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Determination by Gas-Phase EPR of the Absolute Concentration of Species Undergoing Electric Dipole Transitions

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An experimental investigation of the theoretical expressions relating gas-phase EPR signal strengths and absolute concentration of species undergoing *electric* dipole transitions has been carried out. Absolute concentrations of SO($^3\Sigma^-$) have been determined by EPR using NO as a calibrant gas. Concomitant determinations by titration of SO($^3\Sigma^-$) with known amounts of NO_2 are found to be in excellent agreement with the EPR results, once inconsistencies in the published values for the transition moments of NO($^2\Pi$) and SO($^3\Sigma^-$) are reconciled. The agreement supports the validity of each technique, but the EPR method is more convenient once a correct calibration factor is established. Several methods for determining the signal strength from an observed EPR line (first moment, double integral, width squared times height) have been critically examined. All of the methods were found to yield consistent results when properly applied. A choice among them will be dependent upon the particular requirements of any given experiment.

INTRODUCTION

The use of gas-phase EPR detection for determining the reaction rates of small molecules and atoms is now becoming widespread.[1] Westenberg and De Haas,[2,3] have worked out the theory necessary for the determination of relative and absolute concentrations of several atoms and molecules observed by gas-phase EPR. To determine absolute concentrations of species they have recommended spectrometer calibration using the stable paramagnetic gases O_2 and NO. The theoretical relationships used for determining, from O_2 resonances, the absolute concentration of species whose EPR transitions are magnetic dipole in nature, were subjected to extensive experimental verification[3] by these authors. A separate attempt[4] was made to verify experimentally the equations relating the concentrations of species with electric dipole transitions, such as OH and electrons undergoing cyclotron resonance, to those of NO. This attempt resulted in somewhat inconclusive results due to the unavailability of another electric dipole species of sufficient stability and/or the unavailability of reliable alternative methods (such as the chemical titrations used to verify the magnetic dipole relations) to determine the absolute concentration of the electric dipole species.

We have recently carried out[5] a series of kinetic experiments with EPR detection designed to measure the rate of the spin exchange reaction between triplet SO and singlet O_2. In order to obtain rate constants, it became necessary to determine the absolute concentration of ground-state SO($^3\Sigma^-$). Calibration of a known EPR transition of SO seemed the obvious method for this purpose. However, as there has never been a completely satisfactory check on the reliability of EPR concentration determinations for electric dipole species, we were somewhat dubious about the credibility of the EPR results.

We therefore performed a series of independent experiments designed to check the theoretical calculations of ourselves and others, relating the concentration and signal strengths of SO and NO. These experiments utilized the fast reaction of NO_2 and SO reported by Clyne *et al.*[6] for titration of SO. We have also undertaken a number of experiments designed to determine the best measure (first moment, double integral, etc.) of the signal strength for gas-phase EPR lines. We have found that each of several methods have their own unique advantages and disadvantages, and the choice of a particular one may be dependent upon the particular requirements of any given experiment.

EXPERIMENTAL

The experimental apparatus and procedures have been described previously.[5] The reaction of O(^3P) with OCS was again used to generate SO($^3\Sigma^-$). Volume flow rates and pressures were measured as before.[5] Pressures of NO_2 in the calibrated volume were kept low enough that correction for N_2O_4 formation was negligible. The moveable injector was positioned approximately 15 cm upstream from the detection cavity for the titration experiments, a distance sufficient to allow essential completion of the reactions for the flow rates and concentrations used. Some of the measurements reported here were taken with a Fabri-Tek Instruments computer, Model 1072. The computer's chief uses were in obtaining double integrals and numerical determination of line shapes for first moments.

There are certain difficulties involved in measuring SO($^3\Sigma^-$) under the conditions of low power[7] and low modulation amplitude necessary to obtain a "true" EPR line shape. Particularly for small amounts of SO($^3\Sigma^-$), the signal-to-noise ratio can become intolerably small. It was necessary, therefore, to make measurements under conditions where some power and modulation broadening was present, and to relate these measurements to the "true" signal strength at low power and modulation. This was done in the following way. For each particular set of conditions (total pressure, composition of gas mixture) a large enough concentration of SO($^3\Sigma^-$) was generated to

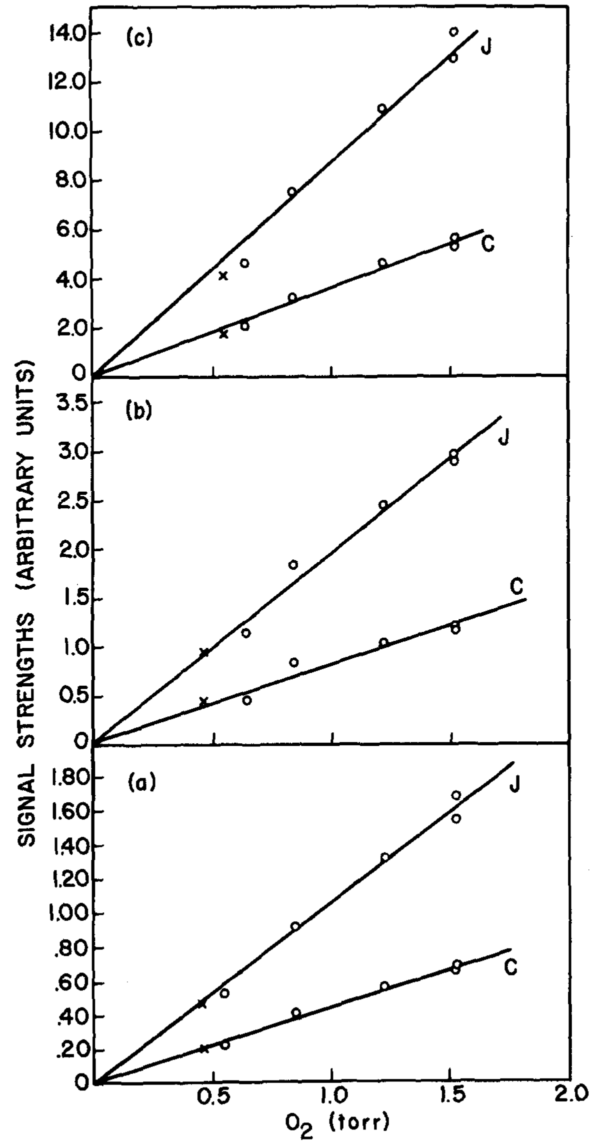

FIG. 1. EPR signal strengths S for the J and C lines of O_2 vs O_2 pressure. In (a) S is determined via the first moments, in (b) via double integrals, and in (c) via the width squared times height method. The data point marked with a × refers to a He–O_2 mixture, 38% O_2 in composition. All other points refer to pure O_2.

obtain measurements with adequate signal-to-noise under known low-power, low-modulation conditions. Immediate measurement at fixed higher-power and modulation amplitude of the apparent EPR signal strength of this amount of SO allowed a calibration curve to be determined which could be used to correct any later measurements of smaller amounts of SO to the true low-power, low-modulation signal strength. Several detailed sets of experiments showed that this correction procedure was quite reproducible. All the measurements reported here were made under conditions of only slight distortion of the SO line shape by modulation or power broadening.

SIGNAL STRENGTH DETERMINATION

The type of formula usually[2,3] employed to relate the observed EPR resonances to the concentration of atoms and molecules is of the form,

$$N_p = KQ(p)\int \chi_p'' dH, \qquad (1)$$

where N_p is the number of paramagnetic atoms or molecules per unit volume. K depends upon instrumental parameters and is exceedingly difficult to calculate. It should, however, have only two unique values. One value is common to all species undergoing electric dipole transitions. The other value is common to all species undergoing magnetic dipole transitions. By using the magnetic dipole calibrating gas O_2 and the electric dipole calibrating gas NO, K can be determined experimentally, assuming $Q(p)$ and $\int \chi_p'' dH$ are known for O_2 and NO.

$Q(p)$ depends upon angular momenta quantum numbers, dipole moments, and partition functions. It should be calculable for most paramagnetic gases. Westenberg[2] and De Haas[2,3] have given values of $Q(p)$ for O_2 and NO, with the former having been subjected to extensive experimental verification. We discuss the similar quantity for SO in the next section, hence we postpone further comment on $Q(p)$ until that point.

The remaining term on the right-hand side of Eq. (1) is the integral over all values of the magnetic field of the complex portion of the magnetic or electric suspectibility. For most practical purposes, we may simply consider this an integration of the line-shape function to give the total signal strength. We will therefore denote the value of this integral by the symbol S.

Unfortunately, in the typical EPR experiment the observed line shape is not given by χ_p''. As Westenberg and De Haas[8] have noted, this complication results from the fact that field modulation is employed and the signal detected by a lock-in amplifier. These workers have also presented equations describing the further modifications of the line shape produced by nearly saturating microwave fields or high-modulation amplitudes. (Mention is made in the Experimental section of our efforts to avoid these latter difficulties.) Experimental results consistent with their equations have been described.[8] We have conducted similar experiments with the intention of determining the most efficient means of measuring S for particular experimental conditions. Some of the earlier results[8] have been confirmed, and certain techniques, especially with respect to NO calibration, have been extended into regions previously uninvestigated.

Several indirect means have been employed to obtain S from the observed EPR resonance. (a) Some investigators[3] have measured the first moment of the line to obtain S. (b) Double integration of the lines with low-modulation amplitude has been the classical means[9] to obtain S from EPR lines. (c) Since completely resolved gas-phase EPR lines of all species can be expected to have a Lorentzian line shape, a product of linewidth squared times height has been employed[10] to obtain S. (d) For the purpose of obtaining relative atomic concentrations, measurement of signal height alone may be sufficient to determine S.[2,3,8]

As far as ease and efficiency are concerned, the methods are listed roughly in descending order of difficulty though methods (a) and (b) are of very comparable difficulty while the difference between (b) and (c) is quite pronounced. As kinetic experiments require numerous determinations of S, rapid measurements are important. Unfortunately, in some cases, e.g., comparison of concentrations of two different atoms or molecules, method (d) is impossible because of different linewidths. We thus have undertaken to determine if method (c) gives results as reliable as, and consistent with, methods (a) and (b).

Data were taken on the C and J lines (see Ref. 3) of the O_2 spectrum which have different field widths. Figures 1(a)–1(c) show plots of the strength of these lines as a function of O_2 pressure. Included in these plots are data taken both with pure O_2 and with O_2–He mixtures. As can be seen from these figures each method [(a)–(c)] shows a linear variation of strength vs O_2 pressure. No deviation is observed for the O_2–He mixture.

In Table I, we list the ratios (J/C) obtained at various pressures as determined by the three methods. One can see that average values agree within experimental error and that the standard deviation is smallest for method (c). It is also worth mentioning that the average value of (J/C) is somewhat different from the theoretical value of Tinkham and Strandberg[11] and the experimental one given in Ref. 3. This is not particularly surprising as our microwave frequency (~8880. MHz) and hence our resonant magnetic field is considerably different from the previous investigators, and the line strengths in O_2 are fairly strongly magnetic field dependent. This result, however, does indicate the need for some caution in using O_2 as an absolute calibrant if one's microwave frequency is several hundreds of megahertz different from those of the previous references.

TABLE I. Ratio of the strengths of the J and C lines of O_2 as a function of pressure. Column 2 gives the ratio of strengths as determined by the width squared times height method. Column 3 gives the same ratio as determined from the double integrals of the lines. Column 4 gives the ratio using the first moment technique.

Pressure (torr)	$(J/C)_{W^2H}$	$(J/C)_{DI}$	$(J/C)_{FM}$
0.55	2.26	2.40	2.35
0.85	2.33	2.22	2.20
1.20[a]	2.36	2.23	2.11
1.23	2.36	2.32	2.35
1.53[b]	2.45	2.43	2.34
Av	2.35±0.06	2.32±0.08	2.27±0.10

[a] Partial pressure O_2, 0.46 torr; partial pressure He, 0.74 torr.

[b] Average of two runs.

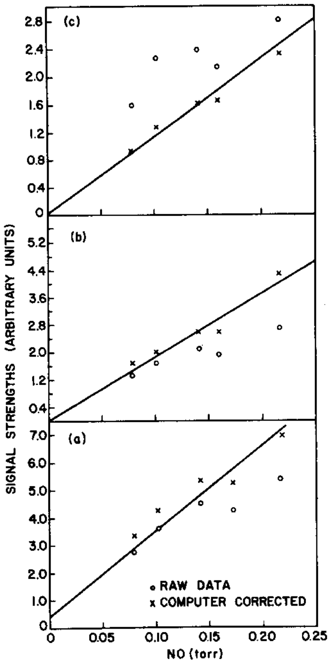

FIG. 2. EPR signal strengths S for an NO line vs NO partial pressure in mixtures of NO and helium (total pressure, 1–2 torr). In (a) S is determined via the first moment, in (b) via the double integral, and in (c) via the width squared times height method. O's indicate raw data points and ×'s indicate data corrected through computer calculations for incomplete resolution in the NO spectrum.

We have also carried out experiments with NO. The transition $J=\frac{3}{2}$, $M_I=-1$, $M_J=-\frac{1}{2}\leftrightarrow M_J'=\frac{1}{2}$, was chosen for study. Figures 2(a)–2(c) show plots of the strength of this line vs NO partial pressure. [The measurements were taken in excess helium at total pressures of 1–2 torr to avoid experimental problems encountered in handling higher pure NO pressures or adsorption, differential pumping, and pressure measurement problems at lower (total) pressures of pure NO.] In these figures, circles denote the raw experimental data, and it is quite apparent that the linear dependence of S upon pressure observed with O_2 is not found with NO.

It was felt that the most likely explanation of this difficulty lay in the incomplete resolution of the NO spectrum at the pressures used. The line studied con-

TABLE II. Molecule-dependent factors for NO and SO($^3\Sigma^-$) entering into a determination of $Q(p)$.

	Z_p	g_{eff}^p	$\exp(-E_i^p/aT)$	$\lvert(\mu_p)_{ij}\rvert^2$ [a]	μ_0^p (D)
NO($^2\Pi$)	1.16×10^3	0.777	0.549	$0.320(\mu_0^{NO})^2$	0.1587
SO($^3\Sigma$)	8.72×10^2	0.636	0.951	$0.102(\mu_0^{SO})^2$	1.55

[a] For NO, the value listed is the sum for both the unresolved Λ–doublet transitions.

sists, in fact, of two separate transitions across the Λ doublet[12] of NO($M_J^+\leftrightarrow M_J^{-\prime}$ and $M_J^-\leftrightarrow M_J^{+\prime}$). At the lowest pressures used, the lack of perfect superposition of these two transitions very seriously affects the determination of S from the observed line by method (c). At the highest pressures used, overlap of adjacent M_I transitions disturbs sufficiently the wings of the line of interest to cause the first moment and double integrals to become inaccurate.

In each case corrections to the line can be obtained if the line shapes of the individual components are known. The assumption was made that χ_p'' is Lorentzian and the equations of Wahlquist[13] for the modulated and phase-detected first harmonic were programmed to obtain correction factors. The **X**'s in Figs. 2(a)–2(c) represent the computer-corrected data, and one can see that a linear variation of S with pressure has been achieved.

Because method (c) seems to show the least scatter and is also the simplest method, we chose it for the remainder of our measurements. Figure 3 gives the computer-generated correction factor for the NO strength determined by method (c) from the observed NO line for a range of linewidths. Superimposed upon the theoretical curve are a number of data points taken to check the validity of the theoretical curve. The point marked with a triangle was assumed to match the theoretical curve and all the other experimental points positioned relative to it.

SULFUR MONOXIDE CONCENTRATION MEASUREMENTS

EPR Strength Relations

The number of paramagnetic molecules present is related to the EPR signal strength by Eq. (1). The factor, $Q(p)$ in Eq. (1), has the explicit form,[2]

$$Q(p)=\frac{kT\beta}{\nu_0 h}\,\frac{Z_p g_{\text{eff}}^p}{\exp(-E_i^p/kT)\,\lvert(\mu_p)_{ij}\rvert^2},\qquad(2)$$

where h is Planck's constant, k is Boltzmann's constant, T is the absolute temperature, ν_0 is the spectrometer frequency, β is the Bohr magneton, E_i^p is the energy of the lowest state of the molecule or atom p involved in the transition, $\lvert(\mu_p)_{ij}\rvert^2$ is the square of the transition moment in the direction of the microwave electric or magnetic field, Z_p is the partition function, and g_{eff}^p is the effective g value.

The values of the p-dependent quantities are listed in Table II for NO and SO. With the exception of the transition matrix element and the dipole moment of NO, for which there now exists a more accurate value,[14] the quantities for NO are the same as those given by Westenberg[2] for the lines (in his notation) d, e, f, at room temperature.

For SO, Z_p and $\exp(-E_i^p/kT)$ can be easily calculated from the known rotational and vibrational structures. The line chosen for the SO measurements was the transition, $K=1$, $J=1$, $M_J=0\leftrightarrow M_J'=-1$, $K=2$, $J=1$, which can be observed at approximately 5.81 kG at a nominal microwave frequency of 8.88 GHz. The effective g value was obtained from the work of Daniels and Dorain.[7] The value of $\lvert(\mu_p)_{ij}\rvert^2$ was taken from the work of Carrington, Levy, and Miller.[8] The value listed in Table II for the transition matrix element squared of NO is one-half the value given by Westenberg.[2] This factor of 2 is discussed in some detail in Appendix I and is absolutely necessary for a consistent determination of the rela-

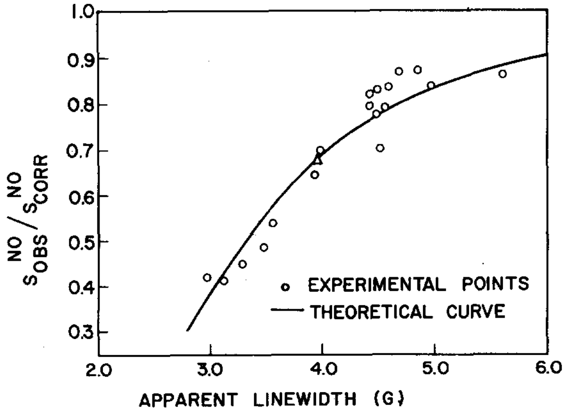

FIG. 3. Plot of the ratio of observed signal strength to corrected signal strength vs apparent NO linewidth. The factor ($S_{\text{obs}}^{NO}/S_{\text{corr}}^{NO}$) gives the ratio of the apparent value of the signal strength, obtained via a linewidth squared times height computation, to that which would be obtained were the NO Λ-doublet transitions perfectly superimposed. The solid curve is based on computer simulation while the points are obtained experimentally by measuring the relative S_{obs}^{NO} for known NO concentrations. To determine the relative position of the data points and the computed curve, a single data point (open triangle) is assumed to lie on the curve.

tive Q's for NO and SO($^3\Sigma^-$). It should be mentioned that $|(\mu_p)_{ij}|^2$ and $g_{\mathrm{eff}}{}^p$ are field dependent for SO and the previous calculations were at slightly different fields than the observed line position. The error so introduced should at most be 2%–3%. The value of the dipole moment of SO is taken from the microwave experiments of Powell and Lide.[15]

Combining the results in Table II with Eq. (1), we obtain

$$N_{\mathrm{SO}}/N_{\mathrm{NO}}=1.05[Q(\mathrm{SO})/Q(\mathrm{NO})](S_{\mathrm{SO}}/S_{\mathrm{NO}})$$

$$=0.0123(S_{\mathrm{SO}}/S_{\mathrm{NO}}). \qquad (3)$$

The factor of 1.05 in Eq. (3) allows for the fact that the observed EPR line originates with $^{32}S^{16}O$ ($^3\Sigma^-$), while ^{32}S accounts for only 95% of all the S isotopes.

TITRATION CHEMISTRY

Clyne *et al.*[6] have recently reported a value of 5× 10^9 liter mole^{-1}·sec^{-1} for the rate constant of the reaction

$$NO_2+SO\rightarrow SO_2+NO. \qquad (I)$$

If this value is correct, and the stoichiometry is accurately implied by the equation, Reaction (1) represents an excellent titration reaction for SO. To verify that Reaction (1) proceeds rapidly and without complications in our system, we carried out a number of experiments.

Figure 4 shows a plot of percent (SO) titrated vs the concentration of added NO_2. In these experiments the relative SO concentration was monitored by means of its EPR signal, and the NO_2 concentration was determined by the metering technique described in Ref. 5. The linearity of the plot would seem to verify that NO_2 is reacting only with SO and that there are no complicating secondary reactions. Results presented in the next section show also that the calibration procedure gives consistent results over a wide range of SO concentrations.

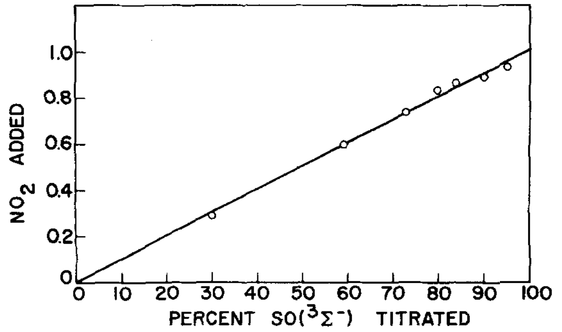

FIG. 4. Plot of percent SO titrated vs NO_2 added. Because the points shown were determined at slightly different SO concentrations, each NO_2 concentration value has been normalized by dividing it by the initial concentration of SO. The ordinate and abscissa are therefore both dimensionless quantities.

TABLE III. Partial pressure of NO produced from a known amount of NO_2, determined (I) from EPR measurements of the products of Reactions (I), (II) from EPR measurements of the products of Reactions (II), (III) by measuring a flow of NO regulated to give a standard EPR signal.

Method	NO production (mtorr)
I	2.5
II	2.5
III	2.8

To further verify the reaction mechanism, we monitored via EPR the NO produced in this reaction. The NO signal was, however, very weak and only limited quantitative use can be made of it. A measured concentration of NO_2 was allowed to react with excess O(^3P) atoms according to

$$O+NO_2\rightarrow NO+O_2, \qquad (II)$$

a reaction whose fast rate and simple stoichiometry are well known.[16] This NO concentration, determined from the flow of NO_2, is listed as entry 1 in Table III. If the O atoms are replaced with an excess of SO the relative (to entry 1) NO concentration produced can be determined from the EPR signal. This relative concentration is listed as entry 2 in Table III. Another measure of the NO concentration can be obtained by eliminating the O atoms and SO from the system and introducing a small flow of NO. This flow may be regulated so that the NO signal is equal or close to equal to that measured in trials 1 and 2. The NO concentration listed as entry 3 in Table III was obtained by measuring this regulated NO flow. These measurements show that within experimental error NO_2 is converted stoichiometrically into NO by SO.

We have also conducted an experiment which at least qualitatively confirms the conclusions of Clyne *et al.*[6] that Reaction (1) is extremely fast. By monitoring the relative changes in O(^3P) and SO concentrations when a small amount of NO_2 was added to a mixture of approximately equal parts of O(^3P) and SO in the main flow tube, we showed that k_1 is larger than k_2, in agreement with the finding of these workers.

CONCLUSIONS

Equation (3) gives a means of determining absolute SO concentration by EPR, and Reaction (1) gives a chemical titration to check theoretical EPR relations. Table IV summarizes the results of several concentration determinations by the two methods. We see that there is excellent agreement between the two techniques. It appears, therefore, that the cumulative effect of any possible small systematic errors associated

TABLE IV. Comparison of determinations of SO by EPR and by NO_2 titration. The error assigned to the ratios in Column 3 is equal to the square root of the sum of the square of the percentage standard deviations of the entries in Columns 1 and 2.

Expt	$(SO)_{titr}$ ($torr\times10^4$)	$(SO)_{EPR}$ ($torr\times10^4$)	$(SO)_{EPR}/(SO)_{titr}$
A	6.35	6.4	1.01 ± 0.06
B	10.2	10.4	1.02 ± 0.07
C	12.7	13.1	1.03 ± 0.07
D	24.5	23.8	0.97 ± 0.08
		Av	1.01 ± 0.07

with either method is less than the uncertainty due to the observed random error of the measurements.

While this report of our work was being prepared for publication, a paper by Cupitt and Glass[17] appeared in which some calculations and experiments concerning absolute gas-phase EPR concentration measurements were described. Calibration factors relative to an NO EPR transition were calculated for various transitions of $SO(^3\Sigma^-)$ and $SH(^2\pi_{3/2})$. However, because an error of a factor of 2 in the NO absolute transition probabilities (discussed above and in Appendix I) was incorporated into these calculations, all the calibration ratios for $SO(^3\Sigma^-)$ reported by Cupitt and Glass should be divided by two.[18]

In their study, determinations were made of the concentration of $SO(^3\Sigma^-)$ produced by an SO_2–Ar discharge, using NO as a calibrant gas. The authors attempted to verify the validity of the calibration procedure by measuring the $SO(^3\Sigma^-)$ concentration independently. The method[6] of Clyne, Halstead, and Thrush was employed to titrate, with added NO_2, the products $O(^3P)$ and $SO(^3\Sigma^-)$ of the SO_2–Ar discharge. The concentration of $SO(^3\Sigma)$ was determined by subtracting the $O(^3P)$ concentration (estimated by EPR using O_2 as a standard) from the total NO_2 which had to be added to titrate $O(^3P)+SO(^3\Sigma^-)$. It was claimed that there was semiquantitative agreement between the absolute EPR method and the indirect titration method for obtaining the concentration of $SO(^3\Sigma)$. However, because the EPR calibration factors used were incorrect, the consistency of the two methods was only apparent. We can offer no certain explanation for the fortuitous agreement reported by Ref. 17, but it is possible that other species which reacted with NO_2 were generated in their SO_2–Ar discharge. This effect would have resulted in too high an estimate of the $SO(^3\Sigma^-)$ concentration by the titration method, causing it to be in apparent agreement with the EPR determination.

In conclusion, on the basis of our work there would seem to be no reasonable preference with respect to absolute reliability for the determination of SO by either of the two methods. The EPR method, however, offers a nondestructive and faster SO determination once an NO calibration is performed. The consistency of the two methods confirms the stoichiometry of Reaction (1). Likewise, this consistency offers the first successful experimental check and verification of a gas-phase EPR concentration determination for a species with electric dipole transitions.

ACKNOWLEDGMENTS

We would like to thank D. H. Levy, D. R. Johnson, and others for helpful discussions regarding the transition matrix elements.

APPENDIX

To determine the transition matrix elements for NO it is perhaps easiest, though not absolutely necessary, to turn to the theory of irreducible tensor operators.[19] The dipole moment is a first-rank irreducible tensor operator with components in the space-fixed cordinate system,

$$T_0^1(\boldsymbol{\mu})=\mu_z,$$

$$T_{\pm1}^1(\boldsymbol{\mu})=\pm(1/\sqrt{2})(\mu_x\pm i\mu_y). \qquad \text{(A1)}$$

For a molecule-fixed coordinate system with the z' direction along the internuclear axis of a diatomic molecule, the only nonvanishing component of $\boldsymbol{\mu}$ is $\mu_{z'}$ or $T_{0'}^1(\boldsymbol{\mu})$. We can transform this molecule-fixed expectation value of the dipole moment to the space-fixed system via a first-rank rotational matrix,

$$T_q^1(\boldsymbol{\mu})=T_{0'}^1(\boldsymbol{\mu})D_{q0}^{1*}(\omega)=D_{q0}^{1*}(\omega)\langle\mu\rangle, \qquad \text{(A2)}$$

where ω relates the molecule and space-fixed axis system and $\langle\mu\rangle$ is the permanent electric dipole moment.

For symmetric top or case (a) basis functions the matrix elements of $T_q^1(\boldsymbol{\mu})$ are just[20]

$$\langle JM\Omega\,|\,T_q^1(\boldsymbol{\mu})\,|\,J'M'\Omega'\rangle=\{[(2J+1)(2J'+1)]^{1/2}/8\Pi^2\}$$
$$\int D_{M\Omega}^{J**}(\omega)D_{q0}^{1*}(\omega)D_{M'\Omega'}^{J'*}d\tau\langle\mu\rangle$$
$$=\langle\mu\rangle[(2J'+1)/(2J+1)]^{1/2}$$
$$\times\langle J'1M'q\,|\,JM\rangle\langle J'1\Omega'0\,|\,J\Omega\rangle. \qquad \text{(A3)}$$

In the typical gas-phase EPR experiment, a microwave electric field is present in *one* of the directions perpendicular to the magnetic field (space-fixed z direction). Let that direction be the x direction, then in the EPR experiment the transition probabilities are proportional to the square modulus of the space-fixed x component of the electric dipole moment.

For the case of the NO molecule, the EPR transitions are of the form $J\leftrightarrow J$, $\Omega\leftrightarrow\Omega$, $M\leftrightarrow M+1$, $\pm\leftrightarrow\mp$ where $+$ and $-$ denote the parities of the levels. Strictly speaking we should use symmetric and antisymmetric combinations of the symmetric-top wavefunctions, but as we have noted before[20] the matrix elements of the tensor $T_q^1(\boldsymbol{\mu})$ that are diagonal in Ω are the same between these combinations as between the simple basis functions, save that odd-rank electric multipoles vanish between states of the same parity and odd-rank magnetic multipoles vanish between states of different parity. Thus we use Eq. (3) and the explicit expressions[21] for the Clebsch–Gordan coefficients to obtain

$$\begin{aligned}\langle +JM\Omega \mid T_{-1}^1(\mu) \mid -JM+1\Omega\rangle &= \langle +JM\Omega \mid +(1/\sqrt{2})(\mu_x - i\mu_y) \mid -JM+1\Omega\rangle \\ &= [(J-M)(J+M+1)/2J(J+1)]^{1/2} \\ &\quad \times \{\Omega\langle\mu\rangle/[J(J+1)]^{1/2}\} \qquad \text{(A4)}\end{aligned}$$

and

$$\begin{aligned}\langle +JM\Omega \mid T_1^1(\mu) \mid -JM+1\Omega\rangle = \langle +JM\Omega \mid \\ -(1/\sqrt{2})(\mu_x + i\mu_y) \mid -JM+1\Omega\rangle = 0. \qquad \text{(A5)}\end{aligned}$$

By substracting the respective sides of Eq. (5) from Eq. (4) we obtain

$$\begin{aligned}\langle +JM\Omega \mid (2/\sqrt{2})\mu_x \mid -JM+1\Omega\rangle = \{\Omega\langle\mu\rangle/[J(J+1)]^{1/2}\} \\ \times[(J-M)(J+M+1)/2J(J+1)]^{1/2} \qquad \text{(A6)}\end{aligned}$$

or

$$\begin{aligned}\mid\langle +JM\Omega \mid \mu_x \mid -JM+1\Omega\rangle\mid^2 = [\Omega^2\langle\mu\rangle^2/4J^2(J+1)^2] \\ \times(J-M)(J+M+1). \qquad \text{(A7)}\end{aligned}$$

The result is for the Λ-doublet transition $+\leftrightarrow-$; there is another transition, $-\leftrightarrow+$, which has an identical transition probability. The two transitions are often not resolved in the EPR spectrum of NO, so the total transition moment in the x direction is twice that given by Eq. (A7).

We note that the result, Eq. (A7), is exactly $\frac{1}{2}$ the value derived for the seemingly identical transition moment by Westenberg.[2] As this discrepancy is important and Westenberg's method of derivation is different from ours we have considered his results, in light of our derivation.

He began with the value of the matrix element of the transition moment squared $\mid(\mu_{ij})\mid^2$ summed over all M' states,

$$\begin{aligned}\mid\mu_{ij}\mid^2 &= \sum_{M'} \mid\langle +JM\Omega \mid \mu_x \mid -JM'\Omega\rangle\mid^2 \\ &\quad + \mid\langle +JM\Omega \mid \mu_y \mid -JM'\Omega\rangle\mid^2 \\ &\quad + \mid\langle +JM\Omega \mid \mu_z \mid -JM'\Omega\rangle\mid^2 \\ &= \sum_{M'}\sum_{q} \mid\langle +JM\Omega \mid T_q^1(\boldsymbol{\mu}) \mid -JM'\Omega\rangle\mid^2 \\ &= [\sum_{M'q} \langle JM \mid J1M'q\rangle\langle J1M'q \mid JM\rangle] \\ &\quad \times\langle\mu\rangle^2\,\langle J\Omega 10 \mid J\Omega\rangle^2 \\ &= \langle\mu\rangle^2[\Omega^2/J(J+1)], \qquad \text{(A8)}\end{aligned}$$

where the penultimate equality is derived from Eq. (A3). The final equality is obtained from the orthogonality of the Clebsch–Gordan coefficients and is in agreement with the value of $\mid\mu_{ij}\mid^2$ (along all axes) quoted by Westenberg.

To find the matrix element we derived in Eq. (A7) he noted that to obtain the total intensity, V_T, along any axis one should divide the total transition moment along all axes by 3 and sum over the $2J+1$ values of M. Thus,

$$V_T = \langle\mu\rangle^2\,\Omega^2(2J+1)/3J(J+1). \qquad \text{(A9)}$$

He then noted that the sum of the intensity of all the Zeeman components (along an axis perpendicular to the magnetic field) must equal the unperturbed line intensity (along that axis). Hence using the M dependence of a T vector[21] he writes

$$\begin{aligned}\mid\langle +J\Omega M \mid \mu_x \mid -J\Omega M+1\rangle\mid^2 \\ = C\tfrac{1}{2}\langle\mu\rangle^2\,\Omega^2(J-M)(J+M+1) \qquad \text{(A10)}\end{aligned}$$

and

$$\tfrac{1}{2}(\langle\mu\rangle^2\,\Omega^2)C\sum_{M=-J}^{J}(J-M)(J+M+1) = V_T \qquad \text{(A11)}$$

and solves Eq. (A11) (after performing the sum) for C, obtains $[C=1/J^2(J+1)^2]$, and the desired matrix element.

We believe that Eq. (A11) is in error. Consider two cases (i) magnetic field energy $\ll\Lambda$ doubling, (ii) magnetic field energy $\gg\Lambda$ doubling. In case (i) the total intensity along the x axis is actually a sum of two sums, one for the $\Delta M=+1$ sum given in Eq. (A11) and an identical sum for $\Delta M=-1$. The latter sum implies that

$$C = [2J^2(J+1)^2]^{-1}, \qquad \text{(A12)}$$

which gives agreement with our Eq. (A7). Alternatively we can work out C in case (ii). Here it is appropriate to consider only transitions $M\leftrightarrow M+1$, *but* the total intensity is now given by the sum of the $+\leftrightarrow-$ *and* $-\leftrightarrow+$ transitions, implying that a factor of 2 should be included inside the summation over M in Eq. (A11). The argument again gives C as in Eq. (A12) and yields a matrix element in agreement with that derived by us in Eqs. (A3) and (A7).

We thus conclude that the matrix elements given by Ref. 2 should be divided by a factor of 2 if they are to be interpreted as the transition moment along *one* axis (say the x axis) perpendicular to the magnetic field. Equivalently they need *not* be altered if one adopts the convention that they refer to the transition moment along *both* axes (x and y) perpendicular to the magnetic field.

Finally, we would note that Westenberg appears to have used the same procedure for obtaining the transition moments for OH. Thus, this same factor-of-2 anomaly exists for the OH transition moments. A consistent anomalous normalization factor is no anomaly at all, so we conclude that the intensity ratios for NO and OH are correct as given. However, if one uses a transition moment for another molecule, calculated without this anomalous normalization procedure, as Cupitt and Glass have done for SO($^3\Sigma^-$), one obtains an intensity ratio which is incorrect by a factor of 2.

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