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Radiative association and inverse predissociation of oxygen atoms

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The formation of O_2 by radiative association and by inverse predissociation of ground-state oxygen atoms is studied using quantum-mechanical methods. Cross sections, emission spectra, and rate coefficients are presented and compared with prior experimental and theoretical results. At temperatures below 1000 K, radiative association occurs by approach along the $1\,^3\Pi_u$ state of O_2 and above 1000 K inverse predissociation through the $B\,^3\Sigma_u^-$ state is the dominant mechanism. This conclusion is supported by a quantitative comparison between the calculations and data obtained from hot oxygen plasma spectroscopy.

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I. INTRODUCTION

Of the 81 molecular electronic states that two $O(^3P)$ atoms can form, the repulsive $1\,^3\Pi_u$ state can make an allowed electric dipole transition to the $X\,^3\Sigma_g^-$ ground state. Thus the formation of an oxygen molecule through the *direct radiative association* reaction

$$O(^3P) + O(^3P) \to O_2(1\,^3\Pi_u) \to O_2(X\,^3\Sigma_g^-) + h\nu \quad (1)$$

can occur and it might be an important molecular oxygen creation process at low temperatures. In Fig. 1 the potential energy curves for the $1\,^3\Pi_u$ and $X\,^3\Sigma_g^-$ states of O_2 are depicted. Wraight [1] had suggested that the process (1) might be responsible for the emission in the near infrared of the nightglow of the planet.

At higher temperatures another process—*inverse predissociation*, an indirect mechanism of association—can occur with the excited $B\,^3\Sigma_u^-$ state serving as an intermediate step in the formation of an oxygen molecule

$$O(^3P) + O(^3P) \to O_2^* \to O_2(B\,^3\Sigma_u^-) \to O_2(X\,^3\Sigma_g^-) + h\nu, \quad (2)$$

where O_2^* denotes any one of the four states $1\,^1\Pi_u$, $1\,^3\Pi_u$, $1\,^5\Pi_u$, or $2\,^3\Sigma_u^+$ that dissociate to $O(^3P) + O(^3P)$ and cross the $B\,^3\Sigma_u^-$ state. The predissociative coupling is due to spin-orbit (any of the four states) or electronic-rotational interaction ($1\,^3\Pi_u$ state) [2]. Reaction (2) may be characterized by an activation energy that is the energy with respect to the $O(^3P) + O(^3P)$ asymptote at which the particular state O_2^* crosses the $B\,^3\Sigma_u^-$ state. The potential energy curve of the $B\,^3\Sigma_u^-$ state, which dissociates to an $O(^3P)$ atom and an $O(^1D)$ atom, is shown in Fig. 1. Because the strength of the electronic-rotational coupling increases with the nuclear rotational angular momentum, while the strength of the spin-orbit coupling is nearly independent of it [3], the $1\,^3\Pi_u$ state is expected to be the most important channel for inverse predissociation. In a shock tube study of the emission from recombining oxygen atoms in a nonequilibrium shocked ozone-argon gas mixture at temperatures between 2500 and 3800 K Myers and Bartle [4] obtained absolute intensity measurements of the spectrum and attributed the emission to the formation of oxygen molecules from ground state oxygen atoms through the inverse predissociation process

$$O(^3P) + O(^3P) \to O_2(1\,^3\Pi_u) \to O_2(B\,^3\Sigma_u^-) \to O_2(X\,^3\Sigma_g^-) + h\nu. \quad (3)$$

The emission has been observed in several later experiments. It was seen in a silent electric discharge in O_2 by Weisbeck and Völkner [5] and Sharma and Wray [6] measured emission intensities at 230 and 325 nm for temperatures in the range 2800–5300 K in shocked oxygen and oxygen–noble-gas mixtures. Sharma and Wray [6] confirmed that the excited levels of O_2 were populated by inverse predissociation, but their emission spectra appear to be modified by vibrational redistribution. Similar conclusions were reached by Wray and Fried [7], who measured the emission intensities in an arc jet in oxygen and and oxygenlike gas mixtures. Hoffmann and Neiger [8,9] measured the absolute intensity of the emission from an equilibrium oxygen plasma at 8800, 9140, and 9420 K, finding a peak at about 260 nm which they attributed to inverse predissociation (3). We return to a discussion of prior work in Sec. V.

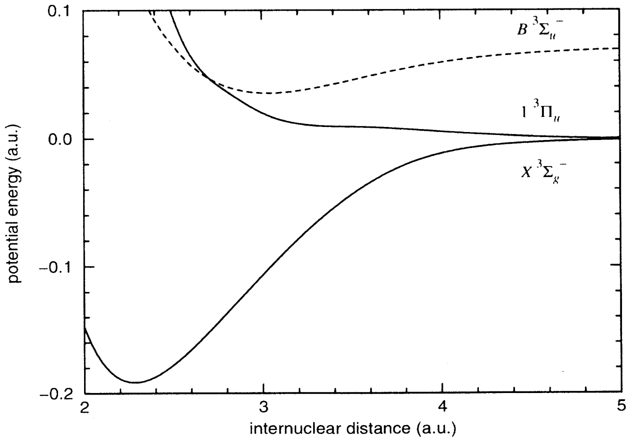

FIG. 1. Adopted $1\,^3\Pi_u$, $B\,^3\Sigma_u^-$, and $X\,^3\Sigma_g^-$ potentials.

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In this paper, we study quantum mechanically the direct radiative association process (1) and the inverse predissociation process (3). Cross sections, emission spectra, and rate coefficients are determined for temperatures from 15 to 15 000 K. Improvements in the knowledge of the $1\,{}^3\Pi_u$ and $B\,{}^3\Sigma_u^-$ state potentials make it possible to get qualitative agreement with many experiments for the emission spectra and quantitative agreement for rate coefficients measured by Myers and Bartle [4].

II. MOLECULAR STATES

In Ref. [10] we constructed two $1\,{}^3\Pi_u$ potential energy curves that were identical except in the range of internuclear distances $2.4 < R < 3.1$ (we shall use atomic units in this section and Sec. III). The first curve was designed to be consistent with the level shifts arising from predissociation of the $B\,{}^3\Sigma_u^-$ state, as analyzed in Ref. [11] where an internuclear distance for the $B\,{}^3\Sigma_u^-$-$1\,{}^3\Pi_u$ crossing $R_x = 2.700$ was obtained, which used *ab initio* energy calculations [12] for $3.1 < R < 10$. The second curve we constructed simply used the *ab initio* calculations [12] for $2.5 < R < 10$. A recent analysis [13] of the photoabsorption cross section measurements [14], an analysis presumably more accurate than that of Ref. [11], yielded a different crossing point of $R_x = 2.748$, which is consistent with the crossing point of the cubic spline fit [13] to the calculations of [12] at $R = 2.5$ and 2.8. We have therefore used the second curve we constructed in Ref. [10] here. As we have discussed [10] the potential curve was supplemented for $R < 2.4$ by the adjusted *ab initio* energies of [15] and was constructed to have the proper asymptotic long-range behavior.

The adopted transition dipole moment function $D(R)$, defined in [16], for the transition from the $1\,{}^3\Pi_u$ to the $X\,{}^3\Sigma_g^-$ state was the semiempirical determination of [17] for $1.5118 \leq R \leq 2.5$ and the *ab initio* calculation of [15] for $2.6 \leq R \leq 5$. The data were smoothly connected using cubic splines. For $R \leq 1.5118$ the function $D(R) = 0.1794 - 0.01945R$ was used and for $R \geq 5$ the function $D(R) = 1.2625/R^3$. The $X\,{}^3\Sigma_g^-$ state potential energy curve was constructed using Rydberg-Klein-Rees data for $1.794\,80 < R < 4.0840$ and fitted to the long-range form $-17.57/R^6$ for $R > 5$ as described in Ref. [18], but with a short-range form

$$V(R) = 5757.0053\exp(-5.7925R). \tag{4}$$

The adopted $X\,{}^3\Sigma_g^-$ and $1\,{}^3\Pi_u$ potential curves, which correlate with the separated atoms $\mathrm{O}({}^3P) + \mathrm{O}({}^3P)$, are shown in Fig. 1. The $B\,{}^3\Sigma_u^-$ potential curve of [18] and the semiempirical $B\,{}^3\Sigma_u^-$–$X\,{}^3\Sigma_g^-$ transition dipole moment of [19] as described in [18] were utilized. In Fig. 1 the adopted $B\,{}^3\Sigma_u^-$ potential is shown. It correlates to the separated atom limit $\mathrm{O}({}^3P) + \mathrm{O}({}^1D)$, which lies 0.072 29 a.u. (1.967 eV) above $\mathrm{O}({}^3P) + \mathrm{O}({}^3P)$.

III. DIRECT RADIATIVE ASSOCIATION

A fully quantum-mechanical theory can be formulated and used to calculate the cross sections at various energies and rate coefficients at various temperatures for direct radiative association (1). Let E be the energy of relative motion of the atoms approaching in the $1\,{}^3\Pi_u$ electronic state. The cross section for a transition to a bound vibration-rotation level $E_{v''N''}$ of the $X\,{}^3\Sigma_g^-$ molecular ground state is given in atomic units by [20,21]

$$\sigma_{v''N''N}(E) = \frac{g_1}{g}\frac{4\pi^2\alpha^3}{3\mu E}(E + E_{v''N''})^3 S_{J'',J}|M_{N'',N}|^2, \tag{5}$$

where $\mu = 14\,583.10$ is the reduced mass for ${}^{16}\mathrm{O}_2$, $g_1 = 3$ is the statistical weight of the $1\,{}^3\Pi_u$ state (the nuclear spin is zero so only one of each lambda-doubling level is populated), $g = 81$ is the statistical weight of the $\mathrm{O}({}^3P)$-$\mathrm{O}({}^3P)$ pair, α is the fine structure constant, $S_{J'',J}$ is the Hönl-London factor, and

$$M_{N'',N} = \int_0^\infty dR\, \psi_{v''N''}(R)\, D(R)\, \chi_N(R), \tag{6}$$

with $\psi_{v''N''}(R)$ the normalized bound state wave function and $\chi_N(R)$ the energy-normalized wave function for the partial wave with angular momentum N of the continuum $1\,{}^3\Pi_u$ state. The wave functions $\psi_{v''N''}$ and χ_N were calculated by integrating the Schrödinger equation using the Numerov method and χ_N was matched to the asymptotic form

$$\chi_N(R) \sim (2\mu/\pi k)^{1/2}\sin(kR + \delta_N - \tfrac{1}{2}N\pi), \qquad R \sim \infty, \tag{7}$$

with $k = (2\mu E)^{1/2}$ and δ_N the phase shift. Due to the presence of identical nuclei in the diatom and the absence of nuclear spin, the $X\,{}^3\Sigma_g^-$ state is allowed only odd values N''. Let $J = |\mathbf{N} + \mathbf{S}|$ be the magnitude of the total angular momentum for the $1\,{}^3\Pi_u$ state, with $\mathbf{S}$ the total spin angular momentum and $|\mathbf{S}| = 1$. Assuming that Hund's case (b) coupling applies, we have for $N \gg 1$, $J \sim N$ [in an unrelated study, case (b) was found to be a satisfactory approximation to intermediate coupling [18]] and then, summing over the rotational branches [22] for the allowed fine structure transitions for a given value of N, we obtain the Hönl-London factors given in Table I, which possess the sum rule property [23,24]

$$\sum_{N''} S_{N'',N} = (2S + 1)(2N + 1). \tag{8}$$

In carrying out the computations N'' was required to be odd, but N could be odd or even.

The total cross section, summed over allowed transitions between partial waves N and final states $v''N''$

$$\sigma(E) \equiv \frac{1}{(2S + 1)}\sum_{v''N''N}\sigma_{v''N''N}(E), \tag{9}$$

TABLE I. Hönl-London factors for transitions from the $1\,^3\Pi_u$ to the $X\,^3\Sigma_g^-$ state.

J''	Branch	$S_{J'',J}/(2S+1)$
$J-1$	R	$J+1$
J	Q	$2J+1$
$J+1$	P	J

is presented in Fig. 2 at various energies. Some structure, due to shape resonances, is apparent in the cross section at low energies. The cross section drops off rapidly for $E \gtrsim 0.4$ due to the loss of Franck-Condon overlap at small R. In computing the total cross sections values of N up to 15 were sufficient for $E \lesssim 2.0 \times 10^{-5}$, up to 30 for $E \lesssim 3.0 \times 10^{-5}$, up to 100 for $E \lesssim 0.015$, and for $E \gtrsim 0.015$ values of N up to 188 were used. Since the $X\,^3\Sigma_g^-$ state has 45 vibrational levels, each total cross section at a given E was a sum of many partial cross sections. Nevertheless, the computations could be carried out readily.

The cross sections obtained at various values of E were used to obtain the rate coefficient at various temperatures by averaging over a Maxwellian velocity distribution

$$\alpha_D(T) = \frac{2}{kT}\left(\frac{2}{\pi\mu kT}\right)^{1/2} \int_0^\infty E\sigma(E)e^{-E/kT}\,dE. \quad (10)$$

The values are given in column 2 of Table II. The rate coefficient is approximated to within 5% for $T < 400$ K by the expression

$$\alpha_D(T) \approx 9 \times 10^{-27} T^{-0.23} \exp(T/70)\ \mathrm{cm^3\,s^{-1}}, \qquad T < 400\ \mathrm{K}. \quad (11)$$

Wraight [1] estimated semiclassically the rate coefficient for the direct process (1) and found

$$\alpha_W(T) \sim 6 \times 10^{-24} T^{1.58}\ \mathrm{cm^3\,s^{-1}} \quad (12)$$

for 200 K $< T <$ 2000 K. He advised caution in applying (12) to high temperatures. Expression (12) was adopted for astrophysical purposes in the tabulation of Prasad and Huntress [25] and of Millar *et al.* [26]. The present computations show that Eq. (12) drastically overestimates the radiative association rate coefficient at low temperatures.

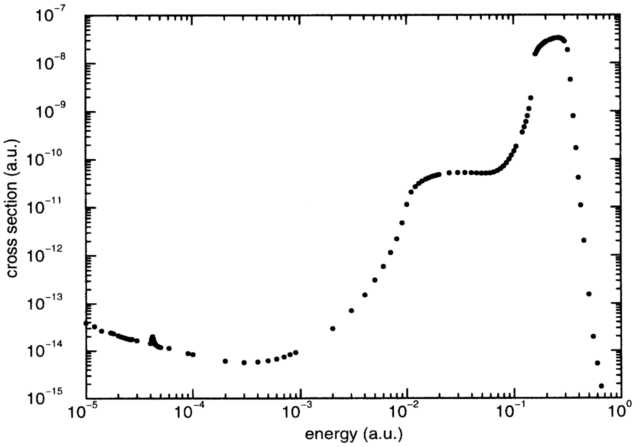

FIG. 2. Cross section $\sigma(E)$ (9) in a.u. (a_0^2) for the direct radiative association process (1) as a function of energy E in a.u. (e^2/a_0).

TABLE II. Rate coefficients in $\mathrm{cm^3\,s^{-1}}$, as a function of temperature T, in K, for direct radiative association process (1), inverse predissociation (3), and the experimentally derived value for the total process (21). Numbers in square brackets represent powers of 10.

T (K)	Direct	Inverse predissociation	Experiment, Ref. [4] α_{expt}, Eq. (20)
15	6.0[-27]		
30	6.4[-27]		
50	7.4[-27]		
100	1.3[-26]		
200	4.6[-26]		
300	1.7[-25]		
400	6.5[-25]		
500	1.9[-24]		
600	4.4[-24]	1.1[-27]	
700	8.3[-24]	2.7[-26]	
800	1.4[-23]	3.1[-25]	
900	2.1[-23]	2.0[-24]	
1000	2.9[-23]	9.2[-24]	
1200	4.7[-23]	8.9[-23]	
1400	6.9[-23]	4.5[-22]	
1600	9.2[-23]	1.5[-21]	
1800	1.2[-22]	3.9[-21]	
2000	1.4[-22]	8.4[-21]	
2200	1.6[-22]	1.5[-20]	
2500	2.0[-22]	3.2[-20]	2.2[-20]
2700	2.2[-22]	4.8[-20]	3.3[-20]
3000	2.5[-22]	7.8[-20]	5.7[-20]
4000	3.7[-22]	2.2[-19]	1.9[-19]
5000	6.1[-22]	3.9[-19]	
10000	1.7[-20]	9.0[-19]	
15000	7.3[-20]	9.3[-19]	

IV. INVERSE PREDISSOCIATION

For inverse predissociation (3), the rate coefficient at temperature T is given by the Breit-Wigner expression [27–29]

$$\alpha(T) = \frac{g_B}{g}\left(\frac{2\pi}{\mu kT}\right)^{3/2} \sum_{v'}\sum_{N'} (2N'+1) \times \frac{\Gamma_r(v',N')\Gamma_d(v',N')}{\Gamma_r(v',N')+\Gamma_d(v',N')} \exp(-E_{v'N'}/kT), \quad (13)$$

where $g_B = 3$ is the statistical weight of the $B\,^3\Sigma_u^-$ state, $g = 81$ is the statistical weight of the O(^3P)–O(^3P) pair, $E_{v'N'}$ is the energy of the level $v'N'$ of the $B\,^3\Sigma_u^-$ state measured with respect to the O(^3P)–O(^3P) asymptote, $\Gamma_r(v',N')$ and $\Gamma_d(v',N')$ are, respectively, the radiative and predissociative widths of level $v'N'$, with

$$\Gamma_r(v',N') = \hbar A(v',N') \equiv \hbar \sum_{v'',N''} A(v'N'v''N''), \qquad (14)$$

and $A(v'N'v''N'')$ is the Einstein A coefficient. The sum in Eq. (13) is taken over levels $v'N'$ with energy greater than the energy of the crossing point. Analysis [13] of the predissociation in the $B\,^3\Sigma_u^-$ state indicates that the $1\,^3\Pi_u$ state crosses at an energy of 0.0435 relative to the O(^3P)-O(^3P) asymptote [11] or about 13 000 K. For the $B\,^3\Sigma_u^-$ state, typically $\Gamma_d(v',N') \gg \Gamma_r(v',N')$ [30], so that

$$\alpha(T) \approx \frac{3}{81}\left(\frac{2\pi}{\mu kT}\right)^{3/2} \hbar^2 \sum_{v'}\sum_{N'} (2N'+1)\Gamma_r(v',N') \times \exp(-E_{v'N'}/kT). \qquad (15)$$

The effect of centrifugal distortion is negligible, so in evaluating (15) we made the approximation

$$A(v'N'v''N'') \approx A(v'0v''0)[(E_{v'N'} - E_{v''N''})/(E_{v'0} - E_{v''1})]^3, \qquad (16)$$

with $N' \approx N''$ leading to the formula

$$\alpha(T) \approx \frac{3}{81}\left(\frac{2\pi}{\mu kT}\right)^{3/2} \hbar^3 \sum_{v'}\sum_{v''} A(v'0v''0) \times \sum_{N'}(2N'+1) \times [(E_{v''N'} - E_{v''N'})/(E_{v'0} - E_{v''1})]^3 \times \exp(-E_{v'N'}/kT). \qquad (17)$$

The intensity of emission from a transition from level (v',N') into level (v'',N'') is then given by the expression

$$I_\nu \approx h\nu_{v'N'v''N''}\tfrac{3}{81}(2\pi/\mu kT)^{3/2}(2N'+1) \times \exp(-E_{v'N'}/kT)\hbar^3 A(v'0v''0) \times [(E_{v''N'} - E_{v''N'})/(E_{v'0} - E_{v''1})]^3. \qquad (18)$$

With $E(v'N'v''N'') \equiv h\nu_{v'N'v''N''}$ and $E_{v'N'}$ both in cm^{-1}, T in K, and $A(v'0v''0)$ in s^{-1}, we can express I_ν in W cm^3 as

$$I_\nu = \tfrac{3}{81}(4.7\times10^{-45})E(v'N'v''N'')(1/T^{3/2})(2N'+1) \times A(v'0v''0)\exp(-E_{v'N'}/0.695T). \qquad (19)$$

V. RESULTS AND COMPARISON WITH EXPERIMENT

Using a program of Allison *et al.* [31,19] and the potentials and transition dipole moments of Sec. II, we determine the radiative widths. They are in good agreement with other computations [31,32]. In Table III we present the values of the emission transition probabilities $A(v',0)$ of the $B\,^3\Sigma_u^-$ state vibrational levels. In Fig. 3 the calculated emission spectra arising in inverse predissociation at 3000 K are shown in W cm^3/nm along with the measurements of Myers and Bartle [4] at 3030 K; the experimental points and error bars were interpolated from absolute emission-intensity spectral distribution curves. Our calculations support the suggestion that the measurements are in error for wavelengths $\lambda \lesssim 300$ nm, a possibility noted by Myers and Bartle [4] and Sharma and Wray [6]. The measurements of Sharma and Wray [6] and Wray and Fried [7] appear to be affected by vibrational redistribution and their spectral data can be better interpreted in terms of an equilibrium model of the vibrational level populations of the $B\,^3\Sigma_u^-$ state [33].

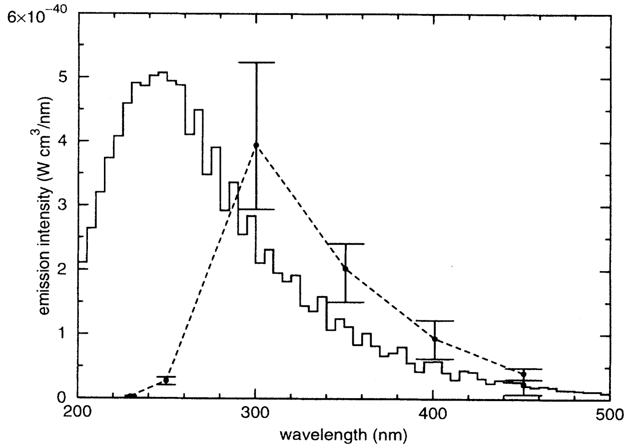

FIG. 3. Absolute emission intensity at various wavelengths calculated for inverse predissociation at 3000 K (solid line), compared to experimental measurements of Myers and Bartle at 3030 K (points with error bars connected by the dotted line). The calculated spectrum has been averaged over bins of width 5 nm. The experimental data are average values over a spectral interval, the width of which is represented by the horizontal span of the error bar.

In the measurements of Hoffmann and Neiger near 9000 K a strong broad continuum feature was observed at around 260 nm. Our calculated emission spectra from inverse predissociation are consistent with the experimental observations. Measurements at higher wave-

TABLE III. Transition probabilities $A(v',0)$ for emission from the $B\,^3\Sigma_u^-$ to $X\,^3\Sigma_g^-$ states in units of 10^7 s^{-1} for various values of the $B\,^3\Sigma_u^-$ vibrational quantum number v' with $N'=0$.

v'	$A(v',0)$	v'	$A(v',0)$
0	1.816	11	1.750
1	1.916	12	1.586
2	2.006	13	1.393
3	2.078	14	1.184
4	2.130	15	0.9709
5	2.157	16	0.7833
6	2.157	17	0.6162
7	2.129	18	0.4710
8	2.073	19	0.3414
9	1.992	20	0.2254
10	1.883	21	0.1195

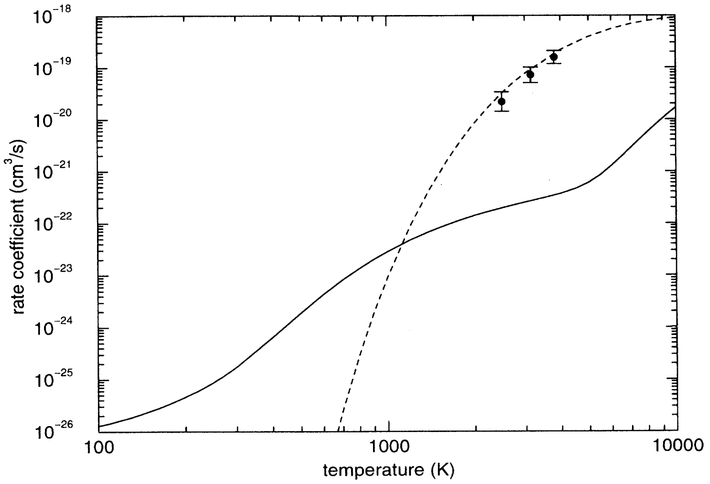

FIG. 4. Comparison of the calculated direct radiative association (solid line) and inverse predissociation (dotted line) rate coefficients and the experimental rate coefficient (points) of Myers and Bartle with the estimated uncertainties shown as error bars.

length resolution should reveal structure arising from the Schumann-Runge bands populated by inverse predissociation. We find an absolute emission intensity of about 5×10^{-39} W cm^3/nm at 250 nm and 9400 K. From the measured absorption coefficient of $K = 2 \times 10^{-5}$ cm^{-1} [8], using Wien's radiation law [9,34], the length 10 cm of the experimental arc column, and estimating the number density of O atoms of about 10^{18} cm^{-3} from Fig. 5 of Ref. [9], we obtain an experimental value of 2.5×10^{-39} W cm^3/nm at 250 nm and 9400 K. The agreement to within a factor of 2 is remarkably close.

A rate coefficient

$$\alpha_{\text{expt}}(T) = 7.3 \times 10^{-18} \exp[(-14540 \pm 1100)/T] \text{ cm}^3\,\text{s}^{-1}, \quad 280 \le \lambda \le 500 \text{ nm}, \quad (20)$$

for the total radiative combination of oxygen

$$\text{O} + \text{O} \to \text{O}_2 + h\nu \quad (21)$$

between 2500 K and 3800 K was deduced by Myers and Bartle [4]. In Table II values of $\alpha_{\text{expt}}(T)$ are given for various temperatures. Our values for the rate coefficient for inverse predissociation $\alpha_{IP}(T)$ are included in Table II. The rate coefficient is fitted to within 10% for $T \le 5000$ K by the expression

$$\alpha_{IP}(T) \sim 6.4 \times 10^{-18} \exp(-13\,455/T) \text{ cm}^3\,\text{s}^{-1}, \quad T \le 5000 \text{ K} \quad (22)$$

and to within 5% for $5\,000 \le T \le 15\,000$ K by

$$\alpha_{IP}(T) \sim (-5.6 \times 10^{-19} + 2.4 \times 10^{-22} T - 9.6 \times 10^{-27} T^2) \text{ cm}^3\,\text{s}^{-1}, \quad 5000 \le T \le 15\,000 \text{ K}. \quad (23)$$

In Fig. 4 the calculated direct α_D and inverse predissociation α_{IP} rates are presented and compared with the α_{expt}. The agreement is very good, confirming that the formation of molecular oxygen from hot oxygen atoms at low densities proceeds by inverse predissociation through the $B\,^3\Sigma_u^-$ state following the approach along the $1\,^3\Pi_u$ state.

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