

Conformational Isomerization of Formic Acid by Vibrational Excitation at Energies below the Torsional Barrier

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Understanding the structural and dynamical conformational properties of molecules is of fundamental and practical value in chemistry. One of the most fascinating issues in this respect is the folding of proteins, which represents a very important but simultaneously extremely complicated and multidimensional problem. The most detailed information can be obtained by studying small molecules. In this respect, formic acid (FA), being the simplest organic acid, represents a good model system for studying the conformational properties of carboxylic acids and the carboxylic group in general. It is known that interconversion of different conformers can be induced in the solid state by vibrational excitation.¹ Coupling of the initially excited state with other modes of the isolated molecule and with lattice phonons leads to the flow of energy into the reaction coordinate, finally promoting the change of the geometry of the molecule from one conformation to another.^{1,2} Usually, it is natural to assume that to induce the conformational conversion, the initially excited state should lie well above the reaction barrier.^{2,3} In this communication, we show that in FA, due to tunneling, the conversion from the lower energy trans to the higher energy cis form can be induced with high efficiency at energies well below the reaction barrier.

In the experiments, FA (KEBO lab, >99%) was mixed with argon (AGA 99.9999%) in a glass bulb with a ratio FA/Ar = 1/2000. The mixture was deposited on a CsI window held at 15 K in a cryostat (APD DE 202 A). After deposition, the sample was cooled to 8 K. The IR pumping was carried out with pulsed (~5 ns) narrowband IR radiation of an optical parametric oscillator (Sunlite with an infrared extension, Continuum, fwhm ≈ 0.1 cm⁻¹). The absolute wavelength was determined with a wavemeter (Burleigh WA-4500), and the pulse energy was measured with a pulsed energy meter (Molelectron). The pulse energies were 0.5–1 mJ, and the repetition rate was 10 Hz. The IR spectra were measured with a FTIR spectrometer (Nicolet 60 SX) with a resolution of 1 or 0.25 cm⁻¹. The experimental setup was arranged in such a way that IR spectra could be recorded during irradiation. Suitable interference filters were used to suppress the effect of the glowbar radiation on the IR induced isomerization. It was also verified that the room-temperature radiation from the surroundings had a negligible effect on the results.

An important value for the present work is the barrier height for the trans → cis conversion. There are various estimates for the barrier in the literature, and the high level ab initio calculations give ~50 kJ/mol (4500 cm⁻¹).^{4,5} We performed additional calculations within the GAUSSIAN 98 program package.⁶ Our value for the barrier height at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level is 3921 cm⁻¹ (corrected for the zero-point-energy (ZPE) using the calculated frequencies at the MP2 level). At the same level of theory, the energy difference between the cis and trans

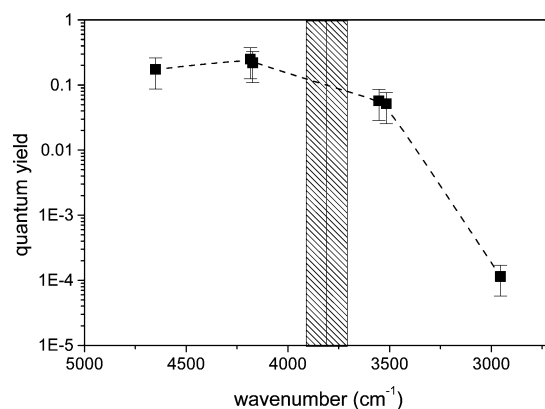


Figure 1. The quantum yield for the trans → cis isomerization of formic acid via pumping various vibrational transitions. The line connecting the points is for guiding the eye. The position of the barrier for the isomerization from the ab initio calculations is indicated in the figure with a vertical line, and the estimated uncertainty is indicated by a shaded region. The points correspond to the following vibrational modes: 4651 cm⁻¹, $\nu_{\text{OH}} + \text{COH}-\text{CO def.}$; 4184 cm⁻¹, $\nu_{\text{OH}} + \tau_{\text{OH}}$; 4174 cm⁻¹, $\nu_{\text{CH}} + \text{CO}-\text{COH def.}$; 3552 cm⁻¹, ν_{OH} ; 3516 cm⁻¹, $2\nu_{\text{CO}}$; 2955 cm⁻¹, ν_{CH} .

forms is 1396 cm⁻¹, the experimental value being 1365 ± 30 cm⁻¹.⁷ An additional factor to consider is the effect of the environment on the energetics. We have estimated the effect of the medium on the barrier height within the PCM (polarized continuum model) solvation model in GAUSSIAN 98 using a dielectric constant of 1.63 for argon.⁸ According to these results, the barrier height is reduced by 111 cm⁻¹ from the gas phase to solid argon. Combining these computational results, we reliably estimated the barrier height for the solid-state trans → cis conversion in an Ar matrix to be 3810 ± 100 cm⁻¹.

Cis FA was prepared by pumping various vibrational transitions of trans FA.⁹ Cis FA decays back to trans FA in a time scale of minutes even at 8 K due to tunneling.^{9,10} In effect, under continuous IR pumping, a photoequilibrium is established, and the equilibrium concentrations of the two forms [cis]_{eq} and [trans]_{eq} are given by the pumping efficiency and the tunneling rate for the backreaction. The pumping efficiency is determined by the radiation intensity, absorption cross section, and the quantum yield for the isomerization, the first two values being experimentally measurable. The backreaction rate can also be measured.¹⁰ Thus, the quantum yield for the isomerization at different excitation wavelengths can be extracted.

The results of these experiments are shown in Figure 1, presenting the quantum yield for pumping several different fundamental and combination vibrations in the energy interval 2900–5000 cm⁻¹. The position of the barrier for isomerization determined from the ab initio calculations is given in the figure as well. The isomerization efficiency remains surprisingly high, being about 20% down to ~4100 cm⁻¹. There is very little difference in

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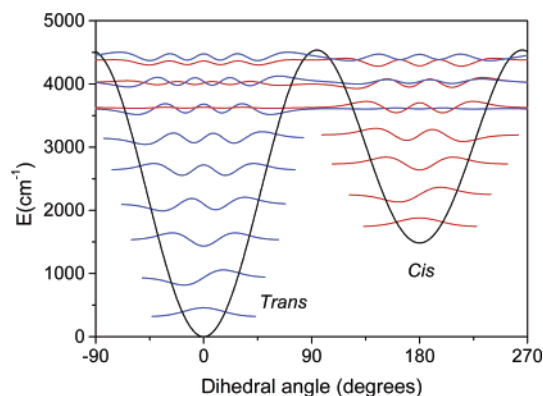


Figure 2. The calculated torsional potential of formic acid. The vibrational energy levels and wave functions are from the variational calculations. The blue and red curves refer to the trans and cis wave functions, respectively.

the quantum yield between different pumped modes in the same energy region. Remarkably, the efficiency decreases only slightly to about 5% at $\sim 3500\text{ cm}^{-1}$ (corresponding to the excitation of the OH stretching or carbonyl stretching overtone) despite these energies being reliably below the barrier. The quantum yield for the isomerization then drops strongly about 3 orders of magnitude at $\sim 3000\text{ cm}^{-1}$ (corresponding to the C–H stretching fundamental) but is still reliably measurable. Therefore, the principal result of these studies is that IR induced rotamerization takes place at significantly lower energies than the torsional barrier height.

The natural explanation for these observations is that the isomerization process occurs by tunneling. Indeed, we have previously observed that cis FA tunnels quite efficiently back to trans FA even from the vibrational ground state.^{9,10} To gain more insight into the mechanism, we have calculated the torsional potential for the FA at the MP2/aug-cc-pVTZ level. At a given H–O–C–H dihedral angle, the other coordinates were fully optimized. The obtained potential was fitted with a cosine series.

$$V = \frac{1}{2} \sum_1^n V_n (1 - \cos n\phi)$$

For this potential, the vibrational Schrödinger equation was variationally solved in the sine and cosine basis sets using the Hamiltonian of Lewis et al.¹¹ The inertial constant as a function of the torsional angle needed for the calculation was obtained using the method of Pitzer,¹² and the resulting data set was also fitted with a cosine series to be used in the vibrational analysis. The geometries needed for the calculation of the inertial constants were taken from our ab initio calculations.

The fitted potential and the obtained energy levels and wave functions are shown in Figure 2. The quality of the potential can, to some extent, be judged by comparing the calculated and experimental torsional frequencies. The calculated torsional frequency for the trans FA is 614 cm^{-1} and for the cis FA is 513 cm^{-1} , while the experimental values are 635 and 503 cm^{-1} , respectively;⁹ that is, the agreement is reasonably good. The most relevant for the present study are the states near the top of the barrier and the extent of delocalization of these states. Because the calculated potential is determined at a lower level than our best estimates for the barrier height and ignoring solvation, it yields somewhat different energetics as well. To make meaningful comparisons with the higher level calculations and with experiments, we discuss the energetics with respect to the barrier top. This is a reasonable approach because we are mainly interested in the region near the top of the barrier. It is seen in Figure 2 that the two torsional states just below the barrier are strongly delocalized over the two wells. The next two

levels below them are also strongly delocalized. For instance, the square of the wave function for the third highest state gives 84 and 16% for the probabilities for the system to be in trans or cis wells, respectively. This state lies $\sim 500\text{ cm}^{-1}$ below the top of the barrier, that is, energetically slightly below the trans OH-stretching fundamental and the carbonyl stretching overtone. Dynamically, this means that at these energies torsional randomization is fast, comparable with the free rotor states, in accordance with the observed high quantum yield for the isomerization. The next two states are already strongly localized in either well with a probability of $\sim 99\%$. These states lie at $\sim 900\text{ cm}^{-1}$ below the top of the barrier, that is, near the CH stretching. The strong localization means dynamically reduced tunneling probability, and it is in accordance with the reduced quantum yield for the isomerization.

The obtained results together with the results of other studies point out the importance of tunneling in the conformational dynamics of the OH group.^{9,10,13,14} Moreover, it is remarkable that the excitation energy is so efficiently transferred to the isomerization coordinate. The initially excited state can relax via cascading vibrational relaxation, and this process is possibly accompanied by phonon emission.¹⁵ At some stage of the relaxation process, the molecule is transferred to a high overtone state of the torsion, and the isomerization can take place.

In summary, it has been shown that formic acid undergoes photoinduced conformational isomerization when the photon energy is significantly lower than the energy barrier for this process. The quantum yield for the isomerization slightly below the top of the barrier is comparable with the quantum yield above the barrier and decreases strongly at lower energies. The conformational isomerization occurs most probably via the tunneling mechanism assisted by solid-state energy relaxation.

Acknowledgment. This work was supported by the Academy of Finland. E.M.S.M. acknowledges a Ph.D. student grant of the Portuguese foundation for science and technology.

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JA0295016