

CH stretch excitation causes conformational interconversion in ground state methyl vinyl ether but not in methyl nitrite

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Molecules exhibiting conformational isomerism have been studied by spectrally resolving the infrared laser induced fluorescence from CH stretch fundamental excitation of methyl vinyl ether and from CH stretch fundamental and N=O overtone excitation of methyl nitrite. By comparison of the resolved fluorescence spectra of methyl vinyl ether with its absorbance spectrum, we have observed the first case of state selected ground electronic state intramolecular conformational interconversion in an isolated molecule. The distribution of conformers is altered drastically by the deposition of energy. The *cis/trans* ratio of the laser excited molecules may also be sensitive to the laser excitation frequency. Excitation of the N=O overtones of both *cis* methyl nitrite and *trans* methyl nitrite, which are well separated in frequency, gives resolved fluorescence spectra which mimic the absorbance spectra for *cis* methyl nitrite and *trans* methyl nitrite, respectively, thereby placing a lower bound for the conformational interconversion energy barrier from *trans* to *cis* of 3325 cm^{-1} . The experiments were performed by exciting either molecule cooled in a pulsed nozzle expansion with light from an infrared optical parametric oscillator. The fluorescence spectra were recorded with a cryogenic Michelson interferometer.

INTRODUCTION

This represents the first of our efforts to study intramolecular conformational interconversion in isolated gas phase ground electronic state molecules, and the first evidence of state selected collisionless conformational interconversion in a ground electronic state molecule.

Polyatomic molecules which have more than one local minimum can have several equivalent minima (e.g., the rotamers of ethane) or differing minima separated by barriers having heights of the order of magnitude of bond energies (e.g., the isomers *cis* and *trans* dichloroethylene) or (the case described in this paper) differing minima with barriers of the order of vibrational energies (called conformers).

We have previously studied a molecule with rotamers, dimethyl ether,¹ and two molecules which exhibit conformational isomerism, *cis* methyl formate² and chair dioxane.³ In each of these we pumped from the ground vibrational state of the lowest minimum. The transitions pumped were approximately 3000 cm^{-1} , and in all three the molecules remained within the well of the lowest minimum.

A search of the literature shows that there are a large number of molecules with barriers to conformational interconversion below the CH stretch region, and a smaller group (still a substantial number!) with barriers above the CH stretch region. Our optical parametric oscillator can excite transitions from 2500 to 7000 cm^{-1} . Of course, combination and overtone bands above the CH stretch region are usually quite weak.

Given appropriate experimental conditions it should be possible to probe conformational interconversions of a great many molecules using infrared excitation. Energy would be deposited in a conformer, and the subsequent dynamical behavior elucidated via some observable. One should learn about:

- (i) possible tunneling effects,
- (ii) state content close to barrier (state selective effects),
- (iii) better determination of barrier energies by direct observation of conformational interconversion,
- (iv) elucidation of overlapped conformer modes,
- (v) time domain effects such as IVR vs interconversion rates.

Our experiment deposits energy at approximately 3000 cm^{-1} in molecules exhibiting conformational isomerism. The resolved fluorescence spectra then tells whether the deposited energy exceeds the barrier energy or not. The two molecules chosen for this study each have two conformers. Methyl nitrite (MEN) exists at room temperature as *cis* MEN and *trans* MEN in about a 60:40 mix.⁴ Methyl vinyl ether (MVE) exists as *cis* MVE and either *trans*⁵ or *gauche*⁶ MVE in an unknown number ratio, but with the *cis* form likely predominating. The equilibrium geometry of the high energy conformer does not affect the analysis presented here.

Methyl vinyl ether is reported to have an energy barrier of 2200 cm^{-1} between *cis* and the high energy conformer.⁶ Methyl nitrite is reported to have a barrier between 3500 and 4400 cm^{-1} .^{4,8} Our MVE resolved fluorescence spectra show a conformational interconversion as a result of photon absorption. From the resolved fluorescence spectra of MEN it is apparent that conformational interconversion as a result of photon absorption does not occur; a lower bound of 3325 cm^{-1} is thereby given to the potential energy barrier for *trans* to *cis* interconversion.

Conformational interconversion can occur by collisional energy transfer or by absorption of photons. The $3N-6$ dimensional potential energy barrier between conformers can be, for MEN and MVE, projected onto the asymmetric torsion. Although this is not in general exact (the normal

modes are not molecular eigenstates) an appropriate criterion of interconversion is that there be sufficient energy in this mode to exceed the barrier energy.

Within each local minimum, the normal mode approximation might be quite good for vibrations which access little of the potential surface (i.e., the harmonic part). However for polyatomics of sufficient energy content the zeroth order modes are not eigenstates. An energy high enough that the vibronic density of states is greater than 20 cm is sufficient.² This is the case for MVE and MEN at CH stretch excitation energies. Excitation of a zeroth order mode can therefore be followed by intramolecular vibrational relaxation (IVR).² After IVR occurs (probably in less than 10^{-10} s) inside one conformer well the relaxed vibrational fluorescence spectrum provides a fingerprint for that conformer if the resultant fluorescence is resolved. This fingerprint matches the same conformer absorbance spectrum with slight shifts due to anharmonicities and different changes in rotational states *PQR* structure. The quantum beats and recurrences which would appear following the initial IVR process would be totally washed out by state averaging in our experiment.

The lifetime of the relaxed fluorescence, in the absence of collisions, would be about 10^{-3} s.

When the internal energy content exceeds the potential energy barrier the fluorescence will contain peaks (slightly shifted due to anharmonicities) from all the infrared active modes (except CH stretches) of both conformers, due to IVR. The converse, that a spectrum containing peaks from both conformers implies that the internal energy content exceeds the potential energy barrier, is not in general true. One must deposit energy in only one conformer (or in both such that the amount deposited in each is known) to say that the internal energy content exceeds the potential energy barrier, and that a conformational interconversion has been caused by the laser.

If one were to excite a single molecular eigenstate, the resolved fluorescence spectrum would again be a fingerprint providing information on whether or not the internal energy content is greater than the potential energy barrier, and would be quite fascinating from the view of mapping out the mixing due to IVR in each conformer well and above the barrier connecting the wells.

Thus in moderate and large size molecules infrared fluorescence following IVR provides the means of identification and the cold beam serves the purpose of having the molecules, following photon absorption, with a well defined internal energy content.

EXPERIMENT

The molecular beam system, pulsed nozzle, Nd-YAG pumped optical parametric oscillator infrared laser system, filter wheel detector system, and cryogenic Michelson interferometer detector system used in these experiments have been previously described.¹⁻³ It should be noted that during our $5 \mu\text{s}$ observation time following the laser pulse there are essentially *no* collisions, even if their cross section were 500 \AA^2 .

The liquid nitrogen cooled heat shield inside the molecular beam box and the cryogenic interferometer are now

filled with liquid nitrogen automatically rather than manually. A control box turns on solenoid valves every 20 min, which stay on for 3 min or until resistors attached below two phase separators sense overflow. This improves signal to noise by keeping background emission always at liquid nitrogen temperature.

Noise bursts are now removed automatically during data collection rather than manually following data collection. A simple comparator circuit discriminates between noise bursts (large voltage spikes lasting 0.5 ms) and good data. When a noise burst occurs, the data collection ignores it and takes the point again.

Total fluorescence excitation spectra were taken with the filter wheel detector system attached to the molecular beam box. Resolved fluorescence spectra were obtained with the cryogenic Michelson interferometer detector system attached to the molecular beam box. Absorbance spectra were recorded with a Nicolet FT-IR. Methyl vinyl ether was obtained from Linde Specialty Gas, Union Carbide Corp., and used without further purification. Methyl nitrite was prepared from reagent grade methanol, sodium nitrite, and cold sulfuric acid.⁹ The MEN gas produced was stored as a saturated solution in cold tetrahydrofuran (typically) or cold diethyl succinate (for one run).

The beams of gas of either MVE or MEN were prepared by the nozzle system previously described. Methyl vinyl ether was pure, and MEN was some (roughly 50:50) mixture of MEN and air.

Some resolved fluorescence spectra of MEN showed a small peak due to tetrahydrofuran. We have obtained resolved fluorescence spectra of pure tetrahydrofuran, and subtracted out this peak. As a check diethyl succinate, a solvent with negligible vapor pressure at room temperature, was used for the preparation of a different MEN saturated solution. The resolved fluorescence spectrum obtained was identical to that of the tetrahydrofuran saturated solution spectrum minus the tetrahydrofuran peak.

Both MVE and MEN were at about room temperature in the valve prior to expansion.

RESULTS

The total fluorescence excitation spectrum of MEN and MVE are shown in Figs. 1 and 2. The relaxed fluorescence spectra of MEN and MVE are shown in Figs. 3 and 4. The number above each spectrum is the excitation energy in cm^{-1} . Notice that the FT-IR absorbance spectrum of MVE is the upper right corner spectrum of Fig. 4. Each molecule is discussed separately.

METHYL NITRITE

The known spectroscopy of MEN is extensive.¹⁰⁻¹⁷ We have confirmed several points. The total fluorescence excitation spectrum of MEN in Fig. 1 has overtone peaks at 3325 and 3220 cm^{-1} . These are identified¹⁰ as *trans* N=O overtone and *cis* N=O overtone, respectively. The zero point energy difference between *cis* and *trans* MEN has been found to be $314 \pm 22 \text{ cm}^{-1}$.¹¹ From Fig. 3, it is evident that the resolved fluorescence at excitation 3220 cm^{-1} and the resolved fluorescence at excitation 3325 cm^{-1} have no coinci-

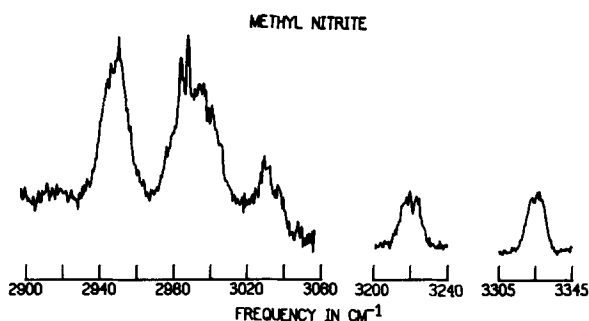


FIG. 1. Total laser induced fluorescence spectrum of the C-H stretching region and N=O overtone regions of methyl nitrite.

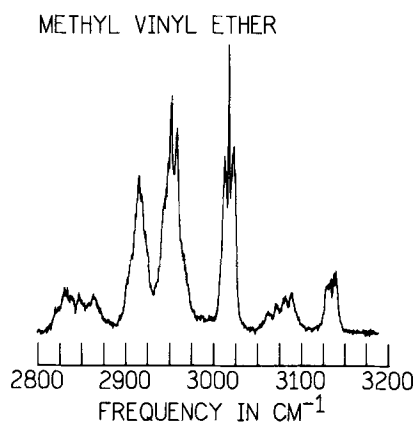


FIG. 2. Total laser induced fluorescence spectrum of the C-H stretching region of methyl vinyl ether.

dent peaks. All peaks in the 3325 cm^{-1} spectrum can be labeled with *T* for *trans*. All peaks in the 3220 cm^{-1} spectrum can be labeled with *C* for *cis*.

The resolved fluorescence spectra at excitation 2954, 2981, 2990, and 3005 cm^{-1} can then be labeled *C* or *T* by reference to the N=O overtone spectra.

Visual inspection of the spectra shows that there are fluctuations present in relative energy content of a given mode (*trans* peaks compared only with each other; *cis* peaks compared only with each other). This relative energy content fluctuation over a fairly narrow excitation energy range has been previously discussed.²

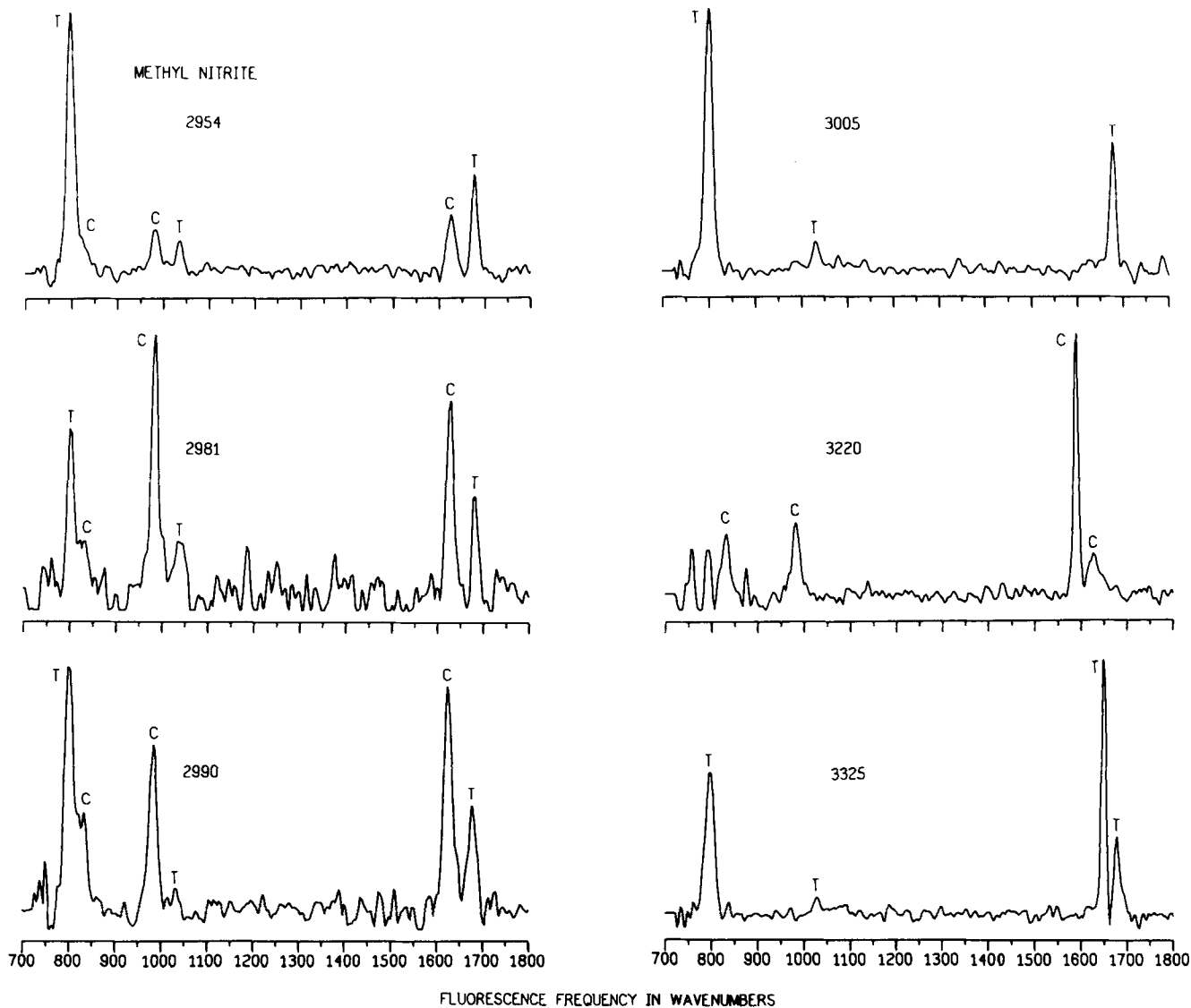


FIG. 3. Resolved fluorescence spectra from C-H stretching region and N=O overtone excitation of methyl nitrite. Spectra are labeled by the laser pump frequency in cm^{-1} . Intensity of fluorescence is in arbitrary units with the most intense peak of each spectrum normalized to the same height. The labels *C*, *T* refer to *cis* and *trans*, respectively.

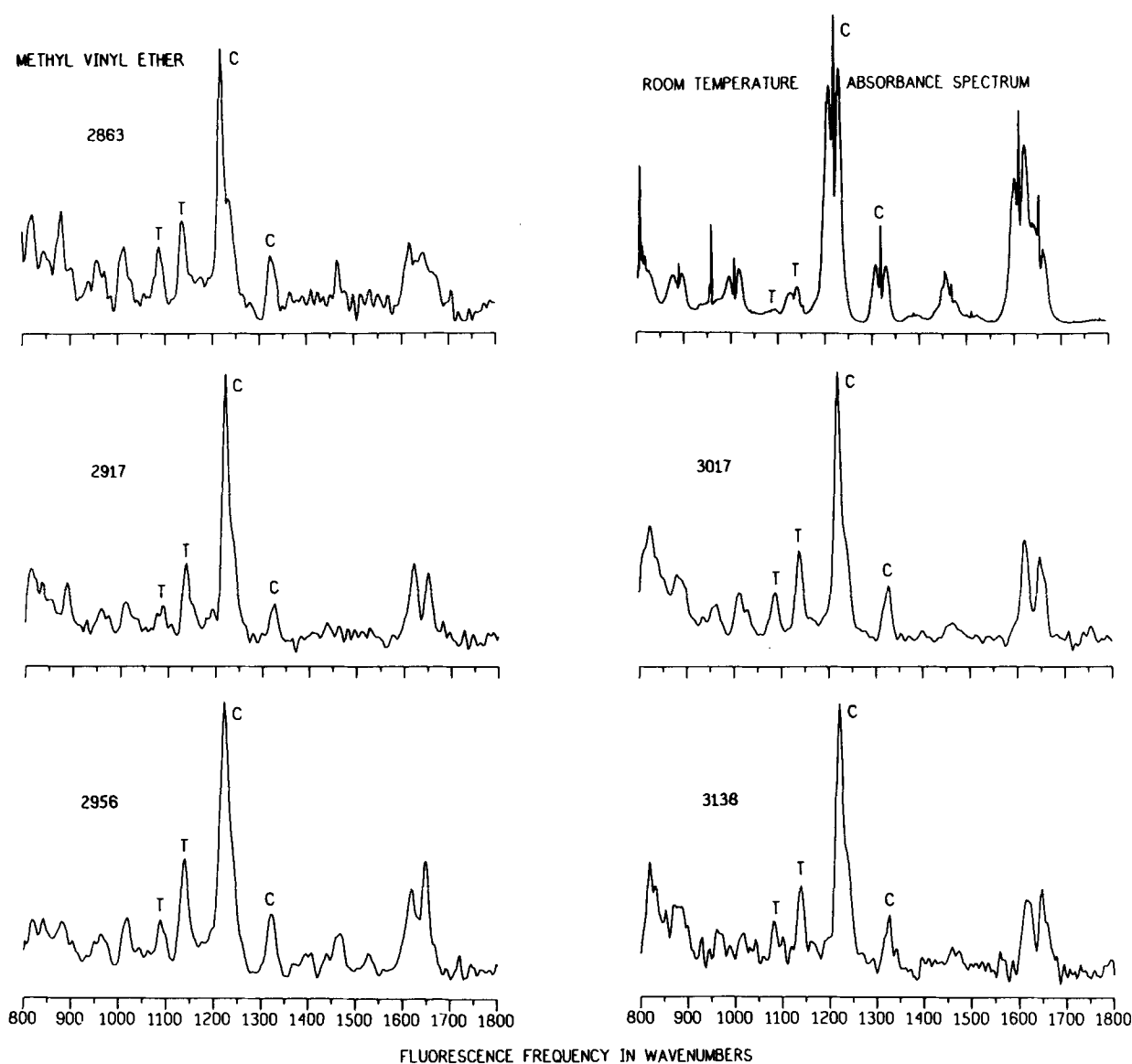


FIG. 4. Resolved fluorescence spectra from the C-H stretching region of methyl vinyl ether. Spectra are labeled by laser pump frequency in cm^{-1} . Top right spectrum is the bulb gas phase absorbance spectrum of methyl vinyl ether. The labels C, T refer to *cis* and *trans*, respectively.

Were the excitation energy greater than the potential energy barrier to conformational interconversion, excitation of the *trans* N=O overtone would cause conformational interconversion and IVR leading to *cis* relaxed peaks. As this is not the case an accurate lower bound of 3325 cm^{-1} relative to the ground state of *trans* MEN can be assigned to the potential energy barrier for *trans* to *cis* interconversion. Taking the zero point energy difference to be $314 \pm 22 \text{ cm}^{-1}$ between the two conformers of MEN,¹¹ the potential energy barrier for *cis* to *trans* interconversion must be above about 3640 cm^{-1} .

While the CH stretch fundamentals show no resonance fluorescence (they are diluted via IVR) the N=O overtones for both *cis* and *trans* MEN have resonance fluorescence clearly present. This is a result of the large Einstein *B* coefficients for absorption of the N=O fundamental and the fact that second overtones fluoresce at about twice the rate of fundamentals. The large anharmonic shift between resonance fluorescence and overtone fluorescence is clearly evi-

dent in Fig. 3, where the sharp peaks at lower wave number are the $\Delta\nu = -1$ overtone fluorescence.

Although not the emphasis of this paper, we present information concerning IVR in *trans* MEN and *cis* MEN. Dilution factors for resonance fluorescence from N=O overtones in both conformers were calculated by the previously presented model.² The *trans* N=O overtone is about four times as dilute as the *cis* overtone. The dilution factors are: $\phi_D(\textit{cis}) = 0.15$ and $\phi_D(\textit{trans}) = 0.04$.

METHYL VINYL ETHER

If only one conformer absorbed at a given wavelength, the evidence for conformational interconversion would be straightforward. Appearance in the resolved fluorescence spectra of relaxed peaks (from IVR) of another conformer would mean that conformational interconversion had occurred.

It is clear from our data that the relaxed *trans* peaks are much stronger (averaging about 4.6 times as strong) com-

pared to the *cis* peaks in the fluorescence spectra than in the room temperature absorbance spectrum.

If it is not obvious which conformer is absorbing, i.e., that both might be simultaneously excited, the spectra must be analyzed in comparison with the bulk gas phase absorbance spectrum obtained at the temperature of the valve. The valve temperature for MVE was 300 K, the absorbance spectrum in Fig. 4 being therefore labeled "room temperature" as this is the appropriate absorbance spectrum to compare with.

The CH stretch region of MVE is known from the literature to be overlapped with both *cis* MVE and the higher energy conformer of MVE.^{18,19} Most authors believe the high energy conformer geometry to be *trans*.⁵ Whether the geometry is *trans* or *gauche* does not affect subsequent analysis here. We have labeled the non *cis* peaks *T* for *trans* for convenience and refer to the high energy conformer as such.

As the CH stretch region is overlapped, it is not known at a given excitation energy what fraction of photons are absorbed by *cis* and what fraction by *trans* MVE.

Therefore we assume simultaneous absorption and present in Appendices A and B analyses which delineate between whether the internal energy content exceeds the potential energy barrier between *cis* and *trans* MVE. Literature estimates have put the barrier substantially less than our excitation energies^{6,18}; analysis proves that in fact the excitation photons are greater in energy than this barrier.

The derivation in the Appendices are cast in terms of the following experimentally measured ratio:

$$R = \frac{I_{\beta}^t a_{\alpha}^c}{I_{\alpha}^c a_{\beta}^t}$$

In this equation, I_{β}^t represents the integrated intensity of the relaxed peak which is related to motion in the β mode of the *trans* conformer, I_{α}^c a similar quantity for mode α of the *cis* conformer; a_{β}^t is the integrated area for mode β in the room temperature absorbance spectrum and a_{α}^c a similar quantity for mode α . The modes could be, e.g., the peaks at 1325 cm^{-1} (α , *cis*) and 1140 cm^{-1} (β , *trans*).¹⁸ In this paper we have in fact used these two peaks; these two peaks were sufficiently unoverlapped and had large enough integrated areas to be reliable.

This ratio R has an average of 4.6 for the CH stretch excitations used, and although roughly uniform, has fluctuations present as shown in Table I. Because the CH stretch region must be treated as if, at each excitation energy, a fraction of the photon flux is absorbed by *cis* and a fraction ab-

sorbed by *trans*, it remains to determine whether the resolved fluorescence spectra result from conformational interconversion or some spectroscopic quirk. As shown in Appendix A it would be necessary to invoke an Einstein B coefficient of absorption for the *trans* of a constant 4.6 times greater than that for the *cis* conformer at each excitation frequency, if the spectra do not represent a conformational interconversion following photon absorption. This cannot be so as we experimentally checked the CH stretch absorption region and saw no change in the total integrated absorbance of this region at several temperatures over a broad temperature range.

Therefore we conclude that the R ratios obtained are explained by a conformational interconversion as a result of absorption of photons whose energy exceeds the potential energy barrier between conformers. Appendix B contains derivations in terms of a statistical model. It is found that it is not important whether the fraction of photons absorbed by *cis* exceeds the fraction of photons absorbed by *trans*; the distribution of conformers following absorption (resulting from the admixture of *cis* zeroth order optically active modes and *trans* zeroth order optically active modes at the excitation energy) calculated by the theory being independent of which conformer absorbs.

The final number ratio of *cis* to *trans* is unknown because as previously mentioned the starting ratio is not known, although it is clear that *cis* predominates. Were the starting ratio known the results obtained here would allow calculation, in terms of the model, of the distribution of conformers following absorption.

An examination of the relative areas of the *cis* and *trans* peaks shows that different excitation frequencies appear to produce slightly different ratios of *cis* to *trans* product, as observed at the equilibrium value attained during our $5 \mu\text{s}$ observation time. This is quite likely evidence for a true initial state selective effect. It is not certain evidence because the peak areas can fluctuate due to the finite density of vibrational states (from about 10 to 50 cm^{-1} depending on the assumed value of the low frequency modes). The *cis/trans* ratio is, in fact, subject to exactly the same kind of fluctuation, and the two are, on the most fundamental level, inextricable.

DISCUSSION

We have demonstrated that infrared fluorescence can be used to observe the presence or absence of conformational interconversion in isolated molecules excited in single vibronic levels. We have also seen evidence that this interconversion can be state selective.

Future experiments should be able to show whether collisions can stabilize the differing *cis/trans* ratios we observe (i.e., whether our laser irradiation can perturb the equilibrium in a bulk sample). *Electronically state selective* isomerizations are of course a commonplace organic chemical process. Although infrared *multiphoton* processes²¹⁻²⁸ can easily be used to perturb bulk equilibrium, there is no evidence to date for truly *state selective* vibrational isomerization (as opposed to *energy selective*), except for one report using overtone excitation.²⁹ We may also be able to locate barriers quite exactly for some molecules and be able to ob-

TABLE I. Observed conformer ratios (fluorescence peak area/absorbance peak area) for methyl vinyl ether.^a

Excitation energy (cm^{-1})	R^b
2863	6.06
2917	5.16
2956	4.70
3017	3.36
3138	3.78

^aThe *cis* peak used is at 1325 cm^{-1} and the *trans* peak at 1140 cm^{-1} .

^b R defined by Eq. (1).

serve tunneling effects.

ACKNOWLEDGMENT

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APPENDIX A

In this Appendix we calculate the ratio R for the case of *no* interconversion of conformers following laser excitation. We are not able to spectrally resolve the fluorescence from overtones and fundamentals of a given vibrational mode in relaxed fluorescence. This is a result of the small variation in anharmonicities of the bath modes and the 8 cm^{-1} spectral resolution of the interferometer. What we do measure is the intensity of the $(\Delta\nu) = -1$ fluorescence of a given relaxed mode, e.g., mode γ .

For a statistical molecule (in the sense of IVR behavior) there is expected little fluctuation in the intensity of the relaxed peak as a function of excitation energy. A molecule such as MVE can be expected to have some fluctuations.² As shown in Table I in the main text the ratio R is roughly uniform with fluctuations present due to these fluctuations in intensities.

Using the usual harmonic oscillator approximation for the A coefficients one obtains²

$$I_\gamma = (1 - \phi_D) \frac{g_s A_{0,s} A_{0,\gamma}}{8\pi\nu_s} \mathcal{L}(\nu_s) \sum_\nu V f_{\gamma=\nu}, \quad (\text{A1})$$

where ϕ_D is the dilution factor of resonance fluorescence, g_s is the degeneracy of the zeroth order state pumped (in the case of MVE the CH stretch pumped), $A_{0,s}$ the Einstein A coefficient for spontaneous emission from the optically pumped mode, $A_{0,\gamma}$ a similar quantity for the relaxed mode γ , ν_s the frequency of the optically pumped mode in cm^{-1} , \mathcal{L} the laser photon flux at frequency ν_s . The quantity $\sum_\nu V f_{\gamma=\nu}$ is the fraction of zeroth order states with V quanta in mode γ in the group of mixed states at excitation frequency ν_s ; it must be calculated by some "statistical" theory.

The sum $\sum_\nu V f_{\gamma=\nu}$ is related to the amount of energy deposited in a given vibrational motion γ , given by

$$E_R = hc\nu_\gamma \sum_\nu V f_{\gamma=\nu}. \quad (\text{A2})$$

If we call the *trans*(t) relaxed peak β , and the *cis*(c) relaxed peak α , the ratio I'_β to I'_α is

$$\frac{I'_\beta}{I'_\alpha} = \frac{1 - \phi'_D}{1 - \phi^c_D} \frac{n'_t n_c}{n'_c n_t} \frac{B'_{0,s}/n_t}{B^c_{0,s}/n_c} \frac{a'_\beta}{a^c_\alpha} \frac{\nu_\beta}{\nu_\alpha} \frac{E'_R}{E^c_R}, \quad (\text{A3})$$

where I'_β is the integrated intensity of relaxed *trans* peak at mode β , n'_t is the number fraction of *trans* following absorption of photons, n_t the number fraction prior to absorption but following expansion and cooling, a'_β the integrated intensity of the room temperature absorbance peak for *trans* mode β , ν_β the frequency in cm^{-1} of the *trans* mode β , E'_R the energy content of *trans* mode β as defined by Eq. (A2), and $B'_{0,s}$ the Einstein B coefficient for absorption of *trans* conformers. Similar definitions hold for the analogous quantities for the *cis* conformer, labeled with c and α .

In terms of the experimentally measured ratio defined

in the main text

$$R = \frac{1 - \phi'_D}{1 - \phi^c_D} \frac{n'_t n_c}{n'_c n_t} \frac{B'_{0,s}}{B^c_{0,s}} \frac{\nu_\beta}{\nu_c} \frac{E'_R}{E^c_R}, \quad (\text{A4})$$

However, the ϕ^c_D and ϕ'_D values must be less than 0.1 because we observed no resonance fluorescence in the resolved fluorescence spectra. Also the calculated ratio $(E'_R \nu_\beta)/(E^c_R \nu_\alpha)$ is approximately one for a wide variety of choices for the low lying fundamentals of the *trans* conformer (about which there exists uncertainty in the literature). The following relation is therefore found.

$$R \approx \frac{n'_t n_c}{n'_c n_t} \frac{B'_{0,s}}{B^c_{0,s}} = n'' \frac{B'_{0,s}}{B^c_{0,s}}. \quad (\text{A5})$$

Note that if cooling of the conformational degree of freedom in the beam occurs one expects $n'' < 1$ because the *cis* conformer is lower in energy than the *trans*. Gunthard *et al.* have shown²⁰ that there is no cooling of the conformational degree of freedom for several conformers with barriers in the range expected for MVE, and if this is the case then $n'' = 1$. Therefore, if the internal energy content following photon absorption were less than the potential energy barrier, it must be true that the Einstein B coefficient for absorption of *cis* is greater by a factor of about 4.6 ($N'' = 1$), or greater than 4.6 ($n'' < 1$), at each excitation frequency. This would be a highly unlikely spectroscopic anomaly, but as an experimental check, the gas phase absorbance spectrum of MVE was measured at several temperatures over a wide range; no perceptible change in the integrated intensity of the whole CH stretch region was measured; one expects a large variation for such postulated large differences in B coefficients between conformers.

Therefore the internal energy content is *not* less than the potential energy barrier and the appearance of the relaxed fluorescence spectra result from intramolecular conformational interconversion. Appendix B presents theory appropriate for this case.

APPENDIX B

If the internal energy content is greater than the potential energy barrier one has for excitation of only the *cis* conformer

$$\frac{I'_\beta}{I^c_\alpha} = \frac{1 - \phi'_D}{1 - \phi^c_D} \frac{E'_R(E - \Delta E_0)}{E^c_R(E)} \frac{\nu_\beta}{\nu_\alpha} \frac{\delta'(E - \Delta E_0)}{\delta^c(E)} \frac{a'_\beta}{a^c_\alpha}, \quad (\text{B1})$$

where ΔE_0 is the zero point energy difference between conformers, E the excitation energy in cm^{-1} , δ^c the density of states of the *cis* conformer at the quoted energy, and all other quantities as defined in Appendix A.

Cast in terms of the equation for R in the main text, and with the experimentally verified assumption that the ϕ_D 's are less than 0.1 one obtains

$$\frac{I'_\beta a^c_\alpha}{I^c_\alpha a'_\beta} = R^c = \frac{E'_R(E - \Delta E_0)}{E^c_R(E)} \frac{\nu_\beta}{\nu_\alpha} \frac{\delta'(E - \Delta E)}{\delta^c(E)} \quad (\text{B2})$$

and a corresponding expression for the excitation of *trans* only

$$R' = \frac{E_R^\beta(E)}{E_R^\alpha(E + \Delta E_0)} \frac{\nu_\beta}{\nu_\alpha} \frac{\delta'(E)}{\delta^c(E + \Delta E_0)}. \quad (\text{B3})$$

Letting the fraction of photons absorbed by *cis* be m_c and the fraction absorbed by *trans* m_t , then the experimentally measured R is given by the model to be

$$R = m_c R_c + m_t R_t. \quad (\text{B4})$$

It is an interesting fact that *calculated* values for R_c and R_t are approximately equal. The calculations assumed a wide range of reasonable ΔE_0 's and several different sets of fundamental frequencies for the *trans* conformer. Once ΔE_0 and the frequencies are set for a given calculation, the ratios obey the approximate equalities shown in Eqs. (A5) and (A6):

$$\frac{E_R^\beta(E - \Delta E_0) \nu_\beta}{E_R^\alpha(E) \nu_\alpha} \approx \frac{E_R^\beta(E) \nu_\beta}{E_R^\alpha(E + \Delta E_0)}, \quad (\text{B5})$$

$$\frac{\delta'(E - \Delta E_0)}{\delta^c(E)} \approx \frac{\delta'(E)}{\delta^c(E + \Delta E_0)}. \quad (\text{B6})$$

In other words these ratios are slowly varying functions of the energy content. The final result, with the fact that $m_c + m_t = 1$, is

$$R \approx R_c \quad \text{or} \quad R \approx R_t. \quad (\text{B7})$$

That is the experimentally measured value of R should be according to this simple statistical theory, about the same for excitation of *cis* only, only *trans*, or any mixture of *cis* and *trans*.

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