Errata

Erratum: Bimolecular processes in a low-density oxygen discharge [Phys. Rev. A 29, 2578 (1984)]

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In a recent publication,[1] Awschalom, Shivashankar, and Robinson (ASR) reported on luminescence bands obtained from microwave discharges in oxygen with total pressures in the range 5–2000 mTorr. The observed luminescence bands were attributed to weakly bound O_2-O_2 complexes. In this Erratum we point out that these bands are due to optical emission from the "first negative-band system" of the oxygen molecular ion, i.e., $O_2^+(b^4\Sigma_g^-) \rightarrow O_2^+(a^4\Pi_u) + \hbar\omega$.

The $O_2^+(b^4\Sigma_g^-) \rightarrow O_2^+(a^4\Pi_u)$ bands are very complex, since 48 rotational branches are expected for each vibrational band.[2] A rotational analysis and tables of line positions and intensities for these bands have been published.[2] A spectrum can be generated from these tabulated line positions and strengths by convolution with an instrumental resolution function. In Fig. 1 we show the calculated emission spectrum for the $O_2^+(b^4\Sigma_g^-) \rightarrow O_2^+(a^4\Pi_u)$ (0,1) band and oxygen atomic lines at 6158 and 6456 Å using the experimental resolution of ASR.[1] The result corresponds quite closely with Fig. 1 of ASR.[1] The complex "quasiperiodic structure" on the molecular-ion emission band is due to unresolved rotational structure.

The 6340-Å emission band of the $O_2(a^1\Delta_g)$-$O_2(a^1\Delta_g)$ bimolecule[3] appears in the same spectral region at the $O_2^+(b^4\Sigma_g^-) \rightarrow O_2^+(a^4\Pi_u)$ (0,1) emission band. Estimates of the emission intensity for the bimolecular process $2O_2(a^1\Delta_g) \rightarrow 2O_2(X^3\Sigma_g^-) + \hbar\omega$ can be made using the measured rate constant for this reaction.[4] These estimates indicate that under the discharge conditions of ASR, emission from excited molecular ions produced by electron-impact ionization of O_2 should dominate the bimolecular emisson by several orders of magnitude. ASR[1] reported a decrease in emission intensity as the oxygen pressure increased in the range 5–500 mTorr. Those observations are consistent with quenching of the long-lived $O_2^+(b^4\Sigma_g^-)$ state[5] by thermal ion-molecule reactions.[6] While bimolecular oxygen species must certainly occur in low-pressure oxygen discharges, their optical-emission spectra, for a wide range of conditions, are expected to be masked by intense emission from the diatomic molecular ions.

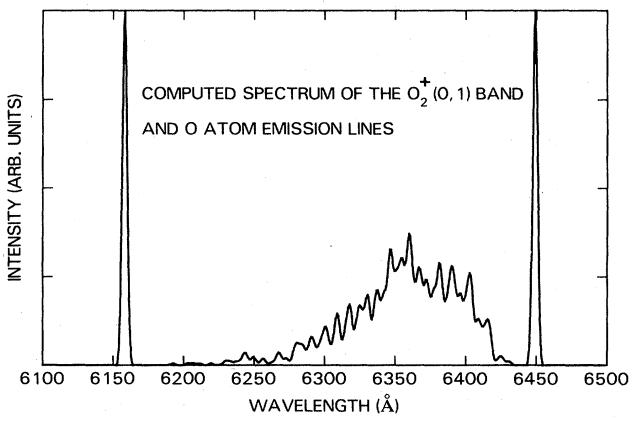

FIG. 1. Calculated emission spectrum for the $O_2^+(b^4\Sigma_g^-) \rightarrow O_2^+(a^4\Pi_u)$ (0,1) band and oxygen atomic lines at 6158 and 6456 Å using the tabulated line positions and intensities of Nevin (Ref. 2) and the experimental resolution of ASR (Ref. 1).

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[1] D. D. Awschalom, S. A. Shivashankar, and B. Robinson, Phys. Rev. A **29**, 2578 (1984).
[2] T. E. Nevin, Philos. Trans. R. Soc. London **237**, 471 (1938).
[3] S. J. Arnold, E. A. Ogryzlo, and H. Witzke, J. Phys. Chem. **49**, 1769 (1964).
[4] P. Borrel and N. H. Rich, Chem. Phys. Lett. **99**, 144 (1983).
[5] The radiative lifetime of the $v=0$ level of $O_2^+(b^4\Sigma_g^-)$ *is* 1 μsec. See K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979), and references therein.
[6] T. O. Tiernan and C. Lifshitz, *Advances in Chemical Physics,* edited by J. Wm. McGowan (Wiley, New York, 1981), Vol. 45, Chap. 2, p. 82. The quenching rate for $O_2^+(b^4\Sigma_g^-)$ by collisions with O_2 is assumed to be similar in magnitude to the large number of known quenching rates, i.e., close to the rate for capture in the polarization potential.