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High-resolution optical spectroscopy of atomic oxygen

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We report sub-Doppler laser spectroscopy of atomic oxygen. The atom is detected as a trace in a noble-gas radio-frequency discharge by means of optogalvanic effect. The fine structure of the $2p^3 3p^5 P_{1,2,3} \rightarrow 2p^3 (4S^0) 4d^5 D_{4,3,2,1,0}$ transitions is fully resolved and preliminary values for the upper level splittings are: $\Delta_{4,3} = 1382(20)$ MHz, $\Delta_{3,2} = 1594(20)$ MHz, $\Delta_{2,1} = 1360(20)$ MHz, and $\Delta_{1,0} = 735(20)$ MHz. The best values so far derived from conventional spectroscopy are one order of magnitude less accurate and in marginal agreement with our data.

Modern laser techniques, such as saturation or intermodulated spectroscopy, have proved to be very efficient in eliminating Doppler broadening. A multitude of atomic species and transitions have been carefully investigated, especially after the demonstration of possible combination with unconventional schemes like optogalvanic detection.¹

Atomic oxygen has so far been elusive to any high-resolution investigation, which on the contrary would be highly desirable. Indeed, this atom is an important intermediate in fundamental physical and chemical processes; it is the third abundant element after hydrogen and helium. Its spectral features, of fundamental interest in the upper atmosphere, are relatively faint in the solar spectrum, in part masked by H₂O absorptions, and accurate laboratory measurements could expedite identification.

The lack of high-resolution investigations of oxygen is caused by the fact that, like for many other light atoms, the resonance lines are in the vacuum ultraviolet (VUV) region, where tunable radiation of high intensity and spectral purity is hard to produce. The use of pulsed sources, which are well suitable for lifetime measurements² or time-resolved spectroscopy, is often necessary. However, the pulsed linewidths limit the precision of the determination of spectral features.^{3,4} The ground-state fine-structure splittings are the only high-accuracy data available for oxygen since they could be directly measured at far infrared frequencies^{5,6} where Doppler effect is negligible. The very low probability transitions in the red from the ground state were detected by cw laser intracavity configuration⁷ but with no high resolution. Rydberg transitions were observed in the infrared.⁸

In this Rapid Communication, we describe the first Doppler-free investigation of atomic oxygen. It is performed in the visible and it promises to be a powerful tool for studying optical transitions in oxygen, including those

involving high-lying states.

We produce atomic oxygen by dissociation of O₂ molecule in a moderate power radio-frequency discharge (about 50 W at 60 MHz). The discharge is sustained by a buffer noble gas (Ne or Ar) at rather high pressure (4–5 mbar) with the addition of O₂ at low partial pressure (a few parts in 10³). As we shall discuss later, the high buffer gas pressure causes significant inhomogeneous velocity changing effects, but does not prevent sub-Doppler resolution with homogeneous linewidths at least one order of magnitude narrower than the Doppler ones. The discharge sample configuration naturally leads to a detection scheme based on the change of impedance under resonant absorption of photons (optogalvanic spectroscopy⁹). We have studied the $3p^5 P_{1,2,3} \rightarrow 4d^5 D_{4,3,2,1,0}$ multiplet transitions at 616 nm. Nine fine-structure components are originated, as shown schematically in Fig. 1. In Doppler-limited spectroscopical investigations, only the splittings of the lower ⁵P state are sufficiently large to be resolved and only three separated lines can be observed at 6158.19, 6156.78, and 6155.99 Å. Indeed, the ⁵P separations are known¹⁰ with the typical uncertainty of a few hundred MHz.

In our experiment, tunable radiation is provided by an actively stabilized rhodamine 6-G ring dye laser (Coherent 699-21). The laser beam is split into two beams of roughly equal intensity. One beam is chopped at a frequency of 350 Hz and the other at 490 Hz by the same mechanical chopper which provides separate reference signals at each of the two frequencies and at the sum frequency of 840 Hz. The two beams counterpropagate through the discharge cell. This is a Pyrex tube 150 mm long containing the oxygen-noble-gas mixture and placed inside two sets of coils of the same diameter of the cell (9 mm). The discharge is maintained by an oscillator fed by

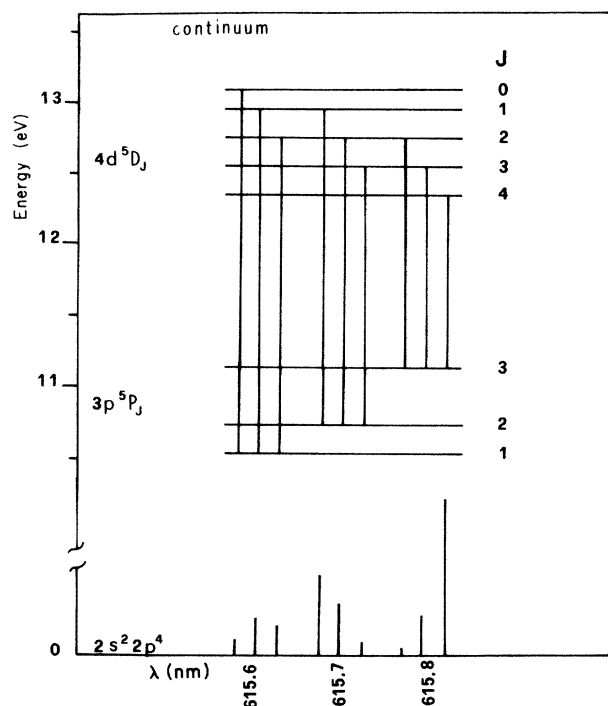


FIG. 1. Partial oxygen-atom level scheme with the transitions used to demonstrate sub-Doppler resolution. In the lower part, the relative oscillator strengths are shown.

a current stabilized power supply. At the resonance, the change in the impedance of the discharge is recorded with high sensitivity by monitoring the change of the feedback signal on the stabilized power supply. The laser wavelength is determined by recording the absorption from a I_2 cell, while the frequency scan is calibrated by means of the markers from a 300-MHz free spectral range confocal Fabry-Perot interferometer.

A Doppler-broadened recording, obtained blocking one of the two counterpropagating beams, is shown in Fig. 2(a) for the unresolved triplet ${}^5P_3 \rightarrow {}^5D_{4,3,2}$ at 6158.2 Å. O_2 -Ne mixture in the ratio of 5×10^{-3} for a total pressure of 9 mbar was used. The recording signal to noise ratio is as good as 100:1 with a time constant of 1 s.

The fine-structure multiplets are directly resolved by

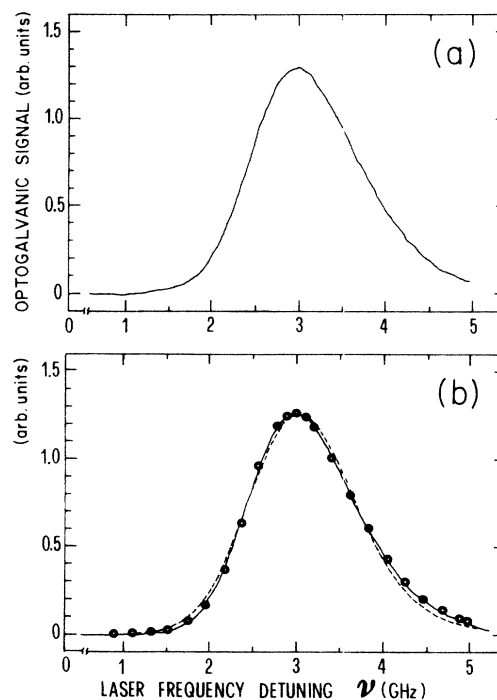


FIG. 2. Doppler-broadened line shape of the ${}^5P_3 \rightarrow D_{4,3,2}$ overlapping transitions. In (a) the experimental optogalvanic recording is reported. In (b) the experimental recording is fitted to the existing data from conventional spectroscopy (dashed line). A better fit (solid line) is obtained using for the parameters of the three overlapping Gaussians the values directly obtained from the present sub-Doppler investigation.

using the intermodulated scheme of detection¹ and the results are shown in Fig. 3 for all the components originating from the 5P levels. These measurements were performed using a O_2 -Ar (1:45; total pressure 4.6 mbar) mixture. Total signals with Ar were comparable with those with Ne, but the contrast between the Doppler-free contribution and the broad pedestal was higher. The observed homogeneous linewidth of about 250 MHz is due primarily to pressure broadening, while a power broadening cannot be excluded since the laser intensity could not be reduced to less than 10 W/cm^2 . In addition to the

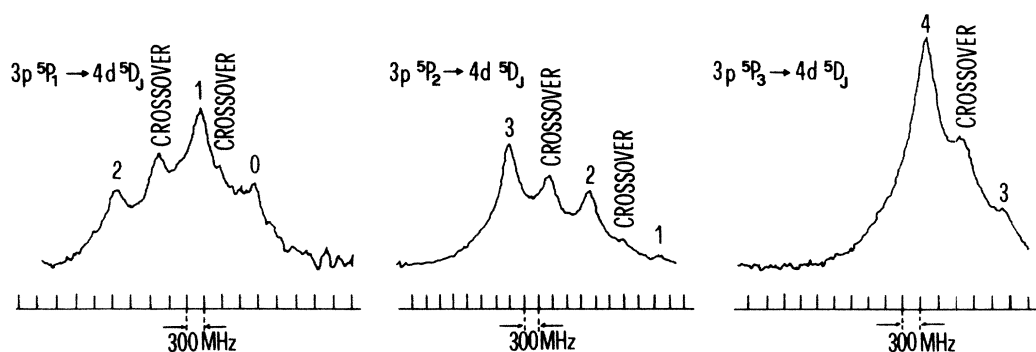


FIG. 3. Doppler-free recording of the oxygen ${}^5P \rightarrow {}^5D_{4,3,2,1,0}$ transitions at 6155.99, 6156.78, and 6158.19 Å using intermodulated radio-frequency optogalvanic technique.

fine-structure components, also the associated crossovers are recorded with comparable intensity. This last feature seems to be common to measurements in relatively high-pressure discharge¹ and it is possibly suggestive of a contribution of the velocity changing collisions also to the crossover signals.

A quantitative analysis of the line shapes has been performed following the model introduced earlier in Ref. 11 and then extended in Ref. 12 to take into account the case of "weak" collisions. In the hypothesis of a homogeneous width γ much smaller than the Doppler one $\Delta\nu_D$, each intermodulated component line shape can be assumed to a good approximation as the superposition of a Lorentzian $L(\nu)$ (Doppler-free signal) and a Gaussian pedestal $G(\nu)$ caused by velocity changing collisions:

$$S = A[L(\nu) + CG(\nu)] \quad (1)$$

where S denotes signal, L has the width γ and G the width $\Delta\nu_D/\sqrt{2}$, A is a normalization constant, and C represents the weight of the collisional pedestal. Under our experimental conditions, involving rather high gas pressures, C is found to range from 0.1 to 0.5.

By fitting the experimental data, we obtain values for the relative positions of the maxima only slightly different (less than 2%) from those directly inferred from the recorded spectra. Moreover, no appreciable deviations have been found when the fits have been performed with Voigt profiles (γ comparable to $\Delta\nu_D$) instead of Gaussian functions. The 5D sublevel separations in some cases (e.g., the $\Delta J_{1,2}$) can be obtained in two independent ways from the recordings, using transitions originating from different 5P sublevels. In this case, the internal consistency is of a few percent for the individual measurements. By repeating the measurements several times, also changing the buffer gas, and fitting all the data we can give for the fine-structure splitting the values in Table I, with quoted uncertainties of 1 standard deviation. In general, the present accuracy is better than 1% except for the 0-1 separation which can be deduced from only one multiplet (6155.99 Å) and in addition is the weakest component of that multiplet. In Ref. 10 the accuracy is given only for levels directly measured (120 MHz), while it is not clearly stated for unresolved fits. The 200-MHz estimate in Table I seems to us to be a reasonable assumption.

The comparison with the data from conventional spectroscopy analysis is interesting not only for the improvement in the accuracy but also in view of verifying the assumptions made in that analysis.¹⁰ In order to fit the line shape to the sum of three overlapping and unresolved Doppler-broadened Gaussians in Ref. 10, it had to be assumed the relative values between the fine-structure intervals in the high 5D terms to be the same as for the $3d\ {}^5D$, the only ones directly observable. The present direct measurements show, for the splitting ratios, a deviation ranging from 2% to 25%. This is stimulating in view of extending similar measurements on even higher 5D multiplets with $n = 5, 6, \dots$, still accessible to dye lasers and in-

TABLE I. Fine-structure splittings in the atomic oxygen $2p^3(4S^0)4d\ {}^5D_{4,3,2,1,0}$ levels as obtained from sub-Doppler spectroscopy. For comparison the data deduced in conventional spectroscopy are reported. Ratios between adjacent splittings are also compared.

Δ_{ij}	Our results (MHz)	Ref. 10 (MHz)
$\Delta_{0,1}$	735(20)	720(200)
$\Delta_{1,2}$	1360(20)	1469(200)
$\Delta_{2,3}$	1594(20)	1769(200)
$\Delta_{3,4}$	1382(20)	1229(200)
$\Delta_{0,1}/\Delta_{1,2}$	0.54	0.49
$\Delta_{1,2}/\Delta_{2,3}$	0.85	0.83
$\Delta_{2,3}/\Delta_{3,4}$	1.15	1.44

vestigating the actual dependence of the splittings at present only postulated to be proportional to n^{-3} . Also, the relative intensity of the resolved components is found to follow the assumptions according to LS coupling¹⁰ only within a few tens of a percent. The better spectral knowledge now available can be qualitatively evidenced also in the Doppler limited measurements that in Fig. 2(b) are fitted using Voigt profile to the previous (dashed line) and present parameters (solid line). The width of the Gaussians obtained from the fit is about 2 GHz, corresponding to the Doppler broadening at 520 K, and the Lorentzian contribution to the linewidth results of 230 MHz.

Our experiment could not improve the accuracy of the splittings in the 5P level because each component position could only be evaluated relative to Doppler-broadened iodine lines, used for laser wavelength calibration.

The present results demonstrate that atomic oxygen can be produced in enough amount even in highly excited states and still under environmental conditions well suitable for high-resolution spectroscopy. Intermodulated radio-frequency optogalvanic spectroscopy has been used for the sub-Doppler recording of $3p\ {}^5P \rightarrow 4d\ {}^5D$ transitions. Improvements in the sensitivity, for instance, using heterodyne technique,¹³ could allow a narrowing of the linewidth. However, the present resolution is already sufficient to increase the knowledge of this fundamental atom. Further developments can be made not only in the direction of a systematic investigation of the fine structure for a light and theoretically still tractable atom, but also of the isotope shifts of the optical transitions. This last possibility seems important because the ${}^{16}\text{O}$ nucleus is doubly magic and the high resolution now accessible should allow investigation of the nuclear structure via the relatively small contribution of the volume change to the isotopic shift.

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