IR Spectrum of the Other Rotamer of Formic Acid, *cis*-HCOOH

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Formic acid is one of the simplest organic acids, and it represents an ideal model compound for understanding more complicated molecules. Apart from being an important industrial product, HCOOH is known to play a role in human metabolism. It is also an important intermediate in the oxidation of unsaturated hydrocarbons in combustion and in atmospheric chemistry.

Formic acid is one of the smallest molecules which can exhibit rotational isomerism representing two planar structures defined by the rotation of the OH group around the C−O bond (see Scheme 1).

In the gas phase the *trans* rotamer is the predominant naturally occurring form, and it has been well characterized by microwave studies,[1−3] electron diffraction,[4−6] and IR spectroscopy.[7,8] Several infrared studies of *trans*-formic acid in low-temperature matrices have also become available.[9−12] Miyazawa and Pitzer[9] published infrared spectra of four isotopic species of HCOOH in nitrogen matrix in the spectral region of 400−800 cm^{-1}. The study was focused on the internal rotation of HCOOH, and some matrix-induced perturbed *trans*-HCOOH bands were incorrectly assigned to *cis*-HCOOH.[8] Hisatsune and Heicklen[8] also reported the detection of *cis*-HCOOH among the reaction products from the gas phase ozonolysis of 1,2-dichloroethylene. The assignment, nevertheless, was based only on tentative assignment of two transient infrared absorption bands. It seems that to our knowledge the only positive identification of *cis*-HCOOH has been made by Hocking and Bjarnov[13,14] by using microwave spectroscopy. In their experiments, very weak signals of six isotopically substituted species of *cis*-formic acid could be resolved directly in the gas phase. Also, they estimated the barrier to internal rotation as seen from the bottom of the *trans* rotamer to be 4842 cm^{-1}. The torsional vibration transition of the *cis*-HCOOH was predicted to lie at 574 cm^{-1}, and the torsional vibration transition of the *trans* rotamer to lie at 618 cm^{-1}. The experimental relative energy difference of 16.7 kJ mol^{-1} between the two conformers[14] is inserted into the Boltzmann equation to estimate the population ratio between the *trans* and *cis* rotamers. At 298 K, we receive a value of 1.2×10^{-3}. This small population of *cis*-HCOOH in the gas phase explains why it has escaped IR detection up till now.

The low-temperature matrices create a good opportunity to study intermolecular interconversions,[15] as the low-temperature
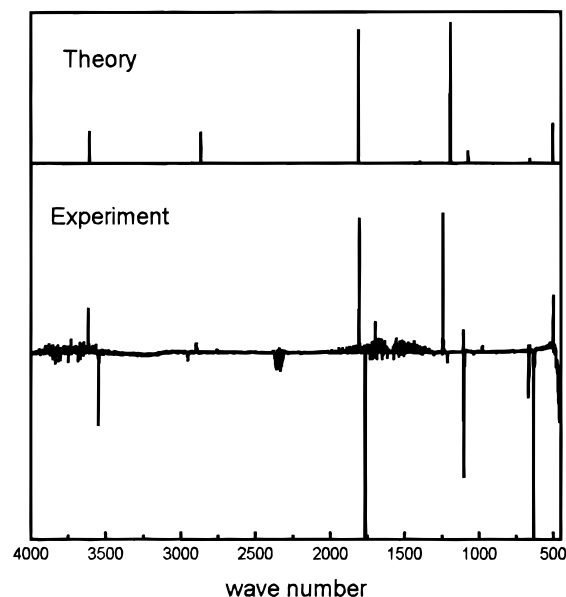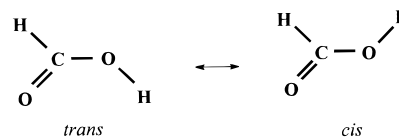

Figure 1. Difference spectrum demonstrating the result of IR pumping (at 6934 cm^{-1}) of *trans*-HCOOH. The appearing (upward) bands belong to *cis*-HCOOH. The upper trace shows the predicted *cis*-HCOOH spectrum, when the calculated shifts (ref 20) between *cis* and *trans* rotamers are applied to the experimentally observed (ref 12) *trans*-HCOOH bands in solid Ar.

Scheme 1

solid matrix prohibits all processes requiring more than a few kJ mol^{-1} of activation energy. However, the torsional barrier of HCOOH is very high[14] (ca. 50 kJ mol^{-1}), and it cannot be overcome by thermal annealing in order to populate the *cis* rotamer enough for IR probing. Also in the gas phase, the thermal excitation of *trans*-HCOOH results in the decomposition of the molecule to neutral molecular species H$_2$ + CO$_2$ and H$_2$O + CO.[16] A different approach must be looked for. We measured the near infrared spectrum of *trans*-formic acid isolated in solid Ar, and observed the ν_{OH} stretching overtone at 6934 cm^{-1}, which corresponds well with the ν_{OH} overtone observed in the gas phase at 6975 cm^{-1}.[17] The OH stretching overtone was pumped with tunable IR (idler) radiation of an optical parametric oscillator (SunLite, Continuum), and thereafter the IR spectrum in the 400−4000 cm^{-1} region was recorded on a Nicolet 60 SX FTIR spectrometer. The experimental setup has been discussed elsewhere.[18,19] The ν_{OH} overtone lies significantly above the torsional barrier from *trans* to *cis* rotamer, so that if vibrational relaxation to the torsional coordinate occurs, *cis*-HCOOH should be formed. Indeed, after IR pumping of the first overtone of ν_{OH}, diminishing of the *trans*-HCOOH bands was observed. Simultaneously, new prominent bands appeared! The difference spectrum before and after IR pumping is shown in Figure 1. When these new absorptions are compared with the experimental values of the

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Table 1. Observed Vibrational Frequencies in Solid Ar (cm^{-1}) Compared with the Calculated Frequencies of the *trans* and *cis* Conformers of Formic Acid

	assignment[a]	*trans*		*cis*			
		obs	calcd[b]	obs	Δ_{c-t} obsd[c]	calcd[b]	Δ_{c-t} calcd[c]
ν_1	ν_{OH}	3550.5	3945	3618	+67.5	4003	+58
$2\nu_3$		3515.8					
ν_2	ν_{CH}	2952.9	3225	2899		3138	−87
$\nu_3 + 2\nu_9$				2760			
$\nu_5 + 2\nu_9$				2207			
$2\nu_6$		2194.8					
ν_3	$\nu_{C=O}$	1767.2	1921	1808	+40.8	1962	+41
ν_4	CH rock	1381.0	1470	1396 (?)	+15.0	1488	+18
ν_5	CO−COH def	1215.8	1366	1244	+28.2	1344	−22
ν_6	COH−CO def	1103.4	1203	1108	+4.6	1174	−29
ν_8	CH wag oop	1037.4	1102			1084	−18
$2\nu_9$				980			
ν_9	τ COH	635.2	687	503	−132.2	507	−180.0
ν_7	OCO scissors	629.2	649	661	+31.8	680	+31

[a] The assignments follow the assignments presented for HCOOH in refs 10 and 11 according to a PED analysis. [b] From ref 20. [c] Calculated vibrational shift *cis*−*trans*.

trans-HCOOH, and the *ab initio* frequencies[20] for both rotamers, the appearing bands can be unequivocally assigned to *cis*-HCOOH. The experimental wave numbers of the two rotamers of formic acid in Ar have been collected in Table 1. This is the first time seven fundamentals, one overtone, and two combination bands belonging to *cis*-HCOOH have been identified in the IR spectrum.

Especially informative in order to prove the existance of the *cis*-rotamer is the 1000−1300 cm^{-1} spectral region. Here the *trans* rotamer absorbs at 1103 and 1216 cm^{-1}, corresponding to the CO−COH and COH−CO deformations, respectively. According to both experimental and computational evidence, the first band is a strong band and the other is quite weak. According to the *ab initio* calculations,[20] in the *cis* rotamer the

higher wavenumber band should be a strong band, whereas the lower wavenumber component should be a weak one. Indeed, the *cis* band at 1108 cm^{-1} is observed to be quite weak while the 1244 cm^{-1} band is the strongest *cis* band observed. These two pairs of bands could, in fact, be considered as good "fingerprints" of the two rotamers of formic acid.

Interesting is that we observed interconversion back to the *trans* rotamer from the *cis* rotamer in the low-temperature argon matrix. As discussed elsewhere,[18] the characteristic halftime of the disappearance at 15 K was found to be a couple of minutes. At the moment we have reason to believe that this is due to resonance-enhanced tunneling through the torsional barrier. Further studies on *cis*-HCOOH are currently underway in our laboratory, including IR pumping of different HCOOH isotopomers as starting points.

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