Intramolecular Vibrational Redistribution at Low State Densities in S_1 Aromatics. Evidence for Rotational Contributions

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Evidence is presented concerning the onset of intramolecular vibrational redistribution (IVR) as one climbs the vibrational manifold of room temperature S_1 aromatics. The onsets of IVR occur at S_1 vibrational energies between 670 and 2000 cm^{-1} for various single and double ring aromatic molecules. The vibrational level densities in the onset region seem too small to support the extensive IVR that is observed in every molecule. Comparisons of room temperature fluorescence spectra with cold supersonic beam spectra from *p*-difluorobenzene support the proposition that Coriolis vibration–rotation coupling makes important contributions to the effective density of states in room temperature IVR.

INTRODUCTION

Speculations concerning intramolecular vibrational redistribution (IVR) within upper electronic states of polyatomics began¹ soon after the first collision-free single vibronic level (SVL) fluorescence spectra were obtained.² The evidence is found in changes of the fluorescence structure as higher S_1 vibrational levels are pumped. While SVL fluorescence spectra have open structure when fluorescence originates

from low vibrational levels, pumping of higher levels often produces congestion, sometimes so dominant that discrete vibrational structure is lost from the fluorescence spectrum. Such congestion is consistent with the proposition that IVR has scrambled the S_1 vibrational identity prior to fluorescence, so that the resulting fluorescence is in effect a superposition of spectra from many S_1 vibrational levels. The superposition submerges discrete structure by congestion.

This simple picture was clouded by uncertainty concerning the extent to which a trivial source of fluorescence congestion, namely thermal inhomogeneous broadening (TIB), contributed to these room temperature spectra. Consequently the issue of IVR was not pursued seriously in the early SVL fluorescence studies, although subsequent developments have shown that the TIB and IVR contributions to congestion in room temperature fluorescence can be separated.³⁻⁶

The first truly convincing arguments pointing to IVR as the cause of congestion were instead derived from SVL fluorescence spectra from molecules in cold supersonic beams where TIB is largely suppressed. Examples can be found in representative early papers of Levy and co-workers,⁷ of Smalley and co-workers,⁸ and of Amirav, Even and Jortner.⁹ Zewail and co-workers¹⁰ have more recently cemented the association of congestion in cold beam fluorescence spectra with IVR. With direct observation, they have characterized quantum beats in the vibrational structure of cold anthracene fluorescence. The beats result from coherent pumping (15 ps pulses) of a small number of S_1 coupled vibronic levels with excess vibrational energy of about 1380 cm^{-1} . Some of the room temperature and beam studies have recently been reviewed.^{5,11}

The cold beam experiments have begun to reveal an apparently general aspect of IVR. The onset of level mixing sufficient to give these indications of IVR occurs relatively early as one climbs the S_1 vibrational ladder in aromatics. Such low onsets were specifically documented in the Tel-Aviv work¹² on ovalene, tetracene and pentacene (10, 4, and 5 rings respectively) where onsets occur with S_1 vibrational energies in the range 1060 to 1900 cm^{-1} . Smalley's group has found the onset in naphthalene¹³ to be near 2400 cm^{-1} , and in alkyl benzenes⁸ it drops to as low as 530 cm^{-1} . Perhaps the largest molecule yet studied in this respect is free base phthalocyanine⁷ where clear indications of the extensive level mixing associated with IVR are in place at 700 cm^{-1} .

The beam studies have emphasized IVR in relatively large and vibrationally complex molecules. Room temperature experiments emerging in coincidence with the beam studies have revealed the same behavior in much smaller aromatics.⁵ In this paper we discuss room temperature examples that are shown in Figure 1. Some studies are old and some new. All contribute documentation of the phenomenon of low onsets of IVR in these smaller aromatic systems. We will show that onsets occur at levels densities so low that one questions whether IVR could operate without the presence of some additional source of level density such as that provided by vibrational-rotation Coriolis coupling. Some preliminary explorations of the importance of such coupling to IVR are obtained by comparisons of room temperature and cold beam fluorescence spectra.

OBSERVATION OF IVR ONSETS BY COLLISION-FREE SVL FLUORESCENCE SPECTROSCOPY

Room temperature studies of IVR in collision-free SVL fluorescence require careful choice of molecules in order to separate fluorescence congestion due to TIB from that due to IVR. Accordingly one seeks molecules that have well defined vibrational structure in their 300 K absorption spectrum so that tuned pumping of a prominent absorption maximum can bias a significant fraction of the initial S_1 population

FIGURE 1 Molecules discussed.

to a single vibrational level. Often this fraction can be estimated so that clear expectations arise concerning the relative intensities of structured components versus background congestion on fluorescence. If IVR occurs after such pumping, one will observe less structured intensity than estimated from absorption characteristics.⁵ Alternatively, one can estimate the contribution of TIB to fluorescence congestion by comparing fluorescence spectra that are generated with a laser tuned and then detuned from an absorption maximum.⁶

Neither of these methods can assign TIB contributions to fluorescence congestion with a quantitative accuracy much better than 10 or 15%. Thus they are not sensitive to the very earliest onset of IVR as excitation climbs the S_1 vibrational ladder. The methods are sufficiently accurate, however, to identify with security even rather modest IVR contributions to fluorescence congestion. Thus the onsets quoted in the following discussions generally concern IVR under conditions where it is sufficiently limited so that structure in fluorescence is not entirely obliterated.

A summary of room temperature IVR onsets, or more accurately, upper limits to these onsets is given in Table I along with estimates of vibrational level densities in those S_1 vibrational regions. Specific discussion of each case is given below.

(i) *p*-Difluorobenzene This is probably the first molecule in which a room temperature IVR onset was securely established.^{3,5} The association of the fluorescence congestion with IVR has been made explicitly

TABLE I
Upper limits to IVR onsets and the corresponding level densities in the S_1 vibrational manifolds of room temperature aromatics

Molecule	Vibrational energy of the IVR onset (cm^{-1})	ρ_{vib} (levels/ cm^{-1}) (levels/ cm^{-1})
<i>p</i> -difluorobenzene	1760	10
<i>p</i> -fluorotoluene	1990	25
coumarone	720	0.2
indole	1440	3
1-azaindolizine	1110	1
azulene	670	0.2

through the use of time-resolved fluorescence spectroscopy³ that showed substantial enhancement of the structured component when fluorescence observation times are reduced to a few tens of psec after excitation. The earlier experiments⁵ placed the onset at $\epsilon_{\text{vib}} \leq 2069 \text{ cm}^{-1}$, checked by time-resolved spectroscopy. Later refinements,⁶ again checked by timing, have lowered the detected onset to $\epsilon_{\text{vib}} \leq 1761 \text{ cm}^{-1}$. This study has also revealed that a low frequency out-of-plane mode (ν_{30}') is especially effective relative to other modes in promoting IVR.

The S_1 level densities are reasonably accurate for *p*-difluorobenzene.¹ The figure quoted in Table I is that for ungerade levels alone, since only those species can couple with the $\epsilon_{\text{vib}} = 1761 \text{ cm}^{-1}$ level initially excited.

(ii) *p*-Fluorotoluene The study of collision-free SVL fluorescence is still in progress, but it has been reported that excitation of an absorption maximum leading to $\epsilon_{\text{vib}} = 1988 \text{ cm}^{-1}$ results in completely unstructured emission.^{4,14} Fluorescence timing confirms the IVR contribution to this congestion.⁴ Other spectra show that the onset is well below this level, but the data are not yet ready for a better estimate.

The level density calculation in *p*-fluorotoluene is complicated by a near free rotor.¹⁵ The density reported in Table I was calculated from a known set of S_0 frequencies with substitution of 8 known S_1 frequencies. The rotor has been omitted from the calculation.

(iii) Coumarone (2,3-benzofuran) An extensive set of SVL collision-free fluorescence spectra are available for this molecule and a few examples of the S_1 level dependence are shown in Figure 2. The spectra follow the typical pattern with abundant structure from low levels and congestion from high levels. The spectra are in fact wholly without structure from S_1 levels with $\epsilon_{\text{vib}} \geq 2142 \text{ cm}^{-1}$. Congestion exceeding that expected for TIB is found for levels above 721 cm^{-1} . Accordingly we set the onset in S_1 coumarone at $\epsilon_{\text{vib}} \leq 721 \text{ cm}^{-1}$.

Coumarone S_1 level densities are calculated from a set of known ground state frequencies adjusted by a uniform drop of 20% to simulate the average S_1 changes. Two low frequency S_1 modes are well known and they have been included accurately.

FIGURE 2 Collision-free $S_1 \rightarrow S_0$ single vibronic level fluorescence spectra of coumarone. The vibrational energy of the S_1 pumped level is given at the right. The position of excitation is denoted by the asterisk.

(iv) *Indole* Only a few room temperature spectra have so far been obtained. Extensive structure is found in zero point level S_1 fluorescence and congestion well beyond TIB contributions is seen in a spectrum from a level with $\epsilon_{\text{vib}} = 1435 \text{ cm}^{-1}$. Further study will almost certainly show an onset below the $\epsilon_{\text{vib}} \geq 1435 \text{ cm}^{-1}$ value that we now adopt.

(v) *1-Azaindolizine (imidazo(1,2a)pyridine)* With a beautiful long Franck-Condon envelope of structure extending $>4000 \text{ cm}^{-1}$ above the $S_1 \leftarrow S_0$ absorption origin,¹⁶ this otherwise obscure molecule is a favorable experimental candidate for S_1 IVR studies. Examples of fluorescence spectra from various S_1 levels are given elsewhere.⁵ Low levels yield fluorescence with discrete structure and almost no congested background. Congestion in excess of that expected from TIB is certainly present in fluorescence from levels above 1100 cm^{-1} . While the IVR onset is probably somewhat lower, the onset limit is securely set at $\epsilon_{\text{vib}} \leq 1110 \text{ cm}^{-1}$.

The S_1 state density quoted in Table I is estimated from the coumarone calculations with substitution of several known low S_1 frequencies for azaindolizine.

(vi) *Azulene* A comprehensive study of IVR in S_2 azulene is in progress using collision free room temperature fluorescence spectra, cold beam spectra, and timed room temperature spectra. The onset is determined from a full set of spectra such as those shown in Figure 3. The spectra clearly show congestion due to IVR at the remarkably low S_1 energy of 670 cm^{-1} . We suspect that more sensitive tests now in progress will place the onset below our current limit of $\epsilon_{\text{vib}} \leq 670\text{ cm}^{-1}$. The S_1 level density reported in Table I is estimated by extrapolation from calculated densities for S_1 naphthalene.¹³

FIGURE 3 Collision-free $S_1 \rightarrow S_0$ single vibronic level fluorescence spectra of azulene. The vibrational energy of the S_2 pumped level is given at the right. The position of excitation is denoted by the asterisks.

VIBRATION-ROTATION COUPLING AS A SOURCE OF LEVEL DENSITY FOR IVR

In addition to the uniform occurrence of low onsets among the aromatic molecules listed in Table I, a remarkable characteristic appears. One can see that the vibrational level densities in the onset regions are extremely low, being commonly of order unity. The situation is actually more severe than the Table indicates, since the method of detecting onsets is not fully sensitive to the initial stages of IVR. Thus the vibrational densities are even lower in the regions of true IVR onsets.

It is difficult to see how such low densities can accommodate the degree of spectral congestion seen in the examples discussed in this paper. Superposition of emission from the order of 10^2 states is generally required. Acquisition of such extensive state mixing among vibration levels with densities of order unity requires interactions over tens of wave numbers. Such mixing, in turn, will obliterate the prominent maxima seen in the absorption spectra.

These considerations suggest immediately that an additional source of level density contributes to IVR in these room temperature systems. The most apparent source is Coriolis rotation-vibration coupling which allows interactions to occur between nearly isoenergetic rotational levels of widely separated vibrational levels. Such involvement of rotational levels is now well documented in radiationless transitions between electronic states,¹⁷ and since IVR is so closely related to these processes it would not be surprising to find similar rotational involvements. In fact Saigusa and Lim¹⁸ have recently argued that data from isoquinoline fluorescence in "cool" and "cold" beams provides evidence for such rotational level contributions to IVR. The possible role of vibration-rotation coupling in IVR has also been discussed⁵ in connection with room temperature fluorescence data concerning *p*-difluorobenzene and *p*-fluorotoluene.

In the case of anharmonic vibrational coupling, the rotational selection rules are $\Delta J = \Delta K = 0$, and the density of states available for interaction is that calculated from vibrational levels alone. With Coriolis coupling, the $\Delta K = 0$ restriction is relaxed, making possible the distribution of energy into a larger number of vibronic levels. This effect is illustrated for the room temperature case in Figure 4a. The net result is an increase in the available density of states by a

FIGURE 4 Schematics of neighboring vibrational levels (heavy lines) with the J, K rotational stacks built up on them. A J, K level in the left vibrational state is coupled to nearly isoenergetic rotational levels of other vibrational states. (a) At room temperature, coupling can occur to isoenergetic vibrational states with $\Delta J = \Delta K = 0$ or to widely separated vibrational states through Coriolis interactions that allow coupling of nearly isoenergetic J, K levels with $\Delta K \neq 0$ ($\Delta J = 0$). (b) At low temperatures, thermal restrictions on J reduce markedly the energy span of other vibrational levels that can be mixed through these interactions.

factor of about J . Since J on order of 100 is accessible at room temperature, such vibration-rotational coupling can easily boost the effective density of states by factors in excess of 10^2 .

An obvious test for Coriolis coupling in the IVR process is to compare room temperature data to that obtained in low temperature molecular beams. Cold supersonic beams will restrict the effective state density in proportion to the cooling of J population as illustrated in Figure 4b.

Early experimental results are shown in Figure 5. Collision-free room temperature fluorescence spectra from *p*-difluorobenzene pumped to an S_1 level at 2069 cm^{-1} and to another level at 2502 cm^{-1} are compared with spectra obtained with similar excitation but under supersonic beam conditions. Marked changes occur. In each case the cold beam spectrum shows a substantial boost in the relative intensity of structured emission from the level initially pumped. The change is most dramatic in emission after $\epsilon_{\text{vib}} = 2502\text{ cm}^{-1}$ pumping where the structured component of emission is almost nil in the room temperature experiments.

FIGURE 5 Comparisons of collision-free room temperature $S_1 \rightarrow S_0$ fluorescence with cold supersonic beam fluorescence from S_1 *p*-difluorobenzene. The top pair are obtained after pumping the 3^2S_1 level at $\epsilon_{\text{vib}} = 2502 \text{ cm}^{-1}$ and the bottom pair are from pumping the 3^1S_1 level at $\epsilon_{\text{vib}} = 2069 \text{ cm}^{-1}$. The excitation position is marked at the right.

Several factors participate in these changes. The contributions associated with IVR must be sorted from the rest. The principal source of non-IVR change must be a reduction of TIB in the cold beam experiments. Congested emission originating from TIB can be gauged for both room temperature and beam experiments by measurements auxillary temperature to the spectra in Figure 5.

One can obtain a qualitative judgement of the IVR contributions to fluorescence congestion by making corrections for the TIB contributions to congestion. After corrections for TIB, all intensity would occur as structured emission if IVR were absent, and conversely, structure would disappear if IVR is extensive.

Table II shows an analysis of the spectra in Figure 5 after contributions to congestion from TIB have been extracted. It is seen for each level that at room temperature over half the remaining intensity occurs as congestion attributable to IVR. It is also seen that congestion drops appreciably when the experiments are repeated in the cold beam, but in neither case is the congestion entirely eliminated. One concludes that vibration-rotation coupling contributes appreciably to the level density used by IVR in both energy regions. Further, since the temperature effect is greater for the lower energy region, it appears that the rotational contributions are here more important.

It is more difficult to assess the significance of the residual congestion in the cold beam spectra. If the rotational temperature is truly low, say a few degrees K, then the congestion implies that substantial IVR occurs in these regions with vibrational coupling alone. We know

TABLE II

A comparison of the fluorescence intensities appearing as congested background in room temperature and cold beam spectra. The percentages include only background appearing as a result of IVR. The S_1 *p*-difluorobenzene level densities include only gerade levels

ϵ_{vib} (cm^{-1})	ρ_{vib} (levels per cm^{-1})	Percent background		Ratio of backgrounds 300 K/cold
		300 K	cold	
2069	5	60	30	2
2502	100	90	60	1.5

that the vibrational temperature of our beam is about 80 K. The degree to which rotational cooling exceeds this is not presently known.

A comparison of hot and cold spectra from a higher vibrational region ($\epsilon_{\text{vib}} = 2888 \text{ cm}^{-1}$, $\rho \approx 300$ levels per cm^{-1}) is given in Figure 6. In this case the behavior is dramatically different than that of the lower levels. Little effect of cooling occurs. Thus we have reached a vibrational level density that is sufficiently high to sustain congestion due to IVR without appreciable contributions from vibrational-rotational coupling. We must emphasize that the spectra do not argue against such coupling. They merely show that $\Delta J = \Delta K = 0$ coupling among levels has become sufficient to remove structure from emission.

FIGURE 6 Comparison of the collision-free room temperature fluorescence spectrum (top) with the cold supersonic beam spectrum (bottom from the $3^1 5^2$ ($\epsilon_{\text{vib}} = 2888 \text{ cm}^{-1}$) S_1 level of *p*-difluorobenzene.

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