Structure and Bonding of Dense Liquid Oxygen from First Principles Simulations

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Using first principles simulations we have investigated the structural and bonding properties of dense fluid oxygen up to 180 GPa. We have found that band gap closure occurs in the molecular liquid, with a "slow" transition from a semiconducting to a poor metallic state occurring over a wide pressure range. At approximately 80 GPa, molecular dissociation is observed in the metallic fluid. Spin fluctuations play a key role in determining the electronic structure of the low pressure fluid, while they are suppressed at high pressure.

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The study of pressure-induced transformations in solids and liquids has become an active field of research in the last decade [1], due to key progress both in experimental methods [diamond anvil cell (DAC) and shock wave experiments] and in accurate computational tools. In particular, molecular systems such as hydrogen [2], oxygen [3], and nitrogen [4] have been investigated with a variety of techniques. Nevertheless, fundamental questions on the nature of these systems in the dense liquid state are yet unanswered.

In this Letter, we focus on the liquid state of oxygen. In particular, we examine the structural and bonding changes induced by pressure, as well as the mechanism leading to the insulator-to-metal transition (IMT) observed experimentally in shock wave experiments [5].

Metallization of oxygen was first observed in the solid state by Desgreniers *et al.* [6] who reported a Drude-type metallic behavior of its reflectivity for pressures P above 96 GPa. These results were later confirmed by Shimizu *et al.* [7] who observed a change in the sign of the resistance-temperature curve at 96 GPa and also discovered superconductivity in dense, solid oxygen [8]. Following measurements by Akahama *et al.* [9], Weck *et al.* [10] showed that in solid oxygen the IMT is accompanied by a structural change between two different crystallographic arrangements of molecules. The magnetic properties of the proposed structures were studied theoretically by Gebauer *et al.* using noncollinear spin *ab initio* calculations [11]. The insulating phase below 96 GPa was also studied with infrared absorption spectroscopy by Gorelli *et al.* [12] who suggested the existence of a lattice of O_4 molecules at high P. However, this hypothesis is not confirmed by recent *ab initio* calculations [13], showing that a geometrical configuration built from extended "herringbone"-type chains is energetically favored over a lattice of O_4 molecules. The structure predicted theoretically is consistent with earlier suggestions based on DAC experiments [14].

In fluid oxygen, metallization was recently reported by Bastea *et al.* [5] who used reverberation shock wave techniques to generate compression states on a quasi-isentrope. For a given shock speed, the thermodynamic states reached in these experiments are at higher P and lower temperatures T than Hugoniot states obtained in earlier shock wave measurements [15]. When increasing P from $\simeq 30$ to 120 GPa (and correspondingly T by several thousands K), Bastea *et al.* [5] observed an increase of the electrical conductivity over 6 orders of magnitude. At about 120 GPa and 3.4-fold compression, the measured conductivity attains values characteristic of a poor metal. As P is further increased from 120 to 190 GPa, the conductivity levels off and is nearly constant as a function of P. These experimental results, which indicate that the IMT occurs at higher P in the liquid than in the solid, are rather surprising. In general, one would expect disorder or dissociation effects to lead to a lower metallization P in the fluid than in the ordered solid.

In order to investigate the mechanism by which the IMT occurs in the fluid, we have carried out a series of *ab initio* molecular dynamics (MD) simulations [16] in the liquid state for different P. Our findings shed light on the microscopic structure and electronic properties of the dense fluid state and on the key role of spin fluctuations present in the fluid before metallization occurs. Our predicted metallization P in the fluid is lower than that reported experimentally [5], as well as lower than the metallization P measured in the solid. Our findings further indicate that the system becomes metallic in a predominantly molecular state, as opposed to other fluids such as hydrogen [17] and nitrogen.

We have carried out *ab initio* MD simulations [16] using a gradient corrected energy functional [18] in the density (ρ) and T range explored in recent shock wave experiments: $2.8 \leq \rho \leq 4.5\ \mathrm{g\,cm^{-3}}$ and $1000 \leq T \leq 6400$ K. In some of our simulations we have treated the spin variable explicitly within the gradient corrected local spin density approximation (GCSDA). We performed constant volume microcanonical simulations [19] with cells containing 54 and 108 oxygen atoms. For each ρ and T, the total simulation time was 4–5 ps, after equilibration.

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Our calculated pair correlation functions [$g(r)$] are shown in Fig. 1. Finite size effects were found to be negligible compared to T and P effects. At $\rho = 2.8\ \mathrm{g\,cm^{-3}}$ and $T = 1000$ K [20], the first sharp peak of $g(r)$ at 1.20 Å, followed by a minimum very close to zero, is indicative of a molecular fluid. The computed P is 24 GPa. The first maximum is at a distance very close to the bond length of an oxygen molecule in the gas phase in its triplet ground state (1.207 Å) [21]. As the T is increased to 3000 K (and correspondingly P to 34 GPa) the first molecular peak is broadened while its position remains unchanged. This trend continues as the fluid is compressed to $\rho = 3.6\ \mathrm{g\,cm^{-3}}$ at $T = 3000$ K ($P =$ 84 GPa). Upon further compression to $\rho = 4.5\ \mathrm{g\,cm^{-3}}$ at $T = 6400$ K ($P = 179$ GPa), the first molecular peak becomes less intense and the second broad peak moves to shorter distances. However, the position of the intramolecular peak remains constant over a P range of 150 GPa and does not shift to larger separations as in dense liquid hydrogen [22].

The ground state of the O_2 molecule is a triplet, and this has been shown to give rise to interesting structural effects in the low density fluid [23]. We therefore explored the effect of explicit spin treatment on the structural properties of the high P fluid and found that spin effects are negligible on average structural properties both at low and high P, consistent with recent *ab initio* calculations for solid oxygen [13] in the same P range. For example, in Fig. 1, $g(r)$ calculated with and without explicit treatment of spin are found to be indistinguishable. However, spin effects are key in determining the optical excitation spectrum of the low-P fluid, as we discuss below.

The microscopic structure of the liquid can be further examined by a cluster analysis. We define a set of atoms as belonging to a given cluster if these atoms are separated by less than a given cutoff distance r_c. (We chose $r_c =$ 1.50 Å, which corresponds to the first $g(r)$ minimum in the molecular regime.) We then define cluster lifetimes by simply computing the duration for which a given cluster remains intact. This analysis yields a very simple picture for our simulations at low density ($2.8\ \mathrm{g\,cm^{-3}}$) and 1000 and 3000 K: we find that the liquid consists entirely of O_2 molecules. A density increase to $3.6\ \mathrm{g\,cm^{-3}}$ at 3000 K leads to a small fraction of dissociated molecules. Although the liquid is still predominantly molecular (94% O_2), we find 1% single atoms and 5% O_3-like clusters. At this density, the average lifetime of O_2 molecules is about 15 vibrational periods of the isolated O_2 molecule (21.1 fs), while O_1 and O_3 exist only for about one molecular vibration. When the T is raised to 5000 K at $3.6\ \mathrm{g\,cm^{-3}}$, the number of molecules decreases to 79%, leading to 7% atoms, 10% O_3, and 4% O_4-like complexes. The lifetime of molecules decreases to about three O_2 vibrations, indicating the presence of a dynamical dissociation equilibrium with molecules still being the predominant and most stable species. At $\rho = 4.5\ \mathrm{g\,cm^{-3}}$ and $T = 6400$ K, we find 9% atoms and 58% molecules and also 16% O_3 clusters. The remaining 17% of the nuclei belong to short-lived complexes composed of four or more atoms. Further inspection reveals that O_4-like clusters arrange predominantly into short zigzag chains. At this high density, the O_2 lifetime is only about 1.5 vibrational periods. The short lifetime of O_3 at all densities clearly indicates that triatomic configurations are closer to scattering states than to stable chemical species. Nevertheless, it is interesting to note that the "bond" angles of O_3 clusters are not randomly distributed but vary between 80° and 150° with an average of 120°. Therefore, the transient structure of O_3 clusters resembles that of the ozone molecule.

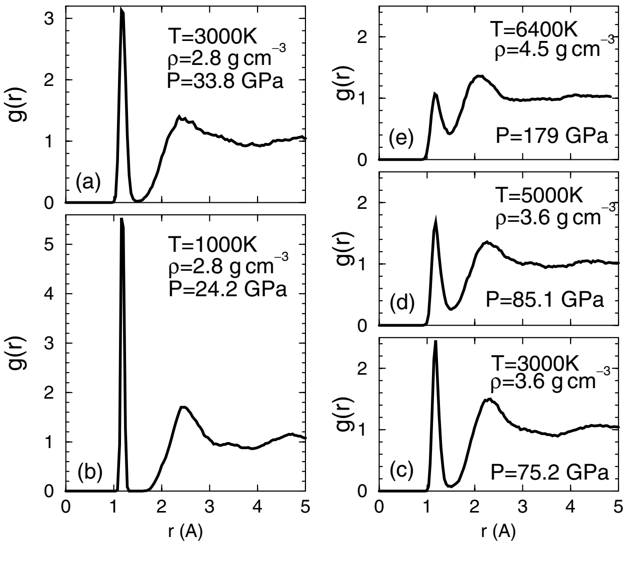

FIG. 1. Pair correlation functions calculated using GCSDA (see text) for different densities, temperatures, and pressures.

While spin effects are negligible for the structural properties of the fluid, it is crucial to include them explicitly in order to understand the electronic properties of liquid oxygen. In the low density regime, the liquid is composed of a disordered arrangement of O_2 molecules carrying a net spin of one as in the gas phase. The left panel of Fig. 2 shows the difference ($\Delta\rho_{\downarrow\uparrow}$) between spin-up ($\rho_\uparrow$) and spin-down densities ($\rho_\downarrow$), for a snapshot at $\rho =$ $2.8\ \mathrm{g\,cm^{-3}}$ and 1000 K, showing a random distribution of up and down spins. At higher P (right panel of Fig. 2), $\Delta\rho_{\downarrow\uparrow}$ has almost vanished throughout the whole system, indicating that spin fluctuations are suppressed. This effect can be characterized quantitatively by the correlation function of the nuclei $\mathbf{r}_i$ and the electronic magnetic moment, $m_z(\mathbf{r}) = \mu_B[\rho_\uparrow(\mathbf{r}) - \rho_\downarrow(\mathbf{r})]$,

$$\rho_e g_{\mathrm{O},m_z}(|\mathbf{r}|) = \frac{1}{N}\left\langle \sum_{i=1}^{N} m_z(\mathbf{r}_i - \mathbf{r}) \right\rangle, \qquad (1)$$

where ρ_e is the electron density, N is the number of atoms,

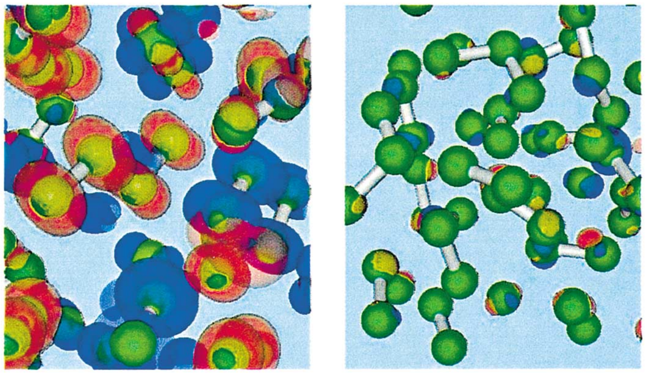

FIG. 2 (color). Difference between spin-up and spin-down densities for two representative snapshots at $\rho = 2.8\ \mathrm{g\,cm^{-3}}$ and $T = 1000$ K (left) and $\rho = 4.5\ \mathrm{g\,cm^{-3}}$ and $T = 6400$ K (right). Positive and negative regions are represented by red and blue isosurfaces. Green spheres represent the atoms.

and $\langle \ldots \rangle$ denotes an average over ionic configurations and the solid angle of **r**. This correlation function is similar to the nuclei-electron pair correlation function. The first, intense peak in the low density correlation function shown in Fig. 3 indicates that the majority of molecules are in the triplet state. At higher density, the intensity of the first peak is decreased by almost an order of magnitude, showing that most of the pairs in the fluid do not carry a net spin.

In order to qualitatively understand the effect of P on the spin state of the oxygen molecule, we carried out calculations of the total energies of O_2 in the singlet ($E_{S=0}$) and the triplet ($E_{S=1}$) state in the presence of a confining potential mimicking an average pressure effect. Interestingly, we found that the difference $E_{S=0} - E_{S=1}$ can be substantially reduced by applying an external confining potential. This difference decreases as a function of the confinement strength.

In order to compare our results with recent shock wave data, we computed the conductivity (σ) of the liquid for selected snapshots taken from our GCSDA simulations at different pressures, using the Kubo-Greenwood formula [24,25]. We note that in the low P regime, where spin fluctuations are present, the results with (GCSDA) and without [generalized gradient approximation (GGA)] explicit treatment of spin are very different. The GGA yields much smaller optical gaps, consistent with the incorrect treatment of excitation in the isolated molecule if spin is not explicitly taken into account. On the other hand, at higher densities, the computed GGA and GCSDA conductivities are very similar.

Our results are reported in Fig. 4 along with the experimental results of Refs. [5,15]. The comparison between theory and experiment is not straightforward: the T in the measurements of Hamilton [15] is in general different from that of Bastea *et al.*'s data [5], and in both experiments, T was not measured but estimated on the basis of empirical equation of state (EOS) models. However, the two sets of experimental data show the same qualitative rise of σ as a function of P and T. In particular, Bastea *et al.*'s data show a 6 order of magnitude rise of σ with increasing shock compression, corresponding to a P and T increase from about 30 to 120 GPa and 1000 to 5000 K, respectively. Our calculations within GCSDA show only a 2 order of magnitude increase in σ in the same P and T range. This increase of σ as a function of T occurs primarily in a state where the fluid is entirely composed of stable O_2 molecules ($\rho = 2.8\ \mathrm{g\,cm^3}$, $T = 1000 \rightarrow 3000$ K). This indicates that in oxygen, metallization is not accompanied by molecular dissociation as found in other first row molecular fluids, in particular, hydrogen [25] and nitrogen. Above 100 GPa both theory and experiment show an almost constant σ as a function of compression, but the theoretical values are about a factor of 7 larger than the experimental ones.

In our calculations, overestimates of σ values could be due to the use of the GCSDA, which is known to underestimate electronic gaps in many systems. In order to qualitatively investigate this effect, we used a scissors

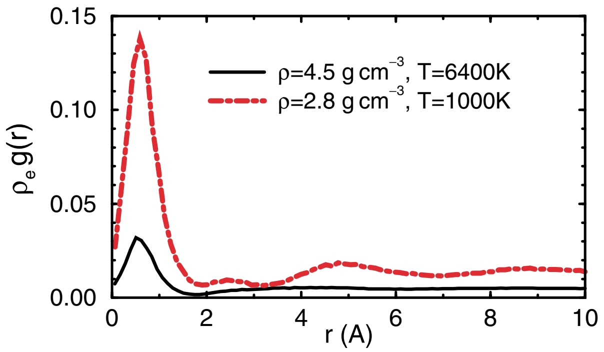

FIG. 3 (color online). Pair correlation function derived from nuclear positions and the absolute difference of the spin density. The first peak characterizes spin fluctuations in the molecular liquid which are suppressed at high density.

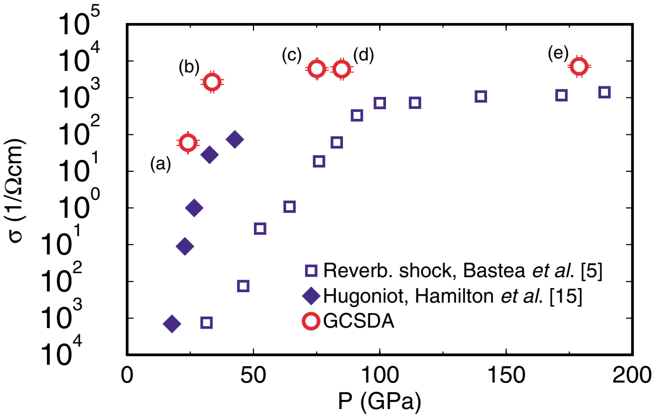

FIG. 4 (color online). Measured and calculated conductivity as a function of pressure. The labels correspond to Fig. 1.

operator and arbitrarily increased the value of the computed gaps by a factor of 2. This lowered the computed conductivity by 1 order of magnitude at $\rho = 2.8\ \mathrm{g\,cm^{-3}}$, both at 1000 and 3000 K. However, even after this "gap correction," our theoretical data show values of σ approaching those of a poor metal at a P much lower (30–40 GPa) than found experimentally. The computed conductivity is then slowly changing as a function of P, and it reaches metallic like values at approximately 80 GPa. This slow metallization of the fluid as a function of P may be related to spin fluctuations and their slow suppression with increasing P. At low P, the molecular fluid, with each oxygen molecule in a triplet state, can be viewed as a disordered spin system. As the P is increased, this system exhibits a highly corrugated potential energy surface (similar to that of a glass) due to the presence of a multitude of local minima, corresponding to a multitude of different spin arrangements. However, in spite of the frustrated spin dynamics, the diffusion coefficient of the system (5×10^{-5} at 24 GPa, $4 \times 10^{-4}\ \mathrm{cm^2/s}$ at 179 GPa) is typical of a high T molecular fluid. With increasing P, the fluid eventually reaches metallization and spin fluctuations are almost completely suppressed. In this respect, compressed liquid oxygen is unique among first row molecular fluids and rather different from, e.g., liquid hydrogen and nitrogen, composed of molecules with spin zero.

In summary, our first principles simulations show that above 30 GPa, over a wide P range of about 50 GPa, liquid oxygen transforms from a semiconducting to a metallic fluid by closure of the band gap in a disordered molecular state. This suggests that disorder present in the liquid state is responsible for lowering the metallization P below the value observed in the solid. For $P \geq 80$ GPa, molecular dissociation is observed, giving rise to short-lived atomic- and ozonelike species. Our results also show that spin fluctuations are suppressed at high P, with no significant magnetic moment present in the high P liquid.

Our findings for the electrical conductivity point to the need for further experimental and theoretical work. Experimentally, in shock wave experiments only P and σ are measured. Data are then analyzed using a model EOS as input for hydrodynamic codes which compute densities. Finally, T is inferred from additional empirical chemical model calculations. This type of analysis may introduce uncertainties in the estimated ρ and T at a given P and σ. Measurements of the oxygen EOS obtained with shock wave experiments and possibly with other techniques, e.g., DAC measurements, may help clarify the existing discrepancies between theory and experiment. Finally, we note that theoretical inaccuracies on calculated conductivity values may arise from the use of an approximate exchange and correlation functional. Although computationally still out of reach, quantum Monte Carlo calculations for liquid oxygen under P might be used in the future to address this issue [17].

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