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Thermoluminescent Charge Recombination in Saturated Hydrocarbons

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Thermoluminescence from the recombination of *N*,*N*,*N*′,*N*′-tetramethylparaphenylenediamine (TMPD) cations with trapped electrons in squalane and *cis*-decalin glasses and in microcrystalline methylcyclohexane is reported. The glasses exhibit distributions of activation energies maximal at 0.20 eV in squalane and 0.19 eV in *cis*-decalin, with half-widths at half-height of approximately 0.03 eV. Microcrystalline methylcyclohexane exhibits a single activation energy at 0.30 eV. These activation energies for thermal electron release are much smaller than photoionization threshold energies determined optically in similar glasses, suggesting that the mechanism of electron release is trap destruction, not electron excitation within a stable trap. The similarity between these activation energies and those determined for quenching of the TMPD phosphorescence also supports this interpretation.

I. Introduction

Low energy electrons produced by ionization can become trapped in nonpolar glasses.[1−21] The physical properties of trapped electrons reflect the excess electron−solvent interactions that are of fundamental and practical interest regarding ionization in amorphous condensed phases. A number of experimental methods have been applied to elucidate the properties of electrons trapped in nonpolar glasses, including absorption spectroscopy,[1−5] photoconductivity,[1,6−8] various forms of magnetic resonance,[1,2,10,11] isothermal recombination luminescence,[12−19] and the effects of electron scavengers.[1−3,10,11,20,21] Complementary to these methods is the technique of thermoluminescence, to which we confine our focus.

A typical thermoluminescence experiment involves cooling the matrix to liquid nitrogen temperature, applying radiation (commonly UV light or γ-rays) to ionize the matrix or solutes, discontinuing the irradiation, and warming the sample. Temperature and luminescence intensity are simultaneously recorded. The light intensity is a measure of the rate of electron-cation recombinations and the temperature is a measure of the energy required to free the electrons from the traps.

The relationship between the thermoluminescence spectrum and electron trapping properties of the matrix has been extensively studied and analyzed in solid-state systems.[22−26] While thermoluminescence is an established technique for typical solid-state materials, it has been less frequently employed in studying organic crystals,[27,28] or glasses.[29−38]

The thermoluminescence studies that have been reported for nonpolar glasses[29−38] have established a number of interesting phenomena but have not particularly focused on the energetics of the process, albeit a few studies have utilized the initial rise method to determine activation energies of electron release in methanol glass[15] and anion release in 3-methylpentane.[29] Thermoluminescence peaks in glasses have been correlated with phase transitions,[27,30,33,37,38] particularly the glass transition at which anion mobility becomes possible. Thermoluminescence spectra frequently supplement studies of isothermal recombination luminescence,[12−16,19] and have facilitated observation of a number of novel emission processes[30,32,35,36] (cation−anion recombination, excimers, dimers, radicals, enhanced phosphorescence).

Herein, we address the following questions: What is the activation energy of thermal electron release? How does thermal ionization from traps compare to optical ionization? What is the mechanism of thermal ionization? In addressing these questions, the thermoluminescence spectra, activation energies, frequency factors, yield, and emission spectra will be shown to be consistent with standard models of thermally activated processes and reasonable conditions regarding electrons photoionized from TMPD and trapped in nonpolar glasses.

II. Theory

A. Functional Form of the Thermoluminescence Curve. Randall and Wilkins[39] were the first to quantify thermoluminescence, and their model, which has been reviewed elsewhere,[22−26] is typical of many thermally stimulated processes.[23] The essential assumption is that thermoluminescence is rate determined by a first-order activated release of electrons from a single type of trap, with rate constant

$$k_1 = \nu \exp\left(-\frac{E_t}{k_B T}\right) \tag{1}$$

Accordingly, with an initial concentration, n_0, of trapped electrons and a yield of luminescence per released electron, q, we obtain the luminescence intensity, $I(t) = n_o q k_1 \exp(-k_1 t)$. Defining a warming rate, $b = dT/dt$, this expression is simply rearranged to the Randall −Wilkins equation

$$I(T) = q n_0 \nu \exp\left(-\frac{E_t}{k_B T}\right) \exp\left[-\int_T^{T_0} \frac{dT'}{b} \nu \exp\left(-\frac{E_t}{k_B T}\right)\right] \tag{2}$$

where T_0 is the initial temperature at which the trapped electron concentration is n_0. In the case that ν/b is independent of T, this equation predicts a maximum when

$$T^2 \exp\left(-\frac{E_t}{k_B T}\right) = \frac{E_t b}{k_B \nu} \tag{3}$$

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In the case that the luminescence arises from recombination of geminate pairs, eq 2 easily accommodates the possibility of retrapping. This is accomplished by replacing the frequency factor, ν by the product of ν with a branching ratio, K where $K = k_3/(k_2 + k_3)$, with k_2 the retrapping rate constant and k_3 the rate constant for geminate recombination of electron and hole. In eq 3 there is the additional constraint that K be only weakly dependent on T. More complicated scenarios in which the recombination is not necessarily geminate will be considered in subsequent sections.

B. Determination of Activation Energy. The activation energy E_t can be determined by warming at two different rates and measuring the shift in the thermoluminescence peak.[22-26] For the case of a single trap energy E_t, the use of two different warming rates b_1 and b_2 in eq 3 and determination of two different peak temperatures T_1 and T_2, permits a simple evaluation of E_t as

$$E_t = k_B \frac{T_1 T_2}{T_1 - T_2} \ln\left(\frac{T_2^2 b_1}{T_1^2 b_2}\right) \tag{4}$$

Alternatively, the activation energy may be estimated from a measurement of the initial rise of the thermoluminescence curve. Clearly, from eq 2, as $T \rightarrow T_0$, the temperature dependence of the thermoluminescence becomes simply proportional to $\exp(-E_t/(k_B T))$, and the activation energy is then obtained from a simple Arrhenius plot, of $\ln I(T)$ vs $1/T$.

III. Experimental Section

Glasses of nitrogen-flushed hydrocarbon solutions containing 10^{-4} M TMPD were formed by rapid cooling of the solution with liquid nitrogen. The glass was allowed to anneal for >15 min, then the TMPD was two-photon ionized with 500 pulses of 308 nm light (XeCl Excimer: 25 Hz, 10mJ, 15 ns, 10^{24} photons s^{-1} cm^{-2} at the cell). After the irradiation, the sample was maintained at 77 K for 45 min to allow some isothermal decay of the recombination luminescence. Warming was then initiated at rates varying from 0.05 to ~0.5 K s^{-1}. The temperature and emission intensity were simultaneously measured at timed intervals to establish the thermoluminescence spectrum and the warming rate. Temperature was measured to 0.5 K by a calibrated iron−constantan thermocouple immersed in the center of the solution and isolated from the cell walls. A photon counting system measured emission intensity through either fluorescence or phosphorescence band-pass filters. In either case, the temperature dependence of the emission was the same. The spectral distribution of the luminescence was recorded using a McPherson 0.3m monochromator at <6 nm band-pass.

The sample cells were made of copper (inner diameter of 1 cm and 1 cm in path length). Quartz windows were sealed to the cell body with indium wire compression seals. The cell was mounted in a nitrogen flushed insulated box and cooled by contact with flowing liquid nitrogen. Excitation occurred at 45° through the front quartz window. The emission was also collected from this front face.

We searched for phase transitions in the *cis*-decalin, squalane, and methylcyclohexane by seeking (a) breaks in the warming curve (WC) dT/dt, (b) sudden changes in the dependence of phosphorescence intensity (P) on temperature, (c) the sudden appearance of anion thermoluminescence peaks (ATL), or (d) by visual (V) differences in the clarity, cracking, or appearance of samples warmed under nitrogen atmosphere. Phase transitions that were observed are listed below with the methods of observation (as abbreviated in parentheses above), and with the apparent nature of the transition specified using the abbreviations: supercooled liquid (SCL), glass (G), crystalline (C), and liquid (L). All temperatures reported here can vary by ~5-10 K, being dependent on direction and rate of temperature change.

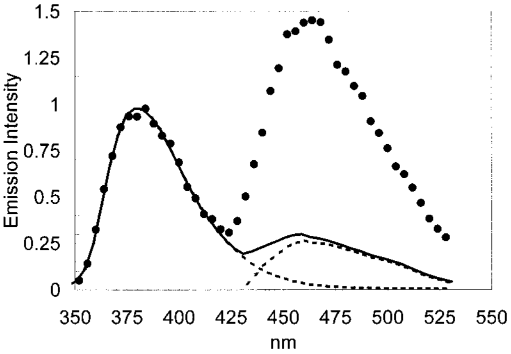

Figure 1. Emission spectrum of TMPD under nonionizing excitation (solid line), separated into fluorescence and phosphorescence (dashed lines), and the recombination emission spectrum during thermoluminescence (●).

cis-decalin: 145 K (P, V; G → SCL), 165 K (WC, V; SCL → C), and 235 K (WC, C → L)

squalane: 135, 150 K (ATL; ?), 185 K (WC, P, ATL, V; G → SCL)

methylcyclohexane crystals: 115 K (WC, P; C1 → C2?), 140 K (WC, P, V; C2? → L)

methylcyclohexane glass: 85 K (WC, P, V; G1 → G2?), 115 K (WC; G2? → SCL), 128 K (WC, P, V; SCL → C), 140 K (WC, P, V; C → L)

For the cases of *cis*-decalin and squalane, their glass temperatures of 145 and 185 K lie well above the temperature interval within which we conducted our measurements on the thermoluminescence (see next section) and we find no other phase transitions intruding within this range.[40]

In the case of methylcyclohexane, a glass phase transition at 85 K caused a sudden drop in temperature from 85 to 80 K despite external warming. This made our examination of the glass thermoluminescence impossible and, accordingly, the thermoluminescence behavior of its microcrystalline phase was examined instead.

Aldrich TMPD (*N,N,N′,N′*-tetramethylparaphenylenediamine) was purified by vacuum sublimation. Aldrich squalane, *cis*-decalin, and methylcyclohexane were purified by percolation through columns packed either with activated silica gel or with silver nitrate treated alumina.

IV. Results

A. Spectral Distribution of the Emission. Figure 1 shows both the steady-state emission spectrum of TMPD in methylcyclohexane glass at 77 K, together with the spectrum that is observed during thermoluminescent recombination. In the former spectrum, the excitation lies below the ionization threshold and exhibits, in addition to the shorter wavelength fluorescence, a longer wavelength part attributed to phosphorescence from the lowest triplet. For the steady-state excitation, this is populated via $S_1 \rightarrow T_0$ intersystem crossing. The separation of the phosphorescence from the fluorescence (indicated by the dotted curves), was obtained using a Stanford Research Systems 260 boxcar with a 10−50 ns gate. The thermoluminescence spectrum (which is measured ca. 45 min after two-photon excitation and arises from the recombination of geminate electron−hole pairs), shows the phosphorescence much enhanced due to spin relaxation. This enhancement has been observed in many similar systems.[7,30,32,36]

The ratio Γ_T/Γ_S of the probabilities for electron−hole recombination to form the triplet to that for the singlet state can be estimated from the experimental ratio, $R = [P_2/F_2]/[P_1/F_1]$, where P and F refer to the integrated areas of phosphorescence and fluorescence, respectively, and 2 and 1 refer to two-photon (above the ionization potential and after 45 min) to one-photon (steady state and below the ionization potential) excitations. The connection is simply established to be $\Gamma_T/\Gamma_S = (R - 1)\chi$ where χ is the TMPD intersystem crossing probability. Although χ is not known for this system, it cannot exceed 0.8 (i.e., the difference between unity and the TMPD fluorescence quantum yield, ca. 0.18 in cyclohexane at 298 K[41]).

For a spin equilibrated recombination, Γ_T/Γ_S would be expected to be 3/1. From our measured $[P_2/F_2]/[P_1/F_1]$, the ratio Γ_T/Γ_S was found to have values in *cis*-decalin, squalane, and methylcyclohexane of ca. 3.5. This ratio was about the same for the isothermal luminescence at 77 K as for the luminescence observed during the limited range temperature scans.

The yield of TMPD phosphorescence at 77 K was observed to increase by only 5−10% when the steady-state excitation was changed to an energy above the ionization threshold (i.e., 185 nm). This very small increase, when compared to the phosphorescence yield in the thermoluminescence spectrum, implies a low value for the product of the ionization probability and the probability of spin relaxation under the 185 nm steady-state conditions. From a variety of measurements on TMPD photoionization in fluid solvents, the ionization efficiency at 185 nm is ca. 0.5.[42] Accordingly, it is possible to estimate that the probability of spin relaxation before recombination is ca. 0.1−0.2.[43] As expected, most electrons have inadequate time to spin relax on the time scale of geminate recombination.

B. Other Parameters of the Emission. The time dependence of the delayed isothermal recombination luminescence of squalane glass was studied with TMPD replaced with 10^{-4} M perylene. Following a single intense 308 nm laser pulse at 77 K, the luminescence was found to follow a t^{-a} dependence with $a = 1.05$ over a time interval ranging from $t = 100-10000$ s. Such power law dependence has been previously observed in similar systems[12−19,44−47] and attributed to tunneling of a trapped electron to its sibling cation, with an exponential distribution of initial electron cation separation distances. In this case, a-1, has the simple interpretation as the ratio of the distance parameter in an assumed exponential form for the tunneling probability, to the average initial separation distance of the geminate pair. A similar power law dependence can be rationalized with activated unimolecular decay from traps with an exponential distribution of trap activation energies but with a-1 having now the interpretation of k_BT divided by the average trap energy.[39]

The phosphorescence yield from TMPD under steady-state illumination below the ionization potential, P_1, was measured together with the phosphorescence lifetime τ_P as a function of temperature in squalane and *cis*-decalin. This is illustrated for squalane in Figure 2. The inset in this Figure shows an Arrhenius plot of the phosphorescence quenching function $Q(T) = [1 - P_1(T)/P_1(T{=}135\text{K})]/\tau_P$ over the temperature range of the falloff. The activation energy of the phosphorescence quenching was found to be 0.21 eV in squalane glass and 0.22 eV in *cis*-decalin glass. These activation energies are interpreted to be the energies at which inadvertent impurities that quench the phosphorescence become mobilized.

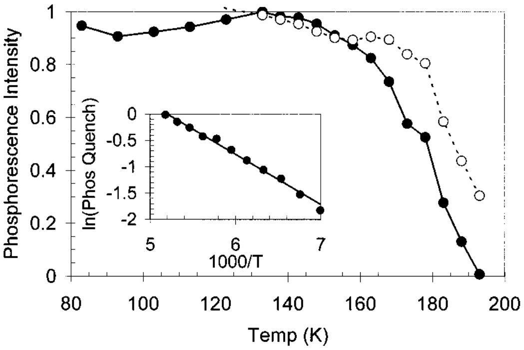

Figure 2. TMPD normalized phosphorescence intensity (●) and phosphorescence lifetime (in units of 2.2 s) (○) as a function of temperature in squalane. Inset: Arrhenius plot for activation energy of phosphorescence quenching.

C. Thermoluminescence Spectra and Activation Energies. Typical thermoluminescence spectra for *cis*-decalin and squalane glasses, warmed at two different rates, are shown in Figure 3A,B. The thermoluminescence spectrum of microcrystalline methylcyclohexane is shown in Figure 3C. The solid lines are theoretical fits that will be described below. Thermoluminescence spectra taken under the same conditions (similar preparation and warming rates) provide very reproducible shapes to those shown in Figure 3.

The slope of the Arrhenius plot for the initial rise of thermoluminescence is the simplest method of determining activation energy. Using a temperature range encompassing less than 8% of the total thermoluminescence area, reasonable Arrhenius plots were obtained with activation energies of 0.17 ± 0.02 eV for *cis*-decalin (4 trials), and 0.20 ± 0.05 eV for squalane (21 trials). For microcrystalline methylcyclohexane, an activation energy of 0.28 ± 0.03 eV (4 trials) was obtained using a somewhat smaller temperature range but encompassing ca. 15% of the total area.

Warming at different rates shifts the peak temperature as seen in Figure 3A,B. The application of eq 4 gives activation energies of $E_t = 0.18 \pm 0.03$ eV (4 trials) for *cis*-decalin and $E_t = 0.21 \pm 0.02$ eV (4 trials) for squalane. Both activation energies are in good agreement with those obtained via the initial slope technique.

The sensitivity of these activation energies to experimental conditions and to reproducibility of the glasses' properties was tested in squalane. Thermoluminescence spectra were measured using different samples on different days. Eighteen fast/slow warming pairs were used to find activation energies. This procedure resulted in a value of $E_t = 0.24 \pm 0.05$ eV.

Substituting the activation energy as determined above into eq 3 gives an estimate of ν (squalane glass, 10^9 s^{-1}; *cis*-decalin glass, 10^8 s^{-1}; methylcyclohexane microcrystal, 10^{14} s^{-1}). It should be noted from eq 3 that the frequency factor is only logarithmically sensitive to the thermoluminescence data

Substitution of E_t and ν into eq 2 predicts the shape of the thermoluminescence curve. These predictions are displayed in Figure 4A, B for squalane and *cis*-decalin and Figure 3C for microcrystalline methylcyclohexane. As will be noted, for methylcyclohexane microcrystal, the prediction is quite good, but for squalane and *cis*-decalin glasses, the experimental distribution is considerably broader than that estimated by eq 2. The disparity is easily accommodated by generalizing eq 2

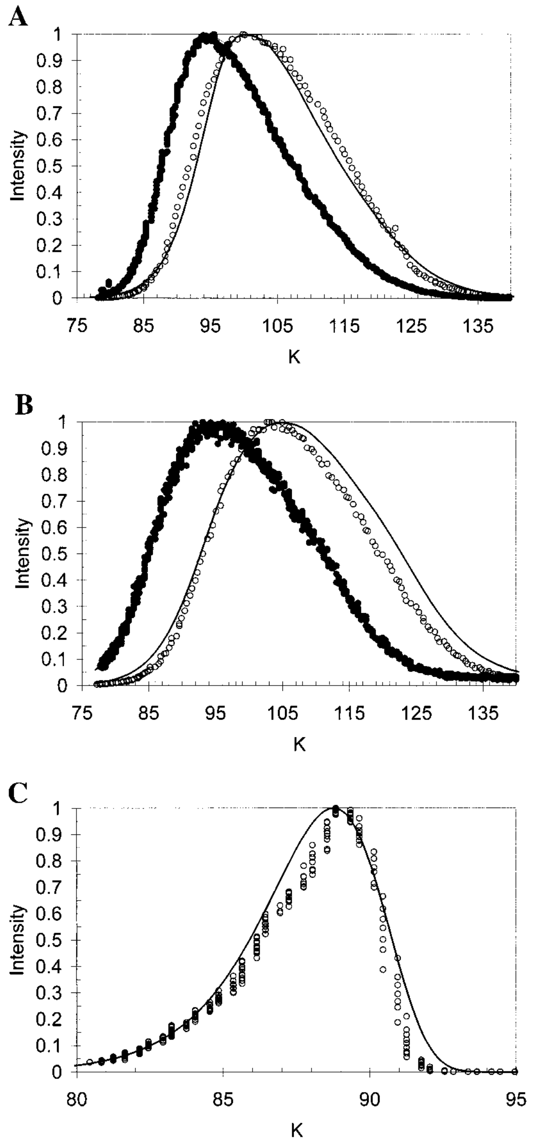

Figure 3. (A) Thermoluminescence spectra in squalane glass. Warming rates of 0.10 (●) and 0.48 (○) K/s. (B) Thermoluminescence spectra in *cis*-decalin glass. Warming rates of 0.068 (●) and 0.57 (○) K/s. (C) Thermoluminescence spectrum in microcrystalline methylcyclohexane. Warming rate of 0.046 (○) K/s. The solid lines are fits of the experimental thermoluminescence spectra to the Randall–Wilkins eq 2 with a distribution of activation energies as described in the text.

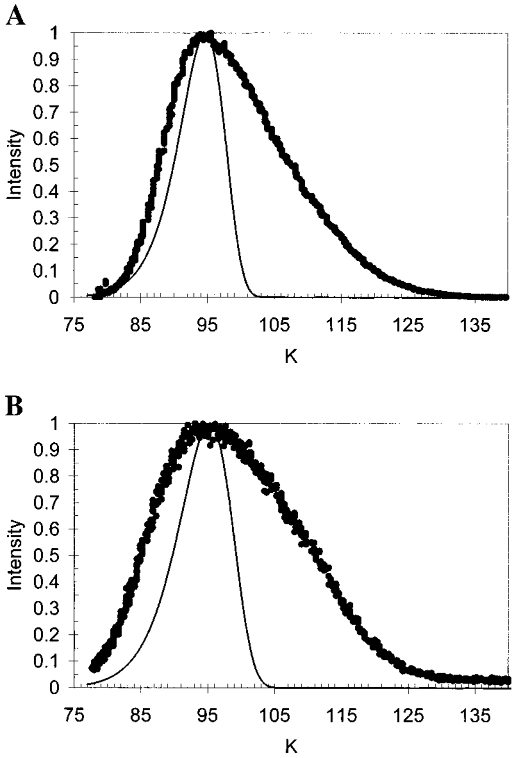

Figure 4. (A) Thermoluminescence spectra in squalane and fit to eq 2 with a single activation energy. (B) Thermoluminescence spectra in *cis*-decalin and fit to eq 2 with a single activation energy.

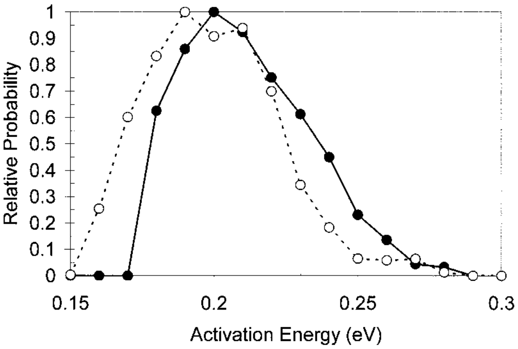

Figure 5. The distributions of thermoluminescence activation energies in *cis*-decalin (○) and squalane (●) glasses.

to allow for a distribution of activation energies. With the frequency factor as determined above, $I(T)$ was fit to a linear combination of basis functions of the form of eq 2 with activation energies evenly distributed every 0.01 eV. The coefficients in this superposition were determined by least-squares fit to $I(T)$. As a partial check on the validity of this technique, the coefficients determined for a slow warming rate were used to predict the thermoluminescence spectrum observed at the faster warming rate.

The predicted spectra for the two warming rates are shown as solid lines in Figure 3. For *cis*-decalin and squalane glasses, the activation energy distribution functions that were used are shown in Figure 5. In the case of microcrystalline methylcyclohexane, as pointed out above, a Dirac delta function distribution works quite well with E_t determined by the initial slope technique and ν determined via eq 2. A slightly better fit for this case is achieved by least-squares fit of eq 2 with E_t and ν as adjustable parameters. The spectrum in Figure 3C uses $E_t = 0.30$ eV and $\nu = 5 \times 10^{14}$ s^{-1}. These are not too disparate (recall the logarithmic sensitivity of ν) from the values obtained from initial slope and from eq 2 of 0.28 eV and 10^{14} s^{-1}, respectively.

D. Thermoluminescence Yield in Squalane Glass. The thermoluminescence yield Y_N (i.e., the area of the thermoluminescence spectrum following a delay of 45 min after an excitation of N pulses at 77 K) was examined as a function of laser intensity, J, laser repetition rate, ω, and number of pulses, N. Y_N was found to be quadratic in J from (0.05 to 1) × 10^{24} photon/s/cm^2. For $J = 1 \times 10^{24}$ photon/s/cm^2 and $N = 10$, Y_N was increased by a factor of ca. 2.5 for an increase in ω from 0.067 to 25 Hz. As will be discussed below, this is consistent with the more efficient route to ionization via the TMPD triplet state (lifetime of 2.5 s at 77 K).

For 1×10^{24} photon/s/cm^2 pulses at 25 Hz, Y_N increased by a factor of 180 as the number of pulses varied from 1 to 10^4. This is displayed in Figure 6 as a plot of normalized yield $\equiv Y_N/Y_{max}$ vs N, where Y_{max} is the saturation yield at $N = 2000$ pulses. The insert in this figure shows a plot of $-\log(1 - Y_N/$

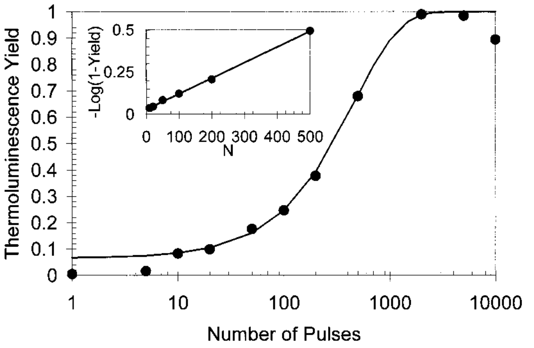

Figure 6. Normalized thermoluminescence yield as a function of number of excitation pulses. Solid line fit described in text. Inset: $-\log_{10}(1 -$ normalized yield) vs number of pulses.

$Y_{\max}$) vs N from $N = 10-500$. The solid lines in both this plot and that of $Y_N/Y_{\max}$ vs N are theoretical fits and will be discussed in the next section.

The thermoluminescence spectrum was found to be independent of J and ω, but was observed to shift slightly to higher temperatures with increasing N. Over the range $N = 1$ to 10 000, the shift in kelvin was ca.1.7 log[N], corresponding to a total change of ca.7 K (or a change in effective activation energy of less than 0.02 eV).

V. Discussion

A. Mechanism of Thermal Ionization in the Glasses. The low energy threshold of trapped electron absorption (which is a lower bound on the ground-state binding energy) has been reported to be 0.46−0.48 eV in a number of saturated hydrocarbon glasses.[4,5] This is significantly greater than the activation energies of ca. 0.2 eV (see Figure 5) for thermal release of trapped electrons. Accordingly, the mechanism of release from the traps cannot involve, as is often assumed, a thermal activation of electrons from stable traps. More plausibly, the thermoluminescence activation energy is an energy that excites solvent motions that alter the trapping potential to make it less binding. Such thermal destruction of traps has been previously suggested[12,30,36] to explain the similarity between the peak temperature of thermoluminescence spectra obtained from anion cation recombination and the temperature of the glass phase transition. In our glasses, the peaks in the thermoluminescence spectra lie well below the glass phase transition temperatures but electron release may be more sensitive to small solvent motions than anion release. Accordingly, we suggest that reconfiguration of the trap molecules occurs with an activation energy of ∼0.2 eV in these glasses and that the observed frequency factors are proportional (see next section) to the frequencies with which the solvent fluctuations visit nonbinding configurations.[48]

Supporting this interpretation is our observation that the phosphorescence quenching (see Figure 2) has essentially the same activation energy (0.21−0.22 eV) as the thermoluminescence. The mobility of phosphorescence quenchers (O_2 and CO_2) is plausibly activated by solvent motions similar to those that destroy the electron trap.

The experimental results are consistent with thermoluminescence predicted using the simple Arrenhius form for the thermal activation in eq 1. Since thermoluminescence in the glasses requires a distribution of activation energies, our results do not rule out modified Arrhenius forms where the effective temperature is reduced to $T-T_0$, where T_0 is related to the glass transition temperature (of 185 K in squalane and 145 K in *cis*-decalin). Such forms also require a distribution of activation energies, but the activation energies would be lower to accommodate the lower effective temperature. However, thermoluminescence in microcrystalline methylcyclohexane fits the simple Arrhenius form of eq 1 with a single activation energy, and is not well characterized by the modified Arrenhius forms. In any case, such forms can only lower the activation energies, maintaining the necessity of the trap destruction mechanism for electron release.

B. Mechanism of Thermal Ionization in Methylcyclohexane Microcrystals. The thermoluminescence spectrum of microcrystalline methylcyclohexane is remarkably similar to the spectrum predicted by eq 2 with a single activation energy of 0.30 eV. This suggests that one activated process is responsible for thermal electron release. The proximity of the thermoluminescence temperature in the crystal to the glass transition temperature additionally signals the possibility of the sudden allowance of some specific solvent motion with a 0.30 eV barrier.[54]

Activation frequencies for thermoluminescence in the glasses of *cis*-decalin and squalane are much lower than that for methylcyclohexane microcrystal of $10^{14}-10^{15}$ s^{-1} (since our spectra are only logarithmically sensitive to ν, this value is known only to within 1 or 2 orders of magnitude but certainly remains significantly higher for methylcyclohexane microcrystal than for the *cis*-decalin and squalane glasses). As pointed out in section II, the appropriate definition of the measured frequency factor is the product of the true frequency factor for the thermal activation from the trap, with a constant, K, which measures the effectiveness of retrapping. In the case of the microcrystal, the very low probability for forming trapped electrons[55,56] suggests that retrapping may also be of low probability. Accordingly, we would suggest that the true frequency factor for thermal activation may be ca. $10^{14}-10^{15}$ s^{-1} in all of these materials, but in the *cis*-decalin and squalane glasses is reduced by extensive retrapping.

C. Retrapping. Electrons released from traps may be retrapped prior to recombination. Photobleaching of trapped electrons in nonpolar glasses has provided evidence that retrapping is important.[2,3] However, to maintain the form of the Randall and Wilkins equation (and our data seem to support this form), it is required to assume that the entire process of trapping, retrapping, and recombination is geminate. With this constraint, as we have already pointed out (see section II), eqs 2 and 3 remain valid so long as the frequency factor ν is simply replaced with a branching ratio K (ratio of recombination rate constant to sum of recombination and retrapping rate constants) times the true frequency factor.

Garlick and Gibson[22,23] have derived thermoluminescence equations analogous to eq 2, but under conditions such that recombination is not necessarily geminate. The second order thermoluminescence equations that result from this homogeneous model predict a narrowing of the spectra and a shift to lower temperatures with increasing number of trapped electrons. Experimentally, however, we find that our thermoluminescence spectra retain their width and shape over a factor of 180 in number of trapped electrons. Indeed, the second-order equations predict a shift of −25 K (for the factor of 180) but the observed shift is +6 K (and this is most probably caused by heating of the sample by the laser or preferential bleaching of low activation energy sites).

The failure of the second order thermoluminescence equations supports the geminate recombination model, but this is not surprising. In our systems, the cation concentration is only $\sim 10^{-5}$ M. After 45 min, all electrons within ∼74 Å of the cation will have recombined by tunneling (see next section), but the average range of the remaining electrons remains well within the Onsager radius of 1000 Å. Accordingly, escape from the sibling cation field would be negligibly small.

D. Thermoluminescent Yield in Squalane Glass. In the case of squalane glass, the normalized thermoluminescence yield is shown in Figure 6 as a function of *N*, the number of laser pulses, operating at a frequency ω. In the simplest model that rationalizes this dependence, we consider that, after a delay of $1/\omega$ following a pulse, the probability of finding a trapped electron per absorption event is *f*. Therefore, after one pulse, the probability Z_1 that there exists a trapped electron per absorption event is $Z_1 = f$, and after *N* pulses will be $Z_N = (1 - Z_{N-1})f + Z_{N-1}$, where $Z_0 = 0$. Accordingly, $1 - Z_N = (1 - Z_{N-1})(1 - Z_1)$ is solved by $1 - Z_N = (1 - Z_1)^N$ with $Z_N = 1$ as $N \rightarrow \infty$. Since the thermoluminescence yield Y_N (which is measured after the *N*th pulse with a delay time of τ) is proportional to Z_N, we have the experimental equivalent that $\log(1-Y_N/Y_{\max})$ should be linear on *N* with a slope of $1 - Y_1/Y_{\max}$ where $Y_{\max}$ is the limit of Y_N as $N \rightarrow \infty$.

This predicted linearity (for $\tau \sim 60$ s and $\omega = 25$ Hz) is demonstrated in the insert of Figure 6 for $N = 10$ to 500. (This linearity extends to $N = 2000$.) The nonzero intercept, we suggest,[57] implies that ca. 7% of the yield accumulates before the mechanism described above begins to apply at $N \approx 10$.

The solid line in Figure 6 is the prediction of this model using $Y_1/Y_{\max} = 2.1 \times 10^{-3}$, as determined from the slope of the insert plot. The decrease in yield above 2000 pulses is due to photodegradation of TMPD.

As discussed above, the parameter $Y_1/Y_{\max} = 2.1 \times 10^{-3}$ is simply the probability/absorption event at 77 K that there remains a trapped electron at the end of $t = 1/\omega = 0.04$ s. This can be expressed as the product of the ionization yield per absorption event times the probability the electron so generated has not disappeared within the delay interval *t*.

The ionization yield for the two-photon process via an intermediate TMPD triplet can be estimated as follows. With an ionization threshold of ~5.5 eV in nonpolar glasses[58] and a TMPD triplet level at 2.9 eV, we expect a 4.0 eV second photon to generate an excited triplet state of TMPD ca. 1.4 eV above the ionization threshold. Were the excited state a singlet, this excess energy would be expected to lead to an ionization probability of ~0.35.[42] For the purpose of the following approximate analysis, we assume a similar probability for ionization from the triplet. Accordingly, we estimate that the probability that the electron has not decayed during the 0.04 s interval to be 0.006 (=0.0021/0.35). To obtain the contribution to this decay from tunneling back to the cation we have proceeded as follows.

The tunneling probabilitywas obtained by computing a WKB approximation to the rate constant, $k = s\,p(r)$ where *s* is a frequency factor and $p(r)$ the transmission of an electron from a spherical well at a position r into a coulomb well ($\epsilon = 3.0$)[45,59] at $r = 0$. The survival probability, $\exp(-k\,t)$, was then averaged over an exponential radial density of separation distances, $f(r) = (\beta^3/2)e^{-\beta\,r}$ where $\beta = 3/\langle r\rangle$. Using transmission parameters obtained from the absorption spectrum of the trapped electron,[5] the average tunneling probability (i.e., $1 - \exp[-kt]$) was determined as a function of β. If the entire decay probability of 0.994 (=1 − 0.006), is due to tunneling, then $\beta = 0.15$ A^{-1}, whereas if only 10% of the decay is due to tunneling (*ie*. tunneling probability is 0.96) then $\beta = 0.10$ A^{-1}. For the exponential distribution, these values suggest average thermalization distances of 20 and 30 Å, respectively.[60]

The thermalization distance in room-temperature liquid squalane (ionization threshold at 5.0 eV) was determined by fitting the dependence of photocurrent on electric field strength (from 5 to 80 kV/cm) to the exponential radial probability density of initial distances.[61] The average ranges so obtained with one photon singlet excitation was $\langle r\rangle = 21$ Å at 0.8 eV above threshold and $\langle r\rangle = 40$ Å at 1.7 eV above threshold. In the ~20% denser glass,[1] a singlet excitation 1.4 eV above threshold would then be estimated to give an average thermalization range of ~28 Å.

Accordingly, if the 28 Å thermalization distance is correct for the triplet excitations that are employed here, our previous calculation would require that tunneling accommodate only 10% of the decay. The remaining 90% would have then to be accommodated by other mechanisms (e.g., diffusive recombination of untrapped electrons).[62] On the other hand, it is also plausible that in the ionization from the triplet, a somewhat larger amount of energy is retained by the cation than for ionization from the singlet and that therefore the range reduces to a value closer to 20 Å. In this case, our calculation would imply that decay is exclusively by tunneling to the cation. Our data do not permit us to go beyond these speculations.

VI. Conclusions

Activation energies and frequency factors for thermoluminescence from 2 photon excited TMPD (at 308 nm/photon) were found to be 0.20 eV and 10^9 s^{-1} in squalane glass, 0.19 eV and 10^8 s^{-1} in *cis*-decalin glass, and 0.30 eV and 10^{14}−10^{15} s^{-1} in microcrystalline methylcyclohexane. The glasses exhibit a small distribution of trap activation energies of ~0.03 eV half-width at half-height, whereas for microcrystalline methylcyclohexane there appear to be only traps with activation energy of 0.30 eV. The smaller frequency factors for the glasses is considered to be due to retrapping of released electrons prior to their geminate recombination with the cation.

The activation energy for electron release in the glasses appears to be much smaller than the trap binding energies (as determined by the onsets of optical absorption). This supports the interpretation that the thermoluminescence is caused by thermally activated solvent rearrangements that destroy the trap. This conclusion is supported by activation energies for phosphorescence quenching that are very close to those for thermoluminescence.

In squalane, the dependence of the thermoluminescence yield on energy and frequency of excitation laser pulses is consistent with a two-photon ionization through the lowest triplet state of the TMPD. The dependence on number of pulses has been analyzed to show that at 77 K there is a probability of 0.0021 that an electron is ionized, trapped, and remains trapped at the end of a 0.04 s time interval. With an ionization quantum yield estimated at 0.35, the decay probability of 0.994 (=1 − 0.0021/0.35) can be entirely accommodated by geminate tunneling into the coulomb field of the cation, if the geminate ion separation distances are distributed exponentially with an average separation distance of ca. 20 Å.

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