Calculation of Absolute Concentrations of SH and SO from their E.S.R. Spectra

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Transition probabilities have been calculated for several lines in the gas phase, X-band e.s.r. spectra of SH and SO, and the results of the calculations have been used to estimate the absolute concentration of the two free radicals in the gas phase. The concentration of SO obtained in this manner has been compared with the results of experimental measurements that were made by titrating mixtures of SO and atomic oxygen with nitrogen dioxide. During the course of this study, the relative rate constants for reactions (a) and (b) were measured:

$$NO_2+O\xrightarrow{k_a}NO+O_2, \qquad (a)$$

$$NO_2+SO\xrightarrow{k_b}NO+SO_2. \qquad (b)$$

k_a/k_b was estimated as 0.63 ± 0.06.

Van Vleck and Weisskopf[1] have shown that for a pressure-broadened non-saturated microwave transition the imaginary part of the susceptibility is given by the expression:

$$\chi''_{ij} = \omega/kT \mid \mu_{ij} \mid^2 f(\omega-\omega_0)\,(N/Z)\exp(-E_i/kT), \qquad (1)$$

where $f(\omega-\omega_0)$ is the normalized line shape, μ_{ij} is the matrix element of the transition dipole between the states i and j, N is the number of absorbing molecules in the sample, Z is the partition function and E_i is the energy of the absorbing state i relative to the ground state of the molecule. The total integrated absorption is $\int_0^\infty \chi''_{ij}\mathrm{d}\omega$.

In conventional electron spin resonance experiments, the magnetic field H is swept rather than the angular frequency ω and the above expression must be transformed using the relationship,[2]

$$f(\omega-\omega_0) = (\hbar/g_{\mathrm{eff}}\beta)f(H-H_0), \quad \text{where} \quad g_{\mathrm{eff}} = \hbar/\beta(\mathrm{d}\omega_0/\mathrm{d}H_0) \qquad (2)$$

to give, after integrating, the following expression for the integrated absorption,

$$\int_0^\infty \chi''_{ij}\,\mathrm{d}H = (\hbar/g_{\mathrm{eff}}\beta)(\omega_0/kT) \mid \mu_{ij} \mid^2 (N/Z)\exp(-E_i/kT). \qquad (3)$$

The total integrated absorption may be calculated if g_{eff}, Z, E_i and μ_{ij} are known.

^{32}SH INTENSITY

The SH radical has an inverted $^2\pi$ ground state, i.e., the lowest level $J = \frac{3}{2}$ of $^2\pi_{\frac{3}{2}}$ lies below the lowest level $J = \frac{1}{2}$ of $^2\pi_{\frac{1}{2}}$, and its angular momentum coupling scheme is intermediate between Hund's case (a) and (b). The electron resonance spectrum of SH has been recorded and partially analyzed by McDonald[3] and by Radford.[4] They observed electric dipole transitions between opposite members of the Λ doublet within the lowest rotational level of the $^2\pi_{\frac{3}{2}}$ state. The spectrum consists of two groups of lines. One group at approximately 7650 G consists of $2J(2I+1) = 6$ lines of the type $\Delta m_J = 1$, $\Delta m_I = 0$, $+\rightarrow-$ with $I = \frac{1}{2}$ for H. The other group occurs at 190 G lower field and consists of the equivalent set of $-\rightarrow+$ transitions. These lines are listed in table 1.

TABLE 1.—TRANSITIONS IN THE E.S.R. SPECTRUM OF SH ($^2\pi_{\frac{3}{2}}$, $J = \frac{3}{2}$) IN ORDER OF DECREASING MAGNETIC FIELD. FIELD MEASUREMENTS WERE MADE AT A FREQUENCY OF 8850 MHz.

line	transition				field (G)
	$m_J m_I \rightarrow m_J+1\, m_I$				
(*a*)	$-\frac{3}{2}$	$\frac{1}{2}\rightarrow$	$-\frac{1}{2}$	$\frac{1}{2}$	7665
	$-\frac{3}{2}$	$-\frac{1}{2}\rightarrow$	$-\frac{1}{2}$	$-\frac{1}{2}$	7659
(*b*)	$-\frac{1}{2}$	$-\frac{1}{2}\rightarrow$	$\frac{1}{2}$	$-\frac{1}{2}$	7646
	$-\frac{1}{2}$	$\frac{1}{2}\rightarrow$	$\frac{1}{2}$	$\frac{1}{2}$	7640
(*c*)	$\frac{1}{2}$	$-\frac{1}{2}\rightarrow$	$\frac{3}{2}$	$-\frac{1}{2}$	7625
	$\frac{1}{2}$	$\frac{1}{2}\rightarrow$	$\frac{3}{2}$	$\frac{1}{2}$	7620
(*d*)	$-\frac{3}{2}$	$\frac{1}{2}\rightarrow$	$-\frac{1}{2}$	$\frac{1}{2}$	7471
	$-\frac{3}{2}$	$-\frac{1}{2}\rightarrow$	$-\frac{1}{2}$	$-\frac{1}{2}$	7465
(*e*)	$-\frac{1}{2}$	$\frac{1}{2}\rightarrow$	$\frac{1}{2}$	$\frac{1}{2}$	7455
	$-\frac{1}{2}$	$-\frac{1}{2}\rightarrow$	$\frac{1}{2}$	$-\frac{1}{2}$	7450
(*f*)	$\frac{1}{2}$	$-\frac{1}{2}\rightarrow$	$\frac{3}{2}$	$-\frac{1}{2}$	7441
	$\frac{1}{2}$	$\frac{1}{2}\rightarrow$	$\frac{3}{2}$	$\frac{1}{2}$	7436

Doublets (*a*), (*b*) and (*c*) are $+\rightarrow-$ transitions. Doublets (*d*), (*e*) and (*f*) are $-\rightarrow+$ transitions.

Since the ground state of SH is inverted, E_i = zero and $\exp\{-(E_i/kT)\} = 1$. The partition function Z for a $^2\pi$ molecule which shows intermediate Hund's case (*a*)/(*b*) coupling is given by [5]

$$Z = 2(2I+1)\left[\sum_{J=\frac{1}{2}}^{\infty}(2J+1)\exp-\frac{E_j}{kT}+\sum_{J'=\frac{3}{2}}^{\infty}(2J'+1)\exp-\frac{E_{j'}}{kT}\right] \tag{4}$$

where E_J refers to the $^2\pi_{\frac{1}{2}}$ molecule and E_J to the $^2\pi_{\frac{3}{2}}$ state. The energy levels are given by the term values,[6]

$$E_J = B\{(J+\tfrac{1}{2})^2-\Lambda^2\pm\tfrac{1}{2}[4(J+\tfrac{1}{2})^2+\lambda(\lambda-4)\Lambda^2]^{\frac{1}{2}}\}, \tag{5}$$

where the + sign refers to $^2\pi_{\frac{1}{2}}$ and the − sign to $^2\pi_{\frac{3}{2}}$ state, $\Lambda = 1$ for π molecules, B is the rotational constant, A is the spin-orbit coupling constant and $\lambda = A/B$.

The electronic absorption spectra of SH has been analyzed by Ramsey.[7] He measured B as 9.461 cm^{-1}, A as -376.9 cm^{-1} and λ as -39.85. Using these values, Z was calculated as 113 by direct summation. g_{eff} has been measured [4] as 0.838.

The matrix elements of the electric dipole moment for transitions of the type $\Delta J = 0$ between the two members of a Λ doublet of a $^2\pi_{\frac{3}{2}}$ state slightly perturbed by a $^2\Sigma$ state have been derived by Dousmanis *et al.*[8] :

$$|\mu_{ij}|^2 = \frac{\mu^2\{\Omega_1^2(X-2+\lambda)^2+\Omega_2^2(X+2-\lambda)^2+2\Omega_1\Omega_2[X^2-(2-\lambda)^2]\}}{4X^2J(J+1)}, \tag{6}$$

where $\Omega_1 = \frac{1}{2}$, $\Omega_2 = \frac{3}{2}$, $X^2 = 4(J+\frac{1}{2})^2+\lambda(\lambda-4)$, and μ is the electric dipole moment, which for SH has been measured as 0.62 ± 0.06 D.[12] The derived expression applies to transitions between any particular m_j state of the initial level to all possible m_j states of the final level that are induced in three-dimensional isotropic radiation.

The application of this formula to particular $\Delta m_j = 1$ transitions induced in an e.s.r. cavity has been discussed by Westenberg.[9] For an e.s.r. transition from a state $|J,m_j\rangle$ to the state $|J, m_j+1\rangle$, the matrix element μ_{ij}^* is given by the expression

$$|\mu_{ij}^*|^2 = \frac{|\mu_{ij}|^2(2J+1)(J-m_j)(J+m_j+1)}{3\sum_{m_j=-J}^{J-1}(J-m_j)(J+m_j+1)}. \tag{7}$$

Upon substituting eqn (6) and (7) into (3) and evaluating the constants for SH, we have for each line of the doublets (*a*), (*c*), (*d*) and (*f*),

$$\int_0^\infty \chi_{ij}''(\mathrm{SH})\,\mathrm{d}H = 9{\cdot}83\times10^{-4}\,N_{\mathrm{SH}}\,h\,\frac{\omega_0}{kT\beta}. \tag{8}$$

In most experiments these doublets are unresolved and thus if χ_{ij}'' is integrated over one of these doublets, its value is twice that above. The integrated absorption for doublets (*b*) and (*e*) is $\frac{4}{3}$ times that for (*a*), (*c*), (*d*) or (*f*).

Westenberg[9] has discussed a method of estimating the concentration of free radicals by measuring the total integrated absorption of their e.s.r. spectra. The method utilizes nitric oxide as an internal standard. He has derived, for several radicals *R*, expressions of the form

$$\frac{N_{\mathrm{R}}}{N_{\mathrm{NO}}} = Q_{\mathrm{R}}\frac{\int_0^\infty \chi_{ij}''(\mathrm{R})\,\mathrm{d}H}{\int_0^\infty \chi_{ij}''(\mathrm{NO})\,\mathrm{d}H}, \tag{9}$$

where N_{R} is the number of radicals present, N_{NO} is the number of molecules of nitric oxide in the calibrating sample and $\int_0^\infty \chi_{ij}''(\mathrm{NO})\mathrm{d}H$ represents the integrated absorption measured for one line of the centre triplet of the NO spectrum at $g = 0.777$. If the expression for the integrated absorption of SH is cast in this form, $Q_{\mathrm{SH}} = 1.00\times10^{-2}$ for each line of the unresolved doublets (*a*), (*c*), (*d*) or (*f*), and equals 7.52×10^{-3} for each line of (*b*) or (*e*).

^{32}SO ($^3\Sigma$) INTENSITIES

The SO ($^3\Sigma$) molecule exhibits an angular momentum coupling scheme intermediate between Hund's case (*a*) and (*b*), but is usually described in terms of a Hund's case (*b*) basis, in which *JKS* and *M* are good quantum numbers. Its electron resonance spectrum has been completely analyzed,[10, 11] and consists, below 10 000 G, of four strong lines due to transitions of the type $JKM \rightarrow JK{+}1M$ where $J = J = 1$. These are listed in table 2.

TABLE 2.—TRANSITIONS IN THE *X*-BAND E.S.R. SPECTRUM OF ^{32}SO ($^3\Sigma$) THAT ARE OBSERVED BELOW 10 kG. THE FIELD IS GIVEN AT A SPECTROMETER FREQUENCY OF 8762 mHz. ^{32}S OCCURS ONLY IN 95 % ABUNDANCE IN NATURAL SULPHUR.

line	field	transition $JKM \rightarrow JK{+}1M$	$-g_{\mathrm{eff}}$	$\lvert\mu_{ij}\rvert^2$
g	2845 G	111→120	1.14	1.16×10^{-1}
h	4642 G	111→121	0.69	2.00×10^{-1}
i	5944 G	110→12-1	0.64	1.02×10^{-1}
j	9110 G	110→120	0.61	1.04×10^{-2}

The initial state of these transitions lies 10.7 cm^{-1} above the ground state, and thus at 300 K, exp $(-E_i/kT)$ can be calculated as 0.95. The partition function Z of the SO molecule at 300 K is, to the accuracy of these quantitative determinations (±5 %), $3\,kT/B$. $B_0 = 0.7179\ cm^{-1}$,[12] and therefore $Z = 871$. Values of g_{eff} can be calculated from the measurements of $d\nu/dH$ tabulated by Dorian and Daniels [10] and the dipole matrix elements are listed by Carrington.[11] Table 2 includes these data. For SO ($^3\Sigma$), the dipole matrix elements are functions of the magnetic field. This is most clearly seen by observing that line (*j*) is rigorously not allowed at zero magnetic field. In fact, the square of the dipole matrix elements for line (*j*) varies by 7 %, if calculated at fields equivalent to a microwave frequency of 8978 and 9375 MHz. However, the matrix elements for lines (*g*), (*h*) and (*i*) vary by less than 1 % as the lines are tuned over the normal X-band frequency range (8800-9600 MHz), and for these lines, Carrington's values, calculated for 8762 MHz are more than adequate.

One important feature of the SO spectra is that lines (*h*) and (*j*), being $\Delta M = 0$ transitions, are excited by the component of the microwave electric field vector that is parallel to the magnetic field, while lines (*g*) and (*i*) are excited by the components perpendicular to the field. Thus, only lines (*g*) and (*i*) should be compared to nitric oxide when it is used as an intensity standard since all of the NO transitions are of the type $\Delta M = 1$.

The electric dipole moment of SO ($^3\Sigma$) has been measured as 1.55±0.02 D.[12] Using this figure and the value of the constants calculated above, we obtain from eqn (3).

$$\frac{N_{\text{SO}}}{N_{\text{NO}}} = 3.68\times10^{-2}\frac{\int_0^\infty \chi''_{ij}(\text{SO})\,dH}{\int_0^\infty \chi''_{ij}(\text{NO})\,dH}\quad\text{for line } (g) \text{ of SO.} \tag{10}$$

The multiplication factor, Q_{SO}, is 1.28×10^{-2} for line (*h*), 2.33×10^{-2} for line (*i*), and 2.21×10^{-1} for line (*j*).

EXPERIMENTAL MEASUREMENT OF THE TRANSITION PROBABILITY FOR SO

When a 1-3 % mixture of SO_2 in argon is subject to microwave discharge, SO and atomic oxygen are produced. Both of these radicals are relatively stable and can be pumped over distances of several meters in a typical fast flow system. Nitrogen dioxide reacts rapidly with these radicals,

$$NO_2 + O \xrightarrow{k_a} NO + O_2 \tag{a}$$

$$NO_2 + SO \xrightarrow{k_b} NO + SO_2 \tag{b}$$

such that the total concentration of atomic oxygen plus SO can be estimated from an NO_2 gas " titration ".[13]

We have carried out the above titration in the apparatus described in a previous paper.[14] A 3 % mixture of SO_2 in argon was discharged in a microwave cavity situated 50 cm upstream of the e.s.r. cavity. The e.s.r. spectra of both atomic oxygen and SO were recorded and NO_2 was admitted to the gas stream through a movable probe situated 7-20 cm upstream of the cavity. The flow rate of NO_2, which was measured as described previously,[14] was slowly increased, and titration curves similar to those shown in fig. 1 were obtained. From such curves the total concentration of SO plus atomic oxygen at the probe could be obtained. Since similar results were obtained with the probe positioned 7 and 20 cm from the cavity, it was assumed that negligible radical concentration decay occurred within the flow tube and that the concentration at the probe represented the concentration at the e.s.r. cavity.

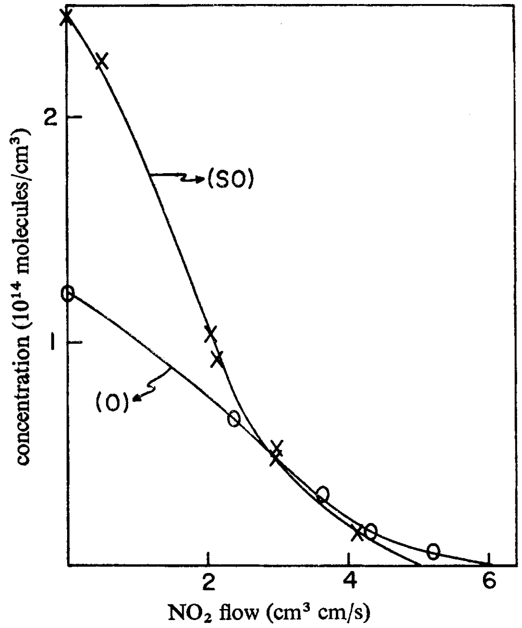

FIG. 1.—Titration of SO and O by NO_2.

The concentration of atomic oxygen, in the absence of NO_2, was measured from its e.s.r. spectrum using the calibration procedure described by Westenberg.[15] Molecular oxygen was used as a calibration standard and the double integrations that are required in this procedure were performed as described earlier.[14]

Table 3 shows the results of several titrations. Column 1 shows the sum of the concentrations of O and SO as determined from the NO_2 titration. The next column gives the O concentration as estimated by the procedure described above. Column 3 shows the experimental estimate of the SO concentration as given by the difference of the first two columns, while column 4 shows the SO concentration that was calculated from the SO spectrum line (*i*) assuming the transition probability to be that given in this paper. This estimate was made using nitric oxide as a calibrating intensity standard as described earlier. To within the experimental uncertainty which was estimated to be ±15 %, the experimental and calculated values of the SO concentration agree. This gives some confidence that the transition probabilities for SO are correct and useful. Unfortunately it does not constitute proof since

TABLE 3.—ALL CONCENTRATIONS ARE GIVEN IN UNITS OF 10^{14} molecules cm^{-3}.

[SO]+[O] from titration	[O] from integrated absorption	[SO] difference of column (1) and (2)	[SO] from integrated absorption
3.52	1.37	2.15	1.89
3.41	1.21	2.20	2.69
5.10	1.87	3.23	3.60
5.51	2.17	3.34	3.14
3.15	0.70	2.45	2.88
4.62	1.26	3.36	2.73

while it is certain that NO_2 does titrate SO and O, it is not certain that other species that react rapidly with NO_2 are totally absent from the products of the SO_2 discharge. However, it is unlikely that such products are present in concentrations that would affect this titration.[13]

Most of the integrated absorption measurements were made using line (*i*) of the SO spectrum. However, a few measurements were also made using lines (*g*), (*h*) and (*j*), and these are shown in table 4. The ratio of the intensity of line (*g*) to (*i*) agrees with theory, but that for lines (*h*) and (*j*) to (*i*) does not. This lack of agreement is probably due to a difference in electric field density in the *x* and *z* directions. Our spectra were obtained using a cylindrical cavity operating in the TE_{012} mode. In this mode $E_y = 0$ and $E_z = E_x$ from cylindrical symmetry. However, if the sample is not located on the cavity axis, this symmetry is lost and thus any relationship between lines (*g*) and (*i*), which are excited by E_x, and lines (*h*) and (*j*) which are excited by E_z, is lost. This explanation is supported by the observation that line (*h*) tended to saturate at much lower powers than did lines (*g*) and (*i*). Thus, when NO is used as a calibration standard, only lines (*g*) and (*i*) should be used for absolute concentration measurements.

TABLE 4.—ALL RELATIVE INTENSITIES WERE MEASURED FROM THE INTEGRATED ABSORPTION OF THE LINE SHOWN, AND WERE NORMALIZED WITH RESPECT TO LINE (*i*).

	line (*g*)	line (*h*)	line (*i*)	line (*j*)
theory	0.63	1.82	1.00	0.11
measurement	0.70	1.43	1.00	0.07
	0.66	1.43	1.00	0.08
	0.70	1.53	1.00	—
	0.59	1.29	1.00	—
	0.71	1.45	1.00	0.11
	—	1.45	1.00	—

Fig. 1 contains sufficient data for the determination of the relative rate constants of reactions (*a*) and (*b*). Using the kinetic analysis described previously,[13] the ratio k_a/k_b was estimated as 0.63 ± 0.06. This number is in excellent agreement with that obtained from experiments in which chemiluminescence was monitored.[13]

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