

Formic and acetic acids in a nitrogen matrix: Enhanced stability of the higher-energy conformer

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Formic acid (HCOOH, FA) and acetic acid (CH₃COOH, AA) are studied in a nitrogen matrix. The infrared (IR) spectra of *cis* and *trans* conformers of these carboxylic acids (and also of the HCOOD isotopologue of FA) are reported and analyzed. The higher-energy *cis* conformer of these molecules is produced by narrowband near-IR excitation of the more stable *trans* conformer, and the *cis*-to-*trans* tunneling decay is evaluated spectroscopically. The tunneling process in both molecules is found to be substantially slower in a nitrogen matrix than in rare-gas matrices, the *cis*-form decay constants being approximately 55 and 600 times smaller in a nitrogen matrix than in an argon matrix, for FA and AA respectively. The stabilization of the higher-energy *cis* conformer is discussed in terms of specific interactions with nitrogen molecule binding with the OH group of the carboxylic acid. This model is in agreement with the observed differences in the IR spectra in nitrogen and argon matrices, in particular, the relative frequencies of the ν OH and τ COH modes and the relative intensities of the ν OH and ν C=O bands. © 2010 American Institute of Physics.

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I. INTRODUCTION

Formic acid (HCOOH, FA) and acetic acid (CH₃COOH, AA) are simple carboxylic acids both identified in the interstellar medium.^{1,2} Carboxylic acids have biological value and provide an insight into prebiotic organic chemistry in the protoplanetary nebula.³ Acetic acid is of particular importance due to its structural proximity to glycine, the simplest amino acid. Formation of acetic acid was detected upon irradiation of binary mixtures of methane (CH₄) and carbon dioxide (CO₂) ices by energetic electrons at 12 K.⁴ Electron bombardment mimics the energy transfer processes that occur in the track of the trajectories of MeV cosmic-ray particles.

Organic acids in the gas phase can partition into aerosol particles⁵ with the aid of foreign nuclei, such as alkaline mineral particles and elemental carbon, and by condensation and co-condensation with NH₃. It is hypothesized that organic acids are at least one of the primary sources of CCN in the atmosphere, especially over the continental forested areas, due to their ubiquitous presence in the troposphere.⁶

FA and AA have two conformers (*cis* and *trans*), which differ by the orientation of the OH group (Fig. 1). They are good model systems for fundamental studies of conformational changes and intramolecular energy redistribution. The *cis* form is higher in energy than the *trans* form by approximately 1365 cm⁻¹ for FA (gas-phase experimental data),⁷ and approximately 1880 cm⁻¹ for AA (theoretical value).⁸ The calculated *trans*-to-*cis* conversion barriers are

44 kJ mol⁻¹ (3921 cm⁻¹) (Ref. 9) and 49 kJ mol⁻¹ (4400 cm⁻¹) (Ref. 8) for FA and AA, respectively. Detailed infrared (IR) spectroscopic data for *trans* and *cis* conformers of these acids and their isotopomers have been reported in rare-gas matrices.¹⁰⁻¹⁴

The *cis* form of carboxylic acids can be obtained by vibrational excitation of the *trans* form.^{10,13,15} Once obtained, the higher-energy *cis* conformer converts back to the ground-state *trans* form. At low temperatures, quantum tunneling dominates the overbarrier reactions. Hydrogen tunneling in FA and AA has been the subject of several studies.^{9,15-19}

cis-CH₃COOH has a shorter lifetime in rare-gas matrices than *cis*-HCOOH [approximately 50 s (Ref. 18) versus 8 min (Ref. 16) in solid argon at 8 K]. Deuteration of the OH group influences greatly the tunneling process, slowing it down by about four orders of magnitude. The conversion process of *cis*-CH₃COOD and *cis*-HCOOD to the *trans* forms in an argon matrix at 8 K takes about 15 days.^{18,19} On the other hand, the tunneling rates in formic¹⁶ and acetic acids¹⁸ increase upon deuteration of CH or CH₃ groups. This secondary isotopic effect is very interesting but lacks an explanation.

The tunneling rates in these species are strongly dependent on the matrix material. The *cis*-HCOOH decay rates change with the matrix polarizability as $k_{Xe} < k_{Kr} < k_{Ar} < k_{Ne}$.^{15,16} However, the decay of *cis*-HCOOD follows almost the opposite trend: $k_{Xe} \approx k_{Kr} > k_{Ar} \approx k_{Ne}$.¹⁹ With respect to the reaction barrier height, which increases in more polarizable hosts, the order of the rate constants in HCOOD is anomalous.^{15,16} Similar “anomalous” behavior was also reported for AA ($k_{Xe} > k_{Ar} \geq k_{Kr}$).¹⁸ Clearly, in addition to the

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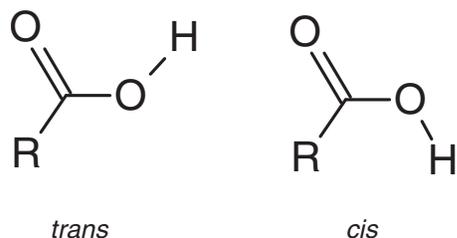


FIG. 1. *Trans* (most stable) and *cis* (higher energy) conformers of formic acid ($\text{R}=\text{H}$) and acetic acid ($\text{R}=\text{CH}_3$).

barrier change upon solvation in polarizable media, other factors can also influence the *cis*-to-*trans* conversion.^{15,16,19}

Some experimental results suggest that the *cis* conformers might be stabilized in media resembling interstellar and atmospheric environments. An experimental study of AA and FA aerosol nanoparticles generated at 78 K and investigated using *in situ* rapid-scan Fourier transform infrared spectroscopy (FTIR) shows that the spectra of the particles have the same characteristic splitting of the $\nu(\text{C}=\text{O})$, $\delta(\text{CH})$, and $\nu(\text{C}-\text{O})$ bands as the crystalline bulk.²⁰ One possible explanation for the observed splitting is the co-existence of the *trans* and *cis* conformations in the chains, which would presumably destroy the planarity of the chains; however, the polymorphism of molecular chains made from *trans* subunits cannot be excluded. Crystalline acetic acid shows similar spectral splitting which might also be attributed to the inclusion of *cis*-oriented subunits.²¹

The tentative observation of the *cis* conformation in hydrogen-bonded systems agrees well with the general idea that complexation, dimerization, or solvation of higher-energy conformers can significantly decelerate or even stop the tunneling decay process.^{15,22} For example, the *cis*- $\text{HCOOH}\cdots\text{H}_2\text{O}$ complex is stable at 9 K on a day scale. The lifetime of *cis*-FA in this complex might be practically infinite at low temperatures, i.e., tunneling to the *trans* conformer is efficiently suppressed.¹⁵ Studies of the interaction of carboxylic acids with nitrogen might lead to a better understanding of the role of conformational isomerism in dark interstellar clouds²³ and the Earth's atmosphere.

In the present work, we report new results on spectroscopy of formic and acetic acids in a nitrogen matrix and on the stabilization of higher-energy *cis* conformers in this medium. The stabilization effect is discussed in terms of specific interactions between the matrix and embedded molecules.

II. COMPUTATIONAL DETAILS AND RESULTS

The quantum chemical calculations were performed using GAMESS, version R1 (24-Mar-2007) (Ref. 24) at the MP2 level of theory²⁵ using the 6-311++G(2d,2p) basis set.^{26,27} This basis set has been shown to reproduce the experimental structural and vibrational properties of FA with an acceptable accuracy.^{11,28,29} The optimization criteria parameter OPTTOL was set to 0.00001 hartree/bohr. This parameter corresponds to the maximum value allowed to the energy gradient and also controls the maximum allowed value of the root mean square gradient, which is given by 1/3 of OPT-

TOL. The optimized structures of all $\text{FA}\cdots\text{N}_2$ and $\text{AA}\cdots\text{N}_2$ complexes were confirmed to correspond to the true energy minima on the potential energy surfaces by inspection of the Hessian matrices. The vibrational spectra were computed at the same level of theory. The calculated MP2/6-311++G(2d,2p) vibrational frequencies and intensities of the fundamental modes for the *cis* and *trans* forms of HCOOH , HCOOD , and CH_3COOH are listed together with the assignments of the observed fundamental transitions (Tables I and II). The calculated spectra of FA and AA are shown in Figs. 2 and 3 (lower traces).

The most stable complex has the N_2 molecule interacting with the OH bond of the carboxylic acid (Fig. 4). This result is in agreement with the previous study on the *trans*- $\text{FA}\cdots\text{N}_2$ system.²⁸ All optimized complexes are presented in Figs. S1–S4.³⁰ Most of the *trans*- $\text{FA}\cdots\text{N}_2$ structures (Fig. S2) were not found previously by Lundell *et al.*²⁸

The interaction energies of the $\text{FA}\cdots\text{N}_2$ and $\text{AA}\cdots\text{N}_2$ complexes were evaluated (see Fig. 4). For the *trans* species, the interaction energy of approximately -4.0 kJ mol^{-1} (zero point and basis set superposition error corrected energy) was obtained for both FA and AA. This value agrees fairly with the interaction energy reported by Lundell *et al.*²⁸ for the *trans*- $\text{FA}\cdots\text{N}_2$ complex (-5.3 to -6.2 kJ mol^{-1} depending on the basis set). The interaction is slightly stronger in the complexes of the *cis* conformers. The calculations reveal a stronger stabilization for AA than for FA (-5.1 kJ mol^{-1} in AA versus -4.4 kJ mol^{-1} in FA; Fig. 4).

The calculated characteristic vibrational frequencies and intensities for the strongest complexes are compared with the data for the monomers in Table III. According to the calculations, the OH stretching frequency decreases by approximately 20 to 30 cm^{-1} and substantially intensifies (three to four times) for both acids in both conformational states. The OH torsional mode shows blue shifts (approximately 60 to 80 cm^{-1}) and its intensity slightly decreases upon complexation except for the *trans*- $\text{AA}\cdots\text{N}_2$ complexes. The $\nu\text{C}=\text{O}$ mode red-shifts by ca. 5 cm^{-1} and slightly gains intensity for the *cis* conformers, whereas the intensity slightly decreases for the *trans* forms. The changes of both frequency and intensity upon complexation of FA and AA are in agreement with the expectations for an H-bond type interaction.^{31–34} The spectral data for other complexes are presented in Table S-I.³⁰

A. Experimental details and results

Gaseous mixtures of FA (HCOOH , Kebo Lab, 99%) and AA (CH_3COOH , Kebo Lab, 99%) with nitrogen (AGA/Linde 6.0) were prepared with a typical ratio of 1:1200. The acids were purified by a few freezing-pumping cycles. Nitrogen was used as supplied. The mixtures were deposited onto a CsI window at 8.5 K in a close-cycle helium cryostat (APD, DE 202A). The spectra were recorded with a Nicolet 60SX FTIR instrument by coadding 200 interferograms with 1 cm^{-1} spectral resolution. HCOOD molecules were pro-

TABLE I. Assignment of the spectra of the *trans* and *cis* forms of HCOOH and HCOOD isolated in argon and nitrogen matrices. The calculated fundamental frequencies (in cm^{-1}) and intensities (in km mol^{-1} , in parenthesis) for *trans* and *cis* conformers of HCOOH and HCOOD were obtained at the MP2/6-311++G(2d,2p) level of theory. Frequencies in *italic* indicate tentative assignments.

Assignment	N ₂ matrix		Ar matrix ^a		Calc.	
	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>
HCOOH						
νOH	3528.2	3598.1	3549	3617	3777.9(81.8)	3844.5(81.6)
νCH	2967.5	2900.6	2955	2898	3127.2(33.6)	3039.4(64.8)
$\nu\text{C}=\text{O}$	1762.2	1803.0	1768	1808	1784.2(334.3)	1824.4(268.3)
γCH	<i>1342 w</i>	<i>1391 w</i>	1383	1392	1424.4(1.5)	1439.3(0.1)
CO—COH def.	<i>1265 w</i>	1275.9	1215	1246	1314.3(9.0)	1285.5(294.4)
COH—CO def.	1119.4	~1120	1103	1106	1119.9(284.2)	1109.4(81.6)
wCH	1040.5	1047.0	1038	...	1060.8(3.8)	1038.8(0.2)
τCOH	672.3	536.2	635	504	674.7(143.5)	535.2(88.1)
δOCO	637.0	667.8	629	662	629.9(39.1)	659.1(11.7)
HCOOD						
νOD	2602.5	2657.4	2619.5	2668.7	3127.7(30.0)	3039.3(63.1)
νCH	2973.7	2899.4	2961.2	2895.3	1777.5(317.7)	1816.8(297.1)
$\nu\text{C}=\text{O}$	1749.6	1790.6	1767.2	1799.3	1415.5(1.4)	1437.9(0.6)
γCH	1374.3	1395.4	1191.7(179.6)	1172.6(303.2)
$\nu\text{C}-\text{O}$	1187.9	1176.8	1181.7	1164.0	1058.2(1.3)	1038.8(0.1)
wCH	1038.2	...	1036.4	1041.0	1000.1(85.0)	925.7(2.9)
δCOD	989.8	929.5	971.0	910.5	564.6(40.1)	631.9(12.1)
OCO—COD def.	571.3	<i>641.2</i>	559.7	633.6	530.2(88.7)	402.5(33.1)
τCOD	528.9	...	506.7	...	3127.7(30.0)	3039.3(63.1)

^aFrom Refs. 11 and 19 (averaged value of two sites).

duced by an H/D exchange with deuterated surfaces in the deposition line. The obtained deuteration degree (~15%) was sufficient to observe and assign the main fundamental frequencies.

The *trans*-to-*cis* conversion was promoted by selective vibrational excitation by using an optical parametric oscillator with IR extension [Sunlite Continuum, full width at half maximum (FWHM) ~0.1 cm^{-1}]. *cis*-AA was produced by

TABLE II. Assignment of the spectra of the *trans* and *cis* forms of CH₃COOH isolated in argon and nitrogen matrices. The calculated fundamental frequencies (in cm^{-1}) and intensities (in km mol^{-1} , in parenthesis) for *trans* and *cis* conformers of CH₃COOH were obtained at the MP2/6-311++G(2d,2p) level of theory. Frequencies in *italic* indicate tentative assignments.

Assignment	CH ₃ COOH (N ₂)			CH ₃ COOH (Ar) ^a		Calc.	
	<i>trans</i>		<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>
	Site I	Site II					
νOH	3544.1	3551.9	3610.7	3563.8	3622.6	3787.3(77.5)	3852.9(63.3)
νHCH_2 s	3035.8	3035.8	...	3051	...	3228.7(2.6)	3221.6(1.9)
νHCH_2 a	3002.4	2995.6	2990.0	2996	...	3187.8(1.8)	3169.8(3.8)
νCH_3	2965.4	2954.0	2942.3	2944	...	3107.6(1.2)	3091.7(3.5)
		2947.4					
$\nu\text{C}=\text{O}$	1775.1	1777.6	1797.2	1779.0	1807.4	1801.0(290.3)	1828.1(247.4)
δHCH_2 a	1445.5	1441.0	1445.7	1438.8	1448.3	1505.4(8.4)	1513.2(7.8)
δHCH_2 s	1435.7	1435.7	<i>1438.8</i>	1433.6	1444.5	1500.3(16.2)	1500.5(7.4)
δCH_3	1387.6	1385.7	1371.9 1370.2	1379.4 1324.4	1368.3	1432.7(48.9)	1420.4(44.3)
CO—COH def.	1275.9	1280.5	1234.0 <i>1210.4</i>	1259.4	1192.9	1350.3(39.0)	1215.0(7.6)
COH—CO def.	1205.9 1183.9	1196.5 1177.4	1301.7 1290.5 ^b	1179.8	1285.4 1271.9 ^b	1208.1(212.8)	1306.3(373.5)
γCH_3 a	1048.1	...	1044.1	1047.2	1042.4	1082.7(5.1)	1076.8(3.3)
γCH_3 s	990.9	985.5	982.2	1009.4(82.4)	1000.4(11.9)
$\nu\text{C}-\text{C}$	856.3	...	857.4	...	848.6	867.8(7.9)	860.6(40.5)
τCOH	663.2	656.1	489.3	637.8	458.0	661.0(90.3)	465.1(101.3)
δOCO	588.3	585.7	600.6	580.4	...	584.6(36.3)	602.3(1.4)
$\gamma\text{C}=\text{O}$	554.2 546.4	556.0 549.4	...	534.2	...	550.7(30.9)	598.6(7.4)
$\delta\text{CC}=\text{O}$	<i>430.2</i>	428	...	425.4(4.1)	434.4(3.7)
τCH_3	75.4(0.2)	92.2(1.2)

^aReference 14.

^bFermi resonance with $\nu\text{C}-\text{C} + \tau\text{C}-\text{O}$.

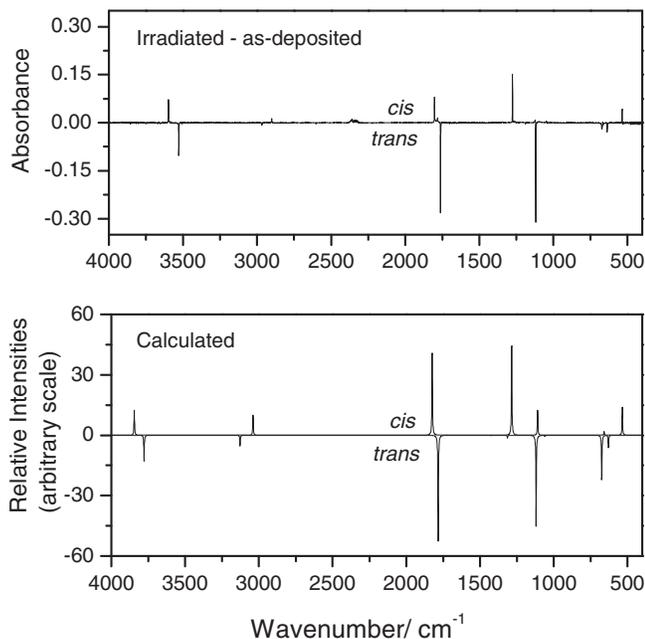


FIG. 2. Top: FTIR difference spectrum of FA in solid N₂. Result of irradiation at 5288 cm⁻¹ showing conversion of *trans*-FA into *cis*-FA. Bottom: MP2/6-311++G(2d,2p) calculated infrared spectra of *trans*-FA (downward peaks) and *cis*-FA (upward peaks). In the calculated spectra, bands were represented by Lorentzian functions centered at the calculated wavenumbers and with FWHM (full width at half maximum) equal to 4 cm⁻¹.

exciting the $\nu\text{OH} + \delta\text{COH}$ combination mode of *trans*-AA at 4724.5 cm⁻¹. *cis*-FA was prepared by exciting the $\nu\text{OH} + \nu\text{C}=\text{O}$ combination mode of *trans*-FA at 5288 cm⁻¹. The *cis*-HCOOD was produced by the IR light source of the spectrometer (Globar).

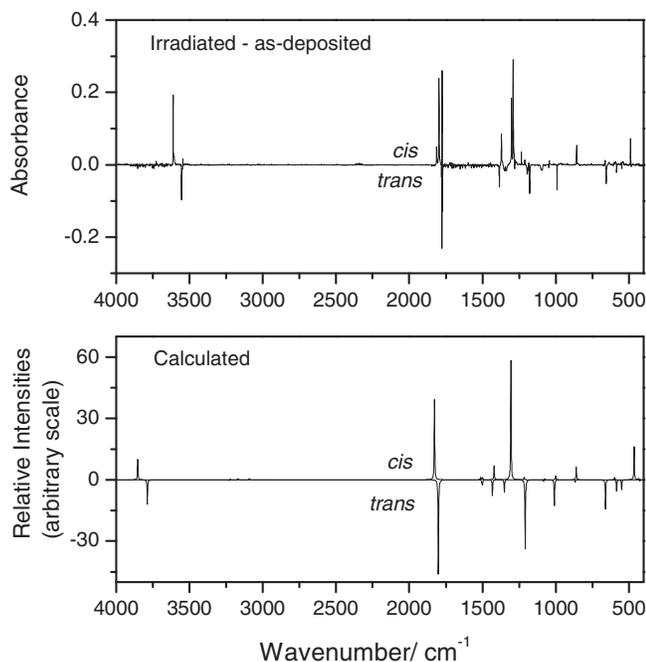


FIG. 3. Top: FTIR difference spectrum of AA in solid N₂. Result of irradiation at 4724.5 cm⁻¹ showing conversion of *trans*-AA into *cis*-AA. Bottom: MP2/6-311++G(2d,2p) calculated infrared spectra of *trans*-AA (downward peaks) and *cis*-AA (upward peaks). In the calculated spectra, bands were represented by Lorentzian functions centered at the calculated wavenumbers and with FWHM equal to 4 cm⁻¹.

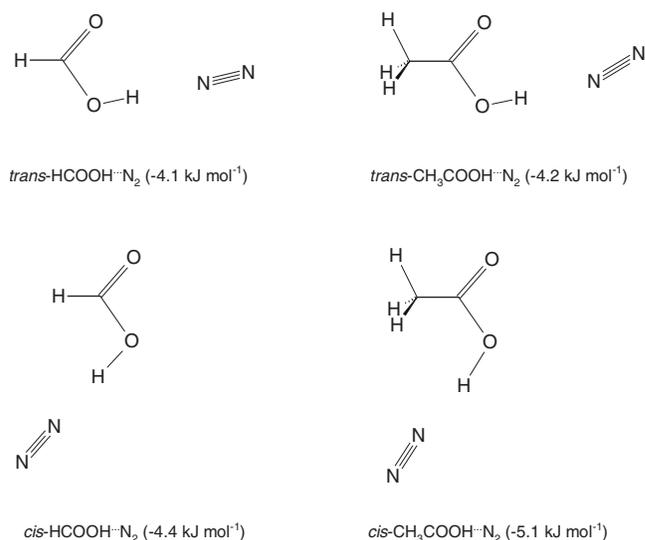


FIG. 4. Schematic structures of the strongest complexes of formic and acetic acids in *cis* and *trans* forms with molecular nitrogen at the MP2/6-311++G(2d,2p) level of theory. The interaction energies of the complexes are given in parenthesis and correspond to zero point and basis set superposition error (BSSE) corrected values. The calculated BSSE for *cis* and *trans* complexes amount to -2.6 and -2.3 kJ mol⁻¹, respectively. Optimized structures for the complexes are provided in Figs. S1–S4 (supplementary material). Calculated N···H distances are 2.199, 2.209, 2.218, and 2.223 Å for *trans*-HCOOH···N₂, *cis*-HCOOH···N₂, *trans*-CH₃COOH···N₂, and *cis*-CH₃COOH···N₂, respectively.

In the kinetic measurements, the *cis*-conformer decay was monitored by measuring the intensity of the CO—COH def. fundamental band of *cis*-HCOOH (1275.9 cm⁻¹) as a function of time. In the case of *cis*-CH₃COOH, the split COH—CO def. band (1301.7 and 1290.5 cm⁻¹) and the δCH_3 band (1370.5 cm⁻¹) were used. A long-pass optical filter (>1500 cm⁻¹) was inserted between the sample and the Globar source in order to suppress high frequency light components which could accelerate the *cis*-to-*trans* conversion process. The Globar light was blocked between the measurements. The OD form of *cis*-FA is very stable over time due to the well-known mass effect on the tunneling rate^{12,15–19} and its decay was not studied here.

The spectra of FA and AA in a nitrogen matrix at ca. 8.5 K are presented in Figs. 2 and 3. The results of vibrational excitation (at 5288 cm⁻¹ for FA and at 4724.5 cm⁻¹ for AA) are shown. The assignments of the observed fundamental transitions are given in Tables I and II, together with the calculated MP2/6-311++G(2d,2p) vibrational frequencies and intensities of the fundamental modes for the *cis* and *trans* forms of HCOOH, HCOOD, and CH₃COOH.

The *cis*-to-*trans* decay curves for FA and AA are shown in Figs. 5 and 6. The decay rates obtained in a nitrogen matrix at different temperatures are compared with the rates previously measured in an argon matrix^{16,18} in Fig. 7.

III. DISCUSSION

A. Spectral assignment

For both acids, the experimental IR spectra are reproduced well by theory, which allows a straightforward identification of the bands (Figs. 2 and 3). The assignments of the

TABLE III. Calculated νOH , $\nu\text{C}=\text{O}$ and τCOH wavenumbers (ν in cm^{-1}) and infrared intensities (I_{IR} in km mol^{-1}) for monomeric *cis* and *trans* forms of FA and AA and their most stable complexes with N_2 . (See Figs. 1–4.)

	νOH		$\nu\text{C}=\text{O}$		τCOH		νOH		$\nu\text{C}=\text{O}$		τCOH	
	ν	I_{IR}	ν	I_{IR}	ν	I_{IR}	ν	I_{IR}	ν	I_{IR}	ν	I_{IR}
	<i>cis</i> -HCOOH						<i>trans</i> -HCOOH					
Monomer	3844.5	81.6	1824.4	268.3	535.2	88.1	3777.9	81.8	1784.2	334.3	674.7	143.5
Complex	3820.3	292.3	1820.6	297.9	620.9	79.0	3747.6	282.1	1779.1	321.0	747.7	118.5
^a	-24.2	3.6	-3.8	1.1	85.7	0.9	-30.3	3.4	-5.1	0.96	73.0	0.8
	<i>cis</i> -CH ₃ COOH						<i>trans</i> -CH ₃ COOH					
Monomer	3852.9	63.3	1828.1	247.4	465.1	101.3	3787.3	77.5	1801.0	290.3	661.0	90.3
Complex	3833.6	233.1	1824.6	270.0	537.5	72.3	3762.6	266.8	1795.2	277.1	718.6	96.9
^a	-19.3	3.7	-3.5	1.1	72.4	0.7	-24.7	3.4	-5.8	0.95	57.6	1.1

^aThe values presented in this row correspond to frequency shifts ($\nu_{\text{complex}} - \nu_{\text{monomer}}$) or intensity ratios ($I_{\text{complex}}/I_{\text{monomer}}$).

observed fundamental transitions are given in Tables I and II, where they are compared with the experimental data obtained in an argon matrix.^{11,14,19}

The assignments for *trans*-HCOOH are doubtless except for the low intensity CO—COH def. and γCH modes, which are tentatively assigned to the weak bands at 1265 and 1342 cm^{-1} in a nitrogen matrix (1215 and 1383 cm^{-1} in an Ar matrix).¹¹ For *cis*-HCOOH, γCH is also predicted to have low intensity (see Table I), and it is tentatively ascribed to the band observed at 1391 cm^{-1} , appearing at almost the same frequency as in an Ar matrix (1392 cm^{-1}).¹¹ The assignment of the COH—CO def. mode of *cis*-HCOOH is complicated by a fact that this vibration almost coincides with the analogous vibration of the *trans* conformer. The band of the *cis* form is hidden by the wing of the *trans*-FA band and even in the difference spectrum is not easy to be noticed. Nevertheless, the theory predicts this band to be intense (see Table I), so that there is no other possibility for assignment.

In the case of HCOOD, the very weak γCH and ωCH modes (see Table I) could not be observed experimentally. The assignment of the OCO—COD def. mode of the *cis* form is uncertain also due to its low intensity.

The results for *trans*-AA indicate trapping into two main matrix sites (named I and II) in a nitrogen matrix. In our experiments, only molecules in site II were vibrationally ex-

cited by IR radiation and consequently converted to the *cis* form.

B. Interaction with nitrogen

The potential energy surfaces of the $\text{FA}\cdots\text{N}_2$ and $\text{AA}\cdots\text{N}_2$ systems reveal that the 1:1 hydrogen-bonded complexes feature the most important interaction in a nitrogen matrix. If a specific interaction dominates one can consider the 1:1 complex surrounded by a matrix. For an Ar matrix, this approach is validated by calculations of $\text{FA}\cdots\text{Ar}$ complexes by Wawrzyniak *et al.*^{35,36} They found that the $\text{FA}\cdots\text{Ar}$ structures with an Ar atom bonded to the OH group of FA have substantially smaller interaction energies (-1.5 to -2.0 kJ mol^{-1}) than in the present case of similar nitrogen complexes. Thus, the substitution of the Ar atom by a nitrogen molecule is energetically favorable. If the $\text{OH}\cdots\text{N}_2$ interaction is dominant, the result of complexation will be accordingly reflected in the vibrational spectra. Adding additional N_2 molecules to the 1:1 complexes to describe the matrix effect is computationally difficult and, in the present case, does not seem to be strictly required.

The data obtained in solid nitrogen can be compared with less perturbing hosts such as neon and argon matrices.^{11,14,22} The experimental observations in a nitrogen

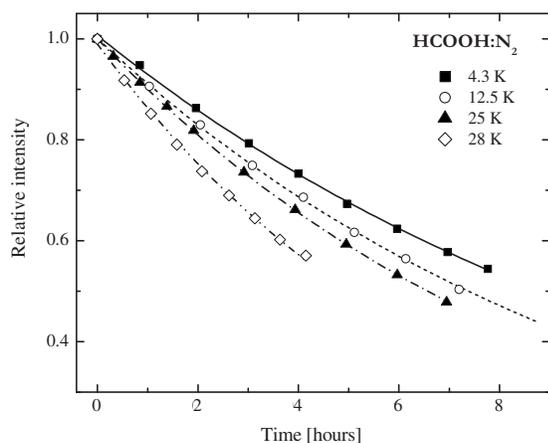


FIG. 5. Decay of *cis*-HCOOH in a nitrogen matrix at different temperatures.

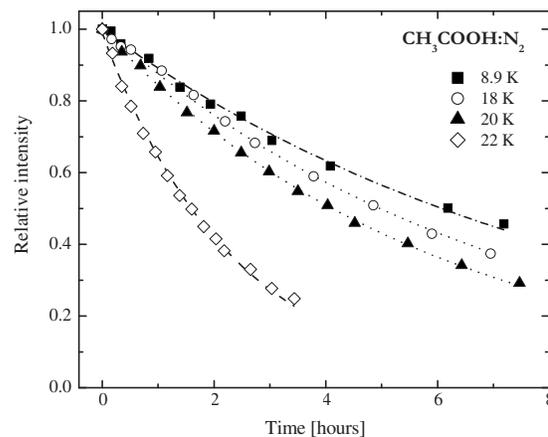


FIG. 6. Decay of *cis*-CH₃COOH in a nitrogen matrix at different temperatures.

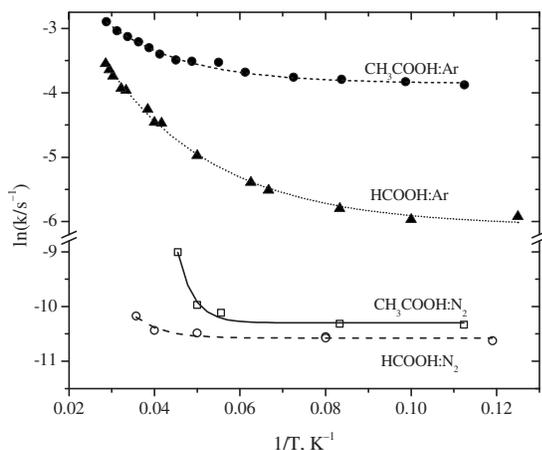


FIG. 7. Tunneling rate constants for *cis*-HCOOH and *cis*-CH₃COOH in nitrogen (this work) and argon (data from Refs. 16 and 18) matrices.

matrix agree with the spectral predictions for the strongest 1:1 complexes. The ν OH frequency of FA decreases by 19 and 21 cm^{-1} for *cis* and *trans* forms, respectively, from the values in an argon matrix (Table IV) and by 39 and 41 cm^{-1} compared to a neon matrix. The τ COH frequency increases by 32 (*cis*) and 37 cm^{-1} (*trans*) from values in an argon matrix and by 39 and 34 cm^{-1} compared to a Ne matrix. For AA, ν OH shows red-shifts by 12 cm^{-1} (*cis*), 20 cm^{-1} (*trans*, site I), and -12 cm^{-1} (*trans*, site II), and τ COH shifts by +31 (*cis*), +25 cm^{-1} , (*trans*, site I) and 12 cm^{-1} (*trans*, site II) compared to an Ar matrix. These trends are in agreement with the calculations for the strongest complexes (Table III). The 1:1 interaction with nitrogen produces larger red-shifts compared to interaction with argon, as calculated for FA.^{35,36}

Analysis of the experimental intensities leads to similar conclusions. We assume that the ν OH/ ν C=O intensity ratio is a fingerprint of the OH \cdots N₂ interaction in a nitrogen matrix because the C=O stretching intensity does not change much upon complexation. For FA, this ratio in a nitrogen matrix increases by a factor of approximately 2 compared to an argon matrix (see Table IV). It should also be remembered that the relative band intensities are already changed in an argon matrix. Wawrzyniak *et al.*^{35,36} reported a twofold increase of the OH stretching intensity for the hydrogen bonded FA \cdots Ar complex. Combining these data, one may estimate that complexation with nitrogen leads to a four-fold

increase of the OH-stretching intensity, which is in reasonable agreement with our theoretical value for the strongest complexes (ca. 3.5). The results for AA follow the same general trends. However, for this compound the uncertainties in the determined experimental intensities are considerably larger due to band overlapping in the carbonyl stretching region making impossible the quantitative analysis. It is also probable that the rest of the matrix (in addition to the specific interaction) somewhat affects the vibrational intensities. Perhaps this leads to the large effect observed for the torsional intensities, which is not so well predicted by the model of specific interactions.

C. Tunneling rates

At the lowest temperatures, the *cis*-HCOOH decay rate in a nitrogen matrix is smaller by ~ 55 and 10 000 times compared to argon and neon matrices, respectively.^{16,22} For CH₃COOH, the *cis*-to-*trans* conversion in a nitrogen matrix is slower by a factor of ~ 600 than in an argon matrix.¹⁸ At ca. 8.5 K, the *cis*-HCOOH decay in a nitrogen matrix is about five times slower than the decay in a xenon matrix¹⁶ and approximately 30 times slower than in a krypton matrix. For CH₃COOH, the tunneling rate is very similar in argon and krypton matrices, but it is five times faster in a xenon matrix.¹⁸ The tunneling rate of AA in a Xe matrix is ca. 3000 times greater than in a nitrogen matrix. *Cis*-to-*trans* conversion accelerates at elevated temperatures (Fig. 7), which suggests the influence of the matrix phonons to the tunneling process.¹⁶ The observed temperature dependence in a nitrogen matrix has a plateau for both acids where the tunneling rate remains practically constant. Such behavior demonstrates that up to a certain temperature (ca. 15 K in our case) the conversion process goes solely by tunneling.

We emphasize three experimental observations: (i) faster decay of *cis*-AA compared to *cis*-FA in all matrices; (ii) slower decay of the *cis* conformers in solid nitrogen than in rare-gas matrices; and (iii) closer decay rates of *cis*-AA and *cis*-FA in a nitrogen compared to argon matrix. The faster decay of *cis*-AA compared to *cis*-FA can be explained by the lower *cis*-to-*trans* barrier for AA. The calculated *cis*-to-*trans* barriers are 4400 and 3921 cm^{-1} for AA and FA, respectively.^{8,9} Indeed, the barrier height is the most important factor controlling the tunneling rate. The different barriers also explain why the decay slows down in solid nitrogen

TABLE IV. Experimental relative intensities of FA and AA in nitrogen and argon (Ref. 14) matrices and the corresponding matrix shift (cm^{-1}).

	N ₂ matrix	Ar matrix	Shift	N ₂ matrix	Ar matrix	Shift
	<i>cis</i> -FA			<i>trans</i> -FA		
ν OH	0.83	0.45	-19	0.57	0.32	-21
ν C=O	1	1	-5	1	1	-6
τ COH	0.45	0.28	+32	0.21	0.50	+37
	<i>cis</i> -AA			<i>trans</i> -AA ^a		
ν OH	0.73	0.09	-12	0.53	0.47	-12 (-20)
ν C=O	1	1	-10	1	1	-1 (-4)
τ COH	0.21	1.02	+31	0.63	0.82	+18(+25)

^aData for site II; shifts for site I in parenthesis.

compared to an Ar matrix. As discussed above, the spectroscopic data indicate the importance of the specific interaction between the hydrogen atom of the OH group and a nitrogen molecule. This interaction lowers the total energy of the system. On the other hand, this interaction is not efficient in the transition state for the case of a short tunneling time when the coordinates of the atoms are fixed (except the tunneling hydrogen). It follows that the *cis-to-trans* barrier becomes higher within the model of specific interactions approximately by the value of the dissociation energy of the corresponding hydrogen-bonded complex. This interaction is substantially weaker for an argon atom than for a nitrogen molecule. In agreement with the model of specific interactions, Marushkevich *et al.*³⁷ have found recently that the *cis*-FA \cdots N₂ complex in an argon matrix has a lifetime of 48 min, i.e., 6.5 times longer compared to the *cis*-FA monomer. The same discussion is relevant to the third experimental observation that the decays of *cis*-AA and *cis*-FA in solid nitrogen become closer compared to an Ar matrix. Indeed, the hydrogen bonding to nitrogen is stronger for AA than for FA (by 0.7 kJ mol⁻¹); hence the *cis-to-trans* barriers become similar for these molecules. It should be mentioned that additional factors exist which influence the tunneling rates.^{15,16,18,19}

IV. CONCLUSION

Formic and acetic acids have been studied in nitrogen matrices. The IR spectra of the *cis* and *trans* conformers of these species are assigned (Tables I and II). The higher-energy *cis* conformer of these molecules is produced by vibrational excitation of the more stable *trans* conformer. The decay of the *cis* forms is observed and explained by tunneling of hydrogen through the *cis-to-trans* torsional barrier, similarly to these species in rare-gas matrices.^{16,18} On the other hand, the tunneling for both molecules is considerably slower in a nitrogen matrix than in rare-gas matrices, for example, the *cis-to-trans* conversion of HCOOH slows down in a nitrogen matrix by four orders of magnitude compared to a neon matrix.

Both spectroscopic and tunneling data indicate that the OH \cdots N₂ specific interactions are important for both acids in a nitrogen matrix. Within the model of specific interactions, the tunneling barrier height should be higher in a nitrogen matrix than in an argon matrix. This conclusion is in agreement with the experimental observations on tunneling decay of AA and FA in a nitrogen matrix.

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