Electrostatic Model for the Interaction Force Constants of the Formic Acid Dimer

Weili Qian and Samuel Krimm*

Biophysics Research Division and Department of Physics, University of Michigan, Ann Arbor, Michigan 48109

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We have developed a new form of the intermolecular potential that is consistent with ab initio structures, interaction energies, interaction forces, intermolecular force constants, and dipole derivatives of four different hydrogen-bonded structures of the formic acid dimer. The ab initio "data" are based on a scaled HF/6-311++G** force field in nonredundant coordinates and reflect a reassignment of some bands in the spectrum. The model incorporates charges, charge fluxes, atomic dipoles, and van der Waals interactions, and its successful reproduction of the intermolecular force constants indicates that it may provide a more general description of detailed features of the hydrogen bond.

Introduction

The cyclic formic acid dimer (FAD) has provided a model system in which to study the physical nature of the intermolecular interactions that give rise to perturbations of intramolecular normal modes, particularly through hydrogen bonding. In this case, the effort has been concentrated on explaining the large frequency splitting between the symmetric and antisymmetric C=O stretch (s) modes, $\Delta\nu$(C=O).[1] As a result, it has been possible to show that charge fluxes, in addition to charges, play a major role in accounting quantitatively for $\Delta\nu$(C=O)[1b,c] and, more recently,[2] that atomic dipole (as well as van der Waals) interactions must be included if consistency with intermolecular energies is also to be achieved (significant through-hydrogen-bond charge fluxes[1a,c] are found not to be important[2]).

However, by limiting the focus to interaction energies and $\Delta\nu$(C=O), we neglect much other "data" available from ab initio calculations, which is our goal to have the model reproduce. In particular, the set of intermolecular force constants provides a much more complete description of the intermolecular interactions, accounting for intermolecular as well as intramolecular spectroscopic properties. And if we include intermolecular forces generated at nonequilibrium structures, we have the possibility, as noted[2] and realized,[3] of obtaining a much more general description of the hydrogen-bond interaction.

In this paper we describe the development of such a complete model for the FAD, one which aims to account for structures, interaction energies, interaction forces, intermolecular force constants, and dipole derivatives. While the latter can be used to uniquely derive the charges and charge fluxes,[4] we find that such values, which served previously,[2] are not consistent with the complete set of intermolecular force constants. It is therefore necessary to allow the flexibility of optimizing the charge fluxes in order to obtain agreement with all of the above properties. (We will see that this is not unreasonable.) Nor at this stage do we wish to explicitly incorporate the changes in intramolecular structure and force field with nonequilibrium geometries, since this might mask the intermolecular interaction characteristics that we seek. We have therefore used the intramolecular part of the ab initio force field for any given geometry. (This creates no major problem in a molecular mechanics (MM) energy function, such as our spectroscopically determined force field (SDFF),[5] since such ab initio variations can be incorporated as functional forms.) Within this framework, it is indeed possible for our previous electrostatic model[2] to account for the intermolecular force constants of the FAD near its equilibrium conformation. It should be noted that, since charge fluxes for out-of-plane displacements are zero for planar molecules,[4] we have limited ourselves to the determination of in-plane interaction force constants.

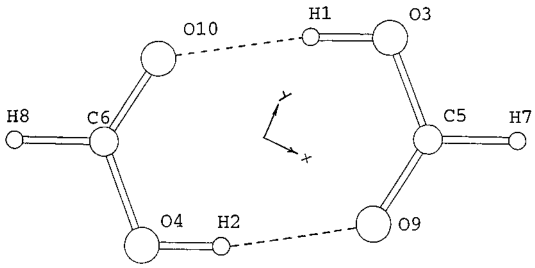

Figure 1. Ab initio (HF/6-311++G**) optimized structure of the formic acid dimer.

We start with a discussion of the ab initio force constant calculation that was the basis for this and our earlier[2] studies. Although there have been a few such calculations,[6] the results have depended on definitions of internal coordinates, selection of scale factors, and assignments of the calculated normal mode frequencies. In distinction to most previous studies, we have used a nonredundant coordinate basis. We also differ in the range of scale factors and in the assignments of some bands. It is therefore important to establish the validity of the force field on which we base the determination of our model for the intermolecular force constants.

Ab Initio Force Field

All ab initio calculations were done with GAUSSIAN 92[7a] and 94.[7b] We compared the results for a number of different basis sets, with and without electron correlation, and found that HF/6-311++G** was most suitable for the determination of the large amount of "data" needed in this study (calculations were also done at MP2/6-31G** and MP2/6-311++G**, and

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* To whom correspondence should be addressed. E-mail: skrimm@umich.edu. FAX: 313-764-3323.

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TABLE 1: Geometric Parameters of Optimized Formic Acid Dimer[a]

parameter	calcd	obs[b]	parameter	calcd	obs[b]
	Intramolecular			*Intermolecular*	
r(C═O)	1.191	1.217 ± 0.003	r(O4···O9)	2.816	2.696 ± 0.007
r(C−O)	1.299	1.320 ± 0.003	r(H2···O9)	1.864	
r(C−H)	1.085	1.079 ± 0.021	θ(O−H···O)	171.41	180[c]
r(O−H)	0.960	1.033 ± 0.017			
θ(O−C═O)	125.73	126.2 ± 0.5			
θ(H−C═O)	122.64	115.4 ± 3.1			
θ(H−C−O)	111.64	(118.4)			
θ(C−O−H)	111.13	108.5 ± 0.4			

[a] Bond lengths in angstroms, bond angles in degrees, calculations at HF/6-311++G**. [b] Quoted from ref 6c. [c] Assumed in refinement of electron diffraction data.

TABLE 2: Nonredundant Internal and Symmetry Coordinates of the Formic Acid Dimer

internal coordinate	symmetry coordinate	description[a]
R1 = Δr(C5H7)	S1 = R1 + R2	CH s A_g
R2 = Δr(C6H8)	S2 = R1 − R2	CH s B_u
R3 = Δr(C5O9)	S3 = R3 + R4	C═O s A_g
R4 = Δr(C6O10)	S4 = R3 − R4	C═O s B_u
R5 = Δr(C5O3)	S5 = R5 + R6	C−O s A_g
R6 = Δr(C6O4)	S6 = R5 − R6	C−O s B_u
R7 = Δr(O3H1)	S7 = R7 + R8	OH s A_g
R8 = Δr(O4H2)	S8 = R7 − R8	OH s B_u
R9 = Δr(O9O10)	S9 = R9	O···O s A_g
R10 = Δθ(H7C5O9)	S10 = 2R14 − R10 − R12 + 2R15 − R11 − R13	OCO d A_g
R11 = Δθ(H8C6O10)	S11 = 2R14 − R10 − R12 − 2R15 + R11 + R13	OCO d B_u
R12 = Δθ(H7C5O3)	S12 = R10 − R12 + R11 − R13	CH d A_g
R13 = Δθ(H8C6O4)	S13 = R10 − R12 − R11 + R13	CH d B_u
R14 = Δθ(O3C5O9)	S14 = R16 + R17	COH b A_g
R15 = Δθ(O4C6O10)	S15 = R16 − R17	COH b B_u
R16 = Δθ(C5O3H1)	S16 = R18 + R19	CO···O b or O···H s A_g
R17 = Δθ(C6O4H2)	S17 = R18 − R19	CO···O b or O···H s B_u
R18 = Δθ(C5O9O10) or Δr(O10H1)	S18 = R20 + R21	CH ob A_u
R19 = Δθ(C6O10O9) or Δr(O9H2)	S19 = R20 − R21	CH ob B_u
R20 = Δω(C5H7)	S20 = R22 + R23	C−O t A_u
R21 = Δω(C6H8)	S21 = R22 − R23	C−O t B_g
R22 = Δτ(C5O3)	S22 = R24 + R25	C═O t A_u
R23 = Δτ(C6O4)	S23 = R24 − R25	C═O t B_g
R24 = Δτ(C5O9)	S24 = R26	O···O t A_u
R25 = Δτ(C6O10)		
R26 = Δτ(O9O10)		

[a] s = stretch, b = bend, ob = out-of-plane bend, d = deformation, t = torsion.

some pertinent results are quoted below). The fully optimized structure, referred to as $\mathbf{D_0}$, is shown in Figure 1, and its geometric parameters are given in Table 1.

The definition of the internal coordinates and the handling of the cyclic redundancies in the FAD has varied in the literature,[6,8] but in all previous cases (except a recent one[6d]) they were based on a full redundant coordinate system. In some cases,[1b,c] intermolecular coordinates were even dropped in investigating Δν(C═O) and the burden of agreement was placed on the intermonomer interaction force constants involving C═O s and C−O s. (The advantage of this is that all interaction force constants between intramolecular and intermolecular coordinates disappear, and Δν(C═O) then depends only on the three C═O s/C−O s interaction force constants. The effect on the intramolecular modes is minimal, indicating a very good separation between high and low frequencies. This is because, as the transformation matrix from full redundant to intramolecular coordinates shows, the diagonal force constants of the intermolecular coordinates and the interaction force constants between these and the C═O s/C−O s coordinates all make contributions to the above three interaction force constants. This is why Δν(C═O) can be reproduced in full redundant coordinates even without intermonomer interaction force constants.[8d]) We did not feel that such an approach was a useful one and have therefore chosen a nonredundant set of internal coordinates (though different from that recently used[6d]) in which to develop the force field.

Since only one type of internal coordinate, such as (C═)O···O(═C) s, belongs to the A_g symmetry species, it is obviously convenient to take it with the two CO···O bend (b) as the in-plane internal coordinates. Similarly, the O···O torsion (t) and the two C═O t were chosen as out-of-plane internal coordinates. Actually, the CO···O b are very similar to the O···H s internal coordinates, so the alternative choice for the in-plane hydrogen-bond coordinates is O···O s and two O···H s, which are also the appropriate choices in MM potential energy functions since they are all nonbonded distance coordinates. Fully redundant in-plane internal coordinates consist of pairs of O···H s, CO···H b, and OH···O b. Ab initio force fields and atomic polar tensors (dipole derivatives) in different internal coordinate systems are equivalent and convertible into each other by transformation matrices **BA**, where **A** is the generalized **B** inverse. However, we found not only that the six intermolecular modes are more "pure" in the nonredundant set of coordinates, being heavily mixed in a redundant set, but that basis effects, electron correlation, force constant scaling, and transformation are easier to study. The internal and symmetry coordinates are given in Table 2.

The proper scaling of force constants of course requires that the normal modes be accurately assigned to the observed bands.[9]

TABLE 3: Influence of Internal Coordinates and Assignments on Hydrogen Bond Normal Modes

Different Coordinates

frequency (cm^{-1})[a]		PED[b]		
		set A[c]	set B[c]	set C[c]
B_u	243	CO···O b(104)	O···H s(104)	O···H s(152) CO···H b(38) OH···O b(48)
A_g	189	O···O s(134) COH b(9)	O···O s(125) O···H s(91) COH b(7)	O···H s(74) CO···H b(18) OH···O b(10)
A_g	162	CO···O b(215) O···O s(40) COH b(29)	O···O s(37) O···H s(68) COH b(29)	O···H s(55) CO···H b(57) COH b(13) OH···O b(25)

Different Assignments

obs	calcd I[d]		calcd II[e]	
$(HCOOH)_2$				
248	238, 219	O···H s(103, 98)	252, 245	O···H s(102, 97)
	188, 188	O···O s(134, 131) O···H s(79, 38) COH b(12, 10)	185, 196	O···H s(157, 124) O···O s(26, 8)
137	161, 169	O···H s(79, 90) COH b(26, 10) O···O s(28, 6)	138, 139	O···O s(137, 130) COH b(37, 18)
$(HCOOD)_2$				
240	233, 214	O···D s(104, 99)	246, 240	O···D s(103, 98)
	187, 187	O···O s(134, 128) O···D s(79, 43) COD b(11, 8)	181, 194	O···D s(156, 126) O···O s(30, 10)
144	157, 165	O···D s(80, 86) COD b(25, 10) O···O s(27, 8)	136, 136	O···O s(132, 128) COD b(36, 17)
$(DCOOH)_2$				
	233, 213	O···H s(103, 98)	246, 239	O···H s(102, 97)
	186, 186	O···O s(136, 133) O···H s(79, 35) COH b(12, 10)	183, 194	O···H s(156, 124) O···O s(25, 8)
140	160, 168	O···H s(81, 94) COH b(26, 10) O···O s(26, 0)	138, 138	O···O s(138, 131) COH b(37, 18)
$(DCOOD)_2$				
227	228, 209	O···D s(103, 99)	241, 234	O···D s(103, 98)
	185, 185	O···O s(135, 129) O···D s(76, 40) COD b(12, 0)	181, 192	O···D s(156, 125) O···O s(29, 9)
130	153, 164	O···D s(81, 89) COD b(34, 10) O···O s(31, 16)	136, 135	O···O s(133, 128) COD b(36, 17)

[a] Unscaled MP2/6-311++G** frequencies (MP2/6-31G** frequencies are 260 (B_u), 195 (A_g), and 168 (A_g) cm^{-1}). [b] Potential energy distribution, contributions ≥ 10. [c] Set A coordinates: CO···O b, O···O s. Set B coordinates: O···H s, O···O s. Set C coordinates: O···H s, CO···H b, OH···O b (redundant). s = stretch, b = bend. [d] Internal coordinate set B (O···H s, O···O s). Scale factors: O···H s = 1.0000 (first entry in frequency, e.g., 238, and PED, e.g., 103, corresponds to MP2/6-311++G**) and 1.0911 (second entry in frequency, e.g., 219, and PED, e.g., 98, corresponds to HF/6-311++G**); O···O s = 0.9588 and 1.1758. [e] Internal coordinate set B. Scale factors: O···H s = 1.0672 and 1.3758, O···O s = 0.6485 and 0.6870.

In this regard, we differ from previous studies on two intramolecular mode assignments. In the first case, as previously discussed,[2] we place the B_u C═O s mode at 1741 cm^{-1} instead of the much-quoted[9a] value of 1754 cm^{-1}. In the second case, we do not assign a quoted band[9a] at 1450 cm^{-1} to a fundamental. This band does not show up in high-resolution gas phase spectra,[9f] and it must, if present, be very weak. Our efforts at scale factor refinement, as those of others,[1c,6d] gave large discrepancies for such a mode. We therefore do not include it in the force field optimization.

TABLE 4: Comparison of the Hydrogen-Bond Normal Modes of $(HCOOH)_2$ with Different Basis Sets

	frequency (cm^{-1})					
	B_u	B_g	A_g	A_u	A_g	A_u
obs	248	230	(190)	163	137	68
HF/D95	249	262	208	188	181	101
HF/D95**	223	249	182	172	165	81
HF/D95++**	217	237	179	170	162	76
HF/6-31G*	237	246	191	167	165	72
HF/6-31G**	229	247	184	168	165	74
HF/6-311++G**	209	227	174	160	161	76
MP2/6-31G**	260	273	195	179	168	72
MP2/6-311++G**	243	217	189	160	162	57

TABLE 5: Optimized Internal Coordinate Scale Factors of the Formic Acid Dimer

coordinate[a]	scale factor
CH s	0.8186
C═O s	0.7652
C−O s	0.8185
OH s	0.6397
O···O s	0.6870
O···H s	1.3758
HC═O b	0.8463
HC−O b	0.8463
OCO b	0.8848
COH b	0.8297
CH ob	0.7707
C−O t	0.9548
C═O t	1.0355
O···O t	0.7943

[a] s = stretch, b = bend, ob = out-of-plane bend, t = torsion.

The intermolecular or hydrogen-bond normal modes need to be discussed in greater detail. The three unscaled in-plane ab initio normal modes (at MP2/6-31G** and MP2/6-311++G**) are listed in Table 3 with three different hydrogen-bond coordinate sets. As we can see from the table, the most pure PED descriptions are achieved with set A (O···O s, CO···O b), which gives an intermediate frequency pure O···O s band and a pair of CO···O b bands. Set B (O···O s, O···H s) gives two mixed A_g modes plus a pure O···H s B_u mode, which shows that the CO···O b modes of set A are most closely described as O···H s modes while O···O s is essentially a hydrogen-bond bending mode. Much more mixing can be seen for set C (O···H s, CO···H b, and OH···H b). The effects of basis set and electron correlation are significant and different from their effects on intramolecular normal modes. The calculated normal mode frequencies are listed in Table 4. While the larger basis sets consistently lead to lower frequencies, MP2 increases the B_u mode tremendously, with MP2/6-311++G** giving the best agreement.

For scaling, we have to make a choice of assignments, which is not obvious. If we select the original experimental assignment,[9d] which has also been followed in a recent ab initio analysis,[6d] the 137 cm^{-1} A_g band would be assigned to a CO···H b (i.e., O···O s) mode. Although this looks reasonable, in that otherwise the 111 cm^{-1} splitting with the B_u O···H s mode seems to be unduly large, it has the unsettling consequence “that the only Raman-active vibration that is not observed is the one whose frequency has been thought to be known for 40 years, the symmetric hydrogen bond stretching vibration”.[9d] The Hartree−Fock (HF) calculations would support the original assignment, predicting splittings of 64 (6-31G**) and 48 (6-311++G**) cm^{-1}, but the MP2 calculations give larger values, viz., 92 (6-31G**) and 81 (6-311++G**) cm^{-1} (although the discrepancy would be minimized if the A_g mode is subject to a large anharmonicity). Although this assignment requires an

TABLE 6: Scaled Internal Coordinate Force Constants of the Formic Acid Dimer[a]

In-Plane

	CH s	C═O s	C−O s	OH s	HC═O b	HC−O b	OCO b	COH b	O···H s	O···O s
intramonomer										
CH s	4.8070									
C═O s	0.3078	11.7058								
C−O s	0.1852	1.3815	7.2290							
OH s	−0.0217	−0.0693	0.1964	5.5651						
HC═O b	0.0230	0.1005	−0.3105	0.0077	0.5121					
HC−O b	0.0750	−0.3170	0.1339	0.0198	−0.1180	0.5298				
OCO b	−0.1002	0.2214	0.1806	−0.0281	−0.4030	−0.4210	0.8425			
COH b	0.0316	0.0303	0.3472	0.1829	−0.0248	0.0508	−0.0266	0.8570		
O···H s	0.0078	0.1508	−0.0875	0.3063	−0.0150	0.0137	0.0013	0.0428	0.3248	
O···O s	0.0040	−0.0681	−0.0745	−0.0793	0.0171	0.0104	−0.0281	−0.1107	−0.0702	0.1842
intermonomer										
CH s	0.0013									
C═O s	−0.0021	−0.0766								
C−O s	−0.0041	0.1385	−0.0607							
OH s	0.0055	−0.0585	0.0796	0.0167						
HC═O b	0.0002	0.0141	−0.0194	0.0163	−0.0021					
HC−O b	0.0002	0.0007	−0.0027	0.0014	0.0000	−0.0007				
OCO b	−0.0004	−0.0151	0.0226	−0.0181	0.0021	0.0007	−0.0029			
COH b	−0.0030	0.0164	0.0373	0.0075	0.0011	0.0027	−0.0039	0.0124		
O···H s	−0.0148	0.1410	−0.0551	0.0596	−0.0123	0.0059	0.0066	0.0429	0.0085	

Out-of-Plane

	CH ob	C−O t	C═O t	O···O t
intramonomer				
CH ob	0.6484			
C−O t	0.0595	0.3491		
C═O t	0.0643	0.2416	0.3167	
O···O t	0.0167	0.0335	0.0393	0.0473
intermonomer				
CH ob	0.0068			
C−O t	0.0097	0.0141		
C═O t	0.0073	0.0018	−0.0258	

[a] Calculations at HF/6-311++G**. Nonredundant coordinate basis. Units: mdyn/Å for stretch and stretch, stretch constants; mdyn for stretch, bend constants; mdyn Å for all others.

unusually small scale factor for O···O s (see Table 3, set II), we have retained it, while presenting the results of both assignments (Table 3). The refinement of the MM potential function gives essentially the same parameters for either assignment.

The set II internal coordinate scale factors, optimized by least-squares fitting to the FAD and its three deuterated derivatives, are given in Table 5, and the scaled force constants are given in Table 6. As is common,[10] in order to reduce the number of parameters we have scaled the off-diagonal force constants by the geometric mean of the diagonal force constants.

The comparison of observed and calculated frequencies, with the above scale factors, is given in Table 7. Ab initio internal coordinate dipole derivatives are given in Table 8, and observed and calculated infrared intensities, based on scaled force field eigenvectors, are compared in Table 7. (Intensities based on MP2/6-311++G** dipole derivatives and scaled force constant eigenvectors are also included.) In addition to the potential energy distribution (PED), we give the dipole derivative distribution (DDD),[11] which provides the contribution of each coordinate to the infrared intensity and is useful because it does not always follow the PED. As can be seen, the frequency agreement is very good (as well for deuterated derivatives; we recall that the difference between observed and calculated $\Delta\nu$-(C═O) is accounted for by anharmonicity)[2], with the MP2 calculation giving comparable results. While the HF intensity agreement is acceptable, the MP2 agreement is quite good.

It is important to note that in many cases the DDD gives a very different description of the origin of a band intensity than does the PED. This is particularly true of modes associated with CH d and OH b, whose assignments have been controversial.[6d] The ab initio PED shows that these are strongly mixed modes and their eigenvectors can be affected by basis set, electron correlation, and scale factor. As to their infrared intensities, the situation is complicated by mixing of these coordinates with C−O s, C═O s, and OCO d. This can be seen by comparing this region in the HF/6-311++G** calculation (Table 7) with that from the MP2/6-311++G** calculation, given in Table 9. From Table 8 we see that the dipole derivatives for CH d and COH b are relatively small, and therefore can be overshadowed by contributions from other coordinates. Thus, while ν_8 and ν_{10} are primarily COH b and CH d in the PED, COH b makes a negative contribution to both modes while CH d makes a negative (ν_{10}) or small positive (ν_8) contribution to the intensities, which are derived mainly from the other coordinates.

The above ab initio studies provide a secure basis for understanding the spectroscopic properties of the FAD, and therefore for exploring whether an electrostatic model can reproduce the 45 in-plane force constants of the intermolecular force field.

Electrostatic Model

A model in which the intermolecular potential *u(r)* is limited only to distance-dependent terms, such as the commonly used forms[12] that contain coulomb interactions between fixed charges plus a fixed van der Waals interaction of the Lennard-Jones type, cannot reproduce the intermolecular force constants of the

TABLE 7: Calculated and Observed Frequencies and Infrared Intensites of the Formic Acid Dimer

ν^a		I^d		
calcd[b]	obs[c]	calcd[e]	obs[f]	PED[g], DDD[h]
(1) 3098 B_u	3110	1281 (1883)[i]	1980 vs	OH s(102)[646] O···H s[627]
(2) 3047 A_g				OH s(107)
(3) 2957 A_g	2949			CH s(100)
(4) 2954 B_u	2957	254 (249)	102 vs	CH s(99)[87] OCO b[50] OH s[34] O···H s[34] C═O s[21]
(5) 1734 B_u	1741	1165 (798)	766 vs	C═O s(85)[806] CH d(15) C−O s(14)[270] COH b(6)[139]
(6) 1683 A_g	1670			C═O s(86) CH d(15) C−O s(12) COH b(10)
(7) 1415 A_g	1415			CH d(56) COH b(17) C═O s(16)
(8) 1411 B_u		47 (8)		CH d(73)[7] C═O s(12)[41] COH b(6)[-9] O···H s[7] OCO d[5]
(9) 1376 A_g	1375			COH b(48) CH d(29) C−O s(18) OCO d(10)
(10) 1357 B_u	1362	58 (34)	55 m	COH b(59)[-42] C−O s(20)[30] OCO d(12)[61] CH d(10)[-3] O···H s[12]
(11) 1220 A_g	1214			C−O s(70) COH b(20) OCO d(7) CH d(5)
(12) 1219 B_u	1217	495 (380)	316 vs	C−O s(64)[304] COH b(26)[155] OCO d(6)[99] C═O s[-60]
(13) 1063 A_u	1063	3 (50)		CH ob(93)[-0.6] C−O t(14)[14] C═O t(8)[-5] O···O t[-5]
(14) 1059 B_g	1060			CH ob(95) C−O t(9) C═O t(8)
(15) 922 A_u	923	358 (214)	145 s	C−O t(98)[328] CH ob(9) O···O t[30]
(16) 874 B_g				C−O t(105)
(17) 692 B_u	699	81 (47)	48 m	OCO d(80)[98] C−O s(8)[-20] COH b[12] O···H s[-11]
(18) 684 A_g	677			OCO d(81) C−O s(8) COH b(5)
(19) 245 B_u	248	40 (54)	s	O···H s(97)[38]
(20) 231 B_g	230			C═O t(193) C−O t(87)
(21) 196 A_g	190			O···H s(124) O···O s(8)
(22) 162 A_u	163	12 (8)	m	C═O t(248)[-8] C−O t(95)[10] O···O t(20)[10]
(23) 139 A_g	137			O···O s(130) COH b(18)
(24) 68 A_u	68	5 (3)	w	O···O t(109)[6] C−O t(20)[-1]

[a] Frequency in cm^{-1}. [b] At HF/6-311++G** with scaled force constants. [c] Reference 9 (see text). [d] Infrared intensity. [e] Calculated with scaled force constant eigenvectors. [f] Reference 1c for numerical and ref 9a for qualitative intensities. [g] Potential energy distribution (in parentheses), contributions ≥5. See Table 2 for designation of internal and symmetry coordinates. [h] Dipole derivative distribution[11] (in brackets), contributions ≥5% of calculated intensity. [i] Intensities calculated with MP2/6-311++G** dipole derivatives and scaled force constant eigenvectors.

TABLE 8: Ab initio Dipole Derivatives[a] of the Formic Acid Dimer

	$\partial\mu_x/\partial r$		$\partial\mu_y/\partial r$		$\partial\mu_z/\partial r$		$\lvert\partial\mu/\partial r\rvert$	
coordinate[b]	SCF[c]	MP2[d]	SCF[c]	MP2[d]	SCF[c]	MP2[d]	SCF[c]	MP2[d]
CH s	−0.544	−0.607	−0.275	−0.323			0.610	0.688
C═O s	−0.047	−0.290	7.219	5.502			7.220	5.509
C−O s	3.281	2.901	−4.406	−4.288			5.494	5.177
OH s	−1.753	−2.241	−0.816	−0.918			1.934	2.422
O···H s	1.860	2.192	0.782	0.923			2.018	2.379
O···O s	0.0	0.0	0.0	0.0			0.0	0.0
HC═O b	1.024	0.737	−0.012	−0.049			1.024	0.739
HC−O b	1.245	1.054	−0.329	−0.325			1.288	1.103
C−H d	−0.156	−0.224	0.224	0.195			0.323	0.297
OCO b	−2.269	−1.791	0.341	0.374			2.294	1.830
COH b	−0.888	−0.698	1.169	0.953			1.468	1.181
CH ob					−0.037	0.215	0.037	0.215
C−O t					1.621	1.491	1.621	1.491
C═O t					0.721	0.730	0.721	0.730
O···O t					1.714	1.275	1.714	1.275

[a] In D/Å or D/rad. [b] s = stretch, b = bend, ob = out-of-plane bend, t = torsion, right monomer only. [c] SCF: HF/6-311++G**. [d] MP2: MP2/6-311++G**.

FAD, and therefore of the hydrogen bond in general.[3] This is because such potentials lead to Cartesian interaction force constants given by[13]

$$F_{i\alpha,j\beta} = -\frac{u'}{r}\delta_{\alpha\beta} + \left(u'' - \frac{u'}{r}\right)\frac{\partial r}{\partial x_{i\alpha}}\frac{\partial r}{\partial x_{j\beta}} \qquad (1)$$

where r is the distance between the ith and jth atoms, α and β are Cartesian components, and $u' = \partial u/\partial r$ and $u'' = \partial^2 u/\partial r^2$. If u is isotropic and all pairwise interaction parameters are fixed, since

$$\partial r/\partial x_{i\alpha} = -\,\partial r/\partial x_{j\alpha} \qquad (2)$$

TABLE 9: CH and OH Bend Region in MP2/6-311++G Calculation of the Formic Acid Dimer**

ν_{calc}[a]	PED[b], DDD[c]
(7) 1423 A_g	COH b(48) CH d(23) C═O s(9)
(8) 1408 B_u	CH d(57)[4] COH b(25)[-11] C═O s(6)[11] O···H s[2]
(9) 1368 A_g	CH d(70) COH b(21) C−O s(15) OCO d(7)
(10) 1356 B_u	COH b(44)[-21] CH d(31)[-8] C−O s(23)[21] OCO d(11)[35] O−H s[3] O···H s[4]
(11) 1222 B_u	C−O s(61)[244] COH b(30)[110] OCO d(7)[72] C═O s(6)[-50] CH d(5)[14]
(12) 1219 A_g	C−O s(70) COH b(24) OCO d(8)

[a] Frequency in cm^{-1}. [b] Potential energy distribution (in parentheses), contributions ≥5. See Table 2 for designation of internal and symmetry coordinates. [c] Dipole derivative distribution[11] (in brackets), contributions ≥5% of calculated intensity.

we find that

$$F_{i\alpha,j\beta} = F_{i\beta,j\alpha} \tag{3}$$

Examination of the ab initio force field shows that this relation is not true (the equality may be relaxed to some extent if the hydrogen-bond potential incorporates an angular dependence,[12a,b] but even this does not assure reproduction of intermolecular force constants). We therefore must look for a more comprehensive model if we want to develop the more detailed description provided by the intermolecular force field.

On the basis of studies of the amide I mode splitting (essentially equivalent to $\Delta\nu$(C═O)) in polypeptides, it was proposed[14] and subsequently verified in polypeptides[15] and in the FAD[1b] that transition dipole coupling is the major intermolecular interaction responsible for such intramolecular mode splittings. Since such coupling can be represented by charge flux interactions,[1b] it is clear that they must be included in an electrostatic model. Our finding[2] that atomic dipoles are needed to give agreement with interaction energies then leads to the obvious question of whether such a model will reproduce the ab initio intermolecular force field, at least near the equilibrium conformation.

We are mainly interested in the behavior near equilibrium because it is in this region that we want an accurate spectroscopic characterization of the hydrogen bond. In regions far from equilibrium, the effect of the hydrogen bond is minimal and a standard molecular mechanics description is appropriate. (Of course, there is no major problem in devising an effective transition between these regions.) For the model to be most appealing, it is desirable that its parameters be constant in the near-equilibrium region, so that any changes in intermolecular force constants be due solely to the changes in intermolecular geometry, and this is a constraint we have imposed on our model. Since the use of valence-type intermolecular internal coordinates would not make this possible (i.e., force constants would have to change with geometry), we keep the nonbonded nature for the intermolecular interactions. Three nonbonded distances, two O···H (O9···H2 and O10···H1) and one O···O (O9···O10), were chosen as intermolecular in-plane coordinates, which together with the 14 intramolecular internal coordinates make a complete set for the dimer.

In this connection, it is worthwhile to note that internal coordinates can be chosen in two ways to calculate the Hessians: rectilinear (which do not involve a second-order **B** matrix calculation) and curvilinear (which do involve such a calculation). This is related to the fact that, in general for a nonbonded coordinate r_k, the force constant is

$$F_{\alpha,\beta} = u' \frac{\partial^2 r_k}{\partial x_\alpha \partial x_\beta} + u'' \frac{\partial r_k}{\partial x_\alpha} \frac{\partial r_k}{\partial x_\beta} \tag{4}$$

where the first term arises from the force $F_k = -u'$ and the second-order **B** matrix element $B_{k,\alpha\beta} = \partial^2 r_k / \partial x_\alpha \partial x_\beta$, and the second term is from the force constant $F_{kk} = u''$ and the first-order **B** matrix elements $B_{k\alpha}B_{k\beta} = (\partial r_k/\partial x_\alpha)(\partial r_k/\partial x_\beta)$. Generally, r_k is a redundant coordinate with respect to a complete set r_m and the force F_k does not vanish. Also, the second-order **B** matrix is not invariant to rotation, so neither is the first term in eq 4. For a system having n degrees of freedom with $m + n$ internal coordinates, we can define n independent and m redundant coordinates such that $B_{n\alpha} \neq 0$ and $B_{m\alpha} = 0$. At the minimum energy structure the F_n vanish but the F_m do not. This is especially relevant in molecular mechanics where all the forces related to valence and nonbonded coordinates are explicitly calculable. For linear redundancies, it can be shown from the redundancy condition that the $B_{m,\alpha\beta} = \sum_{i,j} C_{mij} B_{i\alpha} B_{j\beta}$, where the C_{mij} are constants, vanish and therefore the first term in eq 4 disappears. However, in real systems most redundancies are not linear and this term exists. Nevertheless, it is possible to transform force constants $F_m B_{m,\alpha\beta}$ to a set of force constants $F_{ij} = F_m C_{mij}$ in r_n with rotational invariance, which means that both F_{ij} parameter sets are valid but have different individual values. In practice, both the SDFF transformation and the MM potential parameter refinement should be done in the same coordinate system, which hopefully would avoid lengthy second-order **B** matrix calculations in MM normal mode treatments. As is commonly used in present MM Hessian calculations, curvilinear coordinates are adopted in the following discussion, but we have also done the refinement in a rectilinear coordinate system, and although the optimized parameters are slightly different the ability to reproduce the ab initio data is comparable.

In addition to the ab initio calculation on the equilibrium structure, $\mathbf{D_0}$, we did calculations on three other structures by fixing one intermolecular distance, O···H or H···H, and relaxing all other geometric parameters. In one of these, $\mathbf{D_{-1}}$, the O···H distance was shorter than in $\mathbf{D_0}$, while in the other two, $\mathbf{D_1}$ and $\mathbf{D_2}$, this distance was longer. The intermolecular interaction energy for $\mathbf{D_0}$, $E(\mathbf{D_0})$, was calculated by the counterpoise method to correct for basis set superposition error. The energies for the other structures were taken as

$$E(\mathbf{X}) = E(\mathbf{D_0}) + E'(\mathbf{X}) - E'(\mathbf{D_0}) \tag{5}$$

where E' is the HF energy of the dimer. The ab initio forces for $\mathbf{D_{-1}}$, $\mathbf{D_1}$, and $\mathbf{D_2}$ (which are obviously zero for $\mathbf{D_0}$) in Cartesian coordinates were transformed to the complete internal coordinate set r_k and the three forces for the intermolecular coordinates were taken as part of the "data". (The forces in the intramolecular internal coordinates are appropriately treated by the SDFF transformation method.[5]) The ab initio force constants for $\mathbf{D_{-1}}$, $\mathbf{D_1}$, and $\mathbf{D_2}$ were scaled by the same scale factors as those for $\mathbf{D_0}$. From such force constants in internal coordinates, the intermolecular interaction constants were selected and transformed back into Cartesian coordinates. Dipole derivatives were taken from ab initio values for $\mathbf{D_0}$.

The above set of ab initio "data" satisfactorily overdetermines the number of model parameters to be optimized (by about 7:1). Nevertheless, it would be less physically meaningful in judging the model if one could not at least start with compelling initial values of these, preferably keeping some of them fixed. In this respect a planar system such the FAD is advantageous, since

TABLE 10: Ab initio Molecular Properties of Dimer and Monomer Structures[a] and van der Waals Parameters of Dimer

property		dimer				monomer
		$\mathbf{D}_{-1}$	$\mathbf{D}_0$	$\mathbf{D}_1$	$\mathbf{D}_2$	
geometry[b]						
r(C=O)		1.196	1.191	1.188	1.184	1.177
r(C−O)		1.292	1.299	1.303	1.311	1.321
r(C−H)		1.085	1.085	1.085	1.086	1.086
r(O−H)		0.970	0.960	0.955	0.951	0.947
θ(O−C=O)		125.66	125.73	126.31	126.79	124.92
θ(H−C=O)		122.07	122.64	122.70	123.12	124.58
θ(H−C−O)		112.27	111.64	110.99	110.09	110.50
θ(C−O−H)		111.18	111.13	111.62	112.48	109.42
r(O···H)		1.677	1.864	1.970	2.275	
r(O9···O10)		3.165	3.254	3.146	3.078	
θ(C−O···O)		83.82	86.76	90.71	98.69	
atomic charges[c]						
H1		0.370	0.377	0.383	0.389	0.393
O3		−0.447	−0.453	−0.459	−0.468	−0.481
C5		0.484	0.480	0.477	0.469	0.468
H7		0.076	0.079	0.080	0.080	0.090
O9		−0.483	−0.483	−0.481	−0.471	−0.471
atomic dipoles[d]						
H1	m_x	−0.039	−0.032	−0.040	−0.066	
	m_y	−0.201	−0.234	−0.269	−0.307	
	$\lvert m\rvert$	0.205	0.237	0.272	0.314	0.334[e]
O3	m_x	0.281	0.291	0.270	0.315	
	m_y	0.252	0.281	0.330	0.379	
	$\lvert m\rvert$	0.378	0.405	0.426	0.493	0.579
C5	m_x	−0.456	−0.479	−0.453	−0.452	
	m_y	−0.160	−0.176	−0.210	−0.241	
	$\lvert m\rvert$	0.483	0.511	0.499	0.512	0.311
H7	m_x	−0.087	−0.085	−0.100	−0.117	
	m_y	−0.041	−0.046	−0.050	−0.068	
	$\lvert m\rvert$	0.096	0.097	0.112	0.135	0.045
O9	m_x	0.359	0.372	0.358	0.335	
	m_y	−0.048	−0.018	−0.014	0.067	
	$\lvert m\rvert$	0.363	0.372	0.359	0.341	0.292
van der Waals parameters[f]						
		H1	O3	C5	H7	O9
r^*		0.994[g]	3.180	3.727	0.800	2.674[g]
ϵ		0.418	1.640	1.573	0.084	5.079

[a] Calculations at HF/6-311++G**. The parameters optimized and used in MM potential function, see text. [b] Bond lengths in angstroms, bond angles in degrees. [c] In fractional electron charges. [d] In electron charge·Å. y axis along H2−H1, x axis toward O9, see Figure 1. [e] From Dinur, U. *J. Phys. Chem.* **1991**, *95*, 6201, with a differently oriented coordinate system. [f] From ref 12g, r^* in angstroms, ϵ in KJ/mol. [g] For hydrogen-bond interactions: r^*_{ii}(H1) = 0.584Å, r^*_{ii}(O9) = 2.050 Å.

TABLE 11: Optimized Bond Charge Fluxes for the Formic Acid Dimer

internal coordinate	Bond Charge Flux[a]			
	CH	C=O	C−O	OH
CH s	−0.010267	−0.001491	−0.004848	0.194147
C=O s	0.197218	−0.547439	0.334387	0.082509
C−O s	0.104078	0.471367	−0.476598	−0.091481
OH s	0.012699	0.156801	0.221316	−0.170505
HC=O b	0.026032	0.004720	−0.036836	0.058766
HC−O b	0.043269	−0.122322	−0.140455	0.087628
OCO b	−0.069301	0.117602	0.177291	−0.146394
COH b	0.009858	0.147691	0.041598	−0.063830

[a] Charge in electron unit; r in angstroms.

many of the electrostatic parameters are uniquely determinable within the framework of physically reasonable assumptions.[4] We have used such parameters[2] as starting points in this study.

Since in this approach the effective charge on an atom is simply given by the out-of-plane component of the molecular dipole derivative,[4] we have fixed the charges at these values.[2] The charge fluxes are given by second dipole derivatives, but since these depend significantly on basis set (see Table 8), and we wish to have some flexibility in the refinement process, we have kept the CH bond charge flux fixed at the determined value[2] and allowed the others to optimize. (The bond charge flux $\partial q_{ij}/\partial r_k$ makes a negative contribution to the atomic charge flux $\partial q_i/\partial r_k$ and a positive contribution to $\partial q_j/\partial r_k$.) The atomic dipoles other than those of the hydrogen-bonded O and H atoms were kept fixed at their quadrupole-moment-determined values,[2] with these two being allowed to optimize.

The choice of van der Waals parameters is less straightforward. The optimization process (a least-squares procedure) was successful using our previous potential,[2] but we obtained better results with a recently proposed one.[12g] In this case, a potential in the form

$$E_{ij} = 4\epsilon_{ij}\left(\left(\frac{r^*_{ij}}{r_{ij}}\right)^{12} - \left(\frac{r^*_{ij}}{r_{ij}}\right)^{6}\right) \tag{6}$$

where $\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}$ and $r^*_{ij} = (r^*_{ii} + r^*_{jj})/2$, plus a set of static charges were optimized to fit the ab initio potential surfaces around the minima of seven dimer structures thought to be present in the liquid. These parameters satisfactorily reproduced experimental thermodynamic and structural properties, and we used them except for r^*_{ii} of the hydrogen-bonded O and H atoms, which we allowed to optimize. In the least-squares refinement we used weighting factors of 100 for $\mathbf{D}_0$ forces, 10 for the $\mathbf{D}_{-1}$, $\mathbf{D}_1$, and $\mathbf{D}_2$ forces, and 1 for all other ab initio "data".

TABLE 12: Comparison of Ab Initio and Electrostatic Model Properties of Formic Acid Dimer Structures

	$\mathbf{D}_{-1}$		$\mathbf{D}_0$		$\mathbf{D}_1$		$\mathbf{D}_2$	
property	AI[a]	M[a]	AI	M	AI	M	AI	M
energy[b]	−12.23	−12.41	−13.36	−13.80	−12.63	−12.56	−9.16	−8.78
qq		−15.39		−12.11		−11.03		−7.69
qm		5.95		6.25		6.26		5.85
mm		−8.20		−5.49		−3.99		−1.67
LJ12		28.58		14.47		11.63		6.16
LJ6		−23.35		−16.92		−15.42		−11.42
forces[c]								
O···H	−0.047	−0.113	0.000	−0.003	0.021	0.021	0.037	0.031
O···O	0.000	−0.008	0.000	0.000	−0.034	−0.046	−0.050	−0.044
force constants[d]								
	0.134		0.065		0.053		0.028	
	0.137[e]		0.068		0.054		0.029	
frequencies[f]								
	16.8		5.6		4.6		9.2	
	20.0[e]		5.0		4.3		6.4	

[a] AI = ab initio, M = electrostatic model. [b] In kcal/mol. q = charge, m = atomic dipole, LJ12 = Lennard-Jones r^{-12} term, LJ6 = Lennard-Jones r^{-6} term. [c] Intermolecular coordinate forces, in mdyn. [d] Root-mean-square deviation, in mdyn/Å. [e] From the parameters refined in a rectilinear coordinate system, see text. [f] Root-mean-square frequency deviation for all in-plane modes, in cm^{-1}.

Results and Discussion

In Table 10 we present the ab initio geometric and electrostatic properties of four dimer structures (and include those of the monomer for comparison). As expected, when the hydrogen bond gets weaker (longer), the C═O and O−H bonds get shorter. This is accompanied by a lengthening of the C−O bond. It is interesting that as the O−H distance increases the monomers rotate slightly so as to decrease the O9O10 distance. The charges change by no more than a few percent over this range, so it is justifiable to keep them constant. The magnitudes of the atomic dipoles change more significantly (the directions are less affected), particularly that of H1, and this justifies optimizing the values for the atoms in the O···H hydrogen bond (There is also a large change in the dipole for H7, but because of its location it probably has a smaller effect on the intermolecular force constants). As noted above, although we started with the dipole-derivative derived charge fluxes,[2] only the C−H flux was kept at this value and the others were allowed to optimize.

Before the refinement of parameters in the complete model, we examined optimized models in which charge fluxes and/or atomic dipoles were excluded. In none of these cases was it possible to obtain consistent agreement with the entire range of properties. For example, in the absence of atomic dipoles the interaction energies and intermolecular forces were very poorly reproduced, and in the absence of charge fluxes the intermolecular forces and $\Delta\nu(\text{C═O})^2$ were poorly reproduced. Thus, a minimal model must at least incorporate these two quantities.

The optimization of the complete model gave the following set of parameters. The charges, as noted above, are those of $\mathbf{D_0}$ and are given in Table 10. The refined atomic dipoles are 0.222 for H1 ($m_x = 0.001$, $m_y = -0.222$) and 0.406 for O9 ($m_x = 0.261$, $m_y = -0.309$), the others being those for $\mathbf{D_0}$ given in Table 10. The van der Waals parameters for ϵ_{ii} and r_{ii}^* are those of reference 12g, given in Table 10, except that $r_{ii}^*(\text{O9}) = 2.050$ Å and $r_{ii}^*(\text{H1}) = 0.584$ Å for the hydrogen-bonded pair. The optimized bond charge fluxes are given in Table 11.

The extent of agreement between this optimized model and ab initio "data" is indicated in Tables 12−14. As seen from Table 12, energies of the four structures are well reproduced, indicating that the model provides a good representation of the potential energy function near $\mathbf{D_0}$. Because the charge−dipole interaction is relatively constant, and the changes in the dipole−dipole roughly mirror those in the van der Waals interaction (at least for $\mathbf{D_0}$, $\mathbf{D_1}$, and $\mathbf{D_2}$), it is seen that the changes in the total interaction energy are determined mainly by the changes in the charge−charge interaction. The intermolecular coordinate forces are well reproduced, with the largest discrepancy for $\mathbf{D_{-1}}$ perhaps indicating the need for a repulsive van der Waals potential softer than r_{ij}^{-12} (also suggested by the energy of $\mathbf{D_{-1}}$). The force constants are also well reproduced, the rms error being of the order of 10%. This leads to a very good reproduction of the normal mode frequencies, as shown in Table 13, and in particular to $\Delta\nu(\text{C═O})$ and the intermolecular mode frequencies. In the latter case, if only charge and van der Waals parameters[12g] are used, the latter frequencies are $\nu(\text{O···H}) = 296$ ($\Delta\nu = 51$) and 218($\Delta\nu = 22$) cm^{-1} and $\nu(\text{O···O}) = 75$ ($\Delta\nu = -63$) cm^{-1}. Finally, the optimization to the ab initio dipole derivatives gives good agreement, as seen from Table 14.

TABLE 13: Comparison of Ab Initio and Electrostatic Model In-plane Frequencies of the Formic Acid Dimer

		frequency[b]	
mode[a]		ab initio	model
OH s	B_u	3098	3104
OH s	A_g	3046	3041
CH s	A_g	2957	2956
CH s	B_u	2953	2954
C═O s	B_u	1734	1735
C═O s	A_g	1683	1681
CH d	A_g	1415	1417
CH d	B_u	1411	1409
COH b	A_g	1376	1387
COH b	B_u	1357	1346
C−O s	A_g	1220	1221
C−O s	B_u	1219	1216
OCO b	B_u	692	693
OCO b	A_g	684	683
O···H s	B_u	245	250
O···H s	A_g	196	202
O···O s	A_g	138	133

[a] s = stretch, b = bend, d = deformation. [b] In cm^{-1}.

Conclusion

The search for potentials that can account for intermolecular interactions is an important and ongoing one. In the case of the FAD, if one is satisfied with reproducing structures and some thermodynamic properties then van der Waals and charge

TABLE 14: Comparison of ab Initio and Electrostatic Model Dipole Derivatives of the Formic Acid Dimer

internal coordinate[b]		dipole derivative[a]	
		ab initio	model
CH s	$\partial\mu_x/\partial r$	−0.544	−0.498
	$\partial\mu_y/\partial r$	−0.275	−0.239
	$\lvert\partial\mu/\partial r\rvert$	0.610	0.552
C=O s	$\partial\mu_x/\partial r$	−0.047	−0.148
	$\partial\mu_y/\partial r$	7.219	7.057
	$\lvert\partial\mu/\partial r\rvert$	7.220	7.058
C−O s	$\partial\mu_x/\partial r$	3.281	3.060
	$\partial\mu_y/\partial r$	−4.406	−4.600
	$\lvert\partial\mu/\partial r\rvert$	5.494	5.525
OH s	$\partial\mu_x/\partial r$	−1.753	−1.373
	$\partial\mu_y/\partial r$	−0.816	−0.136
	$\lvert\partial\mu/\partial r\rvert$	1.934	1.380
HC=O b	$\partial\mu_x/\partial r$	1.024	0.600
	$\partial\mu_y/\partial r$	−0.012	−0.340
	$\lvert\partial\mu/\partial r\rvert$	1.024	0.690
HC−O b	$\partial\mu_x/\partial r$	1.245	1.279
	$\partial\mu_y/\partial r$	−0.329	−0.490
	$\lvert\partial\mu/\partial r\rvert$	1.288	1.370
OCO b	$\partial\mu_x/\partial r$	−2.269	−1.879
	$\partial\mu_y/\partial r$	0.341	0.830
	$\lvert\partial\mu/\partial r\rvert$	2.294	2.054
COH b	$\partial\mu_x/\partial r$	−0.888	−0.781
	$\partial\mu_y/\partial r$	1.169	1.068
	$\lvert\partial\mu/\partial r\rvert$	1.468	1.323

[a] In D/Å or D/rad. [b] s = stretch, b = bend, right monomer only.

interactions may suffice.[12g] However, if the requirement is more demanding, viz., to reproduce in addition vibrational spectroscopic properties such as Δν(C=O), we have shown that charge fluxes[1b] and even atomic dipoles[2] are needed. The most demanding requirement would be to have the potential reproduce the entire set of intermolecular force constants (in addition to intramolecular perturbations), and in this paper we demonstrated that this is possible within the framework of the extended model.[2] As an important consequence, we show[3] that the model provides a detailed description of the hydrogen bond (including intermolecular frequencies) near its equilibrium structure.

Our treatment is based on a careful analysis of the band assignments for the FAD and a resulting scaled 6-311++G** ab initio force field in non-redundant coordinates. Starting with electrostatic parameters[2] that can be uniquely determined from a physically reasonable model,[4] we have shown that, with some flexibility, these can be optimized to give agreement with structures, interaction energies, interaction forces, intermolecular force constants, and dipole derivatives of four different hydrogen-bonded structures of the FAD. The success of this methodology suggests that it can be the basis of a general approach to a more accurate MM treatment of intermolecular interactions.

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