

Temperature dependent intersystem crossing and triplet–triplet absorption of rubrene in solid solution

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Relative fluorescence quantum yields and lifetimes of the first excited singlet state (S_1) of rubrene in sucrose octa-acetate glass have been measured as a function of temperature. From the thermal activation of intersystem crossing, it was found that the triplet state to which S_1 intersystem crosses lies $4600 \pm 400 \text{ cm}^{-1}$ above S_1 . System dynamics were measured with picosecond pump-probe experiments as a function of temperature. The data yield the temperature dependent intersystem crossing rate constants and the triplet–triplet extinction coefficient, which was found to be $8800 \pm 600 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 532 nm. The triplet–triplet extinction coefficient provides absolute calibration of the previously reported triplet–triplet absorption spectrum. Inclusion of stimulated emission quantitatively in the analysis of pump-probe experiments involving more than one pair of states is shown to be necessary for a proper analysis of system dynamics.

1. Introduction

The temperature dependence of the fluorescence quantum yield of aromatic hydrocarbons in solid and liquid solutions has been studied extensively [1]. Among the aromatic hydrocarbons, rubrene is unusual in that it has unit fluorescence quantum yield at room temperature [2]. At room temperature, many aromatic hydrocarbons and related substituted compounds display large triplet yields and rapid intersystem crossing following optical excitation into the lowest excited singlet state (S_1) [1,3]. The triplet yield is large in spite of the fact that the lowest energy triplet state, T_1 , and the singlet state, S_1 , both involve π to π^* transitions which produce excited states having the same orbital symmetry. Since the total symmetries of the three spin sublevels of T_1 are the orbital symmetry times the spin symmetry of each sublevel, the symmetries of S_1 and T_1 states differ. Therefore, direct spin–orbit coupling between S_1 and T_1 is forbidden and direct intersystem crossing is

forbidden (although vibronic coupling can make the process weakly allowed) [4–7].

In general, intersystem crossing in the aromatic hydrocarbons is thermally activated [1,8–12]. Excitation of vibronic states of S_1 having energy equal to a higher lying triplet state, T_m , makes intersystem crossing possible. T_m has the necessary symmetry (orbital \times spin equal to the S_1 symmetry) to directly spin–orbit couple to S_1 , making intersystem crossing an allowed process. The activation energy is the difference in the S_1 – T_m energy. In some large molecules, T_m can fall below S_1 , and allowed intersystem crossing occurs without thermal activation [1,8,11]. In moderately sized molecules, T_m may be only slightly higher in energy than S_1 and thermally activated intersystem crossing occurs readily at room temperature [1,8–11]. As will be shown below, in rubrene, T_m is substantially higher in energy than S_1 , i.e. 4600 cm^{-1} . This is responsible for the lack of intersystem crossing at room temperature. Intersystem crossing increases rapidly with temperature above

room temperature, and there is a corresponding decrease in the S_1 lifetime.

Intersystem crossing results in the population of long lived triplet states. This has made it possible to measure triplet-triplet absorption spectra [13–15]. However, there have been large discrepancies in the reported triplet-triplet extinction coefficients for the aromatic hydrocarbons because of the difficulties in applying traditional methods quantitatively [1]. It has been possible to measure the relative triplet-triplet absorption spectrum. The main obstacle to obtaining triplet-triplet extinction coefficients is the determination of the T_1 concentration precisely. In addition, optical transitions from T_1 to triplet states near the first excited singlet have not been well studied due to the small extinction coefficients. As a consequence, the energies of these triplet states are frequently unknown.

In this paper we report fluorescence yield measurements and picosecond pump-probe experiments on rubrene in sucrose octa-acetate (SOA) glass as a function of temperature. Both types of experiments provide a measure of the activation energy for intersystem crossing (ISC). The two determinations are in reasonable agreement. The experiments also give the ISC rate constant as a function of temperature. In addition, by combining the yield measurements and the time dependent measurements, taking into account S_0 absorption, S_1 stimulated emission, and T_1 absorption, the triplet-triplet extinction coefficient of rubrene in SOA was determined at 532 nm. The relative triplet-triplet absorption spectrum has been reported [13,14]. The determination of the extinction coefficient at 532 nm calibrates the reported spectrum.

2. Experimental procedures

Rubrene powder was purchased from Aldrich and used without further purification. Sucrose octa-acetate was purchased from Sigma and was twice recrystallized in ethanol. The sample pre-

paration has been described in detail previously [16]. Briefly, rubrene and SOA were dissolved in acetone and passed through a microfilter to remove dust. The solvent was then removed on a vacuum line. The sample was sealed under vacuum in a 1 mm path length spectroscopic cell. Subsequent slow heating of the sample cell with a heat gun caused SOA to form a glass solution. The cell is placed in an aluminum holder which has windows to thermally isolate the sample from the room air. Temperatures of the samples were controlled by a YSI temperature controller (Model 72). Two resistance thermometers were placed in contact with the sample. One was used to measure the temperature and the other was used as a feedback for the temperature controller. The temperature was regulated to within 0.2°C .

The relative fluorescence yields and the pump-probe experiments were performed using frequency doubled (532 nm) single pulses from a CW-pumped, acousto-optically mode-locked and Q-switched Nd:YAG laser [16]. The single pulses were selected by two Pockels cells. The selectivity is better than 100:1. The pulse width of the laser (full width at half maximum) was 110 ps. The laser was Q-switched at 1 kHz. Only one single mode-locked pulse was selected out of each Q-switched pulse train.

In the yield measurements, fluorescence was collected by a lens and a polarizer whose polarization was set to the magic angle relative to the excitation polarization. This removed any possible contribution to the signal from rotational relaxation at higher temperatures above the glass transition where the viscosity is reduced. Scattered light at 532 nm was removed by a set of three 532 nm cut-off filters which allowed light of only longer wavelengths to pass through. The broad band fluorescence was detected by a dry-ice chilled phototube and the signal was measured with a lock-in amplifier. A second lock-in amplifier monitored the laser intensity to compensate for any drift in the laser power during the yield measurements. In the pump-probe experiments, the excitation beam was chopped at 500 Hz with a mechanical chopper which was synchronized to the Q-switch clock, so that every other pulse was blocked. A lock-in amplifier was used to measure the signal as a

mechanical delay line was scanned. Up to 25 ns of delay was possible. Many scans of the delay line were averaged to obtain a data set. The excitation power was reduced until the decays were independent of laser power. The samples had low optical density (< 0.2 at the peak of the spectrum) to prevent fluorescence reabsorption. In both the yield measurements and the time dependent measurements, a number of data sets were taken at each temperature to assure reproducibility of the results.

As will be discussed in detail below, it is necessary to know the stimulated emission coefficient for the S_1 to S_0 transition at the probe wavelength (532 nm). The stimulated emission coefficient was determined in the following manner. Rubrene, like many other aromatic molecules with allowed singlet absorption spectra, displays mirror image symmetry between the absorption spectrum and the fluorescence spectrum. Therefore, the extinction coefficient at the peak of the absorption spectrum should be essentially identical to the stimulated emission coefficient at the peak of the fluorescence spectrum. The only difference is due to differences in the Frank–Condon factors between absorption and emission. Since this is a π to π^* transition of a many π -electron system, the change in the vibrational potential is very small upon excitation as evidenced by very small changes in vibrational frequencies. Therefore, taking the peak extinction coefficient equal to the peak stimulated emission coefficient is an excellent approximation. The fluorescence spectrum was taken with a SPEX fluorimeter (Model DM1B). The spectrum was corrected for the spectral response of the instrument. The fluorescence maximum was at 545.5 nm. The absorption maximum was at 528 nm. At 532 nm, the fluorescence intensity was 78% of the fluorescence peak intensity at 545.5 nm. The stimulated emission coefficient at 532 nm was obtained by multiplying the ratio of the fluorescence intensity at 532 nm to that of 545.5 nm (0.5) by the absorption coefficient at 528 nm (528 nm extinction coefficient = $11\,600\text{ L mol}^{-1}\text{ cm}^{-1}$). Errors, if any, introduced by this method of determining the stimulated emission coefficient were small and will be discussed in the context of the data analysis.

3. Kinetic equations

Pump-probe experiments are quite common. However, they are usually performed on systems with two states, a ground state and an excited state. These experiments are frequently referred to as ground state recovery experiments. There is actually a contribution to the signal both from ground state depletion, which reduces the optical density, and from excited population, which, because of stimulated emission, amplifies the probe transmission. In a two state experiment, the excited state population and the ground state depletion decay at the same rate. Therefore, it is not necessary to explicitly consider the excited state population and stimulated emission. However, if the excited state can decay into a third state, such as a triplet state considered here, the excited state population and stimulated emission must be considered explicitly. Decay of the excited state population occurs at a faster rate than ground state recovery. Therefore the stimulated emission contribution to the signal decays more rapidly than the ground state depletion contribution. To analyze the time dependent signal, it is necessary to quantitatively include the magnitudes of the excited state and ground state contributions to the signals. If, as in the situation considered here, the third level absorbs at the probe wave length, this must also be taken into account. Therefore, we will briefly outline the equations necessary for the data analysis.

A schematic diagram of the dynamic system is shown in fig. 1. Beer's law for this system takes the following form:

$$dI/dx = -\alpha_a C_g(t)I + \alpha_s C_s(t)I - \alpha_t C_t(t)I, \quad (1)$$

where I is the intensity of the laser beam, x is the distance between the entrance surface of the sample and the point of interest inside the sample. α_a , α_s and α_t are the extinction coefficient of the ground state, the stimulated emission coefficient of the first excited singlet state, and the triplet–triplet extinction coefficient, respectively. $C_g(t)$, $C_s(t)$ and $C_t(t)$ are the time-dependent concentrations of the ground state, the first excited state, and the triplet state, respectively.

In pump-probe experiments, the signal is a

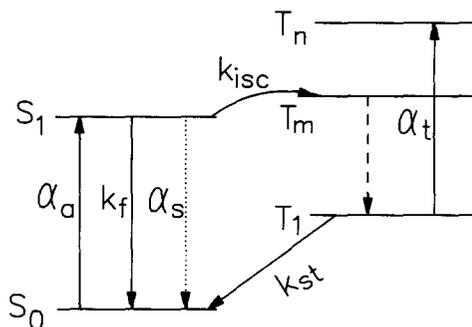


Fig. 1. A schematic diagram of the rubrene system. The system can be optically excited into the S_1 state (extinction coefficient α_a). Decay to S_0 is at rate k_f . The probe pulse can induce stimulated emission (stimulated emission coefficient α_s). The S_1 population can be thermally activated and intersystem cross into the triplet state T_m (with a rate constant k_{isc}). T_m undergoes very fast internal conversion to T_1 . From T_1 , the system can return to S_0 (with rate constant k_{st}). Optical absorption occurs from T_1 to T_n (extinction coefficient α_t).

measure of the difference in the intensities of the probe beam after passing through the sample with the pump beam blocked and unblocked. At the laser repetition rate used in the experiments, the ground state population is completely recovered before the next laser pulse. Therefore, when the pump beam is blocked, there are no excited state populations and the laser light intensity at the detector is

$$I_1 = I_0 \exp(-\alpha_a b C_g^0), \quad (2)$$

where b is the thickness of the sample, I_0 and I_1 are the probe intensity before and after the sample, and C_g^0 is the concentration of rubrene in the sample. When the pump beam is unblocked, the time-dependent probe intensity, $I_2(t)$, can be written as:

$$I_2(t) = I_0 \exp(-\alpha_a b (C_g^0 - C_s(t) - C_t(t)) + C_s(t) \alpha_s b - C_t(t) \alpha_t b). \quad (3)$$

In the experiment, the lock-in amplifier detects the difference between $I_2(t)$ and I_1 . Thus, $S(t)$, the signal amplitude as a function of time (delay line position), has the following form:

$$S(t) = A [I_2(t) - I_1], \quad (4)$$

where A is a proportionality constant which depends on the lock-in amplifier and its sensitivity scale.

Equations (2) and (3) can be rewritten by expanding the exponentials in power series. When the absorbance of the sample is not too high at the pump-probe wavelength, it is straightforward to show that the nonlinear terms in the series are negligible and can be dropped. Using the expansions, the signal amplitude in eq. (4) is

$$S(t) = AI_0 b [(\alpha_a + \alpha_s) C_s(t) + (\alpha_a - \alpha_t) C_t(t)]. \quad (5)$$

The kinetic equations for the excited singlet and the triplet states are:

$$dC_s(t)/dt = -(k_f + k_{isc}) C_s(t), \quad (6)$$

$$dC_t(t)/dt = k_{isc} C_s(t) - k_{st} C_t(t), \quad (7)$$

where k_{st} is the rate constant for ISC from T_1 to S_0 . In eq. (7), the rate constant for internal conversion from the T_m state to the T_1 state is taken to be infinite. (The time for internal conversion in large molecules in condensed phases at room temperature is typically of the order of 1 ps. Since the pulse durations used in these experiments are 110 ps, the assumption of infinitely fast internal conversion is reasonable.) The differential eqs. (6) and (7) are solved using the fact that $k_{st} \ll (k_f + k_{isc})$ (the triplet lifetime is about 100 μ s [14,17,18], which is very long compared to the singlet lifetime). Substituting the results into eq. (5), the pump-probe signal takes the final form

$$S(t) = AI_0 b C_g^0 \times \{ [(\alpha_a + \alpha_s) + (\alpha_t - \alpha_a) k_{isc}/K] \exp(-Kt) + (\alpha_a - \alpha_t) k_{isc}/K \}, \quad (8a)$$

where $K = k_f + k_{isc}$.

The pump-probe data thus can be written in the following simple form:

$$S(t) = C \exp(-Kt) + D. \quad (8b)$$

The constants C and D are the collections of parameters given in eq. (8a) for the pre-exponential factor and the additive constant, respectively.

The ratio of D/C can be used to calculate the triplet-triplet extinction coefficient using

$$\alpha_t = \alpha_a - \frac{(D/C)[(\alpha_a + \alpha_s)(1 + (k_f/k_{isc}))]}{(1 + D/C)}. \quad (9)$$

From eqs. (8a) and (8b), it can be seen that if $\alpha_a = \alpha_t$ ($D=0$), the signal will decay to zero. However, if $\alpha_a > \alpha_t$, the signal will decay (on a few tens of ns time scale) to a positive constant value. If $\alpha_a < \alpha_t$, the signal will decay (on a few tens of ns time scale) to a negative constant value (decay below the baseline). Since the lifetime of the first triplet state of rubrene is $\approx 100 \mu\text{s}$ [14,17,18], at the laser repetition rate the triplet state returns to the ground state completely between laser shots. Therefore, the baseline (signal before $t=0$) is the true baseline with all of the population in the ground state.

Using the relative quantum yield to measure the activation energy for ISC is straight forward. The fluorescence quantum yield can be written as:

$$\Phi(T) = k_f / (k_f + k_{isc}) = I_f(T) / (I_0 \Omega), \quad (10)$$

where $I_f(T)$ is the fluorescence intensity at temperature T collected by the optical system, I_0 is the intensity of the excitation laser beam, and Ω is the total solid angle of the fluorescence collection.

At room temperature the fluorescence quantum yield is unity and thus $k_{isc}(298) = 0$. Using this

and eq. (10), we can use the relative fluorescence yield to obtain $k_{isc} = k_f [(I_f^0/I_f(T) - 1)]$, where I_f^0 is the fluorescence intensity of the sample at room temperature. If we assume the intersystem crossing rate has the form [11] $k_{isc} = A \exp(-E_a/RT)$, then the equation that describes the relationship among the measured fluorescence intensities, the temperature, and the activation energy (E_a) is

$$\ln[(I_f^0/I_f(T) - 1)] = \ln(A) - E_a/(RT), \quad (11)$$

where A is described earlier as being the pre-exponential factor and R is the molar gas constant. Therefore, a plot of $\ln[(I_f^0/I_f(T) - 1)]$ versus $1/T$ should be a straight line and the slope gives the activation energy.

4. Results and discussion

The relative fluorescence yield as a function of the temperature was measured. Figure 2(a) shows the plot of $\ln[(I_f^0/I_f(T) - 1)]$ versus $1/T$. For exponentially activated ISC, the plot should yield a straight with a slope of $-E_a/R$. The activation energy, E_a , obtained from the best fit to the data is 4200 cm^{-1} . The rubrene activation energy is much higher than the observed activation energies of a number of other aromatic hydrocarbons in

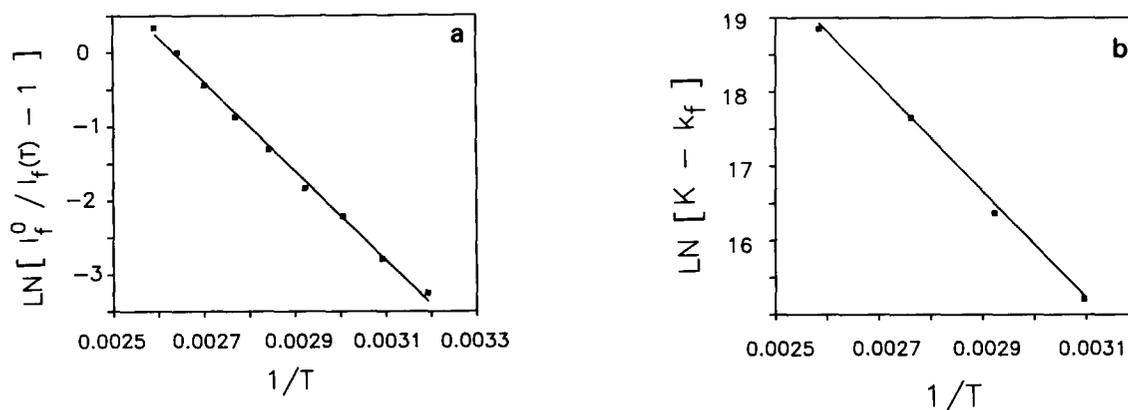


Fig. 2. Determination of the activation energy for the intersystem crossing. (a) Fluorescence yield measurements vs. temperature. Plot of $\ln[(I_f^0/I_f(T) - 1)]$ vs. $1/T$. $I_f(T)$; intensity of fluorescence at temperature T . I_f^0 ; intensity of fluorescence at room temperature where the fluorescence quantum yield is unity. The best fit yields $E_a = 4200 \text{ cm}^{-1}$. (b) Pump-probe experiments give the rate constant for intersystem crossing, $k_{isc} = K - k_f$. K is the measured decay constant and k_f is the rate constant for decay to the ground state (room temperature decay where $k_{isc} = 0$). Plot of $\ln(K - k_f)$ vs. $1/T$. The best fit yields $E_a = 5000 \text{ cm}^{-1}$.

condensed matter systems [1]. This is the reason for the lack of ISC in rubrene at room temperature.

The activation energy of the ISC was also measured by the picosecond pump-probe experiments. The time-dependent pump-probe data were analyzed using eq. (8a). Curve fitting the data gives the total rate constant, $K = k_f + k_{isc}$. Since k_f is temperature independent and corresponds to K at room-temperature, k_{isc} can be found. The activation energy is obtained by plotting $\ln(K - k_f)$ versus $1/T$, as shown in fig. 2(b). A linear fit of the data yields an activation energy of 5000 cm^{-1} . This is in reasonable agreement with the activation energy obtained from the relative fluorescence yield measurements. The yield measurements are probably subject to more systematic errors than the time dependent experiments, e.g., changes in the sample's index of refraction with temperature will change the observed yield [19,20]. Including the temperature dependence of the index of refraction would change the activation energy slightly. Within the context of these experiments, we would place the activation energy at 4600 cm^{-1} .

Typical pump-probe experimental data are shown in fig. 3. The data were fit using eq. (8b) to obtain the parameters C , D and K . K with k_f

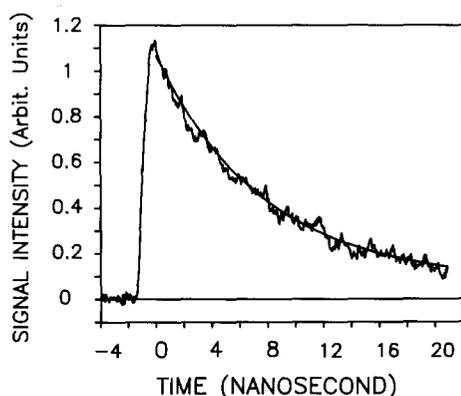


Fig. 3. Pump-probe experimental data and the fit for rubrene in sucrose octa-acetate at 362 K. The functional form is an exponential decay plus a constant (see eq. (8b)). The decay constant (K), the pre-exponential factor (C), the additive constant (D), combined with singlet state spectroscopic data permit the determination of the triplet-triplet extinction coefficient at the probe wavelength. The extinction coefficient at 532 nm is $8800 \pm 600 \text{ L mol}^{-1} \text{ cm}^{-1}$.

gives k_{isc} . Using these parameters, obtained at several temperatures, with α_a and α_s taken from the absorption and fluorescence spectra at room temperature, respectively, eq. (9) yields the triplet-triplet extinction coefficient at the probe wavelength. The triplet-triplet extinction coefficient of rubrene is $8800 \pm 600 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 532 nm. Since the pump-probe experiments and the singlet absorption and fluorescence spectra provide all of the necessary parameters, it is unnecessary to make an explicit measurement of the triplet concentration. Therefore, the absolute error in determining α_t is determined by the quality of the pump-probe data. By averaging, a decent signal-to-noise ratio can be obtained. Thus the accuracy of α_t determined from the picosecond pump-probe experiment is expected to be higher than the values determined using traditional methods.

As discussed earlier, the stimulated emission coefficient was obtained using the mirror symmetry between the absorption and fluorescence spectra (see section 2). The method used could result in some error. If the stimulated emission coefficient is varied $\pm 10\%$ the triplet-triplet extinction coefficient varies from 9000 to 8600 $\text{L mol}^{-1} \text{ cm}^{-1}$. This error falls inside the error bars of the measurement itself. Furthermore, it is important to take into account the stimulated emission during the data analysis process. Omission of the stimulated emission process would result in a 40% error in α_t .

Strong triplet-triplet absorption for rubrene has been observed at $\Delta E = 18600 \text{ cm}^{-1}$ [15,21]. The T_1 state of rubrene is reported to lie in the range $8400\text{--}10400 \text{ cm}^{-1}$ [14]. Thus, the first excited triplet state with strong optical absorption has an energy of $27000\text{--}29000 \text{ cm}^{-1}$, about $9000\text{--}11000 \text{ cm}^{-1}$ above the first excited singlet state. Therefore, the excited triplet state responsible for intersystem crossing must be an optically dark state 4600 cm^{-1} above S_1 .

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