The Other Rotamer of Formic Acid, cis-HCOOH

William H. Hocking

Max-Planck-Institut für Radioastronomie, Bonn, and
Physikalisch-Chemisches Institut, Justus-Liebig-Universität, Gießen

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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 000, 100, 010, 001, 101, 110, 111, 200, 201, and 210 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: \( \mu = 2.65(1) \text{ D, } \mu_b = 2.71(1) \text{ D and } \mu = 3.79(1) \text{ D.} \) 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 \( \pm 30 \text{ cm}^{-1}. \) 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 \( \pi \) 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:

\[
\begin{align*}
H & \quad O \quad C \quad O \quad H \\
\text{trans} & \\
O & \quad C \quad O \quad H \\
\text{cis}
\end{align*}
\]

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 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 100 rotational transition of cis-HCOOH. He concluded that the cis rotamer was at least 4 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 \textit{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 \textit{ab initio} calculations have generally placed the cis rotamer about 8 kcal\(\cdot\)mol\(^{-1}\) higher in energy than the trans rotamer. However, the semi-empirical calculations have consistently given a much lower value (\(~2 \text{ 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(\(\cdot\)O)SH, were identified. The
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. 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, (μ = 0.71521 D).

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. All of these models correspond to a near prolate asymmetric top molecule with \( \alpha \approx -0.96 \). 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(ːO)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
compared in Fig. 1 with the $J = 1 \rightarrow 0$ transitions of trans-\(^{18}\)O\(^{18}\)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 $J = 1 \rightarrow 0$ transition of cis-HCOOH.

The $J = 2 \rightarrow 1$ 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 was employed for this purpose. For the important $J = 2 \rightarrow 0$ 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 $^qR_1$, $^qQ_1$, $^qQ_2$, $^6P_0$, $^6P_1$ and $^6P_2$ 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 in which $\tilde{R}_0$ is set equal to zero. The analysis was performed in the $I^f$ axis representation so that the Hamiltonian may be written as

$$H = \frac{1}{2} (\tilde{B} + \tilde{C}) P^2 + \left[ \tilde{A} - \frac{1}{2}(\tilde{B} + \tilde{C}) \right] P_a^2 + \frac{1}{8}(\tilde{a} - \tilde{c}) (P_b^2 - P_c^2)$$

$$- \Delta \delta P^4 - \Delta \delta [P_a^2 - P_a^4]$$

$$2 \delta \delta [P_a^2 (P_b^2 - P_c^2)] - \delta \delta [P_a^2 (P_b^2 - P_c^2)]$$

$$2 \delta [P_a^2 (P_b^2 - P_c^2)] + \{P_b^2 - P_c^2\} P_a^2$$

where $P_a$, $P_b$, 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 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 constants of formic acid were Watson's reduced rotational constants and the deltas are the quartic centrifugal distortion constants.

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

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed Frequency</th>
<th>Calculated Frequency</th>
<th>Observed - Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-type R-Branch</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J_{1,1} \rightarrow 0_{0,0}$</td>
<td>20713.615</td>
<td>20713.697</td>
<td>0.082</td>
</tr>
<tr>
<td>$J_{1,2} \rightarrow 0_{0,1}$</td>
<td>20715.024</td>
<td>20715.106</td>
<td>0.082</td>
</tr>
<tr>
<td>$J_{1,3} \rightarrow 0_{0,2}$</td>
<td>20716.432</td>
<td>20716.514</td>
<td>0.082</td>
</tr>
<tr>
<td>b-type Q-Branch</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J_{1,1} \rightarrow 0_{0,0}$</td>
<td>20716.215</td>
<td>20716.297</td>
<td>0.082</td>
</tr>
<tr>
<td>$J_{1,2} \rightarrow 0_{0,1}$</td>
<td>20717.624</td>
<td>20717.706</td>
<td>0.082</td>
</tr>
<tr>
<td>$J_{1,3} \rightarrow 0_{0,2}$</td>
<td>20719.032</td>
<td>20719.114</td>
<td>0.082</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table II. Rotational constants and centrifugal distortion constants of formic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-HCOOH</td>
</tr>
<tr>
<td>$A$</td>
</tr>
<tr>
<td>$B$</td>
</tr>
<tr>
<td>$C$</td>
</tr>
<tr>
<td>$\Delta A$</td>
</tr>
<tr>
<td>$\Delta B$</td>
</tr>
<tr>
<td>$\Delta C$</td>
</tr>
<tr>
<td>$\delta A$</td>
</tr>
<tr>
<td>$\delta B$</td>
</tr>
<tr>
<td>$\sigma c$</td>
</tr>
<tr>
<td>$N$</td>
</tr>
</tbody>
</table>

a One standard error.

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a The numbers in parentheses are standard errors.

b Taken from Ref. 42.

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 \( (A_J, A_{JK}, \delta_J, \delta_K) \) have slightly smaller values than those reported for \textit{trans-}HCOOH in its ground state. On the other hand, the \( \tilde{A} \) rotational constant and the \( \tilde{A}_K \) distortion constant are rather larger than in \textit{trans-}HCOOH. All of the observed differences are at least qualitatively consistent with the assignment of the spectrum reported here to \textit{cis-}HCOOH in its ground state.

**V. Molecular Structure**

The moments of inertia and the inertial defect of \textit{cis-}HCOOH were calculated from the rotational constants given in Table II using the conversion factor \( (B^2 - \frac{1}{2}a) = 505379.0(38) \text{ MHz} \cdot \text{u} \cdot \text{Å}^2 \). The small positive value found for the inertial defect \( A = 0.0624 \text{ u} \cdot \text{Å}^2 \) shows that the molecule has a planar configuration. It is also significant that the inertial defect takes on a slightly smaller value in \textit{cis-}HCOOH than in \textit{trans-}HCOOH \( (A = 0.0765 \text{ u} \cdot \text{Å}^2) \). Remarkably similar behavior has been observed for the \textit{cis} \( (A = 0.0735 \text{ u} \cdot \text{Å}^2) \) and \textit{trans} \( (A = 0.0832 \text{ u} \cdot \text{Å}^2) \) planar rotamers of HC(:O)SH.

A structural model was constructed for \textit{cis-}HCOOH as follows: the structure reported for the \textit{trans} rotamer by Bellet et al. 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 \textit{trans} to the \textit{cis}.

![Molecular structures and electric dipole moments of \textit{cis-} and \textit{trans-}HCOOH.](image)

*Fig. 2. Molecular structures and electric dipole moments of \textit{cis-} and \textit{trans-}HCOOH. The arrow heads indicate the positive end of the dipole moment. The dipole moment magnitude given for \textit{trans-}HCOOH was obtained by adjusting slightly the value reported by Kim et al. to conform to the new OCS standard. Two possible orientations have been shown for the dipole moment of \textit{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.

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>Bond angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(C—H) a = 1.097 Å</td>
<td>&lt;(\angle(OCO)) = 122.3°</td>
</tr>
<tr>
<td>r(C=O) a = 1.228 Å</td>
<td>&lt;(\angle(HOC)) a = 106.8°</td>
</tr>
<tr>
<td>r(C—O) = 1.323 Å</td>
<td>&lt;(\angle(HC—O)) a = 110.4°</td>
</tr>
<tr>
<td>r(O—H) a = 0.974 Å</td>
<td>Assumed 15</td>
</tr>
</tbody>
</table>

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 \(1_01—0_01\) 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

\[
\nu = a + \beta V^2 + \gamma V^4
\]

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

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

<table>
<thead>
<tr>
<th>Stark component</th>
<th>(\beta' \times 10^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1_{01—0_{00}}), (M_J = 0)</td>
<td>4.634(38)</td>
</tr>
<tr>
<td>(1_{11—2_{02}}), (M_J = 0)</td>
<td>0.3442(25)</td>
</tr>
</tbody>
</table>

a \(\beta'\) has units of MHz (V/cm)\(^{-2}\).

b The numbers in parentheses are standard errors.

The second order Stark effect energy, \([W_2^{(2)}]_{J_J M_J'}\), of an asymmetric rotor molecule is related to the molecular electric dipole moment by the equation 44, 45

\[
[W_2^{(2)}]_{J_J M_J'} = \sum_{t} \left( \frac{\mu_i^2 S_{J_J M_J'}^2}{2 J + 1} \sum_{\tau} \frac{2 J - M_J^2}{J (2 J - 1)} (2 J - 1) W_{J_J M_J' - W_{J_J M_J'}}^2 \right)

\frac{S_{J_J M_J'}}{J (J + 1)} \left( \frac{M_J^2 - M_J^2}{J (2 J - 1)} \frac{S_{J_J M_J'}}{J (J + 1)} \left( J + 1 \right)^2 \right)

\frac{W_{J_J M_J'}^0 - W_{J_J M_J'}^0}{J (J + 1) (2 J + 3)}

\] (3)

where \(\mu_i\) 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 \(S_{J_J M_J'}\) are line strength factors and the \((W_{J_J M_J'}^0 - W_{J_J M_J'}^0)\) are energy differences between the unperturbed rotational levels designated by \(J\) and \(J'\) 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 and electric dipole moment 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 $\mu_b$. The direction shown with a dotted arrow is that deduced by Kim et al. from an apparent decrease in $\mu_b$ on going from trans-HCOOH to trans-HCOOD. However, this deduction is rather tenuous since the uncertainty in the difference between the two $\mu_b$ values is larger than the difference itself. Furthermore, the variation in the more accurately determined $\mu_a$ 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 and semi-empirical 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 are in good agreement with the dotted arrow in Fig. 2, others are in good agreement with the solid arrow, and yet more 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 and trans-HC(\(\text{O})\)SH may be semiquantitatively accounted for using a simple vector model. 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, $\bar{\mu}_F$, and an oxygen-hydrogen bond moment, $\bar{\mu}_{OH}$. It was assumed that: (i) the $\bar{\mu}_F$ moment has the same magnitude and direction relative to the molecular frame in the two rotamers, (ii) the $\bar{\mu}_{OH}$ moment has the magnitude 1.52 D (estimated from water) 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, $\bar{\mu}_F$ 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 8.5° 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 $\pm (9.0^\circ \pm 3.0^\circ)$ or $\mu = 1.42 \pm 0.01$ D at an angle with the $a$-axis of $\pm (10.5^\circ \pm 1.6^\circ)$] 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

$$\frac{\gamma_c^0}{\gamma_t^0} = \frac{f_c}{f_t} \left( \frac{v_c}{v_t} \right)^2 \left( \frac{\Delta v_c}{\Delta v_t} \right) \left( \frac{\mu_a_c}{\mu_a_t} \right)^2$$

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

- $\gamma^0$ = 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.
- $v$ = the resonance frequency of the rotational transition.
- $\Delta v$ = 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(\(\text{O})\)SH, 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. In order to determine accurately the ratio $f_c/f_t$ it was therefore necessary to measure $\Delta v_c/\Delta v_t$ as well as $\gamma_c^0/\gamma_t^0$. 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.

<table>
<thead>
<tr>
<th>$p$ (mTorr)</th>
<th>$\gamma_i/\gamma_c$</th>
<th>$\Delta v_i$ (kHz)</th>
<th>$\Delta v_c$ (kHz)</th>
<th>$f_i/f_c$</th>
<th>$\Delta E$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>487</td>
<td>505</td>
<td>1200</td>
<td>704</td>
<td>1358</td>
</tr>
<tr>
<td>18</td>
<td>466</td>
<td>485</td>
<td>1065</td>
<td>729</td>
<td>1365</td>
</tr>
<tr>
<td>15</td>
<td>451</td>
<td>440</td>
<td>905</td>
<td>754</td>
<td>1372</td>
</tr>
</tbody>
</table>

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 $(v_c/v_i)^2 = 0.95616$ and $|\mu_a|/|\mu_a|^2 = 3.595$.

in Table V. The experimental uncertainty in the peak intensity and line-width ratio numbers is estimated to be $\sim$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 $f_i/f_c$ numbers using the Boltzmann equation

$$\Delta E = E_c - E_t = kT \ln (f_i/f_c).$$

The exceedingly good agreement between the $\Delta E$ values in Table V is probably to some extent fortuitous. The average of the three $\Delta E$ values is 1365 cm$^{-1}$ and the estimated uncertainty in this final result is $\pm$30 cm$^{-1}$ (16.33 $\pm$ 0.36 kJ$\cdot$mol$^{-1}$ or 3.903 $\pm$ 0.086 kcal$\cdot$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, $\theta$, the torsional angle, and expanded in a Fourier series:

$$V(\theta) = \frac{1}{2} \sum_n V_n (1 - \cos n \theta).$$

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, $\Delta E$, and the frequency of the $v = 1 \leftrightarrow 0$ torsional vibration of the trans rotamer $\nu_2$, $(\nu_2)_c$], 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 to be zero to within an uncertainty of $\pm$5 cm.

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

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

from which it follows directly that

$$V_1 = \Delta E + \frac{1}{2} h [(\nu_2)_c - (\nu_2)_c].$$

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:

$$V_1 + 4V_2 = 8 \pi^2 (\nu_2)_c^2 (Gtt)_c,$$

where $(Gtt)_c$ represents the diagonal element, for the OH torsion, of the $G^{-1}$ matrix. 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 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 $H' = -\frac{V_2}{3} \theta^3$ and the $\nu = 1 \leftrightarrow 0$ torsional frequencies are given by

\begin{align}
(v_9)_t &= (v_9^0)_t + \frac{25.0 \text{ cm}^{-1}}{2}, \\
(v_9)_c &= (v_9^0)_c + \frac{22.1 \text{ cm}^{-1}}{2}.
\end{align}

Equations (8) – (10) were then solved iteratively, using $(v_9^0)_t = 641.8 \text{ cm}^{-1}$ and $\Delta E = 1365 \text{ cm}^{-1}$. The results are: $V_1 = 1409 \text{ cm}^{-1}$, $V_2 = 4093 \text{ cm}^{-1}$ and $(v_9)_c = 553 \text{ cm}^{-1}$. Since $(v_9)_t$ and $\Delta E$ 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(\textrm{O})SH 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. 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.

<table>
<thead>
<tr>
<th>$\Delta E'$</th>
<th>$E^*$</th>
<th>Method</th>
<th>Ref.</th>
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<tr>
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<td>21</td>
</tr>
<tr>
<td>8.1</td>
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<td>ab initio</td>
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<tr>
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<td>ab initio</td>
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<td>18.7</td>
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</table>

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, $V(\theta) = \frac{1}{2}(1409)(1-\cos\theta) + \frac{1}{2}(4093)(1-\cos2\theta)$, in cm$^{-1}$. 

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21-34. See references in the text. 
25-34. 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 $\Delta E'$. 

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63. Polo's method.
66. HC(\textrm{O})SH. 
68. See references in the text. 
72. See references in the text.
Acknowledgements

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