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Rotational isomerism of acetic acid isolated in rare-gas matrices: Effect of medium and isotopic substitution on IR-induced isomerization quantum yield and *cis*→*trans* tunneling rate

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Rotational isomerization of acetic acid (CH_3COOH) is studied in Ar, Kr, and Xe matrices. The light-induced *trans*→*cis* reaction is promoted using resonant excitation of a number of modes in the 3500–7000 cm^{-1} region, and the quantum yields for this process are measured for various acetic acid isotopologues and matrix materials. For excitation of acetic acid at energies above the predicted isomerization energy barrier ($\geq 4400 \text{ cm}^{-1}$), the measured quantum yields are in average 2%–3%, and this is one order of magnitude smaller than the corresponding values known for formic acid (HCOOH). This difference is interpreted in terms of the presence of the methyl group in acetic acid, which enhances energy relaxation channels competing with the rotational isomerization. This picture is supported by the observed large effect of deuteration of the methyl group on the photoisomerization quantum yield. The *trans*→*cis* reaction quantum yields are found to be similar for Ar, Kr, and Xe matrices, suggesting similar energy relaxation processes for this molecule in the various matrices. The IR-induced *cis*→*trans* process, studied for acetic acid deuterated in the hydroxyl group, shows reliably larger quantum yields as compared with the *trans*→*cis* process. For pumping of acetic acid at energies below the predicted isomerization barrier, the *trans*→*cis* reaction quantum yields decrease strongly when the photon energy decreases, and tunneling is the most probable mechanism for this process. For the *cis*→*trans* dark reaction, the observed temperature and medium effects indicate the participation of the lattice phonons in the tunneling-induced process. © 2004 American Institute of Physics. [DOI: 10.1063/1.1760733]

I. INTRODUCTION

A large number of molecules have been found to undergo rotational isomerization upon vibrational excitation of the monomer isolated in low-temperature rare-gas matrices.^{1–16} In general, it is required that the excitation energy is transferred from the initially excited vibrational mode to the reaction coordinate at energies higher than the reaction barrier.³ However, it has been recently shown that isomerization of the carboxylic group can take place due to tunneling even when the excess energy is transferred to the reaction coordinate (C–O torsion) below the reaction barrier.⁷

Isomerization is in competition with other possible energy relaxation channels. In low-temperature matrices, the

guest-guest energy transfer is reduced due to the low concentration of the guest molecules. On the other hand, energy relaxation may involve the transfer of excitation energy to the vibrational modes of the lattice.¹⁷ This process can be viewed as a phonon-assisted intramolecular vibrational energy relaxation (IVR), in which the lattice phonons act like a thermal bath that compensates the energy differences between the relevant intramolecular vibrational states. The relaxation rates are then expected to be dependent on the number of phonons involved and on the temperature of the phonon bath.¹⁷ The IR-induced isomerization quantum yield depends on the proportion of energy relaxation channels depositing energy into the reaction coordinate and the lifetimes of the molecular states involved. In rare-gas matrices, those factors are affected by the excitation energy, the host, and the nature of the excited mode.^{1,11–13,17,18}

Large quantum yields (20%–40%) were obtained for the

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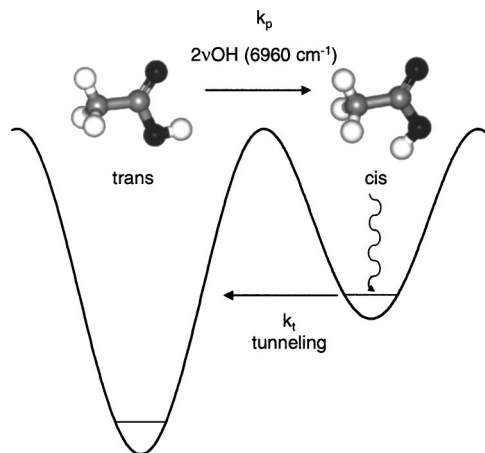


FIG. 1. Isomerization reaction of acetic acid. The *trans*→*cis* isomerization can be induced by excitation of the $2\nu\text{OH}$ mode of the *trans* conformer isolated in rare-gas matrices, while the *cis*→*trans* process occurs in dark via tunneling. The *trans*→*cis* isomerization barrier of 4432 cm^{-1} and the relative energy for the *cis* conformer of 1882.7 cm^{-1} are calculated by *ab initio* methods (Ref. 21).

IR-induced isomerization of formic acid (HCOOH) excited at various modes above the energy barrier in Ar matrices.^{7,19} This high efficiency was connected with the relatively large energy gaps in the vibrational manifold of this molecule that delay energy relaxation within the potential well of the initially excited conformer, allowing isomerization to take place.¹⁹ Similarly, high quantum yields for isomerization were estimated for the HONO molecule excited at the OH stretching mode (νOH) in Kr matrices.¹ In contrast, very low values were reported for $\text{CH}_2\text{FC}(\text{F})=\text{CH}_2$ isolated in solid Ar ($10^{-5}\%$ – $10^{-2}\%$).¹¹

Acetic acid (CH_3COOH) has two stable structures that are interconverted by rotation around the C–O bond, the *cis* and *trans* conformers shown in Fig. 1. Only recently, the higher energy *cis* conformer was detected experimentally, using excitation of the OH stretching overtone of the *trans* conformer isolated in an Ar matrix.²⁰ In that work, *cis*-acetic acid was found to tunnel back to the ground conformational state in dark even at temperatures as low as 8 K. According to the *ab initio* calculations, the *trans*→*cis* energy barrier is about 4400 cm^{-1} and the *cis* form is higher in energy than the *trans* form by about 1880 cm^{-1} .²¹ For formic acid the corresponding calculated values are $\sim 4200\text{ cm}^{-1}$ and $\sim 1400\text{ cm}^{-1}$ for the *trans*→*cis* energy barrier and the relative energy of *cis*-formic acid, respectively.²² Importantly, acetic acid differs from formic acid by the presence of a methyl rotor, which has a low barrier for internal rotation ($\sim 170\text{ cm}^{-1}$ for the *trans* conformer).²¹ In the gas phase, the presence of low barrier internal rotations have been postulated to be responsible for the decrease of the lifetime of excited states associated with vibrations close to the center of flexibility, due to the enhancement of the coupling of vibrational and internal rotational states.^{23–27} In the solid phase, the methyl rotor may also enhance couplings between the intramolecular vibrational states and the phonon bath. Thus, the comparison between the isomerization quantum yields for formic and acetic acids in similar experimental conditions

aids to evaluate the role of the methyl rotor in the dynamics of vibrational energy relaxation.

In acetic and formic acids, the fast *cis*→*trans* conversion by tunneling poses limitations to the detection of the high energy conformers.^{6,28,20} The tunneling rate of matrix isolated *cis*-formic acid was shown to depend on the temperature, the rare-gas host, and even the local environment within the same host (matrix site).²⁸ In that work, a qualitative interpretation of the experimental results was attempted on the basis of the relative position of the initial and final states of tunneling. At least three solvation effects were pointed out as influencing the tunneling dynamics, namely, the changes in barrier height, nature of the states involved, and energy gaps between the tunneling states. For the moment, the relative importance of those factors affecting tunneling is still not well understood. Computational simulations and systematic experimental studies of tunneling in different conformational systems, like acetic acid, are two approaches that are likely to give valuable information on the subject.

In the present work, we study the rotational isomerization of matrix-isolated acetic acid under resonant excitation in the $3500\text{--}7000\text{ cm}^{-1}$ range and the *cis*→*trans* dark reaction. The dependence of the *trans*→*cis* isomerization quantum yield on the excited vibration, excitation energy, and rare-gas host is evaluated. In addition, the effect of isotopic substitution on the isomerization efficiency is investigated. For the hydroxyl deuterated isotopologues, the isomerization quantum yields are obtained for both the *trans*→*cis* and *cis*→*trans* processes. Finally, the medium and temperature effects on the tunneling rates for the *cis*→*trans* dark reaction are investigated and compared with the available data on formic acid.

II. EXPERIMENTAL DETAILS

The gaseous samples were prepared by mixing acetic acid (Sigma-Aldrich, >99%) or its isotopologues (CD_3COOD and CH_3COOD , Sigma-Aldrich, 99.5%), degassed by several freeze-pump-thaw cycles, with high purity Ar, Kr, and Xe (AGA, >99.99) typically in the 1:2000 or 1:1000 proportions. The CD_3COOH form was obtained from the fully deuterated form by exchange of deuterium with H_2O adsorbed on the inner surface of the sample container and the deposition line. The gaseous mixtures were deposited onto a CsI substrate at $15\text{--}35\text{ K}$ (depending on the matrix material) in a closed cycle helium cryostat (APD, DE 202A) and subsequently cooled down to 8 K. The IR absorption spectra ($7900\text{--}400\text{ cm}^{-1}$) were measured with a Nicolet SX-60 Fourier transform infrared (FTIR) spectrometer. A liquid-nitrogen-cooled MCT detector and a Ge/KBr beam splitter were used to record the mid-IR absorption spectra ($0.25\text{--}1.0\text{ cm}^{-1}$ resolution), and a liquid nitrogen cooled InSb detector and a quartz beam splitter were used to record the near-IR absorption spectra (0.5 cm^{-1} resolution). Typically 100–500 interferograms were coadded.

Tunable pulsed IR radiation, provided by an optical parametric oscillator (OPO Sunlite, Continuum, with IR extension) was used to produce *cis*-acetic acid *via* vibrational excitation of *trans*-acetic acid. The pulse duration was ca. 5

TABLE I. Vibrational frequencies of *trans*-acetic acid in the 3500–7000 cm⁻¹ region for acetic acid isolated in solid Ar. The vibrational assignment is based on the observed fundamental modes for the molecule isolated in solid Ar reported in Ref. 29. Symbols: ν , stretching; δ , bending; τ , torsion; and γ , rocking.

CH ₃ COOH assignment	cm ⁻¹	CH ₃ COOD assignment	cm ⁻¹	CD ₃ COOD assignment	cm ⁻¹	CD ₃ COOD assignment	cm ⁻¹
ν OH	3564	ν OD	2629	ν OH	3564		
ν OH + γ C=O	4096	ν CH ₃ + ν CO	4215	ν OH + δ CO=O	3941		
ν OH + τ CO	4201	ν HCH ₂ + ν CO	4264		3946		
ν HCH ₂ + δ CH ₃	4411	ν HCH ₂ + δ CH ₃	4410	ν OH + γ C=O	4041		
ν OH + δ COH	4708	ν OD + ν C=O	4396	ν OH + τ COH	4173	ν OD + ν C=O	4392
ν OH + δ CH ₃	4876	ν HCH ₂ + δ HCH ₂	4464	ν OH + δ CH ₃	4710		
		2 ν OD	5170	ν OH + ν C-O	4881	2 ν OD	5168
ν OH + ν C=O	5351		5148	ν OH + ν C=O	5335		
2 ν OH	6957			2 ν OH	6958		

ns, the spectral linewidth ~ 0.1 cm⁻¹, and the repetition rate 10 Hz. The Burleigh WA-4500 wavemeter was used to control the OPO radiation frequency, providing an absolute accuracy better than 1 cm⁻¹. The pumping beam was quasicollinear with the spectrometer beam allowing simultaneous irradiation and recording of IR absorption spectra, and an interference filter transmitting in the 3300–1100 cm⁻¹ range was attached to the detector to prevent its exposure to the pumping radiation.

For the CH₃COOH and CD₃COOH isotopologues, a photoequilibrium of the *trans* and *cis* forms is established under IR pumping of the *trans* conformers, as a result of the interplay between *cis*-acetic acid photogeneration and its depletion due to tunneling. At the equilibrium, the pumping and tunneling rates are equal:

$$k_p(\nu)[\textit{trans}\text{-CH}_3\text{COOH}]_{\text{eq}} = k_t(T)[\textit{cis}\text{-CH}_3\text{COOH}]_{\text{eq}} \quad (1)$$

It follows that the averaged pumping rate $k_p(\nu)$ can be determined from the tunneling rate $k_t(T)$, and the ratio of the *cis* and *trans* photoequilibrium concentrations, as described elsewhere.¹⁹ For these calculations, the bands corresponding to the CH₃ bending of *trans*-CH₃COOH, the C=O stretching of *cis*-CH₃COOH, the COH bending of *trans*-CD₃COOH and the C-O stretching mode of *cis*-CD₃COOH were used.²⁹ Since deuteration of the hydroxyl group decreases the tunneling rate by orders of magnitude, for the CH₃COOD and CD₃COOD species the pumping rate coefficients were determined directly from the pumping-induced changes in concentration of one of the conformers.²⁰ For these two isotopologues, the concentrations were obtained from the integrated absorption of the bands corresponding to the C-O stretches of the *trans* and *cis* forms.²⁹ To avoid the influence of tunneling on the determination of the pumping rates, only the points obtained in the first 10 min of irradiation were considered for the OD-substituted species. Once the pumping rates are known, the quantum yields of the rotamerization processes $\phi(i)$ can be extracted from the following equation:

$$k_p(\nu) = \phi(i)\sigma_T^i(\nu)I(\nu), \quad (2)$$

where $\sigma_T^i(\nu)$ (in cm²) is the absorption cross section of the excited mode, I (in s⁻¹cm⁻²) is the photon intensity of the pumping beam and i refers to the excited vibrational mode.

The absorption cross section is obtained using the measured IR absorption at the excitation frequency, the known acetic acid concentration, and the matrix thickness. We estimated that the experimental error associated with the quantum yield values is roughly 50%.

III. EXPERIMENTAL RESULTS

After deposition, the matrix-isolated acetic acid is found in the most stable *trans* geometry. The vibrational modes of *trans*-acetic acid observed in the 3500–7000 cm⁻¹ spectral region for the monomer isolated in solid Ar are listed in Table I, and the absorption wavenumbers in the mid-IR region can be found elsewhere.^{20,29,30} The vibrational assignments for the overtone and combination modes presented in this table were based on the reported values for the fundamental modes and on the expected isotopic shifts.^{20,29} For the molecule isolated in Kr and Xe matrices, the observed modes in the 3500–7000 cm⁻¹ range appear shifted to lower frequencies as compared with the values found in an Ar matrix, as a consequence of the known matrix effect caused by guest-host interactions. This effect is illustrated in Table II where the bands observed in the Ar, Kr, and Xe matrices are listed for the CH₃COOH isotopologue.

TABLE II. Vibrational frequencies of *trans*-CH₃COOH in the 3500–7000 cm⁻¹ region in solid Ar, Kr, and Xe. The vibrational assignment is based on the observed fundamental modes for the molecule isolated in solid Ar reported in Ref. 29. The splitting of bands observed for Kr and Xe are due to site effects. Symbols: ν , stretching; δ , bending; τ , torsion, and γ , rocking.

Assignment	Ar	Kr	Xe
ν OH	3564	3552 3551 3549	3546 3538 3532
ν OH + γ C=O	4096	4082 4079	3528 4066
ν OH + τ CO	4201	4190	4171
ν HCH ₂ + δ CH ₃	4411	4400	4403
ν OH + δ COH	4708	4694	4678
ν OH + δ CH ₃	4876	4866	4846
ν OH + ν C=O	5341	5326	5306 5303
2 ν OH	6957	6932	6887 6881

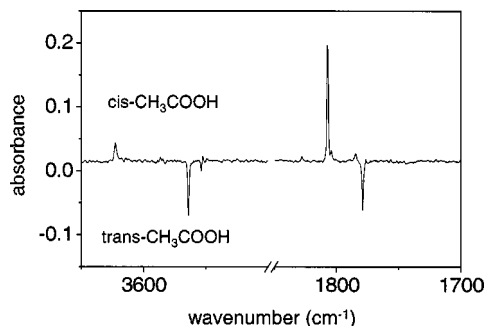


FIG. 2. Difference IR absorption spectrum obtained by excitation of the $2\nu\text{OH}$ mode of the *trans* form. The bands at 3564 and 1779 cm^{-1} belong to the *trans* form of acetic acid, and the bands at 3623 and 1807 cm^{-1} belong to the *cis* form.

The *trans* \rightarrow *cis* isomerization was induced by irradiating the sample at frequencies corresponding to some of the most intense bands in the 3500–7000 cm^{-1} spectral region. In Fig. 2, the spectral changes induced in the regions of the OH and C=O stretches by pumping at the νOH overtone ($2\nu\text{OH}$) of CH_3COOH are shown. The isomerization quantum yields estimated for several excited modes in various matrices are listed in Table III and plotted in Fig. 3. For the CH_3COOH isotopologue, the quantum yield is essentially independent of the excited mode, when the excitation energy is above the calculated isomerization barrier ($\sim 4400 \text{ cm}^{-1}$). The obtained quantum yields are about one order of magnitude smaller than the values measured for formic acid under similar experimental conditions (see Fig. 3).^{7,19,31} At energies below $\sim 4400 \text{ cm}^{-1}$, the quantum yield depends strongly on the excitation energy.

For CD_3COOD , the quantum yields obtained by excitation of the $2\nu\text{OD}$ and the $\nu\text{OD} + \nu\text{C}=\text{O}$ combination mode were found to be 0.011 and 0.016, being similar to the values for CH_3COOH (averaged value for pumping above the cal-

TABLE III. Quantum yields for the IR-induced *trans* \rightarrow *cis* isomerization of acetic acid isolated in rare-gas matrices. The relative error has been estimated as 50% of the quantum yield value.

Excited mode/Energy (cm^{-1})	Ar	Kr
CH_3COOH^a		
νOH	1.4×10^{-4}	1.5×10^{-4}
$\nu\text{OH} + \gamma\text{C}=\text{O}$	2.6×10^{-3}	3.2×10^{-3}
$\nu\text{OH} + \tau\text{CO}$	2.7×10^{-3}	8.4×10^{-3}
$\nu\text{HCH}_2 + \delta\text{CH}_3$	3.0×10^{-3}	...
$\nu\text{OH} + \delta\text{CH}_3$...	2.2×10^{-2}
$\nu\text{OH} + \nu\text{C}=\text{O}$...	2.9×10^{-2}
$2\nu\text{OH}$	2.2×10^{-2}	2.6×10^{-2}
CH_3COOD		
$2\nu\text{OD}$	3.6×10^{-3}	...
CD_3COOH		
$\nu\text{OH} + \nu\text{C}=\text{O}$	8.5×10^{-2}	...
$2\nu\text{OH}$	1.5×10^{-1}	...
CD_3COOD		
$\nu\text{OD} + \nu\text{C}=\text{O}$	1.6×10^{-2}	...
$2\nu\text{OD}$	1.1×10^{-2}	...

^aThe quantum yield determined for pumping at the $2\nu\text{OH}$ mode of the molecule isolated in solid Xe is 3.5×10^{-2} .

^bAverage value used for pumping acetic acid in the Ar and Kr matrices. Symbols: ν , stretching; δ , bending; τ , torsion; and γ , rocking.

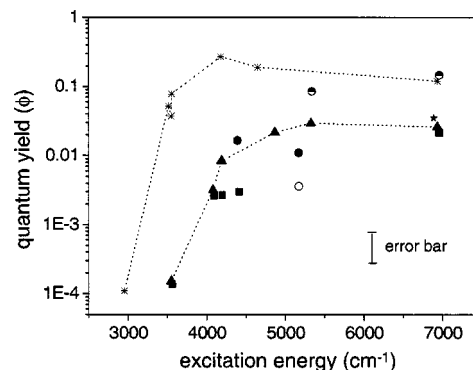


FIG. 3. Quantum yield for the IR-induced *trans* \rightarrow *cis* isomerization of acetic acid [CH_3COOH in solid Ar (\blacksquare), Kr (\blacktriangle); and Xe (\blackstar); and CD_3COOH (\bullet), CH_3COOD (\circ), and CD_3COOD (\bullet) in solid Ar]. The results for the *trans* \rightarrow *cis* isomerization of formic acid in solid Ar are shown for comparison (*). The error bar represents $\pm 50\%$ of the estimated quantum yields. The *trans* \rightarrow *cis* isomerization barriers calculated for acetic and formic acid are ~ 4400 and 4200 cm^{-1} , respectively (Refs. 21, 22).

culated isomerization barrier ~ 0.025). On the other hand, the quantum yields obtained for CD_3COOH (0.15 for $2\nu\text{OH}$, and 0.085 for $\nu\text{OH} + \nu\text{C}=\text{O}$) and CH_3COOD (0.0036 for $2\nu\text{OD}$) differ from each other and from the averaged values for CH_3COOH (~ 0.025 , see Fig. 3).

The concentration of the *cis* conformer is limited by the low *trans* \rightarrow *cis* isomerization quantum yield and by the *cis* \rightarrow *trans* tunneling (Fig. 4).²⁰ Therefore, the data concerning the photoinduced *cis* \rightarrow *trans* process is much more limited. For the OH-isotopologues, the *cis* \rightarrow *trans* tunneling rate is fast (see Fig. 4),²⁰ which practically prevents measurement of the quantum yield for the *cis* \rightarrow *trans* isomerization process. However, in the case of the OD-isotopologues the tunneling is much slower,²⁰ and we could follow the pumping kinetics while exciting the $2\nu\text{OD}$ band of the *cis* form at $\approx 5258 \text{ cm}^{-1}$, i.e., well above the predicted *cis* \rightarrow *trans* isomerization barrier. This enables estimation of the quantum yields for the *cis* \rightarrow *trans* isomerization in CD_3COOD and CH_3COOD . In both cases, the quantum yield was found to be reliably higher than that for the corresponding *trans* \rightarrow *cis* isomerization (by a factor of 40 for CD_3COOD and by a factor of 3 for CH_3COOD).

The effects of temperature and medium on the dark *cis* \rightarrow *trans* reaction of acetic acid were evaluated by following the tunneling kinetics at various temperatures and in different rare-gas matrices. The Arrhenius plots are shown in Fig. 4. The tunneling rate is found to be similar in Ar and Kr matrices, and it is enhanced by a factor of ≈ 5 in a Xe matrix. The tunneling rate increases at higher temperatures. The data for the temperature dependence in a Xe matrix is less accurate because of the large tunneling rates. Deuteration of the methyl group increases the tunneling rate. This is shown by comparing the values measured for CD_3COOH and CD_3COOD ($7.1 \times 10^{-2} \text{ s}^{-1}$ and $1.1 \times 10^{-6} \text{ s}^{-1}$, respectively) with those obtained for CH_3COOH and CH_3COOD ($2.1 \times 10^{-2} \text{ s}^{-1}$ and $7.3 \times 10^{-7} \text{ s}^{-1}$, respectively), as measured in solid Ar at 8 K.

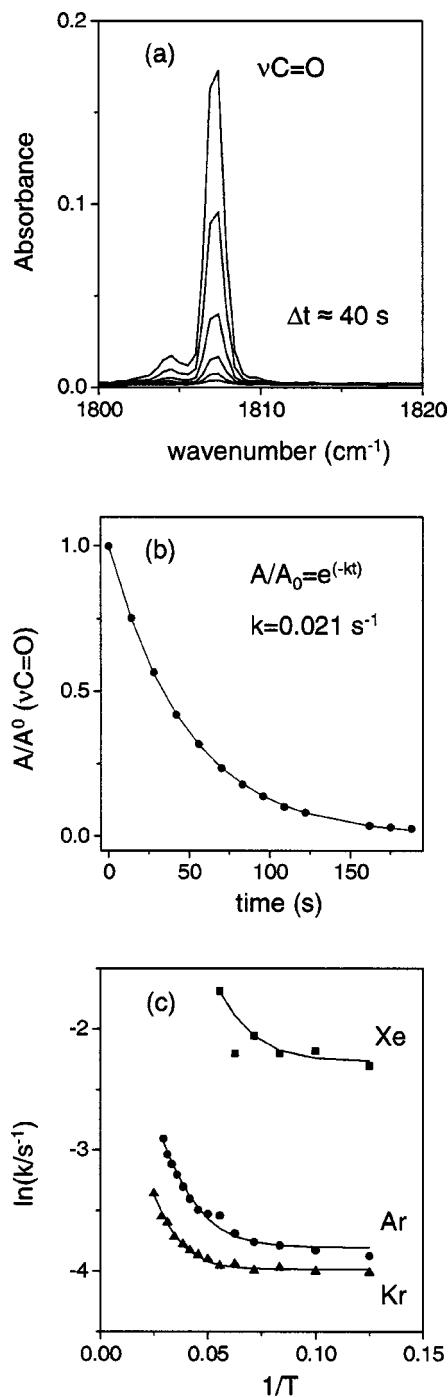


FIG. 4. Tunneling kinetics for the *cis*→*trans* isomerization of acetic acid in rare-gas matrices: (a) time decay of the $\nu\text{C}=\text{O}$ band of *cis*- CH_3COOH in solid Ar at 8 K, (b) exponential fit of the integrated intensity of this band, and (c) Arrhenius plots for the *cis*→*trans* tunneling rate. In plot (c), the experimental data are fitted using an expression for a temperature dependent rate constant $[k(T) = k_0 + k_1 \exp(-E_a/RT)]$, where k_0 , k_1 , and E_a are the parameters. The extracted activation energies (E_a) are (57 ± 4) , (72 ± 4) , and (53 ± 12) cm^{-1} , the k_0 values are (0.0223 ± 0.0007) , (0.0186 ± 0.0002) , and (0.104 ± 0.005) s^{-1} , and the k_1 values are (0.40 ± 0.07) , (0.24 ± 0.03) , and (6 ± 6) s^{-1} for Ar, Kr, and Xe, respectively.

IV. DISCUSSION

A. Quantum yield for the IR-induced isomerizations

For the $2\nu\text{OH}$ mode (~ 7000 cm^{-1}) of the CH_3COOH isotopologue, the quantum yield estimated for the three ma-

trix materials (2.2%, 2.6%, and 3.5%, in Ar, Kr, and Xe, respectively) increases slightly with the polarizability of the rare gas as found previously for other compounds.^{3,4} However, the values here reported for the three matrices are still within a possible experimental error. Therefore, the quantum yield for acetic acid *trans*→*cis* isomerization is not strongly affected by the rare-gas host; in particular, the activated relaxation channels and their efficiency seem to be similar in various matrices.

At excitation energies above the calculated isomerization barrier (>4400 cm^{-1}), the quantum yields for the *trans*→*cis* process in Ar and Kr matrices at 8 K show no difference for various modes (within the experimental error), the obtained values being around 2%–3%. The energy above which the quantum yield reaches a relatively stable value (4500 cm^{-1}) agrees with the computational barrier height, which supports the theoretical estimation. The lack of evident mode specific effects on the quantum yield was also reported for formic acid in solid Ar.^{7,19,31} For both molecules, the range of excitation energies probed corresponds to the discrete region of vibrational states and, thus, mode specific effects are generally possible. We can speculate that the observed lack of mode specificity in the isomerization quantum yield is connected with a slow isomerization rate, allowing effective randomization of the excitation energy between various modes. The coupling of the intramolecular vibrational states with the lattice possibly plays an important role in this randomization process. It should be remembered that the experiment probes the probability of becoming trapped in either well, and after excitation the molecule may undergo isomerization back and forth between the *trans* and *cis* forms before cooling sufficiently to be trapped in either well. The time between initial excitation and trapping may indeed be long enough to allow extensive randomization of energy irrespective of the initially excited mode. Another possibility is that all excited states decay essentially to a few common low energy states with a dominant contribution to the energy relaxation dynamics. The excitation energy introduced into the molecule is still in the low density of states where such bottleneck states could be found.

Deuteration of the methyl group increases the quantum yield for the *trans*→*cis* isomerization from 2%–3% to 8%–15%, as seen from comparison of the values obtained for CH_3COOH and CD_3COOH . This difference shows that the methyl group plays an important role in the isomerization dynamics. It may be that CH_3 yields faster energy relaxation process than CD_3 because its higher energy modes can participate in lower-order couplings leading to a more efficient nonreactive deactivation of the excited states.

Deuteration of the hydroxyl group decreases the quantum yield by almost one order of magnitude (from 2%–3% to 0.4%). This information is provided by the values obtained for the almost isoenergetic vibrations of CH_3COOH and CH_3COOD at ≈ 5250 cm^{-1} . In the case of deuteration of the hydroxyl group, the reaction coordinate is directly affected by the isotopic substitution, which decreases the frequency of the $\tau\text{C}-\text{O}$ mode. Therefore, at similar energies, the $\tau\text{C}-\text{O}$ coordinate should be in a higher excited state in CH_3COOD than in CH_3COOH . Thus, in CH_3COOH the

couplings between the τ C-O and the excited states are expected to be of lower order than those in CH_3COOD , which relatively increases the isomerization efficiency in CH_3COOH .

Remarkably, no significant difference is observed between the isomerization quantum yields for CH_3COOH and CD_3COOD . This observation is in agreement with the previous discussion. Indeed, in the perdeuterated isotopologue, two opposite effects due to isotopic substitution in the methyl group (increase in the quantum yield) and in the hydroxyl group (decrease in the quantum yield) seem to compensate each other, leading to a minor net effect.

Several modes with energies below the computed isomerization barrier (e.g., pumping at ≈ 4200 , 4100 , and 3560 cm^{-1}) were also found to be active in promoting the $trans \rightarrow cis$ process in acetic acid. In this case, a tunneling mechanism is presumably involved. As shown in Fig. 3, for these excitations, the quantum yield increases strongly with the energy. A similar dependence of the quantum yield on the excitation energy is observed for formic acid in solid Ar. The effect was previously explained based on the delocalization of the torsional wave functions between the cis and $trans$ potential wells.⁷

As seen in Fig. 3, the isomerization quantum yield is about one order of magnitude higher for formic acid than for acetic acid. As already mentioned, the presence of the methyl group in acetic acid can enhance the coupling of intramolecular vibrational states with each other and with lattice motion. Additionally, the low-frequency modes originated by the methyl group are capable of participating in the energy relaxation similar to the lattice phonon. Possibly these two effects lead to an increase of the rate for intramolecular energy transfer and/or to an increase in the number of relaxation channels competing with isomerization.²⁵ On the other hand, large-amplitude vibrations such as τ C-O and τ C-C are thought to be considerably anharmonic and, thus, strong coupling between the two internal rotors of acetic acid may also be operating. This is particularly important, since the methyl motion has a lower frequency than τ C-O and part of the energy deposited into the reaction coordinate may also be dissipated through the methyl motion without isomerization. Another interesting observation is that the isomerization quantum yield starts decreasing at energies lower by $\approx 500\text{ cm}^{-1}$ for formic acid than for acetic acid, in qualitative agreement with the predicted lower isomerization barrier for formic acid. The difference between the energy barriers is also experimentally supported by the large gap (roughly two orders of magnitude) between isomerization yields for pumping of formic and acetic acids at the OH-stretching modes.

The reverse, $cis \rightarrow trans$ photoinduced isomerization of acetic acid was also investigated. In this case, excitation of the $2\nu\text{OD}$ mode of $cis\text{-CD}_3\text{COOD}$ and $cis\text{-CH}_3\text{COOD}$ was found to be more efficient in promoting the isomerization than the excitation of the same mode of the corresponding $trans$ conformers to promote the $trans \rightarrow cis$ conversion. The energy barrier for the $cis \rightarrow trans$ process was estimated to be $\approx 1880\text{ cm}^{-1}$ lower than for the $trans \rightarrow cis$ conversion.²¹ Hence, this factor may partially contribute to the observed difference in the isomerization quantum yields.

However, this explanation is not supported by the fact that the $trans \rightarrow cis$ quantum yields here reported are practically insensitive to the excitation energy, as long as it is above the calculated isomerization barrier. Furthermore, the barrier height is the same for CD_3COOD and CH_3COOD , but the relative changes in quantum yield are quite different ($\phi_{c/t} \approx 44$ for CD_3COOD and $\phi_{c/t} \approx 3$ for CH_3COOD , where $\phi_{c/t}$ denotes the ratio of the $cis \rightarrow trans$ and $trans \rightarrow cis$ quantum yields). Accordingly, this factor does not seem to be the dominant one in the studied system. A similar behavior was also observed for HONO isolated in solid Kr ($\phi_{c/t} \approx 7$), where the isomerization barriers (E_i) for the direct and reverse processes are nearly identical ($\Delta E_i = 130\text{ cm}^{-1}$).¹ For the case of HONO, it has been suggested that kinetic or potential couplings between the excited vibrations and nearly resonant vibrational states could be responsible for the more efficient energy transfer from the excited states to the reaction coordinate upon excitation of the cis isomer.^{32,33} These factors may also be relevant for acetic acid.

B. Tunneling rate for the $cis \rightarrow trans$ dark reaction

As mentioned earlier, the $cis \rightarrow trans$ isomerization of acetic acid is observed in dark. As it was discussed for the analogous case of formic acid,²⁸ the initial state in this dark process is essentially the ground state of the cis conformer and the final state is some excited vibrational level of the $trans$ conformer.²⁰ From this excited state the energy relaxes via a cascading process controlled by the energy gaps between intramolecular states and mode couplings. The observed temperature dependence of the tunneling rate for the $cis \rightarrow trans$ isomerization of acetic acid (see Fig. 4) indicates participation of low energy quanta in the tunneling process, which compensates the energy mismatch between the intramolecular levels involved in the process.^{17,18} The fitting of the tunneling kinetics measured in the three studied matrices with a temperature dependent rate of the type $k(T) = k_0 + k_1 \exp(-E_a/RT)$ yields activation energies of $50\text{--}80\text{ cm}^{-1}$ (see Fig. 4). These activation energy values are consistent with the participation of lattice phonon modes in the tunneling process in the various hosts, where the Debye frequencies range from 40 to 70 cm^{-1} .³⁴ In addition, it should be remembered that the methyl torsion (estimated below 100 cm^{-1} in the cis conformer) (Ref. 21) might also be involved in the mechanism.

For acetic acid, the $cis \rightarrow trans$ tunneling rate is larger by at least one order of magnitude (for all hosts at 8 K) than the tunneling rate observed for formic acid.²⁸ The faster tunneling in acetic acid can be primarily connected to its predicted lower barrier for the $cis \rightarrow trans$ conversion as compared with formic acid, the computed difference being $\sim 300\text{ cm}^{-1}$.^{21,22} Note that the increase in the $cis \rightarrow trans$ tunneling rate is quantitatively similar to the decrease in the $trans \rightarrow cis$ isomerization quantum yield, discussed earlier. It follows that the faster tunneling rate for acetic acid can also be a consequence of an efficient deactivation of the excited state of the $trans$ form by the low-energy states of the methyl group.

For acetic acid, the tunneling rate in solid Ar is some-

what higher than in solid Kr, while in solid Xe the rate is faster than in those two matrices by a factor of ~ 5 . A significantly different matrix effect was observed for formic acid, where the tunneling rates increase in the order $k_{\text{Ar}} > k_{\text{Kr}} > k_{\text{Xe}}$.²⁸ This difference indicates a very specific dependence of the tunneling rate on the solute-solvent interactions in the studied systems. For formic acid, the dependence of the tunneling rate with the matrix host was interpreted as resulting from the interplay of three factors determined by solvation effects.²⁸ It was shown that the tunneling rate can also be affected by the local environment within the same host.²⁸ Practically, this means that any detailed interpretation of the observed matrix effect is not realistic at the moment due to the high complexity of the system. Particularly in acetic acid, the lower energy vibrational modes of the methyl group may participate in the tunneling mechanism, in addition to the phonon modes.

Some general ideas can be extracted from the comparison of the tunneling rates for different isotopologues in a given matrix. As expected, the tunneling rate was found to decrease by ca. four orders of magnitude upon substitution of the tunneling particle (OH \rightarrow OD) both for CH₃ and CD₃ containing isotopologues in Ar matrices.²⁰ On the other hand, for the CD₃COOH isotopologue, the tunneling rate in solid Ar at 8 K ($7.1 \times 10^{-2} \text{ s}^{-1}$), is about three times faster than that observed for CH₃COOH in the same experimental conditions ($2.1 \times 10^{-2} \text{ s}^{-1}$). Similarly, the tunneling rate for the fully deuterated species ($1.1 \times 10^{-6} \text{ s}^{-1}$) is almost twice faster than for CH₃COOD ($7.3 \times 10^{-7} \text{ s}^{-1}$). These relative values of tunneling rates can be correlated with an increased efficiency in the energy dissipation within the *trans* well in the acetic acid isotopologues bearing a deuterated methyl group. The smaller energy quanta of the deuterated methyl group can provide a better match with the small energy gap to be overcome in the tunneling process. However, this interpretation is certainly an oversimplification, since the change of the intramolecular vibrational structure occurring upon isotopic substitution may also change both the nature of the states and order of coupling with the phonons involved in the tunneling process.²⁸

V. CONCLUSIONS

Narrowband tunable IR radiation was used to excite selectively various vibrational modes in the 3500–7000 cm^{-1} spectral region of monomeric acetic acid isolated in rare-gas matrices. The isomerization quantum yields for both *trans* \rightarrow *cis* and *cis* \rightarrow *trans* processes were estimated, and the influence of medium, isotopic substitution, and nature of the excited vibrational mode were investigated. The higher energy conformer (*cis*) of acetic acid tunnels back to the conformational ground state (*trans*) even at the lowest working temperature used (8 K). The effects of temperature and medium on the kinetics of the phonon-assisted tunneling process were also addressed.

The main conclusions to be drawn from this study are as follows:

(1) Above the calculated isomerization barrier ($\sim 4400 \text{ cm}^{-1}$), the quantum yield of the IR-induced *trans* \rightarrow *cis* isomerization of acetic acid in solid rare gases is rather in-

sensitive to the excited vibrational mode and the rare-gas host. The IR-induced *cis* \rightarrow *trans* isomerization is more efficient than the *trans* \rightarrow *cis* process. Below 4400 cm^{-1} , the quantum yield for the *trans* \rightarrow *cis* isomerization depends strongly on the excitation energy, and this is probably due to the participation of tunneling in the IR-induced mechanism.

(2) Deuteration of the methyl group increases the *trans* \rightarrow *cis* isomerization quantum yield, while deuteration of the hydroxyl group has the opposite effect. This behavior is probably connected with the different orders of couplings between the excited modes. In the CD₃-isotopologues as compared with the CH₃-isotopologues, the less efficient couplings between the excited modes and the methyl torsion seem to decrease the rate of deactivation of the excited states, increasing the isomerization probability. In the OD-isotopologues as compared with the OH-isotopologues, less efficient couplings between the excited vibrational states and the τ CO mode could be responsible for a lower efficiency of energy transfer to the reaction coordinate.

(3) On average, the *trans* \rightarrow *cis* isomerization quantum yield is one order of magnitude smaller for acetic acid (CH₃COOH) than the values for formic acid (HCOOH).^{7,19} The presence of the low-barrier methyl rotor increases the number of states coupled to the initially excited state, thus probably increasing the number of accessible energy relaxation channels that deactivate the excited mode without transferring energy to the reaction coordinate.

(4) For acetic acid, the *cis* \rightarrow *trans* tunneling rates of the dark reaction follow the trend $k_{\text{Xe}} \gg k_{\text{Ar}} > k_{\text{Kr}}$, which differs from the case of formic acid ($k_{\text{Ar}} > k_{\text{Kr}} > k_{\text{Xe}}$).²⁸ This result indicates that the tunneling kinetics depends on specific solvation effects. The *cis* \rightarrow *trans* tunneling rate is larger for acetic acid than for formic acid by at least one order of magnitude (at 8 K). This difference is presumably connected with the lower isomerization barrier predicted for acetic acid. In addition, this behavior can also be connected with the low-frequency modes of the methyl group in acetic acid increasing the efficiency of the energy relaxation within the *trans* well.

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¹L. Khriachtchev, J. Lundell, E. Isoniemi, and M. Räsänen, J. Chem. Phys. **113**, 4265 (2000).

²A. J. Barnes, J. Mol. Struct. **113**, 161 (1984).

³M. Räsänen, H. Kunttu, and J. Murto, Laser Chem. **9**, 123 (1988).

⁴T. Lotta, J. Murto, M. Räsänen, and A. Aspiala, J. Mol. Struct. **114**, 333 (1984).

⁵S. Sander, H. Willner, L. Khriachtchev, M. Pettersson, M. Räsänen, and E. L. Varetto, J. Mol. Spectrosc. **203**, 145 (2000).

⁶M. Pettersson, J. Lundell, L. Khriachtchev, and M. Räsänen, J. Am. Chem. Soc. **119**, 11715 (1997).

⁷M. Pettersson, E. M. S. Maçôas, L. Khriachtchev, R. Fausto, and M. Räsänen, J. Am. Chem. Soc. **125**, 4058 (2003).

⁸H. H. Gunthard, J. Mol. Struct. **113**, 141 (1984).

⁹R. N. Perutz, Chem. Rev. (Washington, D.C.) **85**, 97 (1985).

¹⁰S. Kudoh, M. Takayanagi, M. Nakata, T. Ishibashi, and M. Tasumi, J. Mol. Struct. **479**, 41 (1999).

- ¹¹A. K. Knudsen and G. C. Pimentel, *J. Phys. Chem.* **95**, 2823 (1991).
- ¹²W. F. Hoffman and J. S. Shirk, *Chem. Phys.* **78**, 331 (1983).
- ¹³P. Roubin, S. Varin, P. Verlaque, S. Coussan, J. M. Berset, J. M. Ortega, A. Peremans, and W. Q. Zheng, *J. Chem. Phys.* **107**, 7800 (1997).
- ¹⁴M. Poliakoff and J. J. Turner, in *Chemical and Biochemical Applications of Lasers*, edited by C. B. Moore (Academic, New York, 1980), Vol. 5.
- ¹⁵H. Frei and G. C. Pimentel, in *Chemistry and Physics of Matrix-Isolated Species*, edited by L. Andrews and M. Moskovits (Elsevier Science, Amsterdam, 1989).
- ¹⁶H. Frei and G. C. Pimentel, *Annu. Rev. Phys. Chem.* **36**, 491 (1985).
- ¹⁷F. Legay, in *Chemical and Biochemical Applications of Lasers*, edited by C. B. Moore (Academic, New York, 1977), Vol. II.
- ¹⁸V. E. Bondybey, M. Räsänen, and A. Lammers, *Annu. Rev. Phys. Chem.* **95**, 331 (1999).
- ¹⁹E. M. S. Maçôas, L. Khriachtchev, M. Pettersson, J. Juselius, R. Fausto, and M. Räsänen, *J. Chem. Phys.* **119**, 11765 (2003).
- ²⁰E. M. S. Maçôas, L. Khriachtchev, M. Pettersson, R. Fausto, and M. Räsänen, *J. Am. Chem. Soc.* **125**, 16188 (2003).
- ²¹M. L. Senent, *Mol. Phys.* **99**, 1311 (2001).
- ²²J. D. Goddard, Y. Yamaguchi, and H. F. Schaefer, *J. Chem. Phys.* **96**, 1158 (1992).
- ²³K. W. Holtzclaw and C. S. Parmenter, *J. Chem. Phys.* **82**, 5283 (1985).
- ²⁴C. S. Parmenter and B. M. Stone, *J. Chem. Phys.* **84**, 4710 (1986).
- ²⁵A. McIlroy and D. I. Nesbitt, *J. Chem. Phys.* **101**, 3421 (1994).
- ²⁶G. A. Bethardy, X. L. Wang, and D. S. Perry, *Can. J. Chem.* **72**, 652 (1994).
- ²⁷D. S. Perry, G. A. Bethardy, and X. L. Wang, *Ber. Bunsen-Ges. Phys. Chem.* **99**, 530 (1995).
- ²⁸M. Pettersson, E. M. S. Maçôas, L. Khriachtchev, J. Lundell, R. Fausto, and M. Räsänen, *J. Chem. Phys.* **117**, 9095 (2002).
- ²⁹E. M. S. Maçôas, L. Khriachtchev, R. Fausto, and M. Räsänen, *J. Phys. Chem. A* **108**, 3380 (2004).
- ³⁰C. V. Berney, R. L. Redington, and K. C. Lin, *J. Chem. Phys.* **53**, 1713 (1970).
- ³¹E. M. S. Maçôas, L. Khriachtchev, M. Pettersson, J. Lundell, R. Fausto, and M. Räsänen, *Vib. Spectrosc.* **34**, 73 (2004).
- ³²Y. Guan, G. C. Lynch, and D. L. Thompson, *J. Chem. Phys.* **87**, 6957 (1987).
- ³³F. Richter, M. Hochlaf, P. Rosmus, F. Gatti, and H. D. Meyer, *J. Chem. Phys.* **120**, 1306 (2004).
- ³⁴H. J. Jodl, in *Chemistry and Physics of Matrix-Isolated Species*, edited by L. Andrews and M. Moskovits (Elsevier Science, Amsterdam, 1989).