On the magnetism of liquid nitrogen-liquid oxygen mixture

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Abstract

The measurements of EPR linewidth in liquid nitrogen-liquid oxygen mixtures are presented. The observed anomalous dependence of linwidth on oxygen concentration can be understood if the existence of $O_2 - O_2 - O_2$ and $N_2 - O_2 - O_2$ molecular clusters is assumed. The provided quantum chemical calculations give the spatial structure as well as the bond energy for these clusters.

Key words: liquid oxygen; liquid nitrogen; electron paramagnetic resonance

In despite of the properties of liquid oxygen have been the subject of investigations by various methods during almost one hundred years the structure of liquid oxygen is not yet understood completely. The possibilities for some short-range order existence in liquid oxygen were discussed, for example, in [1] (neutron diffraction measurements) and in [2] (heat and magnetic measurements near melting point). The additional information about such a short-range order can be obtained from electron paramagnetic resonance (EPR) measurements. Usually EPR linewidth is decreased with the lowering of paramagnetic centers concentration. However it was found [3] a rather strong increasing of the EPR linewidth of paramagnetic oxygen molecules at oxygen concentration close to zero. The reasons for such behavior were not investigated but it is clear that if some short-order exists in liquid oxygen the additional contribution to EPR linewidht has to be appeared. In order to investigate this problem we have provided the EPR measurements in *liquid nitrogen-liquid oxygen* mixtures. Note that this experimental studying is interested also to verify the possibility of paramagnetic oxygen molecules use for the dynamic polarization of noble gas nuclei.

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The results of our EPR measurements are summarized in Fig. 1. Note that EPR linewidth in *liquid nitrogen-liquid oxygen* mixture almost doesn't depend on the amount of O_2 molecules at $35 - 70$ oxygen concentration. The observed anomalous increasing of the linewidth at smaller concentration can be explain by assuming the formation of different clusters in *liquid nitrogen-liquid oxygen* mixtures. These clusters may consist of diatomic diamagnetic N_2 and paramagnetic O_2 molecules. The positions and mutual orientations of molecules in clusters are fixed so a rather strong dipole-dipole interactions inside these clusters are not averaged by motion and the EPR line is a wide. Moreover because of the lower mobility of clusters the additional contribution to the linewidth in comparison with a liquid containing only molecules can be expected due to dipole-dipole interaction between clusters.

The special quantum chemical calculations of electronic and spatial structure of possible clusters have been carried out by an ab initio method at the unrestricted Hartree-Fock self-consistent field (UHF-SCF) level of theory using 6-31G(d) basis set. The influence of electron correlations was taken into account within a framework of the density functional theory (DFT) on the base of the Beckes three-parameter hybrid method

[4] employing the correlation functional [5] which includes both local and non-local terms. The geometry of stationary points was calculated by minimizing the cluster energy. The bond energy for each cluster is determined as the difference between the total energy of a cluster and total energy of free molecules.

It follows from these calculations that three types of molecular clusters are stable at liquid oxygen temperatures (90 K): $O_2-O_2-O_2$, $N_2-O_2-O_2$ and $N_2-N_2-O_2$. The latter cluster doesn't gives any contribution to EPR linewidth so hereinafter we consider only the first two types the structures and bond energies of which are presented in Fig. 2 and Fig. 3.We would like to point out a high anisotropy of the obtained clusters. Note also that our results are correlated with observation of oxygen clusters in work [1].

As mentioned above the assumption about molecular clusters allows to explain the observed concentration dependence of EPR linewidth. At smallest oxygen concentration the clusters can be considered as isolated and non-interacting. Our estimations of the contribution to the second moment of the linewidth determined by dipole-dipole interactions inside cluster with taking into account the random distribution of the angle between cluster orientation and external magnetic field give the values $M_2 = 264.6\ kOe^2$ for $O_2-O_2-O_2$ cluster and $M_2 = 11.8\ kOe^2$ for $N_2-O_2-O_2$ cluster. So we can conclude that at smallest oxygen concentration the clusters $N_2-O_2-O_2$ are preferable. With increasing of the oxygen concentration c the influence of $O_2-O_2-O_2$ has to grow and one would expect the broadening EPR line. But at the same time the probability for two or more clusters to be close is also increased that leads to averaging of dipole-dipole interactions between paramagnetic moments of oxygen. The results of computer simulations of EPR linewidth with taking into account these factors will be published elsewhere [6]. Now we only note that probability to find, for example, two adjacent $O_2-O_2-O_2$ clusters (and consequently the linewidth narrowing) is proportional to c^6 roughly whereas the probability of $O_2-O_2-O_2$ cluster creation is proportional to c^6.

The question about influence of the hindered cluster motion on EPR spectrum is still open. The additional measurements at different EPR frequencies are necessary to study it.

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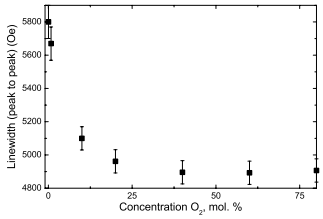

Fig. 1. The dependence of EPR linewidth on oxygen concentration in *liquid nitrogen-liquid oxygen* mixtures.

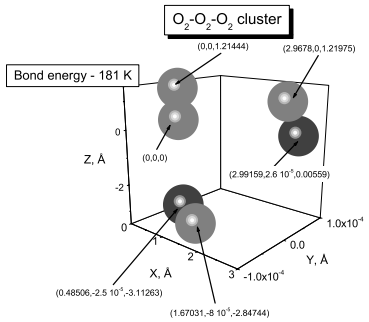

Fig. 2. The spatial structure of $O_2-O_2-O_2$ and the corresponding bond energy. The coordinates of atomic nuclei are given in Å. The more dark circles corresponds to more deeper atoms.

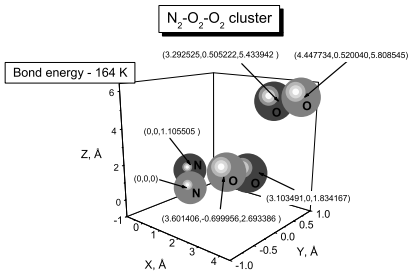

Fig. 3. The same as in Fig. 2 but for $N_2-O_2-O_2$ cluster.

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