

# Intramolecular vibrational relaxation in dimethyl ether

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Intramolecular vibrational energy transfer in isolated gas phase molecules of dimethyl ether 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 3050  $\text{cm}^{-1}$ . By comparing the experimentally observed relative energy content of the IR active modes with that calculated from a statistical model it is concluded that the C–H stretches are strongly mixed with nearby bath states. The observed energy content distribution is best described by a statistical model which assumes coupling over a 20  $\text{cm}^{-1}$  range. Dilution factors for the various C–H stretch modes were observed which vary from 0.01 to 0.20. These values are dependent on the rotational state excited. The experiments are performed by exciting a molecule cooled in a nozzle expansion with light from an infrared optical parametric oscillator. The fluorescence spectra are recorded with a cryogenic Michelson interferometer.

## INTRODUCTION

The intramolecular transfer of vibrational energy is one of the explicit assumptions of statistical unimolecular reaction rate theories (such as RRKM theory).<sup>1</sup> The success of RRKM theory in explaining the gas phase kinetics of unimolecular reactions and bimolecular reactions proceeding through a long lived activated complex highlights the importance of intramolecular energy transfer. However, since RRKM theory is a statistical theory it can provide only limited amounts of detailed dynamical information. Today these details are of vital interest to the emerging technologies of laser isotope separation and chemical lasers. They are also of interest to theoretical studies of chemical dynamics. Interest in the mechanisms, rates, and pathways of vibrational energy transfer has also increased with the development of lasers. A laser's ability to deliver a coherent, monochromatic, and dense packet of photons makes possible the production of highly excited molecules in single vibronic (or even rovibronic states). Although no truly spectacular examples have been observed, it is true that the choice of initial state can affect the rate of reaction by as much as a factor of 3.<sup>2</sup> This makes state selective chemistry a real possibility. This will only be feasible in systems where the rate of energy transfer out of the prepared state or states is slower than the chemical process of interest.

We recently reported on the presence of intramolecular vibrational energy transfer from C–H stretch fundamentals in the ground electronic state for a variety of organic molecules.<sup>3</sup> We are now in the process of studying the variation in the matrix elements that lead to the vibrational state mixing responsible for the intramolecular transfer of energy out of the optically prepared vibronic state into the bath vibronic states of the molecule. Previous work in this area has been reported for methyl formate.<sup>4</sup> This study presents the spectrally resolved infrared laser induced fluorescence from the C–H stretch fundamentals of isolated dimethyl ether molecules. These fluorescence studies are carried out under collisionless conditions. The molecules are initially prepared in

their ground vibronic (though not necessarily ground rovibronic) states by expansion into a vacuum to form a supersonic beam.

An analysis of the fluorescence spectrum allows the direct measurement of relative apportioning of energy amongst the vibrational modes comprising the bath. Excitation of different vibrational transitions results in different energy distributions in the bath manifold. The fluctuations in energy disposal observed at different excitation energies are compared to the fluctuations in energy disposal calculated from a statistical model. It is also possible to calculate the dilution factor of resonance fluorescence  $\phi_d$  from a fluorescence spectrum. The dilution factor is roughly inversely proportional to the number of molecular eigenstates that the optically prepared state is spread over.<sup>3,4</sup>

The molecule chosen for these studies, dimethyl ether, has been the focus of many spectroscopic and theoretical studies.<sup>5–7,9</sup> Its molecular point group for the semirigid molecule is  $C_{2v}$  and there are five IR active C–H stretch fundamentals. In the C–H stretching region the vibronic state density ranges from 15–25 states/wave number. The state density is in the middle of the threshold region for vibrational relaxation of C–H stretch fundamentals. We can also expect extensive state mixing due to Fermi resonances. The argon matrix spectrum of dimethyl ether<sup>5</sup> exhibits no fewer than 10–15 distinct vibrational features in the C–H stretching region. At least some of these must be ascribed to Fermi resonance. Since some of the lower lying vibrational modes have as much if not more oscillator strength in absorption than the C–H stretches, the proper conditions allowing the observation of fluorescence from the bath states are fulfilled.

As in the previous papers<sup>3,4</sup> in this series the following nomenclature will be used. Fluorescence from the original optically excited state will be called unrelaxed fluorescence. This term will be applied both to resonance fluorescence and Fermi resonance fluorescence. Resonance fluorescence is fluorescence at the exciting laser's wavelength (with small shifts due to the rotational selection rules). Fermi resonance fluorescence is fluorescence from overtone and combination bands whose cross section for absorption of light from the ground vibronic state is greatly enhanced by strong mixing

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with a nearby C–H stretch fundamental. In addition to fluorescing to the ground state these states fluoresce to lower lying vibrational states. The latter type of fluorescence we call Fermi resonance fluorescence. Fluorescence from the bath states is called relaxed fluorescence.

## THEORY

The model used to describe the vibrational state mixing and relevant theory has been developed earlier<sup>4</sup> and here we will mainly just summarize the results. The main features of the model are:

(i) The zeroth order optically excited state  $|j\rangle$  is assumed to be equally coupled to all the bath states  $\{|\ell\rangle\}$  within a bandwidth of  $\Delta\omega_j$ .

(ii) The bath states  $\{|\ell\rangle\}$  are formed by premixing all of the states  $\{|\ell\rangle\}$  that are optically dark with respect to an electric dipole allowed transition from the ground vibronic state. This bath is constructed such that a single state  $|\ell\rangle$  is equally coupled to all other states within a bandwidth of  $\Delta\omega_\ell$ .

(iii) All of the above states are vibronic states only, e.g., excited  $J > 0$  rotational states are not considered.

The intensity of resonance fluorescence,  $I_j$ , from a fundamental  $|j\rangle$  measured by our experimental setup is

$$I_j \propto \phi_d (A_{0,j}^1)^2,$$

where  $\phi_d$  is the dilution factor of resonance fluorescence and  $(A_{0,j}^1)^2$  is the square of the Einstein  $A$  coefficient. The Einstein  $A$  coefficient can be measured from the normal IR absorption spectrum. Thus a measurement of the absolute intensity of resonance fluorescence allows the determination of  $\phi_d$ .  $\phi_d$  has the physical significance of being roughly inversely proportional to the number of states  $|j\rangle$  mixes with.

The intensity of  $\Delta V = -1$  relaxed fluorescence from a mode  $\alpha$  is given by

$$I_\alpha \propto (1 - \phi_d) A_{0,\alpha}^1 A_{0,\alpha}^1 \sum_{V=1}^{V_{\max}} V F_{\alpha,V},$$

where  $A_{0,\alpha}^1$  is the Einstein  $A$  coefficient for the  $V = 1 \rightarrow 0$  transition in mode  $\alpha$ ,  $V_{\max}$  is determined by the total amount of energy available from the optical excitation, and  $f_{\alpha,V}$  is the fraction of zeroth order states with  $V$  quanta in the mode  $\alpha$  in the bandwidth  $\omega_\alpha$ . The  $f_{\alpha,V}$  are normalized such that

$$\sum_{V=0}^{V_{\max}} f_{\alpha,V} = 1.$$

The relative energy content  $E$  of the mode is given by

$$E_\alpha = hc\omega_\alpha \sum_{V=1}^{V_{\max}} V F_{\alpha,V},$$

where  $\omega_\alpha$  is the frequency of the transition in wave numbers ( $\text{cm}^{-1}$ ). Thus the experimentally observed fluorescence intensities allow us to determine the final apportionment of energy that was originally deposited in the optically excited state.

In order to compare the experimentally measured relative energy contents with a theoretical description the model is required to calculate the sum  $\sum V f_{\alpha-V}$ . The appropriateness of the model can then be checked by using the relative

intensities of relaxed and unrelaxed fluorescence to measure the dilution factor  $\phi_d$ . The dilution factor obtained via this procedure can then be compared with the  $\phi_d$  measured from the absolute intensity of unrelaxed fluorescence. The later method is valid independent of the model used to describe the intramolecular state mixing.

The sum  $\sum V f_{\alpha,V}$  has been calculated using two methods. The first uses the model described above. We have enumerated all of the vibrational states within the bandwidth  $\Delta\omega_\ell$  by direct state counting and use these states to calculate  $\sum V f_{\alpha,V}$ . The results of these calculations over bandwidths of 2, 4, 10, 20, and 40  $\text{cm}^{-1}$  are labeled DSC 2, DSC 4, DSC 10, DSC 20, and DSC 40, respectively. In performing the direct state counts we assumed all of the vibrational modes were harmonic oscillators with the exception of the methyl torsional modes. The frequencies used are found in the Appendix. As a benchmark we also calculated the  $\sum V f_{\alpha-V}$  using the Whitten–Rabinovitch formulas (called WR hereinafter) for state densities. In this calculation

$$F_{\alpha,V} = \frac{\rho(E - vhc\omega_\alpha)}{\rho(E)},$$

where  $\rho(E)$  is the density of states at a given energy  $E$  for the entire molecule and  $\rho(E - vhc\omega_\alpha)$  is the density of states of the molecule excluding the mode  $\alpha$  at an energy of  $E - vhc\omega_\alpha$ . The relative energy distribution in the bath modes calculated at a total energy  $E$  from this method gives the same results as calculating the average relative energy content of each mode from a canonical ensemble whose temperature is chosen such that  $\langle E \rangle = E$ , where  $\langle E \rangle$  is the average total energy.

The laser used to perform these experiments has a bandwidth of 1  $\text{cm}^{-1}$ . The use of bandwidths  $\Delta\omega_\ell$  greater than 1  $\text{cm}^{-1}$  in the DSC model calculations implies that we are modeling the bath states as being strongly premixed over a bandwidth of  $\sim \Delta\omega_\ell$  (see Ref. 4). This width  $\Delta\omega_\ell$  is also broader than the bandwidth  $\Delta\omega_j$  over which we expect the zeroth order optically excited state  $|j\rangle$  to be mixed.

## EXPERIMENTAL

The infrared fluorescence from isolated molecules in a supersonic beam is measured using the apparatus described previously.<sup>4</sup> The molecules are excited by laser light from an optical parametric oscillator (OPO). As operated for these experiments in the region 2800–3100  $\text{cm}^{-1}$  the OPO produced 5 mJ of energy in a 13 ns pulse. The bandwidth of the OPO is 1  $\text{cm}^{-1}$  in this region. It is focused down to provide fluences of 22  $\text{mJ}/\text{cm}^2$  in the interaction region where it crosses the molecular beam. We carefully checked for evidence of saturation or multiphoton effects and were unable to observe any at this fluence in dimethyl ether.

The molecular beam was produced by the expansion of pure dimethyl ether at a total pressure of 800 Torr through a pulsed nozzle valve with a 0.7 mm hole. This provides a beam of molecules with an average rotational temperature of 25–30 °K (as determined from a rough band contour analysis). At this high a rotational temperature we expect the translational temperature to be in equilibrium with the rotations and the vibrational temperature to be somewhat high-

TABLE I. Relative Einstein  $A$  coefficients of dimethyl ether.

Vibrational frequency <sup>a</sup>	$A$ Coefficient <sup>b</sup>
931	4.8
1104	9.2
1178	21.6
1250	1.1
1400 (five bands)	7.7 (total of five bands)
2814	62.1
2875	40.1
2887	37.3
2923	145.0
3004	72.1

<sup>a</sup> Frequency in  $\text{cm}^{-1}$ .

<sup>b</sup> Arbitrary unit.

er. These beam conditions were chosen because our experience<sup>3</sup> shows that they are sufficient to eliminate vibrational hot band progressions while maximizing the concentration of chemical in the beam.

The method of spectral resolution used for measurement of the absolute intensity of resonance fluorescence has been modified since the previous description of the apparatus.<sup>3</sup> Now instead of using a cooled (77 °K) circular variable filter a cooled infrasil quartz flat is used. The flat acts as a cut-off filter for all radiation below  $2200 \text{ cm}^{-1}$  while having a flat transmission of 95% at frequencies above  $2300 \text{ cm}^{-1}$ . The rest of the detection apparatus used in the measurement of absolute intensities has been left unchanged. The spectrally resolved fluorescence spectra presented here were taken with the cryogenic Michelson interferometer described in Ref. 4.

The Einstein  $A$  coefficients used in this work (shown in Table I) were calculated in the usual way<sup>4</sup> from the pressure broadened gas phase absorption spectrum. The spectrum was taken using a Nicolet FT-IR. The relative absorptions in C-H stretching and  $\text{CH}_3$  bending regions were apportioned with the aid of spectra of dilute dimethyl ether in carbon tetrachloride and the published argon matrix spectrum.<sup>5</sup>

## RESULTS

The laser excitation spectrum of dimethyl ether is shown in Fig. 1. The two outermost peaks (at 2814 and  $3004 \text{ cm}^{-1}$ ) show well defined  $P$ - $Q$ - $R$  branch contours. It is not possible to unambiguously assign a band contour type to these two transitions. However it seems safe to say that they have either an  $A$  or  $C$  type contour and therefore have a symmetry of  $b_1$  or  $b_2$ , respectively. Between 2850 and  $2975 \text{ cm}^{-1}$  the vibrational bands in the spectrum become badly overlapped. With the exception of the  $P$ - $Q$ - $R$  structure in the shoulder at  $2945 \text{ cm}^{-1}$  no distinct band contour structure is visible.

The spectrally resolved fluorescence spectra are shown in Fig. 2. The excitation frequency in  $\text{cm}^{-1}$  is used to label each spectrum. With the exception of the  $\text{CH}_3$  bending modes at  $1400$ - $1500 \text{ cm}^{-1}$  all of the observed nonresonance fluorescence peaks have been assigned<sup>6</sup> to vibrational motions involving the oxygen atom. The broad peak at  $920$

## DIMETHYL ETHER

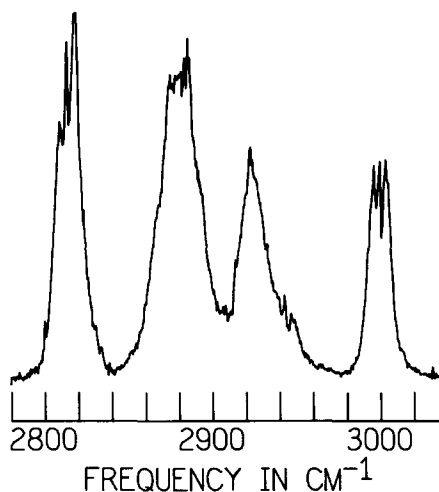


FIG. 1. Total laser induced fluorescence spectrum of the C-H stretching region of dimethyl ether.

$\text{cm}^{-1}$  is assigned to symmetric C-O-C stretch of  $a_1$  symmetry. The two overlapped peaks at  $1100$  and  $1175 \text{ cm}^{-1}$  are assigned to the coupled motions of the asymmetric C-O-C stretch and the in plane methyl rock, both with  $b_1$  symmetry. On the basis of these spectra it is impossible for us to resolve the  $\text{CH}_3$  bending region where there are five IR active vibrational modes.

Table II lists the experimental integrated emission intensities. The resultant relative energy distributions and those calculated from the WR and DSC methods are shown in the spectral plots of Fig. 3. The WR vibrational energy content distribution is the same as the average vibrational energy distribution calculated from a canonical ensemble with a temperature of  $775$ - $880 \text{ °K}$ . The experimentally observed relative energy distributions show substantial fluctuations about the thermal distribution. The DSC results also show fluctuations about the thermal distribution. These fluctuations damp out as the bandwidth  $\Delta\omega_i$  is increased. The best fit between the DSC calculations and the experimentally observed relative energy contents is provided by bandwidths of  $20$ - $40 \text{ cm}^{-1}$ .

The most dramatic fluctuation in the observed energy contents is seen in the  $1425$ - $1500 \text{ cm}^{-1}$  region of the  $\text{CH}_3$  bending modes. Excitation in the region from  $2910$  to  $2975 \text{ cm}^{-1}$  produces spectra with sharp well-defined peaks near  $1460 \text{ cm}^{-1}$  with far more intensity than the statistical energy distribution would predict (see Figs. 2 and 3). Based on this we have tentatively assigned the vibrational features in this area as being combination or overtone bands which borrow absorption intensity from the ground state through Fermi resonance with one or more C-H stretch fundamentals. Using the relative intensities of C-H stretch and  $\text{CH}_3$  bending modes in emission these bands can be estimated to be composed of  $90 + \%$  combination of overtone band in Fermi resonance with a C-H stretch.

There is also substantial fluctuation in the fluorescence spectra obtained by excitation in the vibrational band(s) from  $2850$  to  $2910 \text{ cm}^{-1}$ . This confirms the impression given by

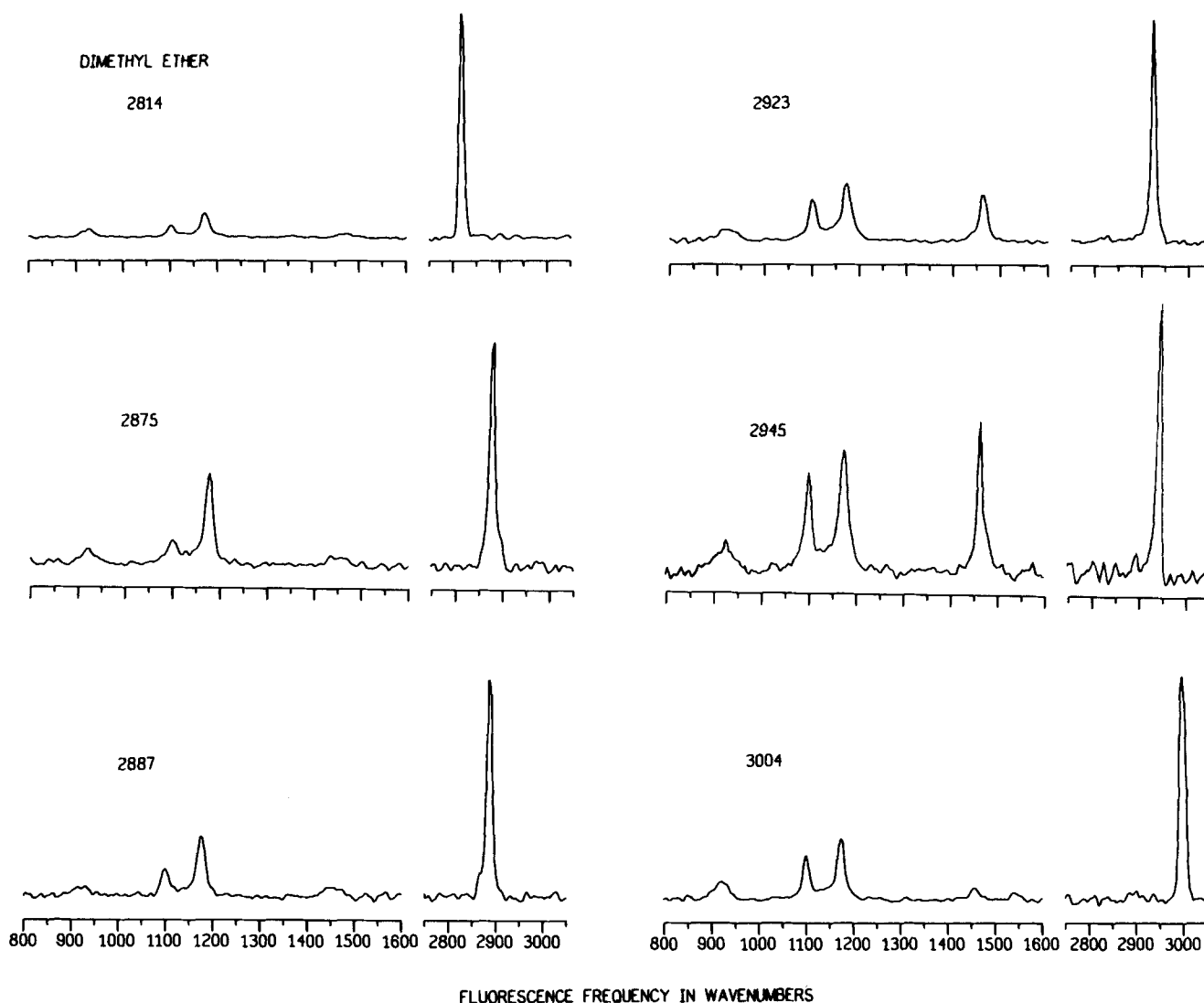


FIG. 2. Fluorescence spectra from the C-H stretching region of dimethyl ether. Spectra are labeled by the laser pump frequency (in  $\text{cm}^{-1}$ ). Intensity of fluorescence is in arbitrary units with the most intense peak of each spectrum normalized to the same height.

Fig. 1 that the excitation spectrum in this region is the result of two or more overlapped vibrational transitions. However, since we do not see extreme fluctuations in the relative energy contents of the various modes we have tentatively assigned this region from the features at 2814 and 3004  $\text{cm}^{-1}$  to be from excitation of C-H stretch fundamentals.

The measured dilution factors are shown in Table III.

TABLE II. Observed integrated fluorescence intensities from C-H stretches in dimethyl ether.

Laser frequency	850-975 $\text{cm}^{-1}$	975-1125 $\text{cm}^{-1}$	1125-1300 $\text{cm}^{-1}$	1300-1550 $\text{cm}^{-1}$	Resonance
2814	0.32	0.39	0.90	0.19	3.20
2874	0.35	0.54	1.49	0.33	2.29
2887	0.42	0.57	1.22	0.31	2.47
2923	0.35	0.74	1.17	0.72	2.03
2950	0.37	0.91	1.43	1.15	1.14
3003	0.46	0.71	1.15	0.24	2.44

Values in brackets represent average values taken over the region of interest. In calculating  $\phi_d$  from the absolute intensity of resonance fluorescence we assumed the presence of two vibrational bands of equal intensity between 2850 to 2910  $\text{cm}^{-1}$  and between 2910 to 2975  $\text{cm}^{-1}$ . If these estimates are wrong the quoted values will be in error by the ratio of the number of vibrational bands present to the number of vibrational bands assumed during the calculation.<sup>3</sup> The tabulated dilution factors measured by our two methods are in good agreement. The worst agreement is in the dilution factors for the combination bands at 2923 and 2945  $\text{cm}^{-1}$ . The disagreement here could well be due in part to systematic errors arising from an incorrect assignment or apportionment of the C-H stretch oscillator strength. The otherwise excellent agreement is an indication of the appropriateness of the model we have used to calculate the relative energy contents of the bath modes.

Although we do not present the results here, we have surveyed the rotational energy dependence of the dilution factors. They appear to decrease with increasing rotational

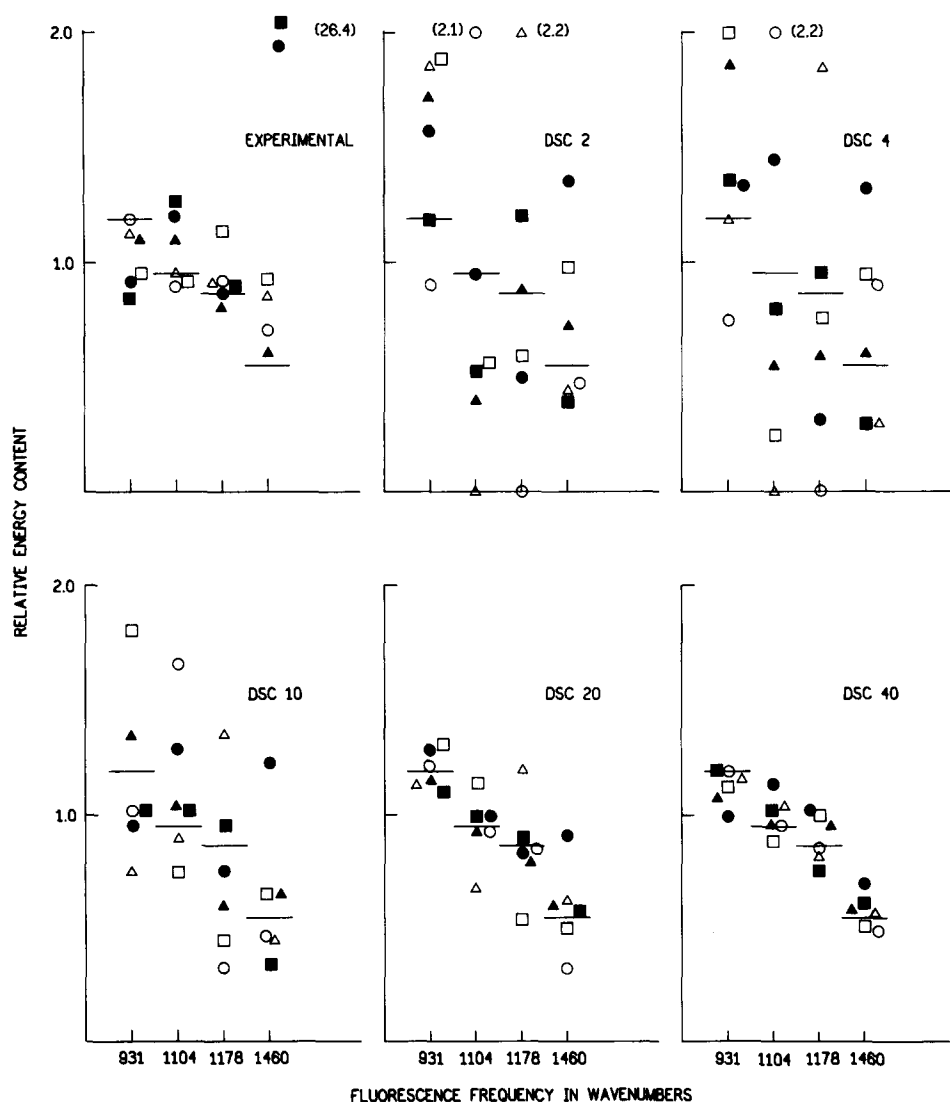


FIG. 3. Relative energy content of vibrational modes following optical excitation. The relative energy contents are obtained from the model calculations and experimentally. Each plot symbol represents a different vibrational band ( $2814\text{ cm}^{-1} = \circ$ ,  $2875\text{ cm}^{-1} = \square$ ,  $2887\text{ cm}^{-1} = \triangle$ ,  $2923\text{ cm}^{-1} = \bullet$ ,  $2945\text{ cm}^{-1} = \blacksquare$ , and  $3003\text{ cm}^{-1} = \blacktriangle$ ). 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 3.0 for the sum of the 931, 1104, and 1178 modes.

energy, by about a factor of 2 from the low  $J$  region presented here to the highest  $J$ 's available at our beam temperature. As the average  $J$  at band center is about 3 or 4, we expect the  $\phi_a$ 's at  $J = 0$  to be higher than our tabulated ones by a factor of perhaps 4.

TABLE III. Dilution factor<sup>a</sup> of unrelaxed fluorescence.

Frequency	From absolute <sup>b</sup> resonance intensity	From relaxed <sup>c</sup> unrelaxed ratio
2814	0.023	0.043
2876	(0.046)	0.036
2887	(0.046)	0.036
2923	(0.032)	0.10
2945	(0.032)	0.19
3004	0.013	0.015

<sup>a</sup> Values in parenthesis are upper bounds.

<sup>b</sup> Accurate to a factor of 3.

<sup>c</sup> Accurate to  $\pm 50\%$ , calculated from the DSC20 results.

## DISCUSSION

The molecule dimethyl ether is physically similar to methyl formate in several ways. They are both strongly asymmetric rotors, they are both prolate, they both have an internal methyl rotor (two in dimethyl ether), and they both have similar densities of states. They differ only in that one hindered rotor in dimethyl ether is replaced by a torsional oscillation in methyl formate. It is not surprising that the internal vibrational relaxation is similar in the two molecules.

With the exception that the extremely strong rotational state dependence of  $\phi_a$  seen in the aldehyde stretch of methyl formate is not seen here, we can state the following similar conclusions.

(i) The estimated  $\phi_a$ 's at  $J = 0$  are about 0.2. This together with a vibronic state density of  $20\text{ cm}^{-1}$  leads to a width of coupled states of  $0.25\text{ cm}^{-1}$  or a relaxation time of about 20 ps. This implies an average matrix element  $\epsilon$  of about  $0.16\text{ cm}^{-1}$ . Because of the lack of single rotational state resolu-

tion this is only a rough estimate.

(ii) In order to explain the similarities of the fluorescence spectra from different C–H stretches we must invoke “premixing” of the bath states. This appears to be induced by Coriolis coupling and by vibrational mixing through the strongly anharmonic rotor modes. The coupled width is a surprisingly great  $20 \text{ cm}^{-1}$ .

(iii) We again see no strong coupling in particular C–H stretch to a *subset* of the bath states.

(iv) The rotational state dependence of the state mixing, while not as great as in methyl formate, is still strong.

We would like to conclude by pointing out that conclusion (iii) above does *not* imply that in some zero order basis (e.g., local modes) a given C–H stretch does not couple most strongly to some single lower energy vibration (i.e., a C–H bend). This occurs because the premixing spreads such zero order character over a very wide bandwidth; because the bandwidth of premixed state  $\Delta\omega_c$  is greater than  $\Delta\omega$ , even time dependent observation might not show a sequential process proceeding through the strongly coupled zero order mode.

#### ACKNOWLEDGMENT

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#### APPENDIX

The following vibrational frequencies (in  $\text{cm}^{-1}$ ) were used in the density of state calculations (they were compiled

from Ref. 7):

$A_1$	2999, 2820, 1485, 1449, 1250, 931, 424,
$B_1$	2999, 2820, 1467, 1432, 1178, 1104,
$A_2$	2922, 1463, 1148,
$B_2$	2935, 1459, 1179.

These states exclude the two torsional vibrations at 202 and  $241 \text{ cm}^{-1}$ . They were treated as two uncoupled hindered rotors whose energy levels were calculated from the potential

$$V(\phi) = \frac{V_3}{2} (1 - \cos 3\phi)$$

in a basis set of rigid free rotor wave functions with the structural parameters  $F = 6.52 \text{ cm}^{-1}$  and  $V_3 = 903.3 \text{ cm}^{-1}$  given in Ref. 8. The WR calculations assumed the rotors to be harmonic.

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