

electronic energy transfer from benzene to acetone is only slightly dependent upon vibrational energy content and vibrational mode for the vibronic states studied ($0, 6^1, 6^{11}, 6^{112}$). The cross sections are approximately 50% of gas kinetic values.

In the case of fluorobenzene, energy transfer from the vibrationless state has been studied for a variety of carbonyl acceptor molecules. Both σ_e^2 and σ_v^2 values are larger than in the case of benzene, the former approaching hard-sphere gas kinetic values. For the series of molecules acetone, 2-pentanone, and 2-heptanone the electronic cross section increases from 21 \AA^2 to 41 \AA^2 while the vibrational cross section increases from 10 \AA^2 to 15 \AA^2 for the same series. The values observed for σ_e^2 imply that nearly all collisions are effective even though the change in molecular size is restricted to the aliphatic side chain. Based on previous studies [2] regarding singlet-singlet electronic energy transfer between benzene and carbonyl compounds, the present results are consistent with the notion that collisions occur over a sufficient time period that an encounter by the aromatic donor at the opposite end of the aliphatic chain from the carbonyl group may eventually result in energy transfer. This would presumably follow appropriate conformational changes which place the carbonyl moiety in close association to the aromatic ring. Results of these studies will be discussed in the light of previous work [2] which indicated that steric effects could be observed in singlet-singlet electronic energy transfer in the gas phase.

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Phosphorescent Benzene: Triplet Sublevel Origins of Decays

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Theory predicts that the radiative emission from the lowest triplet state (phosphorescence) should originate almost entirely from the (nearly degenerate) upper pair of levels. However different kinds of experi-

ments yield rather disparate figures for the sublevel origin of the emission: $\sim 70\%$ from the upper pair from polarization of emission measurements [1, 2] and $\sim 100\%$ from microwave induced delayed phosphorescence results [3].

A third experiment, involving precise intensity and lifetime measurements over the 2 - 30 K range in various solvents has found, for example, a longer lifetime (by 1.8%) at 2.15 K, as compared to 4.13 K. Since spin lattice relaxation times are still short enough at these temperatures, we can confirm the $\sim 100\%$ figure for radiative decay. For the first time, the origin of the non-radiative decay has also been determined: it is similar to the radiative decay's origin.

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Photophysics of Bound and Dissociative Guest Molecular States in Rare Gas Lattices

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Host rigid cage effects have been observed in the photodissociation of matrix isolated ICl and alkyl iodide molecules. In ICl, excitation as much as 6000 cm^{-1} above the $B O^+$ dissociation barrier produces vibrationally relaxed B fluorescence, with near unity quantum yield and a risetime $< 10 \text{ ns}$. A differential matrix shift between the B and C states produces five bound B vibrational levels in Ne and Ar lattices, while only four exist in the gas phase. Excitation spectra in the B dissociative region do not show possible vibrational structure due to constrictive cage forces. Excitation of alkyl and perfluoroalkyl iodides in their ultraviolet dissociative continua produces a near infrared (700 - 1100 nm) spectral progression in the ground state C-I stretching frequency. This fluorescence apparently originates from a bound state in which the alkyl radical and excited I ($^2P_{1/2}$) atom are held together by constrictive cage forces. Photoselection