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An Analysis of the Infrared and Raman Spectra of the Formic Acid Dimer $(HCOOH)_2$

Yan-Tyng Chang, Yukio Yamaguchi, William H. Miller, and Henry F. Schaefer III*

Contribution from the Department of Chemistry, University of California, and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720.
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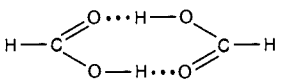
Abstract: Ab initio molecular quantum mechanical methods have been used to study the formic acid dimer and several isotopomers. Structures and harmonic vibrational frequencies have been predicted for the monomer, the equilibrium dimer, and the transition state for simultaneous two-hydrogen transfer. In an attempt to systematize results obtained at various levels of theory, three different basis sets were used: minimum, double-ζ (DZ), and double-ζ plus polarization (DZ+P). The predicted self-consistent-field (SCF) dissociation energies D_e are 15.1 (minimum basis), 19.3 (DZ), and 14.3 (DZ+P) kcal/mol. Further consideration of zero-point vibrational energies and finite temperature effects allows a comparison with several experimental values for ΔH_{300}. The infrared and Raman intensities (as well as the vibrational frequencies themselves) are compared with available experimental results. Where comparison is possible, the agreement is generally good. An exception occurs for ν_{18}, the O–D stretch of the $(HCOOD)_2$ molecule, where it is concluded that the experimental analysis may be incorrect.

I. Introduction

The formic acid dimer



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is one of the simplest examples of a molecular entity held together by two hydrogen bonds.[1-5] As such, it has been the subject of a rather large number of experimental[6-20] and theoretical[21-37] studies. Particularly noteworthy are the classic 1958 infrared study of Millikan and Pitzer[10] and the two definitive investigations (1982, 1986) of the Raman spectrum by Bertie and co-workers.[15,16] Some of these previous studies investigated the geometrical changes[9,34] between monomer and dimer and the energetic stabilization[17,18,20,23,28,34] of the dimer due to hydrogen bond formation. Others were primarily concerned with the double proton transfer

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Table I. Theoretical (Self-Consistent-Field) and Experimental Equilibrium Geometries for the Formic Acid Monomer[b]

	STO-3G	DZ	DZ+P	exptl[c]
$r(C_1{=}O_2)$[a]	1.214	1.210	1.185	1.202
$r(C_1{-}O_3)$	1.386	1.351	1.324	1.343
$r(C_1{-}H_4)$	1.104	1.075	1.088	1.097
$r(O_3{-}H_5)$	0.990	0.956	0.952	0.972
$\angle O_2{=}C_1{-}O_3$[d]	123.6	124.5	125.0	124.6
$\angle H_4{-}C_1{=}O_2$	126.0	125.2	124.5	124.1
$\angle H_4{-}C_1{-}O_3$	110.4	110.4	110.5	
$\angle C_1{-}O_3{-}H_5$	104.8	115.3	109.0	106.3

[a] Bond distances in Å. [b] For atom numbering see Figure 1. [c] Experimental structure is that chosen by: Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619. [d] Angles in deg.

in formic acid dimer along the double well potential.[21,22,27,29-33] Since proton transfer plays an important role in many chemical and biological systems, the knowledge of the total energies and geometries, as well as the vibrational frequencies of the equilibrium state and transition state, is indeed very important to the understanding of such dynamical processes.

Among the experimental studies, the geometry of the monomer has been thoroughly investigated with various techniques such as infrared[38,39] and microwave[40,41] spectroscopy and electron diffraction.[9] The experimental determination of the equilibrium dimer structure is based on electron-diffraction measurements. Infrared and Raman spectra pertaining to the equilibrium between monomer and dimer have also been reported.[10-16] Some of these vibrational motion investigations of the dimer were restricted to the study of the O–H stretching mode[13,14,16] since this stretching mode is subject to a double minimum potential and has evoked significant research interest.

On the other hand, numerous theoretical studies with ab initio quantum chemical methods have been carried out at various levels to predict the structures of the dimer and the potential surface for the double-proton-transfer process. However, most of the geometries used in the potential surface calculation were deduced from experimental[21] data or not fully optimized.[22,27,31] Recently, Mijoule[36] and his co-workers reported the equilibrium and transition-state structures at the 6-31G level with gradient optimization, but they assumed the O–H···O bond angle to be 180°. Two ab initio studies based on 4-31G[33] and (7s3p/3s)[34] basis sets have predicted the fully optimized geometry of formic acid dimer. These two basis sets approach the quality of the double-ζ basis set used in the present work. In order to improve the reliabilities of the energies, geometries, and vibrational frequencies of the formic acid monomer, equilibrium dimer, and transition dimer, studies based on a more complete basis set, namely double-ζ plus polarization, are also reported here.

The primary purpose of this work is to use various levels of ab initio self-consistent-field (SCF) theory, i.e., minimum (STO-3G), double-ζ (DZ), and double-ζ plus polarization (DZ+P) to predict the following: (1) completely optimized geometries for both formic acid and its dimer; (2) vibrational frequencies and infrared and Raman intensities; (3) the dissociation energy of the equilibrium dimer; and (4) the bare barrier height for the two-proton-transfer process.

II. Theoretical Approach

The geometries of the formic acid monomer (C_s structure), equilibrium dimer (C_{2h} structure), and dimer transition state (D_{2h} structure) have been fully optimized by the energy gradient method without setting any constraints on the bond angles and bond lengths. As demonstrated by the vibrational analyses, all three structures turn out to be planar. The basis sets used were minimum (STO-3G), double-ζ (DZ), and double-ζ plus polarization (DZ+P). The DZ basis set is that of Huzinaga and Dunning,[42] which consists of (9s 5p/4s 2p) on carbon and oxygen and (4s/2s) on hydrogen. For the DZ+P basis set polarization functions, a single set of d functions for each heavy atom and a single set of p functions for each hydrogen atom were added to the corresponding DZ basis set. The polarization function exponents were $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$, and $\alpha_p(H) = 0.75$. The DZ+P basis set for the formic acid dimer includes 116 contracted Gaussian functions.

With use of analytic SCF second-derivative techniques,[43] all quadratic force constants and the resulting harmonic vibrational frequencies were determined. The presence of a single imaginary vibrational frequency for the D_{2h} structure proves that it is a true transition state.

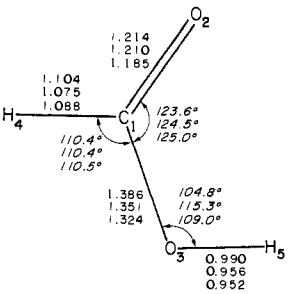

Figure 1. Predicted equilibrium geometries for the formic acid monomer. Bond distances are given in Å. Three levels of self-consistent-field theory are reported for each geometrical parameter.

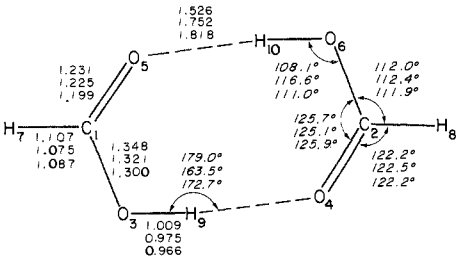

Figure 2. Predicted equilibrium geometries for the formic acid equilibrium dimer. Bond distances are given in Å. Three levels of self-consistent-field theory are reported for each geometrical parameter.

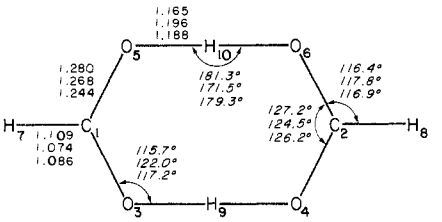

Figure 3. Predicted equilibrium geometries for the formic acid dimer transition state. Bond distances are given in Å. Three levels of self-consistent-field theory are reported for each geometrical parameter.

III. Molecular Structures

The optimized geometries for monomer, equilibrium dimer, and dimer transition state are illustrated in Figures 1–3. Table I reproduces the theoretical geometries of the monomer at all three levels of theory together with the most reliable experimental structure. As shown in Table I, the theoretical geometries are all in reasonable agreement with experiment. Perhaps the only major structural error occurs at the DZ SCF level of theory. There the C–O–H bond angle (115.3°) is predicted to be 9.0 deg larger than experiment. This is a common failure of the DZ SCF

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Table II. Theoretical (Self-Consistent-Field) and Experimental Equilibrium Geometries for the Formic Acid Dimer[c]

	STO-3G	DZ	DZ+P	exptl[a]
$r(C_1{=}O_5)$	1.231	1.225	1.199	1.217 ± 0.003
$r(C_1{-}O_3)$	1.348	1.321	1.300	1.320 ± 0.003
$r(C_1{-}H_7)$	1.107	1.075	1.087	1.079 ± 0.021
$r(O_3{-}H_9)$	1.009	0.975	0.966	1.033 ± 0.017
$r(O_3{\cdots}O_4)$	2.536	2.700	2.779	2.696 ± 0.007
$r(O_3{\cdots}O_5)$	2.296	2.260	2.227	2.262 ± 0.004
$r(C_1{\cdots}C_2)$	3.690	3.847	3.890	
$r(O_4{\cdots}H_9)$	1.526	1.752	1.818	
$\angle O_3{-}C_1{=}O_5$	125.7	125.1	125.9	126.2 ± 0.5
$\angle H_7{-}C_1{=}O_5$	122.2	122.5	122.2	115.4 ± 3.1
$\angle H_7{-}C_1{-}O_3$	112.0	112.4	111.9	
$\angle C_1{-}O_3{-}H_9$	108.1	116.6	111.0	108.5 ± 0.4
$\angle O_3{-}H_9{\cdots}O_4$	179.0	163.5	172.7	(180)[b]

[a] From ref 9 and the compilation by Harmony, et al., footnote *c* to Table I. [b] Geometrical parameter assumed in the refinement of the electron diffraction data. [c] Bond distances in Å, angles in deg.

method, occurring regularly for angles about oxygen.[44]

The theoretical geometries for the equilibrium dimer as well as that from electron-diffraction measurements[9] are listed in Table II. Comparisons between Table I and Table II show that there are some structural changes due to the formation of hydrogen bonds. For example, the C=O double bond is longer in the dimer than in the monomer, whereas the C–O single bond shows the opposite trend. Comparing theoretical geometries for the dimer with data from electron diffraction measurements, one sees generally good agreement. Specifically, the differences between the DZ+P SCF structure and the experimental bond distances are as follows: −0.018 Å (C=O), −0.020 Å (C—O), −0.067 Å (O—H), +0.083 Å (O—H···O). The bond angle differences are −0.3° (O—C=O) and +2.5° (C—O—H).

Several of the differences between theory and experiment are typical of comparisons between DZ+P SCF theory and the truth. However, it does appear that the experimental O–H single bond distance for the dimer is in error by an amount greater than the stated uncertainty of ±0.017 Å. Specifically, it is difficult to see how the DZP SCF prediction of r_e(O–H) = 0.966 Å could be in error by more than 0.02 Å. In addition, the H—C=O bond angle is predicted by all three levels of theory to be 122°, while this angle is found to be 115.4 ± 3.1° from electron diffraction. We doubt that the error in the DZ+P SCF angle H—C=O would be more than 2°.

As will be seen later, the minimum basis set does a good job reproducing energetic predictions from the larger DZ+P basis set. However, the hydrogen bonded distances O···O of the dimer are treated relatively poorly at the minimum basis SCF level of theory. Specifically the STO-3G O···H distances are 1.526 Å, or nearly 0.3 Å less than the comparable DZ+P SCF predictions. The DZ SCF level of theory does much better for the dimer O···O distances but fails (as expected—see above monomer discussion) for the C–O–H bond angles. The DZ SCF method also predicts O–H···O angles 9.2° less than the more reliable DZ+P SCF method.

Since the experimental structure of the transition state dimer is not obtainable, only theoretical results are available. As expected, the previously single bonded C–O distance is shorter for the transition state than for the equilibrium dimer. Comparison between this transition state bond length and the C=O and C—O bond lengths shows that it is characteristic of bond order one and a half. Conversely, the O···O and C···C distances are shorter for the D_{2h} structures. Note that the O–H···O bond angle is not 180° for either C_{2h} or D_{2h} structure. Constraining these bond angles to be 180° results in bond angle errors of the order of 1° for the transition state and 7° for the equilibrium dimer.

Our geometries from DZ basis set calculation for the equilibrium C_{2h} structure are in reasonable agreement with those obtained from 4-31G[33] and DZ contracted (7s 3p/3s)[34] calculations, since these two basis sets approach the level of our DZ basis set. Recall, of course, that the more reliable structures predicted here are the DZ+P SCF structures.

Table III. Vibrational Frequencies and IR Intensities for the HCOOH Monomer[f]

		DZ		DZ+P			
		freq[a]	int[b]	freq	int	exptl	assignment
A′	ν_1	4030	104	4116	116	3569[c]	O—H
	ν_2	3400	34	3293	53	2942[e]	C—H
	ν_3	1872	481	2015	533	1777[c]	C=O
	ν_4	1519	7	1536	10	1381[c]	H—C—O
	ν_5	1382	22	1426	26	1223[e]	H—O—C
	ν_6	1185	335	1268	301	1104[c]	C—O
	ν_7	648	71	690	62	625[c]	O—C=O
A″	ν_8	1160	1	1183	0.3	1033[d,e]	H—C—O oop
	ν_9	680	310	693	201	642[c]	H—O—C oop

[a] In cm^{-1}. [b] km/mol. [c] From ref 15. [d] From ref 43. [e] From ref 42. [f] Note that the theoretical prediction are harmonic frequencies, while the experimental values are the observed (anharmonic) fundamentals.

IV. $(HCOOH)_2$ Vibrational Frequencies and IR Intensities

Tables III–V give the harmonic vibrational frequencies, IR intensities, and normal mode assignments of the molecules studied here. The conventions of Bertie[15,16] were adopted in describing the normal modes. The designations "oop" and "ip" refer to out-of-plane bending and in-plane bending.

It is not surprising[45] that the predicted frequencies from DZ and DZ+P for the monomer and C_{2h} dimer are consistently higher than the observed data. The absolute and relative difference between DZ+P SCF harmonic frequencies ω and the observed monomer fundamentals ν are 547 cm^{-1} = 15.3% (ν_1), 351 cm^{-1} = 11.9% (ν_2), 238 cm^{-1} = 13.4% (ν_3), 155 cm^{-1} = 11.2% (ν_4), 203 cm^{-1} = 16.6% (ν_5), 164 cm^{-1} = 14.9% (ν_6), 65 cm^{-1} = 10.4% (ν_7), 150 cm^{-1} = 14.5% (ν_8), and 51 cm^{-1} = 7.9% (ν_9). These differences between theoretical harmonic frequencies and observed anharmonic frequencies are due to[45] a combination of (a) the tendency of the DZ+P SCF method to overshoot the true harmonic vibrational frequencies and (b) the contributions of anharmonicity; generally speaking $\omega_i > \nu_i$ and anharmonicity corrections of 5% are not unusual.

The classic paper by Millikan and Pitzer[10] labels the dimer infrared intensities as s (strong), m (medium), w (weak), etc. For several of the normal modes, more quantitative information concerning the IR intensities has been given by Marechal.[14] Since the IR intensities have been quantitatively predicted from theory here, an interesting comparison in Table IV is possible. Note, of course, that all A_g and B_g normal modes have zero IR intensity in the "double harmonic" approximation used here. The three greatest IR intensities are predicted theoretically for ν_{17} (1575 km/mol), ν_{19} (1188 km/mol), and ν_{22} (478 km/mol). It is most encouraging that ν_{17}, ν_{19}, and ν_{22} are three of the four frequencies designated "very strong" by Millikan and Pitzer.[10] We predict a significant but smaller intensity (156 km/mol) for the third fundamental (ν_{18}) labeled very strong by Millikan and Pitzer. A designation of simply "strong" would have been more consistent with the ab initio predictions.

The fourth highest theoretical IR intensity (ν_{14}, 357 km/mol) is labeled "strong" by Millikan and Pitzer.[10] This is followed by ν_{23} (85 km/mol) and ν_{21} (75 km/mol), both designated "medium" from the observed IR spectrum. ν_{24} is predicted from DZ+P SCF theory to have an intensity of 48 km/mol, a bit less than expected from Millikan and Pitzer's label "strong". The remaining four fundamentals are predicted to have IR intensities less than 20 km/mol (DZ+P SCF). Those weak intensities concur with the experimental labels,[10,12] except for ν_{15}, which is designated "medium" by Millikan and Pitzer. A success for theory is that among modes with nonvanishing IR intensity, the vibrational frequency with weakest intensity is ν_{13} (1050 cm^{-1}) for which I = 0.4 km/mol (DZ+P SCF). This is in fact the one fundamental (among ν_{13}–ν_{24}) above 200 cm^{-1} that was not observed as a

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Table IV. Vibrational Frequencies and IR Intensities for the Formic Acid Dimer Equilibrium Geometry

		DZ		DZ+P			
		freq	int	freq	int	exptl[a]	assignment
A_g	ν_1	3620	0	3782	0		O—H
	ν_2	3401	0	3303	0	2949	C—H
	ν_3	1800	0	1927	0	1670	C=O
	ν_4	1549	0	1561	0	1415	H—O—C
	ν_5	1503	0	1527	0	1375	H—C—O
	ν_6	1295	0	1357	0	1214	C—O
	ν_7	696	0	732	0	677	O—C=O
	ν_8	209	0	182	0	190	O···O
	ν_9	181	0	164	0	137	O—H···O ip
B_g	ν_{10}	1184	0	1200	0	1060	δC—H oop
	ν_{11}	1029	0	935	0		δO—H oop
	ν_{12}	262	0	250	0	230	O—H···O oop
A_u	ν_{13}	1190	43	1203	0.4	1050	δC—H oop
	ν_{14}	1075	566	985	357	917 strong	δO—H oop
	ν_{15}	188	24	174	13	163 medium	O—H···O oop
	ν_{16}	101	3	81	4	68 weak	twist about C—H bond
B_u	ν_{17}	3686	1551	3835	1575	3110 very strong	O—H
	ν_{18}	3398	130	3300	156	2957 very strong	C—H
	ν_{19}	1840	1145	1983	1188	1754 very strong	C=O
	ν_{20}	1536	5	1551	19	1450 very weak	HOC[b]
	ν_{21}	1495	140	1505	75	1365 medium	HCO[b]
	ν_{22}	1289	549	1358	478	1218 very strong	C—O
	ν_{23}	717	95	747	85	697 medium	O—C=O
	ν_{24}	249	54	223	48	248 strong	O—H···O ip

[a] Experimental fundamentals for the dimer are reviewed in ref 15; intensity labels are from Millikan and Pitzer, ref 10, and Clague and Novak, ref 12. [b] These assignments are from DZ SCF theory and Bertie and Michaelien, ref 15. DZ+P SCF theory reverses the identifications of ν_{20} and ν_{21}.

Table V. Dimer–Monomer Vibrational Frequency Shifts (in cm^{-1}) for Formic Acid[b]

		Δω(DZ SCF)	Δω(DZ+P SCF)	Δν(exptl)	assignment
A_g	1	−410	−334		O—H
	2	+1	+10	+7	C—H
	3	−72	−88	−107	C=O
	4	+167	+135	+193	H—O—C
	5	−16	−9	−6	H—C—O
	6	+110	+89	+110	C—O
	7	+48	+42	+52	O—C=O
B_g	10	+24	+17	+27	δC—H oop
	11	+349	+242		δO—H oop
A_u	13	+30	+20	+17	δC—H oop
	14	+395	+292	+276	δO—H oop
B_u	17	−344	−281	−459	O—H
	18	−2	+7	+15	C—H
	19	−32	−32	−23	C=O
	20	+154	+15	+227	H—C—O[a]
	21	−24	+79	−16	H—O—C[a]
	22	+104	+90	+114	C—O
	23	+69	+57	+72	O—C=O

[a] These assignments are from DZ+P SCF theory. DZ SCF and Bertie and Michaelian reverse the identifications of ν_{20} and ν_{21}. [b] Experimental vibrational frequencies are from ref 10, 15, 42, and 43. Dimer frequencies with no immediate counterpart in the monomer are excluded here.

well-defined feature by Millikan and Pitzer.[10] The reader will appreciate that knowing what *not* to expect in an IR spectrum can be as helpful as knowing what *to* expect. To summarize, the correspondence between theoretical and experimental IR intensities is generallly quite good.

Except for two low-frequency vibrations, all the DZ+P SCF harmonic frequncies ω lie above the corresponding observed fundamentals ν. The two exceptions are the O···O stretch (DZ+P SCF ω_8 = 182 cm^{-1}, ν_8 = 190 cm^{-1}) and the O–H···O in-plane bending vibration (DZ+P SCF ω_{24} = 223 cm^{-1}, ν_{24} = 248 cm^{-1}). Although the theoretical frequencies fall slightly below the experimental fundamentals, the absolute agreement is excellent. This good agreement may augur well for the reliability of the theoretical potential energy hypersurface for dynamical studies of proton transfer. These two modes, O···O and O–H···O, are among the most sensitive to the theoretical description of the HCOOH···HCOOH interaction.

Perhaps more interesting than the vibrational frequencies themselves are the frequency shifts between dimer and monomer. These shifts are displayed in Table V. One sees in Table V that two critical pieces of experimental information are missing, namely $\Delta\nu(\nu_1)$ and $\Delta\nu(\nu_{11})$, predicted by theory to be two of the four largest frequency shifts. However, the remainder of the comparisons between theory and experiment leave little doubt that theory is qualitatively reliable in these predictions.

Not surprisingly (see Figure 2), the largest shifts occur for the O–H frequencies. The antisymmetric dimer O–H stretch ν_{17} is known[15] to be 459 cm^{-1} less than that for the isolated monomer, and theory predicts an even larger shift for the symmetric OH stretch ν_1. The simple explanation, of course, is that the formation of two strong hydrogen bonds in the dimer weakens the two O–H single bonds. In the limit of the D_{2h} transition state, the four O–H linkages become indistinguishable.

The next largest dimer–monomer vibrational shift occurs for ν_{14}, the in-phase combination of monomer out-of-plane O–H bending modes. This large shift is +276 cm^{-1} from experiment,[15] with DZ+P SCF theory predicting +292 cm^{-1}, in good agreement. The comparable out-of-phase combination of oop O–H bending frequencies is not known from laboratory studies, but it should be close to the predicted $\Delta\nu(\nu_{11})$ = +242 cm^{-1}. These vibrational frequencies increase in the formic acid dimer, because the formation of the two hydrogen bonds has the effect of causing the monomers to become much more rigidly planar. That is, the nonplanar excursions of the O–H are now not only accountable to the singly bonded formyl group (HCO) but also to the partner monomer.

A significant dimer–monomer vibrational frequency shift also occurs for ν_4, the symmetric combination of in-plane H–O–C bending frequencies. For the reasons discussed in the previous paragraph, these vibrational modes are shifted to higher frequency in the dimer. DZ+P SCF theory does not do terribly well in predicting this shift: $\Delta\nu(\nu_4)$ = +135 (theory) and +193 cm^{-1} (experiment). Further theoretical work will be necessary to ascertain whether these discrepancies are due to (a) an inadequate description of the potential energy surface, in which case the true harmonic shifts $\Delta\omega$ would be closer to $\Delta\nu$, or (b) neglect of important anharmonic effect.

Insight into the problem between theory and experiment for ν_4 is given by the analogous comparisons for ν_{20} and ν_{21}. For these two shifts DZ SCF theory seems to be doing a reasonable job, while the higher level DZ+P SCF method does very poorly

compared to experiment. The reason is that the separation between H–C–O and H–O–C bending modes is rather murky. Specifically, Bertie and Michaelian[15] identify the higher of these two B_u modes as H–O–C bending. This is consistent with the DZ SCF potential energy distributions (PED's). However, in the DZ SCF case the weightings are quite close, being 0.52 (H–O–C) and 0.36 (H–C–O). At the DZ+P SCF level, the PED's reverse to give 0.71 (H–C–O) and 0.23 (H–O–C). Furthermore, since ν_{20} and ν_{21} are only separated by 85 cm^{-1} experimentally, one cannot be certain that the experimental designations of Bertie and Michaelian are unambigous. The best way to think about ν_4 and ν_5 and about ν_{20} and ν_{21} is that they are strongly interacting combinations of the H–C–O and H–O–C bending modes. This is, of course, confirmed by the accepted assignment that for the monomer the H–C–O bend lies higher, while for the A_g dimer vibrations the H–O–C bend lies higher.

Further insight into the assignments for ν_{20} and ν_{21} is possibly given by examination of the IR intensities. For the formic acid monomer, theory and experiment agree that the H–O–C bend has a higher IR intensity and lower fundamental frequency than the H–C–O bend (DZ+P SCF: $I(4)$ = 10 km/mol, $I(5)$ = 26 km/mol). To the extent that the monomer results may be used to anticipate the dimer intensities, one would thus expect the H–O–C bending assignment to go to the lower dimer vibrational frequency with higher IR intensity. This is precisely what is predicted by DZ+P SCF theory, but it is opposite to the experimental assignments.

The C–O single bond stretching frequencies are shifted upward by ~110 cm^{-1} in the dimer, and DZ+P SCF theory does a good job in reproducing this trend. Inspection of Figure 2 shows that the C–O single bonds are next-nearest neighbors to the H···O hydrogen bonds and take on a small amount of "conjugation" or double bond character upon dimer formation.

Perhaps most widely discussed among the formic acid dimer vibrations are the C=O double bond stretching frequencies. A recent paper by Dybal, Cheam, and Krimm[46] discusses in great detail the origin of the splitting between the symmetric (ν_3 = 1670 cm^{-1}) and antisymmetric (ν_{19} = 1754 cm^{-1}) components of the C=O stretch mode. This shift of 84 cm^{-1} between C=O dimer modes is predicted to be (1983 − 1927) = 56 cm^{-1} at the DZ+P SCF level of theory. With the 4-31G SCF method Morokuma and co-workers[33] predict 44 cm^{-1} for this shift. Karpfen predicts 58 cm^{-1} for this dimer shift in his ab initio study[34] using a small double-ζ basis set in conjunction with SCF theory. The three sets of ab initio harmonic vibrational frequencies are consistent with the conclusions of Dybal, Cheam, and Krimm[46] that the remaining discrepancy (84 − 56 = 28 cm^{-1}) may be due to a difference in anharmonicity between the A_g and B_u modes.

It is encouraging that the smaller dimer–monomer vibrational frequency shifts are also treated in a reasonable manner by the present theoretical methods. For example, the symmetric combination of C–H stretches is predicted to be 10 cm^{-1} higher in the dimer, while the experimental shift is +7 cm^{-1}. In fact the *sign* of every known dimer–monomer vibrational frequency shift is properly predicted with DZ+P SCF theory. DZ SCF theory fails once, for ν_{18}, the asymmetric combination of C–H stretches. In that case $\Delta\omega$(DZ SCF) = −2 cm^{-1}, $\Delta\omega$(DZ+P SCF) = +7 cm^{-1}, and $\Delta\nu$(exptl) = +15 cm^{-1}.

Finally, a brief comparison of the dimer and monomer IR intensities is in order. Based strictly on the formic acid monomer results (Table III), one would expect the dimer C=O stretch (monomer intensity 533 km/mol) to be strongest, followed by the C–O single bond stretch (301 km/mol) and then by the O–H stretch (116 km/mol for the monomer; DZ+P SCF level of theory). Although these three modes do have the largest IR intensities among the B_u dimer fundamentals, the order is different. That is, the O–H stretch has the highest IR intensity (1575 km/mol) and the C–O single bond stretch the lowest (478 km/mol) of the three. Since the IR intensity is proportional to the square of the change in dipole moment with respect to the appropriate normal coordinate, $(\partial\mu/\partial Q)^2$, the order of dimer IR intensities is not trivially deduced from those of the formic acid monomer.

(46) Dybal, J.; Cheam, T. C.; Krimm, S., to be published.

Table VI. Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for HCOOD[b]

		assignment	ω(theory)	int (theory)	ν(exptl)[a]
A′	1	C—H	3294	47	2938/2942
	2	O—D	2995	76	2631
	3	C=O	2010	511	1773
	4	H—C—O	1530	12	1368
	5	C—O	1327	235	1178
	6	D—O—C	1105	59	972
	7	O—C=O	616	59	560
A″	8	H—C—O oop	1182	1	1011
	9	D—O—C oop	544	124	508

[a] Bertie et al., ref 16; Hisatsune and Heicklen, ref 42. [b] All theoretical predictions were made at the DZ+P SCF level of theory.

Table VII. Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for $(HCOOD)_2$[c]

		freq	int[a]	(dimer–monomer)[d]	assignment
A_g	1	3303 (2951)	0	+9 (+9/+13)	C—H
	2	2760 (–)	0	−235 (–)	O—D
	3	1913 (1663/1679)	0	−97 (−110/−94)	C=O
	4	1539 (1383)	0	+9 (+15)	H—C—O
	5	1400 (1261)	0	+73 (+83)	C—O
	6	1175 (972)	0	+70 (0)	D—O—C
	7	670 (624)	0	+54 (+64)	O—C=O
	8	182 (–)	0	NC	O···O
	9	160 (~144)	0	NC	O—D···O ip
B_g	10	1197 (1060?)	0	+15 (+49?)	δC—H oop
	11	692 (–)	0	+148 (–)	δO—D oop
	12	244 (224)	0	NC	O—D···O ip
A_u	13	1198 (1037)	3	+16 (+26)	δC—H oop
	14	741 (693)	221	+197 (+185)	δO—D oop
	15	166 (158)	11 (s)[b]	NC	O—D···O oop
	16	81 (68)	4 (m)[b]	NC	twist about C—H bond
B_u	17	3302 (2960)	102 (m)	+8 (+18/+22)	C—H
	18	2793 (2068)	891	−202 (−563)	O—D
	19	1977 (1745)	1129 (vs)	−33 (−28)	C=O
	20	1542 (1387)	50 (m)	+12 (+19)	H—C—O
	21	1399 (1259)	371 (s)	+72 (+81)	C—O
	22	1145 (1037)	93 (m)	+40 (+65)	D—O—C
	23	690 (651)	91 (m)	+74 (+91)	O—C=O
	24	218 (240)	46 (vs)[b]	NC	O···O

[a] Unless indicated, qualitative experimental intensity descriptions (in parentheses) are from Millikan and Pitzer, ref 10. [b] Intensity labels from far infrared spectrum of ref 11. [c] All predictions were made at the DZ+P SCF level of theory. Experimental results are given in parentheses. Note that theoretical vibrational frequencies are harmonic, while the experimental frequencies are the observed (anharmonic) fundamentals, taken from Bertie, Michaelian, Eysel, and Hager, ref 16. The controversial ν_{18} is from Excoffon and Marechal, ref 13. [d] NC = no comparable monomer vibrational frequency.

V. $(HCOOD)_2$ Vibrational Frequencies and IR Intensities

The theoretical predictions concerning the IR spectra of HCOOD and $(HCOOD)_2$ are summarized in Tables VI and VII. All monomer and dimer assignments are the same as those given from experiment by Bertie, Michaelian, Eysel, and Hager.[16] It is also encouraging that every predicted DZ+P SCF harmonic frequency except ν_{24} lies above the analogous observed fundamental. In the case of ν_{24} the absolute agreement is still quite good, with ω(DZ+P SCF) = 218 cm^{-1} and ν(exptl) = 240 cm^{-1}.

With two exceptions, the dimer–monomer vibrational frequency shifts agree quite well with experiment. The predicted A_g DZ+P SCF dimer–monomer shift for the D–O–C bend is somewhat disappointing, being +70 cm^{-1}, while experiment shows no shift. We might be inclined to blame this on a poor description of the H–C–O and D–O–C mixing, but (a) these are now rather well separated by the deuterium substitution and (b) theory does quite well for the H–C–O shift from monomer to dimer.

The serious disagreement between theory and experiment occurs for the O–D stretching frequency ν_{18}, which Excoffon and Marechal[13] have assigned at 2068 cm^{-1}. The DZ+P SCF ω_{18} is 35.1% greater than the experimental ν_{18}. This is clearly unreasonable and we are forced to conclude that the true ν_{18} must be signifi-

Table VIII. Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for DCOOH[b]

		assignment	ω(theory)	int (theory)	ν(exptl)[a]
A′	1	O—H	4116	118	3566
	2	C—D	2458	87	2218
	3	C=O	1977	523	1760/1724
	4	H—O—C	1413	5	1297
	5	C—O	1311	254	1140
	6	D—C—O	1083	45	970
	7	O—C=O	683	62	620
A″	8	D—C—O oop	1000	9	
	9	H—O—C oop	681	188	665

[a] Bertie et al., ref 16; Millikan and Pitzer, ref 39a; Miyazawa and Pitzer, ref 39b. [b] All theoretical predictions were made at the DZ+P SCF level of theory.

cantly higher. We suggest that it is extremely unlikely that ν_{18} is less than 2200 cm^{-1}. Thus it seems clear that Excoffon and Marechal have made a misassignment.

One of the referees has noted, however, that the present results are based on the harmonic approximation while in ref 13 an attempt was made to include strong anharmonic couplings. As the main effect of these anharmonicities is to broaden the O–D stretching band, it may be reasonable to compare frequencies appearing in an harmonic frame with band centers of these broad anharmonic bands and not with the peculiar transition labeled 0000. In Table II of ref 13 this band center falls at 2281 cm^{-1}, which seems to fit in with the present theoretical predictions.

The theoretical IR intensities for $(HCOOD)_2$ may be compared with the qualitative experimental labels assigned by Millikan and Pitzer.[10] Theoretically, the strongest fundamental is predicted to be ν_{19}, the B_u C=O stretch, for which an intensity of 1129 km/mol is seen in Table VII. This prediction fits perfectly with Millikan and Pitzer's identification of ν_{19} as the only "very strong" fundamental. The second strongest theoretical vibration is ν_{18}, the O–D stretch, for which 891 km/mol is predicted, perhaps surprising considering the above-discussed misassignment of ν_{18}. However, if one looks at Figure 1b of the paper by Excoffon and Marechal,[13] it is clear that there is an intense IR band peaking at ~2300 cm^{-1}. Thus, although the correct assignment of ν_{18} was long concealed, the existence of an IR band of high intensity (consistent with the DZ+P SCF prediction I = 891 km/mol for ω_{18}) is indisputable. Our third strongest fundamental is ν_{21} (371 km/mol), the C–O single bond stretch, and it is encouraging that this band is the only one designated "strong" by Millikan and Pitzer.[10] The four fundamentals (ν_{17}, ν_{20}, ν_{22}, and ν_{23}) experimentally labeled "medium" intensity by Millikan and Pitzer are predicted here to have intensities in the range 50–102 km/mol and thus the agreement is superb.

Three of the experimental $(HCOOD)_2$ fundamentals in Table VII were assigned by Carlson, Witkowski, and Fateley[11] from the far-infrared spectrum. Clearly these intensities fall on a different absolute scale than those of Millikan and Pitzer.[10] Nevertheless, the relative ordering vs (ν_{24}), s (ν_{15}), and m (ν_{16}) agrees perfectly with the ab initio intensities, which are 46, 11, and 4 km/mol, respectively.

VI. $(DCOOH)_2$ Vibrational Frequencies and IR Intensities

Tables VIII and IX give theoretical and experimental information pertinent to the infrared spectra of DCOOH and its dimer. Although seven fundamentals of the dimer are yet unobserved, all 17 known (anharmonic) frequencies lie below the corresponding DZ+P SCF harmonic frequencies.

Again the ab initio IR intensities agree well with the experimental descriptions of Millikan and Pitzer.[10] The three most intense fundamentals in the IR are predicted to be the O—H stretch ω_{17} (1599 km/mol), the C=O stretch ω_{19} (1191 km/mol), and the C—O single bond stretch ν_{21} (389 km/mol). These are the only three fundamentals labeled "strong" by Millikan and Pitzer. Similarly, the C–D stretch is predicted to have substantial intensity (199 km/mol) and is labeled appropriately "ms" in the experimental analysis.

Table IX. Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for $(DCOOH)_2$[c]

		freq	int[a]	dimer–monomer[b]	assignment
A_g	1	3782 (–)	0	–334 (–)	O—H
	2	2459 (2208)	0	+1 (–10)	C—D
	3	1896 (1643)	0	–81 (–117/–81)	C=O
	4	1536 (1385)	0	+123 (+88)	H—O—C
	5	1380 (1230)	0	+69 (+90)	C—O
	6	1101 (994)	0	+18 (+24)	D—C—O
	7	725 (672)	0	+42 (+52)	O—C=O
	8	180 (–)	0	NC	O···O
	9	163 (~140)	0	NC	O—H···O ip
B_g	10	1013 (–)	0	+13 (–)	δC—D oop
	11	934 (–)	0	+253 (–)	δO—H oop
	12	218 (202)	0	NC	O—H···O oop
A_u	13	1014 (890)	28 (m, b)	+14 (–)	δC—D oop
	14	983 (930)	328 (m, b)	+302 (+265)	δO—H oop
	15	148 (–)	9	NC	O—H···O oop
	16	80 (–)	4	NC	twist about C—D bond
B_u	17	3834 (3098)	1599 (s)	–282 (–468)	O—H
	18	2456 (2251/2224)	199 (ms)	–2 (+33/+6)	C—D
	19	1956 (1726)	1191 (s)	–21 (–34/+2)	C=O
	20	1497 (1360)	30 (w)	+84 (+63)	H—O—C
	21	1384 (1239)	389 (s)	+73 (+99)	C—O
	22	1103 (996)	62 (m)	+20 (+26)	D—C—O
	23	740 (695)	85 (m)	+57 (+75)	O—C=O
	24	218 (–)	46	NC	O···O

[a] Experimental intensity descriptions are from Millikan and Pitzer, ref 10. [b] NC = no comparable monomer vibrational frequency. [c] All predictions were made at the DZ+P SCF level of theory. Experimental results are given in parentheses. Note that theoretical vibrational frequencies are harmonic, while the experimental frequencies are the observed (anharmonic) fundamentals, taken from Bertie, Michaelian, Eysel, and Hager, ref 16.

Table X. Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for DCOOD[b]

		assignment	ω(theory)	int (theory)	ν(exptl)[a]
A′	1	O—D	2995	71	2632
	2	C—D	2456	85	2232
	3	C=O	1973	504	1735
	4	C—O	1328	214	1170
	5	D—O—C	1145	3	945
	6	D—C—O	1061	54	1042
	7	O—C=O	611	58	556
A″	8	D—C—O oop	1000	10	873
	9	D—O—C oop	526	111	491

[a] Bertie and Michaelian, ref 15; Millikan and Pitzer, ref 39a; Miyazawa and Pitzer, ref 39b. [b] All theoretical predictions were made at the DZ+P SCF level of theory.

Table IX shows that there is a reversal in the theoretical and experimental descriptions of the A_u vibrations ν_{13} and ν_{14}. In the theoretical analysis ν_{13} is clearly the out-of-plane C–D bending motion. In contrast Bertie, Michaelian, Eysel, and Hager identify the higher frequency of ν_{13} and ν_{14} as the out-of-plane O–H bend. The experimental difference $(\nu_{13} - \nu_{14})$ = 40 cm^{-1} is, however, reasonably predicted by theory, which finds $(\omega_{13} - \omega_{14})$ = 31 cm^{-1}.

The experimental dimer–monomer vibrational frequency shifts (where available) are in general well-reproduced by DZ+P SCF theory. The only disappointment occurs for ν_{17}, the dimer O–H stretch, which is predicted to be 282 cm^{-1} lower than the monomer O–H stretch. In contrast the experimental shift is much greater, namely (3098 – 3566) = –468 cm^{-1}. As noted earlier, an error of the same magnitude is made by DZ+P SCF theory for the $(HCOOH)_2$ species. Future theoretical studies would do well to pursue the source or sources of these rather significant errors.

VII. $(DCOOD)_2$ Vibrational Frequencies and IR Intensities

Comparable theoretical and experimental results for the perdeuteriated species DCOOD and $(DCOOD)_2$ are summarized in Tables X and XI. One sees immediately in Table X a disagreement between the DZ+P SCF methods and experiment concerning the monomer assignment of ν_5 and ν_6, the D–C–O and D–O–C bending motions. From theory the higher of the two frequencies is assigned to the D–O–C bend. However, the assignment is marginal, with the PED's being 0.40 (D–O–C) and

Table XI. Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for $(DCOOD)_2$[b]

		freq	int[a]	(dimer−monomer)[c]	assignment
A_g	1	2759 (–)	0	−236 (–)	O—D
	2	2457 (2211)	0	+1 (−21)	C—D
	3	1887 (1648)	0	−86 (−87)	C=O
	4	1395 (1250)	0	+67 (+80)	C—O
	5	1196 (990)	0	+51 (+39)	D—O—C
	6	1091 (1081)	0	+30 (+45)	D—C—O
	7	665 (617)	0	+54 (+62)	O—C=O
	8	180 (–)	0	NC	O···O
	9	159 (130)	0	NC	O—D···O ip
B_g	10	1012 (892)	0	+12 (+19)	δC—D oop
	11	686 (–)	0	+160 (–)	δO—D oop
	12	214 (194)	0	NC	O—D···O ood
A_u	13	1014 (890)	26 (w, b)	+14 (+17)	δC—D oop
	14	730 (678)	195 (s)	+204 (+187)	δO—D oop
	15	143 (135)	8 (w)	NC	O—D···O oop
	16	80 (68)	4 (w)	NC	twist about C—D bond
B_u	17	2794 (–)	849 (–)	−201 (–)	O—D
	18	2455 (2226)	204 (s)	−1 (−6)	C—D
	19	1952 (1720)	1139 (vs)	−21 (−15)	C=O
	20	1395 (1246)	321 (s)	+67 (+76)	C—O
	21	1173 (1055)	14 (w)	+28 (+13)	D—O—C
	22	1085 (987/976)	88 (s)	+24 (+42/+31)	D—C—O
	23	685 (642)	90 (s)	+74 (+86)	O—C=O
	24	213 (227)	44 (s)	NC	O···O

[a] Experimental intensity designations (in parentheses) are from Millikan and Pitzer, ref 10, and Clague and Novak, ref 12. [b] All predictions were made at the DZ+P SCF level of theory. Experimental results are given in parentheses. Note that theoretical vibrational frequencies are harmonic, while the experimental frequencies are the observed (anharmonic) fundamentals, taken from Bertie and Michaelian, ref 15. [c] NC = no comparable monomer vibrational frequency.

0.20 (D–C–O) for ω_5. Bertie and Michaelian[15] instead assign ν_5 to the D–C–O bending motion. Interestingly, the theoretical difference $(\omega_5 - \omega_6) = 84$ cm^{-1} agrees quite well with the experimental $(\nu_5 - \nu_6) = 97$ cm^{-1}.

It is not surprising, in light of the monomer D–C–O and D–O–C assignments, that the DZ+P SCF dimer assignments are not identical with those based strictly on experimental observations. The fact that these assignments are not trivial is seen in footnote *e* of Table I in the paper by Bertie and Michaelian,[15] who state that ν_{21} and ν_{22} are a mixture of the D–O–C and D–C–O deformations. In fact theory and experiment *agree* for the assignment of ν_{21} (D–O–C) and ν_{22} (D–C–O). However, as seen in Table XI, there is a disagreement for ν_5 and ν_6. The DZ+P SCF PED's identify ν_5 as the D–O–C bend, while Bertie and Michaelian prefer the D–C–O deformation. Again, however, theory and experiment are in good agreement concerning difference in frequencies: $\Delta\omega(5-6) = 105$ cm^{-1}; $\Delta\nu(5-6) = 91$ cm^{-1}.

The C=O stretch ν_{19} is predicted here to have the highest infrared intensity, namely 1139 km/mol. It is encouraging that this is also the strongest fundamental ("very strong") in the designations of Millikan and Pitzer.[10] The next strongest IR fundamental, from theory, should be the O–D stretch ν_{17} (849 km/mol). However, we find no acceptable experimental identification of this fundamental. Bertie and Michaelian[15] cite Excoffon and Marechal for ν(O–D) = 2068 cm^{-1}, but this is apparently from $(HCOOD)_2$, for which the O–D should admittedly be comparable. However, we have already shown that the latter assignment of Excoffon and Marechal must be incorrect. Millikan and Pitzer assign ν_{17}(O–D) = 2323 cm^{-1}, and this is certainly closer to the truth than 2068 cm^{-1}. The remaining fundamentals labeled "strong" by Millikan and Pitzer are (in order of theoretical intensity, with DZ+P SCF values in parentheses) ν_{20} (C–O, 321 km/mol), ν_{18} (C–D, 204 km/mol), ν_{14} (δO–D oop, 195 km/mol), ν_{22} (D–C–O, 88 km/mol), and ν_{23} (O—C=O, 90 km/mol). The fundamentals labeled "weak" all have significant smaller DZ+P SCF IR intensities. Thus one sees again an essentially perfect correspondence between theoretical and experimental IR intensities.

VIII. Raman Intensities

Bertie and co-workers[15,16] have carried out definitive experimental studies of the Raman spectra of formic acid and its dimer, and they include in their papers considerable information concerning the Raman intensities. In the present theoretical study we define the Raman intensity following Gussoni[47] as

$$I = 45\alpha'^2 + 7\gamma'^2$$

where α' and γ' are the derivatives of the trace and anisotropy of the polarizability, respectively. The depolarization is then defined as[47]

$$\rho = 3\gamma'^2/[45\alpha'^2 + 4\gamma'^2]$$

The theoretical Raman intensities reported here were obtained with use of recently developed analytic methods.[48] Since Raman intensities can be quite sensitive to basis set choice,[49,50] only the DZ+P SCF results are reported here.

Table XII. Raman Intensities for the Formic Acid Monomer[c]

		fundamental freq $\nu(cm^{-1})$[a]	exptl int (counts/s)[a]	theor int (Å⁴/amu)	depolarization ratio exptl	depolarization ratio theory
A′	ν_1	3569	6	50.8	<0.1	0.27
	ν_2	2942	sh	78.2	<0.3	0.25
	ν_3	1777	9	8.5	0.1	0.21
	ν_4	1381	high T[b]	6.5		0.57
	ν_5	1223		1.2		0.43
	ν_6	1104	3	2.3	0.1	0.13
	ν_7	625	3	3.0	0.1	0.55
A″	ν_8	1033		0.9		0.75
	ν_9	642	0.5	0.9		0.75

[a] Bertie and Michaelian, ref 15. [b] Observed only at high temperature. [c] The theoretical results reported were obtained at the DZ+P SCF level of theory.

Table XIII. Raman Intensities for the Formic Acid Dimer, with Theoretical Results Obtained at the DZ+P SCF Level of Theory[b]

		fundamental freq $\nu(cm^{-1})$[a]	exptl int (counts/s)[a]	theor int (Å⁴/amu)	depolarization ratio exptl	depolarization ratio theory
A_g	ν_1			147.4		0.28
	ν_2	2949	100	203.1	0.1	0.26
	ν_3	1670	32	12.7	<0.1	0.10
	ν_4	1415	8	12.5	0.5	0.49
	ν_5	1375	7	2.3	0.4	0.65
	ν_6	1214	10	6.3	0.06	0.10
	ν_7	677	14	5.3	0.4	0.67
	ν_8	190		0.1		0.40
	ν_9	137	5	0.2	0.75	0.70
B_g	ν_{10}	1060	3	1.4	0.75	0.75
	ν_{11}			0.5		0.75
	ν_{12}	230	40	5.2	0.75	0.75

[a] Bertie and Michaelian, ref 15. [b] Note that only Raman-allowed fundamentals of the dimer are included here.

The predicted Raman intensities for the HCOOH monomer are compared with experiment in Table XII. There the theoretical predictions are seen to be generally helpful. Specifically, the two fundamentals (ν_5 and ν_8) not observed in the Raman and the one labeled questionable (ν_9) by Bertie and Michaelian[15] have the lowest theoretical Raman intensities, 0.9–1.2 Å⁴/amu. Thus theory "explains" the difficulty of observing these fundamentals in the Raman spectrum. Furthermore the next two highest intensity Raman fundamentals (ν_6 and ν_7) hold this position according to either the theoretical or experimental intensities. A disappointment in the theoretical Raman intensities is their failure to show ν_1 and ν_3 having comparable intensities—DZ+P SCF theory predicts $I(\nu_1)$ to be nearly six times more intense than $I(\nu_3)$.

The formic acid dimer Raman intensities are summarized in Table XIII. The allowed Raman fundamental predicted to have lowest intensity is ν_8, corresponding to the O···O motion. This

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Table XIV. Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) for the Formic Acid Dimer Transition State (Point Group D_{2h})

		DZ		DZ+P		
		freq	int	freq	int	assignment
A_g	ν_1	3412	0	3313	0	C–H
	ν_2	1858	0	1845	0	H–O–C
	ν_3	1479	0	1554	0	C–O
	ν_4	788	0	821	0	H–C–O
	ν_5	536	0	555	0	O–H
B_{1g}	ν_6	1770	0	1910	0	C–O
	ν_7	1486	0	1513	0	H–C–O
	ν_8	237	0	239	0	H–O–C
	ν_9	1663i	0	1695i	0	O–H
B_{2g}	ν_{10}	1189	0	1210.3	0	δC–H oop
	ν_{11}	341	0	338	0	wag (CO_2)
B_{3g}	ν_{12}	1527	0	1460	0	δO–H oop
A_u	ν_{13}	133	0	99	0	twist (CO_2)
B_{1u}	ν_{14}	1574	571	1511	292	δO–H oop
	ν_{15}	1191	25	1209.8	26	δC–H oop
	ν_{16}	266	52	259	35	wag (CO_2)
B_{2u}	ν_{17}	1804	1463	1927	1392	C–O
	ν_{18}	1714	36	1704	1	C–O–H
	ν_{19}	1507	195	1524	134	H–C–O
	ν_{20}	629	19	641	10	O–H
B_{3u}	ν_{21}	3410	56	3311	79	C–H
	ν_{22}	1468	1246	1532	707	C–O
	ν_{23}	930	4034	962	4887	O–H + H–C–O
	ν_{24}	700	2683	779	3508	O–H + H–C–O

theoretical prediction fits well with the fact that ν_8 has not yet been observed in the Raman spectrum.[15] Two other Raman fundamentals are predicted by DZ+P SCF theory to have intensities less than 1 Å^4/amu. Of these two frequencies ν_9 (A_g) has been observed in the Raman, while ν_{11} (B_g) has not to date been identified.

The Raman fundamental with highest theoretical intensity (ν_2, 203 Å^4/amu) is also found in the laboratory to have the greatest Raman intensity (100 counts/s). However, the second most intense Raman fundamental is predicted by theory to be ν_1, the O–H stretch, at 147 Å^4/amu, and ν_1 is not observed at all in the laboratory. The non-identification of ν_1 is discussed in some detail in the paper by Bertie and Michaelian.[15] To summarize their conclusions, there are broad features in the expected region of the Raman spectrum, but these are muddled by the likely presence of overtone and combination bands, making the analysis treacherous. Of course, the mixing of ν_1 with overtones and combinations is not accounted for in the simple harmonic approximation adopted in the present theoretical study.

There is a reasonable correspondence between theory and experiment for the Raman depolarization ratios of the formic acid dimer. For example, the three smallest depolarization ratios occur for ν_6, ν_3, and ν_2 both theoretically and experimentally. Note that the B_g depolarization ratios do not provide a test of the theory since these are required by symmetry to be precisely $^3/_4$. However, there are four Raman fundamentals with nontrivial experimental depolarization ratios in the range 0.4–0.75, and these are predicted by theory to be 0.49–0.70. We conclude that theoretical predictions of depolarization ratios at this level can be reliable and may be very helpful in the future in interpreting complicated Raman spectra.

Although not reported here, DZ SCF Raman intensities for $(HCOOH)_2$ are generally within a factor of 2 of the DZ+P predictions, but they provide a poorer correspondence with the experimental intensities.

IX. Transition-State Vibrational Analysis

Table XIV gives vibrational frequencies and IR intensities for the $(HCOOH)_2$ transition state for double-proton transfer. Recall that the transition-state geometrical structure is given in Figure 3. As expected, the single imaginary vibrational frequency (negative force constant in terms of normal coordinates) corresponds to the out-of-phase combination of O–H stretching motions. The frequency 1695i seems to be indicative of a substantial barrier height, and this is confirmed in the following section.

There are, of course, no "experimental" transition-state vibrational frequencies with which to compare the theoretical predictions of Table XIV. However, such data can be very useful in simple models for the dynamics of double-proton transfer in the formic acid dimer.

Among possible comparisons, those involving the transition-state C–O stretching frequencies are interesting. Recall that for the equilibrium dimer structure the DZ+P SCF predictions are ω_3 = 1927 cm^{-1} and ω_{19} = 1983 cm^{-1} for C=O and ω_6 = 1357 cm^{-1} and ω_{22} = 1358 cm^{-1} for the C—O single bond stretches. For the transition state, of course, all four C–O linkages are equivalent, and the harmonic vibrational frequencies are (see Table XIV) 1554 (A_g), 1910 (B_{1g}), 1927 (B_{2u}), and 1532 cm^{-1} (B_{3u}). While the two higher frequencies would be classified C=O stretches at this level of theory, the two lower frequencies are still higher than expected of C–O single bond stretches. Naively, of course, one might expect all four C–O stretches to display bond order $^3/_2$.

Table XV. Summary of Total (in hartrees) and Relative (in kcal/mol) Energies for the Formic Acid Monomer and Dimer

	STO-3G	DZ	DZ+P	exptl
monomer	−186.2179	−188.7061	−188.8144	
equilibrium dimer	−372.4599	−377.4429	−377.6516	
transition dimer	−372.4517	−377.4203	−377.6268	
D_e for dimerization	15.1	19.3	14.3	
zero-point vib corr	−3.1	−2.5	−2.0	
D_0 for dimerization	12.0	16.8	12.3	≤12.0[a]
ΔH_{300}	12.6	17.2	12.5	14.8 ± 0.5,[b] 14.1 ± 1.5,[c] 11.7 ± 0.1[d]
reaction barrier ht	5.2	14.2	15.6	

[a] Reference 20. [b] Reference 17. [c] Reference 51. [d] Reference 52.

X. Energetics

Total and relative energies for formic acid and its dimer are reported in Table XV. The only piece of energetic information available from experiment concerns the dissociation energy for the process

$$(HCOOH)_2 \rightarrow 2HCOOH \qquad (1)$$

The most widely cited experimental value for ΔH is that reported by Clague and Bernstein[17] in 1969, namely 14.8 ± 0.5 kcal/mol. Earlier experimental dimerization energies fall in the range 15.2–18.0 kcal/mol and are discussed in the classic monograph by Pimentel and McClellan.[1] Clague and Bernstein[17] used the ratio of infrared intensities of the dimeric to monomeric O–H stretching vibrations to determine the equilibrium constant for eq 1 and hence the dissociation energy. A related but independent experimental study, also appearing in 1969, was that of Mathews and Sheets,[51] who reported ΔH_{300} = 14.1 ± 1.5 kcal/mol.

In early 1987, Henderson reported a new value of the dimerization of formic acid based on Fourier transform infrared spectroscopy.[52] Henderson reports $\Delta H(1)$ = 11.7 ± 0.1 kcal/mol. Although we are a bit skeptical concerning the very narrow error bars associated with this new experimental dimerization energy, the fact that the experiment is sufficiently simple to be suitable for undergraduates to carry out as coursework is very impressive. Possible support for the experiment of Henderson[52] is the recent NMR study of Lazaar and Bauer,[20] who conclude that ΔE_0 for formic acid dimer dissociation is no more than 12 kcal. These authors also suggest that

$$D_0 = \Delta H_0 \simeq \Delta H_{300} - 1.5 \text{ kcal} \qquad (2)$$

We have evaluated ΔH_{300} ab initio (see Table XV) and find it to be 0.2 kcal larger than D_0 at the DZ+P SCF level of theory.

As Table XV shows, the formic acid dimer has significantly more zero-point vibrational energy (ZPVE) than do two monomers. At the highest level of theory this ZPVE correction is 2.0 kcal/mol. In this way DZ+P SCF theory predicts D_0 = 12.3

(51) Mathews, D. M.; Sheets, R. W. *J. Chem. Soc. A* **1969**, 2203.
(52) Henderson, G. *J. Chem. Educ.* **1987**, *64*, 88.

kcal/mol for the dimerization energy. Although such hydrogen bond energies are not in general known with great precision from experiment, DZ+P SCF theory does agree satisfactorily with the available data for systems such as the water and hydrogen fluoride dimers.[53] In fact the DZ+P SCF value D_0 = 12.3 kcal is quite consistent with the Lazaar–Bauer result (≤12.0 kcal) when one realizes that the reliability of this level of theory is of the order of 1 kcal/mol for such dissociation energies. The DZ basis set predicts D_0 = 16.8 kcal, clearly larger than experiment, as is also the case for the H_2O and HF dimers.[53] In contrast, the minimum basis set SCF method does a good job of reproducing (to within 0.3 kcal) the more reliable DZ+P SCF result. The reader should recall, of course, that the minimum basis set does not do superbly well in predicting the equilibrium geometrical structure of the dimer.

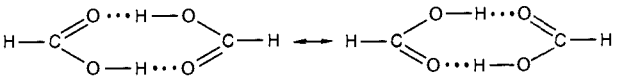
DZ+P SCF theory predicts ΔH_{300} = 12.5 kcal/mol, to be compared with the experimental values 14.8, 14.1, and 11.7 kcal, respectively.[17,51,52] Considering the broad range of experimental dissociation energies, the theoretical prediction is quite satisfactory.

XI. Concluding Remarks

The results presented and discussed here are just a fraction of the information available from the present study. For example, we have not reported theoretical predictions for any of the "mixed dimers", namely HCOOH·HCOOD, HCOOH·DCOOH, HCOOH·DCOOD, HCOOD·DCOOH, HCOOD·DCOOD, and DCOOH·DCOOD. Among the transition states for hydrogen or deuterium transfer, only $(HCOOH)_2$ among the ten distinct possibilities has been considered. Moreover, only for HCOOH and $(HCOOH)_2$ have Raman intensity data been presented. It is apparent that the formic acid dimer is a source of much theoretical and experimental information. As such it provides a unique opportunity for the understanding of hydrogen-bonding and proton-transfer processes.

In this study we find generally good agreement between theory and experimental data, where the latter is available. Particularly encouraging is the close agreement between theoretical infrared intensities and the corresponding experimental designations. An obvious experimental misassignment pointed out by this work is Excoffon and Marechal's ν_{18} = 2068 cm^{-1} for the O–D stretch of $(HCOOD)_2$. This fundamental frequency is extremely unlikely to be less than 2200 cm^{-1}. This conclusion appears to be consistent with the Note Added in Proof to the late 1986 paper by Bertie, Michaelian, Eysel, and Hager.[16]

Finally, it may be of interest to note the very simplest estimate one can make for the rate of double H atom transfer in the dimer with the present potential energy surface information



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More specifically, we estimate the tunneling splitting in the ground vibrational state of the dimer that is caused by this symmetric exchange, utilizing the same first-order model employed by Bicerano et al.[54] in discussing the similar phenomena in malonaldehyde. Referring to eq III.1–III.6 of that paper, the present values for the pertinent parameters are V_0 = 15.56 kcal/mol, V_{eff} = 15.83 kcal/mol, E_0 = 5.48 kcal/mol, $\hbar\omega_i$ = 1695 cm^{-1}. These values give a tunneling splitting ΔE = 0.3 cm^{-1}, which we emphasize in a *very* tentative number. Certainly a more accurate determination of the barrier height (15.6 kcal/mol at the DZ+P SCF level) is needed. Within the simple approximation, decreasing the barrier causes ΔE to increase by about a factor of 2 for each kcal/mol the barrier is reduced. Coupling of the H atom motion to the other degrees of freedom of the molecular system will also have an effect on ΔE, but this awaits a more quantitative treatment.

It is hoped that this theoretical study will simplify the interpretation of existing, unpublished data for the formic acid dimer and stimulate new experimental studies.

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Registry No. Formic acid, 64-18-6; formic acid-*d*, 925-94-0; formic-*d* acid, 917-71-5; formic-*d* acid-*d*, 920-42-3.

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(54) Bicerano, J.; Schaefer, H. F.; Miller, W. H. *J. Chem. Phys.* **1983**, *78*, 259.