

# Molecular electronic energy transfer in bichromophoric molecules in solution and in a supersonic jet expansion

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## Abstract

We present preliminary results showing electronic energy transfer (EET) between benzene and biacetyl and between naphthalene and anthracene in a supersonic jet expansion and in bichromophoric molecules in solution. Excitation of several vibronic levels of benzene (donor) in the presence of biacetyl (acceptor) shows quenching of benzene emission with simultaneous appearance of biacetyl fluorescence emission with similar results for the pair naphthalene (donor) and anthracene (acceptor). The quenching follows Stern-Volmer kinetics as a function of added acceptor pressure, indicative of EET in a binary donor-acceptor complex.

## 1. INTRODUCTION

Electronic energy transfer (EET) processes involve non-radiative transfer of electronic excitation from an excited donor molecule  $D^*$  to an acceptor molecule A. The transfer may be an intermolecular process which can be described in terms of a bimolecular kinetic process



where the bimolecular quenching process is related to an intermolecular energy transfer rate by

$$k_{ET}^{inter} = k_Q[A] \quad (2)$$

Theoretically  $k_{ET}$  is attributed to two possible contributions. The long range coulombic contribution formulated by Förster (ref. 1–3) in terms of dipole-dipole interaction is well documented (ref. 4). It is particularly suitable for describing electronic energy transfer in solution whenever conditions for favourable spectroscopic overlap conditions between the emission of  $D^*$  and the absorption of A are met.

The second contribution to EET can be realized whenever these conditions are not fulfilled. A short range exchange interaction, as formulated by Dexter, can then facilitate EET (ref. 5). It was shown to be the correct mechanism to describe intramolecular EET in bichromophoric molecules of the type D–A (ref. 6–10) in a unimolecular process of the type



These studies were performed in solutions where solvent effects cannot be ruled out. Short range EET processes in the gas phase involve collision which will lead to a collision complex formation for a period long enough for the process described by eq. (3) to take place. There is evidence to support the validity of a modified Dexter formulation for the description of these gas phase EET processes (ref. 11–16). In some cases there is evidence for a formation of a collision complex as part of the EET process (ref. 16).

The unique conditions in a supersonic jet expansion suggest studying these processes in more detail. In particular the dependence of the transfer on a particular vibronic excitation of the donor moiety in a bichromophoric cluster of the type D–A can be studied. These can be van der Waals complex or a more loosely bound bichromophoric complex. One question that may be addressed is whether or not an EET process described by eq. (2) can be observed resulting as in solution by dual fluorescence spectrum (ref. 6–10) typical of a bichromophoric D–A molecule or cluster.

Our choices for a D–A system were the benzene (D) – biacetyl (A) pair and the naphthalene (D) anthracene (A) pair. Studies of intermolecular EET (ref. 17–19) and intramolecular EET (ref. 7–9) in solution as well as gas phase EET studies of the benzene–biacetyl pair (ref. 11–16) indicate that the basic EET mechanism operative in this case is the Dexter exchange interaction (ref. 5), whereas for the naphthalene–anthracene pair solution studies suggests intramolecular EET via dipole-dipole interaction (ref. 20).

We present in this paper preliminary results that demonstrate a short range EET in supersonic jet expansion. Previous studies of EET under similar conditions were performed by Poeltl and McVey (ref. 21) on dimers of benzoic acid, by Tomioka and coworkers (ref. 22) on mixed dimer of benzoic acid and p-toluic acid and by Lahamani and coworkers for the p-xylene p-difluorobenzene pair (ref. 23). In all these studies the extent of spectral overlap rules out exchange interaction as the sole mechanism thus complicating mechanistic interpretation. The choice of benzene-biacetyl pair eliminates this complication.

## 2. EXPERIMENTAL

Samples for the benzene-biacetyl experiment were prepared in a 2 liter stainless steel cylinder. Liquid benzene and biacetyl were held at room temperature in separate containers. Specific pressures of the organic vapors were let into the cylinder, and measured by a mechanical manometer. Finally, helium was added to bring the total pressure up to 5 Atm.

The gas mixture was expanded through a General Valve series 9 pulsed valve with a 0.5 mm orifice into a stainless steel vacuum chamber. The chamber was pumped by an untrapped CVC Goldline 6 inch diffusion pump backed by a Welch model 1397 rotary pump. Typical background pressure was about  $5 \times 10^{-8}$  torr.

For the naphthalene - anthracene experiment mixtures were prepared by passing He at 5 atm over naphthalene held at room temperature in a stainless steel container, into a high-temperature solenoid valve. The valve, built according to Li and Lubman (ref. 24) design, serves as the hot oven and contains the added anthracene. The expansion conditions are the same as those used in the benzene-biacetyl experiment.

The samples were excited by a Quanta Ray PDL-1 Dye laser, pumped by the third harmonic of a DCR Nd:YAG laser, operated at 10 Hz. Coumarin 420 was used to excite biacetyl, while benzene excitation was provided by frequency doubling the output of the dye laser, operating with coumarin 500, using a WEX1 wavelength extender. The laser light is passed through a series of baffles into a vacuum chamber, and intersects the molecular beam about 35 mm from the valve orifice.

Excitation spectra were recorded with a Hamamatsu R1104 photomultiplier tube, using appropriate filters to exclude scattered laser light. A Bausch and Lomb 0.25 meter monochromator was used to record dispersed emission spectra. Signals were averaged over a number of laser shots with a PAR model 162 boxcar, or with a Textronix digital oscilloscope.

Solution work was performed using standard fluorimeter and laser induced fluorescence.

## 3. RESULTS

### 3.1. Benzene-biacetyl pair

The first basic requirement of this study was to obtain the excitation and emission spectra of both benzene and biacetyl in order to examine the extent of spectral overlap under the conditions of supersonic jet expansion.

Figure 1 shows the excitation spectrum of 3 torr benzene jet expansion with 5 atm of helium in the 260 nm wavelength region. This is basically the spectrum observed by Levy and coworkers (ref. 25) and is indicative of insufficient cooling. Thus some of the lines are due to hot transitions. A low resolution dispersed emission spectrum resulting from exciting the  $6_0^1$  transition of benzene at  $38610 \text{ cm}^{-1}$  is shown in Fig. 2. This emission overlaps poorly with the  $S_0 \rightarrow S_1$  absorption spectrum of biacetyl, as can be seen from its jet expansion excitation spectrum shown in Fig. 3. Biacetyl does not show any absorption in the range of the benzene 260 nm bands of Fig. 1 (ref. 26), which allows a specific excitation of benzene in benzene biacetyl jet expanded mixture. The dispersed emission of this mixture is shown in Fig. 4. The 350 nm emission band is the same as that of pure benzene (Fig. 2), whereas the band centered around 480 nm can be attributed to biacetyl.

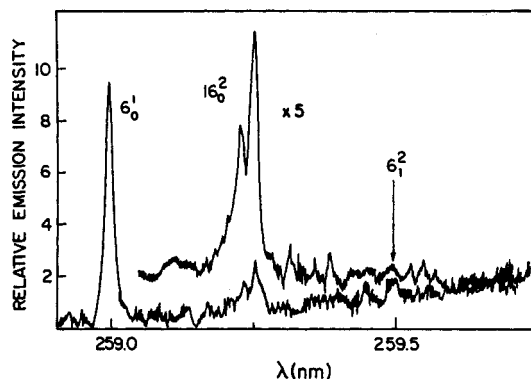


Figure 1: Benzene excitation spectrum, for 3 torr benzene in 5 atm helium. Upper trace taken at 5 times higher sensitivity.

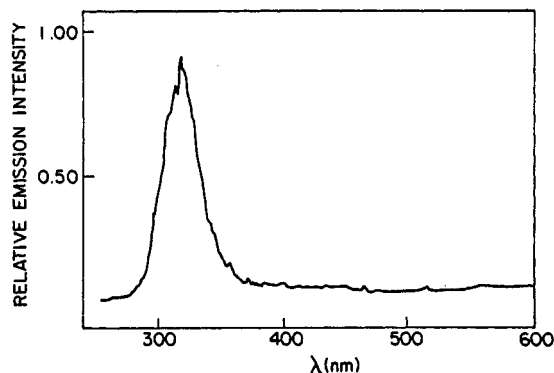


Figure 2: Low resolution (5 nm) benzene emission spectrum (10 torr benzene in 5 atm helium) excited at the  $6_0^1$  transition ( $38610 \text{ cm}^{-1}$ ).

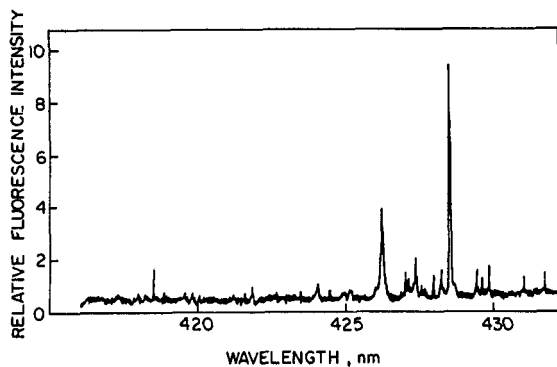


Figure 3: Biacetyl excitation spectrum, for 10 torr biacetyl in 5 atm helium.

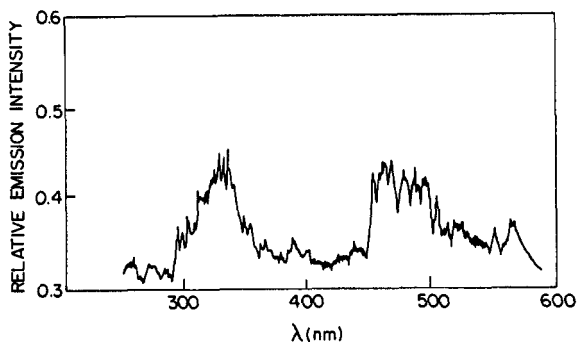


Figure 4: Low resolution (10 nm) emission spectrum of jet expanded benzene - biacetyl mixture (10 torr benzene, 16 torr biacetyl in 5 atm helium), excited at the  $6_0^1$  benzene transition.

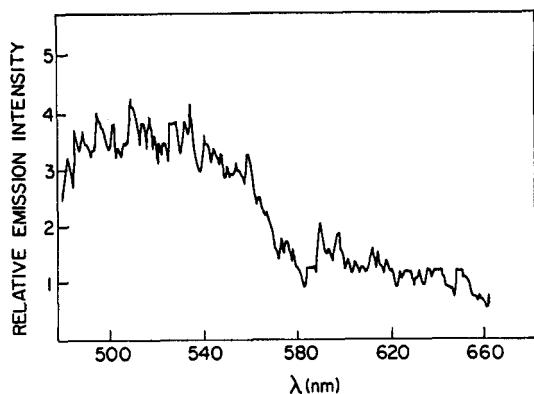


Figure 5: Low resolution (10 nm) emission spectrum of jet expanded biacetyl, excited at 444.5 nm.

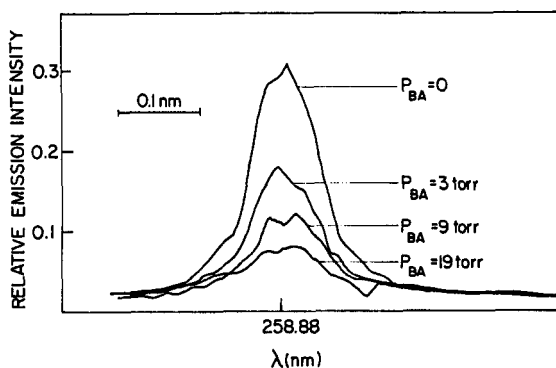


Figure 6: Progressive quenching of the  $6_0^1$  peak of benzene by added pressure,  $P_{BA}$ , of biacetyl (3 torr benzene in 5 atm helium).

The dispersed fluorescence emission from pure biacetyl excited at its 444.5 nm ( $22497 \text{ cm}^{-1}$ ) band (Fig. 3) is shown in Fig. 5, matching the 480 nm emission band of the mixture's dual emission.

This dual fluorescence seems to indicate enlectronic energy transfer from benzene to biacetyl similar to that observed intermolecularly in solution (ref. 17-19), or in the gas phase (ref. 11-15). This is further supported by studying quenching of the  $6_0^1$  excitation peak of benzene upon adding biacetyl (Fig. 6). This quenching seems to follow a Stern-Volmer dependence, shown in Fig. 7 for different excitation lines of benzene. In addition, evidence for EET through complex formation is given in Figure 8 where the excitation spectrum of the benzene is monitored by looking at laser induced fluorescence of the biacetyl band. This spectrum is different from that of pure benzene (Fig. 1).

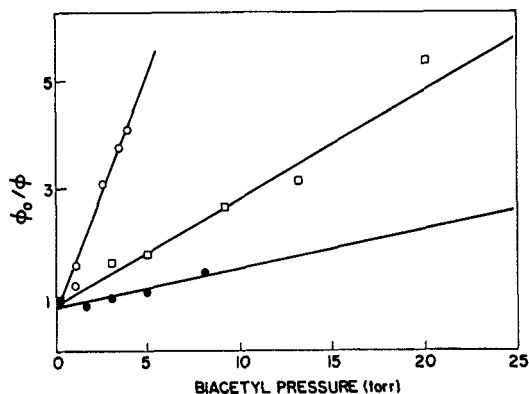


Figure 7: Stern-Volmer plot of quenching benzene emission by added biacetyl in jet expanded mixture, for three excitation wavelengths corresponding to the  $16_0^2$  transition ●,  $6_0^1$  transition ◻ and the  $6_0^1 16_1^1$  transition ○.

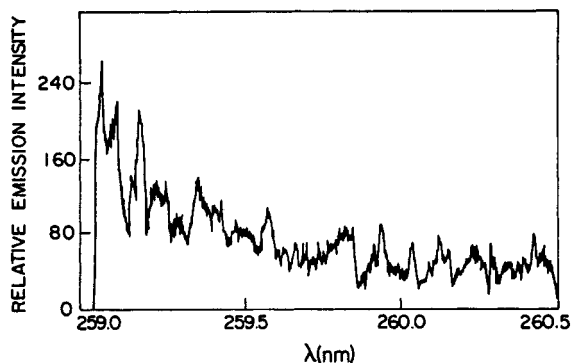


Figure 8: Excitation spectrum of the benzene-biacetyl complex, viewed through a filter that blocks the benzene emission. Sample: 3 torr benzene and 25 torr biacetyl in 5 atm helium.

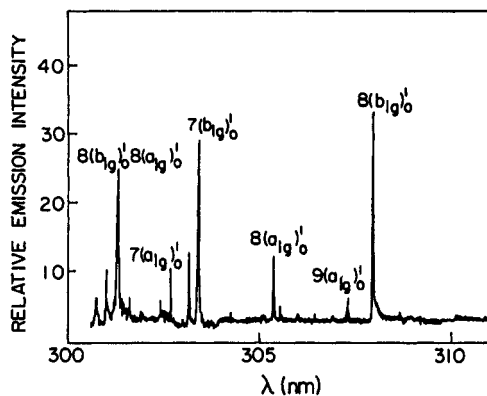


Figure 9: Excitation spectrum of 0.3 torr naphthalene in 5 atm He.

### 3.2. Naphthalene-anthracene pair

The excitation spectrum for jet expanded naphthalene and anthracene is shown in Figures 8. The results are similar to those reported previously (ref. 27, 28). The extent of spectral overlap between naphthalene fluorescence (ref. 29) and anthracene absorption (ref. 30) may determine the mechanism promoting the transfer. Figure 10 shows quenching of the  $8(b_{1g})_0^1$  transition of naphthalene by added anthracene pressure. Again this quenching follows a Stern-Volmer dependence Fig. 11. Examination of the excitation spectrum of the jet expanded naphthalene-anthracene mixtures by looking at anthracene emission at the 380-400 nm range shows (Fig. 12) additional spectral features to those observed for pure naphthalene indicative of complex formation between these molecules in which electronic excitation of the naphthalene moiety is being transferred to the attached anthracene moiety.

### 3.3. Intramolecular electronic energy transfer in bichromophoric molecules

An investigation of intramolecular electronic energy transfer (intra-EET) was conducted on three series of bichromophoric molecules (ref. 6-9, 36). The first series consists of cyclic  $\alpha$ -diketones incorporating a para-substituted benzene ring, connected through two identical polymethylene bridges. These bridges are of varying length, but the total number of methylene groups in the two bridges of all these compounds is equal. This series contains the molecules P-n,m: P-5,5, P-6,4, P-7,3 and P-8,2 as illustrated in Figure 1. The second series consists of cyclic  $\alpha$ -diketones connected through two, equal length, polymethylene bridges to a hydroquinone-dimethyl-ether chromophore: HQ-5,5, HQ-6,6 and DiMeO-P-5,5. The third series includes two molecules from the former series, P-5,5, HQ-5,5 and another molecule 1,4-Naph-5,5, where naphthalene is connected through two bridges to an  $\alpha$ -diketone chromophore. For all three compounds, the bridges and the  $\alpha$ -diketone chromophore are identical, while the aromatic chromophore varies.

The purpose of this study was to map the exchange interactions responsible for the intra-EET between the chromophores, as a function of orientation (series 1 and 2) and of spectral overlap (series 3). The relative orientation of these chromophores was varied and the degree of intra-EET differs accordingly. The spectral overlap between the chromophore pairs in series 3 is varied and the results showed a dependence of intra-EET upon this factor (ref. 36). Earlier studies (ref. 6-9) of singlet-singlet and triplet-triplet intra-EET were performed on symmetrical bichromophoric molecules, so that the main parameter for comparison between the various compounds was the interchromophore distance. Recent study on the asymmetrical bichromophoric

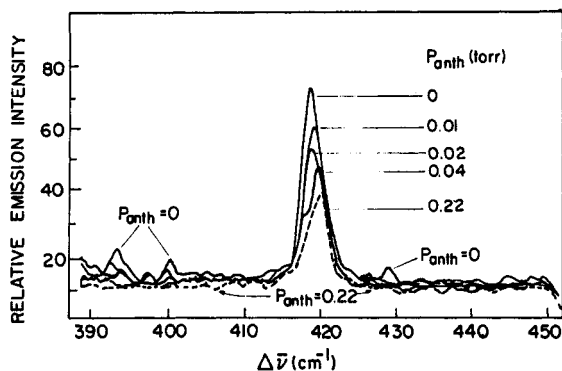


Figure 10: Progressive quenching of the  $8(b_{1g})_0^1$  peak of 0.03 torr naphthalene in 5 atm He by added anthracene pressure,  $P_{anth}$ .

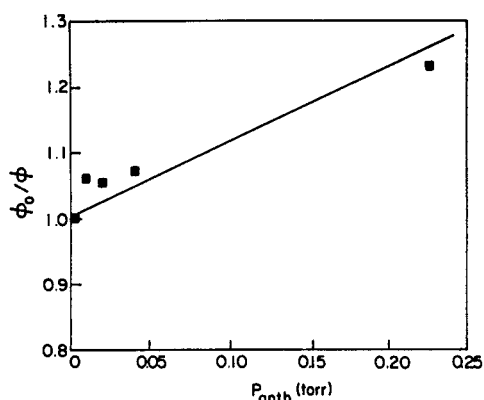


Figure 11: Stern-Volmer plot of quenching naphthalene emission by added anthracene in jet expanded mixture of 0.03 torr naphthalene at 5 atm He.

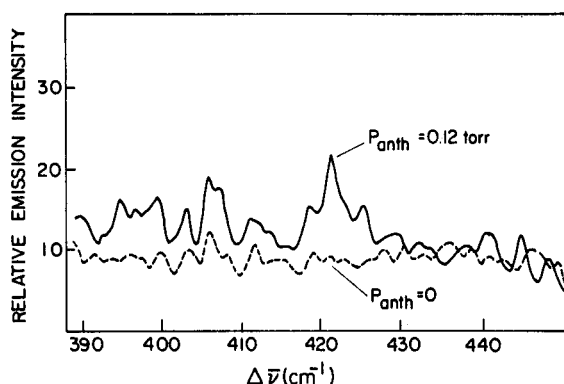


Figure 12: Excitation spectrum of naphthalene observed by monitoring the 380-400 nm spectral range of anthracene fluorescence, indicative of complex formation in 0.06 torr naphthalene with 0.12 torr anthracene in 5 atm jet expanded He. Lower trace shows results with no anthracene present in the jet.

molecules (Fig. 13) enabled us to investigate the influence of additional geometrical dimensions upon singlet-singlet intra-EET (ref. 36). The molecules studied are a variation upon the previously investigated P-5,5 (ref. 8) molecule, shown to exhibit partial intra-EET when the substituted benzene moiety was excited. Absorption spectra were recorded for these compounds together with the separate constituent chromophores. Most spectroscopic properties of the molecules are described by a superposition of those of their constituent chromophores (ref. 37). Unique for the bichromophoric molecules, is the fact that, depending on the molecular geometry, energy absorbed by the aromatic chromophore is transferred in part to the  $\alpha$ -diketone and both chromophores emit their fluorescence spectra. The fluorescence emission spectrum for the compounds and their constituent chromophores was recorded. The molecules of series 1 and 1,4-Naph-5,5 were excited with a 255 nm light beam. The molecules of series 2 were excited at 285 nm.

The fluorescence emission spectrum for the bichromophoric molecules was recorded at different temperatures. The thermal dependence are attributed to conformational factors. All compounds show a temperature dependence for the donor moiety fluorescence emission, thus showing that there is partial intra-EET from a conformational structure that is different from that of the ground state and that the chromophores are all close enough for energy transfer, but not too close for a total energy transfer.

The results indicated that the transfer efficiency is strongly structure dependent, suggesting that the Dexter type exchange interaction is responsible for singlet-singlet intra-EET between the chromophores in a bichromophoric molecule. A previously developed kinetic scheme (ref. 8) was used for the analysis to which a good fit was found. From the analysis,  $\Delta E$ , the energy difference between the ground state conformation and the conformation of efficient intra-EET, was calculated.

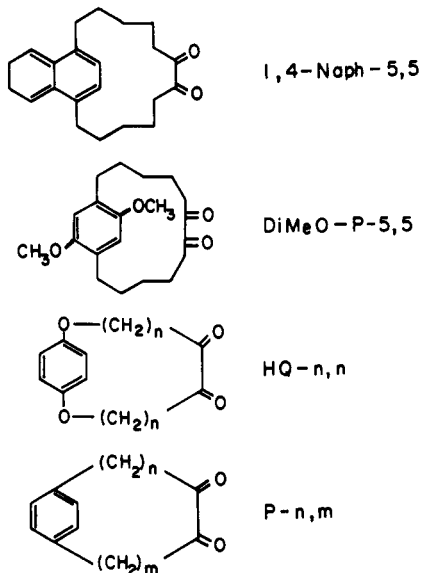


Figure 13: Structure of the bichromophoric molecules studied experimentally (ref. 36) for elucidation of Intra-EET mechanism.

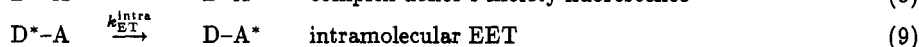
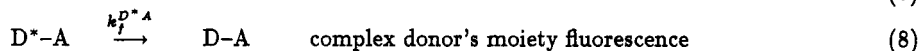
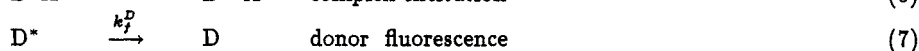
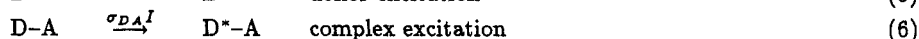
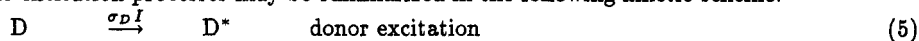
#### 4. DISCUSSION

Our results provide evidence for intramolecular EET is a supersonic jet. In the gas phase this type of behavior is indicative of collisionally induced energy transfer, that might involve an excited  $D^* - A$  complex formation prior to energy transfer (ref. 16). In the jet complex formation precedes the excitation process and can be described by



where  $K$  is the association equilibrium constant. Further assumption made here is that in the excited  $D^* - A$  complex EET process is faster than dissociation and that  $D - A$  is a weakly bound complex where  $D$  and  $A$  maintain most of their spectral identity.

The EET and the excitation processes may be summarized in the following kinetic scheme:



where  $\sigma_D$  and  $\sigma_{DA}$  are the crosssections for donor absorption for the free donor and for its complexed form respectively,  $I$  is the excitation intensity and the  $k_f$ 's are the fluorescence rate constants.

A kinetic analysis of this scheme leads to equation (11) which has the form of a traditional Stern-Volmer relation

$$\phi^o / \phi = 1 + \tau_f^{D^* - A} k_Q [A] \quad (11)$$

where  $\tau_f^{D^* - A} = 1/k_f^{D^* - A}$  and  $k_Q$  is the apparent bimolecular quenching rate constant related to the intramolecular EET rate by

$$k_Q = (\sigma_{DA} / \sigma_D) k_{EET}^{intra} K \quad (12)$$

Table I summarizes  $k_Q$  values for the different excited vibronic states of benzene, obtained from the data presented in Fig. 6 and Fig. 7. It clearly shows that the EET is a function of the excess vibrational excitation, in a specific vibronic state. It is interesting to note that  $k_Q$  values are in the same range as those observed for the gas phase experiments (ref. 13-15), where a Boltzmann distribution of vibronic states is involved in the EET process.

**Table 1:** Quenching constants for benzene quenched by biacetyl, as related to excess vibrational energy of the excited benzene,  $\Delta E_{vib}$ .

Transition	Excitation Wavelength $\text{cm}^{-1}$	$\tau_f^D$ ns (ref. 35)	$k_Q$ $10^6 \text{ torr}^{-1} \text{ sec}^{-1}$	$\Delta E_{vib} \text{ cm}^{-1}$ (ref. 35)
$6_0^1$	38610	79	2.6	521
$16_0^2$	38565	89	2.2	486
$6_0^2$	38525	72	7.8	1042
$6_0^1 16_0^1$	38450	77	10.	767

It should be noted that our kinetic scheme does not include a dissociation channel for  $D^* - A$ . However the emission of biacetyl from the complex (Fig. 4) is blue shifted by about  $2000 \text{ cm}^{-1}$  with respect to that of the uncomplexed molecule (Fig. 5), indicative of emission from hot biacetyl that may have been formed by dissociation of  $D^* - A$ .

Existing EET theories (ref. 1-4, 31, 32) are not directly applicable to the situation in hand. However, it is very probable that the requirement for spectral overlap, under the present conditions where EET takes place without prior vibrational relaxation, is met by a specific vibronic excitation. Our current and future studies will address this problem as well providing further data on the nature of the  $D - A$  complex and resolve some of the problems left open in this preliminary study (ref. 33, 34).

The solution work indicates the same general exchange interaction mechanism is operative regardless of the particular medium in which EET takes place.

## 5. CONCLUSIONS

We have provided evidence for the possibility of electronic energy transfer between an excited donor to an acceptor in a supersonic jet expansion. Due to poor spectral overlap conditions are set for studying EET due mainly to short range exchange interaction in a D-A complex. The transfer is shown to depend on the specific vibronic excitation of the donor.

The solution study provides evidence to the validity of Dexter model for short range exchange interaction mechanisms for Intra-EET.

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