Intramolecular vibrational energy transfer in methyl formate

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(Received 2 May 1983; accepted 29 June 1983)

Intramolecular vibrational energy transfer in isolated gas phase molecules of methyl formate has been studied by spectrally resolving the IR laser induced fluorescence from C–H stretch fundamentals, combination bands, and overtones in the region from 2900 to 3500 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 complete randomization of the energy initially deposited in the zeroth order optically excited state occurs. However, due to the finite density of vibrations, that statistical distribution differs clearly from a thermal distribution. Both the model and experiment agree that different optically excited states deposit different amounts of energy in the carbonyl stretching mode at 1754 cm\(^{-1}\). We also observe a rotational state dependence of vibrational energy transfer in the 2939 cm\(^{-1}\) band. 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 presence of intramolecular vibrational relaxation from C–H stretch fundamentals in the ground electronic state in the gas phase has been demonstrated for a variety of organic molecules.\(^1\)\(^{-3}\) Considering that the vibronic density of states for a molecular excited at 3000 cm\(^{-1}\) can vary from 0.1 to over 10\(^6\) states per wave number, the onset of relaxation occurs in our studied molecules over a very moderate range of 5–100 states per wave number. To date we have seen no completely clear correlation between the threshold density and molecular structure. The variation in the threshold for relaxation can be attributed to the variation in the size of the matrix elements coupling the zeroth order C–H stretches to the bath states of the molecules.

In this work we present the first of our efforts to study the variation in the matrix elements that lead to vibrational mixing. To this end the spectrally resolved infrared laser induced fluorescence from the C–H stretch fundamentals and the first overtone of the carbonyl C=O stretch of isolated methyl formate molecules is presented and analyzed. Utilizing the simple selection rules for fluorescence from excited rovibronic states in the ground electronic state, it is possible to monitor to where the energy is transferred or, equivalently, the relative apportioning of energy amongst the vibrational motions. By then exciting different rotational-rovibrational states we can measure the fluctuations in energy disposal between the various bath vibrational states and the influence of the rotational states within a given vibrational band on the disposal of energy. The fluctuations in energy disposal observed at different excitation energies are compared to the fluctuations in energy disposal calculated from a statistical model.

These fluorescence studies are carried out under collisionless conditions. The collisional time dependence of the spectrally resolved fluorescence is also presented. This helps us to distinguish between unrelaxed fluorescence from the original optically excited zeroth order state and relaxed fluorescence from the bath states.

The molecule chosen for these studies, methyl formate, has been the focus of many spectroscopic\(^4\)\(^{-8}\) studies. Its vibrational and rotational structure have been well characterized. In the C–H stretching region, the vibrational state density ranges from 12 to 17 cm\(^{-1}\) and the vibrational state density in the region of the \(v = 2\) carbonyl overtone at 3497 cm\(^{-1}\) is about 33 cm\(^{-1}\). In the laser excitation spectrum\(^1\) there are five vibrational bands in the 3000 cm\(^{-1}\) region: a combination band at 2913 cm\(^{-1}\) (a combination of the C=O stretch at 1754 cm\(^{-1}\) and the CH\(_3\) rock at 1158 cm\(^{-1}\)), the C–H aldehyde stretch at 2839 cm\(^{-1}\), and three methyl group C–H stretches at 2969, 3008, and 3045 cm\(^{-1}\). In its equilibrium configuration, all of the heavy atoms lie in a plane with one another and the methyl group is in the cis position.\(^9\)\(^7\) The molecular point group is C\(_s\). All of the vibrational bands in the C–H stretching region have \(\tilde{a}'\) symmetry with the exception of the \(\tilde{a}''\) 3008 cm\(^{-1}\) band.

Earlier work on methyl formate showed a slight variation in the dilution of resonance fluorescence amongst the C–H stretches\(^8\) and also showed a strong rotational dependence in the relaxed carbonyl fluorescence in the 2939 cm\(^{-1}\) band.\(^1\) These earlier studies used a circular variable filter with a bandwidth of \(\sim 2\%\) of the passed wavelength. The current experiments were accomplished using a cryogenically cooled Michelson interferometer. The cooled interferometer increases the spectral resolution to 8 cm\(^{-1}\). Given the increased spectral resolution at our disposal, we have reexamined the laser induced fluorescence from methyl formate. In addition to our primary goal of studying vibrational relaxation, we are able to establish the presence of Fermi resonance between the 2913 and 2939 cm\(^{-1}\) bands and calculate the interaction matrix element between them.

In this work three different types of “zeroth order”
states have been optically excited (although one type might be better named "first order"). The states at 2969, 3008, and 3045 cm\(^{-1}\) are simple C=H stretches and, in the limit of no relaxation would emit resonance fluorescence to the ground state (fluorescence at the exciting laser's wavelength plus or minus the P→Q→R branch shift). The zeroth or first order states at 2913 and 2939 cm\(^{-1}\) are a Fermi resonant pair and in the absence of mixing to bath states would emit to the ground state as well as to the states at 1168 and 1754 cm\(^{-1}\). We call these two types of fluorescence resonance and Fermi resonance fluorescence, respectively. It is true that the same mechanism, e.g., anharmonicities in the vibrational modes, is responsible for Fermi resonance mixing and the mixing of vibrational states that eventually results in intramolecular vibrational relaxation. However, the matrix elements responsible for Fermi resonance are generally much larger in magnitude than the matrix elements responsible for ordinary intramolecular energy transfer. This and the collisional time dependence of Fermi resonance fluorescence makes it convenient to treat Fermi resonance fluorescence as unrelaxed fluorescence. The C=O stretch overtone at 3498 cm\(^{-1}\) constitutes a third case which would, in the absence of mixing with the bath, emit \(\Delta V = 1\) fluorescence down to 1754 cm\(^{-1}\). These three types of fluorescence are together called unrelaxed fluorescence. Fluorescence from the bath states is called relaxed fluorescence.

**THEORY**

Methyl formate's state density places it in the "sparse intermediate case" regime. The temporal evolution of the unrelaxed fluorescence in this regime has been described by formal theory\(^{10}\) and monitored by experiment.\(^{11,12}\) The unrelaxed fluorescence first decays irreversibly and rapidly. Next a slower decay follows that is modulated by quantum beats. With our present apparatus we are unable to monitor the intrinsic time dependence of the fluorescence (our laser pulse time is much longer than the probable inverse energy span of the intermediate level structure). However, what we can measure, in principle, is the absolute intensity (rate) of resonance fluorescence,\(^2\) and the relative intensity and frequency of fluorescence from the bath states. To relate these experimental observables to the molecular properties responsible for energy transfer we will assume the following model.

Figure 1 helps to define the nomenclature and the coupling scheme that will be used. We begin with a zero order basis set consisting of anharmonic normal modes which include the anharmonic terms which make bonds Morse oscillators but not those terms which couple different normal modes. This is done so that this basis set approximately represents the infrared oscillator strengths in the molecule. The zeroth order optically excited state is labeled |s\rangle. For the moment we will assume |s\rangle corresponds to the first excited energy level of one particular vibrational mode. This restriction will be lifted later on. The states |l_{a,b,\gamma,...}\rangle are nearly vibronic states that do not contain oscillator strength to the ground state. The Greek indices \(\alpha, \beta, \gamma, \ldots\) are the occupation numbers of the 17 other normal modes of vibration in methyl formate. The bath states |b_i\rangle are formed by diagonalizing the Hamiltonian matrix constructed from the \(|l_{a,b,\gamma,...}\rangle\) states not including the anharmonic terms coupling |s\rangle and the \(|l_{a,b,\gamma,...}\rangle\). The |b_i\rangle are labeled in increasing energy with an index \(i\). Finally, on the bottom half of Fig. 1 are displayed the molecular eigenstates |j_k\rangle. They are formed by diagonalizing the Hamiltonian matrix constructed in the \(|s\rangle \otimes |b_i\rangle\) basis set. The \(|j_k\rangle\) are labeled in increasing energy with an index \(k\). Using the above we can write the following expressions:

\[|b_i\rangle = \sum_{a,b,\gamma,...} C_{a,b,\gamma,...}^i |l_{a,b,\gamma,...}\rangle,\]

and

\[|j_k\rangle = C_k^s |s\rangle + \sum_i C_k^i |b_i\rangle = C_k^s |s\rangle + \sum_i \sum_{a,b,\gamma,...} C_{a,b,\gamma,...}^i C_k^i |l_{a,b,\gamma,...}\rangle = C_k^s |s\rangle + \sum_{a,b,\gamma,...} C_k^a |l_{a,b,\gamma,...}\rangle.\]

The time-independent coefficients \(C\) have the usual physical significance. For example, the probability of measuring a molecule prepared in the state \(|j_k\rangle\) in the observable state \(|s\rangle\) is \(|C_k^s|^2\).

In the development that follows we will use a model...
that assumes the bath states $|b_i\rangle$ are strongly premixed. That is, the states $|I_{z_1z_2\ldots}\rangle$ are strongly coupled to one another over some width $\Delta \omega_i$. The state $|s\rangle$ is assumed to be only weakly coupled to the bath states over some narrower width $\Delta \omega_s$. This situation is displayed pictorially in Fig. 1. The second line of this figure shows the projection of a particular zeroth order state, e.g., $|I_{z_1z_2\ldots}\rangle$ on the bath state manifold. The nominal center of the states $|I_{z_1z_2\ldots}\rangle$ and $|s\rangle$ are also indicated. Line three of Fig. 1 shows the projection of $|I_{z_1z_2\ldots}\rangle$ on the manifold of molecular eigenstates. As drawn the center figures show only slight changes due to mixing in the state $|s\rangle$. The small magnitude of the perturbation is due to the much narrower width over which $|s\rangle$ mixes with $|I_{z_1}\rangle$ and the weak coupling between $|s\rangle$ and the $|I_{z_1}\rangle$.

This model has been chosen to allow us to explain the variation in the relative energy content of the vibrational modes we observe from the relative intensities of relaxed fluorescence of different optically excited states. Now we connect our two experimental observables with the model parameters.

Assuming that all of the molecules start out in the ground vibronic state $|0\rangle$, and that the only allowed transition into or out of $|s\rangle$ is $|0\rangle \rightarrow |s\rangle$; the integrated intensity of unrelaxed fluorescence from a molecular eigenstate $|I_{z_1}\rangle$ will be given by:

$$I_{s,z_1} = \frac{g_s}{8\pi \omega_s} \mathcal{E}(k, \omega) |C_s|^4,$$

where $g_s$ is the degeneracy of $|s\rangle$, $A_{z_1}$ is the $A$ coefficient for the transition $|s\rangle - |0\rangle$, $\omega_s$ is the frequency of the transition in wave numbers and $\mathcal{E}(k, \omega)$ is the light flux in quanta per cm$^2$ per wave number at the eigenstate $|I_{z_1}\rangle$ with the laser tuned to frequency $\omega$.

To date we have not succeeded in cleanly exciting a single molecular eigenstate. This means we must sum $I_{s,z_1}$ over all of the $|I_{z_1}\rangle$ coupled to the state $|s\rangle$ to predict the intensity unrelaxed fluorescence. First of all we will assume that the laser bandwidth 1 cm$^{-1}$ is much broader than the width of $|I_{z_1}\rangle$ states coupled to $|s\rangle$, $\Delta \omega_s$. Next we will assume that all of the states within the bandwidth of $|s\rangle$ are equally coupled. Then $|C_s|^4$ will be equal to $1/N_s$, where $N_s$ is the number of $|I_{z_1}\rangle$ that $|s\rangle$ mixes with, is given by the bandwidth of $|s\rangle$, $\Delta \omega_s$, multiplied by the local rovibrionic density of states. For example, if $\Delta \omega_s = 0.25$ cm$^{-1}$ and the local density of states is 25 states/cm$^{-1}$, then $|C_s|^4 = \frac{1}{25}$. Summing $I_{s,z_1}$ over the bandwidth of $|s\rangle$ we obtain

$$I_s = \sum_{\nu=1}^{N_s} I_{s,z_1} = \frac{1}{N_s} \frac{g_s}{8\pi \omega_s} \mathcal{E}(\omega) |C_s|^4,$$

where we have also approximated all of the $\omega_s$ by $\omega_s$, the nominal frequency in cm$^{-1}$ of $|s\rangle$ and $\mathcal{E}(k, \omega)$ by $\mathcal{E}(\omega)$ the light flux of the laser at $\omega$. If no state mixing were present the intensity of unrelaxed fluorescence would be given by the above expression without the presence of the $1/N_s$ factor. Thus according to our model the dilution factor of unrelaxed fluorescence will be inversely proportional to the number of states $|I_{z_1}\rangle$ that $|s\rangle$ mixes with. Since in real molecules all of the $|C_s|^4$ are not necessarily equal in magnitude the dilution factor $\phi_s$ measured will not be exactly inversely proportional to the number of states that the optically excited state $|s\rangle$ is mixed with. Notice that we sum the intensities rather than amplitudes of the individual eigenstates. This means we ignore the short period after the initial excitation during which the $|I_{z_1}\rangle$ are still "in phase." Since our observation time is more than 1000 times longer than any conceivable transient, this is a good approximation.

Next consider the intensity of relaxed fluorescence from $|I_{z_1}\rangle$ due to the transition $I_{s'=\nu,\lambda'} \rightarrow I_{s,\lambda}$. (Similar expressions occur for $I_{s',\lambda'} \rightarrow I_{s,\lambda}$, etc.). By analogy to the previous results the integrated fluorescence intensity of relaxed fluorescence from $|I_{z_1}\rangle$ will be given by

$$I_{s',\nu,\lambda} = \frac{g_s A_{z_1}' A_{\nu,\lambda}^2}{8\pi \omega_s} \mathcal{E}(k, \omega) |C_s|^4 \frac{1}{N_s} \sum_{\nu'=1}^{N_s} |C_{s',\nu'}|^2.$$

In order to relate this expression to the experimentally observed relative intensities we assume that all of the states $|I_{s'=\nu,\lambda'}\rangle$ are equally mixed over a bandwidth $\Delta \omega_s$ which is larger than $\Delta \omega_s$ (see Fig. 1). For example, if $\Delta \omega_s = 10$ cm$^{-1}$ and the local rovibrionic state density is 25 states/cm$^{-1}$, all of the $|C_{s',\nu'}|^2 = \frac{1}{25}$, where 250 is simply the number of bath states $|I_{z_1}\rangle$ mixes with. Then using the orthogonality of the eigenstates we find that

$$I_{s',\nu,\lambda} = \frac{g_s A_{z_1}' A_{\nu,\lambda}^2}{8\pi \omega_s} \mathcal{E}(k, \omega) |C_s|^4 \left(1 - |C_s|^2\right) \phi_{s',\nu,\lambda},$$

where $\phi_{s',\nu,\lambda}$ is the fraction of zeroth order states with $V$ quanta in mode $\lambda$ in the region $\Delta \omega_s$ wide centered on $\omega_s$. To find the relative intensity of relaxed fluorescence due to $V-V-1$ transitions in mode $\lambda$ we again sum over all the states $|I_{z_1}\rangle$ within the bandwidth of $|s\rangle$. We make the same assumptions as before about $\omega_s$, $\mathcal{E}(k, \omega)$ and $|C_s|^4$. In addition we assume that $\phi_{s',\nu,\lambda} = \phi_{s,s',\lambda}$, a constant, for all $|s\rangle$ within the bandwidth of $|s\rangle$. This produces

$$I_{s',\nu,\lambda} = \frac{g_s A_{z_1}' A_{\nu,\lambda}^2}{8\pi \omega_s} \mathcal{E}(\omega) \phi_{s',\nu,\lambda}.$$ (2)

The above expression relates our experimentally observed relative intensities to two molecular properties, the dilution factor of resonance fluorescence and the average functional number of bath states with a given number of quanta in a specified mode. Both of these quantities are averaged over the bandwidth of $|s\rangle$. In the absence of any experimental evidence to the contrary we have assumed the state $|s\rangle$ is equally coupled to all the states within its bandwidth. If this is not the case we will still get the same results [Eqs. (1) and (2)]; the effective density of states will merely be lower. For example, if $|s\rangle$ is coupled to $1/2$ the states over a 0.25 cm$^{-1}$ bandwidth and the total rovibrionic density of states is 25 states/cm$^{-1}$, then the effective density of states will be 12 states/cm$^{-1}$ and $\phi_s = 1/3$. This situation is illustrated pictorially in Fig. 1 where we show $|s\rangle$ strongly coupled to only a few of the states within its bandwidth.

In practice we are unable to spectrally resolve the fluorescence from the overtone and fundamental of a given vibrational mode in the relaxed fluorescence. This is due to the small variation in the anharmonicities.
of the bath modes and the wide 8 cm$^{-1}$ spectral resolution of the interferometer. What we can measure is the intensity of the $\Delta \nu = 1$ fluorescence of a given mode.

Using the usual harmonic oscillator approximation for the $A$ coefficients, Eq. (2) becomes

$$I_a = (1 - \phi_a) \frac{g_a\phi_a A_{ao}}{8\pi \omega_a} \int \omega \sum_{\nu} V_{f_{a\nu}}.$$  

(3)

The sum $\sum_{\nu} V_{f_{a\nu}}$ is related to the amount of energy $E_{R}$ deposited in a given vibrational motion $a$. $E_{R}$ is given by the expression

$$E_{R} = h\nu \omega_a \sum_{\nu} V_{f_{a\nu}},$$

where $\omega_a$ is the fundamental frequency of the mode $a$. This means that the experimentally observed fluorescence intensities allow us to determine the final apportionment of the energy that was originally deposited in the optically excited mode.

Using our data we can extract the dilution factor of unrelaxed fluorescence $\phi_a$ in two ways. One method is by measuring the absolute intensity of unrelaxed fluorescence and then finding the ratio of the intensity observed to the intensity we would expect to see if no state mixing was present. This first method is independent of the model assumed for the mixing of vibrational states. Using our model $\phi_a$ can also be calculated from relative intensities of unrelaxed and relaxed fluorescence. Solving Eqs. (1) and (3) for $\phi_a$ produces

$$\phi_a = \frac{(I_a/I_0)(A_{ao}/A_{ao,0}) \sum_{\nu} V_{f_{a\nu}}}{1 + (I_a/I_0)(A_{ao,0}/A_{ao}) \sum_{\nu} V_{f_{a\nu}}}.$$  

(4)

The model-dependent measurement of $\phi_a$ allows us to check on the appropriateness of our assumed model by comparison with the $\phi_a$ measured from the absolute intensity of unrelaxed fluorescence.

In order to use the last equation to calculate $\phi_a$, we must calculate the sum $\sum_{\nu} V_{f_{a\nu}}$. We have done this using two methods. The first method assumes that all of the states within a band $\Delta \omega_i$, centered on the frequency of the zeroth order state (1) are equally mixed. We then enumerate all the vibrational states within this bandwidth by direct state counting and use these states to calculate $\sum_{\nu} V_{f_{a\nu}}$. The results of these calculations over bandwidths of 4, 10, and 20 cm$^{-1}$ are labeled by DSC 4, DSC 10, and DSC 20, respectively. In performing the direct state counts, we assumed that all of the vibrational modes were harmonic oscillators with the exception of the methyl torsional mode. The frequencies used are found in the Appendix. As a benchmark we also calculated the sum of $f_{a\nu}$ using the Whitten–Rabinovitch formulas (called WR hereafter) for state densities. In this calculation

$$f_{a\nu} = \phi'(E - \nu h c \omega_a),$$

where $\rho(E)$ is the density of states at the given energy $E$ for the entire molecule, and $\rho'(E - \nu h c \omega_a)$ is the density of states of a molecule excluding the mode $a$ with a vibrational energy $E - \nu h c \omega_a$. The WR method, which treats the density of states as a continuous function, produces essentially the same values for the sum $\sum_{\nu} V_{f_{a\nu}}$ over the range of energies from 2800 to 3600 cm$^{-1}$.

The DSC calculations produce fluctuations in the sum of $V_{f_{a\nu}}$, calculated at the various zeroth order frequencies (1) $\Delta \omega_i$ is made larger and larger. In the limit of large values for $\Delta \omega_i$, the DSC calculations of $\sum_{\nu} V_{f_{a\nu}}$ cluster tightly about the WR result.

Both of these methods exclude the rotational states. Our laser is 1 cm$^{-1}$ wide so we excite several rovibrational states at the same time. Since the initial rotational distribution in the molecular beam is not well characterized we have excluded it from consideration.

In cases where our initially excited zeroth order state is a member of a Fermi resonant pair or is an overtone band the equations used to calculate the dilution factor $\phi_a$ must be modified in a straightforward manner. It is also a simple manner to calculate the matrix elements of the Fermi resonance coupling provided the two bands are spectrally resolved in the laser excitation spectrum and if both members of the Fermi resonant pair have electric dipole allowed transitions.

**EXPERIMENTAL**

The molecular beam system and the optical parametric oscillator (OPO) used in these experiments have been described previously. Briefly, the vacuum system has an interior volume of 64 l in the shape of a cube. This volume is completely surrounded by a liquid nitrogen cooled heat shield. The portion viewed by the detector is a system of louvres in direct contact with a vessel of liquid nitrogen. The pulsed valve is of our own design. The laser multipass cell has been improved by the use of thorium fluoride overcoated silver mirrors. This provides about three time more signal than the previous gold mirrors. The parametric oscillator now normally produces 4–6 mJ per pulse at 2950 cm$^{-1}$. Under the same focusing conditions as before when the OPO is run with a 1 cm$^{-1}$ bandwidth, the fluence is 22 mJ cm$^{-2}$. At this fluence we have observed saturation and multiphoton events in large molecules with large oscillator strengths such as octane and dioxane. We carefully checked for saturation or multiphoton events in methyl formate by varying the laser power. No such evidence was ever observed.

The addition of improved baffles to the laser multipass system has reduced the scattered laser light to a negligibly small level. We have taken advantage of this by increasing the load resistors in the detector circuit. This increases the signal to noise ratio and the detector time constant (to about 0.5 $\mu$s). The gating circuit previously described is still able to completely remove the residual scattered light.

Spectral resolution of the fluorescence is now obtained with a liquid nitrogen cooled Digilab model 296 interferometer. To the original cooling modifications have been added several features to allow data collection in the pulsed mode. The retrace time has been decreased to 60 ms by using a servo controlled retrace. The position of the moving mirror is sensed with a linear mo-
tion transducer. During the retrace, control of the
drive electronics is switched with an analog FET switch
system to a control voltage derived from the trans-
ducer. From the voltage analog of the position is sub-
tracted a dc level corresponding to the desired rest
position. The sum of this error voltage and its deriva-
tive are then applied to the drive motor. By adjusting
the amounts of direct and derivative control signal
the mirror can be made to move smoothly to its zero
position with very little vibration.

For normal operation with an infrared frequency
range of 0–9500 cm⁻¹ the interferometer scans at the
rate of one data point every 400 μs. The laser works
best at a rate of 7.5 Hz; thus only one data point can
be collected every 333rd possible interferometer pos-
tion. Due to thermal focusing in the YAG rod the
laser operates well only if its lamp flashes at a constant
rate. As an example for a 1024 point interferogram,
the computer collects data on the 20th 400 μs clock tick
(derived from the zero crossing of the He–Ne reference
laser interferogram), on the 353rd; on the 686th; and
the 1091th clock ticks during the first interferometer
scan. On the second scan, points are collected on
clock ticks 21, 354, 687, and 1020. The 20 unused clock
ticks are used to prepare the YAG laser for Q switching.
In order to keep the YAG flash lamp firing at a constant
rate the interferometer physical scan continues after
the last data point if necessary. When this occurs ex-
actly one extra laser firing (unused for data collection)
will occur during the mirror retrace.

The actual signal produced by the Michelson inter-
ferometer is the variation in the average value of the
transmitted light. This causes no problem for con-
tinuous, noiseless sources such as blackbodies, but for
pulsed laser collection, laser power fluctuations appear
as noise. Most of this is removed by dividing the signal
accumulated over five "logical" scans (about 1000 phy-
sical scans) point by point by the laser strength accumu-
lated at the same time. That is, two arrays, one of
signal and one of laser intensity, are averaged separately
and then divided point by point. Occasionally a dust par-
ticle in the beam will provide a large noise burst in the
interferogram. These points are removed manually
after the data collection is over. An approximately
accurate value, determined by inspection of the corre-
sponding points in other interferograms of the same
sample, is simply inserted in place of the defective
point.

The variations in sensitivity vs wavelength caused by
the optical system and detector are corrected with a
reference spectrum of a tungsten filament (0.005 in. in
diameter) at 1500 °C. This is done by dividing the re-
corded filament spectrum by that for a known 1500 °C
blackbody times the spectral emissivity of tungsten.
It is also necessary to correct for the electrical fre-
quency response of the filter used in the ordinary
(rather than point by point) collection process of the fila-
ment spectrum. The signal spectrum is divided point
by point by the resulting response function. The final
result is photon flux per unit wave number.

The entire system is controlled by a LSI-11 computer,
which replaces the obsolete NOVA model of the origi-

nal Digilab system. Programs are written in
FORTRAN and assembly language.

Time decays are measured with the circular variable
filter wavelength resolving element described previ-
ously. Spectral linewidths are about 2% of the center
wavelength (e.g., 60 cm⁻¹ at 3000 cm⁻¹ and 20 cm⁻¹ at
1000 cm⁻¹). Data is collected with a Biomation 8100
transient recorder and averaged with the computer.

The nozzle system has a 0.7 mm hole and is crossed by
the laser about 7 cm down stream. Most of the work
reported here was done with a beam of gas prepared by
bubbling air through methyl formate at room tempera-
ture. This produces a mixture of about 75% methyl
formate in 25% air by pressure, and a total pressure of
one atmosphere. The run at 2939 cm⁻¹ used helium in-
stead of air and a mixture of 20% methyl formate in a
nonvolatile liquid (cumene) in the bubbler at a total pres-
sure of two atmospheres. Under these beam conditions
we have never observed any evidence of van der Waals
molecules. The rotational temperature of the air seeded
beams is about 15 K. The rotational temperature in the
He seeded beam is about 1 K. These temperatures are
obtained from an analysis of the rotational band contour
of the laser excitation spectra.

The Einstein A coefficients used in this work were cal-
culated in the usual way from the pressure broadened
gas phase absorption spectrum. The spectrum was
taken using a Nicolet FT-IR. The relative absorption in
the C–H stretching region was apportioned among the
five vibrational bands present with the aid of the argon
matrix IR spectrum published in the literature. The
resultant relative Einstein A coefficients are tabulated
in the Appendix.

RESULTS

Normalized spectra resulting from the absorption of
various laser frequencies in the C–H stretch region are
shown in Fig. 2. Table I lists the experimental inte-
 grated emission intensities. The resultant relative
energy distribution and those calculated by the WR and
DSC methods are shown in Fig. 3. The fluorescence
from 1130 to 1250 cm⁻¹ has been apportioned into con-
tributions from frequencies below 1190 cm⁻¹ and those
above 1190 cm⁻¹. (This corresponds to the location of
the dip at 1190 cm⁻¹ in the 2970 cm⁻¹, low J, spectrum.)
Since the fluorescence from bands near 1150 cm⁻¹ is
badly overlapped the relative intensities in Table I are
normalized to a value of 1.0 for the total fluorescence
intensity from 1130 to 1250 cm⁻¹. In addition for some
of the pumped vibrational bands we were able to mea-
sure fluorescence at 925 cm⁻¹. The experimentally
measured intensities from the 925 cm⁻¹ band, where
available, are included in Table I.

The spectra labeled 2939, 2943, 2947, and 2950 cm⁻¹
in Fig. 2 are the result of pumping various groups of
J states in the δ aldehyde C–H stretch centered at 2939
cm⁻¹. This band is Fermi resonant with the 2913 cm⁻¹
band. All four spectra show resonance fluorescence
which decreases in intensity relative to the relaxed fluo-
rescence as higher and higher \( J \) states are pumped. The width of the resonance fluorescence peak broadens from an instrument limited full width at half-maximum (FWHM) of 8 cm\(^{-1}\) at 2939 cm\(^{-1}\) to a FWHM of 30 cm\(^{-1}\) at 2950 cm\(^{-1}\). This broadening is due to the \( \Delta J = 0, \pm 1 \) selection rules for electric dipole allowed fluorescence. The rotational selection rules are also responsible for the splitting seen in the 2947 cm\(^{-1}\) peak.

**FIG. 2.** Fluorescence spectra from the C–H stretching region of methyl formate. Spectra are labeled by the laser pump frequency (in cm\(^{-1}\)) and the approximate location on the rotational contour of the laser excitation. Intensity of fluorescence is in arbitrary units with the most intense peak of each spectrum normalized to the same height. Beam and laser conditions are described in the experimental section.

**TABLE I.** Observed integrated fluorescence intensities from C–H stretches in methyl formate.

<table>
<thead>
<tr>
<th>Laser frequency(^a)</th>
<th>880–960 cm(^{-1})</th>
<th>1130–1190 cm(^{-1})</th>
<th>1190–1250 cm(^{-1})</th>
<th>1730–1760 cm(^{-1})</th>
<th>1760–1800 cm(^{-1})</th>
<th>Resonance</th>
</tr>
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<tr>
<td>2915</td>
<td>0</td>
<td>0.63</td>
<td>0.37</td>
<td>0.91</td>
<td>0</td>
<td>0</td>
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<tr>
<td>2939</td>
<td>0</td>
<td>0.65</td>
<td>0.35</td>
<td>0.23</td>
<td>1.08</td>
<td>1.14</td>
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<td>2943</td>
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<td>0.33</td>
<td>0.55</td>
<td>0.54</td>
</tr>
<tr>
<td>2947</td>
<td>0</td>
<td>0.67</td>
<td>0.33</td>
<td>0.50(^a)</td>
<td>0.23(^a)</td>
<td>0.29</td>
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<td>0.67</td>
<td>0.33</td>
<td>0.47(^a)</td>
<td>0.10(^a)</td>
<td>0.13</td>
</tr>
<tr>
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<td>0.37</td>
<td>0.71</td>
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</tr>
<tr>
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<td>0.61</td>
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<td>0.43</td>
<td>0</td>
<td>0.05</td>
</tr>
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<td>0.37</td>
<td>0.57</td>
<td>0</td>
<td>0.06(^a)</td>
</tr>
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</table>

\(^a\)Units of wave numbers.
\(^b\)Normalized to intensity from 1130 to 1250 cm\(^{-1}\) (see the text).
\(^c\)Apportioned using dilution factor of unrelaxed fluorescence. See Table II and Eq. (3).
\(^d\)From a more recent, higher signal to noise spectrum than the one presented in Fig. 2.

We observe two kinds of C=O stretch fluorescence in the 2939 cm$^{-1}$ band. At low $J$ we observe mostly fluorescence at 1775 cm$^{-1}$ which has a FWHM of 8 cm$^{-1}$. As the laser is tuned along the rotational contour to higher and higher $J$ states the peak intensity shifts to 1754 cm$^{-1}$ and the fluorescence peak broadens. On the basis of the 21 cm$^{-1}$ blue shift we have assigned the 1775 cm$^{-1}$ fluorescence to the Fermi resonance C=O stretch. The 1754 cm$^{-1}$ fluorescence is relaxed fluorescence from bath states containing C=O stretch oscillator strength.

This assignment is supported by the collisional time dependence of the spectrally resolved fluorescence. These results are shown in Fig. 4. While the resolution of the circular filter machine is not sufficient to totally resolve the 1754 and 1775 cm$^{-1}$ fluorescence the main results are not obscured. Figure 5 shows that the 1775 cm$^{-1}$ and resonance fluorescence are collisionally depopulated at roughly the same rate. The main feature of the 1170 and 1754 cm$^{-1}$ fluorescence decay is the transit of the excited molecules out of the field of view of the detector, a process that takes about 50 $\mu$s. In addition, the 1170 cm$^{-1}$ peak shows a flat top for the first 15 $\mu$s suggesting that it is being collisionally populated. If our spectral resolution were better we would expect to see a similar behavior in the 1754 cm$^{-1}$ fluorescence. All four fluorescence decays show a detector limited rise time. From this we conclude that the fluorescence at 1775 cm$^{-1}$ is unrelaxed fluorescence from the original optically excited zeroth (or perhaps more exactly "first") order state.

The fluorescence in the 1130–1250 cm$^{-1}$ region also changes as the laser is tuned in frequency over the 2939
cm$^{-1}$ band. At low J the peak intensity is at 1185 cm$^{-1}$. At higher J’s the peak intensity is at 1166 cm$^{-1}$ and the proportion of 1130–1250 cm$^{-1}$ fluorescence intensity to the total fluorescence intensity grows larger.

The 2015 cm$^{-1}$ spectrum results from pumping a combination band at 2913 cm$^{-1}$ in Fermi resonance with the 2939 cm$^{-1}$ band. In the laser excitation spectrum of methyl formate, both the 2013 and 2939 cm$^{-1}$ bands have the same B band contour to be expected when the change in the electric motion during the vibration (due to the C=O aldehyde stretch) is nearly parallel to the intermediate moment of inertia. The exact assignment of the zeroth order combination is a little uncertain. The peak intensity of the carbonyl fluorescence slightly is red shifted, as is to be expected, to 1750 cm$^{-1}$. Also as we tune across the rotational band contour the relative fluorescence intensity of the carbonyl fluorescence decreases. However, in the 1130–1250 cm$^{-1}$ region, we cannot sufficiently resolve the fluorescence to identify its red shifted partner. In this region three fundamental frequencies have been assigned at 1167, 1168, and 1207 cm$^{-1}$. They have been approximately described as an $a''$ CH$_2$ rock, an $a'$ CH$_3$ rock, and an $a'$ C=O stretch. Since the overall symmetry of the combination must be $A'$ (the symmetry of the 2939 cm$^{-1}$ band is $a'$), the two choices are 1168 + 1754 = 2922 cm$^{-1}$ or 1207 + 1754 = 2961 cm$^{-1}$. In order to minimize the energy mismatch the combination 1168 + 1754 cm$^{-1}$ combination seems to be most likely.

Using the tabulated Einstein A coefficients in the Appendix, the unrelaxed fluorescence intensities from the 2939 cm$^{-1}$ spectrum, and the positions of the band minimum in the laser excitation spectrum we can calculate the Fermi resonance parameters for the 1168 + 1754 cm$^{-1}$ and C–H aldehyde stretch pair. The same parameters can also be calculated using the blue shift observed in the carbonyl fluorescence of the 2939 cm$^{-1}$ band and the positions of the band minimum in the laser excitation spectrum. Using the relative intensities of the 2939 cm$^{-1}$ fluorescence spectrum we calculate a Fermi resonance interaction matrix element of 9 ± 1 cm$^{-1}$ and an original unperturbed separation of 12 ± 3 cm$^{-1}$. Using the blue shift of the carbonyl fluorescence we find an interaction matrix element of 8 ± 1 cm$^{-1}$ and an original unperturbed separation between the combination band and the C–H stretch of 13 ± 3 cm$^{-1}$. The amount of zero order C–H stretch character at 2939 cm$^{-1}$ is found to be 76% ± 6% and 80% ± 5% by the two methods, respectively.

The spectra labeled 2970, 3012, and 3038 cm$^{-1}$ are from the vibrational bands centered at 2969, 3008, and 3045 cm$^{-1}$ respectively. All three are from vibrational motions that to zeroth order are C–H stretches of the methyl group hydrogens. The 2969 and 3038 cm$^{-1}$ bands both exhibit A type rotational contours in the laser excitation spectrum and have $a'$ symmetry. The 2970 cm$^{-1}$ low J spectrum was produced with the laser pumping the dip between the Q and the R branch. The 3038 cm$^{-1}$ mid J spectrum was produced by pumping the most intense part of the P branch. The 3008 cm$^{-1}$ band exhibits a C type rotational contour in the laser excitation spectrum and therefore has an $a''$ symmetry. The 3012 cm$^{-1}$ mid J spectrum was produced by optical excitation in the most intense part of the R branch. To within the noise level of our experiment we were unable to measure any change in the relative fluorescence intensities of relaxed fluorescence as the laser was tuned over the rotational contour of the 2969, 3008, and 3045 cm$^{-1}$ bands. The spectra chosen for presentation are the ones with the best signal to noise ratio at the lowest possible J.

The fluorescence from the $V=2$ overtone of the C=O stretch is shown in Fig. 5. The laser excitation spectrum exhibits an A/B hybrid rotational band contour centered at about 3498 cm$^{-1}$. By far the most dominant feature of the spectrally resolved fluorescence is the red shifted carbonyl fluorescence at 1745 cm$^{-1}$. This is unrelaxed fluorescence from the $V=2$ to $V=1$ carbonyl stretch transition. The measured integrated intensities of relaxed fluorescence from the carbonyl overtone and those calculated using the WR and DSC methods are given in Table III.

Using the measured relative intensities and the results of the DSC calculations the dilution factor of unrelaxed fluorescence can be calculated. The results are given in Table II and there compared with our earlier determinations. Numbers in parentheses represent upper bounds based on the amount of noise present in the spectra. For this measurement the amount of zero order C–H stretch character in the 2939 cm$^{-1}$ band was assumed to be 80%.

It is clear that collisions have some effect on our spectra taken with a 5 µs gate. In no case was this effect greater than 11% in the measured areas compared to a very short gate (as extrapolated from the time dependent curves). In addition, FTIR spectra taken with a 1 µs gate showed no change in shape of the relaxed peaks, compared to a 5 µs gate. The small errors in the values measured with a 5 µs gate were not corrected for collisions, as the resulting errors which affect only dilution factors are not significant compared to other

<table>
<thead>
<tr>
<th>Frequency</th>
<th>From relaxed$^b$</th>
<th>From absolute$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm$^{-1}$</td>
<td>ratio</td>
<td>resonance intensity</td>
</tr>
<tr>
<td>2915</td>
<td>(0.1)</td>
<td>0.2</td>
</tr>
<tr>
<td>2939</td>
<td>0.23 ± 0.04</td>
<td>0.3</td>
</tr>
<tr>
<td>2943</td>
<td>0.12 ± 0.03</td>
<td>0.3</td>
</tr>
<tr>
<td>2947</td>
<td>0.070 ± 0.014</td>
<td>0.3</td>
</tr>
<tr>
<td>2950</td>
<td>0.033 ± 0.006</td>
<td>0.3</td>
</tr>
<tr>
<td>2970</td>
<td>(0.04)</td>
<td>0.06</td>
</tr>
<tr>
<td>3012</td>
<td>0.032 ± 0.003</td>
<td>0.3</td>
</tr>
<tr>
<td>3038</td>
<td>0.048 ± 0.008</td>
<td>0.2</td>
</tr>
<tr>
<td>3497</td>
<td>0.19 ± 0.03</td>
<td>0.3</td>
</tr>
<tr>
<td>3500</td>
<td>0.14 ± 0.03</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ A dilution factor, $\phi_\alpha = 1.0$ corresponds to no relaxed fluorescence. Values in parentheses are upper bounds.

$^b$ From values in Table I and Fig. 3 using Eq. (4).

$^c$ Measured from IR absorption and laser excitation spectrum using method of Ref. 2. Measured dilution factors are accurate to a factor of 3.
systematic errors (such as possible detector wavelength normalization errors).

**DISCUSSION**

An inspection of the time resolved spectra in Fig. 4 leads to the conclusion that no collisional process could be responsible for the energy transfer we observe. During the 5 μs time period that we normally integrated, the fluorescence intensity only about 1 molecule in 10 on the average collides. When we decreased the number of collisions by either moving the valve further away from the interaction zone or by integrating the fluorescence intensity for a shorter time period we observed no change in the relative fluorescence intensities seen in Fig. 3. Furthermore, all of the time resolved spectra in Fig. 5 show the same detector limited rise time of ~0.25 μs. For this rise time to be due to collisions at the 15 K rotational–translational temperature of our beam would require cross sections on the order of 3000 Å². Barring the presence of such huge cross sections, we are confident that fluorescence spectra we observe are the product of intramolecular energy transfer processes.

The actual collision cross sections we see are 100 (+200–50 Å²). We feel that this is a reasonable size for these weakly state-mixing collisions. We feel that since this type of collision is expected to occur, and we do see them, that seeing no other larger cross section collisional process means that we are safe in believing that the relaxation we see is intrinsically intramolecular. We do admit that we would only feel absolutely safe if we could exclude 15,000 Å² collisions.

The observed fluorescence spectra are the result of the Einstein A coefficient weighted population of states following the optical excitation. To estimate the extent of vibrational energy mixing, the relative apportioning of energy among the IR active modes obtained from the experimental relative fluorescence intensities was compared with the results of the statistical model calculations. The statistical model assumed that all states within a given band of energy centered on a C–H stretch fundamental frequency were equally populated. The required vibronic state densities were calculated using either the WR formulas or by a direct state count. The WR method produces a smoothed density of states. Over the 2500–3500 cm⁻¹ energy range, it produces no variation in the character of the bath states. That is it predicts, e.g., that over this energy range the relative proportions of bath states containing Δν = –1 carbonyl oscillator strength and C–O stretch oscillator strength will be the same in the neighborhood of each vibrational transition. The results of the WR calculation are indicated by the lines in Fig. 3. The experimentally observed relative energy contents for the two vibrational bands lowest in energy (1168 and 1207 cm⁻¹) show minimal variation. This situation does not hold for the higher energy carbonyl stretch mode which, as Fig. 3 makes clear, varies much more in relative energy content from band to band.

In an effort to model the fluctuation in the amount of C=O character in the bath states, we calculated the nearby density of states by the use of direct state counting, assuming bath state "premixing" to produce smoother distributions than a direct model of our 1 cm⁻¹ excitation would produce. The results of the DSC calculations are shown in Fig. 3. When the averaging is done over relatively narrow energy ranges, there are substantial fluctuations in the relative energy content of all of the vibrational modes. As the averaging is done over broader energy ranges the fluctuations in the relative energy content of the lowest energy modes disappear first and approach the WR results. The fluctuations in the relative energy content of the C=O stretch are the last to damp out. The DSC calculated energy content of the carbonyl stretch does not converge to the WR result until the averaging is done over about an 80 cm⁻¹ range. The good agreement of the DSC 20 calculation with the experimental results is at least partly fortuitous. It is in part due to the approximate correction for anharmonicities in the bath states (which can be expected to be on the order of 10 cm⁻¹) that averaging over 20 cm⁻¹ provides. The main result of the DSC calculations is to demonstrate that the greater fluctuation in the relative energy content of the carbonyl fluorescence can be attributed mainly to the lumpiness in the distribution of C=O oscillator strength amongst the bath states. The carbonyl is higher in frequency than the other fluorescence bands, so its combination bands are much less evenly distributed in the C–H stretching region than lower frequency modes. This lumpiness rather than a systematic variation in the matrix elements coupling the various zeroth order C–H stretches to the individual ℓ(abj) explains most of the differences we see in the relative relaxed fluorescence intensity ratios. No evidence is seen that suggest any subset of the bath vibrational motions is substantially decoupled from the others.

Using the experimentally observed relative fluorescence intensities and the populations calculated from our statistical model the dilution factor of unrelaxed fluorescence can be measured. This dilution factor when compared with dilution factors measured from the absolute fluorescence intensity of unrelaxed fluorescence provides another indication of the validity of the statistical model. The dilution factors measured by the two different methods are shown in Table II. The dilution factors measured from the absolute intensity of unrelaxed fluorescence are averaged over the entire rotational band contour of the vibrational states. The dilution factors measured from the relative intensities of unrelaxed and relaxed fluorescence are averaged over a 1 cm⁻¹ wide section of the rotational band contour. To within a factor of 10 the φd measured by the two different methods agree. Since φd can vary by the same factor of 10 over a rotational band contour of a given vibrational state and since the uncertainties in our measured values are rather large, the measurements of φd using the two different methods are in fair agreement. Both measured values of φd vary over roughly the same factor of 10. There is also no striking difference in the magnitude of the dilution factors in the C–H stretch region (state density = 12 to 17 cm⁻¹) and the dilution factor of unrelaxed fluorescence from the C=O stretch overtone (state density ~33 cm⁻¹). The magnitude of the observed dilution factors makes it
TABLE III. Observed and calculated fluorescence intensities* from the $V = 2$ C=O stretch.

<table>
<thead>
<tr>
<th>Laser frequency$^b$</th>
<th>Model$^c$</th>
<th>1130–1190 cm$^{-1}$</th>
<th>1190–1250 cm$^{-1}$</th>
<th>Relaxed C=O</th>
<th>Unrelaxed C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>3497</td>
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<td>0.71</td>
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<td>5.9</td>
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<tr>
<td>3502</td>
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<td>0.27</td>
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<tr>
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<td>DSC 4</td>
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<td>0.36</td>
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</tr>
<tr>
<td></td>
<td>DSC 10</td>
<td>0.66</td>
<td>0.34</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DSC 20</td>
<td>0.60</td>
<td>0.40</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td></td>
<td>WR</td>
<td>0.55</td>
<td>0.45</td>
<td>0.58</td>
<td></td>
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</tbody>
</table>

*Intensities normalized to a value of 1, 0 for 1130 to 1250 cm$^{-1}$.
$^b$Frequencies in cm$^{-1}$.
$^c$See the text for a description of model calculation.

clear that most of the energy originally deposited in the zeroth order optically excited state is transferred to the bath states.

The slight variations in $\phi_4$ between the various optically excited vibrational bands is due to differences in the isoenergetic vibronic density of states and the matrix elements coupling the zeroth order optically excited state to the bath states. These couplings of the C–H stretch and overtone states to the bath vary by about a factor of 3.

The rotational dependence of vibrational energy transfer is shown by the 2939, 2943, 2947, and 2950 cm$^{-1}$ spectra in Fig. 2. All these spectra were recorded at various portions of the band profile of the 2939 cm$^{-1}$ band. The approximate average $J$ pumped is indicated by each spectrum in Fig. 2. As the laser is tuned to higher and higher states the amount of relaxed fluorescence relative to unrelaxed fluorescence grows as is seen also by the tabulated dilution factors in Table II. This behavior can be rationalized in part by the increased degeneracy at higher $J$. Each $J$ state has $2J+1$ $K$ states. Since methyl formate is an asymmetric top these $K$ states can mix essentially like vibrations in that energy transfer between two states of the same $J$ but differing $K$ can take place without violating the conservation of angular momentum. Thus, the net effect is for the effective rovibronic density of states to increase as $J$ is increased. Also in an asymmetric near prolate top such as methyl formate; the width in energy of states populated by a given $J$ increases as $J$ increases due to the $K$ splittings. This effect can help to lessen the energy mismatch between the bath state and the original optically excited state(s). A substantial part of the width $\Delta \omega$, necessary to match our data may be due to rotational coupling.

At this point it seems appropriate to point out that by using a laser with a bandwidth of 1 cm$^{-1}$ we are not exciting individual rovibronic states, but rather a group of them. With the laser tuned to the low $J$ position of the band it is still possible to excite some states with a fairly high $J$. Thus the labels of average $J$ in Figs. 3 and 6 should only be taken as rough averages.

One somewhat surprising feature of the fluorescence spectra in Fig. 2, is that no shift in frequency is seen in the positions of the relaxed (as opposed to Fermi resonant) fluorescence. One would expect that the anharmonicities in the combination modes and overtones comprising the bath states would lead to shifts in frequency on the order of a few (3–10) cm$^{-1}$. This effect should be particularly evident in the relaxed carbonyl fluorescence of the 2939 cm$^{-1}$ band. In this band, the DSC indicates that there is no bath state at 2939–1754 cm$^{-1}$ for the 2939 cm$^{-1}$ band to fluoresce to (see Fig. 4). Yet an inspection of the spectra indicates that the frequency of the relaxed carbonyl fluorescence is always at 1754 cm$^{-1}$. This failure to observe a shift in frequency of the fluorescence can be attributed in part to the randomness of frequency shifts in the vibrational frequencies of the bath modes due to anharmonicities. The remainder of the energy difference could be made up by the averaging in $J$ states produced by our 1 cm$^{-1}$ laser width and the rotational temperature of our beams.

CONCLUSIONS

The amount of data now available on methyl formate allows us to well characterize the fate of vibrational energy deposited in an optically excited state from 2900 to 3500 cm$^{-1}$. Even though the vibronic state densities in this region are rather modest (12–33 cm$^{-1}$); 70% or more of the energy deposited in the optically excited state is essentially randomized among the isoeenergetic bath states. This is true no matter what the zeroth order description of originally excited state. With the usual caveat that we can only monitor fluorescence from those states of high oscillator strengths; there is no subset of the bath vibrational normal modes that is substantially decoupled from the rest. In addition, the magnitude of the matrix elements that produce the vibrational mixing we observe varies (by a factor of 3) for the optically pumped states. This result is consistent with the variation in threshold for the dilution of resonance fluorescence from C–H stretch fundamentals observed earlier.

Even though we have shown that our data agree with a "statistical" model of bath states, there are state population fluctuations caused by varying $s$–$l$ coupling and by the "lumpiness" of the positions of zero order states in the bath. These variations are substantial.

It can also be concluded that under the proper conditions intramolecular vibrational energy transfer can be strongly dependent upon the initial $J$ state. This is evident from the variation in $\phi_4$ across the rotational contour of the 2939 cm$^{-1}$ band and from the failure to observe slight shifts in the frequency of relaxed fluores-
TABLE IV. Relative Einstein A coefficients of methyl formate.

<table>
<thead>
<tr>
<th>Vibrational* frequency (cm$^{-1}$)</th>
<th>A coefficient</th>
</tr>
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<tbody>
<tr>
<td>925</td>
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<tr>
<td>1168</td>
<td>100</td>
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<td>1207</td>
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<tr>
<td>2869</td>
<td>78</td>
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<tr>
<td>3008</td>
<td>41</td>
</tr>
<tr>
<td>3045</td>
<td>28</td>
</tr>
</tbody>
</table>

*Frequency in cm$^{-1}$.

In a basis set of rigid free rotor wave functions with the structural parameters $F = 5.25$ cm$^{-1}$, $V_5 = 361$ cm$^{-1}$, $V_6 = +19$ cm$^{-1}$ given in Refs. 7 and 8. The WR calculations assumed that the methyl rotor was harmonic. Various values for the frequency of the methyl rotor from 50 to 250 cm$^{-1}$ had little effect on the calculated density of states.

The Einstein A coefficients were calculated from the measured pressure broadened gas phase absorption spectrum in the usual way. The crowded C–H stretching region was apportioned using the matrix spectrum of Ref. 6. The A coefficients used (in arbitrary units) are given in Table IV.


For the DSC calculations the energy levels of the methyl rotor (fundamental frequency at 124 cm$^{-1}$) were calculated from the potential function

$$V(\phi) = \frac{V_2}{2} (1 - \cos 3\phi) + \frac{V_4}{2} (1 - \cos 6\phi).$$

Acknowledgment
This work was supported by the National Science Foundation under grant title NSF CHE 80-20454.

Appendix
The following vibrational frequencies (in cm$^{-1}$) were used in the density of state calculations. They were compiled from Refs. 4–6:

\[d'\] 3045, 2969, 2939, 1754, 1465, 1445, 1371, 1207, 1168, 925, 727, 325,

\[d''\] 3008, 2473, 2287, 2032, 341, 124.