

Optical Selectivity and Absence of Intramolecular Vibrational Redistribution In Near-Resonance Laser Excitation

Shaul Mukamel*[†] and Kaiyu Shan

Department of Chemistry, University of Rochester, Rochester, New York 14627 (Received: February 28, 1985)

The problem of optical selectivity in laser excitation of polyatomic molecules and the elimination of intramolecular vibrational redistribution (IVR) processes is discussed. The recent prediction by Tannor, Blanco, and Heller, that off-resonance excitation may achieve such a selectivity in alkylbenzenes, is shown to have some serious difficulties, since it is based on the assumption that the doorway state in these systems is localized in the benzene ring and that a dynamical IVR takes place. This assumption is not supported by the existing experimental data. Moreover, our earlier analysis shows that elimination of IVR may be achieved only when the excitation is detuned away from any molecular state (not just the doorway state). When the quasicontinuum of background molecular levels is properly taken into account, the apparent selectivity predicted by TBH disappears.

In a recent article by Tannor, Blanco, and Heller (TBH), it was proposed that off-resonance excitation of large polyatomic molecules may result in the elimination of intramolecular vibrational redistribution (IVR) processes and allow the performance of laser selective chemistry.¹ As an example they suggested the 12_0^0 excitation of alkylbenzenes.^{2,3} Their analysis leads to the apparent conclusion that, by tuning the excitation frequency sufficiently off resonance (a few hundred cm^{-1}) from the doorway state, it may be possible to dissociate selectively a substituent on the benzene ring, since energy will not flow to the side chain under these conditions. In this Letter, we wish to make the following points:

(i) The series of experiments on alkylbenzenes was initiated following our suggestion and prediction² that, in the statistical limit, this will be an ideal system to observe the onset of IVR from the ring to the side chain. Unfortunately, these steady-state and time-resolved (nanosecond) fluorescence studies contain no evidence whatsoever for the existence of a selective excitation in the ring, followed by a dynamical IVR process. This is mainly due to the insufficient frequency and temporal resolution used in these experiments. There are two different interpretations which are fully consistent with all the existing experimental observables:^{2,4} one is purely static (state mixing), whereby the initial doorway state is delocalized between the ring and the side chain. In this case, no IVR occurs in these systems. The other interpretation is dynamical, i.e., the initial excitation is localized in the ring and undergoes a dynamical IVR process. The prediction of TBH¹ is based on the assumption that the second interpretation holds. This assumption is not supported by the available experimental information. Only experiments, which are both time and frequency resolved with a much better resolution can distinguish between the two cases. Since it appears that, despite our analysis, there is still some confusion on this point, we shall try to clarify it further.

(ii) Even when IVR does take place, we show that the condition for selectivity is that the detuning of the excitation frequency be far off-resonance not only from the doorway state but also from any other molecular state. The predictions of TBH are based on an unphysical molecular level scheme, which ignores the quasicontinuum. This point is clarified by using our earlier analysis^{2,4} which is based on the doorway state formalism⁵ When the correct molecular level scheme is taken into account, the selectivity predicted by TBH corresponding to large detunings (hundreds of cm^{-1}) disappears. There exists, however, a selectivity on a much finer detuning scale (GHz) whenever a gap exists in the molecular eigenstates. This selectivity is well-known theoretically²⁻⁵ and is supported by some recent experimental evidence.⁶

In order to make the analysis, let us introduce the standard level scheme (Figure 1) and review some of the basic results from the

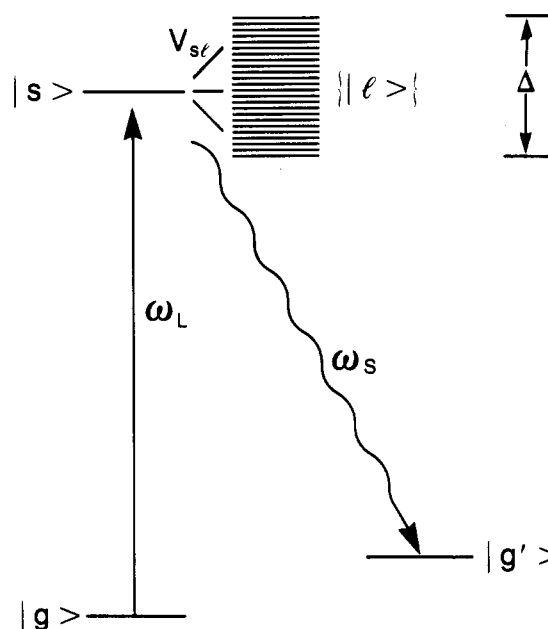


Figure 1. The level coupling scheme. $|s\rangle$ is the doorway state, coupled radiatively to $|g\rangle$ and via V_{sl} to the quasicontinuum $\{|l\rangle\}$, whose spectral width is Δ ($-\Delta/2 < E_l < \Delta/2$). $\{|l\rangle\}$ are vibronic states belonging to the ground electronic state. In a fluorescence experiment the molecule absorbs an ω_L photon and emits an ω_S photon.

theory of radiationless processes.^{2,4,5} Suppose, we have a single doorway state $|s\rangle$ coupled to a manifold $\{|l\rangle\}$ via intramolecular interactions V_{sl} . For the alkylbenzenes, we may take $|s\rangle$ to be a zero-order state, in which this energy is redistributed in the side

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(6) J. Kommandeur, B. J. Van Der Meer, and H. Th. Jonkman in "Intramolecular Dynamics", J. Jortner and B. Pullman, Ed., Reidel, New York, 1982, p 259. For a review see K. E. Drabe and J. Kommandeur in "Excited States", E. C. Lim, Ed., in press.

[†] Camille and Henry Dreyfus Teacher-Scholar.

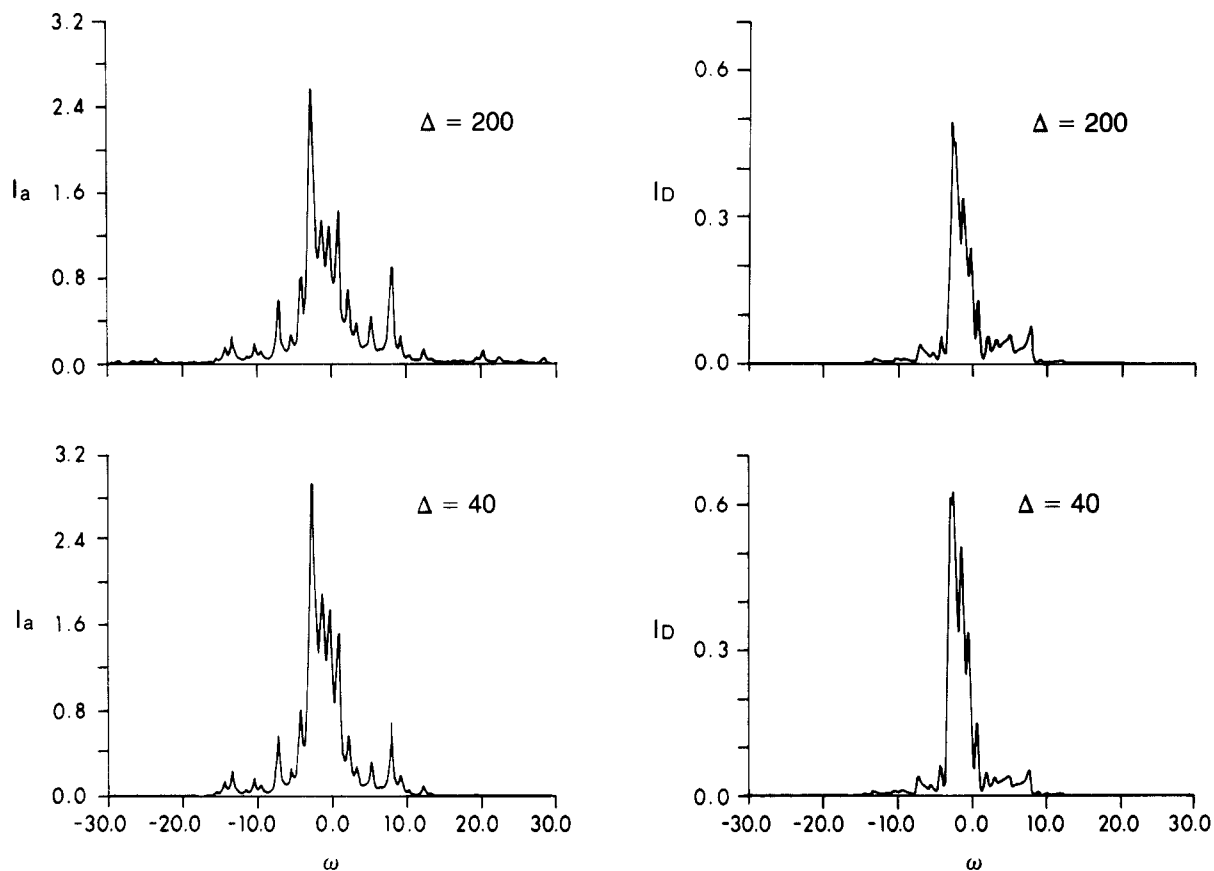


Figure 2. The absorption (I_a) and direct emission I_D rates (eq 4 and 5) as a function of detuning $\omega = \omega_L - \omega_{sg}$. Levels $|l\rangle$ are equally spaced with spacing 1, V_{sl} were random $-W \leq V_{sl} \leq W$ where $W = 3$. Shown are two calculations with $\Delta = 40$ and $\Delta = 200$. The line shapes for both systems are practically the same apart from the background in the wings.

chain. The molecular Hamiltonian is taken to be

$$H = |g\rangle E_g \langle g| + |s\rangle (E_s - i/2\gamma_s) \langle s| + \sum_l |l\rangle (E_l - i/2\gamma_l) \langle l| + \sum_l [V_{sl}|s\rangle \langle l| + V_{ls}|l\rangle \langle s|] \quad (1)$$

For the present discussion, it will be useful to consider the exact electronically excited molecular eigenstates $|j\rangle$, which diagonalize the molecular Hamiltonian H , i.e.

$$|j\rangle = \alpha_j |s\rangle + \sum_l \beta_{jl} |l\rangle \quad (2a)$$

with

$$H|j\rangle = (E_j - i/2\Gamma_j)|j\rangle \quad (2b)$$

Here, α_j and β_{jl} are the mixing coefficients of these states, and E_j and Γ_j are the energy and the width of the $|j\rangle$ state. Note, that if Γ_j is purely radiative, then for our model system it will be independent of j , since $|s\rangle$ and $\{|l\rangle\}$ have the same radiative width ($\gamma_s = \gamma_l = \Gamma_j$). We shall be interested in a steady-state fluorescence process, whereby the molecule absorbs a photon with frequency ω_L and emits a photon ω_s . Under certain conditions, it may be possible to distinguish between a *direct* emission, originating from the doorway state, and a *redistributed* emission, originating from the $\{|l\rangle\}$ states.^{2-4,7-10} (Normally, the direct emission is simple and sharp, whereas the redistributed emission is complex and broad.) Assuming that this is indeed the case, we shall introduce the yield Y of the direct component, i.e., the number of photons emitted in the direct component divided by

the total number of emitted photons. To that end, we introduce Green's function:^{2,4,5}

$$G_{ss}(\omega_L) \equiv \left\langle s \left| \frac{1}{E_g + \omega_L - H} \right| s \right\rangle \quad (3)$$

The absorption line shape (which is identical with the total emission) is given by

$$I_a(\omega_L) = \frac{-2}{\gamma} \text{Im } G_{ss}(\omega_L) \quad (4)$$

and the direct emission rate, resulting from the doorway state, is

$$I_D(\omega_L) = |G_{ss}(\omega_L)|^2 \quad (5)$$

In a frequency-resolved experiment the direct yield, therefore, will be

$$Y(\omega_L) \equiv I_D(\omega_L)/I_a(\omega_L) = \frac{-\gamma |G_{ss}(\omega_L)|^2}{2 \text{Im } G_{ss}(\omega_L)} \quad (6)$$

Here γ is the radiative width of the states $|s\rangle$ and $\{|l\rangle\}$. Equation 6 can be rewritten explicitly by using the molecular eigenstates (eq 2), i.e.

$$G_{ss}(\omega_L) = \sum_j \frac{|\alpha_j|^2}{E_g + \omega_L - E_j + i/2\Gamma_j} \quad (7)$$

Alternatively, Green's function G_{ss} may be written in the form:^{2,4,5}

$$G_{ss}(\omega_L) = \frac{1}{E_g + \omega_L - E_s - \Delta_s(\omega_L) + i/2[\Gamma_s(\omega_L) + \gamma]} \quad (8)$$

Here Δ_s and Γ_s are the real and imaginary parts, respectively, of the self-energy operator:

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$$\Delta_s(\omega_L) = \sum_j \frac{|V_{sj}|^2(\omega_{gj} + \omega_L)}{(\omega_{lg} - \omega_L)^2 + 1/4\gamma^2} \quad (9a)$$

and

$$\Gamma_s(\omega_L) = \sum_j \frac{|V_{sj}|^2\gamma}{(\omega_{lg} - \omega_L)^2 + 1/4\gamma^2} \quad (9b)$$

where $\omega_{\alpha\beta} \equiv E_\alpha - E_\beta$. Using eq 6 and 7 and taking $\Gamma_j = \gamma$, we then have

$$Y(\omega_L) = \left| \sum_j \frac{|\alpha_j|^2}{\omega_{gj} + \omega_L + i/2\Gamma_j} \right|^2 / \left| \sum_j \frac{\alpha_j}{\omega_{gj} + \omega_L + i/2\Gamma_j} \right|^2 \quad (10)$$

Alternately, upon the substitution of eq 8 in eq 6, we get

$$Y(\omega_L) = \frac{\gamma}{\gamma + \Gamma_s(\omega_L)} \quad (11)$$

Equations 10 and 11 allow us to analyze the molecular behavior as follows: suppose we tune the excitation frequency ω_L to be near resonant with an isolated spectral feature, well separated from all other lines. The yield $Y(\omega_L)$ (as well as the molecular dynamics, see eq 16) will depend crucially on the number N of $|j\rangle$ states contained in that feature. It is common to distinguish between case (A), whereby $N = 1$, the intermediate case (B), where N is small but finite, and the statistical limit (C), whereby N is very large and the $\{|j\rangle\}$ manifold forms practically a continuum. In case A, the yield is independent on ω_L , $Y(\omega_L) = |\alpha_j|^2$, reflecting the fact that the doorway state contains an $|\alpha_j|^2$ fraction of $|s\rangle$ character and $1 - |\alpha_j|^2$ redistributed character. This yield merely arises from a *static mixing* and carries no dynamical information. *Neither the appearance of the redistributed component nor its shape or yield contain any dynamical information in this case.* In case B, the yield varies with ω_L , reflecting the dynamical IVR processes. Time-resolved spectra (eq 16) show quantum beats in this case. Finally, in case C the IVR becomes irreversible, $\Gamma_s(\omega_L)$ is constant independent on ω_L , and so is the yield (eq 11). In this case, the yield is *dynamical* in nature and reflects the rate of IVR relative to the radiative width γ . The experiments on alkylbenzenes^{2,3} were performed with a low spectral and temporal resolution (0.5 cm⁻¹ and 10 ns, respectively). We have shown² that these molecules at ~ 2000 cm⁻¹ of vibrational energy clearly do not belong to case C since the time evolution is incompatible with the yield for this case. Those low-resolution experiments were not capable of determining, however, whether these molecules belong to case A or B. For case A, there is no dynamics involved in the experiment, and the observed yield $Y(\omega_L)$ (eq 10) simply reflects the nature of the doorway state (what fraction of the doorway state is localized within the ring). If there are few eigenstates under the observed absorption line (case B), then an intramolecular vibrational dynamics takes place. In principle, a highly resolved absorption (excitation) spectrum should reveal the number of $|j\rangle$ levels, thus yielding the same information contained in the time-resolved quantum beats. In real life, however, the absorption is often dominated by a residual inhomogeneous broadening (sequences, rotations), which obscures this information. In addition, if the widths Γ_j are comparable to the spacings ω_{jj}' , the spectrum becomes difficult to interpret. Therefore, time- and frequency-resolved experiments with a much better resolution are needed in order to distinguish between cases A and B.^{5,7-10} In conclusion, at present, the alkylbenzene experiments do not provide any evidence for dynamic IVR processes, and it is not clear whether the initial excitation is already delocalized. The analysis of TBH is based on the assumption, which is not supported by experimental evidence, that these systems belong to case B.

Let us turn now to our second point, namely, the behavior of the yield $Y(\omega_L)$ with detuning for case B. (In cases A and C, the quantum yield does not depend on detuning.) As pointed out earlier, this may or may not be relevant to alkylbenzenes. It should be noted, however, that case B was unambiguously established in the remarkable picosecond experiments of Zewail et al. on anthracene.^{9,10}

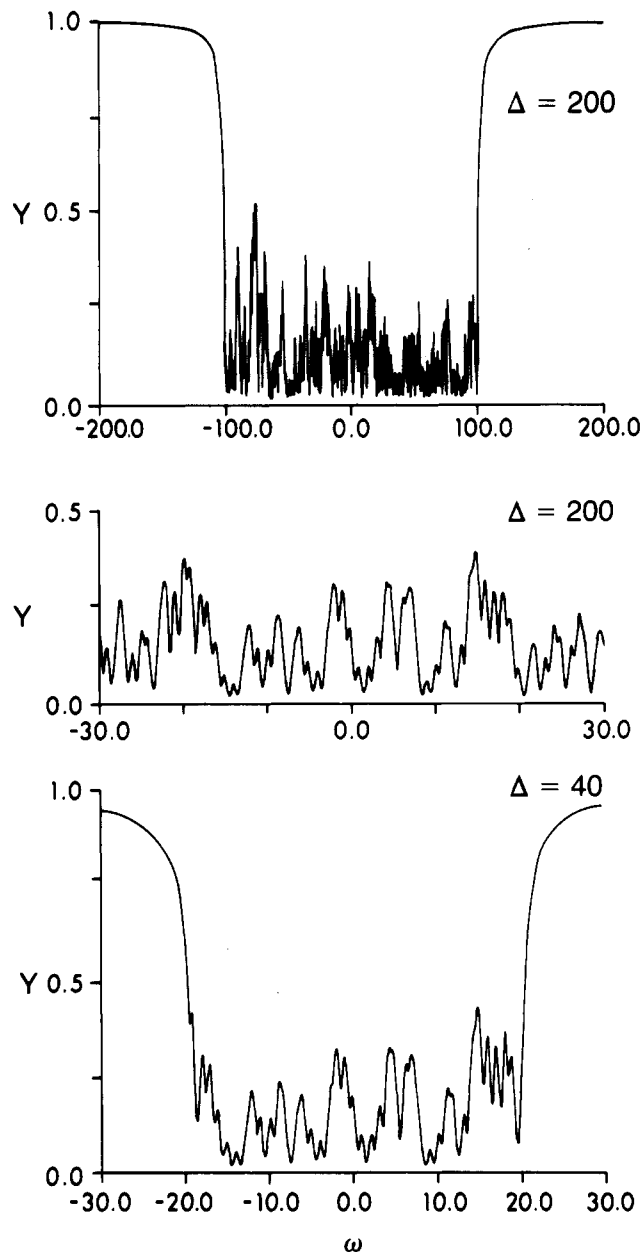


Figure 3. The yield $Y(\omega_L)$ (eq 6) for the two systems of Figure 2. Note that the yield rises sharply to unity as the excitation is detuned off the quasicontinuum $\omega = \omega_L - \omega_{sg} = \pm\Delta/2$ and is very different for the $\Delta = 40$ and $\Delta = 200$ cases. The $\Delta = 200$ calculation is displayed twice, for a small ($|\omega| < \Delta/2$, middle panel) and a large ($|\omega| > \Delta/2$, top panel) detuning range.

The analysis of the dependence of $Y(\omega_L)$ on detuning is most transparent using eq 11 together with eq 9b. It is clear from these equations that whenever $\Gamma_s(\omega_L)$ vanishes, then $Y = 1$. Under these conditions, we get only direct emission, implying that no IVR takes place, and the excitation is selective. Equation 9b shows that this condition will be met for large detunings.

$$|\omega_{lg} - \omega_L| \gg \gamma, V_{sj} \quad (12)$$

whereby Γ_s vanishes as

$$\Gamma_s(\omega_L) \sim (\omega_L - \omega_{lg})^{-2} \quad (13)$$

Note, however, that by large detunings we do not mean just from the doorway state, but rather from all the background levels $|l\rangle$ as well. To illustrate this point, we have considered a model system consisting of equally spaced $|l\rangle$ levels lying between $E_l = -\Delta/2$ to $E_l = \Delta/2$. The coupling matrix elements V_{sl} were taken to be random variables with values bounded between $\pm W$, i.e.

$$E_s = 0$$

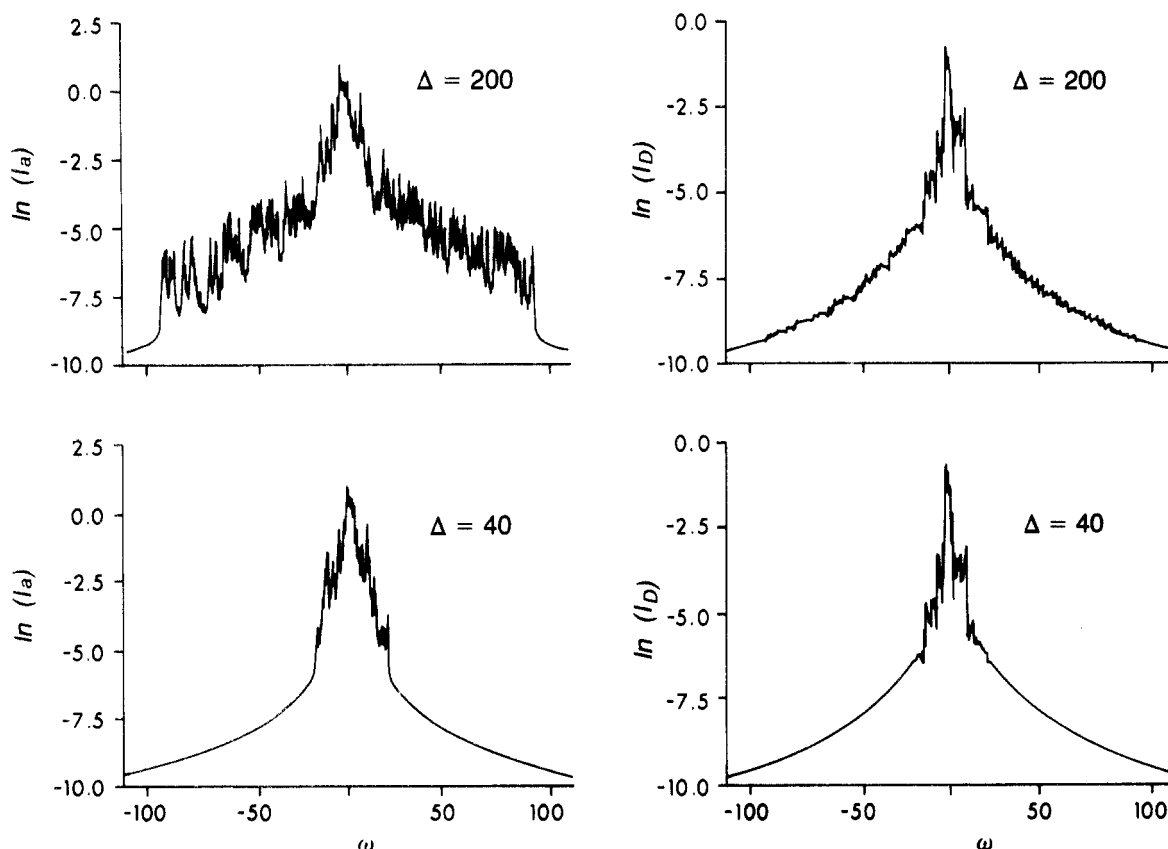


Figure 4. The same line shapes of Figure 2 plotted on a logarithmic scale. I_D for $\Delta = 40$ and $\Delta = 200$ is practically the same. I_a , on the other hand, drops sharply as ω_L is tuned off the quasicontinuum, resulting in a yield of unity $Y(\omega_L) = 1$.

$$-\Delta/2 \leq E_i \leq \Delta/2 \quad (14)$$

$$-W \leq V_{sl} \leq W$$

The spacing between adjacent $|l\rangle$ levels was taken to be 1; we chose $W = 3$ and considered two systems with 40 and 200 $|l\rangle$ levels ($\Delta = 40$ and $\Delta = 200$, respectively). In Figure 2, we show the absorption (I_a) and the direct emission (I_D) for these two systems as a function of detuning $\omega = \omega_L - \omega_{sg}$. Apart from a small noise in the tails, the line shapes for both systems are practically identical. The behavior of the yield $Y(\omega_L)$ for these systems is shown in Figure 3. It is clear that the yield rises sharply to unity as the excitation is detuned away from the quasicontinuum, i.e., $|\omega| = \Delta/2$. Despite the fact that the line shapes I_a and I_D (Figure 2) look similar, the detuning behavior of the yield is very different in both cases. The lower panel shows how the yield for $\Delta = 40$ becomes 1 as $|\omega| > \Delta/2 = 20$. The middle panel displays $Y(\omega_L)$ for the $\Delta = 200$ case on the same frequency scale showing that no selectivity occurs and IVR is not eliminated since $|\omega| < \Delta$. The top panel shows the yield for $\Delta = 200$ on a larger frequency scale and here Y becomes unity as $|\omega| > \Delta/2 = 100$. Figure 3 demonstrates what is clear from eq 9b and 11, namely, that only when the excitation is detuned away from the quasicontinuum will a selective excitation occur. What happens in practice is that, for off-resonance detuning with respect to the doorway state, the fluorescence is dominated by quasicontinuum levels $|l\rangle$, which are near resonance with the radiation field $\omega_{lg} \sim \omega_L$. These levels have a negligible contribution to the absorption line shape but will make the fluorescence to appear "resonance like". A further insight into this effect is provided by Figure 4, which shows I_a and I_D of Figure 2 on a logarithmic scale. I_D for both cases ($\Delta = 40$ and 200) is practically the same in the wings. I_a , however, drops sharply as ω_L is tuned away from the quasicontinuum, and this is why $Y(\omega_L) \rightarrow 1$. For realistic polyatomic molecules, like alkylbenzenes, there is a broad quasicontinuum (Δ is infinite), and we are never "off resonance" with respect to the quasicontinuum. Therefore, the yield will not rise as we go far off resonance. TBH¹ have used an unrealistic level scheme, which took

into account only three, almost degenerate modes. In that level scheme, Δ is restricted, and the true quasicontinuum is absent. This is the reason for their apparent selectivity. As is shown by Figure 3, when the quasicontinuum is properly incorporated, that apparent selectivity will disappear. It should be noted, however, that by using high-resolution (MHz-GHz) excitation, it may be possible to take advantage of *local fluctuations* in the density of states and achieve a selective excitation. On this fine resolution, it is possible to locate groups of bunched molecular eigenstates, separated by a "spectroscopic desert" with no eigenstates. Such an example was analyzed by Kommandeur et al. in the P branch of the 0-0 transition in pyrazine. The P(1) and P(2) transitions contain several lines spread over ~ 3 GHz, and they are separated by an "empty" range of 15 GHz. By tuning the excitation frequency between the P(1) and P(2) transitions, we expect to see enhancement in the direct yield. Kommandeur et al.⁶ have conducted detailed spectroscopic studies of the detuning behavior in pyrazine. Their measurements were time resolved but carry essentially the same information as $Y(\omega_L)$. In order to see that, we shall now analyze their experiment in detail. Suppose we use an excitation pulse whose electric field is given by

$$E_L(t) = \phi(t) \exp(-i\omega_L t) + \text{cc} \quad (15)$$

Let us denote the time-dependent emission rate by $I(t)$ and the "direct" emission rate by $I_D(t)$, i.e.^{4,5}

$$I_D(t) = \gamma |c_s(t)|^2; \quad I(t) = \gamma [|c_s(t)|^2 + \sum_l |c_l(t)|^2] \quad (16)$$

where $c_s(t)$ and $c_l(t)$ is the amplitude of the system to be in the state $|s\rangle$ and $|l\rangle$ at time t . Using standard perturbation theory, we get^{4,5}

$$I_D(t) = I_D^+(t) + I_D^-(t) \quad (17)$$

where

$$I_D^+(t) = \gamma \sum_{j \neq j'} |\alpha_j|^2 |\alpha_{j'}|^2 \int_{-\infty}^t d\tau_1 \int_{-\infty}^t d\tau_2 \phi(t - \tau_1) \times \\ \phi^*(t - \tau_2) \exp[-iE_j\tau_1 + \\ iE_{j'}\tau_2 - 1/2\Gamma_j\tau_1 - 1/2\Gamma_{j'}\tau_2] \exp[i(E_g + \omega_L)(\tau_1 - \tau_2)] \quad (18)$$

and

$$I_D^-(t) = \gamma \sum_j |\alpha_j|^4 \int_{-\infty}^t d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 \phi(t - \tau_1) \phi^*(t - \tau_2) \times \exp[-iE_j(\tau_1 - \tau_2) - 1/2\Gamma_j(\tau_1 + \tau_2)] \exp[i(E_g + \omega_L)(\tau_1 - \tau_2)] \quad (19)$$

When the number of $|l\rangle$ states is large and, provided the excitation pulse $\phi(t)$ is short enough, I_D^+ will decay much faster than I_D^- , since it contains the dephasing due to the energy spread of $|j\rangle$ states. The time-resolved emission will then consist of a "short" component $I_D^+(t)$, followed by a "long" component consisting of I_D^- and the redistributed emission due to the various $|l\rangle$ states.^{5,11,12} The appearance of short and long components is typical to intermediate-size molecules. Kommandeur et al.⁶ have measured the integrated ratio of the short component relative to the total emission, i.e.,

$$Y^+ \equiv \int_{-\infty}^{\infty} dt I_D^+(t) / \int_{-\infty}^{\infty} dt I(t) \quad (20)$$

Using eq 17-20, we can write^{4,5}

$$Y^+ = -\gamma \int d\omega |G_{ss}^+(\omega_L + \omega)|^2 J(\omega) / \int d\omega \text{Im} G_{ss}(\omega_L + \omega) J(\omega) \quad (21)$$

where

$$|G_{ss}^+(\omega)|^2 \equiv \sum_{j \neq j'} \frac{|\alpha_j|^2 |\alpha_{j'}|^2}{(E_g + \omega - E_j + i/2\Gamma_j)(E_g - \omega - E_{j'} - i/2\Gamma_{j'})} \quad (21a)$$

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Here $J(\omega)$ is the power spectrum of the excitation pulse, i.e.

$$J(\omega) = \int d\tau \langle \phi(\tau) \phi(0) \rangle \exp[-i(\omega - \omega_L)\tau] \quad (22)$$

If we use the same pulsed excitation (eq 15) but resolve the direct and redistributed components in frequency (rather than in time), then eq 6 becomes^{4,5}

$$Y = -\gamma \int d\omega |G_{ss}(\omega_L + \omega)|^2 J(\omega) / \int d\omega \text{Im} G_{ss}(\omega_L + \omega) J(\omega) \quad (23)$$

$$|G_{ss}(\omega)|^2 = \sum_{j \neq j'} \frac{|\alpha_j|^2 |\alpha_{j'}|^2}{(E_g + \omega - E_j + i/2\Gamma_j)(E_g + \omega - E_{j'} - i/2\Gamma_{j'})} \quad (23a)$$

For large numbers of $|j\rangle$ states, eq 21 and 23 are practically the same since the restriction $j \neq j'$ becomes statistically insignificant. Far off resonance, they both give

$$Y = Y^+ = \sum_j |\alpha_j|^2 \quad (24)$$

The relative area of the short component Y^+ (eq 21) carries, therefore, essentially the same information as the yield Y (eq 23). Far off resonance, they both achieve a maximum. Kommandeur et al.⁶ have found an oscillatory behavior of Y^+ as ω_L was tuned across the P branch of pyrazine with maxima occurring for detuning inbetween two absorption lines. We predict that these maxima should be observed in a frequency-resolved experiment as well (eq 6 or eq 23).

Acknowledgment. The support of the National Science Foundation, the Army Research Office, the Officer of Naval Research, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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