis of oscillation, a refinement should converge to the average values of the desired set of coordinates rather than to the equilibrium values with a Debye–Waller-like term dependent on the mean-square deviation from the average.

When, however, one considers a structure in three dimensions or a projection that does not fulfill the conditions of the above paragraph, the terms $t_\alpha^2 S/4(a^4+S^2)$ and $t_\beta^2 S/4(b^4+S^2)$ may become quite significant for higher indices, especially if a and b are not too large.

It is interesting to note that the first-order correction term,

$$r\left(\frac{1}{4a^2}+\frac{1}{4b^2}\right)=r\left(\frac{\omega_{yy}''^2}{2}+\frac{\omega_{xx}''^2}{2}\right), \qquad (24)$$

is equivalent to the approximate correction that Cruickshank (1956) gives from other considerations.

The reliability of the above calculation is, of course, dependent upon the approximations made. If $\omega_{yy}''^2+\omega_{xx}''^2$ is much greater than about 0·1, it is likely that the series approximations used in the integration of the scattering function will begin to break down.

The significance of other approximations and corrections may be simply estimated from the resulting series and from the derivation of the probability density function.

4. Conclusions

While noting that the approximations used in the derivation of (10) ($\sin\theta=\theta$ and $\cos\theta=1-\theta^2/2$) may be fairly serious in many cases, the approximations needed to transform (10) to the usual form of the structure factor will also be quite drastic, that is, (16), (17), showing that (10) should give a better picture of scattering than the usual form of the structure factor for some cases. The solution of the librator problem for all amplitudes for the one dimensional case has been indicated by King & Lipscomb (1950) in their paper on 'Scattering from a Hindered Rotator' in the form of an infinite series of Bessel Functions. It is contained in the case $n=1$, using the notation of King & Lipscomb.

It may also be seen from equation (10) that as one adds higher order structure factors to a refinement using the usual form of the structure factor the apparent distance of an atom from the center of libration will increase due to t_α^2, t_β^2 dependance. This effect may be associated with the dependance of Cruickshank's (1956, 1961) correction on the Fourier peak width.

It should also be pointed out that if the integration is carried out to a term of higher order than two in θ, the actual form chosen for the potential function becomes important and the validity of the $(1-\cos\theta)$ dependance for any given case becomes problematical.

A suggested method of using (10) might consist in first refining a structure as well as one could using the usual relationships, then computing the various parameters by methods given by Cruickshank (1956*a*) and this paper and refining for one or two more rounds with a least squares program based on (10).

APPENDIX A

Derivation of the probability density function

To evaluate (2), it is necessary to assume a probability density function on the surface of a sphere of radius $|\mathbf{r}|$. At a given temperature, the exponent in the probability function, D will be proportional to the potential function. A potential function for an oscillating rigid body will then be chosen and related to the displacement of a vector $\mathbf{r}$ from its equilibrium position $\mathbf{r}_0$ on the surface of a sphere of radius $|\mathbf{r}|$.

Let $\mathbf{r}_0$, a vector from the center of oscillation of the rigid body to the equilibrium position of the atom under consideration, be expressed by $x_0\mathbf{i}+y_0\mathbf{j}+z_0\mathbf{k}$ where the unit vectors $\mathbf{i}, \mathbf{j}, \mathbf{k}$ are parallel to the principal axes of oscillation. Then define several coordinate transformations:

$$\begin{pmatrix}x_0\\y_0\\z_0\end{pmatrix}=(T_1)\begin{pmatrix}x_0'\\y_0'\\z_0'\end{pmatrix}, \qquad (A1)$$

$$\begin{pmatrix}x_0'\\y_0'\\z_0'\end{pmatrix}=(T_2)\begin{pmatrix}x_0''\\y_0''\\z_0''\end{pmatrix}, \qquad (A2)$$

$$\begin{pmatrix}x_1\\y_1\\z_1\end{pmatrix}=(T_1)\begin{pmatrix}x_0''\\y_0''\\z_0''\end{pmatrix}. \qquad (A3)$$

T_1 (Fig. A1) brings z_0' parallel to $\mathbf{r}_0$ with x_0' in a plane containing z_0 and z_0' by rotations φ_0 around z_0 and θ_0 around y'.

$$T_1=\begin{pmatrix}\cos\varphi_1\cos\theta_1 & -\sin\varphi_1 & \cos\varphi_1\sin\theta_1\\ \sin\varphi_1\cos\theta_1 & \cos\varphi_1 & \sin\varphi_1\sin\theta_1\\ -\sin\theta_1 & 0 & \cos\theta_1\end{pmatrix}. \qquad (A4)$$

T_2 (Fig. A2) represents a rotation of z_0' to z_0'' through an angle θ about an axis in the x_0', y_0' plane, this axis being perpendicular to a line (also in the x_0', y_0' plane) which makes an angle φ with the x_0' axis.

$$T_2=\begin{pmatrix}\cos^2\varphi\cos\theta+\sin^2\varphi & \cos\theta\cos\varphi\sin\varphi-\cos\varphi\sin\varphi & \sin\theta\cos\varphi\\ \cos\varphi\sin\varphi\cos\theta-\sin\varphi\cos\varphi & \sin^2\varphi\cos\theta+\cos^2\varphi & \sin\theta\sin\varphi\\ -\cos\varphi\sin\theta & -\sin\varphi\sin\theta & \cos\theta\end{pmatrix}. \qquad (A5)$$

It may then be seen that x_1, y_1, z_1 bears the same relationship to $\mathbf{r}$ that x_0, y_0, z_0 bears to $\mathbf{r}_0$. Thus,

$$\begin{pmatrix} x_0 \\ y_0 \\ z_0 \end{pmatrix} = (T_1)(T_2)(T_1)^{-1} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} . \tag{A6}$$

Of the four coordinate systems two are fixed in the laboratory, these being x_0, y_0, z_0 and x_0', y_0', z_0'; the other two systems x_1, y_1, z_1 and x_0'', y_0'', z_0'' are fixed in the rigid body and rotate with the body.

The potential energy of the librational motion is then described in terms of three restoring forces that are proportional to the displacement of the body from its equilibrium position.

Defining two unit vectors (Fig. A3), $\mathbf{x}_0 = \mathbf{i}$ and $\mathbf{x}_1 = x_1\mathbf{i} + y_1\mathbf{j} + z_1\mathbf{k}$,

$$(\mathbf{x}_0 - \mathbf{x}_1)^2 = 2(1 - \mathbf{x}_0 . \mathbf{x}_1) . \tag{A7}$$

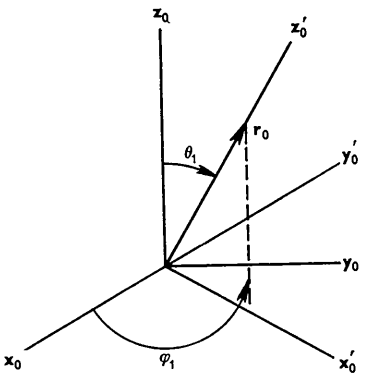

Fig. A1. The relation between the x_0, y_0, z_0 and x_0', y_0', z_0' systems are shown, x_0' being in the plane of z_0, z_0'. The vector $\mathbf{r}_0$ is parallel to z'. It is the vector from the center of oscillation to the equilibrium position of a librating atom.

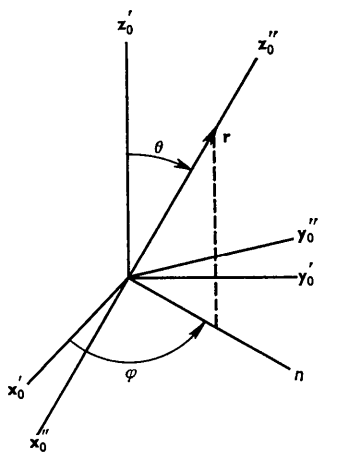

Fig. A2. The relation between the x_0', y_0', z_0' and x_0'', y_0'', z_0'' systems is shown. z_0'' is rotated through an angle θ from z_0' about an axis which is in the x_0', y_0' plane, this axis being perpendicular to line n which makes an angle φ with the x_0' axis and is in the x_0', y_0' plane.

$$V = 2[k_1(1 - \mathbf{x}_0 . \mathbf{x}_1) + k_2(1 - \mathbf{y}_0 . \mathbf{y}_1) + k_3(1 - \mathbf{z}_0 . \mathbf{z}_1)] . \tag{A8}$$

The diagonal elements of the transformation (A6) were used to find the components in (A8). Letting

$$\cos\theta = 1 - \theta^2/2 + \theta^4/24 , \tag{A9}$$

and

$$\begin{aligned} \alpha' &= \theta \cos\varphi \\ \beta' &= \theta \sin\varphi . \end{aligned} \tag{A10}$$

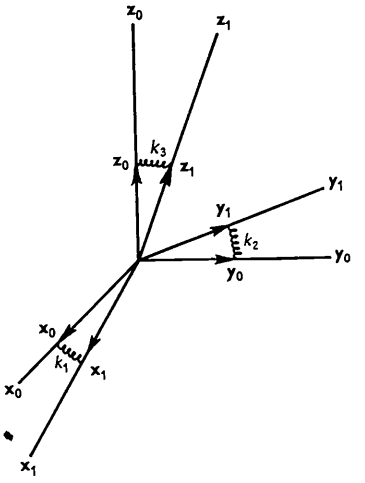

Fig. A3. Model for calculation of the potential function. $\mathbf{x}_0$, $\mathbf{x}_1$, etc. are unit vectors. The potential is obtained for example by squaring the distance $\mathbf{x}_0$–$\mathbf{x}_1$ and multiplying by the spring constant k_1.

To the fourth order in α' and β',

$$\begin{aligned} V = {} & \alpha'^2(k_1 \cos^2\varphi_1 + k_2 \sin^2\varphi_1 + k_3) \\ & + \alpha'\beta'[2 \sin\varphi_1 \cos\varphi_1 \cos\theta_1(k_2 - k_1)] \\ & + \beta'^2[k_1 (\sin^2\varphi_1 + \cos^2\varphi_1 \sin^2\theta_1) \\ & + k_2 (\cos^2\varphi_1 + \sin^2\varphi_1 \sin^2\theta_1) + k_3 \cos^2\theta_1] \\ & + (\alpha'^4/12)(-k_1 \cos^2\varphi_1 - k_2 \sin^2\varphi_1 - k_3) \\ & + (\alpha'^3\beta'/12)[-2 \sin\varphi_1 \cos\varphi_1 \cos\theta_1(k_2 - k_1)] \\ & + (\alpha'^2\beta'^2/12)[-k_1(1 + \cos^2\varphi_1 \sin^2\theta_1) \\ & - k_2(1 + \sin^2\varphi_1 \sin^2\theta_1) - k_3(1 + \cos^2\theta_1)] \\ & + (\alpha'\beta'^3/12)[-2 \sin\varphi_1 \cos\varphi_1 \cos\theta_1(-k_1 + k_2)] \\ & + (\beta'^4/12)[-k_1 (\sin^2\varphi_1 + \cos^2\varphi_1 \sin^2\theta_1) \\ & - k_2 (\cos^2\varphi_1 + \sin^2\varphi_1 \sin^2\theta_1) - k_3 \cos^2\theta_1] . \end{aligned} \tag{A11}$$

Equation (A8) indicates that $(k_2 + k_3)$ is the term associated with ω_{11}^{-1} in the probability function used by Cruickshank (1961) to describe oscillating motion (in an axial system parallel to the principal axes of oscillation); $1/\omega_{22}$ and $1/\omega_{33}$ may be similarly described.

If oscillation is much smaller about one axis than the others, e.g., $k_3 \to \infty$, so that the body must rotate about z, then $\alpha = 0$ and $\theta_1 = \pi/2$ if V is to remain finite. In other words if one force constant is so great that most of the oscillation is about the axis associated with it, the best description would be a

one-dimensional motion about the axis; i.e., $\mathbf{r}_0$ should be perpendicular to the axis of rotation.

In section 2 only the quadratic terms in the distribution function are considered since the only readily discernible way to integrate (4) if higher order terms are used would consist in expanding these terms as a series. This procedure would lead to a function even more unwieldy than the one derived.

The form of the expression used is

$$D=\exp(-V)=\exp[-(C_1\alpha'^2+C_2\alpha'\beta'+C_3\beta'^2)]. \quad \text{(A12)}$$

The rotation about $\mathbf{r}_0$,

$$\begin{pmatrix}\alpha'\\ \beta'\end{pmatrix}=\begin{pmatrix}\cos\psi_1 & -\sin\psi_1\\ \sin\psi_1 & \cos\psi_1\end{pmatrix}\begin{pmatrix}\alpha\\ \beta\end{pmatrix}, \quad \text{(A13)}$$

where

$$\sin^2\psi_1=\left[1+\left(1-\frac{C_2^2}{C_2^2+(C_3-C_1)^2}\right)^{\frac{1}{2}}\right]\Big/2 \quad \text{(A14)}$$

will transform $D(\alpha', \beta')$ to the form

$$D(\alpha, \beta)=\exp[-(a^2\alpha^2+b^2\beta^2)]. \quad \text{(A15)}$$

Here a^2 and b^2 may be interpreted as one over twice the principal mean-square angular displacements on the surface of the sphere.

APPENDIX B

Calculation of average values of coordinates

The average of a function of θ'' and φ'' is

$$\overline{f(\theta'', \varphi'')}=\frac{\int_0^{2\pi}d\varphi''\int_0^{\pi}d\theta''\sin\theta''f(\theta'', \varphi'')\exp[-(a^2\cos^2\varphi''+b^2\sin^2\varphi'')\theta''^2]}{\int_0^{2\pi}d\varphi''\int_0^{\pi}d\theta''\sin\theta''\exp[-(a^2\cos^2\varphi''+b^2\sin^2\varphi'')\theta''^2]}. \quad \text{(B1)}$$

Using the transformation

$$\begin{aligned}\alpha &= \theta''\cos\varphi''\\ \beta &= \theta''\sin\varphi'',\end{aligned} \quad \text{(B2)}$$

these integrals can be written in the form

$$\overline{f(\theta'', \varphi'')}=\frac{\int_{-\infty}^{\infty}d\alpha\int_{-\infty}^{\infty}d\beta\left(1-\frac{(\alpha^2+\beta^2)}{6}+\frac{(\alpha^2+\beta^2)^2}{120}\cdots\right)F(\alpha, \beta)\exp[-(a^2\alpha^2+b^2\beta^2)]}{\int_{-\infty}^{\infty}d\alpha\int_{-\infty}^{\infty}d\beta\left(1-\frac{(\alpha^2+\beta^2)}{6}+\frac{(\alpha^2+\beta^2)^2}{120}\right)\exp[-(a^2\alpha^2+b^2\beta^2)]}, \quad \text{(B3)}$$

where $F(\alpha, \beta)$ is obtained by expanding $f(\theta'', \varphi'')$ in a power series in θ'' and using (B2). The terms $1-(\alpha^2+\beta^2)/6+(\alpha^2+\beta^2)^2/120$ are the first three terms of $\sin\theta''/\theta''$. This term follows from

$$d\alpha\,d\beta=\theta''\,d\theta''\,d\varphi''. \quad \text{(B4)}$$

In general to fourth order in α and β, $F(\alpha, \beta)$ has the form

$$F(\alpha, \beta)=B_1+B_2\alpha^2+B_3\beta^2+B_4\alpha^4+B_5\alpha^2\beta^2+B_6\beta^4, \quad \text{(B5)}$$

where the terms in odd powers of α and β have been omitted since their average is zero.

Integration of (B3) gives

$$\overline{F(\theta'', \varphi'')}=B_1+\frac{B_2}{2a^2}+\frac{B_3}{2b^2}+\frac{1}{a^4}\left(\frac{3B_4}{4}-\frac{B_2}{12}\right)+\frac{B_5}{4a^2b^2}+\frac{1}{b^4}\left(\frac{3B_6}{4}-\frac{B_3}{12}\right). \quad \text{(B6)}$$

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