

Emission of the Atmospheric Oxygen Bands in Discharges and Afterglows

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THE atmospheric bands of oxygen result from an intercombination magnetic dipole transition with a probability of only 0.14 sec^{-1} .¹ Although well known in the solar absorption spectrum, this system was not observed in emission until 1947, when Kaplan² reported the (0, 0) and (0, 1) bands in an oxygen-enriched nitrogen afterglow. Subsequently, the bands have been produced in emission in CO-O₂ explosions,³ in He discharge with a trace of O₂,⁴ and in a high pressure glow discharge in pure O₂.⁵ In addition the (0, 1) band is a prominent feature of the infrared spectrum of the night air-glow.^{6,7}

Under appropriate conditions a sealed-off glass vessel containing spectroscopically pure O₂ at about 1-cm pressure will afterglow very strongly in the infrared. The afterglow spectrum from 3000 to 9100 Å contains only the (0, 0) and (0, 1) atmospheric bands (with heads at 7593.7 and 7685 Å, respectively) and a weak continuum. The rf electrodeless discharge which precedes the afterglow produces these forbidden bands with much greater intensity. This spectrum contains members of the $\Delta v=0$ progression up to $v'=4$, as well as O I lines. O I 8446.8 Å and the O I triplet at 7772 Å are very strong, indicating a high degree of dissociation of the O₂. The (0, 0) band of the direct discharge, photographed in a net exposure of about 30 minutes on a Baird two-meter grating, is shown in Fig. 1.

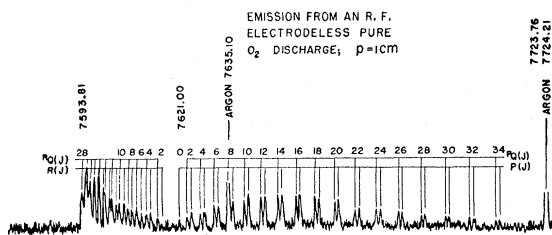


FIG. 1. The (0, 0) $\Sigma-\Sigma$ band of the forbidden oxygen atmospheric system produced in emission. The "rotational temperature" is 710°K .

The spectral composition and pressure requirement suggest that the energy producing the afterglow is stored in the high degree of dissociation and is released by three-body volume recombination. The "active oxygen" of the afterglow is also capable of heating to incandescence tiny flecks of metal for as long as 10 seconds in the afterglow. Because of the high probability of this metallic surface recombination, an electrodeless discharge is propitious for afterglow production.

The rotational and vibrational "temperatures" were measured in both the afterglow spectra and the direct discharge. The rotational distribution in the direct discharge follows very closely the Boltzmann formula with a "temperature" of $710^\circ \pm 10^\circ\text{K}$. The vibrational "temperature" is approximately the same, $670^\circ \pm 80^\circ\text{K}$.⁸ In the afterglow spectra the (1, 1) band does not appear on our plates, placing an upper limit on the vibrational "temperature" of the afterglow of about 450°K . Since the rotational "temperature" computed from the profile of the unresolved (0, 0) band in the afterglow is approximately room temperature (roughly 310°K), the excited oxygen molecules in the afterglow appear to attain thermal equilibrium before radiation, as would be expected from the low transition probability and the moderately high pressure.

The agreement between vibrational and rotational temperatures in the discharge and afterglow shows that many collisions occur before the excited molecule radiates. In excitation by molecule formation in three-body collisions, up to 3.5 volts of vibrational energy in the ${}^1\Sigma_g^+$ state must be removed before equilibrium is attained. Since vibrational energy relaxes much more slowly than

rotation in O₂, we may expect the rotational temperature to agree with the gas kinetic temperature at pressures considerably lower than 1 cm Hg.

The rotational profile of the (0, 1) band of this system has been used by Meinel⁶ and Dufay⁷ to measure the temperature of the upper atmosphere at the altitude of the emitting layer, giving temperatures of 150°K and 130°K , respectively. The normal temperature behavior of the atmospheric bands in the direct discharge and in the afterglow substantiates the interpretations of Meinel and Dufay.

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³ Herman, Hopfield, Hornbeck, and Silverman, *J. Chem. Phys.* **17**, 220 (1949); *J. Chem. Phys.* **17**, 982 (1949).
⁴ R. Herman and L. Herman, *Compt. rend.* **229**, 931 (1949).
⁵ T. Herman and C. Weniger, *Compt. rend.* **230**, 940 (1950).
⁶ A. B. Meinel, *Pub. Astron. Soc. Pacific* **60**, 373 (1948); *Astrophys. J.* **112**, 464 (1950).
⁷ J. Dufay, *Compt. rend.* **231**, 1531 (1950); **232**, 426 (1951).
⁸ The vibrational "temperature" is estimated by comparison of the (0, 0), (0, 1), and (1, 1) band intensities. The relative transition probabilities were taken from *Computation of the Intensities of Vibrational Spectra of Electronic Bands in Diatomic Molecules* (Problem Rep. No. 27) (The Computation Laboratory, Harvard University, Cambridge, Massachusetts, 1951).

Bardeen's Theory of Superconductivity and the f-Sum Rule

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BARDEEN'S^{1,2} derivation of the London equation depends crucially on the assumption that the effective mass of a superconducting electron is very small and that as a consequence the Landau-Peierls diamagnetism is great enough to drive the magnetic field out of the metal. It will be shown below that on Bardeen's model the Landau-Peierls susceptibility is actually paramagnetic and would not, therefore, keep out the magnetic field. Bardeen's model may be characterized briefly as follows: The very weak electron-phonon interaction causes the continuum of levels at the top of the Fermi sea to split up into narrow bands. The superconducting electrons are a group of electrons which occupy the lowest of these bands. Rough arguments indicate that for at least some of these electrons the effective mass is very small. Bardeen argues that for superconductors the effective masses are so small that the Landau-Peierls diamagnetism becomes great enough to keep the magnetic field from penetrating the metal appreciably. In this case the wave functions of the electrons are not disturbed on account of the field and an old argument of London shows that the London equation is valid.

The Landau-Peierls susceptibility³ can be written as

$$\chi = -\frac{1}{2}\mu_B^2 n(\zeta) (\alpha_{xx}\alpha_{yy} - \alpha_{xy}^2). \quad (1)$$

Here μ_B denotes the Bohr magneton, $n(\zeta)$ the density of energy levels at the Fermi surface, $\alpha_{\mu\nu}$ the ratio of the electron mass to the $\mu\nu$ component of the effective mass tensor, and the angular brackets denote an average over the free Fermi surface. x and y are directions perpendicular to the magnetic field. In a normal metal, for which the value of the angular bracket is of the order of unity, Eq. (1) gives a susceptibility of the order 10^{-6} . Therefore, in order to get a susceptibility large enough to keep the magnetic field out of the metal it is necessary that the angular bracket be of the magnitude 10^6 or larger, and positive. For the case of a weak interaction it is possible to express α_{xy}^2 in terms of α_{xx} and α_{yy} and thus to obtain a simpler expression for the susceptibility. The relations we need can be obtained from the following two equations,⁴ which are a consequence of the commutation relations among the p^μ and x^ν operators for the electron.

$$\sum_{n'} p_{nn'} p_{n'n} = \sum_{n'} p_{nn'} p_{n'n}, \quad (2a)$$

$$\sum_{n'} (1/m[E_{n'} - E_n]) (p_{nn'} p_{n'n} + p_{n'n} p_{nn'}) = \delta_{\mu\nu} - \alpha_{\mu\nu}^{(n)}. \quad (2b)$$