

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: ~70% from the upper pair from polarization of emission measurements [1, 2] and ~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 ~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

studies show the transition moment to lie along the C-I bond.

NH(A $^3\Pi$) and OH(A $^2\Sigma^+$) substitutional guests have localized rotational motions. Temperature dependent NH A \rightarrow X emission spectra are analyzed to show that NH(A $^3\Pi$) librates, with a several hundred cm^{-1} barrier to free rotation, while the ground X $^3\Sigma^-$ state almost freely rotates. Both NH (A $^3\Pi$) and OH(A $^2\Sigma^+$) strongly violate a proposed vibrational relaxation energy gap law, in that hydride rates are faster than deuteride rates. This violation, coupled with the absence of typical multiphonon temperature dependence, appears to reflect use of the rotational local mode as the phonon accepting mode. However, intersystem crossing by NH(A $^3\Pi$, $v' = 0$) shows the strong temperature dependence characteristic of stimulated phonon emission, and delocalized lattice phonon modes appear to accept energy in this case.

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Chemiluminescence from the Degradation of Unsaturated Elastomers

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The autoxidation of thin films of *cis*-1,4-polyisoprene in oxygen in the temperature range 25 - 126°C was studied by the weak chemiluminescence emission accompanying the process. The mechanism was assumed to involve a conventional free-radical oxidation chain with electronic excitation in the termination steps. From the time and temperature dependence of the intensity of the emission, activation parameters were obtained for some of the reaction steps. Chemiluminescence emission was also studied from a sample of *cis*-1,4-polyisoprene containing hydroperoxide groups that were introduced by means of singlet molecular oxygen.

An apparatus for measurement of the chemiluminescence was described.

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The Thermodynamics of Photochemical Energy Conversion, and Its Relevance to Photochemical Solar Energy Conversion

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This paper is addressed to the following questions: what is the maximum efficiency with which radiant energy may be turned into other forms of energy, and in particular into electrical energy (as in a photoelectric device) or into chemical free energy (as in an endergonic photochemical reaction)? Are such energy converters subject to thermodynamic restraints of the type that limit the performance of heat engines, or are they capable, at least in principle, of perfectly efficient conversion? What are the implications of any theoretical limitations on maximum efficiency for solar energy conversion?

These questions have been posed and answered in a number of ways in the literature already. Although disagreement with the application of thermodynamic arguments to photon absorption processes has occasionally been expressed [1, 2], it has generally been concluded [3 - 12] that the maximum efficiency of a radiant energy transducer is given by an expression of the type

$$\eta \leq 1 - T_s/T_L \quad (1)$$

Here T_s is the temperature of the absorbing system and T_L is the temperature of the incident light — a concept that is unfamiliar to the majority of physical chemists. It is defined in most general form by the relationship

$$T_L = \dot{E}_L/\dot{S}_L \quad (2)$$

where \dot{E}_L and \dot{S}_L are the rates at which the incident light adds energy and entropy to the absorbing system. In particular cases (e.g. for black body radiation) T_L may be more explicitly defined, and numerical estimates of η may be made.

In energy converters which produce light from work (e.g. from electrical work, as in a light-emitting diode), analogous reasoning [13 - 16] leads to an expression for the maximum efficiency of conversion of work to radiant energy of the type:

$$\eta < (1 - T_s/T_L)^{-1} \quad (3)$$