

Calculation of the Zero Wave Vector Lattice Frequencies of Alpha- and Beta-Oxygen

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The optically active lattice frequencies of α - and β -O₂ have been calculated in the rigid-molecule approximation using an atom-atom Lennard-Jones [6-12] potential, with and without the addition of an intermolecular quadrupole-quadrupole interaction. Both models predict frequencies reasonably close to those observed experimentally for α -O₂ and support the assignment of the higher-frequency librational mode to the torsion about the twofold axis in the crystal. Excellent agreement is obtained between the observed librational frequency and its temperature dependence in β -O₂ and the results calculated using the Lennard-Jones potential. If it is assumed that the molecules in β -O₂ may be tipped from the crystallographic c axis, an increase in the tilt angle as the temperature is raised is predicted, which is consonant with the temperature dependence of the lattice constants for this phase. It is concluded that the Lennard-Jones atom-atom interaction is a satisfactory model for the potential function in solid oxygen, provided that the packing is such that electron overlaps are small.

INTRODUCTION

Crystalline oxygen exists in three distinct phases. The lowest temperature structure, α -O₂, is stable from 0–23.8°K. From 23.8–43.76°K the stable form is called β -O₂. Between 43.8°K and the melting point of oxygen at 54.4°K the third phase, γ -O₂, is stable.¹ Diffraction studies by x rays, electrons, and neutrons have been carried out on these phases, and their crystal structures have been determined.^{1–4} The studies show that α -O₂ and β -O₂ have ordered structures [$C2/m$ (C_{2h}^3) and $R\bar{3}m$ (D_{3d}^5), respectively], but that γ -O₂ is orientationally disordered [$Pm\bar{3}n$ (O_h^3)].

The lattice regions of α -O₂ and β -O₂ have been investigated by infrared⁵ and Raman⁶ spectroscopy. No optically active lattice modes were observed in the infrared; two Raman-active modes were observed in α -O₂, and one Raman-active mode was observed in the β -O₂ phase. These results are in agreement with group-theoretical predictions for the $\mathbf{k}=0$ vibrations. We have performed a series of calculations of the frequencies of these optically active lattice modes by considering the intermolecular forces in the O₂ crystal in terms of a Lennard-Jones [6-12] potential between pairs of non-bonded oxygen atoms and molecular quadrupole-quadrupole interactions between the centers of mass of the molecules.

METHOD

The formalism for calculating the lattice frequencies of a solid was developed by Born and von Karman in 1912.⁷ In their method the lattice vibrations are characterized by the quantum number \mathbf{k} , the reduced wave vector, which arises from the translational symmetry of the crystal lattice. Only those lattice vibrations which have the value of $\mathbf{k}\approx 0$ are infrared or Raman active, however, and it is only these optically active modes with which we will be concerned. When $\mathbf{k}=0$ the

motions of all primitive cells are in phase, which simplifies the frequency calculation considerably. The problem reduces to finding the symmetry coordinates of the molecules in one primitive cell and expressing the energy of the crystal in terms of a potential function. We shall assume the vibrations to be harmonic small displacements and the interactions to be pairwise. The frequencies may then be calculated using classical mechanics. Walmsley and Pople⁸ have calculated the optically active lattice frequencies of carbon dioxide using this approach, and we shall employ their notation in the following development. Walmsley has since considered in detail the treatment of the torsional lattice vibrations in these frequency calculations.⁹

The Lennard-Jones potential function between two interacting particles has the form

$$u(\text{LJ}) = 4\epsilon[(\sigma/R)^{12} - (\sigma/R)^6], \quad (1)$$

where $u(\text{LJ})$ is the energy of interaction between two particles separated by a distance R , ϵ is a parameter equal to the depth of the potential well of the function, and σ is a parameter related to the value of R when the particles are in equilibrium and the slope of the potential curve is zero. The quadrupole-quadrupole interaction energy between two linear molecules is determined by the following electrostatic equation for the interaction of two point quadrupoles¹⁰:

$$u(\text{quad}) = \frac{3}{4}\Theta^{(1)}\Theta^{(2)}R^{-5}\{1 - 5\cos^2\theta_1 - 5\cos^2\theta_2 + 35\cos^2\theta_1\cos^2\theta_2 - 20\cos\theta_1\cos\theta_2(\mathbf{1}^{(1)}\cdot\mathbf{1}^{(2)}) + 2(\mathbf{1}^{(1)}\cdot\mathbf{1}^{(2)})^2\}. \quad (2)$$

The two molecules, superscripted 1 and 2, respectively, have quadrupole moments of $\Theta^{(1)}$ and $\Theta^{(2)}$, and are separated by a distance R . Their orientation in space is in the direction of the unit vectors $\mathbf{1}^{(1)}$ and $\mathbf{1}^{(2)}$, and the angles they make with the intermolecular vector R

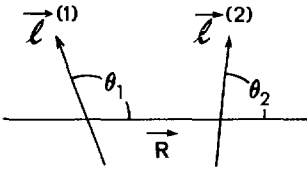


FIG. 1. Coordinate system used to describe the orientations of two linear molecules.

between the centers of mass are θ_1 and θ_2 . Figure 1 shows the correct orientation of the angles in the coordinate system corresponding to the above equation.

The values of the parameters ϵ , σ , and Θ must be determined. From the assumption that the static lattice energy, $U(\text{static lattice})$, of the crystal is equal to the potential energy of the crystal at absolute zero, and the condition that the potential energy is at a minimum when all particles are located at their equilibrium positions, the two Lennard-Jones parameters can be fitted. The quadrupole moment of the molecule in the crystal is taken to be the gas-phase value. Thus none of the parameters required in the calculation are dependent upon the spectroscopic observables.

Let U be the energy of the crystal and $u_{os}(\text{quad})$ be the quadrupole-quadrupole interaction between an arbitrary molecule at lattice point o and its neighbor at lattice point s . Let i be one of a total of m atoms in the molecule composing the crystal, and j be one of the $m(N-1)$ nonbonded neighboring atoms to i . N is Avogadro's number. Then

$$U = \frac{1}{2}N \sum_{s=1}^{N-1} u_{os}(\text{quad}) + \frac{1}{2}N \sum_{i=1}^m \sum_{j=1}^{m(N-1)} 4\epsilon \left[\left(\frac{\sigma}{R_{ij}} \right)^{12} - \left(\frac{\sigma}{R_{ij}} \right)^6 \right]. \quad (3)$$

When all particles are in their equilibrium positions, all $R_{ij} = R_{ij}(\text{eq})$, $u_{os} = u_{os}(\text{eq})$,

$$U_{\text{static lattice}} = \frac{1}{2}N \sum_{s=1}^{N-1} u_{os}(\text{eq}) + \frac{1}{2}N \sum_{i=1}^m \sum_{j=1}^{m(N-1)} 4\epsilon \left[\left(\frac{\sigma}{R_{ij}(\text{eq})} \right)^{12} - \left(\frac{\sigma}{R_{ij}(\text{eq})} \right)^6 \right], \quad (4)$$

and

$$0 = \left. \frac{dU}{dR_{ij}} \right|_{R_{ij}=R_{ij}(\text{eq})} = \frac{1}{2}N \sum_{s=1}^{N-1} u_{os}' - \frac{1}{2}N \sum_{i=1}^m \sum_{j=1}^{m(N-1)} 4\epsilon \left(\frac{12\sigma^{12}}{R_{ij(\text{eq})}^{13}} - \frac{6\sigma^6}{R_{ij(\text{eq})}^7} \right), \quad (5)$$

where u_{os}' is the first derivative of the quadrupole-quadrupole interaction, evaluated at $R = R_{ij}(\text{eq})$.

$U(\text{static lattice})$ is defined by the equation,

$$U(\text{static lattice}) = -(\Delta H_{\text{sub}} + U_{\text{zero pt}}), \quad (6)$$

where ΔH_{sub} is the molar heat of sublimation at 0°K

and $U_{\text{zero pt}}$ is the zero-point vibrational energy of the crystal.

The normal mode frequencies which are optically active can most easily be obtained by expanding the potential function in terms of a Taylor series in the symmetry coordinates of the crystal space group. The members of the set of symmetry coordinates for the crystal will belong to the irreducible representations of the translation group of the crystal. Following the notation of Walmsley and Pople,⁸ they will have the form

$$S_i(\mathbf{k}) = N^{-1/2} \sum_{l=0}^N \exp[2\pi i \mathbf{k} \cdot \mathbf{R}(l)] T_{i,\alpha q} u_\alpha \binom{l}{q}, \quad (7)$$

where N is the number of primitive cells in the crystal, l is the index for these N cells, $\mathbf{R}(l)$ is the position vector of the center of the l th cell, \mathbf{k} is the wavenumber vector,

$$u_\alpha \binom{l}{q}$$

is the α component of the displacement of the q th particle in the l th cell from its equilibrium lattice position, and $T_{i,\alpha q}$ is a member of an $i \times i$ square matrix, where $i = 3n$, n being the number of particles in the primitive cell. When $\mathbf{k} = 0$, Eq. (7) reduces to

$$S_i = N^{-1/2} \sum_{i=0}^N T_{i,\alpha q} u_\alpha \binom{l}{q}. \quad (8)$$

Defining

$$u_\alpha(q) = N^{-1/2} \sum_{l=0}^N u_\alpha \binom{l}{q}, \quad (9)$$

$$S_i = T_{i,\alpha q} u_\alpha(q) \quad (i = 1, \dots, 3n), \quad (10)$$

where we have used the tensor notation convention that a twice-repeated index implies summation over the symbols indexed. These symmetry coordinates are obtained by standard group-theoretical methods.¹¹ They and the normal modes with $\mathbf{k} = 0$ belong to the irreducible representations of the factor group of the space group of the crystal.

The expansion of U about small displacements in S_i takes the form

$$U = U^0 + \sum_{i=1}^{3n} U_i' S_i + \frac{1}{2} \sum_{j=1}^{3n} \sum_{i=1}^{3n} F_{ij} S_i S_j + \dots, \quad (11)$$

where $F_{ij} = \partial^2 U / \partial S_i \partial S_j$, $U_i' = \partial U / \partial S_i$, and U^0 is an arbitrary constant which we shall set equal to zero. In the harmonic approximation used here, the quadratic terms are the highest considered. If the particles in the crystal are at equilibrium, all U_i' must equal zero. Therefore,

$$U = \frac{1}{2} \sum_{j=1}^{3n} \sum_{i=1}^{3n} F_{ij} S_i S_j. \quad (12)$$

The Lagrangian formulation may be used to solve the equations of motion of the $\mathbf{k}=0$ modes. In the harmonic approximation, wave solutions of the form

$$S_j = A_{jj} \sin \omega_j t \quad (13)$$

are assumed, and we are led to the secular equation,

$$|F_{ij} - M\omega^2 \delta_{ij}| = 0, \quad (14)$$

where M is in this case the mass of one oxygen atom. Equation (14) is an equation of order $3n$ in the unknown ω^2 , where ω is the frequency of a normal coordinate.

After the values for the Lennard-Jones parameters have been obtained, and the symmetry coordinates have been generated, the normal mode problem is reduced to expressing F_{ij} in terms of the derivatives of the pairwise potential between atoms. This problem differs slightly for internal, torsional, and translational modes because we are including a molecular quadrupole-quadrupole interaction. However, the form of the potential function is the same for all three cases.

The total energy of interaction in the crystal, U , is assumed to be the sum of all interaction pairs,

$$U = \frac{1}{2} \sum_{l,q} \sum_{l',q'} \psi \begin{pmatrix} l-l' \\ q \quad q' \end{pmatrix}. \quad (15)$$

We define

$$\psi \begin{pmatrix} l-l' \\ q \quad q' \end{pmatrix}$$

as the energy of interaction between the q th atom in the l th cell and q' th atom in the l' th cell. Implicit in this sum is the understanding that for the pair $q=q'$ and $l=l'$,

$$\psi \begin{pmatrix} 0 \\ q \quad q \end{pmatrix}$$

equals zero and all derivatives of

$$\psi \begin{pmatrix} 0 \\ q \quad q \end{pmatrix}$$

do also. This convention is the same as excluding from the sum all interactions of atoms with themselves.¹² During a translational or librational motion the molecule acts as a rigid body. Therefore the derivatives with respect to a particle displacement of

$$\psi \begin{pmatrix} l-l' \\ q \quad q' \end{pmatrix}$$

in Eq. (15), where

$$\psi \begin{pmatrix} l-l' \\ q \quad q' \end{pmatrix}$$

represents the interaction energy of two atoms belonging to the same molecule, must be zero.

Translational Modes

When S_i is a translational symmetry coordinate, the direction of the displacement of each atom in a given molecule is identical; thus there is no change during the vibration in the angular terms inside the braces in Eq. (2). For the purposes of calculating F_{ij} we need consider only nonbonded interactions between atoms on different molecules. Anticipating the simplification, let

$$\psi \begin{pmatrix} l-l' \\ q \quad q' \end{pmatrix} = m^{-2} \psi \begin{pmatrix} l-l' \\ pq \quad p'q' \end{pmatrix}_{\text{quad}} + \psi \begin{pmatrix} l-l' \\ q \quad q' \end{pmatrix}_{\text{LJ}}. \quad (16)$$

The first member of the right-hand side of Eq. (16) is the quadrupolar interaction defined in Eq. (2) multiplied by m^{-2} , where m is the number of atoms in the molecule which forms the crystal. The derivatives are taken only with respect to the R^{-5} term. This quadrupolar term, weighted by m^{-2} is the fraction of the molecule-molecule electrostatic interaction between the two molecules p and p' which can be attributed to the pair of atoms q and q' . The quantity

$$\psi \begin{pmatrix} l-l' \\ pq \quad p'q' \end{pmatrix}_{\text{quad}}$$

interacts between the molecular centers at

$$\begin{pmatrix} l \\ p \end{pmatrix}$$

and

$$\begin{pmatrix} l' \\ p' \end{pmatrix},$$

and has the radial dependence of

$$R^{-5} \begin{pmatrix} l-l' \\ p \quad p' \end{pmatrix}.$$

The second member of the right-hand side of Eq. (16),

$$\psi \begin{pmatrix} l-l' \\ q \quad q' \end{pmatrix}_{\text{LJ}},$$

is the Lennard-Jones interaction

$$\psi \begin{pmatrix} l-l' \\ q \quad q' \end{pmatrix}_{\text{LJ}} = 4\epsilon \left\{ \left[\sigma/R \begin{pmatrix} l-l' \\ q \quad q' \end{pmatrix} \right]^{12} - \left[\sigma/R \begin{pmatrix} l-l' \\ q \quad q' \end{pmatrix} \right]^6 \right\}. \quad (17)$$

It is then fairly straightforward¹³ to derive the expression for F_{ij} ,

$$\begin{aligned}
 F_{ij} &= \partial^2 U / \partial S_j \partial S_i \\
 &= \sum_q \sum_{\alpha, \beta} T_{i, \alpha q} T_{j, \beta q} \\
 &\quad \times \left\{ \sum_{l'q'} \left[\frac{\partial^2 \psi \left(\begin{smallmatrix} l-l' \\ q \quad q' \end{smallmatrix} \right)}{\partial u_\beta \left(\begin{smallmatrix} l \\ q \end{smallmatrix} \right) \partial u_\alpha \left(\begin{smallmatrix} l \\ q \end{smallmatrix} \right)} \right] \right. \\
 &\quad \left. - \sum_{\alpha q} \sum_{\beta q'} T_{i, \alpha q} T_{j, \beta q'} \right. \\
 &\quad \times \left[\sum_{l'} \frac{\partial^2 \psi \left(\begin{smallmatrix} l-l' \\ q \quad q' \end{smallmatrix} \right)}{\partial u_\beta \left(\begin{smallmatrix} l' \\ q' \end{smallmatrix} \right) \partial u_\alpha \left(\begin{smallmatrix} l \\ q \end{smallmatrix} \right)} \right] \}. \quad (18)
 \end{aligned}$$

The expressions for the interaction constants in Eq. (18) are derived directly from Eqs. (16) and (17). For translational lattice modes

$$\begin{aligned}
 &\frac{\partial^2 \psi \left(\begin{smallmatrix} l-l' \\ q \quad q' \end{smallmatrix} \right)}{\partial u_\beta \left(\begin{smallmatrix} l' \\ q' \end{smallmatrix} \right) \partial u_\alpha \left(\begin{smallmatrix} l \\ q \end{smallmatrix} \right)} \\
 &= 4\epsilon \left(\frac{12(14)\sigma^{12}}{R^{16}} - \frac{6(8)\sigma^6}{R^{10}} \right) R_\alpha R_\beta - 4\epsilon \left(\frac{12\sigma^6}{R^{14}} - \frac{6\sigma^6}{R^8} \right) \delta_{\alpha\beta} \\
 &\quad + \frac{3\Theta^2}{4m^2} (35R_\alpha R_\beta R^{-9} - 5R^{-7}) [1 - 5 \cos^2 \theta_1 - 5 \cos^2 \theta_2 \\
 &\quad + 35 \cos^2 \theta_1 \cos^2 \theta_2 - 20 \cos \theta_1 \cos \theta_2 (\mathbf{1}^{(1)} \cdot \mathbf{1}^{(2)}) + 2(\mathbf{1}^{(1)} \cdot \mathbf{1}^{(2)})^2]. \quad (19)
 \end{aligned}$$

Torsional Modes

The derivation of F_{ij} for translational lattice modes involved taking derivatives with respect to the distance between particles. When we look at F_{ij} for librational modes, only

$$\psi \left(\begin{smallmatrix} l-l' \\ q \quad q' \end{smallmatrix} \right)_{LJ}$$

of Eq. (17) is considered as a differentiable function of distance. The quantity

$$\psi \left(\begin{smallmatrix} l-l' \\ pq \quad p'q' \end{smallmatrix} \right)_{\text{quad}}$$

for librations must be considered to undergo only angular variation, since the molecular centers remain fixed during torsional oscillations. Consequently, Eq. (18) is no longer appropriate for expressing F_{ij} for torsional modes. It is correct for

$$\psi \left(\begin{smallmatrix} l-l' \\ q \quad q' \end{smallmatrix} \right)_{LJ},$$

but it must be modified to express angular, rather

than radial, displacements in

$$\psi \left(\begin{smallmatrix} l-l' \\ pq \quad p'q' \end{smallmatrix} \right)_{\text{quad}}.$$

A rigid linear molecule has two degrees of angular freedom. One convenient way to define these degrees of freedom is to express them as rotations about the two principal axes of the molecule perpendicular to the internuclear axis. The effective mass for these motions would then be the moment of inertia, I , of the molecule taken about one of these axes. Actually any two non-parallel axes of rotation, neither of which lie along the internuclear axis, and both of which pass through the center of mass of the molecule will be appropriate as long as the correct moments of inertia are used. We shall use angular displacements about two such axes of rotation to describe the change in

$$\psi \left(\begin{smallmatrix} l-l' \\ pq \quad p'q' \end{smallmatrix} \right)_{\text{quad}}$$

during a torsional oscillation.

We shall now convert the pure displacement symmetry coordinates S_i of Eq. (10) into mass-weighted symmetry coordinates. For the homonuclear molecules considered here, this change multiplies all $T_{i, \alpha q}$ in Eq. (10) by the factor $M^{-1/2}$ and eliminates the mass M from Eq. (14). Only two symmetry coordinates are needed to describe the torsional modes of either α - or β -oxygen, since each phase has only one molecule per primitive cell. These coordinates can be written

$$S_1 = M^{1/2} [u_x(1) - u_x(2)] \quad \text{and} \quad S_2 = M^{1/2} [u_y(1) - u_y(2)], \quad (20)$$

where S_1 corresponds to torsion about an axis parallel to the y axis of the crystal, S_2 corresponds to torsion about an axis parallel to the x axis of the crystal, M is the mass of an oxygen atom, and u_x, u_y are atomic displacements. We can convert these mass-weighted atomic displacement coordinates to mass-weighted angular displacement molecular coordinates by replacing all atomic displacements $u_\alpha(q)$ which belong to molecule p by one molecular angular displacement $\lambda(p)$ and substituting the factor $I_i^{-1/2}$ for $M_i^{-1/2}$ in $T_{i, \alpha p}$. I_i must be the moment of inertia taken about the axis of rotation defined by the displacements of the atom in S_i . Let us specify for an oxygen molecule a set of equilibrium position axes (x_0, y_0, z_0) such that z_0 coincides with the equilibrium position of the molecular axis and y_0 coincides with the twofold symmetry axis of α -oxygen. We can then describe the two optically active lattice modes of each phase as librations about the x_0 and y_0 axes. The primitive-cell symmetry coordinates are then

$$S_1 = I^{1/2} \lambda^{y_0} \quad \text{and} \quad S_2 = I^{1/2} \lambda^{x_0}, \quad (21)$$

where I is the moment of inertia of O_2 and λ^{x_0} and λ^{y_0} are the angular displacements about x_0 and y_0 . This choice of coordinates follows that of Cahill and Leroi⁶; our λ^{x_0} and λ^{y_0} are their θ^{x_0} and θ^{y_0} , respectively.

When the molecules are in their displaced positions from equilibrium during a torsional oscillation, the quadrupolar interaction between two molecules p and p' in unit cells l and l' , respectively, can be written in terms of the angular variables of the interaction as

$$\psi \begin{pmatrix} l-l' \\ p \quad p' \end{pmatrix}_{\text{quad}} = \psi \left\{ \Lambda \begin{pmatrix} l \\ p \end{pmatrix} + \lambda \begin{pmatrix} l \\ p \end{pmatrix}, \Lambda \begin{pmatrix} l' \\ p' \end{pmatrix} + \lambda \begin{pmatrix} l' \\ p' \end{pmatrix} \right\}_{\text{quad}}. \quad (22)$$

In the above expression,

$$\Lambda \begin{pmatrix} l \\ p \end{pmatrix}$$

is the equilibrium angular coordinate of the molecule at

$$\begin{pmatrix} l \\ p \end{pmatrix}$$

and

$$\lambda \begin{pmatrix} l \\ p \end{pmatrix}$$

is the angular displacement from equilibrium. The same meaning is given to the primed symbols on the other molecule. When Eq. (22) is differentiated with respect to angular displacements an expression for the torsional force constants similar to Eq. (18) is derived,

$$\begin{aligned} F_{ij}(\text{quad}) &= \partial^2 U_{(\text{quad})} / \partial S_j \partial S_i \\ &= \sum_p \sum_{\alpha, \beta} T_{i, \alpha p} T_{j, \beta p} \\ &\times \left[\sum_{l' p'} \partial^2 \psi \begin{pmatrix} l-l' \\ p \quad p' \end{pmatrix} / \partial \lambda_\alpha \begin{pmatrix} l \\ p \end{pmatrix} \partial \lambda_\beta \begin{pmatrix} l \\ p \end{pmatrix} \right] \\ &\quad + \sum_{\alpha p} \sum_{\beta p'} T_{i, \alpha p} T_{j, \beta p'} \\ &\times \left[\sum_{l'} \partial^2 \psi \begin{pmatrix} l-l' \\ p \quad p' \end{pmatrix} / \partial \lambda_\alpha \begin{pmatrix} l \\ p \end{pmatrix} \partial \lambda_\beta \begin{pmatrix} l' \\ p' \end{pmatrix} \right]. \quad (23) \end{aligned}$$

Let us define $F_{ij}(\text{LJ})$ to be equal to the expression in Eq. (18) when

$$\psi \begin{pmatrix} l-l' \\ q \quad q' \end{pmatrix} = \psi \begin{pmatrix} l-l' \\ q \quad q' \end{pmatrix}_{\text{LJ}}$$

only. Then for librational modes,

$$F_{ij} = F_{ij}(\text{LJ}) + F_{ij}(\text{quad}). \quad (24)$$

Evaluating the expressions

$$\partial^2 \psi \begin{pmatrix} l-l' \\ p \quad p' \end{pmatrix} / \partial \lambda_\alpha \begin{pmatrix} l \\ p \end{pmatrix} \partial \lambda_\beta \begin{pmatrix} l' \\ p' \end{pmatrix}$$

and

$$\partial^2 \psi \begin{pmatrix} l-l' \\ p \quad p' \end{pmatrix} / \partial \lambda_\alpha \begin{pmatrix} l \\ p \end{pmatrix} \partial \lambda_\beta \begin{pmatrix} l \\ p \end{pmatrix}$$

in Eq. (23) involves taking the derivatives of the angular part of the quadrupolar interaction in Eq. (2) with respect to the angular displacements. After the variables θ_1 , θ_2 , $1^{(1)}$, and $1^{(2)}$ in Eq. (2) are transformed to the angular coordinates chosen to represent the librational motion, there are no difficulties in obtaining the derivatives. The details of this calculation of the second derivatives in Eq. (23) are given by Cahill⁶ and Laufer.¹³

RESULTS AND DISCUSSION

Alpha-Oxygen

Alpha-oxygen has a monoclinic structure with a $C2/m$, b axis unique (C_{2h}^3) space group and one molecule per primitive cell. The unit cell contains two molecules centered on $\frac{1}{2} \frac{1}{2} 0$ and 000 , each molecule positioned with its $O-O$ bond normal to the (001) plane. The unit-cell dimensions are $a = 5.403 \pm 0.005$ Å, $b = 3.429 \pm 0.003$ Å, $c = 5.086 \pm 0.005$ Å, $\beta = 132.53 \pm 0.03^\circ$.¹ Since alpha-oxygen has only one molecule per primitive cell, which lies on a center of symmetry, there should be no translational lattice modes active in the ir, and the torsional modes should be active only in the Raman spectrum. As expected, a study of the far-ir region failed to show any lattice absorption.⁵ Each O_2 molecule has two degrees of rotational freedom. We then expect α - O_2 to have two Raman-active torsional lattice modes. The correlation diagram for α - O_2 , which is given in Fig. 2, shows that the torsion about the y axis of the crystal has A_g symmetry and the torsion about the x axis has B_g symmetry; because of the different symmetry, there is no mixing between the two torsional modes. Recent experimental work on solid oxygen by Raman scattering⁶ disclosed that at about 15°K these two modes have frequencies of 44.5 and 79 cm^{-1} . One of these modes can be described as a torsion of the molecules in the (010) plane and the other one can be similarly described as a torsion in the (100) plane. Alternatively, they may be viewed as motions about axes parallel to the y and x axes of the crystal, respectively; the corresponding angular frequencies are designated ω_y and ω_x . In the present calculations only ω_y^2 and ω_x^2 , which are related to the sums of the pairwise coupling constants K by the harmonic-oscillator dispersion relation, appear. The final torsional frequencies, in wavenumber units, corresponding to the motions parallel to the y and x axes, are designated ν_y and ν_x .

Mode	Molecular Symmetry	Site Symmetry	Factor Group Symmetry	Activity
	$D_{\infty h}$	C_{2h}	C_{2h}	$y=C_2$ screw axis
ν	Σ_g^+	A_g	A_g	$(R_y)(\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xz})$
R_x, R_y	Π_g	B_g	B_g	$(R_x, R_z)(\alpha_{yz}, \alpha_{xy})$
T_z	Σ_u^+	A_u	A_u	(T_y)
T_x, T_y	Π_u	B_u	B_u	(T_x, T_z)

FIG. 2. Correlation diagram for α -oxygen.

Calculations of the torsional lattice frequencies of α -O₂ were carried out in two approximations. The first, Calculation A, assumed a Lennard-Jones atom-atom plus a quadrupole-quadrupole molecular interaction between the pairs of oxygen atoms. In the second, Calculation B, only the atom-atom Lennard-Jones force field in the crystal was considered. Table I summarizes the results of the calculations.

The O₂ molecules in α -O₂ are all parallel. In this orientation, their quadrupole-quadrupole interaction energy is slightly repulsive. The 156 nearest neighbors to a given molecule (out to a distance of 11 Å) were

used to calculate the contribution of the quadrupole-quadrupole interaction to the static lattice energy of the crystal. Interactions beyond 11 Å did not contribute significantly to the lattice energy sum. The magnitude of the quadrupole interaction energy was about 3% of the total lattice energy (see Table I), the remainder being attributed to the Lennard-Jones interaction between nonbonded atoms. Lattice energy sums for atom-atom interactions were taken out to a distance of 10 Å over 234 nearest nonbonded neighbors, and the Lennard-Jones parameters obtained were $\sigma = 2.983$ Å and $\epsilon = 0.7921 \times 10^{-14}$ erg/atom. The contributions to

TABLE I. The quantities and coupling constants K entering into the calculation of the librations of alpha-oxygen.

		$\Theta (10^{26} \text{ esu})^a$	-0.39				
		$\Delta H_{\text{sub}} (\text{cal/mole})^b$	+2294				
		$\Theta_D (\text{°K})^c$	126				
		$(9/8)R\Theta_D (\text{cal/mole})$	282				
		$I_e (10^{40} \text{ g-cm}^2)^d$	19.37				
		$U(\text{static lattice}) (10^{12} \text{ erg/molecule})$	-0.1790				
		$U(\text{quad}) (10^{12} \text{ erg/molecule})$	0.0058				
		Distance to origin	Number of neighbors at distance	LJ+Quad Calc A ν_x	LJ+Quad Calc A ν_y	LJ Calc B ν_x	LJ Calc B ν_y
$\sigma (\text{Å})$				2.983	2.983	2.988	2.988
$\epsilon (10^{14} \text{ erg/atom})$				0.7921	0.7921	0.8007	0.8007
$K(\text{quad}) (\text{dyn/cm})$	3.200	4	-5.9	-34.9			
$K(\text{quad})$	3.429	2	-38.5	-9.6			
$K(\text{quad})$	4.187	4	-3.0	-6.6			
$K(\text{LJ}) (\text{dyn/cm})$	3.153	2	443.0	1192.6	447.9	1205.9	
$K(\text{LJ})$	3.200	4	333.7	881.1	337.4	898.0	
$K(\text{LJ})$	3.210	1	35.4	3398.4	35.8	3436.2	
$K(\text{LJ})$	3.420	4	89.0	77.9	90.0	78.9	
$\omega^2(\text{quad}) (10^{26} \text{ sec}^{-2})$			-0.138	-0.160			
$\omega^2(\text{LJ}) (10^{26} \text{ sec}^{-2})$			0.929	4.695	0.940	5.00	
$\nu_{\text{calc}} (\text{cm}^{-1})$			47.1	113.0	51.5	118.6	
$\nu_{\text{exptl}} (\text{cm}^{-1})^e$			44	79	44	79	

^a D. E. Stogryn and A. P. Stogryn, *Mol. Phys.* **11**, 371 (1966).^b W. F. Giauque and H. L. Johnson, *J. Am. Chem. Soc.* **51**, 2300 (1929).^c M. O. Kostryukova and P. G. Strelkov, *Dokl. Akad. Nauk SSSR* **90**, 525 (1953), quoted by G. E. Jelinek, Ph.D. thesis, University of Washington, 1967.^d G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (Van Nostrand, Princeton, N. J., 1950), 2nd ed., p. 560.^e Reference 6.

the coupling constants from each type of interaction are also listed in Table I, along with the final frequencies calculated: $\nu_y = 113.0 \text{ cm}^{-1}$ and $\nu_x = 47.1 \text{ cm}^{-1}$.

The quadrupole-quadrupole interaction used here is derived from a series expansion of the classical electrostatic interaction of two clusters of charged particles.¹⁴ Implicit in this expansion is the assumption that the distance between the particles in each cluster is much smaller than the distance between clusters. In $\alpha\text{-O}_2$, and in molecular crystals in general, this approximation must be suspect because of the closeness of the packing of the molecules. On a strictly point-atom basis, any oxygen atom sees its bonded neighbor at a distance of 1.207 \AA and its nearest nonbonded neighbor at 3.153 \AA . Barrett and Meyer¹⁵ discuss the packing in $\alpha\text{-O}_2$ from another point of view, in terms of the computed electron density contours of molecular oxygen. They apply to $\alpha\text{-O}_2$ a conclusion of Bader, Henneker, and Cade¹⁶ which states that in general the equilibrium distance between the centers of two homonuclear diatomic molecules is given by the contact of the 0.002 density contours of the molecules. Within the computed 0.002 contour resides over 95% of the electronic charge of the molecule. For O_2 , the predicted equilibrium distance is 3.18 \AA . This value is in very good agreement with the observed distance of 3.20 \AA between nearest molecular neighbors.

In view of the fact that there is probably about 5% overlap between adjacent molecules, one cannot be sure what the value of the quadrupole moment of O_2 is in its lowest-temperature solid phase. The meaning of the frequencies of $\alpha\text{-O}_2$ calculated from a Lennard-Jones plus quadrupole-quadrupole interaction (Calculation A) using the gas-phase value of the quadrupole moment must therefore be somewhat uncertain. The results do show that the $\alpha\text{-O}_2$ crystal is not bonded together by the attraction of the quadrupoles, since their interaction energy sum was repulsive and the negative values of both $\omega_x^2(\text{quad})$ and $\omega_y^2(\text{quad})$ indicate instability.

The frequency calculation was repeated, as Calculation B, with no quadrupolar interaction; the Lennard-Jones potential now represented all interactions. This approximation resulted in values of $\sigma = 2.988 \text{ \AA}$ and $\epsilon = 0.8007 \times 10^{-14} \text{ erg/atom}$. Note that σ remained essentially constant in the two calculations, but that ϵ increased to absorb that part of the static lattice energy which was formerly attributed to the quadrupolar interaction. For a pure Lennard-Jones crystal σ is independent of the static lattice energy and is determined solely by the lattice constants and the geometry of the crystal. When the quadrupolar contribution to the lattice energy is small, as in the case of $\alpha\text{-O}_2$, σ has essentially the same independence from energy values; hence the negligible change in its value between the two calculations. Calculation B yielded values of $\nu_y = 118.6 \text{ cm}^{-1}$ and $\nu_x = 51.5 \text{ cm}^{-1}$. These frequencies are higher than those of Calculation A, the main reason being the absence of the negative values

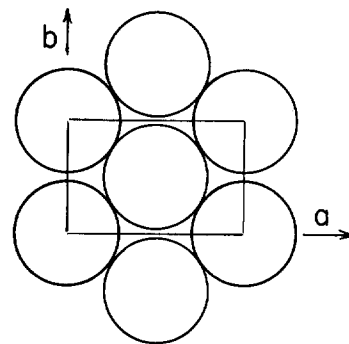


FIG. 3. Projection of molecules in $\alpha\text{-O}_2$ on the ab plane, with the 0.002 contours of electron density indicated.¹⁷

of $\omega^2(\text{quad})$. Table I shows that for both Calculations A and B, the $\omega^2(\text{LJ})$ contributions agree to within about 1%. Both calculations assign the high-frequency mode to the torsion about the y axis and the low-frequency mode to the torsion about the x axis. Figure 3¹⁷ shows the packing in $\alpha\text{-O}_2$ in projection onto the ab plane at the 0.002 electron density contour. One can see that the O_2 molecules are more tightly packed along the a axis than along the b axis. Thus one expects that there will be appreciably more hindrance encountered by the O_2 molecules in the A_g mode than in the B_g mode, and that ν_y will be of higher frequency than ν_x , as our calculations indicate. This assignment is further substantiated by intensity considerations based on the oriented gas model.⁶ Calculations A and B both show good agreement with experiment for the low-frequency mode and only fair agreement with experiment for the high-frequency lattice vibration. The inclusion of the quadrupolar interaction led to frequencies that were somewhat closer to the experimental values than those frequencies derived from only a Lennard-Jones potential, but the two calculations did not differ substantially; the computed A_g torsions agreed with one another to within 5%, and the B_g torsions agreed to within 9%.

It is not necessary to consider molecules at too great a distance from a molecule taken as an origin to obtain a good value for the force constants of the lattice modes. The 10 nearest molecular neighbors, which are within 4.187 \AA , account for over 99% of the value of $\omega_y^2(\text{quad})$, while the 12 nearest molecular neighbors, extending out to 4.231 \AA , account for over 99% of $\omega_x^2(\text{quad})$. The Lennard-Jones potential, which is of shorter range than the quadrupolar potential, gave coupling constants which summed to over 99% of $\omega_i^2(\text{LJ})$ at a radial distance of only 3.635 \AA , which includes only the 14 nearest neighbor atoms.

Beta-Oxygen

Beta-oxygen is the stable form of oxygen between 23.8 and 43.8°K . It is a rhombohedral lattice of space group $R\bar{3}m(D_{3d}^5)$ with one molecule per primitive cell.^{1,4} Figure 4 shows the geometric configuration of the lattice. The two parameters that characterize the structure are c_0 , the length of the c axis of the unit cell

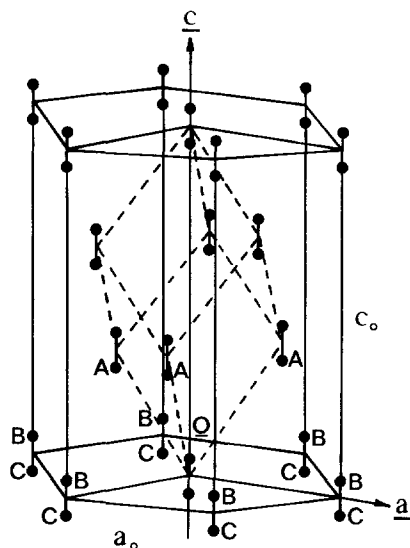


FIG. 4. Schematic representation of the rhombohedral lattice of β -O₂. The oxygen atoms are denoted by solid circles, and the atom slightly above the center of the base hexagon is taken as the origin, O.

which measures the distance between the (001) planes, and a_0 , the length of the a axis which measures the spacing of the hexagonal arrangement of the molecules in the (001) planes. The structure determination of β -O₂ shows the internuclear axis of the oxygen molecules to be aligned parallel to the c axis of the crystal; however, Alikhanov¹⁸ and Barrett and Meyer¹⁵ believe that the molecules are precessing about the c axis and are really tipped off the c direction by an angle of 30° (Alikhanov) or 75° (Barrett and Meyer).

If the molecules are not tilted with respect to the c axis, two Raman-active librational modes are expected, but because of the S_6 symmetry of the lattice about the c axis, these modes should be degenerate. The Raman spectrum does show just one lattice mode, which shifts from 51 cm⁻¹ at 24°K to 46 cm⁻¹ at 42°K.⁶

If the molecules are randomly tilted, the observed diffraction patterns may be produced by motions in which the molecules either precess as rotors about the c axis or flip spontaneously between a set of symmetrically equivalent equilibrium positions situated about the c axis. If the number of equilibrium positions is large enough, or the rate of flipping is rapid enough, the analysis will not be able to distinguish between the precessional motion and the flipping motion. A precessional motion is regarded as a rotation, but a tilted molecule which can spontaneously flip from one orientation to another must be regarded as having only oscillatory motions. In some cases, where a crystal is at a high enough temperature so that its lattice modes are sufficiently excited so that the heat capacity is near the classical limit, the value of C_v can be used to distinguish between flipping and rotational motions in the

crystal¹⁹; however, β -oxygen is at too low a temperature for this method to apply.

A crystal of molecules which undergo motions such as those described above will have over a time average the same equilibrium positions as a crystal of nontilted molecules. However, in this case the coordinates for the positions of the oxygen atoms along the c axis will be the projections of the tilted molecule onto the axis. If the molecules librate at a frequency which is significantly greater than the average time it takes a molecule to flip, the frequencies of the torsional modes of β -O₂ will be independent of the direction of the molecular axis in the (001) plane. Experimental observations of the lattice torsions by Raman spectroscopy show only one broad band, about 16 cm⁻¹ in half-width. For a tilted molecule, one can describe two torsions, one parallel to the (001) plane and one perpendicular to it. Since only one broad band is observed for these torsions, we can conclude that in the flipping-molecule model their frequencies would have to be almost degenerate.

A precessing molecule has only one librational degree of freedom; the other degree of rotational freedom is the precession itself. Because of the isotropic nature of the (001) plane, the librational frequency should be identical to the frequency of the torsion parallel to the (001) plane of the flipping model, assuming that the molecules in both models make the same angle with the c axis. Transitions of a precessional motion have not been observed²⁰; they will not be infrared active because the primitive cell will undergo no change in dipole moment, but they are expected to be Raman active if they do exist.

Free rotation of molecules in crystals has been generally accepted only in the case of solid hydrogen. Blumenfeld²¹ has concluded that the molecules undergo hindered rotation in liquid O₂. It is reasonable to assume that the molecules in β -O₂, at a lower temperature and in a solid phase, do not have greater rotational freedom than in the liquid. Precession, in the sense that it means free rotation about an axis, is therefore highly unlikely in β -O₂. Although our calculation of the torsional lattice mode of β -O₂ would not be different if a precessional motion rather than a flipping one was used, we shall base further discussion of β -O₂ on the supposition that the molecules are tilted at some constant angle, but that they are free to spontaneously flip to a different position about the c axis.

The calculations of the doubly degenerate torsion of β -O₂ were made using the potentials fitted to α -O₂ at absolute zero. It is assumed that Lennard-Jones parameters calculated at 0°K should be equally valid for any temperature or phase of solid oxygen. When calculations of the quadrupole-quadrupole interaction energy were made in a no-tilt configuration for β -O₂, this energy was found to be repulsive. In addition the value of $\omega^2(\text{quad})$ was negative, as it was in α -O₂. The inclusion of $\omega^2(\text{LJ})$ gave final frequencies of 42.0 cm⁻¹ at 26°K and 36.7 cm⁻¹ at 42°K, which are

9 cm^{-1} below the experimental values. When only the Lennard-Jones potential of Calculation B of $\alpha\text{-O}_2$ was used, the theoretical values improved to the point where they were only 1 cm^{-1} below the observed frequencies. Table II compares the results of calculations using only the Lennard-Jones potential with calculations using the Lennard-Jones plus quadrupolar interaction. Since the former model gave better agreement with experiment, it alone was used in subsequent calculations on $\beta\text{-O}_2$.

As the temperature of $\beta\text{-O}_2$ is increased, the crystal expands in the a direction and contracts in the c direction.¹ This negative expansion coefficient in the c direction, which is highly unusual, albeit very small, can be explained if it is assumed that the oxygen molecules are tilted about the c direction in the crystal. At low temperatures the molecules are relatively tightly packed, and the closeness of the molecules in the (001) planes tends to keep the O_2 molecule upright and to minimize the angle of tilt. As the temperature is raised the packing in the (001) planes [ab planes] becomes looser and the molecules can tilt more with respect to the c axis. The distance between nonbonded atoms in the c direction would then be increased and the spacing between the (001) planes could decrease to maintain close packing of the O_2 molecules, establishing a new equilibrium distance and a smaller value of c_0 , the c -axis lattice constant. The molar volume of $\beta\text{-O}_2$ increases with temperature, indicating on the average a greater distance between nonbonded atoms and therefore a weakened interaction between particles with increasing temperature. This weakened interaction results in the decrease of the experimental frequency of the librational lattice mode 6 cm^{-1} between 24 and 44°K.⁶

The frequency of the torsional lattice mode of $\beta\text{-O}_2$ was considered at seven different temperatures ranging from 26–42°K. At each temperature the angle of tilt of the molecules was varied from 0–70.6° and the frequency of the lattice mode was calculated. Lattice constants of $\beta\text{-O}_2$ for each temperature were taken from the data of Barrett *et al.*,¹ and the coordinates of the projection of the oxygen atoms on the c axis were used to define the average position of the randomly flipping molecules. Only Lennard-Jones interactions at a distance of less than 8.00 Å were considered, but this distance was sufficient to include at least the first 111 nearest nonbonded neighbors, which account for more than 99% of the forces. A complete tabulation of the results of these calculations may be found in Ref. 13.

At each temperature the change of the lattice mode frequency with increasing angle of tilt shows the same trend: As the molecules begin to tilt off the c axis the torsional frequency decreases; however, in the vicinity of a tilt of 30° the frequency begins to increase, rising above the value at 0° as the angle is further increased. The explanation of this behavior lies in the distribution of the 15 nearest nonbonded neighbors. As in $\alpha\text{-O}_2$,

TABLE II. Comparison of calculations of the beta-oxygen torsion assuming the O_2 molecules are parallel to c axis.

	a_0 (Å)	c_0 (Å)	$u(\text{quad})(10^{12} \text{ erg/molecule})$	
26°K ^a	3.272	11.2770	0.00580	
42°K	3.332	11.2730	0.00522	
			26°K	42°K
Distance of centers of 6(001) plane nearest molecular neighbors to origin at intersection of a and c axes			3.272	3.332
Distance of centers of six out-of-plane nearest molecular neighbors to origin at intersection of a and c axes			4.207	4.221
Distance of type A atoms to origin $O(\text{Å})$			3.175	3.194
Distance of type B atoms to origin $O(\text{Å})$			3.272	3.332
Distance of type C atoms to origin $O(\text{Å})$			3.488	3.544
$\omega^2(\text{quad})(10^{26} \text{ sec}^{-2})$			-0.150	-0.135
$\omega^2(\text{LJ})(10^{26} \text{ sec}^{-2})$			0.776	0.613
$\nu(\text{cm}^{-1})$			42.0	36.7
$\omega^2(\text{LJ})(10^{26} \text{ sec}^{-2})$			0.885	0.711
$\nu(\text{cm}^{-1})$			49.9	44.7
$\nu(\text{experimental})^b$			51	46

^a Reference 1.

^b J. E. Cahill, Ph.D. thesis, Princeton University, Princeton, N. J., 1968.

these account for almost all of ω^2 . Referring to Fig. 4, which depicts $\beta\text{-O}_2$ at zero tilt, one observes that there are three equivalent nearest neighbors of type A in the plane above the atom at the origin, O , six equivalent next nearest neighbors of type B in the plane of the origin, and then six further neighbors of type C which are bonded to the type B neighbors. At 26°K their distances from the origin atom are 3.175, 3.272, and 3.488 Å, respectively.

Increasing the angle of tilt has a different effect on each of the interaction constants of the three types of neighbors with the atom at the origin. The greater the amount of tilt the closer the coordinates of the projections of the atoms onto the c axis get to the position of the center of mass of the O_2 molecules. Thus type A atoms recede from the origin and their interaction constants decrease. Type B atoms remain at a fixed distance from the origin no matter what the angle of tilt, so their interaction constants are invariant with tilt. Last, type C atoms approach type B atoms as the tilt increases, resulting in a decreased distance of the type C atoms from the origin and an increased interaction. The changes in ω^2 with increasing tilt are therefore due to the net effect of the diminishing interactions of the three type A atoms and the increasing interactions of the six type C atoms.

The initial decrease in frequency from a tilt of 0° to about 30° is due to the dominance of the weakening type A interactions over the increasing type C interactions. Increasing the tilt past 30° gives the interactions of type C atoms greater weight than the type A interactions. The frequency continues to increase as the tilt goes from 30° to 70° . The order of the distances of the nearest neighbors to the origin also changes with the angle of tilt. For the lattice at 26°K , when the tilt reaches an angle of 30° the order of the type of neighbors in increasing distance from the origin changes from A, B, C, to B, A, C. At 42° it has changed to B, C, A, and remains so until an angle of 90° , at which point atoms of type B and C become coincident.

The experimental value of the $\beta\text{-O}_2$ torsion at 26°K is 51 cm^{-1} , which corresponds to a calculated tilt of 41° . At 35°K the librational frequency is 49 cm^{-1} , indicating a tilt of 46° . When the crystal is at 42°K the torsional frequency is 46 cm^{-1} , which correlates with a tilt of 49° . This trend of increasing tilt with increasing temperature is consistent with a picture of the $\beta\text{-O}_2$ structure which gets looser with higher temperature. Our results show that $\beta\text{-O}_2$ is fairly rigid even though the lattice may have orientational disorder. We note that the angle of tilt varies only 8° over a temperature range of 16°K , which is almost the entire temperature range of the beta phase. The amplitudes of the librations are not particularly large. Using harmonic-oscillator wavefunctions, they were calculated to be 10.4° at a temperature of 28°K and a frequency of 51 cm^{-1} .²⁰

Although these calculations of the variation of the torsional frequency are interesting, one must not place too much faith in the numerical value of the tilt angle which precisely reproduces the experimental frequency. Our calculations of the torsional frequency when the molecules are parallel to the c axis (zero tilt) are within the experimental error of $1\frac{1}{2}\text{ cm}^{-1}$ for the observed value of the torsional mode, and this is most satisfying when one considers the many assumptions implicit in the model used. The significance of these calculations is that they correctly predict the decrease in frequency with increasing temperature, and that there is quite satisfactory numerical agreement between the observed frequencies and the ones calculated for acceptable structures. The Lennard-Jones potential predicts the librational frequency very well from the lattice parameters of $\beta\text{-O}_2$. The possibility that the O_2 molecules are tilted with respect to the c axis cannot be ruled out, however, especially since the calculated increase in the angle as the temperature is raised would be expected if such a tilt did exist, on the basis of the observed temperature dependence of the lattice parameters of $\beta\text{-O}_2$ cited above.¹

CONCLUSIONS

Calculations of the optically active lattice modes of α - and β -oxygen have been made using only a Lennard-

Jones atom-atom potential (Calculation B), and with a Lennard-Jones plus quadrupole-quadrupole interaction as the potential function (Calculation A). The latter calculations for beta oxygen in a nontilted configuration are 15%-20% lower than the experimental frequencies, while those of Calculation B give values which agree with the observed frequencies to within experimental error. The alpha-oxygen torsional modes are slightly better predicted with the Calculation A potential; however, neither gives completely satisfactory numerical agreement with experiment. In both ordered solid phases the quadrupolar interaction contribution to the lattice stability is of a repulsive nature, causing the lattice frequencies of Calculation A to be lower than those of Calculation B. We believe that taken as a whole, the inclusion of the quadrupolar interaction fails to improve our potential function, probably because the molecules in the crystal lie too close together to one another for a point molecular quadrupole approximation to be valid.

If the assumption is made that the O_2 molecules are tilted with respect to the c axis of $\beta\text{-O}_2$, and that they can flip randomly about this axis, then a tilt of 41° is predicted using the Lennard-Jones potential and fitting the observed librational frequency and lattice constants at 26°K . Increasing the temperature to 42°K changes the calculated angle of tilt to 49° . Barrett and Meyer¹³ believe that a tilt of 75° is necessary to achieve in $\beta\text{-O}_2$ the contact of the 0.002 electron density contours of the O_2 molecules, which according to Bader, *et al.*¹⁶ should establish the equilibrium intermolecular separation. Although the numerical results are by no means exact, our calculations indicate looser packing in this phase.

In $\alpha\text{-O}_2$ the molecules are situated near enough to one another so that the intermolecular separations predicted from the theory of Bader, Henneker, and Cade are observed. Raman spectroscopy shows two torsional modes at 44 and 79 cm^{-1} . These frequencies calculated using a Lennard-Jones atom-atom potential are 51.5 and 118.6 cm^{-1} . The inability of the Lennard-Jones potential to predict accurately the libration at 79 cm^{-1} is probably because it does not properly take account of electron overlap effects. A quantum mechanical calculation which considers electron interactions would be necessary to more closely predict the observed frequency. Qualitatively, both potential models used in this study support the assignment of the higher-frequency libration as the torsion about the y axis, in agreement with packing and intensity considerations.

The Lennard-Jones potential which gave excellent calculated frequencies for $\beta\text{-O}_2$ was employed without modification of the parameters chosen to fit the equilibrium $\alpha\text{-O}_2$ crystal. These results are evidence that the Lennard-Jones atom-atom potential is a valid approximation to intermolecular forces in solid oxygen provided the molecules are far enough apart so that the intermolecular interactions in the crystal can be considered as a function of the distance between the atomic nuclei.

ACKNOWLEDGMENTS

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Infrared Spectrum and Structure of the SO₂⁻ Radical Ion

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When a sample of SO₂ in a large excess of argon is codeposited at 4 or at 14°K with an atomic beam of an alkali metal, prominent new absorptions appear near 500 cm⁻¹ and between 975 and 1100 cm⁻¹. The pattern of absorptions is somewhat dependent both upon the alkali metal and upon the temperature at which the sample is deposited. Product absorptions which appear at 495, 985, and 1042 cm⁻¹ in samples containing a small concentration of cesium atoms have been demonstrated to be contributed by a single species, shown by isotopic substitution studies to contain one sulfur and two oxygen atoms. A slight splitting in the absorptions of the mixed oxygen isotopic species indicates that the two oxygen atoms are not symmetrically equivalent, either because of a site perturbation or because of a slight nonequivalence of the two S-O bonds. The absorptions have been assigned to the three SO₂⁻ vibrational fundamentals of a charge-transfer complex in which the residual interaction of the cation is sufficiently small that all of the vibrational data can be fitted within experimental error without considering the motion of the cation. The data are consistent with an O-S-O valence angle of 110°±5°. The S-O stretching force constant is significantly lower than that of SO₂, consistent with the addition of an electron to an orbital which is antibonding between the sulfur and two oxygen atoms.

INTRODUCTION

The electron spin resonance spectrum of the SO₂⁻ radical ion has received extensive study. Following the observation by Dunitz¹ that the sulfur-sulfur bond of crystalline sodium dithionite (Na₂S₂O₄) is exceptionally long, investigators in several laboratories obtained electron spin resonance spectra of a species identified by chemical expectation as SO₂⁻ in moist dithionite,^{2,3} in aqueous solutions of dithionite,⁴ and in γ -irradiated sodium dithionite.⁵ The assignment of hyperfine structure in the electron spin resonance spectrum of aqueous solutions of sodium dithionite to ³³SO₂⁻ present in natural abundance, achieved by Atkins, Horsfield, and Symons,⁵ provided a positive identification of SO₂⁻ and demonstrated that the unpaired electron is in a π -type molecular orbital. Hyperfine structure contributed by ³³SO₂⁻ produced on heating sulfur-doped alkali halide crystals in air was reported by Schneider, Dischler, and Räuber.⁶ Dinse and Möbius⁷ also observed the electron spin resonance spectrum of SO₂⁻ produced by the electrolysis of solutions of SO₂ in dimethyl-

formamide. At high concentrations of SO₂ they obtained evidence for species of type (SO₂)_xSO₂⁻. Consideration of molecular orbital theory led these workers to conclude that hybridization involving *d* orbitals does not occur for SO₂⁻.

Despite the familiarity of SO₂⁻ to the electron spin resonance spectroscopist, nothing is known about either the vibrational or the electronic spectrum of this species. Recently, we have found it possible to observe the ultraviolet and infrared absorption spectra of a number of electrically charged species isolated in an inert, nonionic environment at cryogenic temperatures. The first such species to be identified was C₂⁻, produced by photoelectron attachment to C₂ isolated in a rare-gas matrix.⁸ Although the electronic transition assigned in this study to C₂⁻ had previously been observed in a variety of systems, its intensity was found to be dramatically enhanced in experiments involving the vacuum-ultraviolet photolysis of acetylene in an argon matrix in the presence of a small concentration of an alkali metal, which provides a convenient source of