

FIG. 2. Intensity of the SO_2 afterglow as a function of wavelength. [$R_{\text{SO}_2}(\lambda)$ is the uncorrected intensity; $H(\lambda)$ is the instrument sensitivity relative to a value at $500 \text{ m}\mu$; $R_{\text{SO}_2}(\lambda)/H(\lambda)$ is the corrected intensity.]

OCS reacts with O atoms formed in the discharge to produce CO and SO. The SO radicals then react with excess O atoms to produce the violet SO_2 emission. In procedure (a), the emission was monitored by three separate photomultipliers. One, used in conjunction with a Bausch & Lomb monochromator, was set at 2750 \AA , with a half-width of about 15 \AA . A second and third photomultiplier monitored all radiation above 3000 and 4500 \AA , respectively. In procedure (b), intensity was monitored at 3200 \AA , the maximum emission.

In Ref. 1 it was shown that for a chemiluminescent reaction of the form $A+B(+M) \xrightarrow{k} AB(+M)+h\nu$, the ratio of emission intensities before (subscript 1) and after (subscript 2) the shock is given by the product of the ratio of rate constants times the ratio of densities raised to the appropriate power:

$$I_2/I_1 = [k(T_2)/k(T_1)](\rho_2/\rho_1)^{s+2}$$

where $s=0$ or 1 depending on whether the reaction is second or third order. In Fig. 1, we plot $\log(I_2/I_1)(\rho_1/\rho_2)^2$

vs $\log(T_2/T_1)$. The data for all three spectral regimes, regardless of the mode of production of the SO_2 , fall on the same straight line of slope -1.6 when s is taken to be 0 . Thus, the data reinforce the conclusion² that the over-all reaction rate is independent of total pressure and, furthermore, indicate that I varies as $T^{-1.6}$. Our data cover the temperature range of $300^\circ\text{--}1500^\circ\text{K}$, with pressures behind the shock of about $2\text{--}5$ torr.

In an independent series of room-temperature measurements, the absolute total emission intensity of the SO_2 afterglow ($2200\text{--}5000 \text{ \AA}$) was determined. This was obtained by measuring the emission as a function of wavelength, correcting for the spectral response of the monochromator-photomultiplier system, and calibrating absolutely by observing the NO_2 afterglow in the same apparatus (Fig. 2). By use of Fontijn, Meyer, and Schiff's³ absolute quantum yield of the NO_2 chemiluminescence, a room-temperature rate constant for the SO_2 afterglow of $1.9 \times 10^5 M^{-1} \text{ sec}^{-1}$ is obtained. This value compares favorably to the value of $1.5 \times 10^5 M^{-1} \text{ sec}^{-1}$ reported by Clyne, Halstead, and Thrush,² but is lower than other reported values.^{4,5}

Combining the room-temperature absolute measurement with the temperature dependence measured in the shock tube, we obtain the emission intensity $I = 1.9 \times 10^5 (300/T)^{1.6} [\text{O}][\text{SO}] M \text{ sec}^{-1}$.

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Relative Orientation of Molecules Involved in Triplet-Triplet Energy Transfer

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The exchange interaction necessary for the non-radiative triplet-triplet transfer of energy is a short-range interaction sensitive to the overlap of the electronic wavefunctions of the participating molecules.¹⁻³ Hence, there can be an optimum transfer geometry for the sensitizer-acceptor pair.⁴⁻⁷

The aim of this work is to examine this orientation dependence in triplet-triplet transfer using a new technique. It involves the excitation of the sensitizer molecules with polarized light and the measurement of the polarization of the triplet-triplet absorption in the acceptor molecules. Thus, a knowledge of the transition

directions for the absorbing sensitizer molecules ($S_0 \rightarrow S_1$) and the acceptor molecules ($T_1 \rightarrow T_2$) is required. The $T_1 \rightarrow T_2$ polarization in the acceptor is determined relative to the $S_0 \rightarrow S_1$ in the sensitizer transition. Knowing the molecular directions of these transitions, therefore, yields information about the relative orientation of the sensitizer and acceptor molecules.

In order to completely determine the relative orientation for general pairs of molecules, we must determine the polar coordinates θ and ϕ between the two molecules. This may be done by performing measurements involving two orthogonal transitions in the singlet system of the sensitizer relative to a triplet-triplet absorption in the acceptor. An equivalent alternative is the polarization measurements of two orthogonal transitions in the triplet system of the acceptor relative to a singlet transition in the donor. In the present work the measurement of the $T_1 \rightarrow T_2$ transition in the acceptor relative to the $S_0 \rightarrow S_1$ sensitizer absorption is supplemented by the polarization measurement of the acceptor's phosphorescence relative to the sensitizer's $S_0 \rightarrow S_1$ transition.⁴

The systems were studied in EPA glasses at 77°K. All chemicals were carefully purified except phenanthrene- d_{10} (Merck, Sharpe and Dohme) which was used as received. The concentrations of the sensitizer and acceptor were $5 \times 10^{-3} M$. Excitation of the sensitizers at 3660 Å was effected with a 2500-W Hg-Xe lamp and suitable filters. The triplet-triplet absorptions at 4931 and 4602 Å were obtained by using a tungsten source, detected with a 6256S EMI photomultiplier and recorded using a $\frac{3}{4}$ -m Czerny-Truner spectrometer (Spex). The tungsten source and spectrometer were on line, and the Hg-Xe source was at right angles with respect to this direction. A Glan-Thompson polarizer and a Polaroid sheet analyzer were used in the polarization experiments. The precision of the measured polarization was $\pm 1\%$. The polarization of the triplet-triplet absorption is $\epsilon_{\parallel} - \epsilon_{\perp} / \epsilon_{\parallel} + \epsilon_{\perp}$ where ϵ_{\parallel} and ϵ_{\perp} are the molar absorption coefficients, respectively, parallel and perpendicular to the electric field of the excitation light.

The sensitizer-acceptor pairs studied were benzophenone-phenanthrene- d_{10} and anthrone-phenanthrene- d_{10} . The sensitizers were selected for the following reasons. First, their triplet excitation is localized in the carbonyl group and, therefore, might be more sensitive to orientation with respect to the phenanthrene acceptor. Second, steric effects could require different orientations for the sensitizers since benzophenone is nonplanar and anthrone is nearly planar. Third, information about the benzophenone-phenanthrene transfer is available.⁴ Last, the transition directions for $S_0 \rightarrow S_1$ in the sensitizer molecules and the $T_1 \rightarrow T_2$ transition in phenanthrene are known.⁹⁻¹³

The polarization of the phenanthrene phosphorescence

is found to be negatively polarized, $P = -10 \pm 1\%$ with respect to the $S_0 \rightarrow S_1(n, \pi^*)$ transition in benzophenone. This is in agreement with earlier work.¹ Since the $S_0 \rightarrow S_1(n, \pi^*)$ transition in benzophenone is parallel to the $C=0$ axis and phenanthrene phosphorescence is perpendicular to its own molecular plane, the $C=0$ axis of benzophenone must lie parallel to the molecular plane of phenanthrene. However, the angular orientation of the $C=0$ axis with respect to the short and long axes of phenanthrene cannot be determined from the polarization of the phenanthrene phosphorescence. The angular geometry of the benzophenone and phenanthrene can be determined by measurement of the polarization of the $T-T$ absorption in phenanthrene with regard to the $C=0$ axis since the $T-T$ transition is in the molecular plane of phenanthrene along its long axis. Thus, if the $C=0$ axis is parallel to the long axis of phenanthrene, the polarization will be positive; if parallel to the short axis, the polarization will be negative. If there is no preferred angular orientation, the $T-T$ polarization will be zero. The measured polarization of the $T-T$ absorption is found to be zero, thus indicating that there is no preferred angular orientation. These experiments have thus determined the configuration of the benzophenone-phenanthrene pair involved in triplet-triplet transfer.

The $S_0 \rightarrow S_1(n, \pi^*)$ transition in the sensitizer anthrone is primarily perpendicular to the $C=0$ axis and in the plane of the molecule.⁸ The polarization of the phenanthrene phosphorescence with respect to the $S_0 \rightarrow S_1(n, \pi^*)$ transition in anthrone is $P = -8\% \pm 1\%$. Thus, the molecular planes of anthrone and phenanthrene are parallel. The polarization of the $T-T$ absorption in phenanthrene with respect to the $S_0 \rightarrow S_1(n, \pi^*)$ transition in anthrone is likewise found to be zero. Thus, the anthrone-phenanthrene molecules involved in triplet-triplet transfer are found to have the following orientation: (1) The molecular planes are parallel; (2) there is no preferred angular orientation of the molecules in the parallel configuration.

The similar orientations found for the nonplanar benzophenone-phenanthrene pair with the planar anthrone-phenanthrene pair indicates that only the orientation of the $C=0$ group with respect to the phenanthrene plane is important. Although the sensitizer-acceptor distance must be small for exchange transfer to occur, the molecules are not required to be so close that the planarity of the phenyl groups of the sensitizer play a significant role in the transfer geometry of the molecular pair.

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Reduction of the Effect of the Speed Distribution in the Cross Beam on Nonreactive Scattering Experiments*

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The use of velocity selectors and analyzers in molecular-beam measurements of differential cross sections usually both clarifies the interpretation of the results and increases the experimental complications.¹ Thus the selection of the velocities of both primary beams is desirable in principle and difficult in practice. In this Note we show that for one commonly used experimental arrangement, selection of the primary-beam velocity \mathbf{v}_1 by use of a thermal distribution for the velocity \mathbf{v}_2 of the cross beam, the effect of the distribution of speeds v_2 may be substantially reduced for nonreactive scattering by a particular choice of the plane in which the detector scans the angular range.

We take the two beams intersecting perpendicularly and compare two possible ways of scanning the detector: (i) in the plane of \mathbf{v}_1 and \mathbf{v}_2 (*i* plane) and (ii) in the plane containing \mathbf{v}_1 and normal to \mathbf{v}_2 (*o* plane). As an example Fig. 1 shows a velocity vector diagram for a perfectly selected primary beam (\mathbf{v}_1 monochromatic) with two values of \mathbf{v}_2 which represent a distribution of speeds in the cross beam.

For nonreactive scattering conservation of energy requires that the net change in internal energy ΔE be related to the relative speeds before ($v_{12} = |\mathbf{v}_1 - \mathbf{v}_2|$) and after ($v_{34} = |\mathbf{v}_3 - \mathbf{v}_4|$) the collision by

$$\Delta E = \frac{1}{2}\mu(v_{34}^2 - v_{12}^2), \quad (1)$$

where $\mu = m_1 m_2 / (m_1 + m_2)$ is the reduced mass. Conservation of linear momentum requires that C , the tip of the center-of-mass velocity vector \mathbf{v}_c , divide

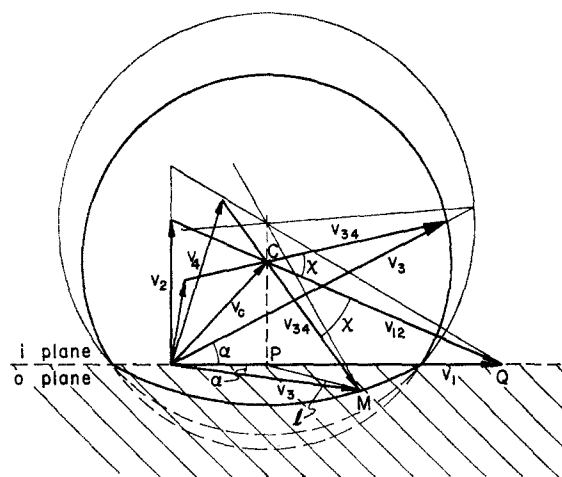


FIG. 1. Velocity vector diagram for inelastic scattering. The circles show the intersections of spheres generated by the tips of the vectors v_{34} as they intersect the plane of \mathbf{v}_1 and \mathbf{v}_2 (*i* plane) and the plane containing \mathbf{v}_1 and normal to \mathbf{v}_2 (*o* plane). The dashed arcs below \mathbf{v}_1 show the continuation of the circles in the *i* plane below the *o* plane. The laboratory and center-of-mass scattering angles are α and χ , respectively. The light lines show a redrawing for a different \mathbf{v}_2 .

\mathbf{v}_{12} and \mathbf{v}_{34} so that the fractions to the right of C in Fig. 1 become $\mathbf{v}_1' = \gamma \mathbf{v}_{12}$ and $\mathbf{v}_3' = \gamma \mathbf{v}_{34}$ with

$$\gamma = m_2 / (m_1 + m_2).$$

Because \mathbf{v}_2 is perpendicular to \mathbf{v}_1 the fraction of \mathbf{v}_1 to the right of point P is also $\gamma \mathbf{v}_1$. Now Eq. (1) becomes

$$\Delta E = (\mu/2\gamma^2)(v_3'^2 - v_1'^2) = (\mu/2\gamma^2)(l^2 - \gamma^2 v_1^2), \quad (2)$$

where we have used the relations (Fig. 1)

$$v_1'^2 = (CP)^2 + \gamma^2 v_1^2, \quad v_3'^2 = (CP)^2 + l^2. \quad (3)$$

Thus we obtain

$$l^2 = \gamma^2 [v_1^2 + (2\Delta E/\mu)], \quad (4)$$

so l is independent of v_2 . Inspection of Fig. 1 shows that this implies v_3 (*o* plane) is also independent of v_2 but v_3 (*i* plane) is not. For reactive scattering in which the product masses are m_3 and m_4 and particle 3 is the one detected, l does depend on v_2 , but, as is easily shown, this dependence vanishes as m_1/m_2 approaches m_3/m_4 .

Of course, there is an advantage in having a selector in the cross beam (\mathbf{v}_2) as well as the primary beam (\mathbf{v}_1), for then not only is the relative kinetic energy of the colliding molecules more closely specified but also scattering measured at one laboratory angle α occurs only at one (or, for $v_c > \gamma v_{34}$, two) center-of-mass angles χ . We believe that the advantage of the *o*-plane measurement with one selector is that it gives more intensity than the two-selector arrangement because a range of v_2 with a corresponding range of χ yields scattering at one α for a given ΔE . Some earlier