



FIG. 2. Interferogram of a rightward-propagating Mach 4.24 shock wave into 60 Torr of 1.5% H_2 in O_2 . The density increase due to vibrational relaxation is followed by a density decrease due to reaction of the H_2 . Height of the field of view is 1.3 cm.

times observed for the various mixtures are multiplied by the shocked gas pressure in atmospheres and given by the circles and triangles. The squares represent relaxation times deduced for the vibrational relaxation of oxygen infinitely dilute in hydrogen, $\tau_{\text{O}_2-\text{H}_2}$. A least-squares fit yields $p\tau_{\text{O}_2-\text{H}_2} = 10^{-8} \exp(36T^{-1})$, where p is in atmospheres, τ in seconds, and T is the average relaxation zone temperature in Kelvin degrees.

Ultrasonic measurements of O_2 - H_2 mixtures at room temperature have been made by Parker² and the value of $\tau_{\text{O}_2-\text{H}_2}$ derived from his data, represented by the solid square, is seen to be in good agreement with the present shock-tube data. These data correlate with those of many other systems as a function of the reduced mass and the energy-level spacing,³ and hence are interpretable as due to a simple collision process. They contain no suggestion of anomalies which might suggest "chemical effects" or even "sticky collisions."

At temperatures above about 1000°K, the density decrease due to reaction of the hydrogen is visible in the interferograms, as in the $T=1240^\circ\text{K}$ experiment of Fig. 2. With increasing temperature, the intervening region of uniform density decreases in length. Only data below 1500°K, where the reaction is clearly separated from the relaxation, were used in the least-squares analysis.

The experiments with average relaxation zone temperatures above 1500°K were reduced assuming that the maximum observed density corresponds to vibrational equilibration without reaction. The approach of the density to this maximum is still exponential, and the relaxation times so obtained are seen to be consistent with an extension of the lower temperature data.

The scatter in $\tau_{\text{O}_2-\text{H}_2}$ increases at the higher temperatures because collisions with other oxygen molecules become relatively more important in exciting oxygen vibration, and the observed time for the mixture is a less sensitive measure of excitation by O_2 - H_2 collisions.

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Triplet-Triplet Transfer in Plastic at 298° and 77°K

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THE occurrence of triplet-triplet transfer for the benzophenone naphthalene pair in Lucite at room temperature and at 77°K has been observed by the authors. This has been shown by noting the decrease in benzophenone phosphorescence as a function of the naphthalene concentration upon selectively exciting the benzophenone donor. The decay of naphthalene phosphorescence was also observed. The transfer of triplet energy in a rigid environment between benzophenone and naphthalene was first noted by Terenin and Ermolaev¹ at 77°K in an ether-ethanol glass. It has been observed subsequently by other workers²⁻⁵ in hydrocarbon glasses and in single crystals at 77°K. Prior demonstrations of triplet-triplet transfer at room temperature were made by Porter and Wilkinson⁶ and by Bäckström and Sandros⁷ using flash techniques on a solution containing the donor-acceptor pair.

Since triplet-triplet transfer in noncrystalline media is generally thought to result from short-range exchange interactions,^{4,5,8,9} one must consider the possible formation of donor-acceptor complexes in the course of making the glasses used in these experiments. Although the attractive interactions between the donor and acceptor molecules in solution might be too weak at room temperature to form a "complex" this may not be true at lower temperatures. Thus in the formation of a glass the lower temperatures which are realized while the solution is still fluid might lead to a system in which the donor and acceptor molecules are closer to one another than one would expect for weakly interacting molecules at room temperature. One possible way of avoiding complexing which results from lowering the temperature is to prepare the donor and acceptor molecules in a suitable plastic. In this latter method the donor and acceptor molecules are dissolved in a monomer solution and a rigid environment, i.e., a plastic, is achieved by raising the temperature above room temperature rather than by lowering it. Hence, the presence

of weak forces between the donor and acceptor molecules which might result in "complex" formation at lower temperatures can be avoided by maintaining the solution at temperatures above room temperature until a rigid environment is realized. It must be emphasized, however, that the possible "clumping" together of donor and acceptor molecules due to polymerization of the monomer cannot be excluded.

The methyl methacrylate monomer was distilled from P_2O_5 and the 90°–100°C fraction was retained. The benzophenone was purified by recrystallization, and its concentration was $5 \times 10^{-2} M$ in the solution at room temperature before polymerization. Its concentration was constant in the course of these experiments. The volume change accompanying polymerization and temperature change were not considered. Reagent grade naphthalene was sublimed. The catalyst used in the polymerization was benzoyl peroxide. The spectra at room temperature and at 77°K were obtained using an Aminco spectrophosphorimeter. The naphthalene lifetime measurements were obtained by photographing the decay from an oscilloscope.

The naphthalene lifetimes measured at 77°K were the same for concentrations of 0.2, 0.3, and 0.4M and were found to be 2.2 sec. The lifetimes of the first samples prepared at 0.2, 0.3, and 0.4M were measured at 77°K using both the Aminco spectrophosphorimeter and the lifetime measurement apparatus made by H. Melhuish, and were found to agree. The lifetimes of the second batch of samples, at naphthalene concentrations of 0.3, 0.2, 0.1, and 0.05M, were measured at 77°K and at room temperature using Melhuish's apparatus. The light source for these latter experiments was a G.E. HA4 Hg lamp. A combination of filters were used which could remove all light at wavelengths less than 365 m μ .

The reliability of the measurements is felt to be no better than $\pm 10\%$. The decay curves at 77°K were all found to be exponential. At room temperature, however, the decay curves of the same samples were non-exponential at the beginning of the decay. The longer-lived component was the more intense one and had the same lifetime value for all the different naphthalene concentrations used. The naphthalene lifetime at room temperature was 1.2 sec. Measurements which were made on the same samples several weeks after the first studies indicated no changes in lifetime at 77°K although there was a significant decrease in the naphthalene intensity. This decrease is thought to result from oxygen entering the plastic between the times that the studies were made.

Preparation of new samples at a benzophenone concentration of 0.05M and naphthalene at 0.3, 0.2, 0.1, and 0.05M were then studied. Once again there was no dependence of naphthalene lifetime on naphthalene concentration, either at room temperature or at 77°K. Furthermore the lifetimes were the same for both the old and new samples. The pure naphthalene sample did not phosphoresce when irradiated with a source per-

mitting light of wavelength less than 365 m μ to pass into the system, was to be expected. However, irradiation at all wavelengths yielded decay curves which were initially nonexponential both at room temperature and at 77°K. The lifetime obtained from the long-lived component was 2.3 sec at 77°K.

The results of these experiments in plastic hosts formed at elevated temperatures supports the idea that triplet-triplet transfer in noncrystalline media is not dependent on the formation of donor-acceptor complexes.⁵ Furthermore the observed insensitivity of the naphthalene lifetime to the presence of benzophenone indicates that the donor-acceptor interaction is very weak. These results, however, do not rule out exchange interactions (not necessarily between nearest neighbors) as the mechanism of energy transfer. In agreement with the theoretical results of Perrin¹⁰ and the observations of Terenin and Ermolaev¹ the ratio of the benzophenone intensities in the presence and absence of naphthalene is found to be exponentially dependent on the naphthalene concentration.

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Anisotropy of the Fluorine Chemical Shift Tensor in Xenon Tetrafluoride

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In our recent fluorine magnetic resonance study of polycrystalline XeF_4 ,^{1,2} the derivative spectra were found to be definitely asymmetric and anisotropy of the chemical shift tensor δ has been proposed^{1,2} as a possible origin of this asymmetry.

In view of the fact that although significant anisotropy is expected on theoretical grounds for a number