Intramolecular vibrational relaxation in 1,4 dioxane

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Intramolecular vibrational energy transfer in isolated gas phase molecules of dioxane has been studied by spectrally resolving the IR laser induced fluorescence from C–H stretch fundamentals, combination bands, and overtones in the region from 2800 to 3000 cm^{-1}. By comparing the experimentally observed relative energy content of the IR active modes with that calculated from a statistical model it is concluded that substantial randomization of the energy initially deposited in the zeroth order optically excited state occurs. This statistical distribution differs from a thermal distribution due to fluctuations in the local state density. The energy content distribution is best described by the model if coupling over a range of 4 cm^{-1} is assumed. Dilution factors for the various C–H stretch modes were observed which vary from 0.018 to 0.13. These values are dependent on the rotational state excited. Collisional time dependent spectra of several relaxed modes are presented. The experiments are performed by exciting molecules cooled in a nozzle expansion with light from an infrared optical parametric oscillator. The fluorescence spectra are recorded with a cryogenic Michelson interferometer.

INTRODUCTION

A primary goal of our study of intramolecular vibrational relaxation is the identification of any relation between the structure of a molecule and the characteristics of energy transfer between its vibrational states. Our first results[1] demonstrated that the dilution of resonance fluorescence from a variety of organic molecules excited with one quantum of CH stretch energy increased with the density of vibronic states in the vicinity of the excitation. This is equivalent to saying that the number of bath modes "effectively coupled" to the CH stretch increases with the state density. While this first order rule holds in general, there are other factors which contribute to the relaxation. Thus, for a given state density there exists a range of dilution factors dependent on the molecule studied or the mode studied within a given molecule. In turn, the "threshold density" for relaxation was observed to span values from 5 to 50 states/cm^{-1}. Later, unpublished results from norbornadiene ($\rho \sim 70$ cm) and acetaldehyde ($\rho \sim 3$ cm) further expand this range. These findings demonstrate, in part, the contributions from a variety of anharmonic and rotational matrix elements. In order to obtain any further predictive rules it is necessary to correlate the magnitude of these elements with structural aspects of the molecules. Our data from that first study was not detailed enough to reveal any systematic variations.

The more recent work[2,3] we have done employs frequency resolved fluorescence to monitor the distribution of the excess CH stretch energy among the bath states. As in all the experiments, the molecules are isolated in a pulsed molecular beam and excited with a tunable infrared laser. The fluorescence is resolved with a cryogenic Michelson interferometer. Though we do not observe fluorescence at the frequency of the "dark" combinations and overtones, we see emission at the energies of the fundamentals of which they are composed. To derive meaning from this data, we compare the fluctuations in the energy contents of these modes as a function of excitation energy to the fluctuations predicted

by a statistical model in which all the bath states within a given energy range are equally coupled to the CH stretch fundamental.

To explain the behavior of the first two molecules we studied (methyl formate and dimethyl ether) it was necessary to assume a very large width (about 20 cm^{-1}) in the statistical model. This is equivalent to stating that the energy from the CH stretch is communicated to states which, at zeroth order, lie up to 10 cm^{-1} above and below the CH stretch. Given a typical dilution factor of 0.1 for these molecules, this would indicate that the CH state interacts with ten bath states over a 20 cm^{-1} area. If this were true we would expect the optical activity to be spread over a similar range, leading to the appearance of several small Fermi resonance like perturbations to the band contours. Because this is not observed, we assume either that the CH stretch is coupled strongly over a narrow width, but that the bath states are extensively premixed among themselves over a much broader energy range or that differing vibrations are mixed by high order Coriolis coupling or both.

In this paper we present the results of a study which shows that while a large statistical width was applicable for dimethyl ether and methyl formate, 1,4 dioxane requires a premixing range of only 2–4 cm^{-1}. In terms of its skeletal structure, dioxane is also very different from the other two cases. Dimethyl ether and methyl formate are each strongly asymmetric prolate rotors. Each has an internal rotor (two in dimethyl ether). Thus both have rather "floppy" skeletons. 1,4 dioxane is a six membered ring which exists only in the chair conformation at room temperature with a barrier to inversion of ~ 12 kcal/mol. It does not have any of the low frequency, highly anharmonic rotor or torsional modes which the other two molecules have. Its rotational constants also differ, placing it in the near oblate symmetric top limit. It does, however, have about the same density of states (19–23 cm) and dilution factors near 3000 cm^{-1}. This makes it a good candidate for comparison.

The statistical model and the pertinent theory are summarized in the preceding paper. For a more thorough discussion, the reader is directed to Refs. 1 and 2.

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EXPERIMENTAL

Our experimental apparatus is briefly described in the preceding paper. For a more extensive discussion of the dilution factor measurements see Ref. 1. For a detailed description of the cryogenic interferometer system see Ref. 2.

Effects due to multiphoton absorption were observed in our initial dioxane data. These were eliminated by reducing the laser power until a linear variation of fluorescence intensity with laser power was observed.

The time decay data was collected on a Biomation 8100 transient recorder and averaged on our computer. The emission was resolved with our circular variable filter apparatus. The data were treated by performing a running average of seven adjacent points for all points after the initial 2 μs fast rise. The time dependences as observed represent a product of the collisional behavior and decay due to the molecules drifting out of the field of view of the detector. The drift was compensated for by multiplying by a rising exponential with an appropriate time constant. Since the loss of molecules is not necessarily an exponential, the presented curves are not really flat at long times. This is definitely an experimental artifact.

RESULTS

Figure 1 contains a normalized spectrum of the total fluorescence intensity as a function of laser frequency for the CH stretching region. A scan (not shown) was also made of resonance (CH stretch) emission only. Four peaks are present at frequencies 2860, 2898, 2919, and 2970 cm^{-1}. Of the four infrared active CH stretch modes expected for dioxane, two have a_u symmetry and two have b_u symmetry. Those with a_u symmetry will have B type contours while the b_u bands will have A/C hybrid contours.[5] The band at 2970 cm^{-1} has either a B contour or is an overlap of two peaks of unknown shape. The remaining three bands have pronounced Q branches giving them either C or A/C hybrid contours. This is one more than expected and thus leads us to believe that a Fermi resonance is present. A convenient way to identify the modes participating in a Fermi resonance involves monitoring the collisional time dependence of the flu-
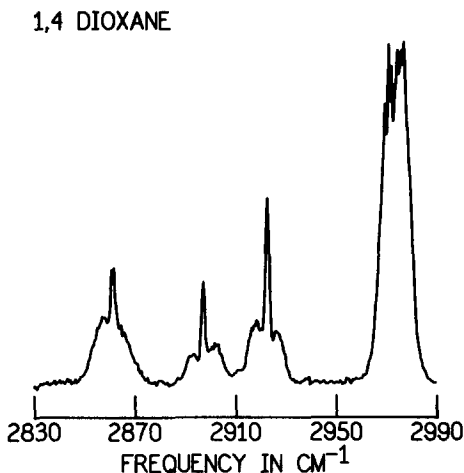
1,4 DIOXANE

FIG. 1. Total laser induced fluorescence spectrum of the C–H stretching region of dioxane.

orescence from the lower energy modes which add to form the combinations and overtones that are the bath states. If a particular mode emits light with the same time dependence as the resonance fluorescence we assume that it is involved in a combination or overtone which has been initially populated by the laser through a strong Fermi resonance interaction with a CH stretch. It is true that relaxed fluorescence originates from the same kind of interaction, but since the coupling is so much stronger in the Fermi resonance case it is convenient for us to label it resonance fluorescence.

The results of our time resolved study are presented in Fig. 2. The only emission with a time decay closely resembling that of the resonance fluorescence comes from the band at 1453 cm^{-1} in molecules excited at 2919 cm^{-1}. A previous assignement[5] has labeled the 2919 band as a combination of an a_u CH$_2$ scissoring mode at 1449 cm^{-1} and a b_g Raman active CH$_2$ scissoring mode at 1459 cm^{-1} (liquid). This is the only viable assignment involving the 1449 cm^{-1} mode which gives the correct symmetry to have the observed band contour. Our frequency resolved spectra, displayed in Fig. 3, show that the 1453 cm^{-1} band is shifted about 3–5 cm^{-1} to the blue from the corresponding peak in this region at the other excitations. This gives further evidence of the correctness of the assignment. Using the observed intensities we find that the 2919 mode is composed of 72% combination and 28% CH stretch character. These figures are valid if there is no overlap between the two members of the Fermi resonance pair.

The 2898 cm^{-1} band has also been assigned as a combination of methylene scissoring bands.[5] The frequency resolved spectra do not, however, show unusually high intensities for them. Therefore, it seems unlikely that the assignment is true. Because of the weakness of the bands, it was not possible to get a good time decay. The remaining bands at 2860 and 2970 cm^{-1} have been assigned as two coincidentally overlapping pairs of the CH stretch fundamentals.

From the intensities of the bands in the resonance scan we are able to calculate the dilution factors. These are displayed in Table I. Also shown in Table I are the dilution factors calculated from the frequency resolved fluorescence spectra using Eq. (4) in Ref. 2 and the Whitten–Rabinovitch density of states function. With the exception of the value for 2919 cm^{-1}, the results of these two methods agree quite well. This indicates that no subset of states is favorably coupled and that our statistical model is appropriate.

The frequency resolved fluorescence spectra were obtained by tuning the laser to the center of each of the CH stretch containing bands. The rotational state dependence of the relaxed fluorescence was investigated by probing further into the P or R branches. This had no effect on the relative intensities of the relaxed peaks, and thus we do not include these results. The dilution factors, however, did decline (numerically) by as much as a factor of 1.6 at higher J states.

The motions corresponding to the observable relaxed states all involve scissoring, wagging, or twisting of the methylene groups, with the exception of the ring stretches at 882 and 1133 cm^{-1}.[5] It is evident that the distribution of their intensities is not the same as one would expect in a
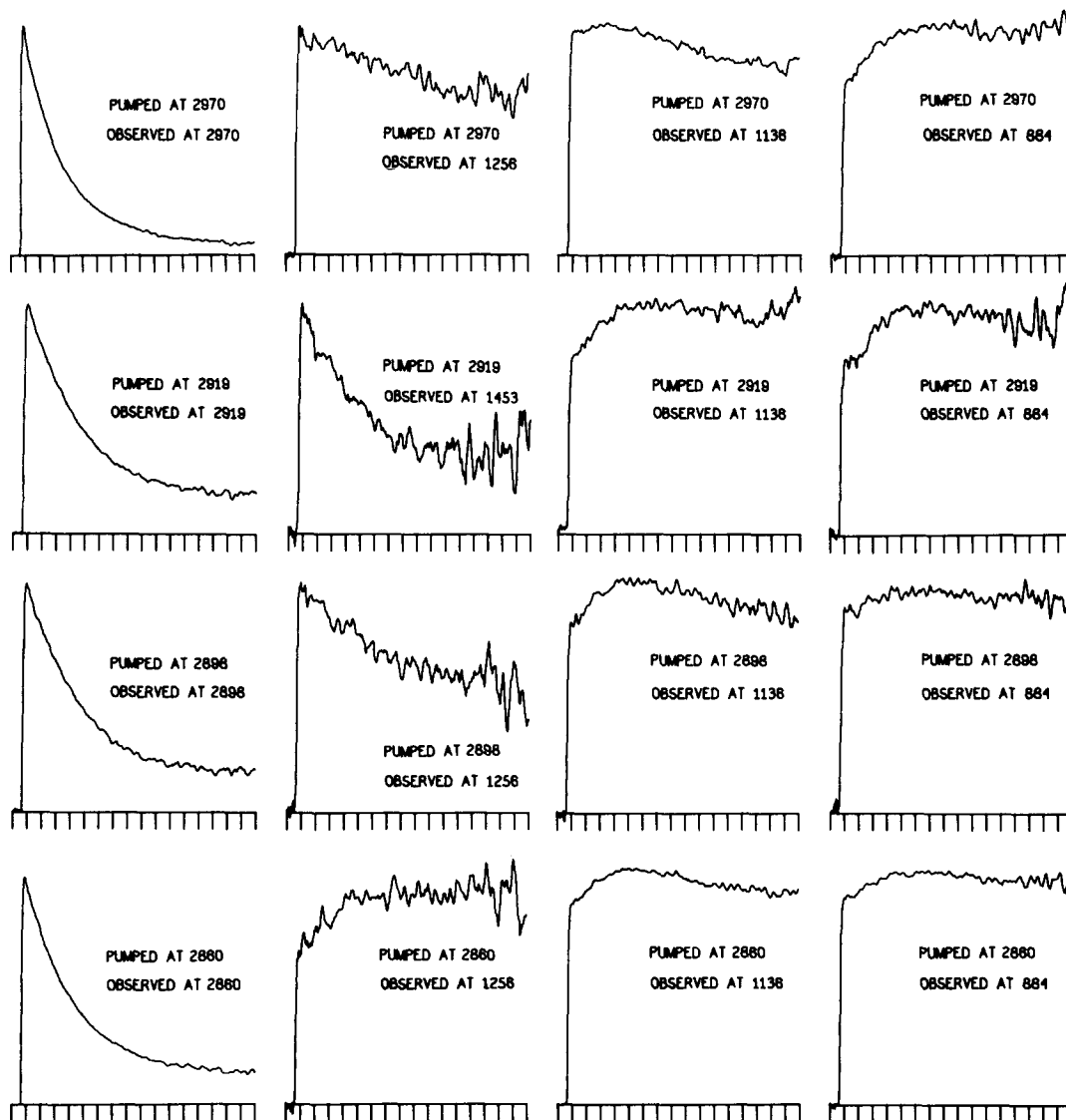
FIG. 2. Time resolved fluorescence from dioxane. The center of filter bandpass (~2% of central wavelength) and excitation energies are indicated on each spectrum. Each tic on the time axis represents 5.0 μs.

thermal distribution. Some of the peaks exhibit quite large fluctuations in intensity as the laser energy is varied. Besides the previously discussed case of the 1453 cm^{-1} band, the CH$_2$ twist at 1256 cm^{-1} is the best example. When excited at 2970 and 2898 cm^{-1} the relative intensity increases and the position shifts to the blue by ~3–5 cm^{-1}. The time resolved spectra do not show a sufficient similarity between the behavior of this mode and the C–H stretch in either case to cause us to consider Fermi resonance. Rather, we attribute the emission to relaxed fluorescence whose intensity is dependent upon the local density of states containing the given mode in the bath. Shifts can be explained by a nonsymmetrical distribution of these states within the coupling width. The linewidths (FWHM) for the resonance fluorescence are in all cases very near to the instrumental resolution of 8 cm^{-1}. The relaxed bands, where there is no overlap of adjacent peaks, have widths of 12–15 cm^{-1}.

The relative fluorescence intensity of all lines was quantitatively obtained by integrating their areas. These intensities and the regions of the integration are displayed in Table II. Several of the bands overlapped others, making it necessary to visually apportion the area among them. For example, the CH$_2$ rock at 1085 cm^{-1} was integrated from the dip at 1065 cm^{-1} to the dip at 1100 cm^{-1}. These divisions were used consistently for all four excitations unless a peak was shifted to an extent which required a new separation. In some cases overlap was so extreme that any division was impossible. This was true for the band labeled 884, which is the superposition of the ring stretch ν_{18} and the CH$_2$ rock ν_{34}. Another band whose shape suggested two overlying peaks is the ring stretch at 1136 cm^{-1}. For the purposes of our analysis these overlapped contours were treated as single bands.

Relative A coefficients for all observed bands are listed in Table III. They were obtained from a gas phase absorption spectrum. Due to crowding in the CH stretching region, it was necessary to use a liquid phase (in CCl$_4$) spectrum to help apportion the areas.

Figure 4 contains plots of the relative energy contents of the relaxed modes. The graph labeled experimental was obtained directly from the observed intensities and the A coefficients. The remaining plots were made using the energy contents predicted by our statistical model. The various symbols represent the energy contents calculated using the direct
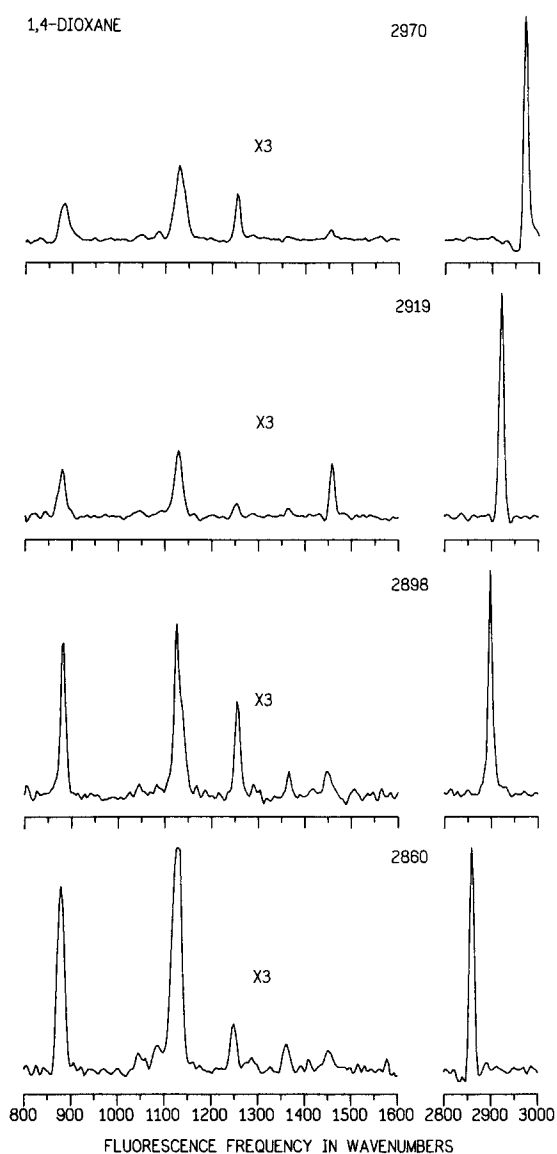
FIG. 3. Fluorescence spectra from the C–H stretching region of dioxane. Spectra are labeled by the laser pump frequency (in cm^{-1}). Intensity of fluorescence is in arbitrary units with the most intense peak of each spectrum normalized to the same height.

state count. Each plot represents the distribution of energy contents expected with a particular coupling width. These are indicated by the DSC numbers at the top of the graphs. As the width is increased, the fluctuations in energy content as a function of excitation frequency diminish. These fluctuations arise from local irregularities in the density of states

containing a given mode as a function of energy. The smoothed Witten–Rabinovitch function does not represent the lumpiness of the actual state density function in a molecule of this size. Thus, the energy contents predicted by it (plotted as lines in the graphs) are constant for a given mode with respect to excitation energy.

In comparing the results of the model to the observed results, the important parameter is this fluctuation in energy content. Because we have not included anharmonicities in our calculation, we cannot expect to produce predictions which agree in magnitude to the experimental results. However, the breadth of the fluctuations at a given energy should not be affected greatly by the inclusion of anharmonicities. Thus we may obtain a rough idea of the width over which the states participate in the coupling. From Fig. 4 it is seen that a DSC size of 2–4 cm^{-1} describes our data adequately.

The error bars in Fig. 4 were obtained by assuming an error equal to 2 SD of the baseline in the intensity of the relaxed peaks. In all instances but one the energy contents for a given excitation frequency were normalized such that their sum is 8. The exception is the 2919 excitation, where the fluorescence at 1453 is predominantly resonance. Here, the remaining contents were normalized to a sum of 7.

At this point it is interesting to return to the time resolved spectra. First of all, we may note that since our detection system employs a gate width of $\sim 5\,\mu$s our data is affected negligibly by collisions. Secondly, we note that we may predict whether a state will be populated or depopulated through collisions by consulting the experimental graph of Fig. 4. Those modes which have energy contents lower than the WR values show rising exponentials while those which are energy rich with respect to WR are depopulated. The effect of collisions on this time scale is to provide near resonant vibrational energy transfer between the molecules. This allows randomization within a bath of states just as the intramolecular anharmonic coupling does. However, here the energy range of the coupling is much wider, and a much larger DSC size is needed to reproduce the final energy contents. This data emphasizes the fact that the intramolecular coupling in dioxane is limited. There is not a heavily premixed bath to extend the range of the energy transfer.

DISCUSSION

It is evident from the dilution factors that the energy deposited in a given zeroth order mode is randomized to a great extent. With a typical dilution factor of ~ 0.05 and the average rovibronic density of states (about 100 cm) we esti-

TABLE I. Dilution factor of unrelaxed fluorescence.

Frequency	From absolute[a] resonance intensity	From relaxed[b] unrelaxed ratio
2860	0.023	0.018
2898	0.11	0.10
2919	0.067	0.13
2970	0.062	0.047

[a] Accurate to a factor of 3.
[b] Accurate to $\pm$ 50%, calculated from the WR results.

TABLE II. Observed integrated fluorescence intensities from C–H stretches in dioxane.

Laser frequency	Fluorescence intensity[a]								
	850–925	1015–1065	1065–1100	1100–1160	1230–1265	1265–1340	1340–1390	1430–1490	Resonance
2860	1.59	0.14	0.30	2.75	0.35	0.15	0.21	0.22	3.29
2898	1.26	0.062	0.13	1.87	0.73[b]	0.088[c]	0.12	0.28	4.46
2919	0.70	0.086	0.11	1.12	0.13	0.049	0.12	0.54[d]	6.15
2970	0.63	0.051	0.11	1.56	0.46	0.13	0.039	0.14	5.88

[a] Normalized to a sum of 9 for each excitation frequency.
[b] Actually integrated from 1230–1280.
[c] Actually integrated from 1280–1340.
[d] Actually integrated from 1430–1480.

mate that the coupling width is about $0.2 \ cm^{-1}$. Because we do not have the capability to excite single rovibronic states yet, this is a very rough estimate.

These values are very similar to those we saw for methyl formate[2] and dimethyl ether.[3] In terms of state densities all three molecules are about the same "size." While dioxane is physically a larger molecule than either of the other two, it does not have the low frequency torsion or rotor modes which build up the density of states. Symmetry of the vibronic states must be considered in comparing the state densities of the three molecules. This requires that the vibronic density of dioxane and dimethyl ether be divided by a factor of 4, while that of methyl formate must be divided by 2. This places the effective vibronic state densities of all three molecules in the small range of $4-8 \ cm^{-1}$. The similarity of these densities, along with the similarity of the dilution factors indicates that the average anharmonic interactions which couple the zeroth order CH stretch to the bath are approximately equal in these cases. This gives a convenient starting point for comparing the distribution of the energy in these structurally different molecules.

The way the energy is distributed within the bath is clearly much different for dioxane. From the plot of the experimental energy contents, we see that there are substantial fluctuations present. This requires that we invoke a bath "premixing" of only $2-4 \ cm^{-1}$—a factor of 5–10 lower than in methyl formate or dimethyl ether. The time resolved data demonstrated nicely that these energy contents approach the smooth Witten–Rabinovitch values when coupling over a

much greater width is allowed by collisions. While dimethyl ether and methyl formate are not randomized to the extent that they are describable by the WR distribution, they are certainly much closer to it than dioxane. Some mechanism must exist which causes these differences.

Other indications of a smaller range of intrabath coupling in dioxane have been noted. We observed shifts in a relaxed peak (the CH_2 twist at 1256) for the first time. While they are to be expected, they are normally averaged out when many combinations and overtones of random anharmonicity are fluorescing. Also, the relaxed peaks are narrower $(12-15 \ cm^{-1})$ than in methyl formate $(> 20 \ cm^{-1})$ and dimethyl ether $(> 22 \ cm^{-1})$.

Given the comparable values of the dilution factors, it seems likely that the CH stretch is coupled within $\Delta\omega_s$ by the same types of motions in all three molecules. The strong anharmonic interactions known to occur between CH stretches and overtones of CH deformation modes make them likely candidates for the bath mode most directly coupled to the CH stretches. Especially strong interactions are expected in methoxy groups of esters. Since all the CH groups we excited were adjacent to an oxygen atom, this type of enhancement may be present in ethers also.

The major effect which accounts for the wider coupling width in methyl formate and dimethyl ether, at least at high J's, is the mixing of rotational states by Coriolis coupling. Since rotation-vibration interactions can couple not only states of the same J, K quantum numbers but also states of different K quantum numbers, this allows vibrational states which are several wave numbers apart to be mixed by Coriolis coupling. Being a near oblate symmetric top causes dioxane's K states to be very close together, unlike the other two highly assymmetric molecules. This results in a narrower width in dioxane.

Since differences in mixing widths appear to persist at low J, substantial differences in the relaxation must also be due to the differences in the mixing of states within $\Delta\omega_l$ by vibrational anharmonicity. We speculate that this is dependent on the skeletal rigidity of the molecule. The internal rotors and torsions present in the floppy molecules are also extremely anharmonic both in the sense of being rotors rather than oscillators, but also in the sense that the rotors or torsions are strongly coupled to the other skeletal modes. Thus it is expected that they will be more effective in distributing the energy to the rest of the molecule. In a more rigid structure these modes do not exist and the energy flow is more restricted.

TABLE III. Relative Einstein A coefficients of dioxane.

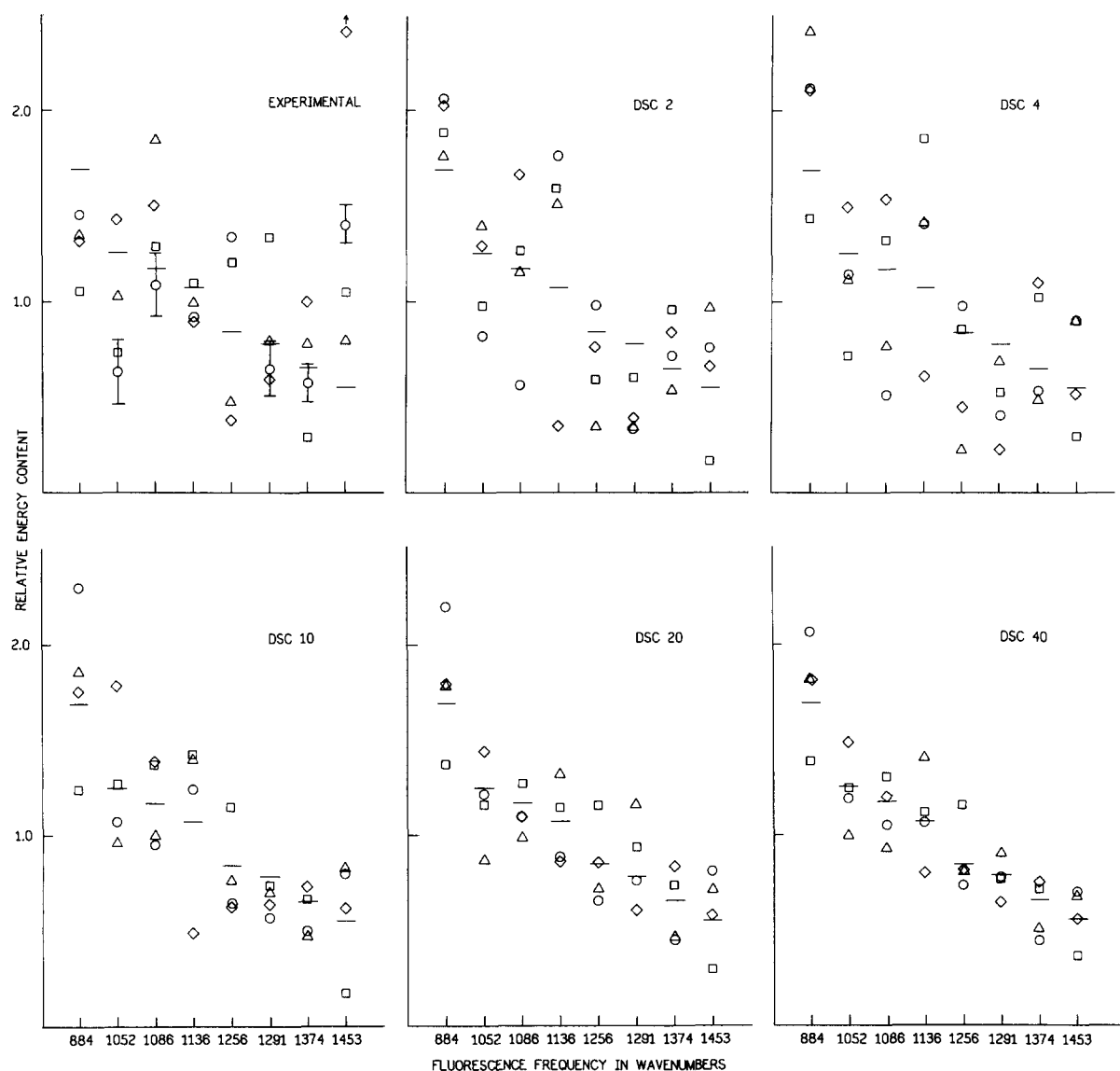| Vibrational frequency[a]	A coefficient[b]
884	7.32
1052	1.00
1086	1.25
1132	22.22
1256	6.60
1291	1.69
1374	2.64
1453	2.77
2860	84.97
2898	27.19
2919	43.46
2970	109.15

[a] Frequency in cm^{-1}.
[b] Arbitrary units.

FIG. 4. Relative energy content of vibrational modes following optical excitation. The relative energy contents are obtained from the model calculations and experimentally. Each plot symbol represents a different vibrational band $(2919\ \text{cm}^{-1} = \Diamond, 2970\ \text{cm}^{-1} = \square, 2860\ \text{cm}^{-1} = \triangle$, and $2898\ \text{cm}^{-1} = \bigcirc)$. The WR calculations gave identical results for each vibrational band. The WR calculations are indicated by a line on each graph. The relative energy contents are normalized to a value of 8.0 for the sum of all bands except for the experimental distribution where they are normalized to a value of 7.0 for the sum of all bands except that at $1453\ \text{cm}^{-1}$.

It is not possible at this point to state with certainty what is causing the narrower coupling in dioxane. More data is necessary on other molecules in order to compare the effects of rigidity to that of rotational constants.

ACKNOWLEDGMENT

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