

## Preliminary Note

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### Energy transfer from single vibronic levels of benzene

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The study of electronic energy transfer between polyatomic molecules has occupied the attention of photochemists for the past two decades<sup>1</sup>. Investigations in both the gas phase and the liquid phase have resulted in many observations of energy transfer from both the singlet and triplet excited states. Work with benzene as an energy donor in the gas phase has been particularly prominent. The studies of singlet energy transfer from benzene have been performed at pressures for which the initially formed excited vibronic states undergo a relatively large number of collisions prior to the electronic energy transfer process. As a result the measured energy transfer cross-sections are determined by several of the lower vibronic levels of the excited singlet state. From the distribution of vibronic states populated in benzene at pressures of 15 Torr the transfer of electronic energy from the  ${}^1B_{2u}$  state of benzene to acetone is quite efficient ( $\sigma^2 = 10.4 \text{ \AA}^2$ )<sup>2</sup>.

In order to explore the nature of electronic energy transfer from individually selected vibrational levels of the  ${}^1B_{2u}$  state of benzene we have initiated a program of low-pressure energy transfer measurements using reasonably monochromatic excitation sources ( $\leq 0.4 \text{ nm}$  half-width). In this paper the results obtained for four of these vibronic levels are described.

The strongest transitions in the  ${}^1A_{1g} \rightarrow {}^1B_{2u}$  absorption band of benzene are denoted  $A_0^0$ ,  $A_1^0$ ,  $A_2^0$  and occur at 259.0 nm, 253.0 nm and 247.4 nm, respectively<sup>3</sup>. Each of these transitions is sufficiently separated from nearby absorption bands so that excitation light of 0.4–0.5 nm halfwidth will almost exclusively lead to the formation of upper vibronic states characterized by one quanta of  $\nu_6$ ,  $\nu_6 + \nu_1$ , and  $\nu_6 + 2\nu_1$ , respectively. A much weaker transition in this spectral region, commonly designated  $B_0^0$ , leads to excitation of the vibrationless excited singlet state. This transition can also be isolated for the most part from adjacent bands with an appropriately narrow excitation band pass. The mean lifetimes of these vibronic states have been measured by Selinger and Ware<sup>4</sup> and by Spears and Rice<sup>5</sup>.

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### Results

Energy transfer from these four states to acetone and propane has been studied by monitoring the intensity of fluorescent transitions from each upper state to specific vibronic levels of the ground electronic state as a function of added acetone or propane. The Stern–Volmer slopes obtained from the quenching data, the lifetimes, and the cross-sections for energy transfer are shown in Table 1. If it is assumed that propane removes only vibrational energy under the conditions of these experiments, and that the removal of vibrational energy by acetone is equivalent to that by propane, the cross-sections for pure electronic energy transfer shown in Table 2 can be calculated.

TABLE 1  
QUENCHING RESULTS

(a) Low pressure					
Vibronic state	$\epsilon_{\text{vib}}$	Acceptor	Stern–Volmer slope (Torr <sup>-1</sup> )	$\tau^*$ (nsec)	$\sigma^2(\text{A}^2)$
0	0	acetone	0.75	87	19.5
		propane	0.165		4.3
6 <sup>1</sup>	521	acetone	0.721	75	22.2
		propane	0.31		9.4
6 <sup>1</sup> 1 <sup>1</sup>	1444	acetone	1.06	62	38.7
		propane	0.67		24.5
6 <sup>1</sup> 2	2367	acetone	1.09	46	53.6
		propane	0.75		36.9
(b) High pressure					
		acetone	0.508	75	15.3

(a) [Benzene] = 0.27 Torr, Temp. = 30°C  
 (b) [Benzene] = 14.8 Torr, Temp. = 30°C,  $\lambda_{\text{ox}} = 254.0 \text{ nm}$

\* Values interpolated from the pressure study of Selinger and Ware.

TABLE 2  
CROSS-SECTIONS FOR ELECTRONIC ENERGY TRANSFER

Vibronic state	$\sigma^2(\text{acetone}) - \sigma^2(\text{propane})$
0	15.2 A <sup>2</sup>
6 <sup>1</sup>	12.4
6 <sup>1</sup> 1 <sup>1</sup>	14.2
6 <sup>1</sup> 2	16.7

### Discussion

It is clear from the propane results that vibrational energy transfer occurs with increased efficiency as the vibrational energy content increases. In fact a plot

of  $\sigma^2$  (propane) vs.  $\epsilon_{\text{vib}}$  is linear. Since the density of states also increases, these data are consistent with a model in which energy is removed in a multistep fashion, each step becoming more efficient as the energy of that step decreases. That "deactivation" can also be accompanied by "activation" is clearly indicated by the result with propane on the 0 state. The "strong collision" model<sup>6</sup> of vibrational energy transfer requires that propane remove increasing amounts of energy with increasing efficiency. Although these results do not rule out such a model, it would seem to be less likely, since "Boltzmanization" requires much larger pressures<sup>7</sup> than are consistent with the cross-sections obtained in this work if they are a measure of complete removal of the vibrational energy of the excited singlet state. In addition emission spectra show that nearby vibronic states are populated during the vibrational deactivation of the  $6^1$  state. It may be noted that excitation of quanta of  $\nu_1$  (C-C stretch or "breathing" mode) in addition to  $\nu_6$  (C-C bending mode) does not result in a deviation from the linear relationship between  $\sigma_{\text{T}}^2$  (propane) and  $[\epsilon_{\text{vib}}]$ .

The variation in electronic energy transfer is very small if, in fact, there is any variation at all. The precision of the measurements, however, definitely places transfer from the  $6^1$  state below that of the 0 and  $6^{11}$  states, even though energetically it is between these two states. Whether this is indicative of a dependence on the vibrational mode for electronic energy transfer can only be conjecture at this time. The presence of 2 quanta of  $\nu_1$  ( $6^{12}$  state) seems to increase the transfer cross-section, and this result could support either an energy dependence or a vibrational mode dependence.

It is interesting to note that the cross-section for the 0 state is equivalent to that obtained at high pressures. However, this result is not surprising since the high pressure experiment was performed by monitoring fluorescence at the same wavelength as was used to study the 0 state. Hence, the two values simply provide further experimental verification for one another. Parmenter and Schuyler<sup>8</sup> have pointed out that fluorescence from a high pressure benzene sample is due only partly ( $\sim 18\%$ ) to emission from the 0 state, and thus energy transfer in the high pressure case must involve some average cross-section from the several low frequency vibrational modes of the excited singlet state. Total emission measurements on another apparatus yield  $\sigma^2 = 10.4 \text{ A}^2$  at 15 Torr of benzene. This may indicate that transfer is characterized by cross-sections below  $10 \text{ A}^2$  for some of the low frequency vibrational modes which are not optically allowed. The value of  $12 \text{ A}^2$  for the  $6^1$  state ( $521 \text{ cm}^{-1}$ ) is not inconsistent with such a conclusion. Possible implications of these observations must await further experimental results currently in progress.

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