

Limits on the lifetimes of intramolecular rovibrational relaxation

Thomas Kulp, Rodney S. Ruoff, and J. D. McDonald

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

(Received 12 October 1984; accepted 19 November 1984)

Rotationally resolved infrared laser induced fluorescence spectra are presented for dimethyl ether and methyl formate. Q branch spectra are presented for 1,4-dioxane, methyl formate, and dimethyl carbonate. It has been demonstrated earlier that all of these states intramolecularly vibrationally relax. Lower limits on the lifetime of this process are inferred from the present data. For methyl formate and dimethyl ether the $J = 1$ and 2 states have linewidths $< 0.31 \text{ cm}^{-1}$. This sets a lower limit on the lifetime of 15 ps, although for the limited number of coupled states an exponential decay is not expected. This is also the lower limit for relaxation in the higher $J = 20$ states of 1,4-dioxane and methyl formate, for which exponential decays probably do occur. Dimethyl carbonate relaxes in greater than 10 ps. All measurements were performed in a pulsed supersonic beam with an infrared optical parametric oscillator.

INTRODUCTION

The vast majority of the accumulated data concerning intramolecular vibrational relaxation (IVR) rates indicate that the process is very rapid (from 10^{-10} – 10^{-14} s lifetimes). These studies involve a variety of molecular sizes, excitation energies, and excitation methods. They include lifetimes inferred from branching ratios for competing reactions,¹ fluorescence gated by collisional quenching,² spectral linewidth studies at a variety of excitation energies,^{3–6} and, most recently, an actual measurement of the fast exponential decay of a coherently excited rovibronic wave packet in the first singlet state of stilbene.⁷ While a large amount of spectroscopically derived work has been done in the electronically excited manifold, relatively little has been done in the ground state, and less still at those density of states regions in which IVR just begins to occur. Also, because of the difficulty inherent in resolving individual rotational lines in polyatomic molecules, many of the existing studies are averaged over several J states. Each of these J states is an individual "zeroth order" state in that it conserves a particular angular momentum value and can therefore couple differently than others through rotational-vibrational interactions. In this paper we attempt to estimate the lifetimes of ground state CH stretch rovibronic states in some of the molecules which we have studied in our vibrational relaxation experiments.^{8–11} Our data consists of total infrared fluorescence excitation spectra obtained by exciting molecules cooled in a supersonic expansion with a tunable infrared optical parametric oscillator (OPO). The resolution of the OPO has been increased through the use of intracavity etalons and careful tuning of the YAG Q switch opacity. The linewidths of the transitions (which are unfortunately in some cases still limited by the width of the laser) provide limits on the lifetime of the zeroth order state.

Because Coriolis coupling causes the magnitude of rovibronic coupling to vary as a function of J it is

desirable to measure the widths of both low and high J states. At our present resolution this requires two types of data. We measured the widths of low J , K states by cooling to very low temperatures (~ 1 K) so that we were able to actually resolve the rotational structure. This also allowed us to see some very weak, closely spaced Fermi resonances which were previously concealed under the rotational contours. Widths of higher J states were estimated by measuring the widths of Q branches at higher temperature (~ 30 K). This temperature is high enough to populate J 's as high as 20, but low enough to prevent vibrational hot bands from appearing.

The molecules which we have chosen for the low temperature measurements, methyl formate and dimethyl ether, both show strong rotational dependencies in their relaxed fluorescence. Preliminary, unpublished, results from our spectrally resolved fluorescence studies demonstrate that the individual rovibronic states which we resolve ($J = 1, 2$) are, in fact, mixed. The data indicates that the dilution factors are between 0.1 and 0.15 for dimethyl ether and ~ 0.3 for methyl formate. If equal coupling is assumed, this would mean that the CH stretches are mixed with 6 to 10 bath states in the first case and 3 in the latter. For the high J measurements we chose dioxane, methyl formate, and dimethyl carbonate. (Dimethyl ether does not have pronounced Q branches.) We have published data on the relaxation of dioxane¹¹ and methyl formate⁹ at $T = 30$ K in earlier papers. We have data on dimethyl carbonate which shows that it is a very strongly relaxing molecule which emits no unrelaxed fluorescence in the CH stretching region.

EXPERIMENTAL

Methyl formate and dimethyl carbonate were purchased from Aldrich, dioxane was purchased from MCB, and dimethyl ether was supplied by Matheson. All chemicals were used as they came without further purification.

The molecular beam was produced by expansion

into a vacuum through a pulsed solenoid valve. The higher temperature experiments used a valve of our own design with a 0.8 mm diameter orifice. For the lower temperature measurements we used a pulsed valve produced by General Valve. Its orifice was the same size, but it was more reliable in opening against the higher back pressures. The ambient pressure in the chamber was maintained at $<10^{-4}$ Torr. For the higher temperature data the chemicals were seeded in air and heated in some cases to increase vapor pressure. The lower temperature scans required that the molecules be seeded in ~ 40 psi of helium and, for the case of methyl formate, diluted in cumene to reduce vapor pressure. This allowed us to achieve temperatures of ~ 1 K. Higher pressures (up to 100 psi He) produced colder beams, but the S/N quality in these scans was not good enough to consider including them.

The laser used was a YAG pumped homebuilt optical parametric oscillator (OPO) which has been described previously.^{8,9} Its beam was multipassed approximately 40 times through the molecular beam at a distance of 7 cm, downstream from the nozzle. The average energy per 10 ns pulse varied between 4–6 mJ. The electric field of the laser was polarized in the plane formed by the molecular beam and the line of sight of the detector, although measurements were also made with perpendicular polarization to confirm that this variable has no effect on the linewidths. To achieve the narrower linewidths used in this study both the OPO and the YAG were run with intracavity etalons. This limited the width of the YAG to ~ 0.25 cm^{-1} . The low frequency output of the OPO (idler) has a spectrum given by the convolution of the YAG and the signal. This gives it a width of 0.31 cm^{-1} , the width used in our Q branch studies. During our colder runs we narrowed the YAG to a greater degree (0.18 cm^{-1}) by adjusting the Q switch voltage. When the Q switch voltage is lowered, the YAG is allowed to "prelase" on the highest gain modes of the cavity while the Q switch is on. When the switch is fully opened the stored energy is dumped into only a few or possibly only one cavity mode. Which mode it chooses, is however, not controllable. This causes it to hop from mode to mode each shot, and the time averaged sum of these frequencies determines the effective output. This tends to give the laser output a trapezoidal shape.

The total fluorescence was detected with a mercury doped germanium crystal operated at liquid helium temperatures. The signal was integrated for 5 μs following the laser pulse. Background emission is reduced by cooling the entire vacuum chamber to liquid nitrogen temperatures.

The effect of collisions on our data has been investigated previously by time resolving both the resonance and relaxed fluorescence from 1,4-dioxane¹¹ and methyl formate⁹ in air seeded beams. Measurements have also been made on molecules in helium seeded beams such as methane and 2,3-dihydrofuran. In no case could more than 11% of the relaxed fluorescence, integrated with the 5 μs gate be attributed to intermolecular processes. In addition, calculations comparing this data to genuinely

collisionally relaxed data show that collisions could not cause the preliminary state selective fluorescence spectra taken on this molecule.

The data was analyzed with the help of a computer program, provided by Dr. William Murphy of the Canadian National Research Council, which simulates the absorption contours of asymmetric top molecules. We have modified the code to allow it to run on a VAX 11-780, and have added code to correctly account for the freezing of the nuclear spins at their high temperature limiting state distribution.

RESULTS AND DISCUSSION

The region from 2850 to 2975 cm^{-1} in dimethyl ether is highly overlapped when viewed at 30 K. At colder temperatures (Fig. 1) at least four major structures are evident. In our earlier work we suggested that the region between 2853 and 2893 cm^{-1} is due to predominantly CH stretch containing bands. The transitions above 2910 cm^{-1} were observed to produce a large amount of fluorescence at ~ 1450 cm^{-1} , indicating a strong Fermi resonance between combinations or overtones containing CH bending modes and CH stretch vibrations. In each of these regions the cold spectrum clearly resolves two major bands and leaves open the possibility of other minor overlapped features.

More detail may be obtained by greater cooling and higher resolution. This is demonstrated in the lower half of Fig. 1 for a scan of the 2864 to 2890 cm^{-1} region. All visible peaks are limited in width by the resolution of the laser which is ~ 0.31 cm^{-1} in this case. One immediately notices two distinct rotational contours which appear to

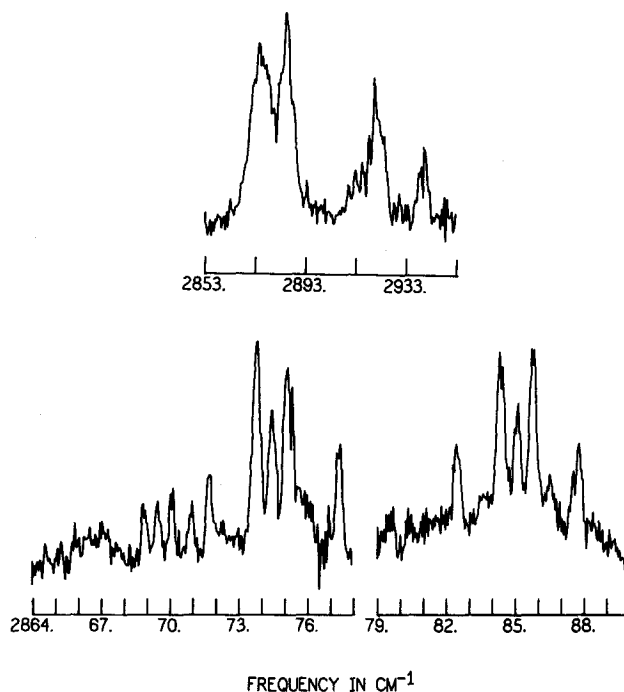


FIG. 1. Above: Fluorescence excitation spectrum of dimethyl ether at intermediate cooling, low resolution (1 cm^{-1}). Below: Fluorescence excitation spectrum scan of dimethyl ether at ~ 2 K, ~ 0.31 cm^{-1} resolution.

be centered at 2874.5 and 2885 cm^{-1} . These correspond to the two major bands observed at lower resolution. Synthesis of the rotational structure of dimethyl ether allowed us to determine that both bands obey *C* type selection rules. The temperature which best fits the data is ~ 2 K.

In addition to these two main bands, other smaller features are present. Four peaks are visible at ~ 2870 cm^{-1} which probably represent the rotational structure of a single vibrational transition. It is not readily apparent what type of transition it is. Also, a weaker unresolved "lump" can be seen at 2867 cm^{-1} . Because any assignment of the CH stretching region of dimethyl ether is highly uncertain, it is not possible to firmly identify the nature of these states. However it does seem quite likely that they are due to weaker, more closely spaced Fermi type resonances.

By altering the *Q* switch voltage, resolutions as high as 0.18 cm^{-1} are attainable. This method (along with additional cooling) was used to produce the spectra shown in Fig. 2 for methyl formate and dimethyl ether. Below each spectrum is a synthesized contour using conditions which best fit the data. For both cases the intensities were calculated assuming no cooling of the nuclear spins during the expansion.

The dimethyl ether scan is of the *C* contour absorption at 2885 cm^{-1} . Its temperature is 1.5 K. The methyl formate transition is the aldehyde CH stretch at 2939

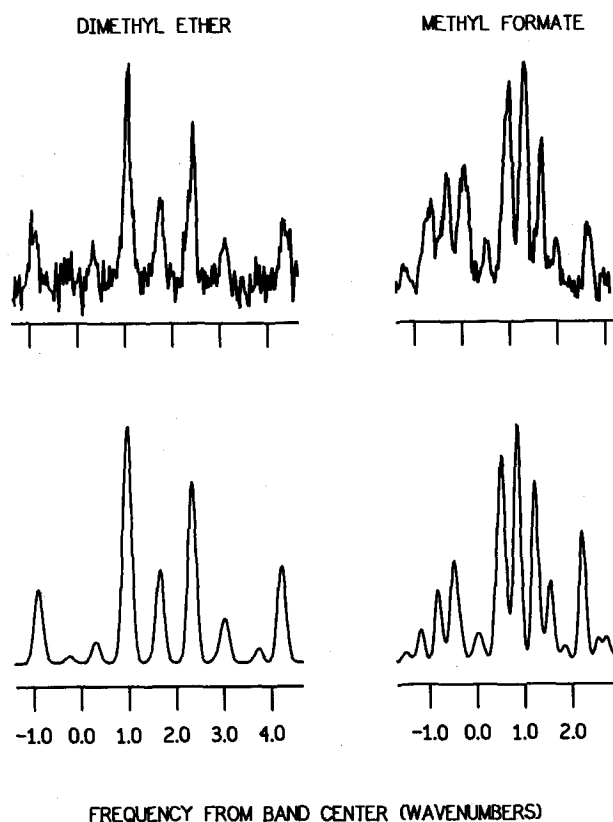


FIG. 2. Above: High resolution (0.18 cm^{-1}) scans of dimethyl ether (2885 cm^{-1} line) and methyl formate (2939 cm^{-1}). Below: Computer simulations of the rotational structure. For dimethyl ether the band is a 1.5 K *C* contour. For methyl formate a 1 K, 1:9 *A*:*B* hybrid gave the best fit.

TABLE I. Dominant rotational lines in Fig. 2.

Relative frequency (cm^{-1})	Assignment	Relative intensity
Dimethyl ether		
-0.958	$1_{01} \leftarrow 1_{11}$	0.46
-0.920	$2_{02} \leftarrow 2_{12}$	0.57
-0.264	$1_{10} \leftarrow 2_{02}$	0.11
0.264	$2_{02} \leftarrow 1_{10}$	0.33
0.920	$2_{12} \leftarrow 2_{02}$	0.58
0.958	$1_{11} \leftarrow 1_{01}$	2.70
1.628	$1_{10} \leftarrow 0_{00}$	1.40
2.298	$2_{11} \leftarrow 1_{01}$	2.70
2.988	$3_{12} \leftarrow 2_{02}$	0.45
2.992	$2_{20} \leftarrow 2_{12}$	0.17
3.699	$4_{13} \leftarrow 3_{03}$	0.21
4.176	$2_{20} \leftarrow 1_{10}$	1.06
4.214	$2_{21} \leftarrow 1_{11}$	0.46
Methyl formate		
-1.197	$1_{01} \leftarrow 2_{12}$	0.75
-0.815	$2_{12} \leftarrow 3_{03}$	0.20
-0.843	$0_{00} \leftarrow 1_{11}$	1.49
-0.547	$2_{02} \leftarrow 2_{11}$	0.93
-0.489	$1_{01} \leftarrow 1_{10}$	2.07
-0.407	$0_{00} \leftarrow 1_{01}$	0.56
-0.373	$1_{11} \leftarrow 2_{02}$	0.51
-0.053	$1_{11} \leftarrow 1_{10}$	0.41
-0.053	$1_{10} \leftarrow 1_{11}$	0.45
-0.373	$2_{02} \leftarrow 1_{11}$	0.87
-0.407	$1_{01} \leftarrow 0_{00}$	1.01
0.489	$1_{10} \leftarrow 1_{01}$	4.18
0.547	$2_{11} \leftarrow 2_{02}$	2.04
0.809	$2_{02} \leftarrow 1_{01}$	1.11
0.815	$3_{03} \leftarrow 2_{12}$	0.64
0.843	$1_{11} \leftarrow 0_{00}$	5.00
1.197	$2_{12} \leftarrow 1_{01}$	4.18
1.526	$3_{13} \leftarrow 2_{02}$	1.79
1.823	$4_{14} \leftarrow 3_{03}$	0.42
2.175	$2_{21} \leftarrow 1_{10}$	2.07
2.233	$2_{20} \leftarrow 1_{11}$	2.10
2.529	$3_{22} \leftarrow 2_{11}$	0.66
2.711	$3_{21} \leftarrow 2_{12}$	0.69

cm^{-1} with a temperature of 1 K. This state is actually one member of a strong Fermi resonance pair which contains $\sim 80\%$ CH stretch character and 20% of a combination between a CH_3 rock at 1168 cm^{-1} and the carbonyl stretch at 1754 cm^{-1} . While its rotational structure has previously been labeled as a *B* contour, our data was best fit by assuming a 1:9 *A*:*B* hybrid ratio. This makes physical sense since the aldehyde CH bond is located at an angle between the *A* and *B* axes causing the dipole moment change to have components in both directions.

The assignments of the various rotational transitions are listed in Table I. It is clear that the features at 1.197 and 1.526 cm^{-1} in methyl formate and 1.628 and 2.298 cm^{-1} in dimethyl ether are due to individual zeroth order rotational states. Following the collection of the spectra, a scan was made of the rotational structure of ethylene oxide, a molecule which should provide very narrow Doppler limited linewidths. In no case could we state with confidence that these lines were any narrower than those observed in the data. Thus our low temperature

measurements are limited by the laser width and provide upper limits on the widths of the rotational lines.

Because the data represent total fluorescence spectra rather than absorption spectra, the relation of the linewidth to the dephasing rate of the coherently excited zeroth order state requires special consideration. Each rotational line represents a contour which outlines the unresolved molecular eigenstates that contain the zeroth order optical activity. The spectrum can be described by a phenomenological model⁹ abridged from the theory used to describe vibrational relaxation in excited electronic states.¹² Each molecular eigenstate can be written as a linear combination of basis states:

$$|j_k\rangle = C^k |j_s\rangle + \sum_{\alpha,\beta,\gamma,\dots} C_{\alpha,\beta,\gamma,\dots}^k |l_{\alpha,\beta,\gamma,\dots}\rangle,$$

where $|j_s\rangle$ is the active rovibronic state and $|l_{\alpha,\beta,\gamma,\dots}\rangle$ is an inactive rotational state of a nearby combination or overtone. Here $\alpha, \beta, \gamma, \dots$ specify rotational and vibrational quantum numbers. The probability of observing the molecule in state $|j_s\rangle$ is given by $|C^k|^2$, leading to the expression for the absorption intensity:

$$I_{k,s} = \mathcal{L}(k, \omega) N_0 B_{0,s} |C^k|^2,$$

where N_0 is the molecule density in the lower state, $\mathcal{L}(k, \omega)$ is the photon flux in quanta per cm^2 per wave number at the excitation frequency, and $B_{0,s}$ is the Einstein B coefficient for absorption into the zeroth order state. B can be considered to be a product of a rotational and vibrational factors:

$$B_{0,s} = (B_{\text{rot}})(B_{\text{vib}})_{0,s}.$$

The emission intensity can be written as

$$I_{k,s} = \mathcal{L}(k, \omega) N_0 B_{0,s} |C^k|^4 \sum_r A_{s \rightarrow 0,r},$$

where the emission to all allowed rotational states (r) of the ground vibrational state is summed. Here we are only considering emission out of the optically active zeroth order state. Emission also occurs from the $|l_{\alpha,\beta,\gamma}\rangle$ states with which $|j_s\rangle$ is mixed. However, by using a filter which passes only resonance fluorescence we have determined that the fluorescence is predominantly from the optically active fundamental. At the levels of rotational excitation involved the states are mixed, but not very extensively. Thus we will neglect the contribution of relaxed fluorescence to the total intensity.

All of the terms in the above expression are constant for C^k (assuming the wavelength differences between the eigenstates are negligible). The contour is defined by the apportionment of the $|j_s\rangle$ character among the eigenstates. In the absorption spectrum I_k is proportional to $|C^k|^2$, whereas the fluorescence spectra has I_k proportional to $|C^k|^4$. Thus, to relate the width of the line to the dephasing rate we must take the square root of its spectrum. Equivalently, we may also measure the full width at quarter maximum.

Care was taken up to insure that saturation did not affect the linewidths measured. By attenuating the laser

by known amounts and viewing the fluorescence it was established that all data was taken in the linear regime. Polarization of the fluorescence with respect to the detector configuration also presents a possible source of error. This may effect the relative total emission intensities of the different zeroth order rotational lines due to retention of some degree of spatial polarization under conditions in which the molecule rotates but does not undergo collisions.¹³ Rovibrational state mixing may affect the polarization of fluorescence also. In this case states which are described as statistical mixtures of many different K states are expected to emit light which is more depolarized than that from a corresponding rigid rotor state.¹⁴ By comparing the spectra obtained by using laser light polarized in each plane it was determined that polarization effects did not influence our data on linewidths.

The widths of the individual rotational states in methyl formate and dimethyl ether are limited to $\leq 0.31 \text{ cm}^{-1}$ at quarter maximum. This corresponds to a relaxation time of $\geq 16 \text{ ps}$. From our preliminary spectrally resolved dimethyl ether data, which gives dilution factors of 0.10–0.15 for the individual rotational states, we calculate that these states are coupled to 6 to 10 bath states (if equal coupling is assumed). Coherent excitations of the entire rotational line would be likely to result in intermediate case behavior in which an initial falloff of fluorescence occurs with a fall time of $\geq 16 \text{ ps}$ followed by quantum beats at longer times.

The 30 K Q branch measurements are shown in Fig. 3. The average J state present in the Q branch at this temperature is ~ 11 for methyl formate, ~ 13 for dioxane, and uncertain for dimethyl carbonate. We could not make a measurement for dimethyl ether since it does not have sharp Q branches.

In all the Q branch measurements, the total fluorescence is predominantly relaxed. Thus, here a measurement of the full width at half-maximum provides the lifetime limit.

The dioxane spectrum is taken from the A/C hybrid CH stretch at 2898 cm^{-1} . Its width is limited by the laser to 0.31 cm^{-1} . The methyl formate band is the C contour CH stretch at 3004 cm^{-1} . Its width is 0.4 cm^{-1} which is definitely broader than the laser. This is exactly the width which we calculate with our program (assuming equal ground and excited state rotational constants) by convoluting a 0.025 cm^{-1} resolution spectrum with a 0.3 cm^{-1} Lorentzian laser function. While it is impossible to do more than place a limit on the width of the higher J states, it does seem likely that they are quite narrow.

The dimethyl carbonate peak is difficult to analyze because it has conformers and its rotational constants are not well known. We have included it because it is an example of a molecule which relaxes very extensively. The Q branch shows a very strange shape which is about 0.5 cm^{-1} wide at half-maximum. It is likely that we are seeing effects due to lifetime broadening here. Unfortunately, the intensity of the fluorescence when cooled to lower temperature was so low as to make it impossible to measure a single rotational state.

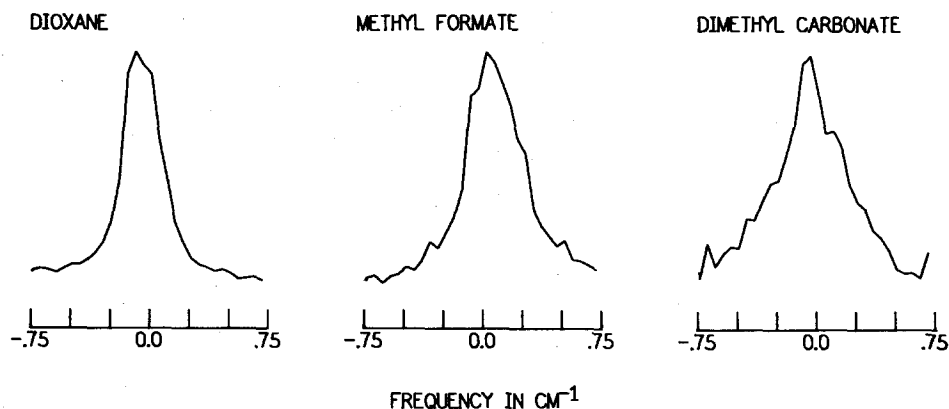


FIG. 3. Q branches for 1,4 dioxane (2898 cm^{-1}), methyl formate (3004 cm^{-1}), and dimethyl carbonate (3006 cm^{-1}). Laser width is 0.31 cm^{-1} .

CONCLUSIONS

Because the measured widths of the low J rotational states match the widths of the rotational lines of ethylene oxide (a molecule whose rotational lines are expected to be Doppler limited to $\sim 500\text{ MHz}$) measured with our laser, it seems we can speculate that the actual widths are quite a bit less than 0.31 cm^{-1} . At the level of coupling involved in these rovibronic states we do not expect to see homogeneous Lorentzian line shapes at infinite resolution. Rather we expect to resolve a cluster of eigenstates. It is possible that higher resolution of our lines would reveal a narrow, central peak surrounded by a few small resonances. It is also possible that in some cases at low J all the relaxed fluorescence is due to nearby Fermi resonances of the type observed above in dimethyl ether, and that the rotational lines represent true molecular eigenstates. This is the type of behavior one might expect at low J in intermediate molecules which have strong rotational dependences in their relaxation. Our preliminary spectrally resolved data supports the conclusion that the rotational dependencies in their relaxation. Our preliminary zeroth order feature. The dilution factors for dimethyl ether of 0.10–0.15 and the $J = 1$ rovibrational state density of $\sim 75\text{ states/cm}^{-1}$ are consistent with linewidths of $0.08\text{--}0.13\text{ cm}^{-1}$. There do not appear to be enough of the Fermi multiplets to account for the measured dilution factors.

The Q branch data demonstrates that the widths at higher J are also not very great in methyl formate and dioxane. In no case can we say that the relaxation time is less than 15 ps, and in reality it is probably quite a bit greater. To truly answer these questions, higher resolution is needed.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation.

- ¹ I. Oref and B. S. Rabinovitch, *Acc. Chem. Res.* **12**, 1979 (1966).
- ² C. S. Parmenter, *J. Phys. Chem.* **86**, 1735 (1982).
- ³ K. V. Reddy, D. F. Heller, and M. J. Berry, *J. Chem. Phys.* **76**, 2814 (1982).
- ⁴ H.-R. Dubal and M. Quack, *Chem. Phys. Lett.* **72**, 342 (1980).
- ⁵ E. Abramson, R. W. Field, D. Imre, K. K. Innes, and J. L. Kinsey, *J. Chem. Phys.* **80**, 2298 (1984).
- ⁶ S. M. Beck, D. L. Monts, M. G. Liverman, and R. E. Smalley, *J. Chem. Phys.* **70**, 1062 (1979).
- ⁷ J. W. Perry, N. F. Scherer, and A. H. Zewail, *Chem. Phys. Lett.* **103**, 1 (1983).
- ⁸ G. M. Stewart and J. D. McDonald, *J. Chem. Phys.* **78**, 3907 (1983).
- ⁹ G. M. Stewart, M. D. Ensminger, T. J. Kulp, and R. S. Ruoff, *J. Chem. Phys.* **79**, 3190 (1983).
- ¹⁰ G. Stewart, R. Ruoff, T. Kulp, and J. D. McDonald, *J. Chem. Phys.* **80**, 5353 (1984).
- ¹¹ T. Kulp, R. Ruoff, G. Stewart, and J. D. McDonald, *J. Chem. Phys.* **80**, 5359 (1984).
- ¹² K. F. Freed and A. Nitzan, *J. Chem. Phys.* **73**, 4765 (1980).
- ¹³ G. W. Loge and C. S. Parmenter, *J. Chem. Phys.* **74**, 29 (1980).
- ¹⁴ G. M. Nathanson and G. M. McClelland, *J. Chem. Phys.* **81**, 629 (1984).