

Dual Photon Emission from the Chemiluminescent SO+O Reaction

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density and η the viscosity. The quantity $\langle A_{11}^* \rangle$ is a ratio of collision integrals (essentially the ratio of the viscosity and diffusion cross sections) and is quite insensitive to temperature and the details of the intermolecular force law. Thus, the above equation yields D_{11} from experimental viscosity which is effectively independent of any molecular model. Diffusion coefficients calculated by this method are only slightly lower than the other values below 326.4°K, and are in excellent agreement above this temperature.

This research was undertaken to test the ability of current theory to predict the diffusion coefficient of polar gases. For the case of highly polar ammonia over the indicated temperature range, the above results demonstrate that the theory is indeed adequate.

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Dual Photon Emission from the Chemiluminescent SO + O Reaction*

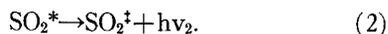
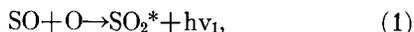
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The nitric oxide-oxygen atom reaction has been studied extensively over the last years¹ and clear evidence has been published that the light emission produced at low pressures is the result of a two-body collisional process.² Due to the complex nature of the reaction, however, there still is some dispute in the literature. The analogous mechanism for the reaction of SO and O to produce light emission is generally accepted.³ In this paper evidence is presented that not one, but two photons are emitted in the SO+O reaction. Similar dual photon emission due to excited atoms is well known.⁴

The present results can be explained in terms of the following steps:



That is, a primary reaction involving the formation of SO₂ in an excited state with the loss of part of the energy of recombination due to photon emission followed by emission of the second photon from the excited state (SO₂^{*}), to a lower level (SO₂[†]) near the ground state.

The chemiluminescence was produced using either CS₂ or COS reacting with O atoms in a flow system at

about 40 mtorr total pressure. Part of the flow was bypassed through a 4 mm i.d. Pyrex tube. A small section of this tube was between two 8575 RCA photomultipliers used as detectors. Each photon observed, produced a low amplitude fast pulse. The pulse output at the anode was amplified by a LeCroy 133 linear amplifier and directcoupled to a LeCroy 161 dual discriminator. The negative output pulses from the 161 discriminators were counted using Canberra 1492 scalers to obtain the single pulse rate from each photomultiplier. The positive outputs of the discriminators were coupled to a Canberra 840 coincidence analyzer where the output coincidence pulses were counted using a Canberra 871 scaler. Counting intervals were set via a Canberra 890 scaler/timer by the use of a gating pulse. The accidental coincidence rate using a light bulb was used to measure the resolving time of the coincidence circuit for various control settings. Most experiments were performed under conditions where approximately 10⁶ counts/min were counted by each singles scaler. At this level an accidental coincidence rate of 833 counts/min, for example, corresponded to a resolving time of 25 nsec. With no light of any kind the random background pulses yielded a 5 counts/min coincidence.

The SO+O reaction produced dual photon emission observed as net coincidence counts above the accidental background rate. The ratio of this dual emission to background was found to decrease as resolving time increases. From this the average half-life time for the excited SO₂^{*} species was determined to be 3(±1) × 10⁻⁸ sec.

The dual photon emission is estimated to be at least 10% of the total. A more precise determination is precluded at present by the limitations of geometry, spectral response, and counting efficiencies of the photomultipliers. This dual emission also is compatible with the absorption spectrum, the fluorescence⁵ and the emission spectrum⁶ of SO₂.

Using the present arrangement such dual emission could not be seen from NO+O reaction. The total energy of the two photons emitted from such a reaction cannot have an energy exceeding the exothermicity of the reaction, but may be somewhat less. The SO+O reaction is 5.6 eV exothermic⁷ and if each photon would have the half, this would correspond to a wavelength of 4400 Å. If one photon is of higher energy, the second must be lower. In this study the 8575 RCA photomultiplier tubes used were sensitive from the uv region to about 6000 Å. Therefore many combinations of energy for the two quanta could be counted. However, the reaction of NO+O→NO₂ is 3.1 eV exothermic⁸ and half would be 1.5₅ eV (~7900 Å) and could not be expected to be observed with these tubes. Indeed no coincidence effect above the accidental rate was found for the NO+O reaction, nor for the SO+O reaction if filters were used where the observed spectral region corresponded only to energies greater than 3.5 eV,

The authors would like to thank Prof. Paul Harteck for many helpful comments and suggestions.

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Vanadium-51 Quadrupole Coupling Constants in Solid Vanadium Oxytrihalides*

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I have used ⁵¹V nuclear magnetic resonance of polycrystalline VOCl₃ and VOF₃ to determine the ⁵¹V quadrupole coupling constant (eQq) in these compounds. The results are given in Table I, with other known ⁵¹V eQq values. The NMR measurements were made at -106°C for VOCl₃ and 28°C for VOF₃, on a Varian variable-frequency wide-line NMR spectrometer, at 9.798 and 15.6 MHz. The observed derivative of the absorption spectrum of VOCl₃ at 15.6 MHz is shown in Fig. 1. It is a typical second-order powder pattern for the case of a small or zero asymmetry parameter (η).¹⁻⁴ The total width of the VOF₃ spectrum at 15.6 MHz is much larger, and each peak is also very broad. The absorption signals at 9.798 MHz were too weak to use. In the dispersion mode a useful signal was obtained from VOCl₃ but not from VOF₃, due to partial overlap with a ²⁷Al signal from the Varian probe. Since there were not enough data to use the extrapolation method suggested by Casabella,⁵ the ⁵¹V eQq of VOCl₃ was evaluated at each frequency, with no detectable difference in the two results.

As expected for large eQq , only the second-order powder patterns were observed. A large field sweep revealed no first-order satellites.

TABLE I. Vanadium-51 quadrupole coupling constants.*

Compound	eQq (MHz) ^b	η	Reference
VOF ₃	8.9 ± 0.4	≤ 0.4	This work
VOCl ₃	5.4 ± 0.2	≤ 0.2	This work
VO ₂	6.86 ± 0.14	0.49 ± 0.02	c
KVO ₃	4.36 ± 0.06	0.75 ± 0.10	d
NaVO ₃	3.65 ± 0.06	0.60 ± 0.10	d
V ₃ Si	2.924 ± 0.015	≈ 0	e
NH ₄ VO ₃	2.88 ± 0.06	0.3 ± 0.10	d
C ₇ H ₇ V(CO) ₃ ^f	$2.0 \pm 0.5^*$		h
V ₂ O ₅	0.805	0.04	i

* Nearly all known ⁵¹V quadrupole coupling constants are listed. Some intermetallic systems are omitted.

^b Unless otherwise stated, these are "room-temperature" values, measured in the solid. For the oxytrihalides, see text.

^c Reference 4, p. 2723. See also J. Umeda, H. Kusumoto, K. Narita, and E. Yamada, J. Chem. Phys. **42**, 1458 (1965). There is a typographical error in the definition of the function νQ in Ref. 4. The correct definition is given in Ref. 1, Eq. (8.4).

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^f π -Tropyliumvanadium (-I) tricarbonyl.

^g Indirectly determined in solution, from the ⁵¹V spin-lattice relaxation time (which was also obtained indirectly from proton NMR line shapes). The main uncertainty here is the value of the rotational correlation time in the liquid, which was estimated. An error larger than stated is quite possible.

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Known equations¹ were used in the data analysis. I assumed that $\eta=0$, but the effect of this assumption on the accuracy of eQq was evaluated, as was the upper limit to η (see Table I). The main effect of $\eta \neq 0$ on the derivative of the second-order powder pattern is to split each of the two peaks.²⁻⁴ Other effects, such as ⁵¹V-¹⁹F dipolar coupling, may broaden the lines enough to prevent resolution of the splitting so that the spectrum will have the appearance of one with $\eta=0$. One can estimate the upper limit for η and the error in eQq by assuming that the width of each of the two peaks in

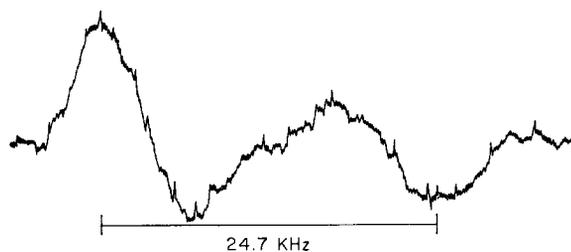


FIG. 1. Vanadium-51 NMR spectrum of solid VOCl₃ at -106°C , taken at 15.6 MHz in the derivative absorption mode using magnetic field sweep, increasing from left to right. Other instrumental parameters: 80-Hz audio modulation frequency; about 4-G peak-to-peak modulation amplitude; about 1-G/min sweep speed; 50-sec output time constant; very low rf level (50 μA on transmitter rf field indicator of V-4210A unit); about 8-mm sample diameter.