ELECTRONIC RELAXATION IN ISOLATED SUBSTITUTED BENZENES*

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Summary

Data on the rate constants for radiative and non-radiative decay of isolated substituted benzenes as a function of excess energy are considered with reference to current theories. The possible role of vibrational redistribution in these isolated molecules is discussed, and the assumptions inherent in the use of theoretical models stressed.

Introduction

In recent years a fruitful interaction between experimentalists and theoreticians has led to the development of extensive quantum-mechanical treatments with which the major features of non-radiative decay of molecular species can be understood [1]. At the same time an extensive, and increasing, body of experimental information has been accumulated with which to test the predictions of such theories. The methods by which the experimental information is obtained usually generate simultaneously information concerning the radiative decay of the molecular species and this aspect of the electronic relaxation of molecules has also been treated theoretically, although to a lesser extent. One of the particular problems which has attracted attention recently has been the energy dependence of non-radiative and radiative decay in polyatomic molecules. In the particular case of benzene, the experimental decay characteristics of single-vibronic levels [2] have been investigated from a theoretical standpoint [3], and exact agreement reached with some slight manipulation of adjustable parameters. This treatment also provides a basis for a rationale of the non-radiative decay of fluorobenzene and hexadeuterobenzene, although quantitative predictions are not possible in the case of the fluorinated compound. Until very recently, the energy dependence of the rate constant for

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radiative decay of such molecules has been largely ignored from a theoretical standpoint, but a simple treatment has been given which explains some of the features for a variety of molecules [4].

Benzenoid hydrocarbons provide an attractive subject for such studies since the molecules are generally volatile, and relatively strongly fluorescent. Moreover, simple substitution in the benzene ring reduces the symmetry of the molecule, and generally results in an increase in the oscillator strength for the S_0-S_1 transition, which makes experiments easier to perform since simultaneously more light is absorbed in the system, and higher pressures can be obtained while retaining the isolated molecule condition. The major, and very important disadvantage in the study of substituted benzenes is that concomitant with the absorption transitions becoming allowed, there is a dramatic increase in the density of upper-state vibronic levels which can be reached optically from the ground state. Single-vibronic levels thus become difficult to populate exclusively, and except in the case of some simply fluorinated and deuterated benzenes, excitation produces a distribution of emitting levels. Nevertheless, it is felt that the results of such experiments can provide information of relevance to the current theories of radiative and non-radiative decay of molecules, and some recent results are discussed here.

Experimental

The results reported here are either derived from the literature, or were measured in our laboratories. These latter results include measurements of fluorescence decay times, fluorescence quantum yields, O_2-perturbed S_0-T_1 absorption measurements, and low pressure fluorescence spectra under moderate resolution. The apparatus used for measurement of fluorescence decay times has been described fully in earlier reports [5, 6], and briefly consisted of a free-running N_2 flash lamp, Bausch and Lomb high-intensity monochromator, or Rank Precision D330 monochromator with 10 Å (or better) band-pass, T-shaped quartz fluorescence cell, and Ortec time-correlated single-photon counting equipment with a Northern multi-channel analyzer. Calibrations of the system were carried out frequently with acetone ($\tau = 1.7$ ns), toluene ($\tau = 54$ ns) and a convolution procedure was adopted to obtain the fluorescence decay curves for decays less than 5 ns. The chief disadvantage of the system is the relatively low repetition rate of the flash lamp (about 3 kHz) and the fact that there is still some line structure in the N_2 spectral output when operated at 25 lb/in^2. Nevertheless, in general good exponential decay for all compounds reported here over at least two decades of decay was observed, and results were reproducible within at worst 10% but usually within 2%.

Quantum yields of fluorescence were measured using again a quartz T-shaped cell, high intensity 500 W xenon arc source, Bausch and Lomb grating monochromator with grating blazed at 300 nm, with a band-pass of 10 Å, with an RCA 935 photodiode to measure the number of photons

absorbed, and an RCA 1P28 photomultipler tube to measure emitted photons. The system was calibrated with benzene vapour excited at 253.7 nm, and the quantum yield of emission of this compound in the region 2 - 20 Torr was taken as 0.18 [7]. Corrections for the fact that viewing geometries produce non-linear relationships between observed emitted photon intensity and optical density were applied in the manner described fully elsewhere [5].

Fluorescence spectra were recorded using a 450 W xenon arc source and Rank Precision D330 monochromator with 10 Å band-pass, or a Coherent Radiation 52 B argon ion laser frequency-doubled to 257.25 nm with the Model 144 UV generator as light source; a 10 cm × 10 cm fluorescence cell in the shape of a cross with 3 cm diameter windows throughout; a Rank Precision Monospek 1000 analyzing monochromator, and a Brookdeal 5C1 photon-counting detector system used in conjunction with an EMI 6256 QB photomultipler tube [8]. The digital output from the 5C1 was converted to an analogue signal and was displayed on a strip chart recorder as a function of wavelength.

O_2-perturbed S_0–T_1 absorption spectra were recorded in the presence of 170 atm. of O_2 in a specially constructed cell which has been described elsewhere [9], using a Unicam SP700 recording spectrophotometer.

Results and discussion

Assumptions in interpretation of the results

The results outlined below can be interpreted on the basis of the simple scheme below:

$$A + h\nu \quad \rightarrow \quad {}^1A_n \qquad I_a \tag{1}$$

$$^1A_n \quad \rightarrow \quad A + h\nu \qquad k_R \tag{2}$$

$$^1A_n \quad \rightarrow \quad {}^3A_m \qquad k_{NR} \tag{3}$$

There are several assumptions implicit in the adoption of such a scheme. For our results, the composition of the emitting states, ^1A_n, will be those states populated by the electronic transition from the Boltzmann distribution of ground state absorbing levels, plus those populated by any intramolecular vibrational redistribution process [10]. The effects of the latter process will be discussed below. At the pressure of aromatic molecules used on most of the decay time and quantum yield measurements, 0.25 Torr, it has been assumed that collisions with surrounding molecules do not take place significantly within the radiative lifetime of the excited singlet state of the aromatic species. There is some evidence to indicate that this might be valid, since over the pressure range 0.1 to 0.5 Torr, the fluorescence spectrum, quantum yield, and decay time of a typical example studied here, *p*-fluorotoluene (PFT), was invariant with pressure. Over the range 2 - 8 Torr of the same compound, however, some variations were observed indicating that at these elevated pressures bimolecular processes which noticeably affected the electronic relaxation characteristics of the compound were of importance.

This is not to say that in the pressure range 0.1 - 0.5 Torr there do not occur some long-range bimolecular interactions which disturb the population of rovibronic levels initially produced, and which could give rise to such phenomena as rotational line-broadening in absorption [11], but it does appear that should such interactions occur, they do not grossly affect the electronic relaxation phenomena observed. Given that for the most part, owing to the complexity of the molecules studied, the 1 nm excitation band-pass used excites a wide distribution of emitting levels initially, especially since sequence congestion may be very marked in these molecules, it is not perhaps surprising that small changes in rovibronic make-up might not lead to observable differences in electronic relaxation phenomena.

The second, and more serious assumption has been used in the evaluation of rate constants for radiative (k_R) and non-radiative (k_{NR}) decay that eqns. (4) and (5) are valid. For excitation to a single vibronic level these equations are rigorously correct provided electronic relaxation is not dependent upon degree of rotational excitation within the vibrational envelope, and this appears to be the case for benzene [12]. When a distribution of vibrational levels is being observed, however, the possibility exists that some of the excited vibrational levels, by virtue of their particular vibronic make-up, may undergo fast non-radiative relaxation processes which are not available to the other levels. Under these circumstances the initially prepared levels will be partitioned into observable fluorescent states and non-observable states undergoing non-radiative decay on a time-scale shorter than fluorescent decay. Quantum yield measurements apply to both types of states, whereas fluorescence decay measurements are made upon only the longer-lived fraction of initial states, and thus eqns. (4) and (5):

$$k_R = \Phi_F / \tau_F \tag{4}$$

$$k_{NR} = \frac{(1 - \Phi_F)}{\tau_F} \tag{5}$$

may not be meaningful. If the fraction of observable states remains constant in any set of experiments, then use of eqns. (4) and (5) will give rise to values of k_R and k_{NR} which are incorrect by a constant factor, and thus comparison of relative measurements will be permissible. It might be expected, however, that the fraction of observable states produced under such circumstances would be strongly dependent upon excess energy in the excited states, and values of k_R and k_{NR} would not be correct. The best test of partitioning is the addition of large pressures of moderating gas to the system, since the quantum yield of fluorescence for higher excited levels will approach that of the Boltzmann distribution obtained at excitation near the zero point level upon addition of the moderating gas if partitioning is absent, but will reach some lower asymptotic value if it occurs. Comprehensive testing of all compounds for this phenomenon has not been carried out, but some results at higher pressures would suggest that, at least in some cases, it is not important [13].

The final assumption in the discussion below is that non-radiative decay in these molecules is accounted for exclusively by intersystem crossing to the triplet manifold. This is a contentious assertion, since no physical proof can be obtained with current experimental techniques in low pressure experiments. The methods of evaluation of triplet-state quantum yields available include observation of triplet–triplet absorption spectra [14, 15], use of the spectrophone technique [16], and use of chemical quenchers such as olefins [17], and biacetyl [18]. In the case of chemical addition the success of the method depends upon there being a significant difference in singlet state and triplet state lifetimes such that addition of the triplet scavenger does not perturb the singlet manifold. Given the requirement in isolated molecule experiments that total pressures may not exceed 0.25 Torr, the fact that for some relaxed triplet-state levels of substituted benzenes the triplet lifetimes are already sub-microsecond and are expected to shorten perhaps exponentially with increasing excess energy [19], it can be seen that scavenging experiments are not practicable in these cases. In the triplet absorption and spectrophone experiments performed to date, high pressures were employed, and thus the triplet state may be populated through the vibrationally relaxed singlet state. There was some evidence in the spectrophone experiments on benzene [16], in which the triplet state is monitored directly, that the quantum yield of triplet formation decreased as successively higher levels in the singlet manifold were excited. The method, however, may only detect relatively long-lived triplet states, and it is conceivable that non-radiative decay of higher excited singlet levels occurs initially in a rate-determining manner, to levels in the triplet manifold, which then decay before detection to a high level of the ground state, or to some other species. Clearly a good physical method capable of use at low pressures is required in order to detect such likely short-lived excited triplet states, but in the absence of any such evidence, the assumption has been made that in benzene the non-radiative decay of the singlet manifold up to 2,800 cm^{-1} above the zero-point level is best represented in terms of intersystem crossing. Data for the substituted benzenes are compared on the same basis.

Radiative decay

The energy dependence of the radiative rate constant for excitation in a progression in benzene [2], hexadeuterobenzene [20], and fluorobenzene [20], has been shown to be linear and decreasing, except where the transition is symmetry-forbidden and the progression being excited is that of a promoting mode for the optical transition [4]. Results for isolated substituted benzenes studied here are shown in Fig. 1, and it can be seen that except at high excess energies where strong deviations are observed in PFT, a linear decrease of radiative rate constant for nominal excitation of the ν_1 (C–C totally symmetric ring breathing mode) progression with excess energy (solid symbols) can be said to hold in these cases, although it should be noted that results for other pumped levels (open symbols) also fall on the same line.
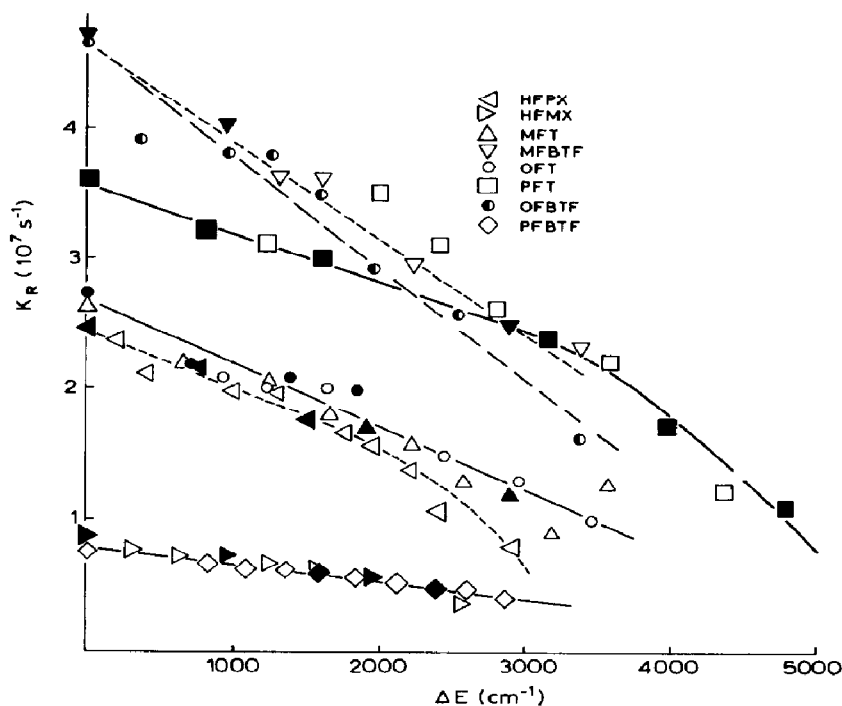
Fig. 1. Plots of rate constant for radiative decay of isolated substituted benzenes (k_R) against excess energy, 25 °C. HFPX = 1,4-bis(trifluoromethyl)benzene; HFMX = 1,3-bis(trifluoromethyl)benzene; MFT = 1,3-fluoro(methyl)benzene; MFBTF = 1,3-fluoro-(trifluoromethyl)benzene; OFT = 1,2-fluoro(methyl)benzene; PFT = 1,4-fluoro(methyl)-benzene; OFBTF = 1,2-fluoro(trifluoromethyl)benzene; PFBTF = 1,4-fluoro(trifluoro-methyl)benzene. Solid symbols represent members of ν_1 progression.

A qualitative understanding of this behaviour can be obtained by consideration of the simple treatment of Lin *et al.* [4], which in a revised form [21] predicts the energy dependence of the radiative decay rate constant for pumping a progression υ_i as:

$$k_R(\upsilon_i') = 4R_{bu}^2(0)\omega_{ba}^3/3\hbar c^3[1 + \frac{3}{4\omega_{ba}} \sum_j \frac{(\omega_j'^2 - \omega_j''^2)}{\omega_j'} + \frac{3\upsilon_i'}{2\omega_{ba}} \frac{(\omega_i'^2 - \omega_i''^2)}{\omega_i'}]$$

(6)

where $R_{ba}(0)$ is the electronic transition moment, ω_{ba} the difference in electronic energies of ground and excited states, and ω_j' and ω_j'' the upper and ground-state vibrational frequencies respectively. The treatment is based upon the Born–Oppenheimer separation of electronic and vibrational wave functions, assumption of the simple harmonic oscillator approximation for evaluation of Franck–Condon factors, and in its simplest form, neglects displacement of the upper potential surface with respect to the lower. The equation clearly shows the linear dependence of $k_R(\upsilon_i')$ upon vibrational quantum number υ_i', and since in general $\omega_j' < \omega_j''$, the negative slope of plots of $k_R(\upsilon_i')$ against υ_i' is also explained. Quantitatively, however, the expression does not predict observed behaviour. This can be demonstrated

for compounds for which all frequencies are known, such as fluorobenzene (Table 1) [20]. Denoting $\sum_j (\omega_j'^2 - \omega_j''^2)/\omega_j'$ as $\Sigma f(\omega)$, it can be seen from Table 1 that the total value of this quantity is -8700 cm^{-1}, which is small compared with ω_{ba} ($\sim 40{,}000$ cm^{-1}), which results in k_R (v_i') being less sensitive to the changing value of v_i' than experiment shows to be the case. For the other aromatic molecules for which variation in k_R with v_i' has been obtained (Fig. 1), complete assignment of vibrational frequencies has not been carried out. The agreement of eqn. (6) can be tested in an approximate fashion, however, by the following procedure.

Writing:

$$\frac{(\omega_j'^2 - \omega_j''^2)}{\omega_j'} = (\omega_j' + \omega_j'')\,(\omega_j' - \omega_j'')/\omega_j' \tag{7}$$

$$\simeq 2(\omega_j' - \omega_j'')$$

$$\simeq 2(\Delta\omega_j)$$

Table 1 shows that this approximation is reasonable, since $2\Delta\omega_j$ for fluorobenzene is only a factor of 1.38 less than $\Sigma f(\omega)$ obtained rigorously, and the equivalent ratio for benzene is only 1.2.

Thus we can write:

$$k_R(v_i') = 4R_{ba}^2(0)\omega_{ba}^3/3\hbar c^3 \left[1 + \frac{3}{2\omega_{ba}} \sum_j (\Delta\omega_j) + \frac{3v_i}{2\omega_{ba}} f(\omega_i')\right] \tag{8}$$

Plots of k_R (v_i') against v_i' should be straight lines with values of slope/intercept, denoted by S, given by:

$$S = \frac{3f(\omega_i')}{2\omega_{ba}} \,/\, \left(1 + \frac{3}{2\omega_{ba}} \sum_j (\Delta\omega_j)\right) \tag{9}$$

Given that:

$$\omega_{ba} = \omega_{00} - \tfrac{1}{2}\sum_j (\Delta\omega_j) \tag{10}$$

eqn. (9) can be rearranged to give:

$$\sum_j \Delta\omega_j = \frac{3}{2} f(\omega_i)/S - \omega_{00} \tag{11}$$

Experimental slopes, S, for all compounds are given in Table 2, from which it can be seen that values of $f(\omega_i)/S$ are very small compared with ω_{00}, again giving rise to impossibly large values of $\sum_j (\Delta\omega_j)$. This is shown by dividing $\sum_j (\Delta\omega_j)$ by the number of vibrational modes, N, leading to average values of $\Delta\omega_j$ shown in the last column of Table 2. The results are clearly at least an order of magnitude too large, and the discrepancies are undoubtedly due at least in part to the neglect of displacement in the simple treatment. If included, eqn. (6) would be rewritten:

TABLE 1

C_6H_5F frequencies [20]

Assignment	ω'' (cm^{-1})	ω' (cm^{-1})	$\Delta\omega$ (cm^{-1})	$f(\omega)$ (cm^{-1})	$\dfrac{f(\omega)}{2\Delta\omega}$
a_1 (C—C stretch)	1597	1465	−132	−275.9	1.05
b_1 (C—C stretch)	1595	1512	−83	−170.2	1.03
a_1 (C—C stretch)	1496	1498	+2	+4.0	1.00
b_1 (C—C stretch)	1458	1405	−53	−108.0	1.02
b_1 (C—C stretch)	1325	1207	−118	−247.6	1.05
$b_1\beta$ (C—H in plane bend)	1290	1183	−107	−223.5	1.04
$a_1\beta$ (C—H in plane bend)	1179	1108	−71	−146.5	1.03
$b_1\beta$ (C—H in plane bend)	1156	1098	−58	−119.1	1.03
$b_1\beta$ (C—H in plane bend)	1066	1004	−62	−127.9	1.03
$a_1\beta$ (CH in plane bend)	1021	937	−84	−175.6	1.05
a_1 (ring breathing)	1010	968	−42	−85.8	1.02
b_2 Y (C—H out of plane bend)	981	762	−219	−500.7	1.14
a_2 Y (CH out of plane bend)	955	706	−249	−585.5	1.18
b_2 Y (CH out of plane bend)	896	661	−235	−553.4	1.18
a_2 Y (CH out of plane bend)	830	585	−245	−593.1	1.21
b_2 Y (CH out of plane bend)	755	533	−222	−536.5	1.21
b_2 Φ (C—C out of plane deformation)	685	285	−401	−1368.2	1.71
b_1 d (C—C—C in plane deformation)	614	546	−68	−144.5	1.06
a_2 Φ (C—C)	400	243	−157	−415.4	1.32
a_1 (C—F stretch)	1219	1209	−10	−20.1	1.00
a_1 (ring deformation)	806	751	−55	−114.0	1.04
a_1 (ring deformation)	519	454	−65	−139.3	1.07
b_1 (C—F in plane bend)	406	315	−91	−208.2	1.14
b_2 (out of plane deformation)	499	121	−378	−1936	2.56
b_2 (out of plane deformation)	2242	292	+50	+91.4	0.91

$\Sigma\Delta\omega$ = −3153 cm^{-1} $\Sigma f(\omega)$ = −8700 cm^{-1}

$2\Sigma\Delta\omega$ = −6306 cm^{-1} $\dfrac{\Sigma f\omega}{2\Sigma\Delta\omega}$ = 1.38

TABLE 2

Radiative decay of substituted benzenes [21]

Excitation of ν_1 progression of isolated molecules

Compound[a]	S[b]	ω' (cm^{-1})	ω'' (cm^{-1})	$f(\omega_i)$[c] (cm^{-1})	$f(\omega_i)/S$	ω_{00} (cm^{-1})	$\sum_j(\Delta\omega_j)$ (cm^{-1})	N[d]	$(\Delta\omega_j)_{av.}$ (cm^{-1})
OFT	−0.13	707	749	−86.5	665.4	37576	−36,577.9	39	−937.9
MFT	−0.179	965	1003	−77.5	433.0	37398	−36,748.5	39	−942.3
HFMX	−0.186	963	(1009)	−94.2	506.5	37606	−36,846.2	48	−767.6
HFPX	−0.16	770	890	−178.7	1116.9	37460	−35,784.0	48	−745.5
			809	−54.0	337.5	37460	−36,953.8	48	−769.9
PFT	−0.0835	794	825	−63.2	756.9	36876	−35,740.6	39	−916.4
PFBTF	−0.137	792	837	−92.6	675.9	37866	−36,852.1	39	−944.9
MFBTF	−0.149	963	1009	−94.2	632.2	37355	−36,406.7	39	−933.5
FB[e]	−0.22	968	1010	−85.8	390	37819	−37,234	30	−1,241.1

[a] OFT = o-fluorotoluene; MFT = m-fluorotoluene; HFMX = $\alpha,\alpha,\alpha',\alpha',\alpha'$-hexafluoro m-xylene; HFPX = $\alpha,\alpha,\alpha',\alpha',\alpha'$-hexafluoro p-xylene; PFT = p-fluorotoluene; PFBTF = p-fluorobenzotrifluoride; MFBTF = m-fluorobenzotrifluoride; FB = fluorobenzene.

[b] Values of slope/intercept of plots of k_R against quanta of ν_1 vibration in upper state.

[c] $f(\omega_i) = (\omega_i'^2 - \omega_i''^2)/\omega_i'$ where ω_i is optically excited mode.

[d] Number of vibrational degrees of freedom.

[e] Data from A. S. Abramson, K. G. Spears and S. A. Rice, J. Chem. Phys., 56 (1972) 2291.

$$k_{\mathrm{R}}(v_i') = 4R_{\mathrm{ba}}^2(0)\omega_{\mathrm{ba}}^3/3\hbar c^3 \left[1 + \frac{3}{4\omega_{\mathrm{ba}}} \sum_j \left(\frac{\omega_j'^2 - \omega_j''^2}{\omega_j} \right) + \right.$$

$$\left. \frac{3v_i}{2\omega_{\mathrm{ba}}} \frac{(\omega_i'^2 - \omega_i''^2)}{\omega_i} - \sum_j \frac{\omega_j'^2 \delta^2}{\hbar} \right] \tag{12}$$

where δ is a measurement of the displacement. For fluorobenzene, the magnitude of $\sum_j (\omega_j'^2 \, \delta^2 \, /\hbar)$ required to give exact agreement with experiment can be evaluated as 0.65, and a similar treatment for benzene in which the $6^1 \, 1^i$ progression is excited yields a corresponding value of ~ 0.75. These values are not unreasonable when compared with values of displacements given by Ross and McCoy [22]. Displacement terms may be of even greater importance in some of the methyl and trifluoromethyl benzenes which have lower symmetry and therefore larger number of totally symmetric modes for which displacement terms may be significant. Displacement is clearly of importance in PFT, since in absorption (Fig. 2) the $v_i' = 6$ member of the ν_1 progression is visible, whereas for zero displacement it would not be anticipated that members above the $v_i' = 3$ level would have significantly large Franck—Condon factors. Unfortunately displacement terms are not simple to evaluate, and thus quantitative calculations are difficult to carry out. The effects of anharmonicity may also severely distort the simple picture presented by the theory of Lin et al., which nevertheless is of considerable interest.

The phenomenon of unimolecular vibrational redistribution is pertinent to the current discussion, since the results for excitation to other vibrational levels (Fig. 1) do not appear to deviate significantly from those obtained for excitation of the ν_1 progression, and one cause of this could be the redistribution process, leading to a smooth dependence of k_{R} upon ΔE. Alternatively, the behaviour could simply be a reflection of the fact that many levels are populated by the excitation process in these complex molecules, although most of the oscillator strength in absorption is apparently carried by the ν_1 frequency. Recent studies on p-difluorobenzene (PDFB) do not show such a smooth dependence [23], and we considered it of interest to compare the fluorescence spectra of this compound and those of PFT in which redistribution may occur. Spectra are given in Figs. 3 and 4 from which it can be seen that differences exist. In PDFB excited to the zero-point level, $e, e + \nu_1, e + 2\nu_1,$ and $e + 3\nu_1$ there is good evidence for resonance fluorescence (Fig. 3) and even at the highest level considerable vibrational structure is in evidence, although an underlying continuum is also observed at this relatively high excitation energy. By contrast, excitation of the same progression in PFT gives spectra which are considerably red-shifted with respect to the exciting radiation, and moreover are largely structureless. This behaviour is that expected if redistribution (Fig. 5) were to occur, and spectra from the other substituted benzenes studied parallel this behaviour. The fact that the absorption spectrum of PFT and related compounds are crowded makes it difficult to ascribe the spectral characteris-
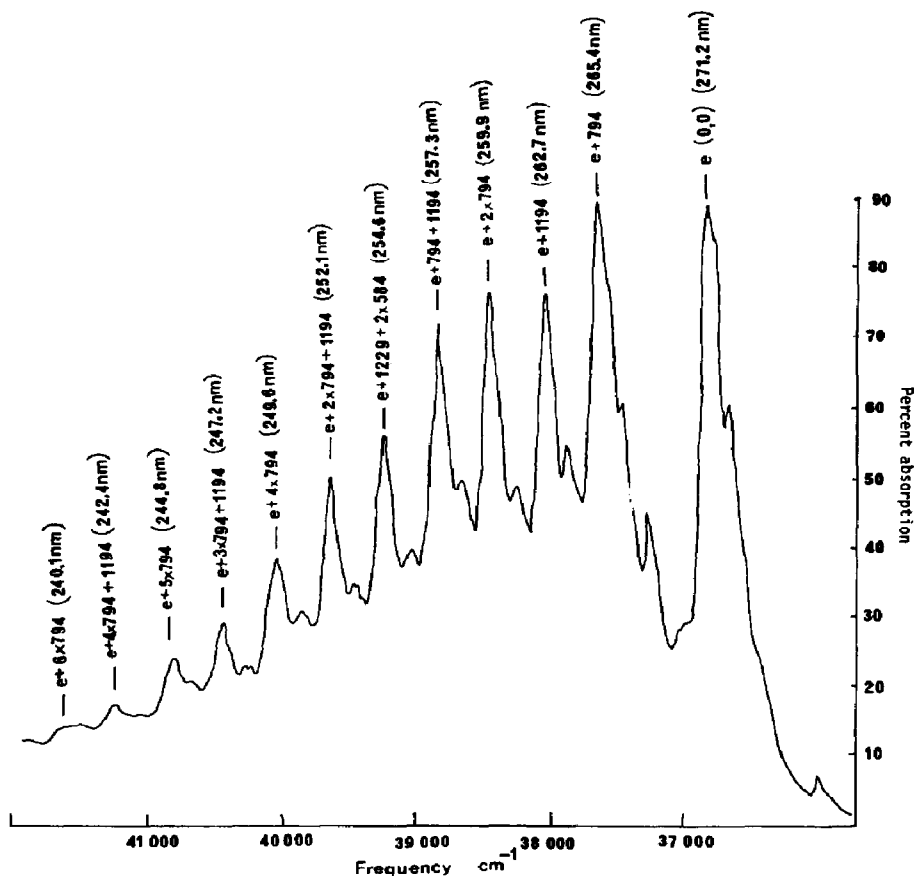
e+6×794 (240.1nm)
e+4×794+1194 (242.4nm)
e+5×794 (244.8nm)
e+3×794+1194 (247.2nm)
e+4×794 (249.6nm)
e+2×794+1194 (252.1nm)
e+1229+2×584 (254.6nm)
e+794+1194 (257.3nm)
e+2×794 (259.9 nm)
e+1194 (262.7nm)
e+794 (265.4nm)
e (0,0) (271.2nm)

Percent absorption

90 80 70 60 50 40 30 20 10

41 000   40 000   39 000   38 000   37 000

Frequency cm^{-1}

Fig. 2. Absorption spectrum of PFT vapour, 1.9 Torr, 22 °C, 5.5 cm path length. Assignment of frequency at 1194 cm^{-1} is ambiguous, and can also be due to 794 + 398 cm^{-1}.

tics solely to the effects of redistribution since spectral congestion might also give rise to such effects. However, excitation at 257.25 nm with the frequency-doubled argon ion laser which has very narrow spectral band-pass produced spectra identical to that seen in Fig. 4, and some differences might have been expected if congestion were the sole cause of the difference in this spectrum and that of PDFB. There is in addition no evidence of resonance fluorescence for excitation at this frequency, and yet as Fig. 2 shows, the 0 - 3 band appears very strongly in absorption, indicating favourable Franck—Condon factors which would have been expected to give rise to bands observable in emission. Should redistribution occur on a time-scale comparable to electronic relaxation, a time-dependent fluorescent spectrum should result, and experiments are currently being carried out to test this and other pressure effects using a mode-locked cavity dumping accessory to the doubled argon-ion laser. Temperature studies are also being carried out to evaluate the role of sequence congestion in this system.

A further effect may be of importance in this system, as has been found in NO [24] and glyoxal [25] recently. This is vibrational relaxation which occurs *via* an electronic energy transfer mechanism:
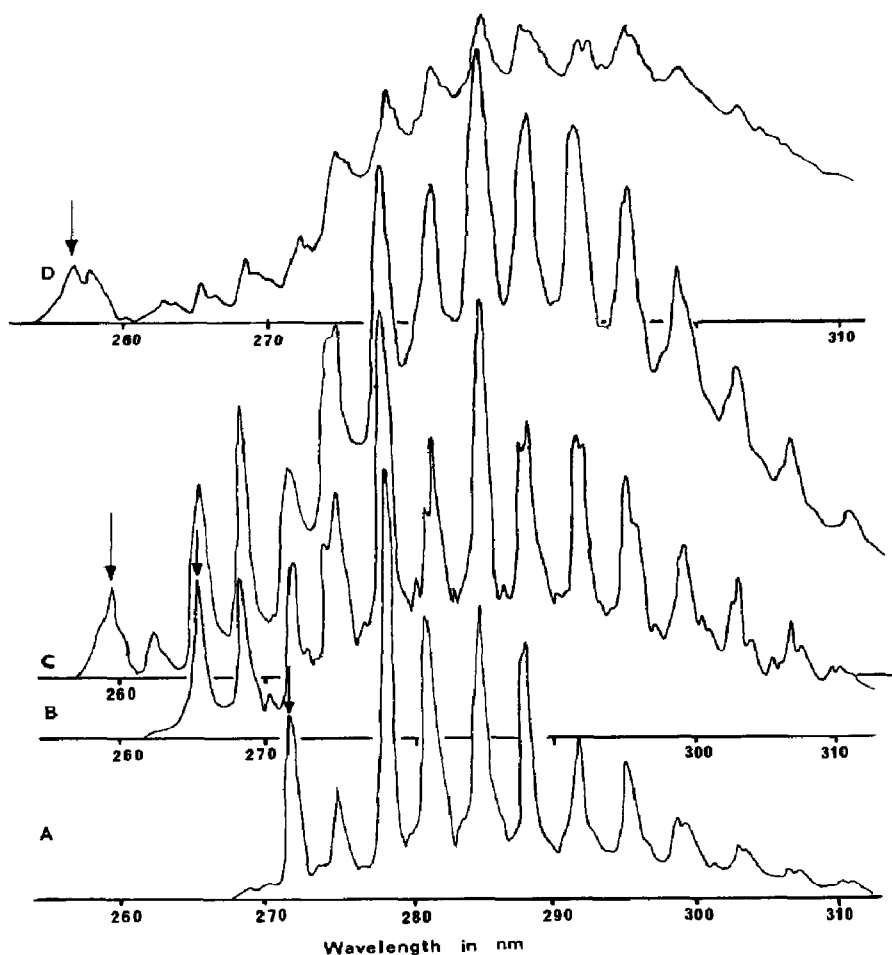
Fig. 3. Fluorescence spectra of 0.1 Torr PDFB excited at different wavelengths (arrowed) corresponding to (A) zero-point level, (B) one, (C) two, and (D) three quanta of ν_1 (totally symmetric C—C breathing mode) respectively.

$$^1A_m^* + A_0 \rightarrow A_m + {}^1A_0^* \qquad\qquad (13)$$

and is more efficient than the gas-kinetic collision efficiency, since it occurs *via* the transition dipole-transition dipole interaction which can extend over long-ranges [26]. It is possible that the effect may occur strongly in compounds such as PFT, and results in red-shifted emission spectra even at low pressures, but the effect would be pressure dependent and there is no strong evidence for its occurrence in these compounds to date. Careful low-pressure studies will be required on the systems to evaluate the importance of mechanism (13).

Non-radiative decay

As stated above, a model has been developed which is capable of describing accurately the non-radiative decay of benzene molecules in terms of intersystem crossing to the triplet manifold [3]. The scheme is shown in
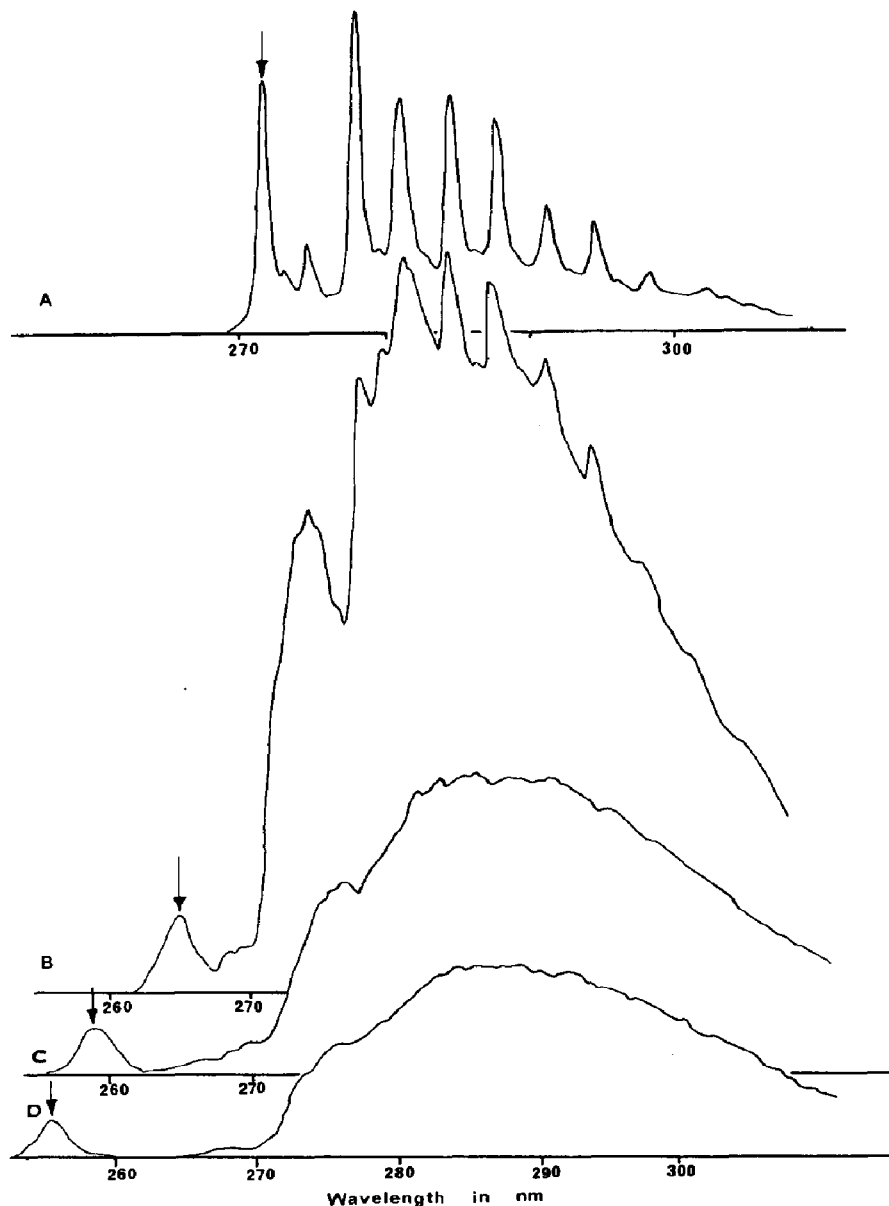
Fig. 4. Fluorescence spectra of 0.125 Torr PFT excited at different wavelengths (arrowed) corresponding to (A) zero-point level, (B) one, (C) two quanta of ν_1, (D) one quantum of ν_1 + 1194 cm^{-1} respectively.

Fig. 6, and consists of a method of evaluation of averaged Franck–Condon factors for the transition from the optically pumped member of the progression ω_a to the isoenergetic levels of the triplet manifold. If the transition is symmetry forbidden as in the case of benzene, the amount of energy to be partitioned among the triplet levels is ΔE, given by

$$\Delta E = \Delta E_{ST} + (v_a + \tfrac{1}{2})\, \hbar\omega_a - \tfrac{1}{2}\hbar\omega_k \tag{14}$$
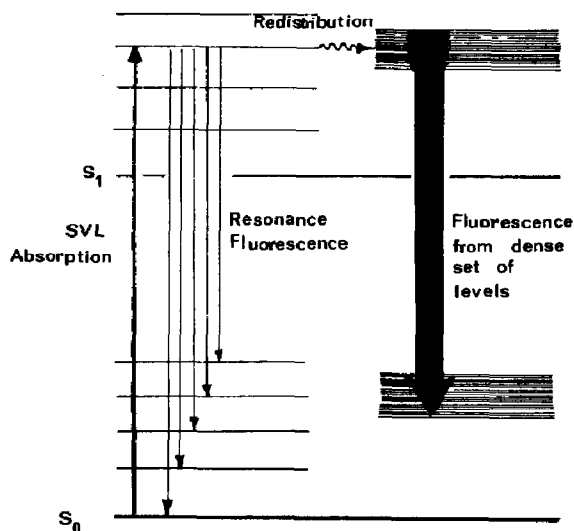
Fig. 5. Scheme illustrating vibrational redistribution process. Resonance fluorescence is structured, fluorescence from dense set of levels is structureless, red-shifted. Spectra similar to the latter can also be due to sequence congestion in the excitation process.
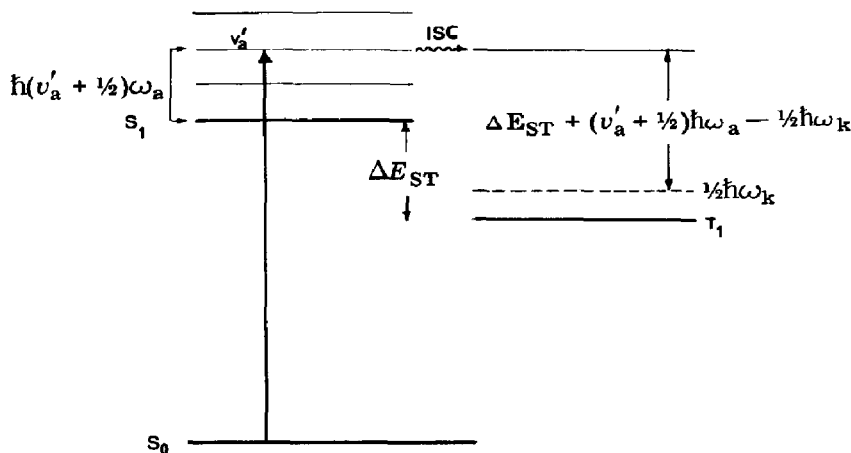

Fig. 6. Scheme illustrating model for non-radiative decay in benzene [3].

where ω_k is the promoting mode frequency. Only totally symmetric vibrational modes have non-zero displacements between singlet and triplet manifolds, and therefore have large Franck—Condon factors. The energy is thus partitioned essentially into the a_1 totally symmetry carbon skeletal breathing mode and the totally symmetric C—H stretching frequencies in benzene. The calculation of absolute values of k_{NR} in this way depends upon a knowledge of ω_k, but this obstacle can be overcome by consideration of the value of k_{NR} for excitation in a progression relative to its value for excitation of the zero-point level. Exact agreement of the relative value of k_{NR} as a function of excess energy with experiment was obtained by consideration of small frequency changes in the optically pumped mode in going from singlet to triplet manifolds, and these were fixed at 25 cm^{-1} for the ring breathing mode [3]. The model was extended to hexadeuterobenzene

and fluorobenzene, and qualitative predictions made which were in agreement with observation. Thus in the deuteriated compound, the lower frequency of the C—D totally symmetric mode renders it a less effective acceptor in the triplet state, and the relative value of k_{NR} is thus a more sensitive function of excess energy than in the case of benzene. For fluorobenzene by contrast, the reduction in symmetry introduces two more totally symmetric C—H vibrations which may act as good acceptors, and the relative values of k_{NR} are thus a less sensitive function of excess energy than is the case of benzene. We may consider the model in the case of the molecules studied here. The values of the rate constants relative to that of the zero-point level are shown in Fig. 7 as a function of excess energy, with members of the ν_1 progression denoted by solid symbols. Values are also shown in Table 3, from which it can be seen that up to an excess energy of around 3000 cm^{-1} the increase in k_{NR} with excess energy is smooth and very close to that for benzene with the exception of PFT which shows a much stronger dependence upon ΔE. There is some evidence that above 3000 cm^{-1} MFT also shows an increase in k_{NR}, although there is only a single result to substantiate this behaviour. Most molecules therefore behave similarly to benzene, and it may be correct to make the assumption that the non-radiative decay is intersystem crossing to the triplet state. PFT poses a problem, since its behaviour seems markedly different. Within the framework of the model proposed for benzene, a stronger dependence of k_{NR} upon energy than expected could be caused by larger frequency changes, of the order of 80 cm^{-1} in the ν_1 mode, in going from the singlet state to the triplet state. We have attempted to observe these frequencies in absorption using the O$_2$-perturbed S$_0$-T$_1$ method [9]. The results are somewhat
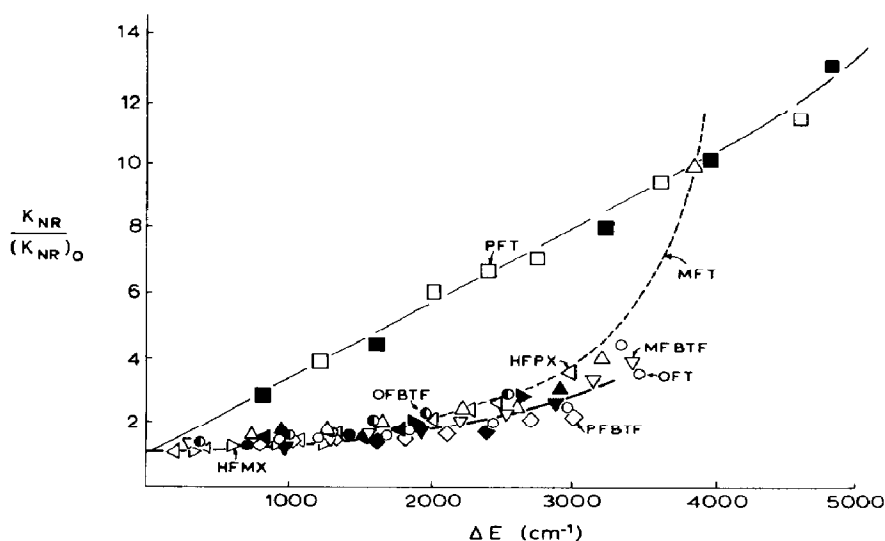

Fig. 7. Plots of rate constant for non-radiative decay of selected levels of isolated substituted benzenes relative to that for zero-point level in each case against excess energy. Symbols as for Fig. 1; solid symbols represent members of ν_1 progression.

TABLE 3

$(k_{NR})/(k_{NR})_0$ for ν_1 progression

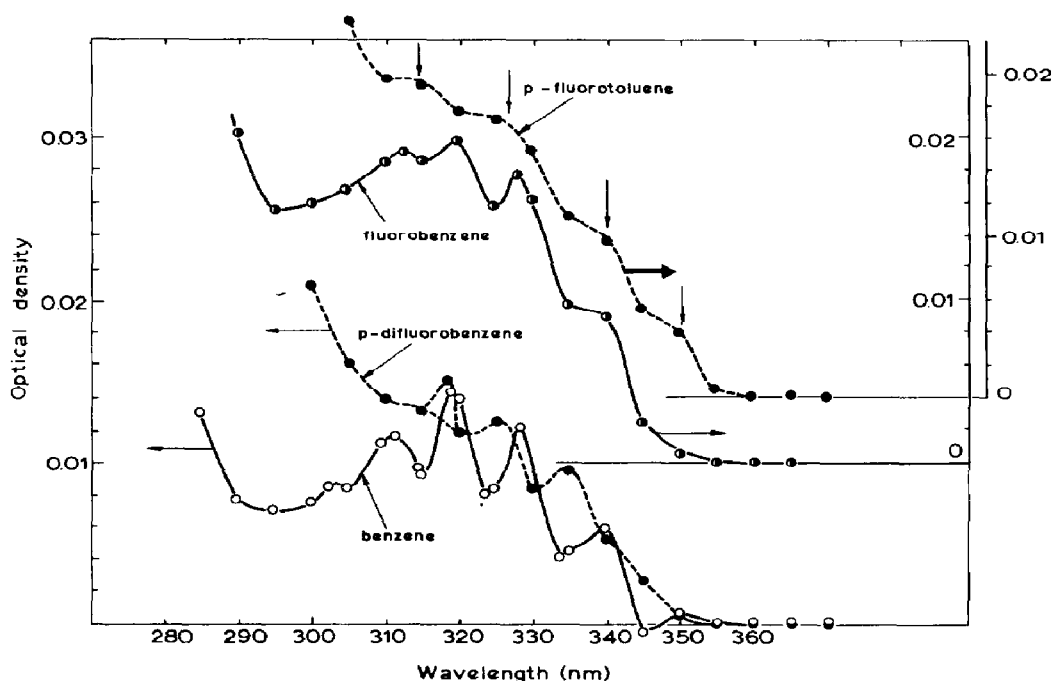| Compound	ν_1(cm^{-1})	$(k_{NR})_0 \times 10^7$(s^{-1})	$k_{NR}/(k_{NR})_0$ for no ν_1 excited						
			0	1	2	3	4	5	6
Benzene	923	—	(1.00)	1.22	1.73	2.42	—	—	—
MFT	965	5.4 ± 0.4	(1.00)	1.61	2.00	3.20	—	—	—
OFT	707	6.9 ± 0.5	(1.00)	1.25	1.57	—	—	—	—
PFBTF	792	5.4 ± 0.3	(1.00)	—	1.53	2.22	—	—	—
MFBTF	963	11.0 ± 1.1	(1.00)	1.32	1.89	2.55	—	—	—
HFPX	770	9.2 ± 0.7	(1.00)	1.27	1.64	—	—	—	—
HFMX	963	4.0 ± 0.2	(1.00)	1.28	1.90	—	—	—	—
PFT	794	1.9 ± 0.3	(1.00)	2.78	4.41	—	8.04	10.4	13.0

Fig. 8. O_2-perturbed S_0–T_1 absorption spectra for PFT, fluorobenzene, benzene and p-difluorobenzene.

self-defeating, however, since the presence of the O_2, while perturbing the system to make the spin-forbidden transition observable, simultaneously broadens the features one is attempting to observe. The results obtained are shown in Fig. 8, from which it can be seen that there are some features in the spectrum of PFT which have a mean separation of 900 ± 100 cm^{-1}, some 100 cm^{-1} greater than the known frequency of the ν_1 vibration in PFT of 794 cm, but it would be foolhardy to ascribe these features to the ν_1 progression in the triplet state.

Having considered the effects of vibrational redistribution upon the

singlet state spectra and radiative decay, it is pertinent to enquire what the effects might be on intersystem crossing rates. Lin has shown [19] that exponential increase in k_{NR} with excess energy should be expected in such circumstances. The effect is known to be absent in benzene, and yet for most of the molecules studied here, the variation in k_{NR} with excess energy is similar to that for benzene. The data for PFT certainly do not appear to be strongly exponentially increasing with excess energy but do resemble the kind of result obtained for naphthalene using the model of communicating states [27]. This model does involve vibrational redistribution, and it may well be therefore that the phenomenon occurs in this compound. There is a very small barrier to rotation of the methyl group in the compound, and this may provide a means of scrambling vibrational energy in the excited state.

Channel III process

It is well known that in benzene at an excess energy of ~ 2800 cm^{-1}, a new non-radiative decay channel appears which has been termed the Channel III process [11]. This process gives rise to vanishingly small quantum yields of fluorescence [7] and considerable broadening of the rotational structure of the absorption spectrum [11]. It is perhaps remarkable that in the case of PFT, the increase in k_{NR} with excess energy is a smooth function up to excess energies even as high as 5000 cm^{-1}, demonstrating the apparent absence of this phenomenon in PFT. Only in the case of MFT is there any evidence of a sudden increase in k_{NR} (at 3800 cm^{-1}), and this is based only upon a single datum-point. The Channel III process has been ascribed in benzene to a crossing to a new state, perhaps a $\sigma\pi^*$ $^3E_{2u}$ state [11], and the absence of the process in these compounds would apparently suggest that such a level lies to higher energies in these species. It will be of interest to probe these compounds further to discover the reasons for the apparent absence of the Channel III phenomenon.

Acknowledgements

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