of the shower, channeling effects in the water, and correlation detection techniques. Each 6-dB (0.3 dyne/cm^2) increase in signal will increase the detected EAS events by approximately a factor of 4.

The contribution to the acoustic signature of an EAS by the various particles in the shower should be different, since they differ in this radial distribution from the core, total energy, and radiation absorption length. The strongest signal will come from the small region near the core where the nuclear particles strike. The electrons will contribute a weaker signal from a larger surface area, whereas the muons will contribute a similar signal whose origin is a larger surface area and a thicker layer because of their reduced interaction with matter. The muon energy distribution is peaked near the core, even though the particles are widely distributed.

The use of detectors with angular sensitivity should make it possible to pinpoint the position and area of the shower and thus the energy of the primary cosmic-ray particle. The spectral content and the radial distribution of sound generated at various distances from the core may allow one to obtain detailed information about the particles in the shower.

As stated earlier, the U.S. Navy has several sophisticated hydrophone listening stations that have operated for extensive periods of time. These stations have probably detected signals from EAS. The signals should appear as a broadband "rumbling" noise of moderate duration, with occasional short higher-frequency "clicks."

W. LOUIS BARRETT
*Physics Department,
Western Washington University,
Bellingham 98225*

References and Notes

1. D. A. Andrews, D. M. Edge, A. C. Evans, R. J. O. Reid, R. M. Tennent, A. A. Watson, J. G. Wilson, A. M. Wray, *Proc. 12th Int. Conf. Cosmic Rays* **3**, 995 (1971).
2. W. F. Clifford, in *Present and Future Civil Uses of Underwater Sound* (National Academy of Sciences, Washington, D.C., 1970), pp. 112–129.
3. K. L. Greisen, *Annu. Rev. Nucl. Sci.* **10**, 63 (1960).
4. R. M. White, *J. Appl. Phys.* **34**, 3559 (1963); L. R. Sulak, paper presented at the Clyde L. Cowan Memorial Symposium on Long-Distance Neutrino Detection, Washington, D.C., 25 April 1978.
5. L. S. Gournay, *J. Acoust. Soc. Am.* **40**, 1322 (1966).
6. K. R. Foster and E. D. Finch, *Science* **185**, 256 (1974).
7. Report of the Committee on Underwater Telecommunication, National Research Council, in *Present and Future Civil Uses of Underwater Sound* (National Academy of Sciences, Washington, D.C., 1970).
8. I thank the faculty and staff of the Electrical Engineering Department of the University of Washington for their support during the preparation of this manuscript.

19 May 1978; revised 17 July 1978

Metastable Oxygen Emission Bands

Abstract. *Recombination of ground-state oxygen atoms populates six different bound electronic states of molecular oxygen. Of the six optical transitions expected between the three upper states at 4 to 4.5 electron volts and the two lowest states, five have been observed in the afterglow of a conventional helium-oxygen microwave discharge in both* $^{16}O_2$ *and* $^{18}O_2$*, three of them for the first time in gas-phase spectra. Generation of these emissions from oxygen atoms in a system free of molecular oxygen establishes that atom recombination is the production mechanism.*

The spectroscopy of O_2 has been studied for the better part of a century (*1*, *2*), but a great deal still remains to be learned. Of particular importance in atmospheric chemistry are the six bound electronic states of O_2 which can arise from recombination of ground-state O atoms. The kinetic processes of production, radiation, and relaxation of these states are only now beginning to be understood. The relevant calculated potential energy curves are shown in Fig. 1 (*3*).

A peculiarity of O_2 is that all of these states are optically metastable with respect to each other; that is, the emission of radiation between any two states is a very slow process compared to the collisional mechanisms by which the excited molecule may lose its electronic energy. Typical radiative lifetimes for allowed electronic transitions are $\approx 10^{-8}$ second, whereas the average times required for isolated $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$ molecules to emit a photon and relax to the $X^3\Sigma_g^-$ ground state are 12 and 3900 seconds, respectively (*4*). This reluctance of the excited molecules to radiate has limited observations of the three upper O_2 states, $A^3\Sigma_u^+$, $C^3\Delta_u$, and $c^1\Sigma_u^-$. For the same reason, these molecules represent a potential energy reservoir in systems containing atomic O and are thus of kinetic importance. All three states have been observed in absorption from the ground state, and the transitions are known (*2*) as the Herzberg I, III, and II systems, respectively. However, only the $A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$ transition has been observed in emission (*5*), except for a very weak pair of bands observed by Degen (*6*), which he was able to rotationally analyze and ascribe to the $c^1\Sigma_u^- \rightarrow X^3\Sigma_g^-$ transition.

Table 1. Band intensities of the $C^3\Delta_{1u} \rightarrow a^1\Delta_g$ system.

Band	Observed peak wavelength (Å)	Observed relative intensity	Calculated relative intensity
0-3	4553	0.03	0.07
0-4	4863	0.22	0.23
0-5	5212	0.58	0.49
0-6	5606	0.88	0.80
0-7	6055	1.00	1.00
0-8	6572	0.92	1.02
0-9	7172	0.59	0.83

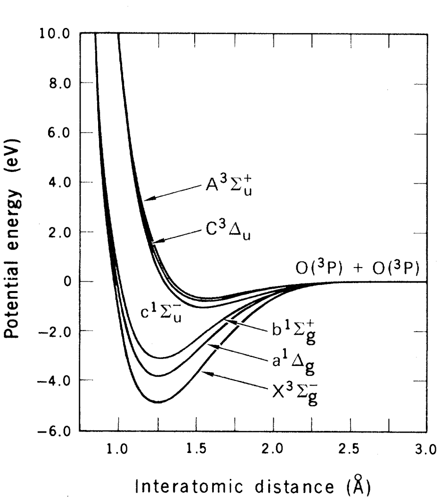

Fig. 1. Bound O_2 potential energy curves from the first dissociation limit (*3*).

When the Russian Venera 9 spacecraft sent back a spectrum of the dark side of Venus taken in the visible region (*7*), a very simple and intense spectrum of eight bands was observed, which was correctly identified by Lawrence *et al.* (*8*) as the 0-v'' progression of the $c^1\Sigma_u^- \rightarrow X^3\Sigma_g^-$ transition. This was a quite unexpected result, there being a very small amount of O_2 present in the venusian atmosphere as compared to the dominant gas, CO_2. Lawrence *et al.* then carried out laboratory experiments and were able to duplicate the Venus spectrum by passing a flowing He-O_2 mixture through a microwave discharge, adding CO_2 downstream and observing the resulting luminescence.

The mechanism of $c^1\Sigma_u^-$ formation was of considerable interest to me, particularly the question of the role of CO_2. The most obvious source of the $c^1\Sigma_u^-$ state is O atom recombination, yet, if the state is seen only in systems containing CO_2, a more complex mechanism must be postulated.

To learn more about c-X bands, I set up a conventional flowing afterglow apparatus and was soon able to duplicate the results of Lawrence *et al.*, obtaining intense c-X emission if I used a mixture of 30 mtorr O_2, 20 torr He, and 7 torr CO_2. Spectra were recorded photographically with a high-speed transmission grating image-tube spectrograph (*9*), with

0036-8075/78/1117-0751$00.50/0

exposure times of 30 seconds to 5 minutes.

Upon turning off the CO_2, I discovered that the *c-X* bands were still present but weaker, and that the entire visible spectral region was partially obscured by the NO_2 continuum. This radiation, from an excited NO_2 state (*10*), is the result of the recombination of O atoms and NO after the discharge, the NO being generated from traces of N_2 in the He carrier gas. The effect of adding CO_2 is both to quench the NO_2 emission and to enhance the *c-X* bands, thus strongly accentuating them.

As it was not clear that O atom recombination was the source of the *c-X* bands (He metastable states might excite O_2 through Penning ionization and subsequent charge exchange), I attempted to generate the bands in the absence of O_2 by titrating the N atoms in a flowing N_2 discharge with NO, thereby effectively converting N to O. The results were the same—the *c-X* bands were as strong as before. I found that the 20 torr He-O_2 mixture could be replaced with 20 torr N_2, or with a N_2-Ar mixture, with little effect on the *c-X* bands. This is a convincing demonstration that the $c^1\Sigma_u^-$ state is produced strictly by O atom recombination and requires neither O_2 nor CO_2 for its generation.

Although the *c-X* bands were weaker in the absence of CO_2 than in its presence, it was apparent that there were other bands present when CO_2 was not used. In order to improve the quality of the spectra, I used a heated Ti getter to reduce the concentration of N_2 in the He, which greatly reduced the NO_2 continuum. Figure 2 shows a typical improved spectrum of the He-O_2 afterglow. The inability to observe such a spectrum in the past is perhaps related to the masking effect of the NO_2 continuum. In addition to the *c-X* bands, there are a variety of other emission features, some even stronger than the *c-X* bands. Figure 3 shows a spectrum with added CO_2, demonstrating the extent to which the other bands are thereby suppressed.

The previously established identifications in Fig. 2 are the $A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$ Herzberg I system analyzed by Broida and Gaydon (*5*), the $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$ 0-0 atmospheric band, and the $c^1\Sigma_u^- \rightarrow X^3\Sigma_g^-$ system described above. In order to analyze the other bands, I carried out experiments with $^{18}O_2$ and with $^{16}O_2$-$^{18}O_2$ mixtures. Large isotopic shifts were observed, and analysis of the data established that all of the bands belong to progressions arising from $v = 0$ levels of an upper state to high vibrational levels of either the $a^1\Delta_g$ or the $X^3\Sigma_g^-$ state. It was thus possible to establish the presence of three new band systems (in terms of gas-phase laboratory spectroscopy), identified in Figs. 2 and 3 as $C^3\Delta_u \rightarrow a^1\Delta_g$, $C^3\Delta_u \rightarrow X^3\Sigma_g^-$, and $c^1\Sigma_u^- \rightarrow a^1\Delta_g$. The $b^1\Sigma_g^+$ state has a radiative lifetime comparable to that of the $c^1\Sigma_u^-$ and $C^3\Delta_u$ states, and considerably longer than that of the $A^3\Sigma_u^+$ state (*11*); however, the $b^1\Sigma_g^+$ state is quenched only very slowly, making the $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$ 0-0 band at 7618 Å stronger by two orders of magnitude than any other feature in Figs. 2 and 3. The OH vibration-rotation overtone bands are observed in all the spectra taken in the absence of CO_2 but do not interfere with the identifications.

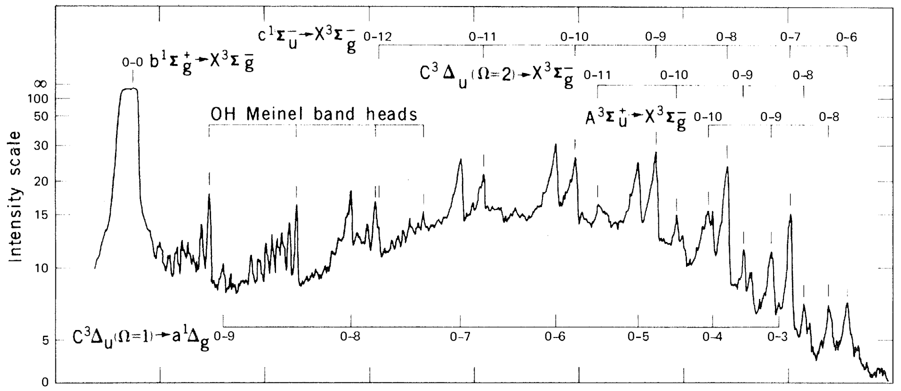

Fig. 2. Microdensitometer trace of the O_2 emission spectrum from 4000 to 8000 Å. Conditions: 38 mtorr O_2, 20 torr He, 2-minute film exposure.

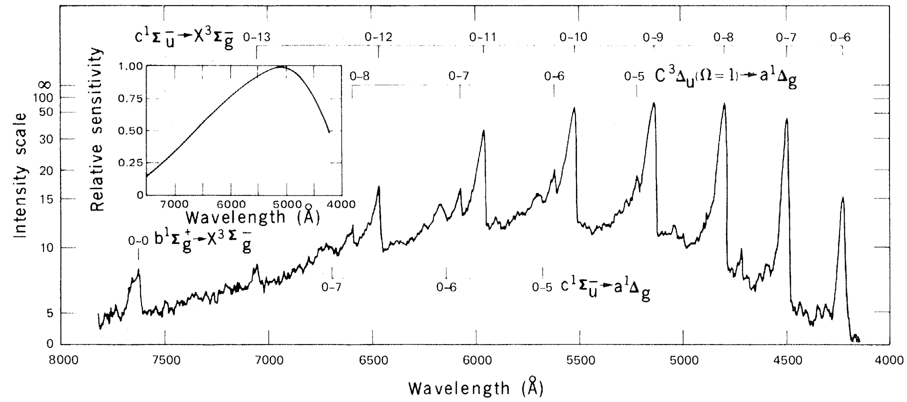

Fig. 3. Microdensitometer trace of the O_2 emission spectrum from 4000 to 8000 Å. Conditions: 35 mtorr O_2, 20 torr He, 7 torr CO_2, 5-minute film exposure. (Inset) Wavelength sensitivity curve.

Five of the six transitions between the upper three and the lower two electronic states are clearly identified in Figs. 2 and 3. The sixth, $A^3\Sigma_u^+ \rightarrow a^1\Delta_g$, should be weaker by as much as two orders of magnitude than the observed $A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$ bands. The $C^3\Delta_u \rightarrow a^1\Delta_g$ and $c^1\Sigma_u^- \rightarrow a^1\Delta_g$ bands represent the first examples of a gas-phase transition involving a substantial range of vibrational levels in the $a^1\Delta_g$ state. Previous spectroscopic constants for this state have been derived from the $v = 0$ and $v = 1$ levels alone (*12*). Of the three new transitions, the $c^1\Sigma_u^- \rightarrow a^1\Delta_g$ and $C^3\Delta_u \rightarrow X^3\Sigma_g^-$ bands have recently been seen in matrix isolation experiments at 4° to 10°K (*13*), and the $C^3\Delta_u \rightarrow X^3\Sigma_g^-$ bands had in fact been seen in matrices in 1960 but were misidentified as $A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$ (*14*). The $C^3\Delta_u \rightarrow a^1\Delta_g$ system, known as the Chamberlain bands, has been provisionally identified by Chamberlain (*15*) in the airglow. The most clear-cut bands in his assignment (*16*) are the 5-2 and 6-2 bands, in which only the $\Omega = 1$ spin component seems to be present. This is also the case in the present spectra and is best explained if it is assumed that the $^3\Delta_{1u}$ component is mixed by spin-orbit interaction with a nearby $^1\Pi_{1u}$ state. There are three weak bands on the short-wavelength side of the 0-8, 0-9, and 0-10 *C-X* bands which have not yet been identified.

Transitions down to the $b^1\Sigma_g^+$ state from the *A*, *C*, and *c* states are not observed. The most likely reason is that these transitions would have their maximum intensities in the region from 6500 to 9000 Å (for $v' = 0$), where the photocathode sensitivity is low and OH emission would interfere.

Table 1 shows the observed wavelengths of the principal new system, the $C^3\Delta_{1u} \rightarrow a^1\Delta_g$ bands, from which new spectroscopic constants for the $a^1\Delta_g$ state may be determined. Observed and calculated band intensities are also listed, on the assumption of a constant electronic transition moment. The calculated intensities are based on interpolations between sets of Franck-Condon factors calculated for the A-a and c-a transitions (*17*).

Now that it is known that there are easily observable transitions from the $A^3\Sigma_u^+$, $C^3\Delta_u$, and $c^1\Sigma_u^-$ states, it should be practical to carry out a variety of measurements. It is evident that all three states will be generated by recombination of O atoms in both the terrestrial and the venusian atmospheres. The fact that Earth's atmosphere shows principally A-X bands, whereas only c-X bands appear in the venusian nightglow, suggests that the difference lies in the quenching and relaxation kinetics of the two systems, as the peak O atom densities are not very different (*18*). Thus quenching rate coefficients by O atoms, O_2, N_2, and CO_2 are needed to clarify the emission features (it is already obvious that quenching of $c^1\Sigma_u^-$ by N_2 and CO_2 is very slow, whereas $C^3\Delta_u$ and $A^3\Sigma_u^+$ quenching by CO_2 is more rapid). Such data will also lead to relative values of the radiative lifetimes.

The O atom recombination into these energetic states of O_2 is likely to be an important process, and the difficulty in observing emission only reflects their weak radiative properties. It may be that both in the atmosphere and in combustion reactions these O_2 states play important roles. Furthermore, subsequent studies should establish significant details about the recombination process, such as the relative initial distribution among the electronic states and the efficiency of cross relaxation interactions.

TOM G. SLANGER
Molecular Physics Laboratory,
SRI International,
Menlo Park, California 94025

References and Notes

1. G. H. Dieke and H. D. Babcock, *Proc. Natl. Acad. Sci. U.S.A.* **13**, 670 (1927).
2. G. Herzberg, *Can. J. Phys.* **30**, 185 (1952); *ibid.* **31**, 657 (1953).
3. R. P. Saxon and B. Liu, *J. Chem. Phys.* **67**, 5432 (1977).
4. P. H. Krupenie, *J. Phys. Chem. Ref. Data* **1**, 423 (1972).
5. H. P. Broida and A. G. Gaydon, *Proc. R. Soc. London* **222**, 181 (1954).
6. V. Degen, *Can. J. Phys.* **46**, 783 (1968).
7. V. A. Krasnopol'skii, A. A. Krys'ko, V. N. Pogashev, P. A. Parshev, *Cosmic Res. (USSR)* **14**, 687 (1977).
8. G. M. Lawrence, C. A. Barth, V. Argabright, *Science* **195**, 573 (1977).
9. R. L. Sharpless and R. A. Young, *Rev. Sci. Instrum.* **41**, 1628 (1970).
10. A. Fontijn, C. B. Meyer, H. I. Schiff, *J. Chem. Phys.* **40**, 64 (1964).
11. T. G. Slanger, *ibid.*, in press.
12. L. Herzberg and G. Herzberg, *Astrophys. J.* **105**, 353 (1947).
13. J. L. Richards and P. M. Johnson, *J. Chem. Phys.* **65**, 3948 (1976); J. Goodman and L. E. Brus, *ibid.* **67**, 1482 (1977).
14. H. P. Broida and M. Peyron, *ibid.* **32**, 1068 (1960); L. J. Schoen and H. P. Broida, *ibid.*, p. 1184.
15. J. W. Chamberlain, *Astrophys. J.* **128**, 713 (1958).
16. A. L. Broadfoot and K. R. Kendall, *J. Geophys. Res.* **73**, 426 (1968).
17. Calculations of the Franck-Condon factors for these transitions were provided by D. L. Albritton.
18. N. D. Sze and M. B. McElroy, *Planet. Space Sci.* **23**, 763 (1975); T. G. Slanger and G. Black, *ibid.* **25**, 79 (1977).
19. This work is dedicated to the memory of Prof. H. P. Broida, whose recent death has saddened his many friends in the scientific community. Herb was involved in the study of the O_2 metastable states from his classic publication in 1954 to the present time, and I acknowledge his enthusiastic encouragement during the course of the present work. I think that the outcome would have pleased him. I thank G. Black, D. L. Huestis, and R. P. Saxon for valuable discussions. I thank D. L. Albritton for providing me with calculations of the Franck-Condon factors. This work was jointly supported by NASA contract NASW-2849 and Army Research Office contract DAAG29-77-C-0018.

5 June 1978; revised 18 July 1978

Size Fractionation Methods: Measuring Plutonium in Respirable Dust

Abstract. *Methods used to evaluate the inhalation hazard of soil contaminated with plutonium were investigated. Four soil fractionation procedures were used to separate three size fractions of soil particles taken from two locations at the Department of Energy's Rocky Flats facility. The results show that increasing amounts of soil mass and plutonium activity (0.5 to 38 percent and 7 to 84 percent, respectively) remain in the fraction of soil smaller than 10 micrometers as the in situ particle associations are increasingly disrupted by physical and chemical forces. The introduction of forces of dispersion unrelated to ambient conditions yields results that are unrelated to the original particle associations.*

In the past, the purpose of most environmental surveys for plutonium in soil has been to establish the total inventory for a particular location. More recently, questions regarding the inhalation potential for contaminated soil have prompted investigators to recommend different methods of soil sampling and analysis to evaluate the inhalation potential. Unfortunately, the different methods recommended can yield conflicting results. For example, Tamura (*1*) recommended a procedure in which particle dispersion is minimal. His stated objective was to retain the association of the plutonium with the soil particles. On the other hand, Johnson *et al.* (*2*) recommended a procedure in which particle dispersion is maximized. Their stated objective was to disperse the soil microaggregates to expose the plutonium as much as possible. With such opposing objectives, dissimilar results can be expected.

The following study was initiated to establish the magnitude of the differences one might expect if one were to use four soil fractionation methods (described below) on two soil samples taken from the Department of Energy's Rocky Flats facility. The basis for the sample site selection was an observed difference in surface character and plutonium activity in the soil at the two locations. Sample 1 was taken from a site that was densely covered with prairie grasses. The surface soil was fine-grained and rich in organic litter. The plutonium activity at this site averages about 2 dpm/g as established by an analysis of surface core samples (10 by 10 by 5 cm deep) taken in the summer of 1975. Sample 2 was taken from a site that was nearer to the release point and sparsely covered by prairie grasses. The surface was rocky, and the soil was intermixed with many small pebbles. The plutonium activity at this site averages about 80 dpm/g, as determined by the same sampling technique.

I resampled these two sites in October 1976, using the collection method specified by Johnson *et al.* (*2*) (0.5-cm-deep surface sample). Each sample was field-sifted through a 10-mesh screen, yielding fractions larger and smaller than 2000 μm. Mass, moisture, and plutonium data were obtained from the two fractions. The fraction of each sample smaller than 2000 μm was separated into even smaller fractions (2000 to 37 μm, 37 to 10 μm, and < 10 μm) according to the following four methods.

Method A, dry sift. About 100 g of the < 2000-μm fraction were sifted through a series of screens to obtain the desired subfractions. A stack of vibrating screens was used to separate the larger particles (2000 to 37 μm). One gram of the 37-μm fraction was placed in an ultrasonic sifter on a 10-μm screen to sepa-

0036-8075/78/1117-0753$00.50/0 Copyright © 1978 AAAS