Luminescence of pairs of laser-excitated oxygen molecules

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Excitation of an O_2-Ar crystal simultaneously with an He-Ne laser (up to the bimolecular level $^1\Delta_g{}^1\Delta_g$) and a Cd laser leads to the appearance of luminescence from the molecular level $^3\Sigma_u^+$, thereby proving directly that the radiation from this level belongs to the $[O_2]_2$ paired centers.

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The absorption of solid binary mixtures O_2–Ar and O_2–N_2 has been investigated in[1–3]. The luminescence of oxygen under resonant photoexcitation was obtained in O_2–Ar crystals from the molecular ($^3\Sigma_u$) and bimolecular (cooperative) levels $^1\Delta_g{}^1\Delta_g$ and $^1\Sigma_g + {}^1\Sigma_g^+$.[3,5] But the question of whether the same centers are responsible for the observed transitions remains unanswered.

1. When an O_2–Ar crystal (~5% O_2) is excited by an He–Ne laser (6328 Å) at 4.2 °K, radiation bands appear at 7030 and 7636 Å. As discussed in [4] the 7030 and 7636 Å bands should be interpreted, respectively, as vibromic transitions 0′–1 from the level $^1\Delta_g{}^1\Delta_g$ and 0′–0 from the level $^1\Sigma_g^+$. The measured damping times were found to be $\tau(^1\Sigma_g{}^1\Sigma_g) = 0.1$ sec1) and $\tau(^1\Sigma_g^+) = 3$ sec. We note that laser excitation of liquid oxygen also leads to the appearance in the emission of a weak band with a maximum at 7030 Å.

2. When the crystal is simultaneously excited by He–Ne and Cd (4416 Å) lasers, additional bands appear in the radiation at 3765, 3977, and 4216 Å; the positions of the bands coincide with the vibronic bands 0′–6, 0′–Γ, and 0′–8 of the electronic transition $^3\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$ in the resonantly photoexcited O_2–Ar crystal.[4] Thus, transitions appear in the radiation, with energy higher than the excitation quantum energy of each of the sources separately, i.e., we are dealing with a two-step excitation of the $^3\Sigma_u^+$ level. The two-step character of the process is demonstrated in Fig. 1, which shows the flareup and the extinction of the luminescence measured in the 2977 Å band. Turning off either the Cd laser (section *B*) or the He–Ne laser (section *C*) leads to a decrease of the signal.

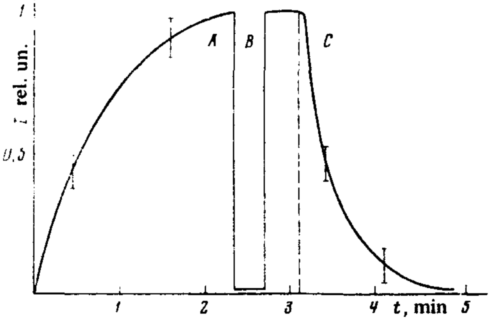

Fig. 1. Flareup (*A*) and extinction (*B* and *C*) of the luminescence of oxygen from the $^3\Sigma_u^+$ level following excitation with He–Ne and Cd lasers: *A*—both lasers in operation; *B*—Cd laser obscured; *C*—only He–Ne laser obscured.

3. Consider the emission from the levels $^1\Delta_g{}^1\Delta_g$, and $^1\Sigma_g^+$, which accompanies the first excitation step. It is seen from Fig. 2 that the vibronic bands of the bimolecular $^1\Delta_g{}^1\Delta_g$ transition are partly overlapped the $^1\Sigma_g^+$ bands. We shall show, however, that the observed luminescence is the result of the decay of a bimolecular level, and not of resonant interaction in $^1\Sigma_g^+$. Excitation by the 6328 Å line is close to the energy of the pure electronic transition $^1\Delta_g{}^1\Delta_g$, whereas the nearest 2′–0 ($^1\Sigma_g^+$) vibronic transition has an energy 80 cm^{-1} higher and cannot be excited. Direct measurement of the excitation spectrum for the 7636 Å radiation has shown a 6320 Å band corresponding to 1′–0 ($^1\Delta_g{}^1\Delta_g$) but no bands at the locations of the $^1\Sigma_g^+$ vibronic transitions.

4. The general scheme whereby radiation from the $^3\Sigma_u^+$ level is produced is shown in Fig. 2. It presupposes the decay $^1\Delta_g{}^1\Delta_g \rightarrow {}^1\Sigma_g^+ + {}^3\Sigma_g^-$[7] is followed by production of a number of molecules excited to $^1\Sigma_g^+$, which are further excited to the state $^3\Sigma_u^+$. Let us examine this scheme from the point of view of the lifetimes of the intermediate states (see Fig. 1). The kinetics of the buildup of the signal on section *A* depends on the excitation intensity. Turning off the excitation by the

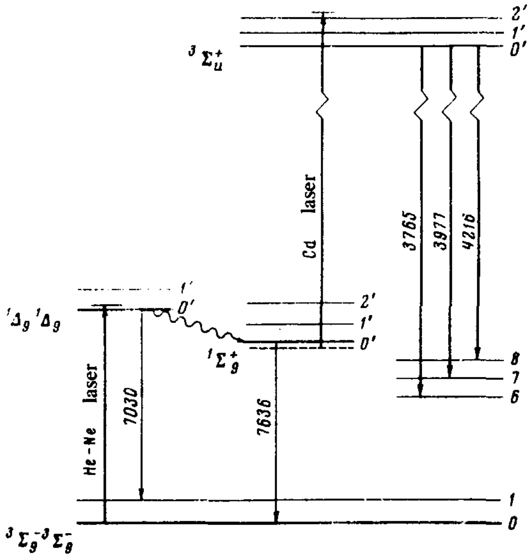

Fig. 2. Scheme of two-step excitation of the luminescence of paired oxygen molecules. The positions of the vibronic transitions are given in angstroms. The dashed line marks the suggested long-lived sublevel of the $^1\Sigma_g^+$ state.

Cd laser (section B) leads to a damping corresponding to the lifetime of $^3\Sigma_u^+$. This time was measured with direct excitation in the $^3\Sigma_u^+$ vibronic bands and is equal to $\tau(^3\Sigma_u^+) = 10^{-4}$ sec. The section C corresponds to depletion of the $^1\Sigma_g^+$ level and the damping proceeds slowly (~30 sec). The lifetime of this level, determined from the luminescence damping (see Sec. 1), turned out to be shorter by one order of magnitude. It appears that the centers that participate in the two-step absorption accumulate on some long-lived level near $^1\Sigma_g^+$.

We note in conclusion that observation of a two-step excitation of the oxygen molecules in the crystal O_2–Ar settles the argument whether the triplet structure of the vibronic bands of the Harzberg series belong to transitions in paired or single[8] oxygen molecules in favor of the paired molecules, and also makes it possible to determine the decay probabilities of bimolecular states.

The results of this study do not allow us to assess the degree of distortion of the molecular level $^3\Sigma_u^+$ in a paired center.

[1)] The result in [6] was $\tau(^1\Delta_g{}^1\Delta_g) = 0.05$ sec.

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[1] A. F. Prikhot'ko, Zh. Eksp. Teor. Fiz. 8, 671 (1938).

[2] Yu. G. Litvinenko, V. V. Eremenko, and T. Y. Garber, Phys. Stat. Solidi 30, 49 (1968).

[3] A. F. Prikhot'ko, V. A. Pavloshchuk, and L. I. Shanskiĭ, Ukr. Fiz. Zh. 18, 490 (1973).

[4] I. Sil'dos, A. Lykhmus, and L. Rebane, Izv. AN EstSSR, ser. Fiz.-mat. 21, 121 (1972); ibid. 21, 316 (1972).

[5] A. Prikhot'ko, L. A. Rebane, I. R. Sil'dos, O. S. Pakhomova, and L. I. Shanskiĭ, Izv. AN SSSR 37, 871 (1973).

[6] I. R. Sil'dos, Fiz. Tverd. Tela 16, 1168 (1974) [Sov. Phys.-Solid State 16, 749 (1974)].

[7] A. U. Khan and M. Kasha, J. Am. Chem. Soc. 92, 3293 (1970).

[8] I. N. Douglas, R. Grinter, and A. J. Thomson, Mol. Phys. 28, 1377 (1974).