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Optogalvanic study of the atomic-oxygen laser lines at 844.5 nm

Namic Kwon
Physics Department, Hankuk University of Foreign Studies, Yongin 449-791, Korea

Young-Hwan Yun and Wonho Jhe
Physics Department, Seoul National University, Seoul 151-742, Korea

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The $3\,^3S_1$–$3\,^3P_{0,1,2}$ laser lines at 844.5 nm of atomic oxygen are studied in a weak discharge cell with argon buffer gas, using the optogalvanic effect. Three Doppler-limited peaks are observed at the center frequencies of the three fine-structure transitions. The measurements of the spectral widths indicate that the atoms in the lower state ($3\,^3S_1$) are at room temperature or "cold." This excludes the previous assumption that all the triplet states are very "hot" and moreover is consistent with the long-range atom-ion interaction model [Kwon *et al.*, Phys. Rev. A **42**, 4408 (1990); Bjerre and Keiding, Phys. Rev. Lett. **56**, 1459 (1986)]. Based on the results, one can understand the unexplained observations such as the anomalously broadened spectra associated with the $3\,^3P$ triplet state, the peculiar four-peak emission spectra of the laser lines, and the absence of the $J=0\rightarrow J=1$ transition.

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Atomic oxygen is the most abundant element in the upper atmosphere. It has been widely used in several physical and chemical processes and has attracted much interest due to its close relationship with biological systems. However, most of the resonance and transition lines are in the vuv wavelength range, so that not many high-resolution laser spectroscopic studies have been done. With recent advances in laser technology, there have been several laser optogalvanic (OG) studies of oxygen atom. Using radio-frequency discharge, atoms can be populated at excited states by collisions with energetic metastable buffer-gas atoms. The excited-state atomic levels are closely spaced so that high-resolution spectroscopy is possible with a tunable dye laser or semiconductor lasers.

Inguscio and co-workers [1,2] reported an interesting observation, that the spectral width of the OG signal for the $3\,^3P_{0,1,2}$–$6\,^3S_1$ transitions at 604.8 nm is anomalously broadened by 5.7 GHz, which corresponds to a motional temperature of 9000 K [2]. Their subsequent higher-resolution results showed [3] that each wide spectrum was actually superimposed by a narrower signal with their center frequencies slightly different. They explained the observed phenomena in the following way: (i) the broad part of the spectra is due to the highly energetic ("hot") oxygen atoms in the triplet states, produced by electron collision of oxygen atoms in the metastable singlet states, which are also highly energetic due to the energy defect ΔE in the isothermal process,

$$O_2+Ar^*\rightarrow Ar+O^*(^1S,^1D)+O(2\,^3P)+\Delta E \quad ; \qquad (1)$$

(ii) the narrow part is due to the room-temperature ("cold") triplet states, which are produced from the room-temperature ground-state ($2\,^3P$) oxygen atoms that undergo thermalyzing collisions with the containing wall. Unfortunately, some of the main features, such as the slight shift of the center frequencies of the wide and narrow signals, could not be explained within their model.

The above model of broad velocity distribution due to "hot" triplet states was essentially based upon the earlier studies by Bennett *et al.* [4] on the laser transitions ($3\,^3P_{0,1,2}$–$3\,^3S_1$ at 844.5 nm) in atomic oxygen. Soon after their work, Feld *et al.* [5] observed four anomalous laser lines (two pairs of doublets for each of the $J=2\rightarrow J=1$ and $J=1\rightarrow J=1$ laser transitions), whereas the spontaneous emission profile showed three peaks corresponding to the three fine-structure frequencies, but with anomalously broadened widths. They explained the peculiar two-pair spectra by the selective reabsorption of resonance radiation from the lower laser level by ground-state oxygen atoms, resulting from the assumption that the velocity distributions of the upper and lower laser levels are considerably wider than that of the ground state, as mentioned before [5,6]. They also observed that the midpoint of a pair of laser lines was slightly shifted (0.01 cm^{-1}) with respect to the center of the corresponding fine-structure line. They conjectured that the shift might be due to the existence of the ^{18}O isotope. Moreover, they could not explain the absence of laser oscillations for the $J=0\rightarrow J=1$ transition, despite the fact that its spontaneous-decay intensity is only three times smaller than that of the $J=1\rightarrow J=1$ line.

Recently, Kwon *et al.* [7] performed a similar optogalvanic spectroscopy study for the $3\,^3P_{0,1,2}$–$5\,^3S_1$ lines in atomic oxygen at 725.4 nm and found that each anomalously broadened line was also superimposed by a sightly shifted (0.01 cm^{-1}), narrow line as in [3]. Note that the slight shift, found in Refs. [5,6] and mentioned above, now can be easily understood by the shift of the superimposed narrow and broad lines. Kwon *et al.* then proposed an alternative model for the OG spectra and explained the peculiar shifts as follows: when highly excited molecular oxygen ions (O_2^+) are produced by collisions with energetic metastable Ar atoms, there exists a weakly bound state with large vibrational amplitudes just below the lowest dissociation limit $O^+(^4S_0)$ + $O(^3P_{2,1,0})$. This means that an atomic oxygen ion (O^+) and a neutral atomic oxygen O in the $3\,^3P$ excited state can be

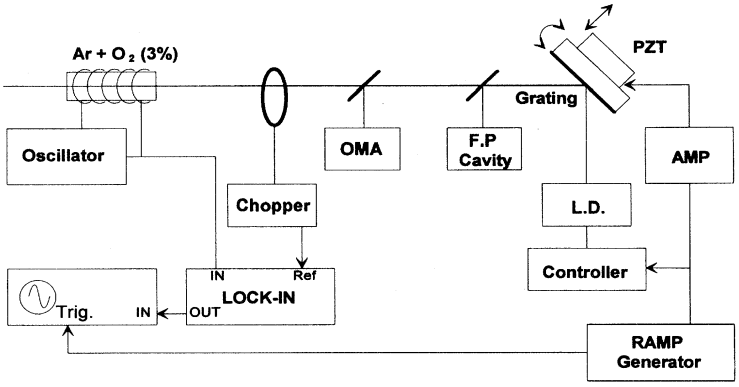

FIG. 1. Experimental setup for the optogalvanic study of the oxygen atom. OMA, optical multichannel analyzer; L.D., laser diode; F.P. cavity, Fabry-Pérot cavity spectrum analyzer.

weakly bound by the long-range atom-ion interaction, and the $3\,^3P$ atomic states are presumably "hot" [8]. This predissociation state of the atom and ion was found to be responsible not only for the very wide OG spectra but also for the slight shift of the center frequencies of the wide and the narrow signals. They found that the observed spectra are in quantitative agreement with the proposed mechanism. Note that, in this model, only the $3\,^3P$–state atoms are "hot" and are responsible for the anomalously wide spectra, whereas all the other triplet states are "cold" and responsible for the narrow lines.

In this work, therefore, we have performed an OG spectroscopy for the laser lines in atomic oxygen ($3\,^3S_1 \rightarrow 3\,^3P_{0,1,2}$) and measured the velocity distribution of the lower laser level ($3\,^3S_1$) as an independent check of the newly proposed model [7]. We have found that the $3\,^3S_1$ state is "cold," which is consistent with the above long-range atom-ion interaction model. The OG study for the laser lines is also interesting from the point of view that an absorption from the short-lived lower laser level (lifetime = 2.6 ns) could be experimentally realized. Moreover, we find that the new model can also be consistently applied to the case of the laser oscillations in atomic oxygen, and the unexplained absence of lasing between $J=0$ and $J=1$ fine structures can be easily resolved.

The experimental setup is shown in Fig. 1 and the experimental parameters are similar to those in the aforementioned references [3–7]. Three percent of oxygen molecules is mixed with argon buffer gas and flows through a 1-cm-wide, 10-cm-long radio-frequency discharge cell. A slow and steady flow of the oxygen is needed, since the OG signals cannot be obtained in a sealed cell due to the chemical activity of the oxygen. A stable pressure near 3 Torr is maintained in the cell with an automatic pressure-regulating system. A weak rf glow discharge is driven by a homemade solid-state oscillator [9]. For atomic excitation, we have used a commercial diode laser (SDL5420-C) emitting a 843-nm radiation at room temperature. Laser frequency scanning was achieved using optical feedback from a diffraction grating in an extended-cavity configuration.

An optical multichannel analyzer (EG&G 1460) was used to monitor the diode laser frequency, and the coarse tuning to the correct atomic lines was done simply by using the strong fluorescence from the $3\,^3P$–$3\,^3S$ transition as a reference. Continuous frequency scanning of about 8 GHz was accomplished by simultaneously adjusting the grating angle and the diode laser current. An optical spectrum analyzer (Newport SR-100), which has a 782-MHz transverse mode for the 2.5-cm Fabry-Pérot cavity, was used for fine calibration of the frequency intervals of the OG spectra. The change in the impedance of the discharge cell was measured with a lock-in amplifier and recorded with a digitizing oscilloscope.

A typical optogalvanic spectrum due to the three absorption lines from the $3\,^3S_1$ level at 844.5 nm is shown in Fig. 2. Because the laser sweeps only 8 GHz without hopping, the OG signal for the $J=1$ to $J=1$ transition was taken separately, and plotted in the same graph. Each fine-structure line fits well to a single Gaussian function with a width of 1.3 GHz, clearly indicating that the $3\,^3S$–state atoms are at room temperature. In our experiment, the atomic density of oxygen is so low that no photoassociation of O^+ and $O(3\,^3P)$ forming the $O_2{}^+$ ion takes place. Note that the four vertical marks above the spectrum in Fig. 2 represent the positions of the observed laser oscillation [5].

Therefore, based upon our observations, the previous assumption that all the triplet-state atoms are "hot" should be excluded, and it is likely that only the $3\,^3P$ atoms are "hot" due to the ion-atom interaction, as explained in [7]. And consequently, the explanation of the peculiar laser oscillations by the "hot" excited atoms [5,6] should also be modified as follows: the atoms in the upper laser level ($3\,^3P$) are not isolated, but exist in a weakly bound state with the atomic ion (i.e., in the predissociation state). When they de-

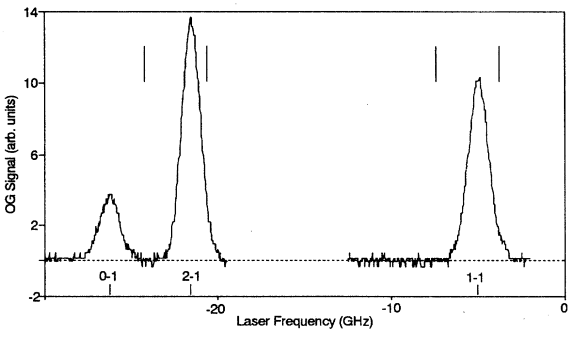

FIG. 2. Optogalvanic spectra for three absorption lines due to the $3\,^3S_1$–$3\,^3P_{0,1,2}$ transition at 844.5 nm. Each line fits well to a Gaussian function with a width of 1.3 GHz, indicating that the $3\,^3S$–state atoms are at room temperature. The vertical marks above represent the positions of the observed four laser oscillations [5].

cay to the lower laser level, the laser lines cannot be observed at the center frequencies of the fine-structure lines but rather split into pairs around each center, since the "cold" atoms in the lower laser level occupy the area near the center of the velocity distribution. Moreover, based upon the fact that the upper laser level is in a weakly bound state, one can also easily understand the absence of lasing for the $J=0$ to 1 transition: for the fine-structure state $3\,^3P_{J=0}$, which consists of the terms p^2 and p^4, the important atom-ion (or charge-quadrupole) interaction vanishes [10], so that a weakly bound state cannot be formed for the $3\,^3P_1$ state (note that the interaction is possible only for a partially filled p subshell). The slight shift of the center of each pair of laser lines with respect to the center of the corresponding fine-structure line, which was tentatively explained by the existence of ^{18}O [5,6], may now be attributed to the spectral shift due to the atom-ion interaction [7].

Our results may also be very useful in understanding and possibly improving the mechanism for measuring the oxygen concentration in plasma processing: The 844.5-nm emission line has been used to measure the relative density of the ground-state oxygen atoms in plasma processing. It was recently found that the emission intensity is not proportional to the number of ground-state oxygen atoms [11], which still remains an unanswered question; however, it can be easily understood by the fact that the emission intensity should be proportional to the number of oxygen atoms in the $3\,^3P$ level that are weakly bound in the predissociation state, which does vary depending on the discharge conditions.

In summary, we have observed three Doppler-limited OG resonances for the $3\,^3S_1$–$3\,^3P_{0,1,2}$ transitions at 844.5 nm of discharge-produced atomic oxygen. The narrow spectral widths of 1.3 GHz indicate that the atoms in the $3\,^3S_1$ state are at room temperature. Our results are in good agreement with the model showing that the anomalously broad OG spectra associated with the $3\,^3P$ state arise from the weakly bound state due to the long-range atom-ion interaction, as proposed by [7]. We also have presented qualitative but consistent explanations for the peculiar laser oscillations in atomic oxygen. Experiments of the type reported here are in progress for a future quantitative study of long-range interactions in other atomic systems, as well as in oxygen.

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