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The Fluorescence Characteristics of Hydrocarbon
Liquids Excited in the Region of
Their Photoionization Thresholds*†

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Abstract

The fluorescence efficiencies of some representative hydrocarbon liquids have been determined as a function of exciting wavelength from their absorption onsets to energies slightly above their vapor phase ionization potentials. The effects of adding quenchers and fluorescent energy acceptors have also been studied. The relevance of this data to the determination of liquid phase ionization thresholds is discussed.

I. Introduction

For most polyatomic molecules in condensed phases, internal conversion from upper singlet states, S_n , to the lowest excited singlet S_1 is sufficiently rapid that the most intense singlet emission has its origin in S_1 .⁽¹⁾ The ratio of the S_1 fluorescence quantum yield observed on excitation into S_n , $\phi_f(\lambda_n)$, to the fluorescence quantum yield observed on excitation into S_1 , $\phi_f(\lambda_1)$, is a measure (after suitable corrections)^(2,3) of the efficiency of the $S_n \rightarrow S_1$ internal conversion. Clearly, if this internal conversion proceeds by means of a cascade through all of the intermediate electronic states, we would expect $\phi_f(\lambda_n)$ to be either invariant or to monotonically decrease with decreasing λ_n .

For neat liquid benzene and toluene, $\phi_f(\lambda_n)$ indeed decreases with decreasing λ_n for excitation in the spectral region extending from the absorption onset of S_2 to the absorption maximum of S_3 .⁽⁴⁾ At shorter exciting wavelengths however, $\phi_f(\lambda_n)$ begins to increase and to continue its rise to at least $\lambda_n \approx 1200\text{\AA}$.^(4,5,6,7)

In previous communications^(8,9) we reported fluorescence quantum yields for a variety of liquid alkanes excited at 1470\AA and have recently extended these measurements to include excitation at 1650\AA.⁽¹⁰⁾ For all molecules studied, the ratio $\phi_f(1476)/\phi_f(1650)$ is either equal to or less than unity. However, preliminary measurements at 1236\AA indicated that, at least for cyclohexane, $\phi_f(1236)$ was larger than $\phi_f(1470)$. A related observation had been made earlier by Laor and Weinreb^(7,11) who noted that the efficiency with which cyclohexane and hexane sensitize the emission of 2,5-diphenyloxazole (PPO) decreases at first with decreasing λ_n but then increases for $\lambda_n < 1400\text{\AA}$.

In an attempt to elucidate the mechanism responsible for the rise in the $S_n \rightarrow S_1$ internal conversion efficiency at high excitation energies, we have studied, for a number of saturated hydrocarbons, the exciting wavelength dependence of their fluorescence efficiency and/or energy transfer efficiency (to PPO). The effect of a quencher on these efficiencies is also reported.

II. Experimental

(12) The light source consisted of two titanium-gettered electrodeless lamps placed in tandem as illustrated in Fig. 1.⁽¹²⁾ The lamp closest to the monochromator was filled with 100 torr of argon and the second lamp with 100 torr of krypton. The source was butted onto the entrance slit of a 0.5 meter, f/11 McPherson monochromator (model 235) with 600G/mm grating blazed at 1500A and evacuated to ca 2×10^{-5} torr. The monochromator was operated at a band-pass of 66A. A typical lamp spectrum as determined with a sodium salicylate monitor placed at the monochromator exit slit is shown in Fig. 2.

The exit slit of the exciting monochromator was vacuum-sealed with a LiF window which also served as entrance to a nitrogen-flushed sample compartment. The exciting light was sharply focussed here by an f/1.8 polished LiF lens onto the face of the sample cell at normal incidence. Two Suprasil quartz lenses, f/1.0 and f/4.0 focussed the sample fluorescence onto the entrance slit of a 0.3 meter f/5.3 McPherson model 218 monochromator with 600G/mm grating blazed at 1500A. The optical axes of exciting and analyzing systems made a 45° angle. The remainder of the analyzing system consisted of a dry ice cooled EMI 6256S photomultiplier, Keithley 417 picoammeter and a 1 sec potentiometric recorder. The entire analyzing system was flushed with dry nitrogen.

The sample cell was constructed from a Pyrex tube, 13 mm in diameter, to which was attached a LiF window 0.5 mm thick. The window was freshly cleaved and annealed and showed no fluorescence (from ca 1800A to 5000A) over the entire spectral range of exciting light. However, after prolonged use, a weak fluorescence did appear at which time the window was replaced with a new one.

The intensity of sample fluorescence, at each exciting wavelength, was compared with that from sodium salicylate powder packed in the same sample cell under an atmosphere of nitrogen. Thus correction for the attenuation of the exciting light by the window was not necessary. The pertinent vacuum ultraviolet

optical constants required for determination of reflection losses at the window-sample interfaces are not known for all of the liquids studied and as a consequence such corrections could not be made. However, if cyclohexane is typical of the (13,14) other saturated hydrocarbons, this correction is always less than 4%. (13,14)

A typical scan of the exciting monochromator lasted about 30 minutes and during this time fluctuations in lamp intensity were monitored by a sodium salicylate coated wire mesh which intercepted the light beam between the exit slit of the exciting monochromator and the LiF condensing lens. The sodium salicylate fluorescence intensity was detected by an RCA 1P28 photomultiplier and displayed on a potentiometric recorder.

All saturated hydrocarbons used were of the highest purity commercially available and further purified by passage through Woelm silica gel (activated by heating at 200°C for 24 hr.). Scintillation grade 2,5-diphenyloxazole (PPO) was obtained from Pilot Chemicals, Inc. and used without further purification.

III. Results

In Fig. 3 is plotted the fluorescence quantum yield, ϕ_f , of a number of neat saturated hydrocarbon liquids (at 25°C) as a function of exciting wavelength λ_e . The emission intensities were measured at the wavelength maxima, λ_f , of the emission spectral distributions of each compound⁽¹⁰⁾ and quantum yields were obtained by normalizing the intensities at 1650A to quantum yields previously determined at this wavelength.⁽¹⁰⁾ Since the continuum lamp employed in this work was much less intense than the resonance lamps previously used, we have been limited here to compounds with relatively high fluorescence yield. However, even for these compounds, their fluorescence intensities at the shorter exciting wavelengths (i.e. $\lambda_e < 1400\text{\AA}$) become extremely weak. Therefore, although we are confident that $|d\phi_f/d\lambda_e|$ is approaching zero at ca 1400A, the reality of the rise that we show at shorter λ_e remains, to some extent, uncertain.

In Fig. 4 we compare the action spectra of neat cyclohexane liquid with a 10^{-2} M PPO solution in cyclohexane. For the latter system, only PPO emission was monitored (at $\lambda = 3600\text{\AA}$) and its intensity is indicated in arbitrary units on the RHS ordinate. For $\lambda_e < 1600\text{\AA}$, light absorption is almost exclusively by cyclohexane and, as a consequence, the PPO emission arises predominantly via cyclohexane sensitization.^(15,16) For longer λ_e , PPO begins to compete favorably with cyclohexane for absorption of light and is responsible for the development in this spectral region of a strong increase in $|dI_{\text{ppo}}/d\lambda_e|$ as compared to $|d\phi_f/d\lambda_e|$ for neat cyclohexane. Since PPO has about a 250 fold larger fluorescence quantum yield than cyclohexane, sufficient intensities were obtained from the solutions to make reliable our measurements over the entire spectral region. A minimum in I_{ppo} at $\lambda_e \approx 1420\text{\AA}$ is now definitely observed and suggests that perhaps the observed minimum for/neat liquid, which occurs at about the same λ_e , is similarly real.

Further examples of this effect in PPO solutions are presented in Figs. 5 and 6. For the three n-alkanes (Fig. 5), the minima appear to be somewhat blue-shifted as compared to cyclohexane whereas for both 3-methylhexane and 2,3-dimethylbutane (Fig. 6) the minima are not much different than observed for cyclohexane. However, the exact locations of the minima are still somewhat uncertain since correction has not yet been made for the finite spectral band width of the exciting beam. The rapid rise in I_{ppo} for $\lambda_e \approx 1600\text{\AA}$ is again attributed to direct absorption by PPO.

Fig. 7 presents our results for cis-decalin both as neat liquid and as solvent for a 10^{-2} M PPO solution. For neat decalin, ϕ_f remains constant from ca 1700 $\text{\AA}$ to 1420 $\text{\AA}$. For $\lambda_e < 1420$ there is observed now a decrease in ϕ_f rather than the previously observed increase. (17) Results for the PPO solution show parallel behavior except of course for $\lambda_e > 1600$ where once again PPO absorption becomes large.

All of the saturated hydrocarbons that we have so far discussed (8,9,10) have fluorescence yields, for excitation at 1650 $\text{\AA}$, greater than 2×10^{-4} . (8,9,10) However, for the compounds presented in Figs. 8 and 9, no fluorescence at all has yet been observed and from this we have estimated their quantum yields to be less than 1×10^{-5} . (10) The origin of this low yield has been attributed to a much larger rate of a non-radiative process (10) that always appears to dominate the decay of saturated hydrocarbons. (10)

On this basis we would have predicted lifetimes of these molecules to be too short to permit sensitization of PPO at $10^{-2}M$. For isooctane and neohexane (Fig. 8) at $\lambda_e \approx 1450A$ this may, in fact, be true. The ca 0.5 units of PPO emission intensity observed for λ_e between 1600A and 1450A could be attributed to a small residual absorption of light by PPO,⁽¹⁶⁾ and, clearly, for $\lambda_e \approx 1600A$, light absorption by PPO becomes increasingly important. It is only for $\lambda_e \approx 1450A$ that we believe light absorption to be sufficiently dominated by the hydrocarbon liquid as to permit interpretation of I_{ppo} as due to a sensitization.⁽¹⁸⁾ Also, it will be noted that in this spectral region, I_{ppo} slowly rises with decreasing λ_e , in a manner very similar to that observed for the "fluorescent" solvents. For cyclopentane (Fig. 9), a similar rise is observed for $\lambda_e \approx 1400A$ and again we suggest that it is attributable to a true sensitization.⁽¹⁸⁾ From $\lambda_e \approx 1400A$ to 1600A, I_{ppo} slowly rises, unlike the behavior observed in this region for isooctane and neohexane, and is also generally larger. Nevertheless, the uncertainties in the liquid extinction coefficients continues to make it impossible to decide definitely whether or not these results are attributable to residual PPO absorption.⁽¹⁶⁾ Of course, beyond 1600A, direct absorption by PPO is again definitely dominating.

The effect of N_2O (0.1M) on a typical action spectrum is shown in Fig.10 by plotting, against, λ_e the ratio of the PPO emission intensity in the presence of N_2O , $I(N_2O)$, to its intensity in the absence of N_2O , I_0 . Since N_2O does not significantly quench excited PPO but is an effective quencher of excited cyclohexane,⁽¹⁵⁾ the initial decrease in $I(N_2O)/I_0$ as λ_e decreases from 1800A to 1650A is simply attributed to a decreasing fraction of light absorbed by cyclohexane. For $\lambda_e \approx 1650A$, absorption by cyclohexane seems to be

complete since the quenching efficiency holds now effectively constant at least to $\lambda_e \approx 1400\text{\AA}$. The slight increase in $I(\text{N}_2\text{O})/I_0$ at $1500\text{\AA}$ is real and may be due to an increased concentration of photochemically developed quenchers as the cyclohexane absorptivity rises thus causing a reduced effectiveness of the N_2O quenching.⁽²⁾ At $\lambda_e \approx 1400\text{\AA}$, where we have previously noted minima to appear in the action spectra of both neat cyclohexane and its PPO solution (Fig. 2), a break occurs in the quenching efficiency curve, and, for shorter λ_e , there is observed increasing quenching.

IV. Discussion

In the gas phase, a molecular ionization potential, I_g , is usually defined as the minimum energy required to remove an electron and place it at infinity with zero velocity. Of course the molecule is considered to be in a gas of sufficiently low pressure as to make negligible all intermolecular perturbations on this process. In a condensed phase, this latter condition is clearly impossible to achieve and, as a consequence, the definition of ionization potential must be amended to include a more detailed specification of the final state. One possibility is to take as final state the electron completely ejected from the condensed phase (at infinity and with zero velocity) and the ion quasi-free in the sense that although it is not bound to a specific solvent molecule, it is stabilized by an electronic polarization of the surrounding solvent. For anthracene crystal, Lyons⁽¹⁹⁾ has calculated this polarization energy to be $W_+ \approx 1 \pm 0.3$ ev and from this calculates an ionization potential, based on the above definition, to be $I_c = I_g - W_+ \approx 6.2 \pm 0.3$ ev which is not too far from the experimental value of 5.6 ev. (20)

Alternatively, a condensed phase ionization potential could be defined with both positive ion and electron, in their final states, remaining in the same phase, but both quasi-free (i.e. not attached to solvent). Again for anthracene, Lyons⁽¹⁹⁾ estimates the polarization energy of the quasi-free electron, W_- , to be about equal to W_+ . As a consequence, the energy required to produce an unbound, free, electron-hole pair should be

$$\begin{aligned} I_s &= I_g - W_+ - W_- \\ &= I_c - W_- \\ &= 2I_c - I_g. \end{aligned}$$

taking $I_c = 5.6$ ev and $I_g = 7.4$ ev gives $I_s = 3.8$ ev which is again reasonably close to the measured onset of charge carrier generation of 3.65 ev. (21)

For no pure liquid hydrocarbon has either I_c or I_s been directly measured.

(22) However, Holroyd and Allen⁽²²⁾ have recently determined the shifts in work functions of various metal surfaces when they are moved from vacuum into hydrocarbon liquids. If it be assumed that the final state of the photoejected electron is quasi-free, then these shifts can be interpreted as equal to W_- and thus are obtained the values $W_- \approx 0$ for hexane, $W_- \approx 0.43$ ev for neopentane, $W_- \approx 0.28$ ev for cyclopentane and $W_- \approx 0.18$ ev for 2,2,4-trimethylpentane. If we were to assume further that $W_+ \approx W_-$, then for these liquids $I_g - I_s \leq 0.9$ ev.

(23) Takeda, Houser and Jarnagin⁽²³⁾ have determined a monophoton threshold for photocurrent from TMPD (tetramethyl-para-phenylenediamine) in hexane to lie at ca 4.5 ev. Their measurements appear to indicate an electron mobility sufficiently high^(24,25) to imply a final electron state which is indeed quasi-free and accordingly we will assume $I_s = 4.5$ ev. Since $I_g = 6.7$ ev for TMPD, $W_+ + W_- \approx 2.2$ ev in hexane. Using Holroyd and Allen's value of $W_- \approx 0$, it follows that $W_+ \approx 2.2$ ev. The situation here is then much different than for anthracene where $W_+ \approx W_- \approx 1$ ev and it is not clear why.

(26) Nakato, Ozaki and Tsubomura⁽²⁶⁾ report a threshold of 4.20 ev for photocurrent from TMAE (tetrakis-(dimethylamino)-ethylene) in pentane. Again, with the assumption that the ejected electrons are quasi-free, it follows that $I_s = 4.2$ ev. Since $I_g = 5.4$ ev, $W_+ + W_- = 1.2$ ev in pentane. Using a Born cycle they estimate $W_+ \approx 1.1$ ev (similar to anthracene) and therefore obtain $W_- \approx 0.1$ ev. This value is close to that of Holroyd and Allen's value for hexane but, again indicates a large disparity between W_+ and W_- for an alkane.

(27) In a somewhat different type of experiment, Bernas, Gauthier and Grand⁽²⁷⁾ have photoionized TMPD (and other solutes) in different low-temperature matrices to produce trapped electrons. These are then optically stimulated to recombine

with the positive ion. By measuring the energy dependence of the photoionizing beam that is required to give an emission on application of the stimulating beam, they obtain a threshold for production of a trapped electron. Calling this threshold I_t , we have

$$I_t = I_g - (W_+ + W_-) - V - e^2/\epsilon r$$

- where V is the binding energy of the trapped electron and $e^2/\epsilon r$ the coulomb energy of the positive ion-trapped electron pair at the distance r . From the extensive measurements of Albrecht and coworkers,⁽²⁸⁾ the last term is estimated to not exceed ca 0.2 ev. Since Bernas, et. al. find $I_g - I_t \approx 0.9$ for TMPD in methylcyclohexane and 3-methylpentane, it follows that $W_+ + W_- \leq 0.9$. Somewhat consistent with this are some early measurements of Vermeil, Matheson and Leach⁽²⁹⁾ who determined both photoconductivity and ionic polymerization thresholds for isopentane and obtained $0.3 \leq I_g - I_s \leq 0.9$ ev.

Thus all of these results taken together give a rather unclear picture of the energetics of electron photoejection in hydrocarbon solvents. All that really emerges is an expectation that $I_g - I_s$ should be of the order of ca 1 - 2 ev unless V is very large.

- For most of the molecules we have studied, $I_g \approx 10$ ev⁽³⁰⁾ and therefore, we expect to find $I_s \approx 8 - 9$ ev (i.e. 1350 - 1550A). Interestingly enough this is about where we have observed peculiarities in the emission action spectra. Also N_2O , which is generally considered to be an efficient electron scavenger, is observed (Fig.10) to increase its quenching efficiency in about the same spectral region.

Neglecting for the moment the results obtained with the "non-fluorescent" solvents, we might explain our results as follows. As λ_e decreases from ca 1650A, the fluorescence quantum yield of the hydrocarbon also decreases due to increasing inefficiency of the cascade from S_n to S_1 . This continues until a state S_t is achieved at $\lambda_e = \lambda_t$ which is the threshold for electron ejection.

At this energy, the electron may be ejected with probability p into a quasi-free state which subsequently localizes with binding energy V . Recombination then of the positive ion with the localized electron produces a neutral excited state S_n with $n \leq t$. Thus is avoided all of the intermediate states between S_n and S_t ($E_t - E_n \approx V_0$) and as a consequence the fluorescence quantum yield is increased. It continues to increase with decreasing λ_e , we would suggest, simply because the autoionization probability, p , increases with decreasing λ_e .

In the case of decalin, there appears to be no inefficiency in the cascade to S_1 for all S_n . Accordingly, our model would force us to predict that for decalin at λ_t , ϕ_f could not possibly be increased and, indeed, unlike all other hydrocarbons studied, no increase is observed. The decrease in decalin ϕ_f at λ_t can be explained if recombination of the positive ion and localized electron does not always produce a singlet excited solvent (e.g. a triplet, or ground state may be formed). The continued decrease in ϕ_f with λ_e for $\lambda_e < \lambda_t$ would again follow from increase in p . The action of N_2O , we postulate, is to first trap the electron followed then either by

which would give quenching were N_2O^* unstable; or $N_2O^- + S_0^+ \rightarrow (N_2O + S_n) \rightarrow (N_2O + S_1) \rightarrow N_2O + S_0$ which because of the close proximity of N_2O to S_1 would give much more quenching than expected from the homogeneous N_2O concentration of 0.1M.

The function of PPO according to this scheme is simply to trap the S_1 excitation, i.e.

For "non-fluorescent" solvents an alternative mechanism must be invoked to explain the PPO sensitization in view of our assumption that the lifetimes of their lowest neutral excited states are now too short for reaction with PPO. Since for these compounds the only real evidence we have for a sensitization of PPO is in the spectral region $\lambda_e \leq \lambda_t$, it is tempting to invoke an ionic

(31,32) mechanism/which is initiated at $\lambda_e \approx \lambda_t$. Two possibilities exist,

(33) Since N_2O has also been observed to quench the cyclopentane sensitized emission of PPO(excited at 1236A,⁽³³⁾) we require, for mechanism i) the additional reaction

and for mechanism ii), either

(15) Efficiencies of energy transfer from cyclohexane or heptane are not found to depend too strongly on the nature of the acceptor.⁽¹⁵⁾ Essentially the same efficiencies were observed for 1470A excitation using PPO or p-xylene as acceptors. However, for the ionic mechanisms suggested above, a rather crucial dependence on acceptor is predicted. In the case of mechanism i) the higher is the ionization potential of the acceptor, the less efficiently we might expect the sensitization to occur. On the other hand for mechanism ii) a low electron affinity probably

will signal a low sensitization efficiency.

(30) Although the ionization potential of PPO is not known, it is probably
for for
less than/p-xylene (8.45 ev) which is in turn less than/benzene (9.25 ev). (30)

Therefore, were mechanism i) correct, we would expect I_A (cyclopentane)/ I_A (cyclohexane) to decrease in the order A = PPO, p-xylene and benzene. Unfortunately, electron affinities are not known for either PPO or p-xylene and, even for benzene, its value is uncertain. Nevertheless, since most oxygen containing compounds have positive affinities, whereas benzene (and very likely p-xylene too) has a

(34,35) negative affinity/we would expect from mechanism ii), I_A (cyclopentane)/ I_A (cyclohexane) to be larger for A = PPO than/benzene, and for p-xylene to have probably an intermediate value.

(36) At $[A] = 10^{-2} M$, the ratio was found to be 0.34, 0.12 and 0.04/for PPO, p-xylene and benzene respectively. Although this does not permit us to distinguish the two mechanisms, it nevertheless argues for a difference in sensitization mechanism for cyclopentane and cyclohexane and is explained simply by at least some ionic mechanism operating for the "non-fluorescent" compound.

We have not yet been able to distinguish which of the ionic mechanisms predominates in the "non-fluorescent" solvent case, nor in fact, to determine to what extent such ionic mechanisms may contribute to the sensitization for the "fluorescent" solvents. However, at $\lambda_e = \lambda_t$ some new channel clearly opens up for the production of fluorescence and it is plausible, as we have attempted to demonstrate, that some form of electron photoejection is involved. For the case of "fluorescent" solvents, the addition of PPO is, in principle, unnecessary for the determination of λ_t and merely complicates the interpretation. With

more intense lamps, perhaps this complication can be eliminated. Ultimately, with a more thorough understanding of the emission properties of the neat hydrocarbons in the electron photoejection spectral region, the problem of unraveling the solute's role will hopefully be somewhat simplified.

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References and Footnotes

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17. The decalin emission is sufficiently intense to make our measurements reliable even in this spectral region.
18. Although LiF does not fluoresce above 1800Å (See Section II) there may be some fluorescence from the window at shorter wavelengths. If this emission is excited at $\lambda_e \lesssim 1450$, it could be absorbed by PPO and be responsible for the observed PPO fluorescence. To check this point we studied the action spectrum of a 10^{-2} M solution of PPO in methanol but could find no evidence in this case for any change in the PPO fluorescence intensity at $\lambda_e \lesssim 1450$.
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Fig.1 SKETCH OF Ar + Kr LAMP

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10