



# Emission of Light during the Oxidation of Hydrogen Sulfide

J. N. Bradley and D. C. Dobson

Citation: The Journal of Chemical Physics **47**, 1555 (1967); doi: 10.1063/1.1712119 View online: http://dx.doi.org/10.1063/1.1712119 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/47/4?ver=pdfcov Published by the AIP Publishing

# Articles you may be interested in

Controllable atomistic graphene oxide model and its application in hydrogen sulfide removal J. Chem. Phys. **139**, 194707 (2013); 10.1063/1.4832039

Exoelectron emission during oxidation of Cs films J. Chem. Phys. **95**, 3756 (1991); 10.1063/1.460826

Oxidation of Hydrogen Sulfide in Shock Waves. II. The Effect of Added Hydrogen on the Absorption of OH and SO2

J. Chem. Phys. 46, 2872 (1967); 10.1063/1.1841146

Ultraviolet Light Emission from Townsend Discharges in Hydrogen J. Appl. Phys. **36**, 743 (1965); 10.1063/1.1714212

Observation of a Separation of the Emission Light during Plasma Injection Phys. Fluids **6**, 311 (1963); 10.1063/1.1706733



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.82.252.58 On: Tue, 23 Dec 2014 02:15:48



FIG. 1. (a) Proton resonance signals of bulk and complexed water molecules in a solution containing 1 mole of  $AlCl_3$  and 18 moles of water. (b) Appearance of the signal arising from the waters of hydration in the same solution, as a function of temperature.

of the fact that Connick and Fiat,<sup>8</sup> by an <sup>17</sup>O NMR study, measured a value of 11 kcal for  $\Delta H^{\ddagger}$  for the exchange of entire water molecules from the solvation shell of Ni(II). The kinetic data in Table I depend critically on  $\delta_0$ , which in turn is affected by the viscosity of the medium and possibly by the interaction of the solvating water molecules with the nuclear quadrupole of Al(III). Thus, although  $\Delta H^{\ddagger}$  was measured with a precision of about 15%, the accuracy of the value of 24 kcal remains doubtful at the present time. A refinement of the experimental techniques to include a consideration of all parameters is now underway. Further, proton magnetic resonance coordination numbers and kinetic studies of a wide variety of metal ions in water and in aqueous solvent mixtures are being conducted.

This work was supported by Grant No. 14-01-0001-762 from the Office of Saline Water, U. S. Department of the Interior.

<sup>1</sup> J. A. Jackson, J. R. Lemons, and H. Taube, J. Chem. Phys. **32**, 553 (1960). <sup>2</sup> R. E. Connick and D. N. Fiat, J. Chem. Phys. **39**, 1349 (1963). <sup>3</sup> R. E. Connick and D. N. Fiat, J. Chem. Phys. **44**, 4403 (1966). <sup>4</sup> D. N. Fiat and R. E. Connick, J. Am. Chem. Soc. **88**, 4754 (1966).

#### Notes

## Emission of Light during the Oxidation of Hydrogen Sulfide

J. N. BRADLEY AND D. C. DOBSON

Department of Chemistry, University of Essex, Colchester, England (Received 9 March 1967)

During a study of the oxidation of hydrogen sulfide in shock waves,<sup>1</sup> the emission of light was observed. In order to determine the nature of the excited species responsible, the emission from 32 successive reflected shocks in 2% H<sub>2</sub>S, 3% O<sub>2</sub>, and 95% Ar mixtures, at a temperature of ~4000°K, was superimposed on a single plate using a Hilger E517 quartz spectrograph. The spectrum consisted of a series of broad bands on a continuum background. The bands in the range 2760– 2409 Å with heads at 2750, 2725, 2625, 2584, 2550, 2525, and 2409 Å were attributed to SO<sub>2</sub><sup>2</sup> and lines at 3945, 3810, 3503, 3428, 3270, 3245, 3166, 3051, 2961, and 2748 Å were identified as belonging to the spectrum of SO.<sup>2,3</sup> No evidence for SH, S<sub>2</sub>, or other molecular species was obtained.

The emission from incident shock waves was investigated by simultaneously isolating two wavelength regions using a Hilger D323 monochromator with vitreous silica optics and a Hilger D285 monochromator with quartz optics. The signals were detected by E.M.I. 9526B photomultipliers, the outputs being displayed on oscilloscopes and the traces recorded photographically. Identical time-dependent behavior was observed at all wavelengths in the range 2100–5500 Å indicating that the emission spectrum is primarily a continuum.

The variation of peak intensity with wavelength was obtained by comparing the output in each region with that from a simultaneous measurement at 2800 Å, correcting as far as possible for the change in sensitivity of the photomultipliers and in transmission of the quartz optics at different wavelengths. The resulting envelope



FIG. 1. Comparison of the induction-time-vs-temperature relations for OH absorption (A); SO<sub>2</sub> absorption (B); and light emission (C).

showed a broad maximum lying between 2600 and 3400 A. If the luminous gas were assumed to behave as a blackbody source, the corresponding temperature would lie in the range 8500-11 000°K. Although some fluctuations were observed in the time dependence of the emission, it is unlikely that the emission is due to solid particles. The emission spectrum appeared to correspond very closely to spectra observed from shock-heated sulfur dioxide,4 from flash photolysis of H<sub>2</sub>S-O<sub>2</sub> mixtures,<sup>5</sup> and from luminescence associated with the recombination of SO and O.6 The emission is therefore attributed to excited states of  $SO_2$ , both <sup>3</sup>B and  ${}^{1}B$  states probably contributing.

The light could be detected only after an induction period, the duration of which was measured by isolating the wavelength region 3900 to 2850 Å using a Kodak 18A filter. For 4% H<sub>2</sub>S, 6% O<sub>2</sub>, and 90% Ar mixtures, over the temperature range 1660-2535°K, the induction time was best represented by the relation

 $\tau(\text{sec}) = 10^{-6.02} \exp(22.09 \pm 1.64 \text{ kcal}/RT).$ 

Comparison of this relation with the results of the previous work (Fig. 1) shows that the  $SO_2$  emission appears after the appearance of  $SO_2$  in absorption but before the appearance of OH in absorption.

In the studies on direct shock heating of  $SO_2$ ,<sup>4</sup> no significant time lag was reported, and it is therefore suggested that the emission is not due to direct thermal excitation of ground-state SO<sub>2</sub> formed during the reaction but that excited SO<sub>2</sub> is produced by a different mechanism. The ground state molecule is probably formed by the reaction

$$SO+O_2 \rightarrow SO_2+O_2$$

and the most likely alternative, which is also believed to be responsible for the appearance of a similar spectrum in the flash-photolysis studies,<sup>5</sup> is

$$SO+O\rightarrow SO_2^*$$
.

This would seem to imply that the induction-time measurements refer to a steep rise in the product of the SO and O concentrations. Qualitatively, this interpretation is probably allowed by the mechanism for the oxidation proposed previously,<sup>1</sup> although it can only be confirmed when the rate constants for the individual steps have been determined.

<sup>1</sup> J. N. Bradley and D. C. Dobson, J. Chem. Phys. 47, 2865

<sup>1</sup> J. N. Bradley and D. C. Dobson, J. Chem. Phys. 47, 2865 (1967).
<sup>2</sup> E. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra* (Chapman and Hall, London, 1963), 3rd ed.
<sup>3</sup> J. J. McGarvey and W. D. McGrath, Proc. Roy. Soc. (London) A278, 490 (1964).
<sup>4</sup> B. P. Levitt and D. B. Sheen, J. Chem. Phys. 41, 584 (1964); Trans. Faraday Soc. 61, 2404 (1965).
<sup>6</sup> R. G. W. Norrish and A. P. Zeelenberg, Proc. Roy. Soc. (London) A240, 293 (1957).
<sup>6</sup> A. G. Gaydon, Proc. Roy. Soc. (London) A146, 901 (1934);

 <sup>6</sup> A. G. Gaydon, Proc. Roy. Soc. (London) A146, 901 (1934);
 <sup>7</sup> C. J. Halstead and B. A. Thrush, Nature 204, 992 (1964); Photochem. Photobiol. 4, 1007 (1964); B. A. Thrush, Chem. Brit. 2, 005 (1964); 287 (1966).

#### Nonintegral Elliptical Orbital Studies on LiH

### JAMES R. HOYLAND Battelle Memorial Institute, Columbus, Ohio (Received 13 April 1967)

It has been recently suggested<sup>1</sup> that the use of a basis set written in elliptical coordinates and including nonintegral powers of the coordinate  $\xi$  may have some advantages in convergence over the usual integral elliptical orbitals for diatomic molecule calculations. Studies carried out on H<sub>2</sub>+, H<sub>2</sub>, and HeH+1 indicate that this speculation may be valid for these small systems, but the improvement brought about by the use of such nonintegral powers was of little significance in some cases. Therefore, calculations have been carried out on the ground state of LiH in an attempt to ascertain whether or not worthwhile improvements in the energy can be obtained through introduction of these nonintegral powers.

The functional form of the orbitals employed is

$$(n, m, \delta, \zeta) = \xi^n \eta^m \exp(-\delta \xi - \zeta \eta).$$
 (1)

Hartree-Fock-Roothaan calculations<sup>2</sup> have been carried out using a basis of four, five, or six functions utilizing both integral and nonintegral values of n at an internuclear separation (R) of 3.00 bohrs. An additional six-basis integral n calculation was also performed at R=3.02 bohrs. In all of these calculations two orbitals are employed for the representation of the Li inner shell while the remaining functions serve mainly to describe the bonding orbital. An open-shell valencebond calculation of the type carried out by Harris and Taylor<sup>3</sup> and using a single configuration was also made at R = 3.00.

The energy results are summarized in Table I along with the computed values of the dipole and quadrupole moments. It is evident from inspection of these results that the use of nonintegral values of n has only a small

TABLE I. Values of the energy, dipole and quadrupole moments.

Basisª	R	Туреь	Energy <sup>c</sup>	Dipole <sup>d</sup> moment	Quadrupoleº moment
4	3.00	SCF. I	-7.98224	-6.039	-4.961
4	3.00	SCF. N	-7.98305	-6.050	-4.954
5	3.00	SCF, I	-7.98712	-5.994	-4.500
5	3.00	SCF, N	-7.98719	-5.993	-4.465
6	3.00	SCF, I	-7.98722	-6.012	-4.504
6	3.00	SCF, N	-7.98724	-6.009	-4.497
6	3.02	SCF, I	-7.98725	-6.035	-4.537
4	3.00	VB, I	-8.00416	-5.933	-4.871
4	3.00	VB, <i>N</i>	-8.00525	-5.937	-4.896

<sup>a</sup> Number of basis functions used in the calculation.

<sup>b</sup> Type of calculation (I denotes an integral basis, N a nonintegral basis).

<sup>e</sup> Energy in hartrees.

<sup>d</sup> Dipole moment in debyes.

<sup>e</sup> Quadrupole moment in units of 10<sup>26</sup> esu · cm<sup>2</sup>.