though the data obtained were not related to the mass of material deposited because of background particle contamination, the overall amounts of Zn released were greater than the amounts of Pb. Moreover, most of the radioactivity measured was associated with particles larger than 5 μm. Since no foliage chambers were used in these experiments, the amounts collected could not be related to surface area. However, when chambers were used and the water transpired from the vegetation was collected, the rates of metal loss during rapid transpiration under sunny conditions were comparable to those found in the laboratory for plants having similar concentrations of metals in their leaves.

Our results show that metal-containing particles of various sizes can be generated from the surfaces of plants. Submicrometer-sized particles are probably released under all conditions, particularly when plants are undergoing rapid growth or have high transpiration rates. Larger particles are almost certainly generated by mechanical disturbances at the plant surfaces. Surface abrasion and leaf bending induced by wind action or thermal plumes could dislodge salt particles, wax rodlets, and cuticular and other surface fragments. Microbiological activity could also disrupt the plant surfaces and so produce potential fragments (*11*). All these effects probably play a part in the process of metal release to the environment. There is every reason to believe that a whole range of elements are available for release within the plant, although the amount released will vary with the element, as shown by Zn and Pb above. In principle, biologically important elements such as K, Na, Ca, and Mg should occur at much higher concentrations in plant-derived particulates as compared with trace elements such as Zn, and indeed there is evidence for this (*12*).

It is unlikely that large metal-containing particles from plants play any significant role in the global atmospheric distribution of elements since their residence times would be relatively short. On the other hand, submicrometer-sized particles released from plants could disperse over large areas and give rise to the unexplained metal-enriched particles collected in remote regions of the globe (*1*). At present, we are unable to quantify this effect since the rate of movement of metals into the atmosphere from plants depends on the element in question, its concentration and availability in the soil, seasonal and meteorological conditions, and the sizes of the particles involved. Our experiments, based on leaf area and a background concentration of 1 ppm for both elements in the soil water, indicate that the loss of Zn could be about 20 pg hour^{-1} cm^{-2} and of Pb about 10^{-2} pg hour^{-1} cm^{-2}. Since the leaf area index is about 5, these rates correspond to approximately 9 kg of Zn and 5 g of Pb released from 1 km^2 of vegetation per year. Clearly, since a great deal of the earth's landmass is covered by vegetation, it is conceivable that a proportion of the trace metal composition of the atmosphere is derived from metal-containing particles released by plants. Moreover, it would be expected that, in regions where vegetation grows in highly mineralized soil, plant-derived particles would be rich in metals; this idea has recently been applied in the development of techniques for geochemical exploration from the air (*12*).

W. BEAUFORD
J. BARBER
Department of Botany,
Imperial College,
London SW7 2BB, England
A. R. BARRINGER
Barringer Research Ltd.,
Rexdale, Ontario, Canada

References and Notes

1. D. H. Pierson, P. A. Cawse, R. S. Cambray, *Nature (London)* **251**, 675 (1974); R. A. Duce, G. L. Hoffman, W. H. Zoller, *Science* **187**, 59 (1975); W. H. Zoller, E. S. Gladney, R. A. Duce, *ibid.* **183**, 198 (1974).
2. F. W. Went, *Proc. Natl. Acad. Sci. U.S.A.* **46**, 212 (1960).
3. ______, D. B. Slemmons, H. N. Mozingo, *ibid.* **58**, 69 (1967).
4. R. C. Schell and G. Vali, *Nature (London)* **236**, 164 (1972); *ibid.* **246**, 212 (1973).
5. J. Moorby and H. M. Squire, *Radiat. Bot.* **3**, 163 (1963); P. Arpino, A. Van Dorsselaer, K. D. Sevier, G. Ourisson, *C. R. Acad. Sci.* **275**, 2837 (1972); B. R. Fish, *Science* **175**, 1239 (1972).
6. G. E. Nemeryuk, *Fiziol. Rast.* **17**, 673 (1970).
7. W. Beauford, J. Barber, A. R. Barringer, *Nature (London)* **256**, 35 (1975).
8. P. Goldsmith and F. G. May, *Diffusiophoresis and Thermophoresis in Water Vapour Systems in Aerosol Science*, C. N. Davies, Ed. (Academic Press, London, 1966), p. 163.
9. British Coal Utilisation Research Association minicyclone (Airflow Developments Ltd. model 7033701).
10. Sites were located at the Imperial College field station, Silwood Park, Ascot, Berks; soil, Bagshot green sand.
11. T. F. Preece and C. M. Dickinson, Eds., *Ecology of Leaf Surface Microorganisms* (Academic Press, London, 1971), p. 3.
12. A. R. Barringer, "Applications of remote sensing mineral and mineral fuel exploration," paper presented at the First William T. Pecora Memorial Symposium, Sioux Falls, S.D., 1975; *U.S. Geol. Surv. Prof. Pap.*, in press.
13. We thank H. M. White for assistance with the Pb experiments and M. Martin for help with the electron microscopy. We acknowledge the technical assistance of M. J. Barber, R. Dawes, and J. Whittick.

15 June 1976; revised 13 September 1976

Excitation of the Venus Night Airglow

Abstract. *The strongest spectral features in the Venus night airglow between 3000 and 8000 angstroms are identified as the Herzberg II* ($c^1\Sigma_u^- - X^3\Sigma_g^-$) *bands of molecular oxygen. These bands have been produced in a laboratory afterglow by the recombination of oxygen atoms in the presence of carbon dioxide molecules. It is hypothesized that the same mechanism produces this emission in the upper atmosphere of Venus.*

During orbital operations of the Venera 9 and Venera 10 spacecraft, observations were made of nighttime emissions from the upper atmosphere of Venus (*1*). From an analysis of spectra obtained in November 1975 Krasnopolsky concluded that the 11 spectral emissions arose from one molecular band system, but the identities of the band system and of the molecule were not determined (*2*). In this report we identify the emission spectrum of the Venus night airglow to be the Herzberg II ($c^1\Sigma_u^- - X^3\Sigma_g^-$) system of molecular oxygen (*3*). In addition, in an effort to understand the excitation mechanism in the Venus airglow, we have produced the oxygen Herzberg II bands in a laboratory afterglow under conditions that simulate the upper atmosphere of Venus.

In the laboratory experiment, we produced oxygen atoms by pumping a 0.3 percent oxygen-helium mixture through a microwave discharge at a total pressure of 22 torr. Downstream of the discharge, carbon dioxide at a partial pressure of 10 torr was added to the stream of oxygen atoms. This glowing gas was pumped through an observation tube 7 cm in diameter and 1.8 m long. The spectral emissions from this afterglow tube were measured with a scanning spectrometer having a spectral resolution of 27 Å and a relative spectral sensitivity determined by the response of a tri-alkali photomultiplier and a grating blazed at 3000 Å. The principal emissions from the oxygen–helium–carbon dioxide afterglow were a progression of bands from the lowest vibrational level ($v' = 0$) of the $c^1\Sigma_u^-$ state of molecular oxygen. In 1968, Degen (*4*) had observed and analyzed the 0,7 and 0,8 bands of this progression in an oxygen-argon afterglow. Using the wavelengths of these bands and of the absorption bands measured by Herzberg (*3*), Degen calculated a table of wavelengths for the entire band system (*4*). The wavelengths of the bands observed in the laboratory afterglow correspond to the first row of the Degen wavelength table (*4*). In addition, the relative intensities of the laboratory afterglow bands are in agreement with relative intensities of the Herzberg II bands calculated by Albritton (*5*). Table 1 lists the wavelengths of the band origins together with the relative intensity for each band.

A comparison of the Herzberg II bands as produced in the laboratory and the Venus night airglow bands as observed by Venera 9 and Venera 10 is shown in Fig. 1. When account is taken of the different relative sensitivities of the two spectrometers, the relative intensities of the bands, the band shapes, and the wavelengths are found to be similar. From this comparison we identify the spectral emissions of the Venus night airglow as the $\nu' = 0$ progression of the Herzberg II ($c^1\Sigma_u^- - X^3\Sigma_g^-$) system. The atomic oxygen line at 5577 Å does not appear in the laboratory afterglow or in the Venus night airglow.

We hypothesize that the excitation mechanism in the laboratory afterglow and in the Venus airglow are the same and are due to the recombination of oxygen atoms in the presence of carbon dioxide molecules. The net process may be represented as the three-body reaction

$$O + O + CO_2 \rightarrow O_2^* + CO_2$$

where the oxygen molecule in the $c^1\Sigma_u^-$, $\nu' = 0$ level (4.08 ev) acquires the major part of the energy of recombination of the oxygen atoms (5.12 ev). An analogous process occurs in Earth's upper atmosphere where the third body in the atomic oxygen recombination is either molecular nitrogen, molecular oxygen, or atomic oxygen. In Earth's night airglow, however, the principal ultraviolet emission from the excited oxygen molecule is the Herzberg I ($A^3\Sigma_u^+ - X^3\Sigma_g^-$) system. The Herzberg II bands do not appear in Earth's night airglow (*6*). In the analogous laboratory experiments, Herzberg II bands do not appear in oxygen afterglows with molecular oxygen as the third body (*7*). The difference in the excitation mechanisms in the Venus night airglow and Earth's night airglow is in the very special role that carbon dioxide plays as a third body in the Venus night airglow.

Table 1. Intensities of the $c^1\Sigma_u^- - X^3\Sigma_g^+$ bands of molecular oxygen compared with Venus night airglow intensities.

ν', ν''	Band origin (*4*) (Å)	Relative intensities	
		Theory (*5*)	Observation (*1*)
0,3	3562	0.04	0.10
0,4	3761	0.13	0.08
0,5	3980	0.30	0.32
0,6	4222	0.54	0.57
0,7	4491	0.83	0.84
0,8	4792	1.00	1.00
0,9	5129	0.99	0.94
0,10	5510	0.81	0.80
0,11	5945	0.57	0.59
0,12	6445	0.33	0.43
0,13	7026	0.16	0.12

Some implications from the identification of the excitation mechanism for the Venus night airglow relate to the two planets in the solar system that have carbon dioxide atmospheres. Mars should have a similar airglow at an altitude where the atomic oxygen density is at a maximum. Since on Mars the total pressure is much less than on Venus, the altitude region most favorable for the production of the airglow is close to the surface where, however, reactions involving the photodissociation products of water vapor catalytically consume atomic oxygen (*8*). The most favorable location on Mars to search for the night airglow is over the winter polar region where, because of the very low temperatures, the atmosphere is very dry and the atomic oxygen density is at a maximum, as shown by the appearance of ozone (*9*).

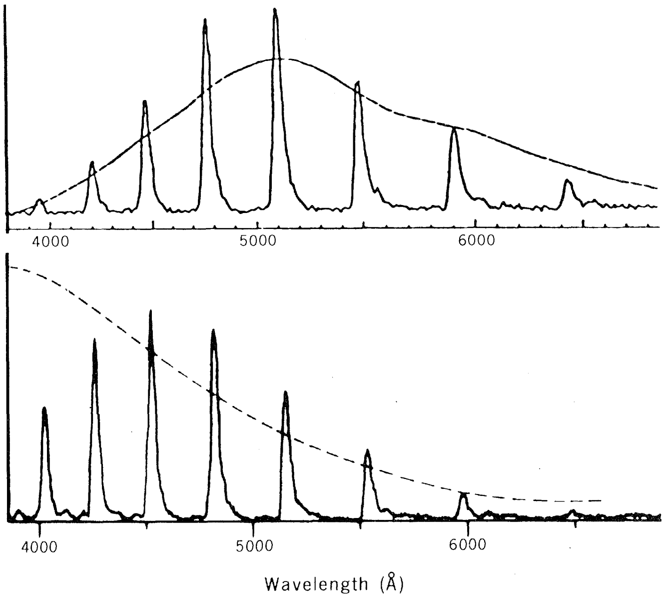

Fig. 1. Herzberg II ($c^1\Sigma_u^- - X^3\Sigma_g^-$) bands of molecular oxygen. (Top) Venus night airglow as observed from Venera 9 (*1*). (Bottom) Venus night airglow as produced in laboratory afterglow. Dashed lines through each of the spectra show the relative sensitivities of the two spectrometers.

On Venus where the surface rotates very slowly, the upper atmosphere appears to have a circulation pattern with a 4-day period (*10*). Oxygen atoms are produced on the dayside of the planet and recombine slowly during the night. Their density at any time and place is controlled by chemical recombination and by transport. Krasnopolsky *et al.* (*1*) have proposed that the mapping of the night airglow is a method of measuring the distribution and transport of atomic oxygen in the Venus atmosphere. With the identification of the excitation mechanism, this technique of observing the circulation of the nightside of Venus can be considered with some confidence.

G. M. LAWRENCE
C. A. BARTH
V. ARGABRIGHT
Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder 80309

References and Notes

1. V. A. Krasnopolsky, A. A. Krysko, V. N. Rogachev, V. A. Parshev, "Spectroscopy of the Venus night airglow from the Venera-9, 10" (preprint D-243, Space Research Institute, Academy of Sciences of the U.S.S.R., Moscow, 1976); V. A. Krasnopolsky, A. A. Krysko, V. N. Rogachev, in *COSPAR 19th Plenary Meeting Program/Abstracts, Philadelphia, 18–19 June 1976* (Committee on Space Research, Paris, 1976), p. 434.
2. V. A. Krasnopolsky, "The spectrum of the Venus night airglow: Identification problem" (preprint D-244, Space Research Institute, Academy of Sciences of the U.S.S.R., Moscow, 1976).
3. G. Herzberg, *Can. J. Phys.* **31**, 657 (1953).
4. V. Degen, *ibid.* **46**, 783 (1968); see also B. Rosen, in *International Tables of Selected Constants 17: Spectroscopic Data Relative to Diatomic Molecules* (Pergamon, New York, 1970), p. 424; P. H. Krupenie, *J. Phys. Chem. Ref. Data* **1**, 423 (1972).
5. We appreciate the efforts of Dr. D. Albritton in calculating the Franck-Condon factors for this band system.
6. J. W. Chamberlain, *Astrophys. J.* **121**, 277 (1955); *ibid.* **128**, 713 (1958).
7. C. A. Barth and J. Kaplan, *J. Mol. Spectrosc.* **3**, 583 (1959); H. P. Broida and A. G. Gaydon, *Proc. R. Soc. Ser. A London* **22**, 181 (1954).
8. For a review of the martian atmosphere, see C. A. Barth, *Annu. Rev. Earth Planet. Sci.* **2**, 333 (1974).
9. C. A. Barth, C. W. Hord, A. I. Stewart, A. L. Lane, M. L. Dick, G. P. Anderson, *Science* **179**, 795 (1973).
10. B. C. Murray, M. J. S. Belton, G. E. Danielson, M. E. Davies, D. Gault, B. Hapke, B. O'Leary, R. G. Strom, V. Suomi, N. Trask, *ibid.* **183**, 1307 (1974).
11. We appreciate receiving preprints of the Venera data. Our analysis was supported under NASA grant NGL 06-003-052.

27 August 1976