

Determination of the distance for triplet energy transfer in the faujasite NaY [☆]

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Abstract

Triplet energy transfer from xanthone to 1-methylnaphthalene in the faujasite NaY involves a rapid component which occurs in < 100 ns. This process has been examined with laser techniques. The yields of detectable triplet xanthone and 1-methylnaphthalene are interpreted in terms of a statistical model that assumes that the sphere for energy transfer includes the original excitation supercage and its four nearest neighbor supercages; i.e. the donor and acceptor are not required to be in the same supercage. For 1-methylnaphthalene, extensive self-quenching (occurring in the same distance regime as energy transfer) controls the yields of detectable triplets.

1. Introduction

The control of photochemical and photophysical processes by solid hosts is a subject of current interest [1]. Among the numerous hosts that have been examined, zeolites have the advantage of a well-defined structure, thus offering the possibility of detailed interpretation of structure–reactivity relationships. In order to test the distance dependence of triplet energy transfer in zeolites, we have examined the quenching of triplet xanthone by 1-methylnaphthalene in the faujasite NaY. We find that most of this transfer involves sensitization in time scales shorter than ≈ 100 ns; for the purposes of this Letter we describe this as rapid quenching. The dynamic decay of both xanthone and 1-methylnaphthalene triplets occurs in a longer time domain, even in aerated samples (vide infra); this Letter deals only with

the rapid component, observed immediately after laser excitation.

2. Experimental

The laser system uses the third harmonic from a Surelite Nd:YAG laser for excitation. The diffuse reflectance setup is similar to that described by Wilkinson [2], and uses a Tektronix 2440 digitizer to capture the signals which are then transferred to a Macintosh-IIci computer. Software has been written using the LabVIEW 2.2 package from National Instruments. A combination of scattered light and luminescence from the samples tends to limit the time resolution of the experiments; for these samples the resolution was limited to 50–100 ns.

Experiments were carried out by 355 nm laser excitation [2] of a series of composites (under air) containing a constant concentration of xanthone and

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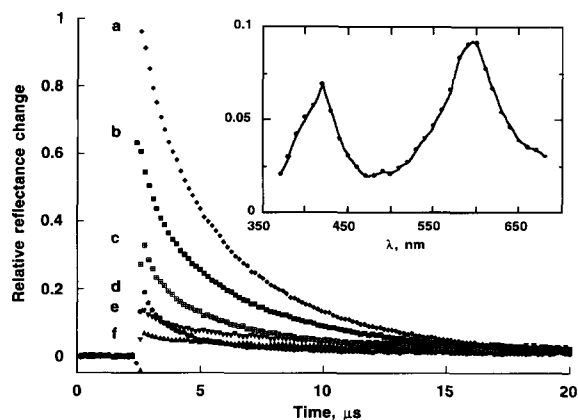


Fig. 1. Decay traces for xanthone triplets for different xanthone:methylnaphthalene ratios ((a)–(f): 1:0.1, 1:0.5, 1:1, 1:1.8, 1:2.5 and 1:3.7) recorded in aerated samples following excitation at 355 nm. Normalized to the intensity of the xanthone-only sample (not shown). Inset: Transient diffuse reflectance spectrum recorded 1 μ s after excitation for a sample containing a 1:1 ratio of xanthone and 1-methylnaphthalene.

variable amounts of 1-methylnaphthalene. Naphthalene chromophores are transparent at 355 nm.

Samples were prepared in the following way: The faujasite NaY was heated to 400°C for 18 h at atmospheric pressure. The sample was allowed to cool down to about 100°C and 1 g of the zeolite added to a solution of 20 mg of xanthone in 30 ml of dichloromethane. The mixture was stirred for 2 h in a closed container to allow the free diffusion of xanthone into the zeolite host. The mixture was then filtered and the solid treated with 30 ml of dichloromethane and stirred for 2 h and filtered again. The solid was then dried under vacuum and stored in a desiccator. The combined filtrates were examined by UV in order to determine the amount of xanthone remaining. It was thus possible to estimate the amount of xanthone included in the zeolite. Typically, ≈ 15 mg/g were included, corresponding to an occupancy of about one for every six cavities, assuming that only the major α -cage is occupied. These samples were later treated with 1-methylnaphthalene in CH_2Cl_2 in a similar way, except that the solvent was removed by rotoevaporation, followed by vacuum drying.

3. Results and discussion

The transient spectra recorded show (insert in Fig. 1) the characteristic signals for 1-methylnaphthalene

triplets ($\lambda_{\text{max}} = 420$ nm) and xanthone triplets ($\lambda_{\text{max}} = 595$ nm) [3]; the position of the latter is indicative of a relatively polar environment [4]. The decay traces (displayed as relative changes in reflectance, $\Delta J/J$) recorded at 600 nm show a monotonic decrease in the observable yield of ketone triplets with increasing quencher concentration. In contrast, the yields of naphthalene triplets show a ‘bell shape’ dependence on occupancy, peaking at around 18% average supercage occupancy (vide infra). Changes in decay lifetime are complex and a comprehensive study will be reported at a later time.

In an attempt to interpret the variations in triplet yield with quencher concentration, we have tested three models. In model ‘A’ we assume that donor and acceptor must share the same supercage at the time of excitation for quasi-static energy transfer to occur. In model ‘B’ we assume that transfer can occur in the same supercage and in any of its four immediate neighbors (5 supercages), and in model ‘C’ we assume that in addition to those in model ‘B’, transfer is also possible in second neighbor cages (for a total of 17 supercages). The following equation gives the dependence between the probability of xanthone triplet survival (i.e. of triplet detection), P_s , and the average fraction of cavities occupied by 1-methylnaphthalene (R_N):

$$P_s = (1 - R_N)^n, \quad (1)$$

where n has values of 1, 5 and 17 for models A, B and C, respectively. Fig. 2 shows calculated plots for the three models, along with normalized experimental data

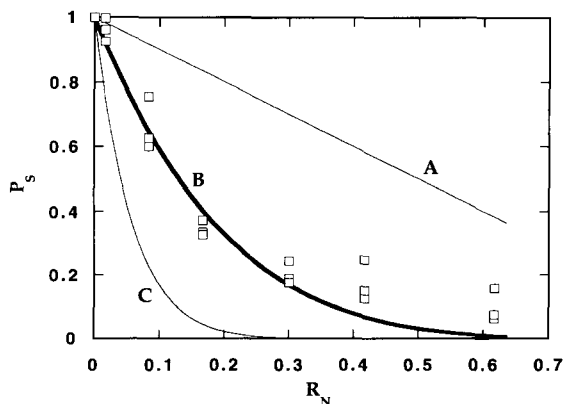


Fig. 2. Yield of xanthone triplets as a function of 1-methylnaphthalene occupancy (as average fraction of cavities occupied) and calculated dependencies for models (A), (B) and (C) (see text).

for three independent sets of experiments. The dispersion of these data provides a visual indication of the reproducibility of the experiments. Quite clearly, model 'B' should be preferred, indicating that quenching does not require sharing of the same supercage, but rather that it can also occur in less than 100 ns between neighboring cages. This does not imply that the same kinetics applies to transfer within the same or neighboring supercages, but rather that both processes are complete in < 100 ns.

It is interesting to compare the results of this analysis with those of the more conventional Perrin formulation [5], which assumes a quenching sphere in which quenching occurs with 100% probability. A plot of $\ln(S_0/S)$ (where S is the signal intensity, $\Delta J/J$) as a function of 1-methylnaphthalene molarity, calculated using a unit cell size of 24.7 Å for NaY [6], leads to a reasonably linear plot ($R=0.949$) and a critical radius of ≈ 11.2 Å. We believe that application of the Perrin model is questionable for a system with discrete geometric features. In spite of this, the value is in line with that expected for a vicinal intercage transfer, given the size of the supercages (≈ 13 Å) [7]. A similar conclusion was reached by application of the Perrin model to the quenching of pyrene fluorescence by Cu^{2+} [8].

Interpretation of the data is somewhat more complex in the case of naphthalene triplet yields. It is reasonable to assume that the probability of formation of an acceptor triplet (P_F) will be given by the number of xanthone triplets quenched, i.e.

$$P_F = 1 - P_S = 1 - (1 - R_N)^n \quad (\text{for } n=5), \quad (2)$$

The calculated line in Fig. 3 shows that Eq. (2) does not provide an adequate interpretation of the data. A clear distinction should be made between *generating* a triplet naphthalene and *detecting* it. If we assume that a triplet naphthalene can only be detected (i.e. survives long enough) if there are no other molecules of 1-methylnaphthalene in the same or in nearest-neighbor supercages, then the probability that a triplet will be formed *and* will survive (P_D) is given by the product of Eqs. (1) and (2), i.e.

$$P_D = (1 - R_N)^n [1 - (1 - R_N)^n] \quad (\text{for } n=5). \quad (3)$$

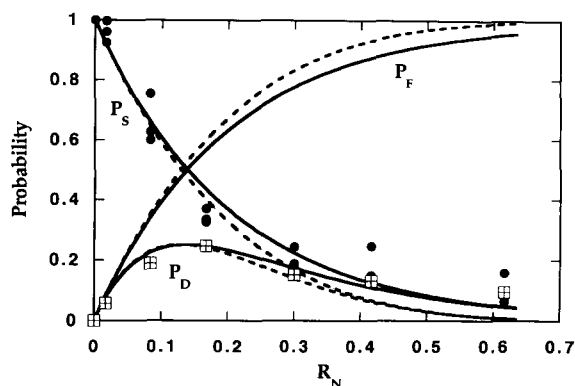


Fig. 3. Experimental and calculated yields of xanthone (●) and 1-methylnaphthalene (◻) triplets based on simple statistics (dashed lines) or employing a Poisson distribution (full lines). Note that Eqs. (5) and (7) give indistinguishable plots within the resolution of this graph.

Fig. 3 also includes a plot according to Eq. (3), showing a good fit to the data². We interpret this unusual observation in terms of triplet naphthalene self-quenching with a distance dependence similar to that observed for xanthone–naphthalene transfer. Such self-quenching is in fact not unprecedented; Lim [9–13] has shown several examples of this type, where the process is believed to involve 'L-shaped' short-lived triplet excimers. This may occur at the *window* site. Our results do not provide direct evidence for such excimers, but are fully consistent with this explanation.

Some self-quenching may also occur in the case of xanthone [4], but this should be a constant in our set of experiments.

The model can be further refined by assuming that multiple naphthalene occupancy may lead to a somewhat increased number of naphthalene-free cavities, i.e. the probability of finding a naphthalene-free cage, P_{NF} ,

$$P_{NF} > 1 - R_N. \quad (4)$$

Thus, we assume that the term $1 - R_N$ in Eqs. (1)–(3) should be replaced by P_{NF} , calculated taking into account multiple occupancy. In a first approximation, we can use a Poisson distribution, in which case

² The actual amplitudes of the 1-methylnaphthalene triplet signals are a function of its extinction coefficient in the solid. These were normalized to match the amplitude of the calculated curve. Only shape comparisons are meaningful in this case. For xanthone the signals were normalized to one (since this is the absorber) and both shape and amplitude comparisons are meaningful.

$$P_{\text{NF}} = \exp(-R_{\text{N}}) . \quad (5)$$

At our highest occupancy (0.62) this model includes a probability of 0.33% of quadruple naphthalene occupancy. This and higher occupancies have no physical meaning, since molecular modeling shows that it would be impossible to fit this number of 1-methylnaphthalenes in the supercage. While it makes no difference in our examples, in the more general case one may want to truncate the Poisson distribution for unoccupied cages,

$$P_{\text{NF}} = 1 - \exp(-R_{\text{N}}) \sum_{n=1}^{\infty} \frac{R_{\text{N}}^n}{n!} , \quad (6)$$

at a maximum occupancy of three,

$$P_{\text{NF}} = 1 - \left(\frac{R_{\text{N}}}{1!} + \frac{R_{\text{N}}^2}{2!} + \frac{R_{\text{N}}^3}{3!} \right) \exp(-R_{\text{N}}) . \quad (7)$$

Fig. 3 shows that Eqs. (5) or (7) provide an improved fit in the region of high occupancy, although they do not change the basic conclusions of the simpler model of Eqs. (1)–(3). Clearly a Poisson distribution is not ideal for a system where either exclusion or cooperative effects could be in play, although it appears to accommodate well the relatively minor adjustments applied here.

4. Conclusion

In conclusion, rapid triplet energy transfer in faujasites, requiring no intercavity migration, can occur in an intracage or nearest-neighbor mode, but not further. It is likely that donor–acceptor interactions occur from opposite sides of the ≈ 7.4 Å window, given that molecular hopping between supercages probably occurs in a much longer time scale [14]. The yields of detectable 1-methylnaphthalene triplets appear to be controlled by self-quenching in a manner similar (but with enhanced efficiency due to confinement) to that which is well documented in solution [9–11,13]. A

simple statistical model that takes into consideration the discrete arrangement of neighbors in a zeolite, explains quantitatively the salient features of intrazeolite quenching in short time scales. The model proposed applies to both xanthone quenching and 1-methylnaphthalene self-quenching, and possibly to many other systems [15].

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