The Other Rotamer of Formic Acid, *cis*-HCOOH[1]

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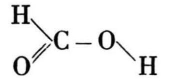
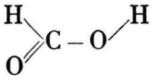
The rotational spectrum of the planar *cis* rotamer of formic acid, *cis*-HCOOH, has been detected for the first time. Twenty transitions belonging to the ${}^qR_K$, ${}^qQ_1$, ${}^qQ_2$, ${}^rP_0$, ${}^rP_1$ and ${}^rP_2$ branches of the parent isotopic species in its ground state have been assigned and measured. The rotational constants and quartic centrifugal distortion constants have been determined using Watson's reduced Hamiltonian. Stark effect measurements have yielded the molecular electric dipole moment: $\mu_a = 2.65(1)$ D, $\mu_b = 2.71(1)$ D and $\mu = 3.79(1)$ D. The energy difference between the ground vibrational states of *cis*- and *trans*-HCOOH has been determined by microwave relative intensity measurements. The *cis* rotamer is found to lie at higher energy than the *trans* rotamer by $1365 \pm 30\ \mathrm{cm}^{-1}$. A one dimensional potential energy curve has been calculated for the OH torsional vibration of formic acid.

I. Introduction

Formic acid, HCOOH, has played a prominent, but hitherto essentially negative, role in the study of rotational isomerism[1]. Due to delocalization of the π electrons over the heavy atom chain[2, 3], the molecule is firmly held in a planar configuration. Thus in principle one could expect to find two rotameric forms:



trans



cis

Early infrared[4, 5] and electron diffraction[6] work indicated that the *trans* rotamer was the predominant naturally occurring form. This was later confirmed by further infrared[7, 8] and electron diffraction[9–11] studies. More recently, a series of progressively refined molecular structures have been determined for *trans*-HCOOH by microwave[12–15] and electron diffraction[16] work.

The *cis* rotamer of formic acid has proved to be a more elusive species than the *trans* rotamer. Negative results from early attempts to observe *cis*-HCOOH have been reviewed by Mizushima[17]. In 1959, Miyazawa and Pitzer[18] claimed to have assigned the OH torsional bands of four isotopic species of the *cis* rotamer of formic acid. From infrared relative intensity measurements, they estimated the energy difference between the two rotamers to be $2.0\ \mathrm{kcal \cdot mol^{-1}}$. However, these results were later disputed by Lide[19] who searched the microwave spectrum of formic acid very carefully, but without success, for the $1_{01} - 0_{00}$ rotational transition of *cis*-HCOOH. He concluded that the *cis* rotamer was at least $4\ \mathrm{kcal \cdot mol^{-1}}$ higher in energy than the *trans* rotamer. Finally, Hisatsune and Heicklen[20] have reassigned the bands observed by Miyazawa and Pitzer[18] as difference bands of the *trans* rotamer of formic acid. In the same paper, Hisatsune and Heicklen also reported the detection of *cis*-HCOOH among the reaction products from the gas phase ozonolysis of 1,2-dichloroethylene. Their claim is based, however, entirely on the tentative assignment of only two transient infrared absorption bands.

The possibility of rotational isomerism in formic acid has also been the subject of numerous *ab initio*[21–25] and semi-empirical[26–34] theoretical investigations. All of these studies indicate that there should indeed be minima in the OH torsional potential at both the *trans* and *cis* planar configurations. The *ab initio* calculations have generally placed the *cis* rotamer about $8\ \mathrm{kcal \cdot mol^{-1}}$ higher in energy than the *trans* rotamer. However, the semi-empirical calculations have consistently given a much lower value ($\sim 2\ \mathrm{kcal \cdot mol^{-1}}$) for this energy difference.

Very recently, the results of a thorough investigation of the rotational spectrum of monothioformic acid have been reported[35–38]. Two planar rotamers of the thiol form, HC(:O)SH, were identified. The

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cis rotamer was found to lie higher in energy than the *trans* rotamer by only 0.661 kcal·mol^{-1}.

In the light of the situation outlined above it seemed worthwhile to make yet one more attempt to detect *cis*-HCOOH. Accordingly, the microwave spectrum of formic acid was re-examined. A new set of very weak absorption lines has been identified. The purpose of this paper is to show unequivocally that the carrier of these lines is *cis*-HCOOH.

II. Experimental Procedures

Formic acid (analytical grade) was purchased from Merck and used without further purification. All frequency measurements were made at room temperature with ~10 mTorr pressure of HCOOH in the microwave cell. The samples were stable in the gold-plated two meter X-band Stark cell.

Microwave frequency measurements were made in the 8 – 53 GHz region using a Hewlett-Packard model 8460 A MRR spectrometer. The X, P and K bands (8 – 26.5 GHz) were covered using the fundamental output from three different backward wave oscillators (BWO). Measurements in the 26.5 to 53 GHz region were made by doubling the P- or K-band BWO radiation. This was accomplished by applying P- or K-band power to a parametric varactor diode in a crossed wave-guide mount [39]. Square wave Stark modulation at 33.333 kHz was employed to obtain high sensitivity. The uncertainty in the measured transition frequencies is estimated to be less than ± 50 kHz.

The electric dipole moment of *cis*-HCOOH was determined from Stark effect measurements. Stark shifts were produced by applying a large dc voltage to the septum of the microwave cell. Modulation was achieved by floating a small ac voltage, in the form of a 33.333 kHz square wave, on top of the dc signal. The dc voltage was monitored using a Hewlett-Packard model 3462 A digital voltmeter. The spacing of the septum in the microwave cell was calibrated by measuring the Stark effect of carbonyl sulfide, OCS, ($\mu = 0.71521$ D) [40].

Relative intensity measurements were made in the K-band spectral region with the aid of a bridge-arm system. Microwave power in the Stark cell was attenuated to a level 10 – 15 dB below that required to saturate the absorption signal being studied, while power in the bridge arm was adjusted to maintain a constant detector crystal current of 100 μA. The line-widths and the peak intensity coefficient ratio of the two absorption lines chosen for comparison were determined from the same set of measurements. Each line was recorded on chart paper by linearly sweeping the source frequency across the absorption signal profile. The full-width at half-height and the peak intensity of the absorption line were then read directly off the chart paper.

III. Rotational Spectrum and Assignment

The rotational constants of *cis*-HCOOH were estimated using various reasonable structural models [14, 15, 37]. All of these models correspond to a near prolate asymmetric top molecule with $\varkappa \approx -0.96$. From the estimated B and C rotational constants, the $1_{01} - 0_{00}$ transition of *cis*-HCOOH was predicted to fall at 21950 ± 300 MHz. By analogy with HC(:O)SH it was expected that the Stark effect of the $1_{01} - 0_{00}$ transition would be much faster for *cis*-HCOOH than for *trans*-HCOOH. Indeed, with the aid of the dipole moment vector model discussed in Sect. VII, the ratio of the Stark coefficients of this transition for the two rotamers was estimated to be approximately four (*cis*/*trans*).

A careful search of the formic acid microwave spectrum in the frequency region 21250 – 22550 MHz revealed one and only one absorption line which could be conceivably assigned as the $1_{01} - 0_{00}$ transition of *cis*-HCOOH. This absorption line, which is very weak, falls at 21973.145 MHz in good agreement with the prediction given above. It is

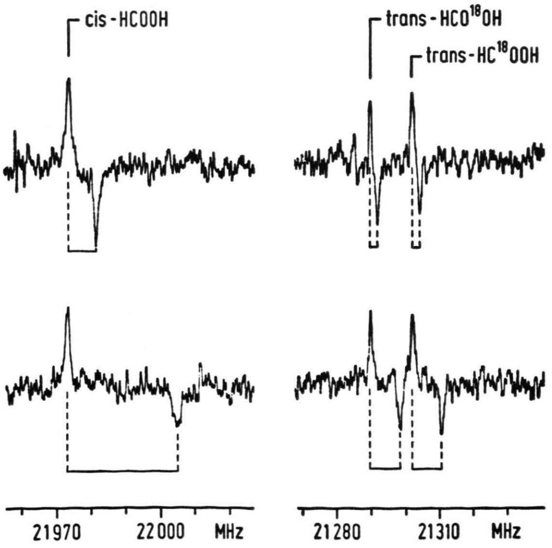

Fig. 1. Comparison of the $1_{01} - 0_{00}$ transition of *cis*-HCOOH with the $1_{01} - 0_{00}$ transitions of *trans*-HCO^{18}OH and *trans*-HC^{18}OOH observed in natural isotopic abundance. The upper traces were recorded with a Stark field of 200 V and the lower traces with 400 V. The *cis* rotamer line is distinguished from the *trans* rotamer lines by its fast Stark effect.

compared in Fig. 1 with the $1_{01}-0_{00}$ transitions of *trans*-$HC^{18}OOH$ and *trans*-$HCO^{18}OH$ observed in natural isotopic abundance (0.204%). As expected, the Stark component of the 21973.145 MHz line moves out approximately four times as fast with increasing voltage as those of the two oxygen-18 substituted *trans* rotamer lines. On the basis of the observed Stark effect and the agreement of the observed and predicted frequencies, the line at 21973.145 MHz was tentatively assigned as the $1_{01}-0_{00}$ transition of *cis*-HCOOH.

The $J=2 \leftarrow 1$ *a*-type R-branch transition of *cis*-HCOOH was searched for next. The $K_a=0$ component and both of the asymmetry split $K_a=1$ components were located without difficulty. In each case, the assignment was confirmed by observation of the $M_J=0$ and $M_J=1$ Stark components ($\Delta M_J=0$). A systematic search for *a*-type Q-branch transitions and *b*-type P-branch transitions was then undertaken. The bootstrap procedure described previously[36] was employed for this purpose. For the important $1_{11}-2_{02}$ *b*-type transition the assignment was further confirmed through the Stark effect. Eventually a total of 10 *a*-type and 12 *b*-type transitions, belonging to the ${}^{q}R_K$, ${}^{q}Q_1$, ${}^{q}Q_2$, ${}^{r}P_0$, ${}^{r}P_1$ and ${}^{r}P_2$ branches, were assigned for *cis*-HCOOH.

IV. Centrifugal Distortion Analysis

The observed rotational transitions of *cis*-HCOOH were analysed using the reduced Hamiltonian reported by Watson[41] in which $\tilde{R}_6$ is set equal to zero. The analysis was performed in the I^r axis representation so that the Hamiltonian may be written as

$$\begin{aligned}\mathcal{H} = {} & \tfrac{1}{2}(\tilde{B}+\tilde{C})P^2 + [\tilde{A}-\tfrac{1}{2}(\tilde{B}+\tilde{C})]\,P_a{}^2 \\ & + \tfrac{1}{2}(\tilde{B}-\tilde{C})\,(P_b{}^2-P_c{}^2) \\ & - \Delta_J P^4 - \Delta_{JK} P^2 P_a{}^2 - \Delta_K P_a{}^4 \\ & - 2\,\delta_J P^2 (P_b{}^2-P_c{}^2) - \delta_K [P_a{}^2 (P_b{}^2-P_c{}^2) \\ & + (P_b{}^2-P_c{}^2) P_a{}^2] \qquad (1)\end{aligned}$$

where P, P_a, P_b and P_c are the operators for the total angular momentum and its components along the principal inertial axes. The parameters designated $\tilde{A}$, $\tilde{B}$ and $\tilde{C}$ are Watson's reduced rotational constants and the deltas are the quartic centrifugal distortion constants.

An iterative least squares procedure[42] was used to fit the observed spectrum to the above Hamiltonian. The observed and calculated transition frequencies are listed in Table I. The derived molecular constants, which are all well determined, are reported in Table II. The $\tilde{B}$ and $\tilde{C}$ rotational con-

Table I. Observed and calculated frequencies of *cis*-HCOOH in MHz.

Transition	Observed Frequency	Calculated Frequency	Observed – Calculated
a-type R-Branch			
$1_{0,1}-0_{0,0}$	21973.145	21973.130 (06)[a]	0.015
$2_{0,2}-1_{0,1}$	43926.440	43926.447 (13)	−0.007
$2_{1,2}-1_{1,1}$	42541.360	42541.364 (14)	−0.004
$2_{1,1}-1_{1,0}$	45351.350	45351.324 (14)	0.026
a-type Q-Branch			
$5_{1,4}-5_{1,5}$	21068.030	21068.041 (11)	−0.011
$6_{1,5}-6_{1,6}$	29486.190	29486.175 (13)	0.015
$7_{1,6}-7_{1,7}$	39295.953	39295.955 (14)	−0.002
$12_{2,10}-12_{2,11}$	18579.040	18579.014 (11)	0.026
$13_{2,11}-13_{2,12}$	24889.890	24889.898 (14)	−0.008
$14_{2,12}-14_{2,13}$	32499.725	32499.712 (18)	0.013
b-type P-Branch			
$1_{1,1}-2_{0,2}$	30843.830	30843.814 (11)	0.016
$4_{0,4}-3_{1,3}$	16350.150	16350.184 (09)	−0.034
$7_{2,6}-8_{1,7}$	26032.845	26032.831 (19)	0.014
$10_{1,9}-9_{2,8}$	30361.590	30361.581 (18)	0.009
$9_{2,7}-10_{1,10}$	52935.160	52935.221 (15)	−0.061
$12_{2,10}-13_{1,13}$	26182.600	26182.591 (17)	0.009
$13_{2,11}-14_{1,14}$	21083.395	21083.362 (17)	0.033
$16_{2,14}-17_{1,17}$	18551.750	18551.759 (16)	−0.009
$17_{2,15}-18_{1,18}$	22106.215	22106.216 (23)	−0.001
$14_{3,12}-15_{2,13}$	17341.005	17340.992 (25)	0.013
$16_{3,13}-17_{2,16}$	26092.585	26092.592 (23)	−0.007
$20_{2,19}-19_{3,16}$	17776.900	17776.898 (27)	0.002

[a] One standard error.

Table II. Rotational constants and centrifugal distortion constants of formic acid[a]

	cis-HCOOH	*trans*-HCOOH[b]	
$\tilde{A}$	86461.565 (22)	77512.232 (21)	MHz
$\tilde{B}$	11689.1767 (30)	12055.1061 (30)	MHz
$\tilde{C}$	10283.9868 (30)	10416.1157 (27)	MHz
Δ_J	8.353 (35)	9.9902 (44)	kHz
Δ_{JK}	−71.07 (77)	−86.32 (10)	kHz
Δ_K	2357.2 (45)	1702.1 (6)	kHz
δ_J	1.4185 (22)	1.9459 (22)	kHz
δ_K	41.102 (82)	43.09 (42)	kHz
σ[c]	25.5		kHz
N[d]	22	166	

[a] The numbers in parentheses are standard errors.
[b] Taken from Ref. [43].
[c] Standard deviation of the fit.
[d] The number of equally weighted transitions included in the fit.

stants and four of the quartic centrifugal distortion constants (Δ_J, Δ_{JK}, δ_J, δ_K) have slightly smaller values than those reported for *trans*-HCOOH in its ground state[43]. On the other hand, the $\tilde{A}$ rotational constant and the Δ_K distortion constant are rather larger than in *trans*-HCOOH. All of the observed differences are at least qualitatively consistent with the assignment of the spectrum reported here to *cis*-HCOOH in its ground state.

V. Molecular Structure

The moments of inertia and the inertial defect of *cis*-HCOOH were calculated from the rotational constants given in Table II using the conversion factor $(\tilde{B} \cdot I_b) = 505379.0(38)$ MHz·u·Å². The small positive value found for the inertial defect $\Delta = 0.0624$ u·Å²) shows that the molecule has a planar configuration. It is also significant that the inertial defect takes on a slightly smaller value in *cis*-HCOOH than in *trans*-HCOOH ($\Delta = 0.0765$ u·Å²). Remarkably similar behavior has been observed for the *cis* ($\Delta = 0.0735$ u·Å²) and *trans* ($\Delta = 0.0832$ u·Å²) planar rotamers of HC(:O)SH[37].

A structural model was constructed for *cis*-HCOOH as follows: the structure reported for the *trans* rotamer by Bellet et al.[15] was adopted as a starting point and then the OCO angle and the CO single bond length were adjusted to bring the calculated $\tilde{A}$ and $\tilde{B}$ rotational constants into agreement with the experimental values. This required only a very slight increase (0.006 Å) in the CO single bond length, but a rather larger decrease (2.7°) in the OCO angle. Corresponding, but slightly larger changes have been observed in the structure of HC(:O)SH on going from the *trans* to the *cis*

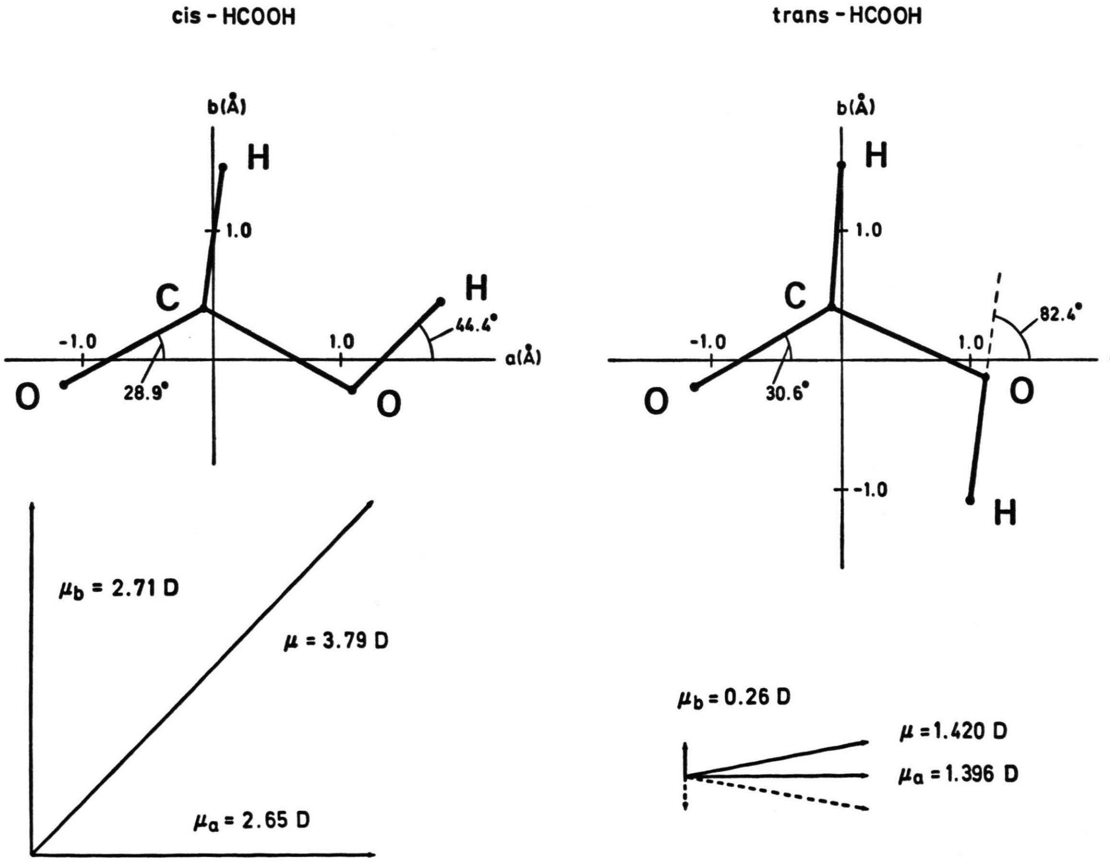

Fig. 2. Molecular structures and electric dipole moments of *cis*-and *trans*-HCOOH. The arrow heads indicate the positive end of the dipole moment. The dipole moment magnitude given for *trans*-HCOOH was obtained by adjustang slightly the value reported by Kim et al.[48] to conform to the new OCS standard[40]. Two possible orientations have been shown for the dipole moment of *trans*-HCOOH; the dotted arrow indicates the direction proposed by Kim et al., the solid arrow indicates the direction adopted in this work.

Table III. The molecular structure of *cis*-HCOOH.

Bond lengths	Bond angles
$r(\mathrm{C-H})^{a} = 1.097$ Å	$\sphericalangle(\mathrm{OCO}) = 122.3°$
$r(\mathrm{C=O})^{a} = 1.228$ Å	$\sphericalangle(\mathrm{HOC})^{a} = 106.8°$
$r(\mathrm{C-O}) = 1.323$ Å	$\sphericalangle(\mathrm{HC-O})^{a} = 110.4°$
$r(\mathrm{O-H})^{a} = 0.974$ Å	

[a] Assumed [15].

rotamer. The complete molecular structure of *cis*-HCOOH is reported in Table III and is illustrated in Figure 2.

With the aid of the structure given in Table III, the $1_{01}-0_{00}$ transitions of *cis*-DCOOH and *cis*-H^{13}COOH were predicted to fall at 21531.3 MHz and 21937.2 MHz respectively. A search was then made for these transitions in the spectra of 90% isotopically enriched formic acid samples. Weak absorption lines having the appropriate Stark effect were easily located at 21528.09 MHz for DCOOH and at 21937.14 MHz for H^{13}COOH. The good agreement of the observed and calculated frequencies confirms the assignment of the spectrum reported in this paper to *cis*-HCOOH in its ground state.

VI. Stark Effect Measurements

Stark effect measurements were made on the $1_{01}-0_{00}$, $M_J=0$ and $1_{11}-2_{02}$, $M_J=0$ transitions ($\Delta M_J=0$) of *cis*-HCOOH. The frequencies of both of these Stark components were determined at a number of different dc voltages. Each set of data was then fit, using the least squares procedure, to an expression of the form

$$\nu = \alpha + \beta V^2 + \gamma V^4 \qquad (2)$$

were ν is the frequency of the Stark component, V is the dc voltage and α, β and γ are parameters to be determined in the fit. This procedure was also applied to measurements on the $J=2\leftarrow 1$, $M_J=0$ Stark component of OCS. In all three cases, the γ coefficient was found to be very small but still significant, while the α coefficient was observed to be in good agreement with the frequency of the zero-field line. The β coefficient determined for OCS was used to calculate the cell constant, d. The β coefficients of the two *cis*-HCOOH Stark components, scaled by the cell constant squared ($\beta' = \beta \cdot d^2$), are reported in Table IV.

Table IV. Stark coefficients of *cis*-HCOOH [a, b].

Stark component	$\beta' \times 10^5$
$1_{01}-0_{00}$, $M_J = 0$	4.634 (38)
$1_{11}-2_{02}$, $M_J = 0$	0.3442 (25)

[a] β' has units of MHz·(V/cm)$^{-2}$.

[b] The numbers in parentheses are standard errors.

The second order Stark effect energy, $[W_S^{(2)}]_{J\tau M_J}$, of an asymmetric rotor molecule is related to the molecular electric dipole moment by the equation [44, 45]

$$[W_S^{(2)}]_{J\tau M_J} = \sum_i \frac{\mu_i^2\,\mathcal{E}^2}{2J+1} \sum_{\tau'}{}' \left[\frac{J^2 - M_J^2}{J(2J-1)} \frac{{}^iS_{J\tau,\,J-1\tau'}}{W^0_{J\tau} - W^0_{J-1\tau'}} + \frac{M_J^2}{J(J+1)} \frac{{}^iS_{J\tau,J\tau'}}{W^0_{J\tau} - W^0_{J\tau'}} + \frac{(J+1)^2 - M_J^2}{(J+1)(2J+3)} \frac{{}^iS_{J\tau,\,J+1\tau'}}{W^0_{J\tau} - W^0_{J+1\tau'}} \right] \qquad (3)$$

where μ_i is the component of the dipole moment along the a, b or c principal axis and J and M_J are quantum numbers for the total rotational angular momentum and its projection along the space fixed direction respectively. The ${}^iS_{J\tau,J'\tau'}$ are line strength factors and the $(W^0_{J\tau} - W^0_{J'\tau'})$ are energy differences between the unperturbed rotational levels designated by $J\tau$ and $J'\tau'$ respectively.

The quadratic Stark coefficients reported in Table IV were analysed using Eq. (3) to obtain the electric dipole moment of *cis*-HCOOH. Since the molecule is known to be planar, it was presumed in this analysis that the c-component of the dipole moment was zero. The results are: $\mu_a = 2.647(11)$ D, $\mu_b = 2.708(9)$ D and $\mu = 3.787(10)$ D, where the numbers in parentheses are one standard error.

VII. Electric Dipole Moment Directions

On the basis of simple electronegativity arguments [46], and by analogy with *cis*-HC(:O)SH [38], the only reasonable orientation for the total electric dipole moment of *cis*-HCOOH is that shown in the first half of Figure 2. The second part of Fig. 2 shows the molecular structure[15] and electric dipole moment[47, 48] of *trans*-HCOOH for comparison. Two different orientations have been indicated for the total dipole moment of *trans*-HCOOH, corresponding to the two possible signs for μ_b. The direction shown with a dotted arrow is that deduced by Kim et al.[48] from an apparent decrease in μ_b on going from *trans*-HCOOH to *trans*-HCOOD. However, this deduction is rather tenuous since the uncertainty in the difference between the two μ_b values is larger than the difference itself. Furthermore, the variation in the more accurately determined μ_a values leads to the opposite conclusion (solid arrow).

Numerous attempts have been made to theoretically calculate the electric dipole moment of *trans*-HCOOH by both *ab initio*[23, 49–52] and semi-empirical[28, 30, 34, 53–56] methods. Unfortunately, these calculations do not seem to be of much help in distinguishing between the two possible orientations of the dipole moment discussed above. Some of the calculated directions[50] are in good agreement with the dotted arrow in Fig. 2, others[30, 49, 53, 54] are in good agreement with the solid arrow, and yet more[23, 51, 55] fall almost halfway between the two. The calculated magnitudes show a similar scatter, ranging from 0.87 D up to 1.88 D.

There have also been several theoretical studies on the dipole moment of *cis*-HCOOH[23, 28, 30, 34, 54]. The calculated magnitudes range from 2.59 D up to 5.24 D. In only one instance was the calculated direction reported[23], and this is in reasonably good agreement with experiment.

Very recently, it has been shown that the difference between the electric dipole moments of *cis*- and *trans*-HC(:O)SH may be semiquantitatively accounted for using a simple vector model[38]. A similar approach was therefore applied to the formic acid dipole moment data. The total dipole moment in each rotamer was resolved into a frame moment, $\vec{\mu}_F$, and an oxygen-hydrogen bond moment, $\vec{\mu}_{OH}$. It was assumed that: (i) the $\vec{\mu}_F$ moment has the same magnitude and direction relative to the molecular frame in the two rotamers, (ii) the $\vec{\mu}_{OH}$ moment has the magnitude 1.52 D (estimated from water[57]) and is directed along the OH bond with hydrogen positive. The slight structural differences between the two rotamers were ignored. From the measured dipole moment of *cis*-HCOOH, $\vec{\mu}_F$ was calculated to have a magnitude of 2.27 D and an orientation of 18.3° relative to the CO double bond (directed from $C=O$ toward $C-H$). The total dipole moment of *trans*-HCOOH was thus predicted to have a magnitude of 1.31 D and to point into the first quadrant of the axis system defined in Fig. 2 at an angle of 8.8° with the *a*-axis. Comparison of this result with the experimental data from two independent studies [$\mu = 1.35 \pm 0.02$ D at an angle with the *a*-axis of $\pm(9.0° \pm 3.0°)$[47] or $\mu = 1.42 \pm 0.01$ D at an angle with the *a*-axis of $\pm(10.5° \pm 1.6°)$[48]] then strongly suggests that the hitherto accepted direction for the electric dipole moment of *trans*-HCOOH be abandoned in favor of that shown by the solid arrow in Figure 2.

VIII. Relative Intensity Measurements

Relative intensity measurements were made on the $1_{01} - 0_{00}$ transitions of *cis*- and *trans*-HCOOH. The experimental data were analysed using the relation[45, 58, 59]

$$\frac{\gamma_c^0}{\gamma_t^0} = \left(\frac{f_c}{f_t}\right)\left(\frac{\nu_c}{\nu_t}\right)^2\left(\frac{\Delta\nu_t}{\Delta\nu_c}\right)\left(\frac{|\mu_a|_c^2}{|\mu_a|_t^2}\right) \qquad (4)$$

where the subscripts c and t denote *cis* and *trans* respectively and:

γ^0 = the intensity coefficient at maximum absorption of the narrow pressure-broadened absorption line in the limit of low microwave power.

f = the fraction of molecules in the ground vibrational state of the *cis* or *trans* rotamer.

ν = the resonance frequency of the rotational transition.

$\Delta\nu$ = the line-width of the rotational transition.

$|\mu_a|^2$ = the square of the *a*-component of the electric dipole moment.

As was previously observed for HC(:O)SH[38], the *cis* rotamer of HCOOH was found to have much broader absorption lines than the *trans* rotamer. This behavior is illustrated in Fig. 3 and may be attributed to the fact that the *cis* rotamer has a substantially larger electric dipole moment than the *trans* rotamer[45]. In order to determine accurately the ratio f_t/f_c it was therefore necessary to measure $\Delta\nu_t/\Delta\nu_c$ as well as γ_t^0/γ_c^0. Measurements were made at three different pressures; the results are collected

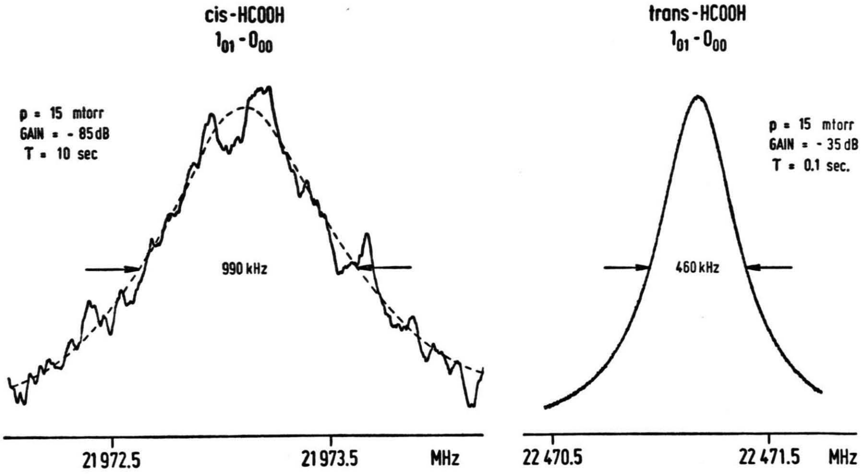

Fig. 3. Line-widths of the $1_{01}-0_{00}$ transitions of *cis*- and *trans*-HCOOH. The *cis* rotamer line has been recorded with much higher sensitivity than the *trans* rotamer line.

Table V. Relative intensity measurements on the $1_{01}-0_{00}$ transitions of *cis*- and *trans*-HCOOH.

p [a]	$\gamma_t{}^0/\gamma_c{}^0$	$\Delta\nu_t$ [b]	$\Delta\nu_c$ [b]	f_t/f_c	ΔE [c]
22	487	505	1200	704 [d]	1358
18	466	485	1065	729	1365
15	451	440	905	754	1372

[a] Approximate pressure in mTorr at a temperature of 298 K.
[b] Full-width at half-height in kHz.
[c] Measured in cm^{-1}; the *cis* rotamer lies higher in energy.
[d] Calculated from Eq. (4) with $(\nu_c/\nu_t)^2 = 0.95616$ and $|\mu_a|_c{}^2/|\mu_a|_t{}^2 = 3.595$.

in Table V. The experimental uncertainty in the peak intensity and line-width ratio numbers is estimated to be ~10%.

Three values for the energy difference between the ground vibrational states of *cis*- and *trans*-HCOOH are also reported in Table V. These were calculated from the f_t/f_c numbers using the Boltzmann equation

$$\Delta E = E_c - E_t = k\,T \ln (f_t/f_c)\ . \qquad (5)$$

The exceedingly good agreement between the ΔE values in Table V is probably to some extent fortuitous. The average of the three ΔE values is 1365 cm^{-1} and the estimated uncertainty in this final result is $\pm 30\ \text{cm}^{-1}$ ($16.33 \pm 0.36\ \text{kJ}\cdot\text{mol}^{-1}$ or $3.903 \pm 0.086\ \text{kcal}\cdot\text{mol}^{-1}$).

IX. Torsional Potential Energy

In studies of rotational isomerism it is usually presumed that the torsional potential energy, V, may be treated as a function of one variable, θ, the torsional angle, and expanded in a Fourier series[1]

$$V(\theta) = \tfrac{1}{2} \sum_n V_n (1 - \cos n\,\theta)\ . \qquad (6)$$

It is further usually assumed that this series converges rapidly. For HCOOH, it is necessary to terminate the above series after the V_2 term, since only two useful pieces of experimental data are available [the energy difference between the ground vibrational states of the *cis* and *trans* rotamers, ΔE, and the frequency of the $v = 1 \leftarrow 0$ torsional vibration of the *trans* rotamer[20], $(\nu_9)_t$], and hence at most only two potential constants can be determined. Some justification for this is provided by comparison with HC(:O)SH for which the V_3 constant has been shown[60] to be zero to within an uncertainty of ±5 cm.

The torsional potential energy function of formic acid was therefore taken to have the form

$$V(\theta) = \tfrac{1}{2} V_1 (1 - \cos\theta) + \tfrac{1}{2} V_2 (1 - \cos 2\,\theta)\ , \qquad (7)$$

from which it follows directly that

$$V_1 = \Delta E + \tfrac{1}{2} h\,[(\nu_9)_t - (\nu_9)_c]\ . \qquad (8)$$

Two additional useful relations are obtained if the potential is expanded about both minima in a Taylor series and this series is terminated after the quadratic term[61]

$$V_1 + 4\,V_2 = 8\,\pi^2 (\nu_9{}^0)_t{}^2\,(G_{tt}^{-1})_t\,, \qquad (9)$$

$$-V_1 + 4\,V_2 = 8\,\pi^2 (\nu_9{}^0)_c{}^2\,(G_{tt}^{-1})_c \qquad (10)$$

where G_{tt}^{-1} represents the diagonal element, for the OH torsion, of the G^{-1} matrix[62]. The vibrational frequencies have been given a zero superscript to denote that these relations are valid only in the harmonic oscillator approximation. As previously shown by Miyazawa and Pitzer[18] the next higher order nonzero term in the Taylor expansion of $V(\theta)$ for HCOOH is not insignificant. This term is most conveniently accounted for by treating it as a first order perturbation. If only the dominant V_2 part is retained then the perturbation Hamiltonian has the simple form $H' = -V_2 \theta^4/3$ and the $\nu = 1 \leftarrow 0$ torsional frequencies are given by

$$(\nu_9)_t = (\nu_9^0)_t - h/[8\pi^2 c (G^{-1}_{tt})_t] , \qquad (11)$$

$$(\nu_9)_c = (\nu_9^0)_c - h/[8\pi^2 c (G^{-1}_{tt})_c] . \qquad (12)$$

The two G^{-1} matrix elements which appear in the above equations were calculated using Polo's method[63]: $(G^{-1}_{tt})_t = 0.6742\ \text{u}\cdot\text{Å}^2$ and $(G^{-1}_{tt})_c = 0.7620\ \text{u}\cdot\text{Å}^2$. It thus follows that

$$(\nu_9^0)_t = (\nu_9)_t + 25.0\ \text{cm}^{-1} , \qquad (13)$$

$$(\nu_9^0)_c = (\nu_9)_c + 22.1\ \text{cm}^{-1} . \qquad (14)$$

Equations (8) – (10) were then solved iteratively, using $(\nu_9)_t = 641.8\ \text{cm}^{-1}$ [20] and $\Delta E = 1365\ \text{cm}^{-1}$. The results are: $V_1 = 1409\ \text{cm}^{-1}$, $V_2 = 4093\ \text{cm}^{-1}$ and $(\nu_9)_c = 553\ \text{cm}^{-1}$. Since $(\nu_9)_t$ and ΔE have been accurately measured, the uncertainties in these numbers are most likely determined largely by model errors. Such errors are very difficult to estimate, but comparison with HC(:O)SH[60] suggests that they are less than 10%. The formic acid OH torsional potential energy function is illustrated in Figure 4.

The barrier to internal rotation, E^*, and the energy difference between the two potential minima, $\Delta E'$, of formic acid have been calculated by various theoretical methods[21–34]. The results from these calculations are compared with experiment in Table VI. Several generalizations can evidently be made. Firstly, the primitive semi-empirical extended Hückel (EHT) method gives spurious results. Secondly, the other semi-empirical methods (discounting those from Ref. [27]) consistently underestimate both $\Delta E'$ and E^*. However, of all the calculations, the Neglect of Diatomic Differential Overlap (NDDO) method does give the best agreement with experiment. Lastly, the *ab initio* calculations generally predict E^* reasonably well, but seriously overestimate $\Delta E'$.

Table VI. Barrier to internal rotation and *cis-trans* energy difference determined for formic acid by different methods[a, b].

$\Delta E'$	E^*	Method	Ref.
8.1		*ab initio*	21
9.46	14.20	*ab initio*	22
8.1	13.0	*ab initio*	23
14.4	18.3	*ab initio*	24
13.2	18.7	*ab initio*	24
6.3	12.2	*ab initio*	25
−1.6	0.7	EHT	26
+	34.9	CNDO/2	27
0.6		CNDO/2	28
−3.0		EHT	29
0.69		CNDO/2	29
1.99	4.65	CNDO	30
2.27	6.06	INDO	30
1.27	5.32	CNDO	31
1.76	7.35	INDO	31
2.65	13.42	NDDO	31
1.97		INDO	32
1.97	6.45	INDO	33
1.99	4.65	CNDO/2	34
2.23	6.78	CNDO/2-NO	34
2.27	6.06	INDO	34
2.64	9.72	INDO-NO	34
4.09	13.8	experiment	

[a] $\Delta E'$ is the energy difference between the potential minima (*cis-trans*) in kcal·mol^{-1}.

[b] E^* is the barrier to internal rotation as seen from the bottom of the potential minimum corresponding to the *trans* rotamer in kcal·mol^{-1}.

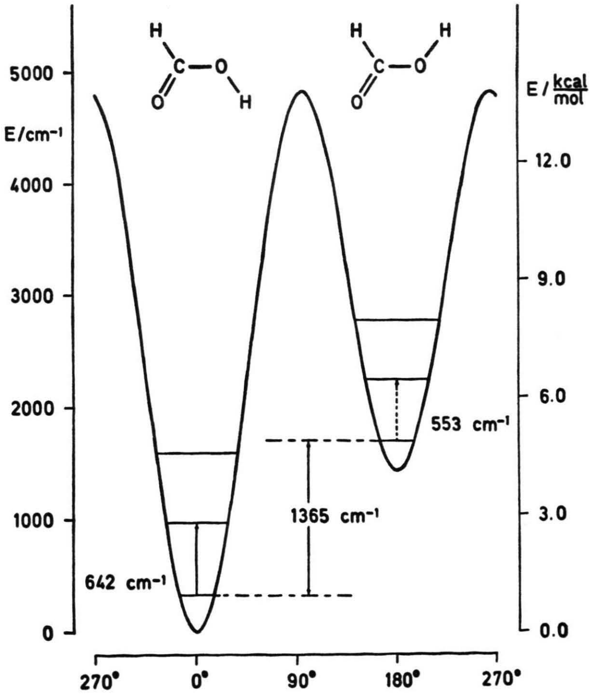

Fig. 4. Torsional potential energy function, $V(\theta)$, of formic acid. $V(\theta) = \frac{1}{2}(1409)(1\text{-}\cos\theta) + \frac{1}{2}(4093)(1\text{-}\cos 2\theta)$, in cm^{-1}.

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