Magnetic coupling and lattice dynamics in solid $O_2$

A. P. J. Jansen and A. van der Avoird

Institute of Theoretical Chemistry, University of Nijmegen, Toernooiveld,
6525 ED Nijmegen, The Netherlands

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The properties of solid $O_2$ are studied by means of an integrated lattice-dynamics-spin-wave approach which uses the random-phase approximation. This approach is based on a Hamiltonian from first principles, which includes the structural dependence of the spin coupling parameters. The calculated magnon and libron frequencies in $\alpha$ oxygen are in satisfactory agreement with experiment and the anomalously large libron splitting at the $\beta$-$\alpha$ phase transition is explained.

Solid $O_2$ is particularly interesting because the $O_2$ molecules possess an extra degree of freedom, the orientations of their triplet electron spins, in addition to the positional and orientational coordinates which characterize the more common closed-shell molecules. In the condensed phases the molecular spin orientations are coupled by spin-dependent terms in the intermolecular potential. Extra collective excitations (magnons) occur in combination with the phonons and librations, and the various phases of solid $O_2$ show magnetic as well as structural order. In the $\alpha$ and $\beta$ phases, which have been studied most extensively, the molecules are packed in layers with their axes perpendicular to the layer planes (the $a-b$ planes, see Fig. 2 of Ref. 1). In the $\beta$ phase the structure of these layers is hexagonal; in the monoclinic $\alpha$ phase the hexagons are slightly distorted. The distorted structure is stabilized by the antiferromagnetic exchange coupling. The $\alpha$ phase is a twofold sublattice collinear antiferromagnet, with the spins preferentially aligned in the $\pm b$ directions. The $\beta$ phase probably has short-range antiferromagnetic order, with a three-sublattice $120^\circ$ spin arrangement.

Although it has been concluded from the occurrence of the so-called magnetoelastic $\beta$-$\alpha$ phase transition that the magnetic coupling and the structure are related, the lattice vibrations in solid $O_2$ and its magnetic excitations have always been treated separately. Lattice-dynamics calculations on $\alpha$- and $\beta$-oxygen have used the standard harmonic model with a spin-independent empirical atom-atom potential. The fitting of the parameters in this potential has made mean-field and spin-wave calculations possible, which yield the magnetic, optical, and thermodynamic properties of $\alpha-O_2$. Comparison of the results with experimental data leads to empirical values of the coupling constants $J$, $A$, and $B$. The situation is unsatisfactory, however, in that various studies yield very different sets of coupling constants (varying typically by factors up to 10), depending on the models used and the experimental data fitted. This discrepancy has most clearly been illustrated in De Fotis's 1981 review, but later studies still show a substantial scattering in the empirical $J$, $A$, and $B$ values.

In this Rapid Communication, we present a new integrated lattice-dynamics-spin-wave approach. This approach is based on a Hamiltonian from first principles, which is directly related to the properties of the individual $O_2$ molecules and their interactions. Such a Hamiltonian, which applies not only to $\alpha$-oxygen, but to all the condensed phases, is written as follows:

$$H = H_0 + H_{\text{spin}}.$$  

$$H_0 = \sum_i \left( -\frac{\hbar^2}{2M} \nabla^2(i) + \frac{\hbar^2}{2I} L^2(\mathbf{r}_i) \right) + \sum_{i<j} V(\mathbf{R}_{ij}, \mathbf{\tau}_i, \mathbf{\tau}_j).$$

The Heisenberg exchange term, with $J_0 < 0$ for nearest neighbors, is isotropic in the spin; the other two terms have been added in order to obtain the experimentally observed spin anisotropy. The single-particle term $\Delta S^2(i)$ keeps the spin momenta perpendicular to the molecular axes (i.e., to the $x$ axis); it is probably due to the intramolecular spin-orbit and spin-spin interactions. The term $BS^2(i)$ imposes the $a-b$ plane anisotropy, which forces the spins in the $\pm b$ (i.e., $\pm z$) directions; this term probably represents the magnetic dipole-dipole interactions between the molecular spin momenta. Using this phenomenological spin Hamiltonian one has made mean-field and spin-wave calculations which yield the magnetic, optical, and thermodynamic properties of $\alpha-O_2$. Comparison of the results with experimental data leads to empirical values of the coupling constants $J$, $A$, and $B$. The situation is unsatisfactory, however, in that various studies yield very different sets of coupling constants (varying typically by factors up to 10), depending on the models used and the experimental data fitted. This discrepancy has most clearly been illustrated in De Fotis's 1981 review, but later studies still show a substantial scattering in the empirical $J$, $A$, and $B$ values.

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$$H_{\text{spin}} = -\sum_{i<j} 2J_0 S(i) \cdot S(j) + \sum_i [\Delta S^2(i) + BS^2(i)].$$
\[ H_{\text{spin}} = - \sum_{i<j} 2J(R_{ij}, \mathbf{r}_i, \mathbf{r}_j) \mathbf{S}(i) \cdot \mathbf{S}(j) + \sum_i A_{-m-m}^{m-m}(\mathbf{r}_i) S_m(i) S_m(i) \left( \begin{array}{ccc} 1 & 1 & 2 \\ m & m' & -m-m' \end{array} \right) \]

\[ + \sum_i S_m(i) T_{-m-m}^{m-m}(R_q) S_m(j) \left( \begin{array}{ccc} 1 & 1 & 2 \\ m & m' & -m-m' \end{array} \right) . \]  

Equation (2b) denotes the usual spin-independent Hamiltonian, which governs the lattice vibrations for closed-shell molecules. It contains the translational and rotational kinetic energy terms, with \( M \) being the \( \text{O}_2 \) mass and \( I \) its moment of inertia, and the potential \( V \), depending on the distance vectors \( \mathbf{R}_q \) and the orientations \( \mathbf{r}_i \) and \( \mathbf{r}_j \) of the molecules in the crystal. Equation (2c) describes the coupling between the \( \text{O}_2 \) triplet spin momenta; the structure dependence of the coupling parameters is included explicitly. (We find it convenient to express this dependence in spherical tensor form, with the larger brackets denoting a 3-j coefficient, and to use the summation convention for \( m \) and \( m' \).) The geometry dependence of the Heisenberg exchange parameter \( J \) is known, analytically, from \textit{ab initio} calculations on the (\( \text{O}_2 \))\(_2 \) dimer.\(^{13,14} \) The "molecular" spin-anisotropy term depends on the angle between the spin direction \( \mathbf{S}(i) \) and the orientation \( \mathbf{r}_j \) of the molecular axis; this dependence is correctly described by the second-rank tensor \( A_m(\mathbf{r}) = \frac{1}{4} A \sqrt{30} C_m^{(2)}(\mathbf{r}) \), with the Racah spherical harmonic \( C_m^{(2)} \). For \( A \) we take the free-molecule value \( A = 5.72 \) \( \text{K} \). Especially for the third term, the change between the phenomenological spin Hamiltonian (1) and Eq. (2c) is drastic. The \textit{ad hoc} single-particle term \( B S_j^2 \) that imposes the observed spin direction is replaced by a two-body operator which represents exactly the dipole-dipole interactions between the magnetic momenta \( g_e \mu_B \mathbf{S}(i) \) and \( g_e \mu_B \mathbf{S}(j) \), with \( g_e = 2.0023 \), and \( \mu_B \) being the Bohr magneton. The dipole-dipole interaction tensor is given by

\[ T_m(R) = -g_e^2 \mu_B^2 \sqrt{30} R^{-3} C_m^{(12)}(R) . \]

When summing this interaction over the lattice, in the calculations described below, we invoke the Ewald method.\(^{15} \)

With this new Hamiltonian (2) we have performed combined lattice dynamics and spin-wave calculations. The formalism used is the random-phase approximation (RPA), which has been applied to spin waves long ago.\(^{16} \) The method has been extended to librons and phonons, using bases of spherical harmonics and three-dimensional (3D) harmonic oscillator functions, respectively, and it has been demonstrated on solid \( \text{N}_2 \) that large-amplitude librons, anharmonic phonons, and their coupling are very well described.\(^{17} \) For studying solid \( \text{O}_2 \) we have further extended this formalism in order to treat magnons, librons, and phonons simultaneously. The coupling terms included consist of all operators which are bilinear in the magnon, libron, and phonon creation and/or annihilation operators. For the single magnon excitations such terms are absent, however, and thus the main role of the combined formalism is to correctly average ("renormalize") the spin-interaction parameters over the lattice vibrations and, vice versa, to average the effective intermolecular potential for the lattice dynamics over the spin. For the spin-independent potential \( V(R_q, \mathbf{r}_i, \mathbf{r}_j) \), we have taken the analytic form of the anisotropic-exchange repulsion and the electrostatic multipole interactions from the \textit{ab initio} calculations,\(^{18} \) while

<table>
<thead>
<tr>
<th>( \omega ) (( \text{cm}^{-1} ))</th>
<th>First principles</th>
<th>From Eq. (1), ( B = 0.26 ) ( \text{K} )</th>
<th>Experiment (Ref. 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3</td>
<td>4.2</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>20.9</td>
<td>20.7</td>
<td>27.5</td>
<td></td>
</tr>
</tbody>
</table>
TABLE II. Optical (q = 0) libron frequencies.

<table>
<thead>
<tr>
<th>$\omega$ (cm$^{-1}$)</th>
<th>First-principles calculation (T = 0 K)</th>
<th>Experiment (Ref. 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Putting $J = 0$</td>
<td>Including $J(R_y, \bar{r}_i, \bar{r}_j)$</td>
</tr>
<tr>
<td>$\alpha$-O$_2$</td>
<td>$B_x$</td>
<td>38.9</td>
</tr>
<tr>
<td></td>
<td>$A_y$</td>
<td>50.7</td>
</tr>
<tr>
<td>$\beta$-O$_2$</td>
<td>$E_x$</td>
<td>42.9</td>
</tr>
</tbody>
</table>

The large splitting of the $A_y$-$B_x$ libron frequencies in $\alpha$-O$_2$ appears to have the following explanation. The structural change from $\beta$-O$_2$ to $\alpha$-O$_2$ is small indeed. The magnetic order in these phases is very different, however, which yields a strong discontinuity of the quantity $\langle S(i) \cdot S(j) \rangle$ at the phase transition. For $\beta$-O$_2$ we have found the 120° spin arrangement with $\langle S(i) \cdot S(j) \rangle = -0.5$, for $\alpha$-O$_2$ the order is antiferromagnetic with $\langle S(i) \cdot S(j) \rangle = -1$, for nearest neighbors. If we substitute these values into the effective Hamiltonian for the lattice vibrations, the Heisenberg exchange term $J(R_y, \bar{r}_i, \bar{r}_j)$ gets a very different weight in $\beta$-O$_2$ and $\alpha$-O$_2$. This parameter is extremely anisotropic and, thus, it has a strong influence on the libron frequencies. Use of the analytic representation of $J(R_y, \bar{r}_i, \bar{r}_j)$ from the ab initio calculations yields good agreement with experiment, both for the splitting of the peaks in $\alpha$-O$_2$ and for the relative positions of these peaks with respect to the peak in $\beta$-O$_2$ (see Table II). Omitting the Heisenberg exchange term from our calculations, we find a much smaller splitting, just as the earlier lattice-dynamics calculations. This confirms the crucial role of this term: it not only drives the so-called magnetoelastic $\beta$-$\alpha$ phase transition, but it is also responsible for the anomalous libron splitting at this transition.

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