cularly polarized appears in the literature. The existence of a new dimension in animal communication cannot be excluded.[8,9]

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(3) (a) In order to perform the chemiluminescence experiments at temperature *T* a cell was constructed to meet three main requirements: (i) sample should reach temperature *T* rapidly, (ii) *T* must be constant during the measurement, (iii) large optical aperture. Essentially the cell consists of a massive copper block, electrically heated, containing a small cylindrical hole covered with a suprasil plate. After the cell is brought slowly to temperature *T*, the sample is injected. (b) Detection system: monochromator (Spex Minimate), bandwidth 5 nm; photomultiplier (EMI 6256B). (c) Average of the measurements. Time constant 30 s. To exclude artifacts, it was verified that ΔI is zero in the chemiluminescence of the optically inactive adamantylideneadamantane-1,2-dioxetane: J. H. Wieringa, J. Strating, H. Wynberg and W. Adams, *Tetrahedron Lett.*, 169 (1972).

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Direct Measurement of the Lifetimes of the $^3B_1$ State of Sulfur Dioxide in Air at Atmospheric Pressure

Sir:

To date, the lifetime and rates of quenching of SO_2 phosphorescence by various gases have been measured at pressures lower than 20 Torr.[1-5] It has generally been assumed that a linear, Stern–Volmer, extrapolation of the low pressure data would yield reasonable values for the quenching of the triplet SO_2 species under atmospheric conditions. We report here direct measurements of the lifetimes of SO_2 phosphorescence in air which show that the lifetime of the $^3B_1$ state is longer than expected from extrapolation of low pressure data to atmospheric conditions.

The lifetimes were measured using a single photon counting instrument. The details of the apparatus are described elsewhere.[6] Excitation was into the excited singlet state of SO_2 at 3159 Å. The phosphorescence emission was isolated from scattered exciting light and cell emission by an interference filter. Emission spectra obtained over the pressure range of lifetime measurements were found to be identical with those previously attributed[2] to the $^3B_1$ state of SO_2.

Low intensity prohibited the measurement of accurate lifetimes in air for SO_2 pressures below 20 Torr. This necessitated obtaining data as a function of SO_2 pressure to permit an extrapolation to the low pressures of SO_2 which are of atmospheric interest. One set of experiments involved a constant 760 ± 10 Torr of dried laboratory air, a second set involved 745 ± 10 Torr of dried air with 15 Torr of water vapor added, and a third set involved 600 ± 10 Torr of dried laboratory air. In each of the above the SO_2 pressure was varied between 20 and 300 Torr. In a final set of experiments the water vapor pressure was varied from 0 to 20 Torr while the SO_2 pressure was maintained at 130 Torr and the pressure of dried air was maintained at 760 ± 10 Torr. In all cases the laboratory air was dried by passage through a dry ice trap. The pressure and lifetime measurements were made at temperatures of 24 ± 2 °C.

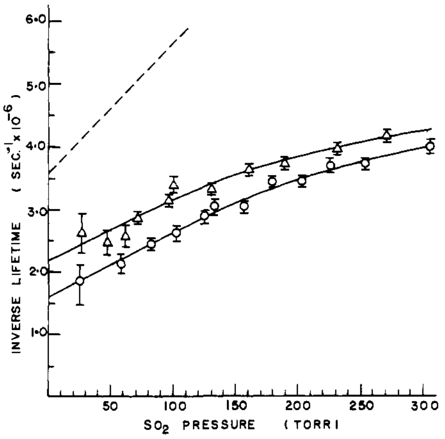

Figure 1. Phosphorescence decay rate of SO_2 in air. Circles are in 760 Torr of dry air; triangles are in 745 Torr dry air plus 15 Torr of water vapor. The dashed line shows values calculated from low pressure rate constants.[5]

The rates of phosphorescence decay are plotted as a function of SO_2 pressure for the first two sets of data in Figure 1. The extrapolated low pressure SO_2 phosphorescent lifetime in 760 Torr of dry air is $(6.3 \pm 0.3) \times 10^{-7}$ s, and the lifetime in 760 Torr of air containing 15 Torr of water vapor is $(4.5 \pm 0.3) \times 10^{-7}$ s. For comparison, the dashed line shows the decay rates calculated for 760 Torr of dry air by extrapolation of the low pressure data of Calvert and co-workers[5] assuming Stern–Volmer behavior. Clearly, the observed lifetime is about twice as long as would be expected from low pressure data.

For the sake of clarity, the last two sets of data are not included in Figure 1. The decay rates in 600 Torr of dry air are uniformly slightly lower than in 760 Torr. The extrapolated lifetime at low SO_2 pressure is $(7.1 \pm 0.3) \times 10^{-7}$ s. This represents an 11% decrease in decay rate for a 21% decrease in the air pressure. Thus the air pressure dependence of the lifetime is about half as great as that predicted from Stern–Volmer behavior. When the water vapor pressure was varied holding the SO_2 and air pressure constant, a water quenching rate of $(6.9 \pm 1.4) \times 10^8$ L mol^{-1} s^{-1} was obtained. This is quite close to the value of $(8.9 \pm 1.2) \times 10^8$ L mol^{-1} s^{-1} obtained by Calvert and co-workers[5] at low pressures.

The lifetime of the $^3B_1$ state of SO_2 in air is longer than expected because quenching of this state by many gases shows strong deviations from Stern–Volmer behavior. In particular, inert gases like N_2 and CO_2 quench by collision induced intersystem crossing to the ground state, and this process is found to saturate at high pressures, with the lifetime becoming independent of quencher gas pressure. Quenching by SO_2 itself partially saturates. The effects of O_2 and H_2O are more complicated; quenching by O_2 at least does not appear to saturate. To our knowledge, this is the first report of pressure saturation of intersystem crossing in gases. Deviations of quantum yields at high pressures have been observed by other workers,[7,8] but were interpreted in other ways. Pressure saturation of intersystem crossing has been predicted theoretically.[9] Our observations have important theoretical consequences, and the details will be discussed elsewhere. The purpose of the present note is only to present the lifetimes which should be useful in studying the photochemistry of SO_2 in the atmosphere.

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A Quadruply Hydrogen-Bridged Metal-Metal Bond. The Neutron Diffraction Analysis of $H_8Re_2(PEt_2Ph)_4$

Sir:

While investigating the chemistry of rhenium polyhydride complexes of the type H_7ReL_2 (L = tertiary phosphine), Chatt and Coffey noticed in 1969 that these unusual compounds often decomposed in solution to give a red crystalline product which they formulated as $[H_xReL_2]_2$.[1] This product was called a rhenium agnohydride complex because of the unknown number of hydrogen atoms in the molecule. In this communication we report an x-ray and neutron diffraction analysis of the structure of this compound (with L = PEt_2Ph), which gives a value of $x = 4$, or eight hydrogen atoms per dimeric unit. We also discovered in this compound the unprecedented feature of a metal-metal bond (formally a triple bond) bridged by *four* hydrogen atoms.

$H_8Re_2(PEt_2Ph)_4$ [octahydridotetrakis(diethylphenylphosphine)dirhenium(IV)] was prepared in the manner of Chatt and Coffey[1] and recrystallized as deep-red bricks from *n*-hexane. A small crystal was selected for x-ray analysis and larger ones were grown for neutron diffraction work. The compound crystallizes in the monoclinic space group $C2/c$, with $a = 23.309$ (7), $b = 12.353$ (4), $c = 19.634$ (6) Å, $\beta = 129.38$ (1)°, $Z = 4$, ρ(calcd) = 1.59 g cm^{-3}, ρ(obsd) = 1.60 g cm^{-3}. X-ray data were collected at room temperature on a Nonius CAD-3 diffractometer with Mo Kα radiation up to a $(\sin \theta/\lambda)$ limit of 0.54 Å^{-1}. The x-ray analysis yielded the positions of all the nonhydrogen atoms in the molecule, and revealed the skeleton of the molecule as a planar, ethylene-like Re_2P_4 fragment with a rather short Re-Re distance [2.538 (4) Å]. The final agreement factors for the x-ray data are R_F = 0.053 and R_{wF} = 0.057 for 2367 reflections with $I > 2\sigma$; R_F = 0.061 and R_{wF} = 0.061 for all data (2557 reflections).[2]

The subsequent neutron diffraction analysis was carried out on a crystal of volume 5.0 mm^3 at the Brookhaven high flux beam reactor.[3a,b] Data were collected up to a $(\sin \theta/\lambda)$ limit of 0.62 Å^{-1} with neutrons of wavelength 1.1598 Å. Because of the lower temperature used in the neutron data collection (80.0 ± 0.5 K), the unit cell is slightly smaller than that found in the x-ray study: $a = 23.137$ (7), $b = 12.276$ (4), $c = 19.438$ (5) Å, $\beta = 129.51$ (2)°. The Re, P, and C positions derived from the x-ray analysis were used to phase the neutron data, and a subsequent difference-Fourier synthesis revealed the positions of the hydrogen atoms in the molecule. After full-matrix least-squares refinement (in which the parameters were divided into two blocks),[3c] the final agreement factors[2] stand at R_{F^2} = 0.117 and R_{wF^2} = 0.098 for all data (3565 reflections); R_F = 0.086 and R_{wF} = 0.049 for data with $I > 2\sigma$ (2729 reflections). The observation/parameter ratio for all data is 6.9.

Table I. Selected Distances and Angles in $H_8Re_2(PEt_2Ph)_4$[a]

Distances (in Å)			
Re–Re′	2.538 (4)	H(3)···H(4)	3.005 (8)
Re–P(1)	2.336 (4)	Re–P(2)	2.333 (5)
Re–H(1)	1.882 (7)	Re–H(2)	1.885 (7)
Re–H(1)′	1.862 (7)	Re–H(2)′	1.883 (8)
Re–H(3)	1.682 (7)	Re–H(4)	1.656 (6)
H(1)···H(2)	2.042 (8)	H(1)···H(2)′	1.870 (8)
H(1)···H(3)	2.323 (11)	H(2)···H(3)	2.317 (11)
H(1)′···H(4)	2.280 (10)	H(2)′···H(4)	2.333 (11)
H(1)···H(1)′	2.752 (8)	H(2)···H(2)′	2.785 (8)
Angles (in Degrees)			
Re′–Re–P(1)	129.2 (1)	Re′–Re–H(3)	115.4 (3)
Re′–Re–P(2)	128.0 (1)	Re′–Re–H(4)	116.3 (3)
P(1)–Re–P(2)	102.7 (2)	H(3)–Re–H(4)	128.3 (4)
H(1)–Re–H(1)′	94.6 (3)	H(2)–Re–H(2)′	95.3 (3)
H(1)–Re–H(2)	65.6 (3)	H(1)–Re–H(2)′	59.6 (3)
Re–H(1)–Re′	85.4 (3)	Re–H(2)–Re′	84.7 (3)
H(1)···H(2)···H(1)′	89.3 (3)	H(2)···H(1)···H(2)′	90.7 (3)

[a] The values in this table are those derived from the neutron diffraction analysis. For comparison, some corresponding x-ray values are Re–Re′ = 2.530 (1), Re–P(1) = 2.340 (5), Re–P(2) = 2.327 (5) Å, Re′–Re–P(1) = 129.6 (2), Re′–Re–P(2) = 127.7 (1), P(1)–Re–P(2) = 102.6 (2)°.

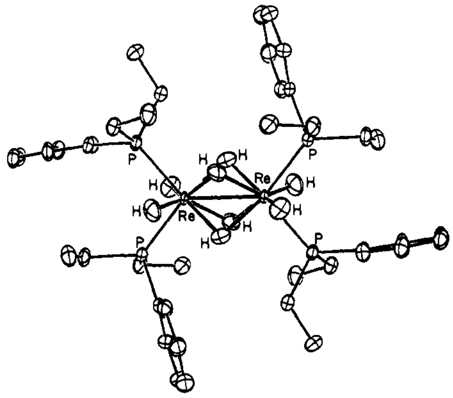

Figure 1. The molecular geometry of $H_8Re_2(PEt_2Ph)_4$, with the hydrogen atoms of the ethyl and phenyl groups removed for clarity. Thermal ellipsoids correspond to 50% probability.

The molecular geometry is depicted in Figures 1 and 2, and selected distances and angles are given in Table I. A crystallographic center of symmetry situated mid-way between the Re atoms relates the two halves of the molecule to each other. The core of the molecule consists of four bridging hydrogen atoms tightly clustered around the rhenium-rhenium bond, at an average distance of 1.38 Å from the center of this bond. These four hydrogen atoms define a distorted square, with one side ~9% longer than the other [2.042 (8), 1.870 (8) Å]. The quartet of hydrogen atoms is essentially normal to the Re-Re bond and is required to be planar by crystallographic symmetry. The other four hydrogen atoms are terminal, with two on each metal. The terminal H_2P_2 units and the bridging H_4