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Rapid Communications

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Anomalous line shapes associated with the $3\,^3P$ state of atomic oxygen

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The $3\,^3P$-$5\,^3S$ transition in atomic oxygen at 725.4 nm has been studied in a weak discharge using the optogalvanic effect with a cw tunable dye laser. The transition appears as a superposition of at least two components with different centroids and widths. The anomalous line shape is probably due to the long-range interaction of ^3P oxygen with $^4S_0$ oxygen ions.

Anomalous effects associated with atomic oxygen in the $3p\,^3P$ state have been observed by different groups over several years. Inguscio *et al.*[1,2] studied the $^3P_{0,1,2}$-$^3S_1$ transition at 604.6 nm by means of the laser optogalvanic effect in a noble-gas–oxygen rf discharge. They reported a 5.7-GHz Doppler-broadened linewidth for the transition corresponding to a "temperature" of 4500 K. Several other atomic oxygen transitions that they studied[3] in the same discharge showed a normal thermal Doppler broadening corresponding to a temperature near 300 K. Earlier Feld *et al.*[4] had measured the fluorescence spectrum of the ^3S-^3P atomic oxygen laser transition at 844.6 nm obtaining a linewidth of 4.5 GHz in a dc discharge. In both of these experiments, the cause of the anomalously large linewidth was not explained, but reference was made to an early hypothesis of Bennett *et al.*[5,6]

Bennett *et al.* had proposed that oxygen molecules are primarily dissociated in a rare-gas discharge by collisions with metastable argon (Ar^*) atoms:

$$Ar^* + O_2 \rightarrow Ar + O + O^* + E_{KE}\,, \qquad (1)$$

where O^* represents a metastable atomic oxygen level, and E_{KE} represents the kinetic energy. The oxygen metastables are subsequently raised to the higher laser levels by electron impact. The energy defect in the dissociation process (1) is several electron volts, giving the excited oxygen atoms a velocity spread considerably wider than that of a room-temperature gas. This distribution in velocity was presumed to be maintained to some extent during the subsequent electron excitation. The Bennett hypothesis must be incorrect, however, as velocity changing collision rates are high, other levels do not show the broadening, and argon is not necessary for its observation.

Independent of the cause of the linewidth, however, Feld *et al.*[4] provided a convincing explanation for four observed laser oscillations originating on the ^3P level, on the basis of anomalously broadened upper laser levels and normal Doppler-broadened lower laser levels. The questions of the source of the population inversion, which as is shown below is due to direct dissociation, and the observed asymmetry about the atomic line center of these oscillations remained unanswered.

In this Rapid Communication we report the results of high-resolution optogalvanic experiments in a weak rf discharge that greatly expands on the observations of previous investigators and demonstrates the existence of two groups of ^3P oxygen in the discharge: normal and broadened. The broadened component is also shifted towards higher energy by approximately 226 MHz. As we describe below, this effect is most likely due to long-range interactions of ^3P oxygen with O^+ ions.

The details of the rf discharge and laser optogalvanic (LOG) system used in these experiments are described elsewhere.[7] Three percent oxygen in argon is flowed through the discharge cell. A stable pressure near 3 Torr is maintained in the cell. A cw actively stabilized tunable dye laser operating with pyridine two dye is wavelength scanned, via computer control, through the atomic oxygen resonances. The change in the impedance of the discharge is detected with low background using a lock-in amplifier and recorded with a computer interfaced analog-to-digital converter. The oxygen transitions and O_2^+ potential curves associated with the $3\,^3P$ state relevant to this work are shown in Fig. 1.

The optogalvanic signal from the $3\,^3P_{2,1,0}$-$5s\,^3S_1$ transitions at 725.4 nm are shown in Fig. 2 as a function of laser frequency. For each of the three fine-structure transitions, a sum of two Gaussian functions, one narrow and one broad, are fit to the data and shown in the figure as a dotted curve. The amplitude of the broad peaks are about three times larger than those of the narrower peaks. The Gaussian fit is unsatisfactory in the line-shape wings.

Atoms in the ^3P state produced by electron collisional excitation from ground or metastable states lead to the narrower peak, which represents a Doppler-broadened distribution with a temperature, characteristic of the

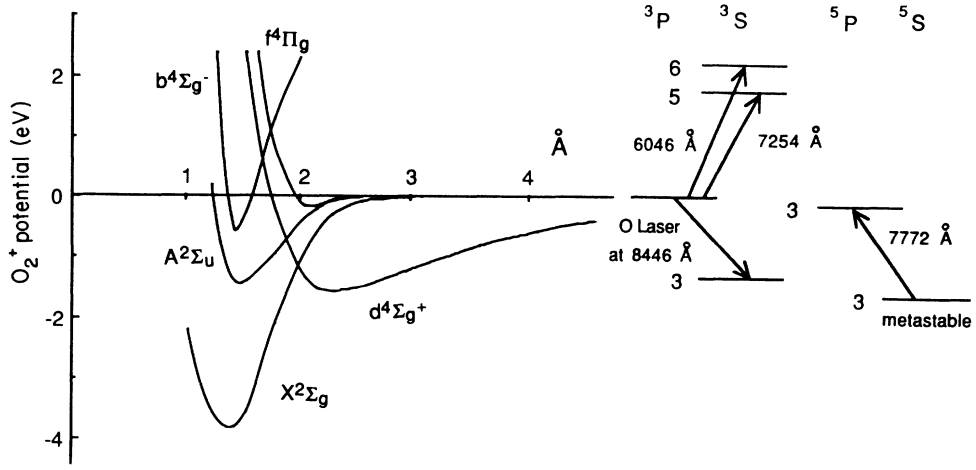

FIG. 1. O_2^+ potential curves associated with $3\,^3P$ oxygen are plotted as a function of internuclear distance. The ^3P atomic state is taken as zero potential. Relevant excited states and transitions in neutral atomic oxygen are also indicated.

discharge, of 300 K. Atoms produced directly by dissociation from states of O_2^+ molecular ions have the large kinetic-energy spread and yield the larger broadened distribution equivalent to a "temperature" of 5000 K.

Consideration of O_2^+ molecular ions, in fact, leads to understanding the cause of broadening. Dissociation channels from state of O_2^+ [$^{2,4,6}(\Sigma^+,\Pi)_{g,u}, A\,^2\Pi_u$ state] to the $3\,^3P$ state of atomic oxygen have been studied theoretically and experimentally by several groups.[8-11] The emergence of energetic fragments from the dissociation of molecular ions was predicted early,[12] and the O^+ time-of-flight spectra[10] from the dissociation of O_2^+ ($c\,^4\Sigma_u^-$ state) into O^+ and O in the ^3P state shows that the O^+ fragments have a high kinetic-energy distribution extending to 2.9 eV. The $O(^3P)$ fragments should also be energetic and have an equivalent kinetic-energy distribution. This inhomogeneous hot atomic oxygen produces the broad LOG spectrum, which as is noted in Fig. 2 does not fit well to a Gaussian distribution function. (The broad spectrum was not seen in a single frequency two-photon excitation process pumped directly from ground oxygen atoms.[13]) A relevant O_2^+ study in the literature is that of Bjerre and Keiding who demonstrated a long-range $O\text{-}O^+$ interaction by means of field-dissociation spectroscopy.[14] They determined the ion-atom interaction potential ($d\,^4\Sigma_g^+$ state) at distances of 10–20 Å.

Another extremely interesting feature of the data shown in Fig. 2 is that the centroid of the broad peaks is shifted on average by 226 ± 28 MHz to the lower-frequency side from that of the narrower peaks. It is likely that part of the signal is due to $O(3\,^3P)$ slightly bound to the O^+ fragments. Such weakly bound molecular states at large intermolecular separation are possible, due to charge-quadrupole interactions and higher-order interactions of the ionic charge with the charge induced dipole moment in the neutral atom.[15] The charge-quadrupole interaction is given by

$$V(R) = qQ/2R^3. \tag{2}$$

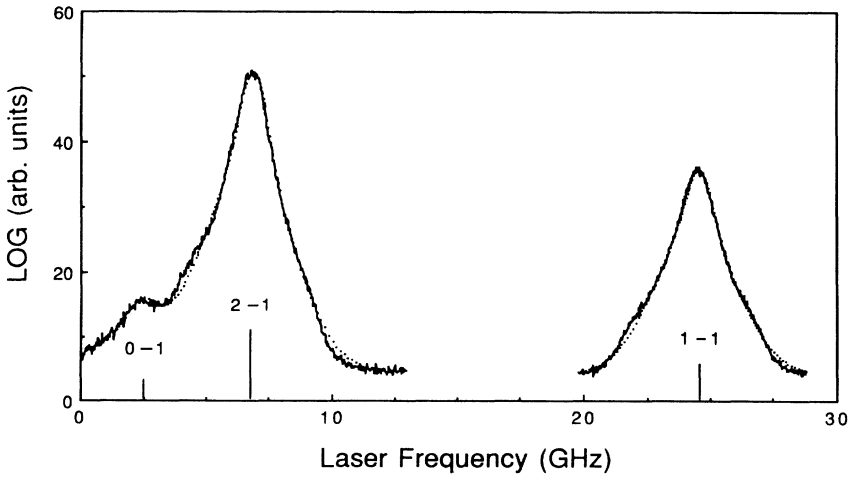

FIG. 2. Optogalvanic signal of $3\,^3P_{2,1,0}$–$5\,^3S_1$ transitions at 725.4 nm is plotted as a function of laser frequency. The dotted lines are fits to sum of two Gaussian functions: one narrow and one broad.

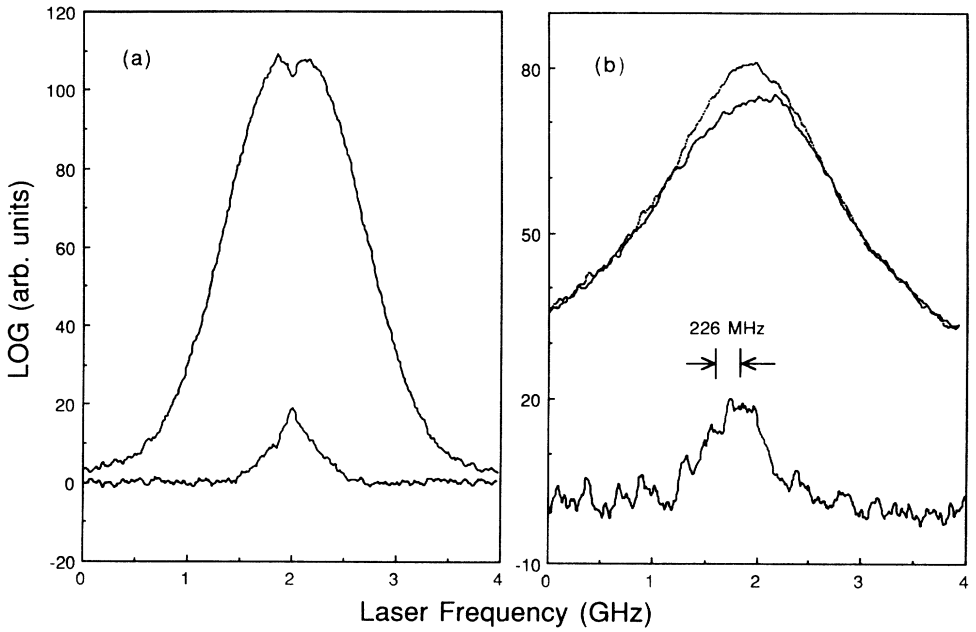

FIG. 3. (a) Optogalvanic signal of $3\,^5S_2$–$3\,^5P_3$ transition at 777.2 nm with reflected beam. Difference of signals with and without reflected beam is plotted at the bottom of the figure. (b) Optogalvanic signals of $3\,^3P_2$–$5\,^3S_1$ transition with and without reflected beam are compared. The difference is multiplied by 5 and plotted at the bottom.

An order of magnitude estimation for R, the internuclear separation, which would shift the ^3P state by 226 MHz yields 28 Å. A quadrupole moment Q, of -0.448 eÅ^2 for ^3P oxygen is used in the estimation.[16] This deduced value for R agrees with Bjerre's O_2^+ measurements. The positive ions slightly perturb the valence electrons via a quadrupole interaction shifting the $3\,^3P$ state higher. Therefore, the centroid of the laser frequency pumping to the higher level shifts to lower frequency.

This shift may also explain the previously noted asymmetric placement of the oscillation lines in the 844.6 nm atomic oxygen laser.[4,17] There are four laser oscillation lines at the $3\,^3P_{2,1,0}$–$3\,^3S_1$ transitions, one pair is around the $J=2$ to 1 transition, the other pair is around the $J=1$ to 1 transition. Lines in each pair are separated by 0.13 cm^{-1}, which is close to the full width at half maximum of the broad lines observed in this work. As explained in Ref. 17, sufficient gain for lasing is only achieved in the wings of the normal Doppler distribution of the lower laser level. The centroids of pairs are shifted from the spontaneous emission lines by 0.01 and 0.05 cm^{-1} for 1 to 1 and 2 to 1 transitions, respectively. In Fig. 2 the centroids of the broad distributions observed in this work are shifted from that of the narrower distributions by 0.01 cm^{-1} for both 1 to 1 and 2 to 1 transitions. The laser shift for the 1 to 1 transition agrees with the LOG data. The larger shift at the laser oscillation pair at the 2 to 1 transition is possibly due to the nearby $J=0$ to 1 transition.

In order to further study properties of the broad peaks, a saturation spectroscopy experiment was carried out by retroreflecting the laser beam through the discharge. When the reflected laser beam overlaps the incident beam, an optogalvanic signal for longitudinally static atoms is saturated, leading to a narrow Lamb dip at the center of the peak. A scan of the LOG signal near the center of the $J=2$ to 1 transition peak with saturation spectroscopy geometry is shown in Fig. 3(b). The difference between the two beam signal and the single beam signal on an expanded scale is shown at the bottom of the figure. A normal Lamb dip appears at the position of the narrower peak superimposed on a broader line feature centered approximately 226 MHz lower in frequency. It is difficult to resolve effects due to velocity changing collisions from a possible broad distribution of atomic levels perturbed by O^+ fragments. For comparison, a typical Lamb dip for a transition not associated with the ^3P level is shown in Fig. 3(a), for the 777.2-nm transition from a metastable atomic oxygen state $3\,^5S$, to the $3\,^5P$ state.[18]

In summary, LOG studies of the $3\,^3P$ level of discharge produced atomic oxygen have shown that an anomalous line shape observed is due to direct dissociation of O_2^+. Analysis of the line shapes obtained can explain previously noted phenomena. The laser studies complement many earlier ion time-of-flight studies of O_2^+ and long-range ion-atom interaction experiments. Experiments of the type reported here can be extended to further evaluate long-range interactions in other systems of current interest.

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