Spectroscopic Observation Radiative Recombination of Ground State Oxygen Atoms

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Measurements of uv-radiation emitted from a low current oxygen arc plasma show continuous emission, which can be attributed to radiative molecular recombination of ground state oxygen atoms.

Detailed knowledge of the continuous radiation processes contributing to the emission and absorption of low temperature plasmas, as encountered in e.g. laboratory electrical discharges, high pressure discharge lamps and shock-tube plasmas is still missing in many cases. This is the reason why active research is continuing in such a classic field of plasma spectroscopy [1, 2, 3, 4]. In a recent experiment [5] the uv, visible and near ir radiation emitted from the axis of a low current oxygen arc with a temperature near 9000 K was measured. Dominant contributions to the radiation of this plasma are the oxygen affinity continuum, resulting from electron-atom attachment, the oxygen electronion free-bound and free-free continuum and the so-called O_2^+-association continuum, resulting from positive ion-neutral atom recombination [1]. Additionally, a continuous molecular bandlike radiation was observed near the short wavelength end of the spectral region investigated, i.e. between 200 and 300 nm, with a maximum at $\lambda \sim 260$ nm.

Figure 1 shows the relative spectral emission coefficient in the visible and uv spectral range for three different plasma temperatures. The features annoted in Fig. 1 belong to the oxygen ^{5}P-recombination threshold (1), the oxygen ^{3}S-recombination threshold (2), the negative oxygen ion ^{3}P-attachment threshold (3) and the continuous band (4) which will be discussed here. The purpose of this communication is to present an explanation of the

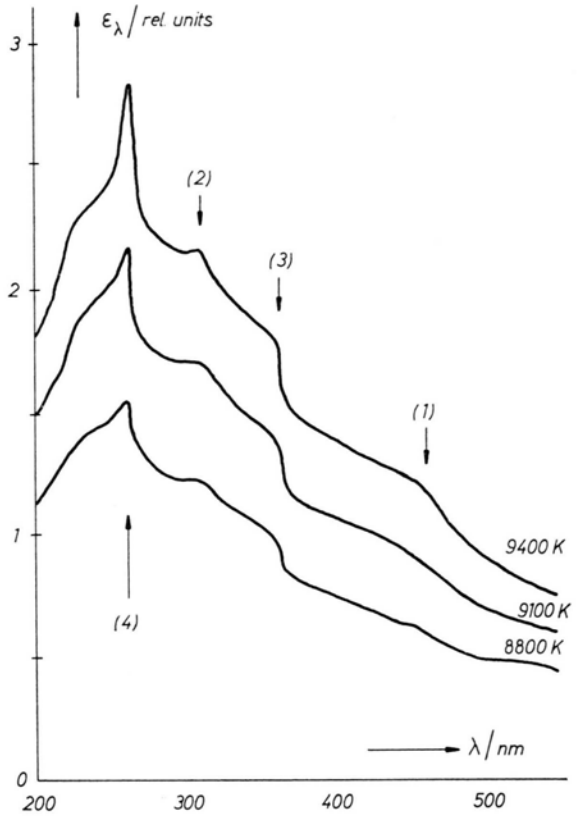

Fig. 1. Spectral emission coefficient.

radiation mechanism which is responsible for this contribution to the total emission coefficient.

For a discussion of the temperature and wavelength dependence of such continuous emission, the background radiation has to be subtracted from the total emission coefficient. This is done following the procedure described in [5]. For this purpose, the results of the absolute emission measurements were converted into absorption coefficient at the corresponding temperatures. The solid line in Fig. 2 shows the absorption coefficient $K(\lambda, 9400\ \mathrm{K})$. Maximum radiation occurs at $\lambda \sim 260$ nm, independent of temperature. This holds not only for the temperature range 8800–9400 K, covered in this experiment, but also for the temperature range 11000 to 13000 K, as was observed by Kupschus [6] in a similar arc experiment. The temperature dependence in our experiment of the absorption coefficient at maximum intensity can be approximated, as already mentioned in [5], by

$$K \sim n_0^2 \exp(+3,6\ \mathrm{eV}/kT), \qquad (1)$$

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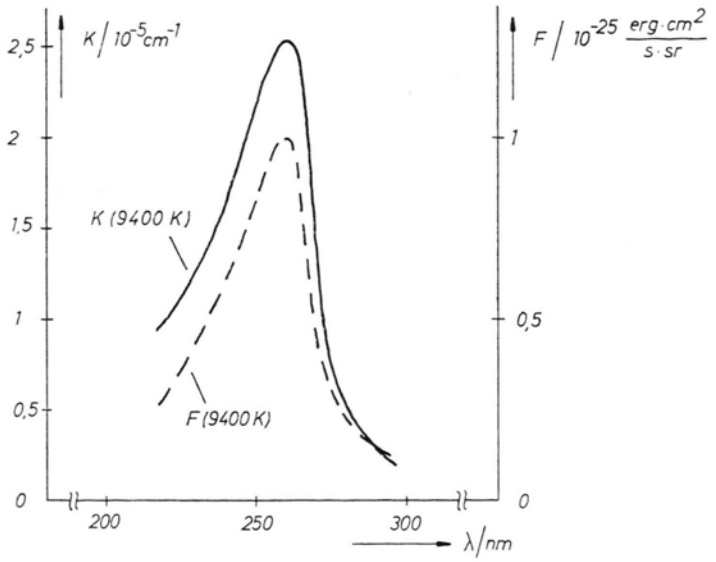

Fig. 2. Absorption coefficient (K) and function F (see text) for $T = 9400$ K.

where n_0 represents the particle density of neutral oxygen ^{3}P ground state atoms in the plasma. The corresponding temperature dependence for the emission coefficient is given by

$$\varepsilon_\lambda \sim n_0^2 \exp(-1{,}2\ \mathrm{eV}/kT)\,. \tag{2}$$

The same temperature dependence is expected for the radiation process, which involves photodissociation of the $X\ ^3\Sigma_g^-$ ground state of the O_2 molecule in absorption, or radiative recombination of ^{3}P ground state oxygen atoms in emission, respectively. The corresponding molecular potential energy curves [7, 8, 9, 10] are shown in Figure 3.

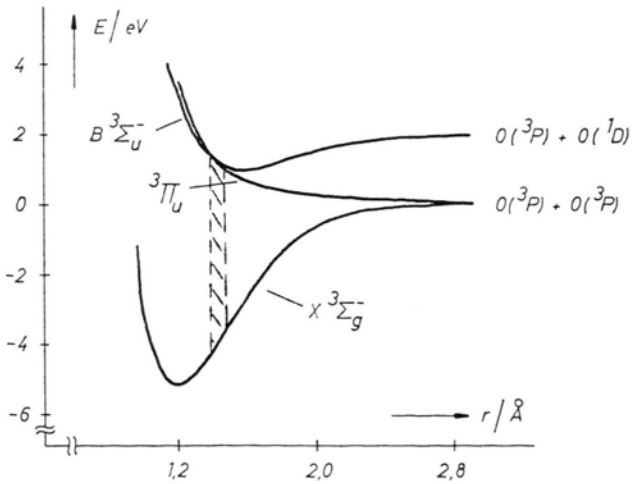

Fig. 3. O_2 potential energy curves.

Possible radiation emission processes are

$$[\mathrm{O}(^3\mathrm{P}) + \mathrm{O}(^3\mathrm{P})]_{^3\pi_u} \xrightarrow{h\nu} \mathrm{O}_2(X\ ^3\Sigma_g^-) \tag{3}$$

and

$$[\mathrm{O}(^3\mathrm{P}) + \mathrm{O}(^3\mathrm{P})]_{^3\pi_u} \rightarrow \mathrm{O}_2(B\ ^3\Sigma_u^-) \xrightarrow{h\nu} \mathrm{O}_2(X^3\ \Sigma_g^-)\,. \tag{4}$$

The first of these processes represents a true molecular continuum with a short wavelength threshold beyond the range investigated. Its intensity maximum is expected to shift to shorter wavelengths with higher temperatures. This fact is in contradiction to our experimental evidence and to the results of [6] and [11]. The contribution of the undisturbed process (3) should thus be negligible in our case. The second process (4) involves inverse predissociation due to level crossing [8, 12, 13, 14] into vibrational $O_2\ B^3\Sigma_u^-$ states, from which Schumann-Runge transitions originate. This mechanism was suggested in [11] as an important ultraviolet radiation source in shock heated plasma of low temperatures $T \sim 3000$ K. According to [13, 14, 15] the predissociation and its inverse process in this case occur mainly at vibrational levels $v = 4$ and $v = 11$ of the $B^3\Sigma_u^-$ state. An important feature of such potential energy curve crossing is that the molecular wave functions of both states become mixed, and a distinction between processes (3) and (4) becomes difficult. One interpretation of the continuous spectrum discussed here can thus be given in terms of process (3), but with enhanced transition probabil-

ities (Frank-Condon factors) in the region of level crossing. Another interpretation, which is nearly equivalent, is in terms of process (4) as emission of Schumann-Runge bands which are smeared out to continuous radiation due to level crossing [15]. Both interpretations are consistent with an intensity maximum between 200 and 300 nm and with a temperature independent wavelength position of this maximum. Our measurements exhibit maximum intensity at $\lambda \sim 260$ nm, which is within the above wavelength range. It is interesting to note that the experimental emission continuum was partly superimposed by weak, band-like structures. This also fits into the above scheme as the $B^3\Sigma_u^-$ state, the thermal population of which should be negligible for our experimental conditions, can be partly populated by the inverse predissociation process.

For a quantitative comparison of the absolute intensities of our measurements with those reported in [11] we consider the function $F(\lambda, T)$, which is defined by

$$F(\lambda, T) = \varepsilon_\lambda / n_0^2 . \quad (5)$$

As an example, the broken line in Fig. 2 represents $F(\lambda, 9400\ \mathrm{K})$. Figure 4 is a plot of $F(260\ \mathrm{nm}, T)$ as a function of the reciprocal plasma temperature. The crosses and the solid line represent our result, the circles and the broken line are taken from the measurements reported in [11]. Both results exhibit the same temperature-dependence, which is in accordance with processes (3) and (4). The agreement with respect to absolute magnitude is within a factor of two. This can be considered satisfactory in view of the large temperature difference of a factor of three and the very different plasma sources (transient shock tube and stationary arc plasma) which were used in these experiments.

Finally we mention that $F(\lambda, T)$ can be expressed as a function of temperature and molecular parameters in the following way [16]:

$$F(\lambda, T) = \frac{1}{4\pi} \frac{hc}{\lambda} g A(r) r^2 \frac{\mathrm{d}r}{\mathrm{d}\lambda} \exp\left(-\frac{E(r)}{kT}\right), \quad (6)$$

with g being the statistical weight ratio of the radiating potential curve to all other curves, r the distance between both oxygen molecules in the moment of photon emission, $A(r)$ the transition probability for the transition considered and $E(r)$ the potential energy according to Figure 2. The other symbols have their usual meaning.

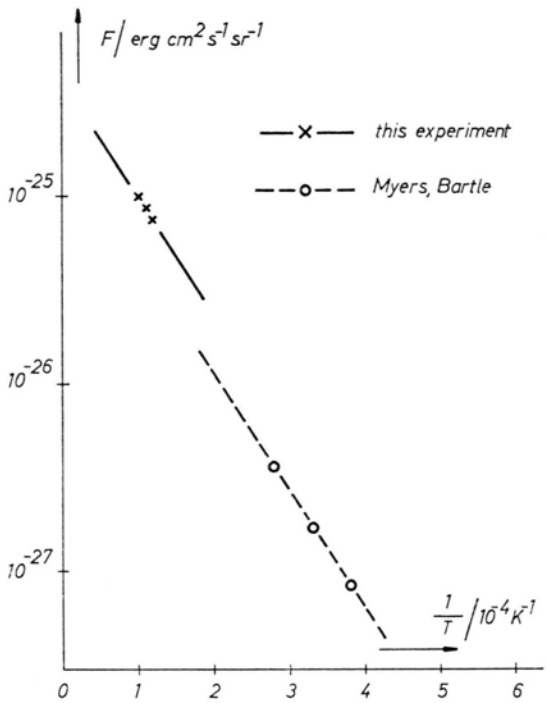

Fig. 4. Absolute values of F (see text) for $\lambda = 260$ nm.

We conclude that the ultraviolet continuous emission band, which can be observed in low temperature oxygen plasmas, originates from radiative recombination of ground state oxygen atoms into the molecular O_2 ground state. This interpretation is consistent with both temperature and wavelength dependence of the measured spectra. The absolute intensities in our arc experiment are in satisfactory agreement with those from a shock tube study. Finally we mention that an experimental investigation of a silent electric discharge in oxygen [15] showed continuous radiation between 200 and 300 nm, which was tentatively interpreted as the recombination continuum described here.

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