Electron paramagnetic resonance of γ oxygen

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A procedure is described for obtaining γ oxygen by pumping off liquid-oxygen vapor. The spectrum of the electron paramagnetic resonance of γ oxygen is described.

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It is known[1] that solid oxygen has three modifications: an α phase (up to 23.9 K), a β phase (from 23.9 to 43.8 K), and a γ phase (from 43.8 to 54.4 K). Investigations of these phases of oxygen by the method of electron paramagnetic resonance (EPR) have not yet been carried out. The only exception is the detailed EPR study[2] of mixtures in which molecular oxygen is present with a small concentration in nitrogen and argon matrices at low temperatures. Measurements have shown the presence of a narrow (up to 70 G in the 3-cm microwave band) EPR signal of asymmetrical shape in fields of approximately 11 kOe, in agreement with the theory of EPR of triplet states randomly disposed in a matrix and having in a zero field a splitting constant close to the splitting constant of the first rotational state of the oxygen-gas molecule. It turns out that with increasing oxygen concentration or with decreasing temperature the signal broadens and it becomes impossible to register it at approximately 25 K.

Nonetheless, an investigation of the α, β, and γ phases of oxygen by the EPR method (if it were found possible) would be of fundamental importance. The point is that the EPR method can yield, in principle, direct information on the character of the interaction of the spins in these states and on the change of these interactions at the phase-transition points. The most important, in our opinion, is the determination of the γ-phase EPR spectrum at a temperature close to the point of the transition of the solid oxygen into a liquid. This makes it possible to compare the spectra of the solid and liquid oxygen and to trace the variation of the character of the interaction between the molecules.

To obtain the EPR spectrum of γ oxygen we used the following procedure: a quartz dewar 1

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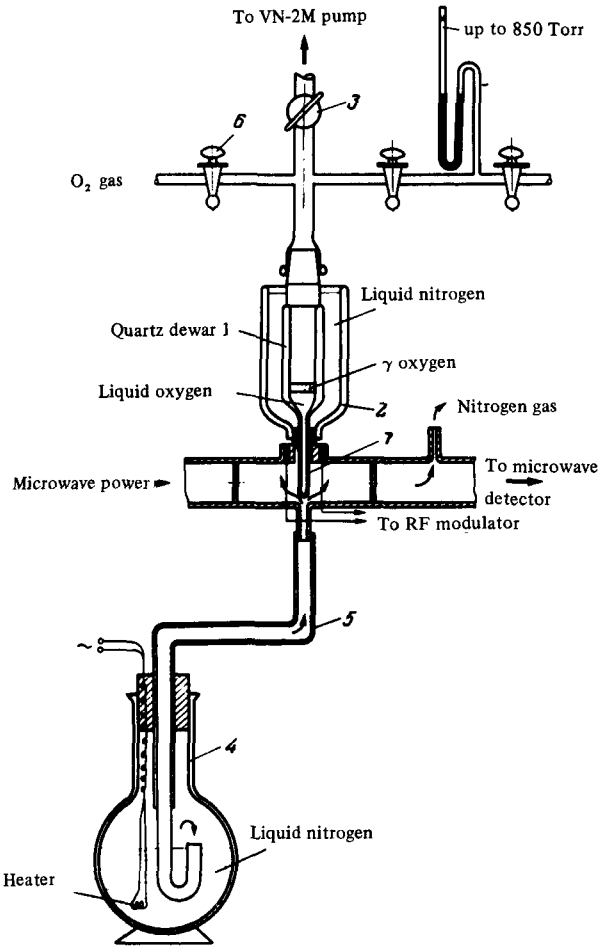

FIG. 1. Apparatus used to obtain the EPR spectrum of γ oxygen.

(see Fig. 1) with a stub 7 was surrounded by another dewar 2 and the stub was placed in the resonator (H_{012} mode) of an EPR spectrometer with high-frequency modulation of the magnetic field. The spectrum plotted with an automatic recorder has a shape close to the absorption-signal derivative. The maximum value of the constant magnetic field, at a gap of 25 mm between the magnet poles, reached 12 kOe. The frequency of the klystron, with automatic frequency control relative to the natural frequency of the loaded resonator was of the order of 9610 MHz.

After evacuating dewar 1 with a forevacuum pump through valve 3 over the ground-glass joint of vessel 1, liquid nitrogen was poured into dewar 2 and the heater in the dewar 4 with liquid nitrogen was turned on.

The current flowed through the U-shaped dewar 5 and around the stub of quartz dewar 1 through a lower opening in the resonator. After the lapse of approximately 1 hour, the dewar 1 was cooled to nitrogen temperature. Valve 6 was then opened with valve 3 closed and oxygen gas at a pressure ~500 Torr was fed into dewar 1, where it was liquified and filled the stub. Valve 6 was

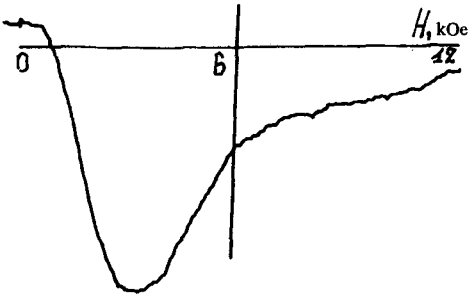

FIG. 2. EPR spectrum of γ oxygen.

then closed and equilibrium established, after which the saturated vapor pressure of the liquid oxygen ($\sim$160 Torr) was registered.

The heavy-duty VN-2MG forevacuum pump, joined through a pipe of 60 mm diameter to valve 3 of dewar 1, was evacuated beforehand by a RVN-20 pump. Valve 3 was then opened and the vapor over the liquid oxygen was pumped out from the dewar 1 by the VN-2MG pump. The oxygen vapor pressure soon became less than 1.2 Torr (the vapor pressure of the solid oxygen at a point close to the melting point) and the solid phase was produced. The process of the complete conversion of the liquid oxygen into solid in stub 7 in the course of evacuation took about 1 hour.

As a result, the γ oxygen was obtained at the thin end of the stub 7 in the form of a transparent casting of delicate blue color with dimension $7\times3\times3$ mm, and was slowly sublimated in the course of evacuation. The process of formation of the γ oxygen was observed both continuously, in a transparent system that imitated a blow-through resonator, and directly under the working conditions, periodically, with removal of the quartz dewar with the oxygen after the plotting of the spectra.

The obtained spectrum of the γ oxygen (the derivative of the absorption line) is shown in Fig. 2.

The spectrum is a broad symmetrical line with a maximum at zero magnetic field.

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[1]A.S. Borovik-Romanov, M.P. Orlova, and P.G. Strelkov, Dokl. Akad. Nauk SSSR **99**, 699 (1954).
[2]R. Simoneau, J.S.M. Harvey, and G.M. Graham, J. Chem. Phys. **54**, 4819 (1971).