PHYSICAL REVIEW A VOLUME 29, NUMBER 5 MAY 1984

Bimolecular processes in a low-density oxygen discharge

D. D. Awschalom, S. A. Shivashankar, and B. Robinson
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 4 January 1984)

When excited by a microwave discharge, pairs of gaseous oxygen molecules radiate strong luminescence and display bimolecular oscillatory transitions. At low pressures the intensities of both processes have an unusual density dependence, increasing with decreasing density, indicating molecular competition between radiative and nonradiative decay schemes. The data provide the first direct observation of a weakly bound O_2-O_2 structure.

For nearly half a century[1] it has been known that molecular oxygen participates in a cooperative process in which pairs of molecules pool their energies to produce a single photon. These "double transitions" dominate the visible spectra of oxygen since no single-molecule transitions lie in this range.[2] Although it has been witnessed in condensed phases,[3] gaseous discharges,[4] and chemical reactions,[5] the fundamental mechanism concerning the bimolecular interaction remains a mystery.

Recent attempts to study these radiative properties have involved methods of isolating the molecules, such as rare-gas matrix isolation[6,7] and molecular physisorption,[8] in an effort to suppress nonradiative processes. Encouraged by these results we report preliminary optical measurements in very low pressure oxygen gas, where the pair interaction may be studied in an environment which minimizes the role of molecular collisions.

A 2.45-GHz microwave generator is coupled to a unique low-loss rectangular waveguide,[9] within which runs a coaxial quartz tube 5 cm in diameter. The design of the waveguide leads to an intense, 30 cm long, uniform discharge in a continuous flow of ultrahigh-purity oxygen, allowing measurements to be made over three decades of pressure. The gas flow is maintained at a fixed rate and the system density ρ altered by varying the conductance. An emission signal is collected using a 2-mm fiber optic bundle placed midway along the glass discharge column, and analyzed with a 27-cm monochromator employing a 25-μm entrance slit. The 1200-line per mm monochromator grating is held fixed and the dispersed light scanned with a 1024 element diode array, yielding a spectral resolution of 2.0 Å. To ensure that the gas is at a fixed ambient temperature (and hence remained a constant parameter as the discharge pressure was varied) the quartz tube was air cooled continuously and the optical signal collected rapidly, typically as 32 signal-averaged scans in 90 msec.

The majority of spectra were collected between 6000 and 6500 Å, thereby encompassing the $(^1\Delta^1\Delta)\leftarrow(^3\Sigma^3\Sigma)$ double transition for which both molecules have zero-vibrational final states. Mention will be made later of the (1,0) band in which the final state of one of the molecules is the first vibrational level of the $^1\Delta$ state.

Figure 1 shows a typical oxygen emission spectrum. Noteworthy are the following features:

(i) A pair of narrow *atomic* oxygen transitions appear at 6158 and 6456 Å. These lines belong to the excitation series of neutral atomic oxygen, are well understood, and serve as ideal calibration markers. Both are triplet transitions, and as such have linewidths which are a sum of their respective component spacings and intensities.

(ii) Flanked by the two atomic oxygen lines rests a broad *bimolecular* luminescence band whose peak is located at 6350 Å. The general profile and position of this band are independent of gas pressure, as is the band width of 80 Å. The asymmetric peak profile has been described elsewhere and is attributed to the formation of biexcitons.[10] This band corresponds to luminescence from the $(^1\Delta^1\Delta)$ zero-vibrational state to either the zeroth-vibrational or first-vibrational levels of the $(^3\Sigma^3\Sigma)$ ground state, and has been previously observed[4-6] at high gas pressures.

(iii) At low pressures, quasiperiodic structure appears as a modulation of the broad luminescence band. This structure is visible only within the luminescence band and extends over the entire profile, with a spacing which ranges from 8 Å on the short-wavelength side of the peak to 13 Å on the high-wavelength side. We identify these features with relative vibrational and torsional oscillations of the weakly bound molecular pairs, and as such provide the first direct observation of a weakly bound O_2-O_2 complex. This is consistent with earlier high-resolution gas-phase absorption measurements[11] which suggested the existence

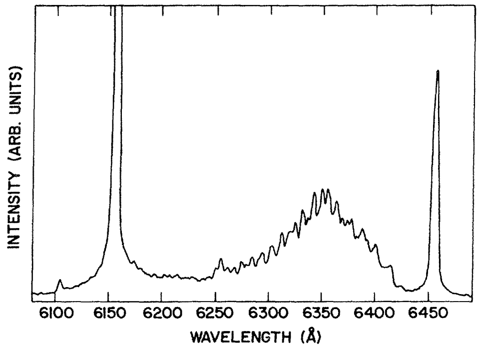

FIG. 1. Emission spectrum of oxygen at 4 mTorr. The broad bimolecular luminescence band rests between two atomic oxygen peaks. The net absorbed microwave power is 850 W.

of a weakly bounded van der Waals bimolecule. Although clearly visible at low pressures, these peaks disappear at higher pressures and the luminescence peak returns to its normally smooth profile. The structure remains at the same position independent of gas pressure.

The pressure dependence of the bimolecular luminescence is plotted in Fig. 2. Note that this behavior is exactly opposite to what is seen in the high-pressure gas phase,[12] where collision-induced electronic transitions between molecular pairs give rise to bands whose intensity is proportional to ρ^2. We believe the density dependence of the intensity shown in Fig. 2 reflects the onset of competing nonradiative decay modes. At low densities, bimolecular radiation prevails as collisions are less important. However, as the density is increased, collisions provide an alternative deexcitation channel, either by dissociating the pairs or perturbing them to permit other internal decay modes. This process is then similar to what has been seen in adsorbed systems,[8] where concentration quenching arises from the proximity of other oxygen molecules. Eventually, a sufficiently high densities ($P > 50$ Torr), collision-induced electronic transitions create radiative pairs and the bimolecular luminescence crosses over to the ρ^2 dependence.

The intensity of this feature is thus governed by different radiative lifetimes in the low-pressure regime where collisions are unimportant, and in the higher-pressure regime where collisions play a vital role. By pulsing the discharge assembly, we have measured an upper limit to the bimolecular radiative lifetime of 10 msec for the former, at a pressure of 30 mTorr. This is somewhat shorter than the radiative half-life of 25 ms reported[4] previously and still dramatically shorter than the 3.6×10^3 sec lifetime of an unperturbed $^1\Delta$ O_2 molecule.[13] Clearly, in order to better understand the competitive nature of the bimolecular process, a time-resolved study of the luminescence should be performed. In this manner it would be possible to examine the interactions over a large density range and follow the crossover behavior into the condensed phases.

In order to obtain a characteristic energy for the low-density behavior, the temperature dependence of the band intensity is plotted logarithmically in Fig. 3. We assume an intensity dependence of the form $I \propto (-E/k_BT)$, where k_B is the Boltzmann constant, T is the effective temperature determined from the pressure, and E is a characteristic energy. E then has a value ~ 100 K, nearly equal to what has been seen in the low-density adsorbed gas.[8] This may be associated with the interaction strength of a bimolecular pair responsible for the double transition. Although several theories have been advanced to explain the origin of this interaction,[10,14] an attractive possibility is to associate this energy with the binding energy of biexcitons.[8]

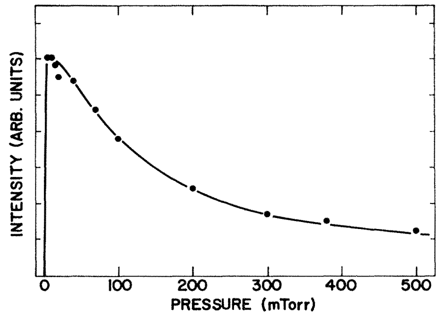

FIG. 2. Pressure dependence of the integrated 6350-Å luminescence band intensity.

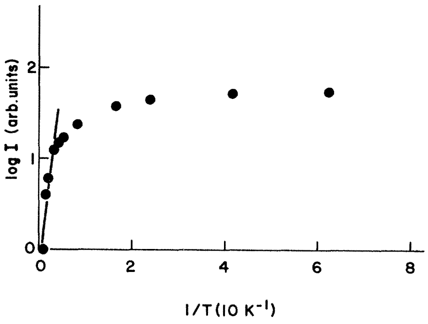

FIG. 3. Temperature dependence of the 6350-Å luminescence band intensity. The high-temperature behavior yields a characteristic energy for the bimolecular interaction.

The quasiperiodic structure seen in Fig. 1 is somewhat unusual when viewed from a condensed-matter perspective. The periodic spacing is too large (10—30 cm^{-1}) to be free molecular rotation and there are no single-molecule transitions in this spectral region. However, if bimolecular oxygen is weakly bound in both ground and excited states, a relative vibration *between molecules* would produce a series of vibrational transitions beginning at low wavelengths and progressing to higher wavelengths. At $T > 0$ (i.e., finite pressures) there would also be transitions from higher initial levels as well as possible torsional oscillations superimposed upon these. The strength of the different progressions and their extent would depend on the displacement between ground- and excited-state equilibrium positions for each of these modes, which are presumably nonlinear due to an anharmonic potential. Thus it may be that the series responsible for some of the structure on the low-wavelength side dies out leaving only the series with approximately 13-Å spacing on the right. Note that the spacings of these features are not very different from those seen in solid oxygen,[15] and as such are not unreasonable for pair interactions. In addition, there seem to be interference "beats" in the pattern.

As a further check of the data integrity an oxygen emission spectrum was recorded from a low-density 13.5-MHz rf discharge. This data, obtained at 30 mTorr, also revealed bimolecular luminescence and quasiperiodic structure.

A few measurements were made of the (1,0) emission band at 5800 Å. These showed similar but not identical structures. Presumably the ground-state levels are the same but the weighting for different transitions could vary.

In summary, we have seen intense luminescence and quasiperiodic spectral structure arising from bimolecular transitions in gaseous oxygen. At low pressures, the luminescence exhibits a density dependence suggestive of molecular competition between radiative and nonradiative decay modes. Moreover, the spectral structure confirms the bimolecular nature of these features by indicating the existence of a weakly bound oxygen bimolecule.

We would like to thank D. B. Fitchen for help with analysis of the data, and Bruce Bumble for technical assistance.

---

[1] J. W. Ellis and H. O. Kneser, Z. Phys. 86, 583 (1933).
[2] E. J. Wachtel and R. G. Wheeler, J. Appl. Phys. 42, 1581 (1971).
[3] A. Landau, E. J. Allin, and H. L. Welsh, Spectrochim. Acta 18, 1 (1962).
[4] J. S. Arnold, R. J. Browne, and E. A. Ogryzlo, Photochem. Photobiol. 4, 963 (1965).
[5] R. J. Browne and E. A. Ogryzlo, Proc. Chem. Soc. London 1964, 117.
[6] I. R. Sil'dos, L. A. Rebane, A. B. Treschchalov, and E. A. Lykhmus, Zh. Eks. Teor. Fiz. Pis'ma Red. 22, 321 (1975) [JETP Lett. 22, 151 (1975)].
[7] J. Goodman and L. E. Brus, J. Chem. Phys. 67, 4398 (1977).
[8] D. D. Awschalom, K. Iwahana, D. B. Fitchen, and S. Gregory, Phys. Rev. B 25, 4185 (1982).
[9] L. J. Bailin, B. L. Hertzler, and D. A. Oberacker, Environ. Sci. Technol. 12, 673 (1978); B. Robinson and S. A. Shivashankar (unpublished).
[10] Yu. B. Gaididei, V. M. Loktev, A. F. Prikhotko, and L. I. Shanskii, Fiz. Nikh. Temp. 1, 1229 (1975) [Sov. J. Low. Temp. Phys. 1, 653 (1975)].
[11] C. A. Long and G. E. Ewing, J. Chem. Phys. 58, 4824 (1973).
[12] G. C. Tabisz, E. J. Allin, and H. L. Welsh, Can. J. Phys. 47, 2859 (1969).
[13] A. V. Jones and A. W. Harrison, J. Atmos. Terr. Phys. 13, 45 (1958).
[14] R. Bhandari and L. M. Falicov, J. Phys. C 6, 479 (1973).
[15] J. E. Chill and G. E. Leroi, J. Chem. Phys. 51, 97 (1969).