Direct detection of singlet oxygen O$_2$ ($a^1\Delta_g$) by absorption at the $a^1\Delta_g \rightarrow b^1\Sigma_g^+$ transition using intracavity laser spectroscopy

V S Pazyuk, Yu P Podmar'kov, N A Raspopov, M P Frolov

Abstract. **The absorption spectrum of singlet oxygen O$_2$ ($a^1\Delta_g$) is detected in a gas phase at the $a^1\Delta_g \rightarrow b^1\Sigma_g^+$ transition by the method of intracavity laser spectroscopy using a broad-band Co : MgF$_2$ laser emitting 200-μs pulses at a wavelength 1.91 μm. In the case of Doppler broadening of absorption lines at room temperature, the sensitivity of detection of O$_2$ ($a^1\Delta_g$) is $\sim (2-5) \times 10^{14}$ cm^{-3}. It is shown that the gas temperature can be calculated from the dependence of absorption cross sections for individual lines on the rotational quantum number.**

Molecular oxygen in the first excited electronic state O$_2$($a^1\Delta_g$) is called singlet oxygen (SO). On the one hand, it attracts attention in connection with some biological and medical problems, in particular, the photodynamic [1] or light-oxygen [2] therapy of tumors, where, according to modern concepts, SO plays an important role. On the other hand, SO is an important component of the active medium of chemical oxygen–iodine laser [3], which is today one of the most powerful lasers.

Because SO is involved in many processes, its detection is of particular interest. The SO concentration is conventionally measured by the intensity of emission at the $a^1\Delta_g \rightarrow X^3\Sigma_g^-$ transition at a wavelength of 1.27 μm [4, 5] using a calibrated photodetector. This method uses a simple equipment, however, the absolute calibration of the photodetector is a difficult problem and may introduce errors. In addition, considerable problems may arise in such measurements due to a background illumination (e.g., in a gas discharge plasma), because the 1.27-μm line intensity is low, due to a low probability of the radiative transition from the O$_2$($a^1\Delta_g$) state (the radiative lifetime of the O$_2$($a^1\Delta_g$) state in a gas phase is 45 min [6]).

For this reason, methods based on absorption spectroscopy attract interest. For example, the authors of [7] determined the SO concentration in the active medium of an oxygen–iodine laser by measuring the concentration of oxygen in the ground state and subtracting the concentration of unexcited oxygen from the known total oxygen concentration. They used high-sensitivity diode laser spectroscopy for measuring absorption at the $X^3\Sigma_g^- \rightarrow b^1\Sigma_g^+$ transition at a wavelength of 760 nm. It was shown [8] that in this method the intracavity laser spectroscopy (ICLS) based on an Ti^{3+} : Al$_2$O$_3$ laser can be also used. Unfortunately, the method can be applied only when the concentration of foreign impurities in oxygen is low and the content of SO is high (tens percent).

The authors of [9] measured the SO concentration in a gas phase by its absorption in the vacuum UV spectral region. However, the absorption caused by unexcited oxygen molecules should be taken into account in this case.

SO can be detected directly by measuring absorption at the $a^1\Delta_g \rightarrow b^1\Sigma_g^+$ transition at 1.91 μm. This transition was first observed by J F Noxon [10] in the emission spectrum of the discharge in the oxygen–helium mixture. This is the electric quadrupole transition and its probability in a gas phase is as low as 0.0017 s^{-1} [10,11]. In solutions, this probability may increase 5-6 orders of magnitude due to the interaction with solvent, allowing the authors [12] to observe the absorption of SO at the $a^1\Delta_g \rightarrow b^1\Sigma_g^+$ transition in some organic solvents. Similar measurements in a gas phase require highly sensitive methods of absorption spectroscopy.

Intracavity laser spectroscopy [13, 14] is one of such methods. By placing a sample with the line absorption spectrum into the cavity of a broad-band laser, for example, a dye laser one can detect spectral lines with absorption coefficients down to $\sim 10^{-11}$ cm^{-1} [14], which is far beyond the capabilities of conventional absorption spectroscopy. A Co : MgF$_2$ laser that was successfully used in ICLS [15, 16] in the range 1.6–2.5 μm extended the spectral range of the method to the near-IR region and the number of substances that can be detected by this method increased significantly.

In this paper, we detected for the first time the absorption spectrum of gaseous SO at the $a^1\Delta_g \rightarrow b^1\Sigma_g^+$ transition by ICLS using a Co : MgF$_2$ laser. The experimental setup is schematically shown in Fig. 1. A Co : MgF$_2$ crystal *1* was longitudinally pumped by a Nd : YAlO$_3$ laser *2* operated in the free running mode at 1.34 μm. The pump radiation was focused to the centre of the crystal by lens *3*. The pulse duration of a Co : MgF$_2$ laser was 220 μs, its cavity was formed by two spherical mirrors *4* ($R = 20$ cm) and *5* ($R = 50$ cm) and has a length of 62 cm. The emission spectrum of a Co : MgF$_2$ laser was determined by the spectral characteristics of the cavity mirrors and at the moment $t = 200$ μs relative to the leading edge of the laser pulse the width of the spectrum centred at 1.91 μm was ~ 5 nm.

V S Pazyuk, Yu P Podmar'kov, N A Raspopov, M P Frolov P N Lebedev Physics Institute, Russian Academy of Sciences, Leninsky prosp. 53, 119991 Moscow, Russia
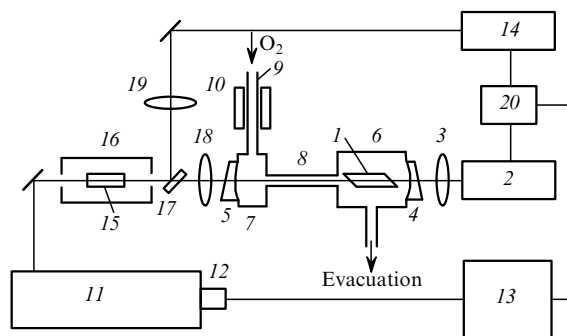
Figure 1. Schematic of the experimental setup: (*1*) Co : MgF$_2$ crystal; (*2*) pumping Nd : YAlO$_3$ laser; (*3, 18, 19*) focusing lenses; (*4, 5*) mirrors of the Co : MgF$_2$ laser cavity; (*6*) metal chamber; (*7*) outlying flange; (*8, 9*) quartz tubes; (*10*) HF discharge; (*11*) diffraction spectrograph; (*12*) optical multichannel analyser; (*13*) PC; (*14*) narrow-band Nd : YAG laser; (*15*) nonlinear LiNbO$_3$ crystal; (*16*) oven; (*17*) dichroic mirror; (*20*) synchronising unit.

The Co : MgF$_2$ crystal was placed inside a hermetic metal chamber *6*, mirror *4* being a window of the latter. Mirror *5* was attached to a outlying flange *7* made of organic glass. Flange *7* was connected to the chamber *6* by quartz tube *8* with an inner diameter of 16 mm and a length of 40 cm. The oxygen flew was supplied through the quartz tube *9* with an inner diameter of 9 mm and crossed the laser cavity at a pressure of $1-5$ Torr. SO was produced in tube *9* in HF discharge *10* with frequency 2375 MHz and power 100 W.

To eliminate atomic oxygen that was also produced in the discharge and quenched SO, the HgO ring was deposited on the walls of tube *9* below the discharge region. The gas flow velocity in tube *8* was 9 m s^{-1}. Because of the low probability of SO decay on the quartz surface [17], the high velocity of oxygen flow provided minimum losses of SO upon its transfer in tube *8*. Because the flow velocity in chamber *6* decreased approximately by two orders of magnitude, the SO concentration in the chamber also drastically decreased due to its heterogeneous relaxation. Thus, in our experiments, SO filled only two thirds of the cavity length.

The output spectrum of the Co : MgF$_2$ laser was detected with a diffraction spectrograph *11* (with a spectral resolution of 0.018 cm^{-1}) coupled to an optical multichannel analyser *12* equipped with an MORS-1/3648 CCD linear array (Multichannel Optical Recording Systems) and PC *13*.

The broadband IR radiation from a Co : MgF$_2$ laser was first converted to visible spectral range by mixing it with the monochromatic radiation from a Nd : YAG laser *14* ($\lambda = 1.064$ μm, the linewidth is 0.02 cm^{-1}, the pulse duration is 5 μs, and the pulse energy is 1 mJ) in a nonlinear lithium niobate crystal *15*, which was heated in oven *16* to achieve the 90° phase matching. Dichroic mirror *17* and lenses *18* and *19* were used for combining and focusing two laser beams inside the nonlinear crystal. The emission at a sum frequency was incident on the entrance slit of spectrograph *11*.

The synchronisation unit *20* provided the variable delay between the Nd : YAG laser pulse and the leading edge of the pulse from a Co : MgF$_2$ laser. Thus, we could detect the emission spectrum of the Co : MgF$_2$ laser at any specified moment of time without using any additional equipment.

Fig. 2 shows intracavity absorption spectra obtained at the oxygen pressure of 1.9 Torr in the discharge and in the absence of the discharge. The spectra correspond to the 200-μs delay relative to the leading edge of the laser pulse and are averaged over 200 laser pulses.
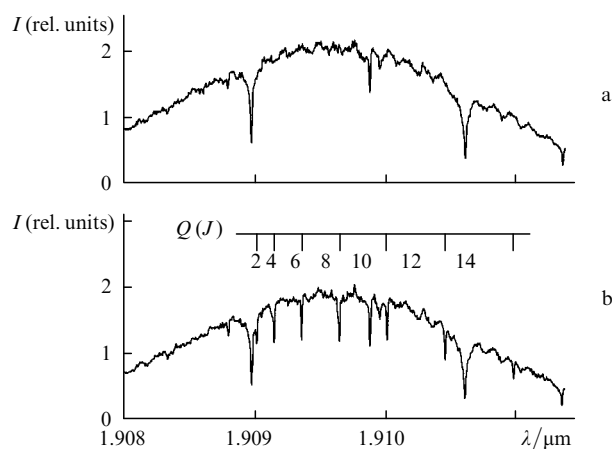
Figure 2. Intracavity absorption spectra obtained 200 μs after the lasing onset at the oxygen pressure of 1.9 Torr (a) in the absence of the HF discharge and (b) during the HF discharge. The results are averaged over 200 laser pulses.

The absorption lines detected in the absence of the discharge belong to water vapour [18] that is present in the atmosphere (the path of the IR output radiation from the Co : MgF$_2$ laser between the output mirror and the lithium niobate crystal was 65 cm). In addition, the trace water vapour in the laser cavity may also contribute to these lines (according to [18], the sensitivity of our setup ensures the detection of water vapour at a pressure of as low as $\sim 10^{-4}$ Torr). Fig. 2 shows that additional absorption lines appear when the discharge is switched on.

By using the absorption spectrum of CO$_2$ for calibration, we measured the frequencies of these lines and found that they coincided with good accuracy with those of the lines of the Q branch of the $0-0$ $a^1\Delta_g \rightarrow b^1\Sigma_g^+$ vibrational band of molecular oxygen [19].

We estimated the sensitivity of our setup with respect to the detection of SO molecules by two independent methods: based on the data on the SO concentration in a discharge available in the literature and using the calculated cross-section for the $a^1\Delta_g \rightarrow b^1\Sigma_g^+$ transition.

It is known that the typical concentration of O$_2(a^1\Delta_g)$ obtained in the electric discharge under conditions that are close to those in our experiment is a few percent of the initial oxygen concentration [20, 21]. This suggests that at the oxygen pressure of 1.9 Torr, the SO concentration was $(1-3) \times 10^{15}$ cm^{-3}. Because the intensity of the most intense absorption lines detected in the experiment exceeded that of the random noise in the output spectrum of the laser by more then six times, our estimate of the method sensitivity based on these data yields the minimum detectable concentration of SO as low as $(2-5) \times 10^{14}$ cm^{-3}.

By averaging the spectrum over 200 pulses we reduced the random noise in the laser output spectrum to approximately 5 % and could detect the absorption lines for which the condition $kctL_{\mathrm{so}}\Delta\omega_{\mathrm{D}}(L_{\mathrm{c}}\Delta\omega_{\mathrm{in}})^{-1} \geqslant 0.05$ was satisfied. Here, $k = \sigma(N_a g_b/g_a - N_b)$ and σ are the absorption coefficient and the absorption cross section at the line centre, respectively; N_a, N_b are the concentrations of O$_2(a^1\Delta_g)$ and

$O_2(b^1\Sigma_g^+)$, respectively; $g_a = 2$ and $g_b = 1$ are the degeneracy factors for these states; $\Delta\omega_D = 0.0113$ cm^{-1} is the Doppler width of the absorption line at room temperature; $\Delta\omega_{in} = 0.03$ cm^{-1} is the width of instrumental function of our optical setup determined by the width of the output spectrum of a Nd : YAG laser used for the up-conversion and by the resolution of our spectrograph; t is the time delay between the instant of the intracavity spectrum detection and the onset of the Co : MgF$_2$ laser action; $L_{SO} = 40$ cm is the length of the cavity region filled with SO; $L_c = 62$ cm is the total cavity length.

If we neglect the concentration of $O_2(b^1\Sigma_g^+)$, then $k \approx 0.5\sigma N_a$, and, taking into account the parameters given above, we find the minimum concentration $N_a \geqslant 0.4(\sigma ct)^{-1}$ that can be detected. It is shown in [22, 23] that the absorption cross section for the strongest rotational line of an electronic transition in a two-atomic molecule can be represented, for the case of Doppler broadening, in the form $\sigma = 2.7 \times 10^{-6}(BM)^{1/2}(\tau\omega^3 T)^{-1}qf(v)$. Here, $B = 1.41784$ cm^{-1} is the rotational constant for the lower state; M is the molecule mass expressed in atomic units; τ is the radiative lifetime in seconds; ω is the transition frequency in wavenumbers; T is the gas temperature in kelvins; q is the Franck–Condon factor; $f(v)$ is the distribution function of molecules over vibrational energy levels. Assuming that $q \approx 1$ for the $0 - 0$ band of the $O_2(a^1\Delta_g \to b^1\Sigma_g^+)$ transition and $f(0) \approx 1$ (i.e., all the particles are in the ground vibrational level) and using the transition probability $\tau^{-1} = 0.0017$ s^{-1} [10,11], we estimated the cross section $\sigma \sim 7 \times 10^{-22}$ cm^2 at room temperature, which yields $N_a \geqslant 10^{14}$ cm^{-3} for $t = 200$ μs.

It should be taken into account that the Doppler broadening of absorption lines under our experimental conditions is comparable to the separation between longitudinal modes, which was 0.0081 cm^{-1} for the cavity length of 62 cm. Due to the instability in the optical length of the cavity, the spectral positions of modes may noticeably vary. As the result, the cavity mode can fall either at the centre of the absorption line or at its wing, reducing the detection sensitivity. In this case, the effective absorption cross section can decrease approximately by a factor of two ($\sigma_{eff} \sim 3.5 \times 10^{-22}$ cm^2). By measuring the depth of dips in the intracavity absorption spectra shown in Fig. 2 and using the above cross section, we found the SO concentration in our experiments $\sim 1.5 \times 10^{15}$ cm^{-3}. The threshold detectable SO concentration limited by the random noise level was $\sim 2 \times 10^{14}$ cm^{-3}, in accordance with the above estimate obtained by the first method.

Because several rotational absorption lines from a vibrational band fall within the emission spectrum of our laser, this method can be used not only for measuring the SO concentration but also for monitoring the gas temperature based on the dependence of the absorption coefficient of molecular lines on the rotational quantum number. On the one hand, this allows one to measure the SO concentration more reliably, because in general the absorption coefficients for individual rotational lines depend on temperature. On the other hand, to describe adequately processes involving SO, one should know the temperature.

In our case, the dependence of the absorption coefficients of rotational lines for the Q-branch on J in the case of rotational equilibrium is determined by the expression $k(J) \sim S(J)\exp[-BJ(J+1)T^{-1}]$, where $S(J) = 2(2J+1) \times (J+1)(J-1)(2J-1)^{-1}(2J+3)^{-1}$ [19], where T is the gas temperature expressed in wavenumbers. Fig. 3 presents the

experimental data obtained for $Q(2) - Q(14)$ lines plotted in coordinates $\ln[k(J)/S(J)]$ versus $J(J+1)$ and the fitting straight line. The slope of the straight line gives the temperature $T = 305 \pm 15$ K for the state $a^1\Delta_g$.
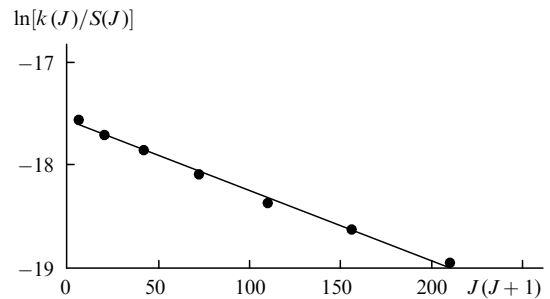
Figure 3. $\ln[k(J)/S(J)]$ as a function of $J(J+1)$. The slope of the straight line corresponds to the temperature $T = 305 \pm 15$ K.

Note that a broad tuning range of our laser along with the high sensitivity of intracavity laser spectroscopy make it possible in principle to detect SO not only at the $v = 0$ vibrational level but at excited vibrational levels as well. Thus, the $1 - 1$ and $2 - 2$ vibrational bands of the $a^1\Delta_g \to b^1\Sigma_g^+$ system are located at 1.938 μm and 1.969 μm, respectively [10] and also can be detected using a Co : MgF$_2$ laser. This opens up new possibilities, for example, for studying electric discharge plasma in oxygen-containing mixtures, because a considerable number of SO molecules can be in vibrationally excited states in this case.

Thus, we detected for the first time the absorption spectrum of gaseous SO at the $a^1\Delta_g \to b^1\Sigma_g^+$ transition by the method of intracavity laser spectroscopy. The high sensitivity $\sim (2 - 5) \times 10^{14}$ cm^{-3} demonstrated in our experiments makes this approach promising for studying gas-phase processes involving singlet oxygen. If necessary, a higher sensitivity can be achieved by filling a greater part of the cavity by the substance under study (recall that the absorbing layer of SO in our setup filled only 2/3 of the cavity length). In addition, the sensitivity can be enhanced by reducing the intermode separation by using longer cavities and increasing the pulse duration of a Co : MgF$_2$ laser.

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