CO stretch mode splitting in the formic acid dimer: Electrostatic models of the intermonomer interaction

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C=O STRETCH MODE SPLITTING IN THE FORMIC ACID DIMER: ELECTROSTATIC MODELS OF THE INTERMONOMER INTERACTION

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ABSTRACT

The physical origin of the large (74 cm^{-1}) splitting between the symmetric (A_g) and antisymmetric (B_u) components of the C=O stretch mode in the formic acid dimer has previously been attributed to tautomerism effects, transition dipole—dipole coupling, or dynamical charge transfer through the hydrogen bonds. We show that an electrostatic model involving atomic charge—charge interactions can account for a splitting of 56 cm^{-1}, provided the atomic partial charges are allowed to vary in magnitude during vibrational motion. The charges and charge derivatives have been obtained from ab initio Hartree—Fock calculations up to the 6-31G** level. An additional 13 cm^{-1} of the remaining discrepancy in the splitting is shown to be due to a difference in diagonal cubic anharmonicity between the A_g and B_u modes. The charge—charge model plus anharmonicity thus lead to a predicted splitting of 69 cm^{-1}, compared to the observed value of 74 cm^{-1}.

INTRODUCTION

In carboxylic acid dimers, which form cyclic centrosymmetric hydrogen-bonded structures, the symmetric and antisymmetric carbonyl stretching modes show large splittings; for example, in the formic acid (FA) dimer [1], the splitting $\nu(B_u)-\nu(A_g)$ is 74 cm^{-1}. These splittings can be reproduced in normal mode calculations by introducing some intermonomer force constants with relatively large values [2—4]. The physical origin of these interaction force constants between non-adjacent coordinates has been debated. Tautomerism caused by double proton transfer was suggested as an explanation [2]. However, a large splitting of the C=O stretch (str) modes has also been observed in crystalline diketopiperazine [5], where a similar cyclic hydrogen-bond configuration exists but where tautomerism is not likely. Based on studies of the amide I mode in polypeptides, it was proposed [6] that the splittings in carboxylic acid dimers could be caused by transition dipole—dipole coupling. According to Bosi et al. [7, 8], however, the effect of the dipole—dipole interaction is negligibly small, both in acid dimers and in polypeptides. In an ab initio calculation of the FA dimer [8], these authors

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computed the interaction force constant between the C=O bond-stretching coordinates and derived a magnitude for the splitting of 20 cm^{-1}. Noting that charge redistribution takes place throughout the hydrogen-bonded ring during the vibration of a C=O group, they suggested that dynamical charge transfer through the hydrogen bonds is a cause of the vibrational interaction. More recent ab initio studies [9, 10] of the FA dimer have also found a large splitting (44 and 58 cm^{-1}, respectively) for the C=O str mode, but no explanation of the interaction was attempted.

We have already shown [11] that the objections of Bosi and Zerbi [7] concerning dipole—dipole coupling are not valid for the amide I mode in polypeptides, and that the splittings observed in polypeptides are consistent with transition dipole interaction. In the present work, we have analyzed, with the help of ab initio Hartree—Fock calculations, the carbonyl band splitting in the FA dimer on the basis of electrostatic models of the inter-monomer interaction energy. We show that the dipole—dipole coupling mechanism results in a splitting of about 30 cm^{-1}, and is therefore not negligible although it is still considerably smaller than that observed. Because the dipole—dipole interaction is only the first term in the multipole expansion of the electrostatic energy,we have considered ways to include higher-order contributions. An obvious extension is to calculate the dipole—quadrupole and quadrupole—quadrupole terms. We have found, however, that the required quadrupole moment derivatives are extremely sensitive to basis set, even up to the 6-31G** level, and the resulting contributions to the splitting are therefore not reliable. We have therefore considered the representation of the electrostatic energy in terms of Coulombic interactions between atomic partial charges, thus implicitly accounting in a simple way for the effects of higher-order molecular multipole moments.

In the fixed partial charge (FPC) model commonly used to calculate various molecular properties, point charges are located at the atomic centers. The atomic charges follow the vibrational motion of the atoms but do not change in magnitude. In our present work using dynamical partial charges (DPC), changes in the magnitude of the partial charges are allowed. We show that the contributions of the partial charge fluxes to the intermomoner interaction force constants are essential, and that the DPC model gives a splitting of up to 56 cm^{-1}. Most of the remaining discrepancy is shown to be due to a difference in diagonal cubic anharmonicity of the A_g and B_u modes.

Similar extensions of the FPC model to include charge redistribution during vibration have been made in the calculation of IR intensities [12] and vibrational circular dichroism [13, 14]. In molecular mechanics calculations in which Coulombic terms are included [15, 16], it may be important to allow for DPC effects.

THEORY

The total potential energy of two molecules A and B may be written as $V = V_A + V_B + V_{AB}$, where V_A and V_B are the intramolecular energies of the isolated molecules. Changes in the interaction energy V_{AB} during vibratinal motion in general lead to shifts of the corresponding normal mode frequencies. V_{AB} can be decomposed into terms describable as electrostatic, exchange repulsion, polarization, charge-transfer, and dispersion interactions [17]. In a medium-strength hydrogen-bonded system such as the FA dimer, the electrostatic energy is known to be the primary stabilizing term, and often approximates the total interaction energy [17—19]. It is therefore reasonable to seek an electrostatic explanation of the carbonyl band splitting. We note that using conventional representations of van der Waals interactions, such as the atom—atom 6-12 potential with empirical parameters, fails to give any significant splitting of the C=O str mode in the FA dimer and in diketopiperazine [20].

The electrostatic energy V^{ES} is usually defined as the interaction between the undistorted charge distributions of the monomers [17]. Knowing the monomer wavefunction, one can get the intermonomer force constants directly from the second derivatives of V^{ES}. It is preferable, however, to derive a physical model of the interaction which, besides yielding an intuitive understanding of the mechanisms involved, would allow calculations of other configurations of FA molecules and extension of the model to other systems without having to do a complete ab initio calculation for each case.

One approach is to expand V^{ES} in a series of interactions between molecular point multipole moments. The dipole—dipole term is

$$V^{dd} = |\vec{\mu}^A| |\vec{\mu}^B| X_{AB} \tag{1}$$

where

$$X_{AB} = (\hat{e}_A \times \hat{e}_B - 3\hat{e}_A \times \hat{r}_{AB} \hat{e}_B \times \hat{r}_{AB})/r_{AB}^3 \tag{2}$$

is a geometrical factor, $\hat{e}_i$ being the direction of the dipole $\vec{\mu}^i$, and $\vec{r}_{AB}$ is the vector between the centers of the dipoles. Changes of the multipole moments during intramolecular vibrational motion give rise to restoring forces, which can be included in a normal mode calculation using the GF method by means of the corresponding quadratic force constants. These force constants can be expanded either in the normal coordinate basis $\vec{Q}$ or in the internal coordinate basis $\vec{S}$. In the dipole—dipole coupling model, they are given by [11]

$$f_{\alpha\alpha} = \left|\frac{\partial\vec{\mu}^A}{\partial Q_\alpha^A}\right| \left|\frac{\partial\vec{\mu}^B}{\partial Q_\alpha^B}\right| X_{AB}^\alpha \tag{3}$$

or

$$f_{ij} = \left|\frac{\partial\vec{\mu}^A}{\partial S_i^A}\right| \left|\frac{\partial\vec{\mu}^B}{\partial S_j^B}\right| X_{ij} \tag{4}$$

where X_{AB}^{α} and X_{ij} are given by the directions and locations of the derivatives $\partial\vec{\mu}/\partial Q$ and $\partial\vec{\mu}/\partial S$, respectively. To first order, only interactions between like normal modes Q_{α} on A and B need to be considered. Expressions (3) and (4) can be easily extended for higher-order multipole terms.

In an atomic partial charge model of V^{ES}, the molecular charge distribution is represented by partial charges q_i located on the atoms. The intermolecular Coulombic energy is then

$$V^{qq} = \sum_{i,j=1}^{N} \frac{q_i^{A} q_j^{B}}{r_{ij}} \tag{5}$$

where N is the number of atoms in a molecule and r_{ij} is the distance between atom i of molecule A and atom j of molecule B. In this expression, as in eqn. (1), we assume a unit dielectric constant. In the DPC model, both the charges and the interatomic distances are allowed to change during intramolecular vibrational motion. The force constants expanded in the $\vec{Q}$ basis are then

$$
\begin{aligned}
f_{\alpha\alpha} &= \frac{\partial^2 V^{qq}}{\partial Q_{\alpha}^{A} \partial Q_{\alpha}^{B}} \\
&= \sum_{i,j}^{N} \frac{\partial q_i^{A}}{\partial Q_{\alpha}^{A}} \frac{\partial q_j^{B}}{\partial Q_{\alpha}^{B}} \frac{1}{r_{ij}} + \sum_{i,j}^{N} q_i^{A} \frac{\partial q_j^{B}}{\partial Q_{\alpha}^{B}} \frac{\partial}{\partial Q_{\alpha}^{A}} \frac{1}{r_{ij}} \\
&+ \sum_{i,j}^{N} \frac{\partial q_i^{A}}{\partial Q_{\alpha}^{A}} q_j^{B} \frac{\partial}{\partial Q_{\alpha}^{B}} \frac{1}{r_{ij}} + \sum_{i,j}^{N} q_i^{A} q_j^{B} \frac{\partial^2}{\partial Q_{\alpha}^{A} \partial Q_{\alpha}^{B}} \frac{1}{r_{ij}}
\end{aligned}
\tag{6}
$$

The last term in eqn. (6) represents the FPC model, and the other terms involve the charge fluxes $\partial q/\partial Q$. Cross terms of the form $\partial q^{A}/\partial Q_{\alpha}^{B}$, corresponding to the partial charge changes in A caused by vibrational motion of B, are not included in eqn. (6); these fluxes represent polarization and charge-transfer effects. Using the relation $\vec{X} = L\vec{Q}$, where L is the Cartesian eigenvector matrix, the derivatives of $1/r_{ij}$ in eqn. (6) can be evaluated as

$$\frac{\partial}{\partial Q_{\alpha}^{A}} \frac{1}{r_{ij}} = \sum_{s=1}^{3N} L_{s\alpha}^{A} \frac{\partial}{\partial X_s^{A}} \frac{1}{r_{ij}} \tag{7}$$

and

$$\frac{\partial^2}{\partial Q_{\alpha}^{A} \partial Q_{\alpha}^{B}} \frac{1}{r_{ij}} = \sum_{s,t=1}^{3N} L_{s\alpha}^{A} L_{t\alpha}^{B} \frac{\partial^2}{\partial X_s^{A} \partial X_t^{B}} \frac{1}{r_{ij}} \tag{8}$$

Force constants f_{ij} in the $\vec{S}$ basis are given by expressions analogous to (6); the derivatives of $1/r_{ij}$ with respect to $\vec{S}$ are evaluated using

$$\vec{X} = M^{-1} \tilde{B} (BM^{-1} \tilde{B})^{-1} \vec{S} \tag{9}$$

where B is defined by $\vec{S} = B\vec{X}$ and **M** is the matrix of atomic masses.

In the absence of empirical means of obtaining reliable values for the charges and charge derivatives, we have computed these quantities by quantum mechanical methods. Whereas molecular multipole moments are well-defined quantities, atomic charges are not; we have used Mulliken populations in our work. On the other hand, the location of a point molecular moment is arbitrary; we have placed the dipole derivatives $\partial\vec{\mu}/\partial Q_\alpha$ at the center of mass of the FA monomer, and the derivatives $\partial\vec{\mu}/\partial S_i$ at bond centers (for bond-stretch coordinates) or between bonds (for angle-bend coordinates).

CALCULATIONS

The formic acid dimer geometry used in all our calculations was the 4-31G optimized structure of Hayashi et al. [9]; the same bond lengths and angles of each moiety were used in calculations on the FA monomer. Dipole moment and partial charge derivatives were evaluated by numerical differentiation; the atoms were displaced along the normal coordinates $\vec{Q}$ (by ± 0.1 Å $u^{1/2}$ for the C=O str mode, u being the atomic mass unit), or along the local symmetry coordinates $\vec{S}$ (bonds were distorted by ± 0.01 Å and angles ± 0.025 rad). The corresponding Cartesian displacements are given by $\vec{X} = L\vec{Q}$ or by eqn. (9). The $\vec{S}$ coordinates for a monomer are given in Table 1, and the Cartesian axes are oriented as in Fig. 1. To get the eigenvector matrix L, we used the empirical valence force field of Ovaska [4], which gives better frequency agreement than the ab initio sets [9, 10]. (Karpfen's ab initio intramonomer force constants [10] give a very similar eigenvector for the C=O str mode.) This force field was refined for the FA dimer and includes some intermonomer terms; we used only the intramonomer part, resulting in degenerate g and u frequencies in the dimer, since our aim is to derive a set of intermonomer force constants.

In keeping with the usual definition of the electrostatic energy as the interaction between the undistorted charge distribution of the monomers, we computed the partial charges and the dipole and charge derivatives for the FA monomer. To see the effect of dimerization, we computed the dipole derivatives with respect to $\vec{S}$ for a monomer in the dimer configuration. From these dipole and charge parameters, we derived the intermonomer force constants as described in the Theory section. To compare with these force constants obtained from dipole—dipole and charge—charge interaction models, we also computed the interaction terms directly by the energy-gradient method [21]; that is, in the dimer configuration, the atoms were displaced along $\vec{S}$ and the force constants were obtained from the analytical first derivatives of the SCF energy. Lastly, by displacing the dimer along the zero-order g and u C=O str normal coordinates given by the empirical force field, $Q_g = 2^{-1/2} (Q_\alpha^A + Q_\alpha^B)$ and $Q_u = 2^{-1/2} (Q_\alpha^A - Q_\alpha^B)$, Q_α^A and Q_α^B being the normal coordinates for the isolated monomers, we calculated the

TABLE 1

Dipole moment derivatives (in D A^{-1} or D rad^{-1}) for in-plane coordinates of formic acid calculated with the 4-31G basis

S	Monomer			Dimer		
	$\dfrac{\partial\mu_x}{\partial S}$	$\dfrac{\partial\mu_y}{\partial S}$	$\left\|\dfrac{\partial\vec{\mu}}{\partial S}\right\|$	$\dfrac{\partial\mu_x}{\partial S}$	$\dfrac{\partial\mu_y}{\partial S}$	$\left\|\dfrac{\partial\vec{\mu}}{\partial S}\right\|$
C=O str	−1.920	5.465	5.792	−3.000	+5.830	6.557
C—O str	−1.520	−5.225	5.442	−1.570	−4.590	4.851
COH bend	0.448	1.784	1.839	−0.154	1.836	1.842
OCO bend[a]	2.418	1.545	2.869	2.229	1.680	2.791
C—H rock[b]	−0.080	0.240	0.253	−0.109	0.307	0.326
C—H str	0.305	0.015	0.305	0.345	0.075	0.353
O—H str	1.315	0.380	1.369	4.195	0.050	4.195

[a] Defined as $(2\Delta\theta(O=C-O) - \Delta\theta(H-C=O) - \Delta\theta(H-C-O))/(6)^{1/2}$. [b] Defined as $(\Delta\theta(H-C=O) - \Delta\theta(H-C-O))/(2)^{1/2}$.
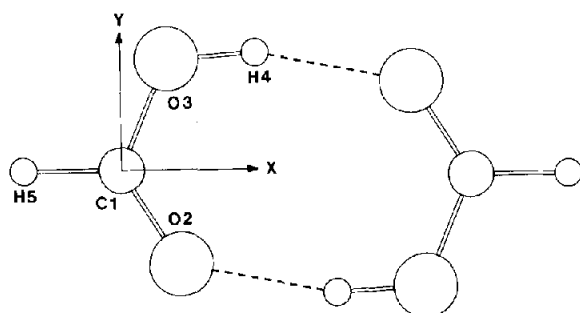

Fig. 1. Structure and coordinate axes for formic acid dimer.

respective diagonal force constants, $\partial^2 V/\partial Q_g^2$ and $\partial^2 V/\partial Q_u^2$, and hence the perturbed g and u frequencies and their splitting. The relation used here is $4\pi^2 c^2 \nu^2 = \lambda$, where $\lambda = \partial^2 V/\partial Q^2$ is the normal coordinate force constant, and from which we get ν (cm^{-1}) = 1302.78 $(\lambda(\text{mdyn Å}^{-1} \text{ u}^{-1}))^{1/2}$.

Thus, the intermonomer force constants were evaluated in three ways: (i) from the electrostatic models using ab initio dipole and charge parameters; (ii) from the ab initio energy gradient with respect to $\vec{S}$; and (iii) from the ab initio energy gradient with respect to Q_g and Q_u. The 4-31G, 6-31G and 6-31G** basis sets were used in (i); only the 4-31G and 6-31G bases were used in (ii) and (iii).

In doing displacements along $\vec{S}$ in the dimer configuration, the cyclic redundancies among the internal coordinates in the ring must be considered. Because the coordinates are not independent, it is impossible to stretch a C=O bond, for instance, without also deforming other coordinates. To allow

inversion of the $BM^{-1}\widetilde{B}$ matrix in eqn. (9), which otherwise would be singular, we arbitrarily removed the redundancies by ignoring the $H \cdots O$ stretch and the $O-H \cdots O$ and $C=O \cdots H$ bend coordinates. Consequently, the dipole derivatives and force constants in the $\widetilde{S}$ basis in the dimer implicitly contain contributions from these coordinates.

The frequency shifts caused by the intermonomer force constants were calculated by the perturbation expression [11]

$$\Delta\nu_\alpha = (848619/\nu_\alpha)\,f_{\alpha\alpha} \text{ cm}^{-1} \tag{10}$$

where $f_{\alpha\alpha}$ is in mdyn $\text{Å}^{-1}\,\text{u}^{-1}$ and the unperturbed frequency ν_α has the value 1700 cm^{-1} (for both A_g and B_u carbonyl modes) with Ovaska's [4] force field. Splittings result from the opposite directions of the shifts for the g and u modes.

For the ab initio calculations, we used a version of the GAUSSIAN76 program [22], augmented by Schlegel's gradient program FORCE [23]. Quadrupole moments, for which no results are reported here for the reason given in the Introduction, were evaluated with the properties package of GAUSSIAN79 [24].

RESULTS AND DISCUSSION

Table 1 shows the dipole moment derivatives $\partial\vec{\mu}/\partial S_i$ for the FA monomer and dimer. For brevity, we list only the 4-31G results. This basis gives an equilibrium dipole moment of 1.870 D for the FA monomer, compared to an experimental value [25] of 1.415 D; with the larger bases, the overestimation of the static moment is worse. Furthermore, using the 4-31G set and the empirical force field of Ovaska [4], we get an integrated IR intensity for the C=O str mode in the monomer of 445 km mol^{-1}; the measured value for this mode in acetic acid [26] is 390 km mol^{-1}. The results show that the O—H str derivative increases by three times on dimerization; this agrees with the factor of 8.7 increase in the intensity of the O—H str mode in acetic acid [26] from monomer to dimer. The increase in the C=O str derivative is less, and the C—O str derivative unexpectedly decreases on formation of the hydrogen bonds.

The partial charges and their derivatives calculated with the 6-31G** basis are given in Table 2. It can be seen that all charges and derivatives add up to zero (columnwise). The arbitrary nature of atomic partial charges derived from Mulliken population analysis is well known [27]. Nevertheless, recent studies [28] of IR intensities show that atomic charges derived using bond-charge models to fit experimental intensities agree very closely with Mulliken charges at the 6-31G** level. Our 6-31G** charges may be compared with the set of empirical charges found by Lifson et al. [29] from an analysis of amide and carboxylic acid structures (their 6-9-1 set III): $q(C_1) - q(H_5) =$ 0.39, −0.46, −0.46, 0.42, and 0.11 electron units. A further comparison is possible with the set of atomic charges derived by Cox and Williams [30]

TABLE 2

Atomic partial charges (in atomic units) and partial charge derivatives of the formic acid monomer in the 6-31G** basis

Atom	q	$\dfrac{\partial q}{\partial Q_{carb}}$	$\dfrac{\partial q}{\partial S_i}$						
			C=O str	C—O str	COH b	OCO b	C—H r	C—H str	O—H str
C_1	0.602	−0.004	0.207	0.310	0.027	0.039	0.042	−0.133	0.069
O_2	−0.549	−0.318	−0.735	0.344	0.025	0.042	−0.014	0.069	−0.035
O_3	−0.578	0.162	0.181	−0.770	0.044	−0.021	−0.023	0.006	0.316
H_4	0.381	0.078	0.106	−0.043	−0.104	0.035	0.012	0.072	−0.351
H_5	0.144	0.083	0.241	0.156	0.008	−0.095	−0.016	−0.015	0.001

by fitting to the electrostatic potential field of a monomer computed from the 6-31G** wavefunction for FA: $q(C_1) - q(H_5) = 0.674, -0.628, -0.568, 0.462$, and 0.059 electron units. Finally, we note that it is possible that charge derivatives may be less sensitive than the charges themselves to the problems inherent in the Mulliken partitioning.

That the computed dipole and charge parameters are physically reasonable may also be seen from Table 3. This table shows the values for the three intermonomer force constants in the $\vec{S}$ basis ($f_{C=O,C=O}$, $f_{C-O,C-O}$, and $f_{C=O,C-O}$) that are responsible for most of the B_u-A_g splitting of the C=O str mode. These values were obtained directly from the SCF energy gradient, and from the dipole—dipole and charge—charge interaction models. Also shown are the empirical force constants used by various workers [2—4]. Larger magnitudes of these force constants correspond to larger splittings, and the signs consistent with $\nu(B_u) > \nu(A_g)$ are −, −, and +, respectively. We see that while the dipole—dipole model yields force constants with the proper signs, their magnitudes are only about half the energy-gradient values, indicating the need to include higher multipole moments. On the other hand, the force constants given by the charge—charge model agree very well with those derived from the SCF energy gradient. By examining the separate contributions to these force constants from the charge-flux and FPC terms (analogous to eqn. (6), but in the $\vec{S}$ basis), the importance of the charge fluxes is seen: for the 6-31G** $f_{C=O,C=O}$, compared to the $(\partial q^A/\partial S^A)(\partial q^B/\partial S^B)$ term of −0.130 mdyn Å^{-1}, the FPC term is +0.032 mdyn Å^{-1} and is therefore small and of the wrong sign. The decomposition of $f_{C-O,C-O}$ is similar, and for $f_{C=O,C-O}$, while the FPC term has the correct sign, its magnitude is only 10% of the total.

Comparison of our results in Table 3 with the other force fields is complicated by the different procedures used in handling the cyclic redundancies. The empirical force fields were either defined in a redundant basis [2, 4] or a different set of coordinates was removed to eliminate the redundancies [3]. Nevertheless, except in one instance, the signs of the force

TABLE 3

Some intermonomer interaction force constants (in mdyn Å^{-1}) of the formic acid dimer, in the S basis

	SCF energy gradient (4-31G)	Dipole—dipole[a]		Charge—charge			Empirical		
		I	II	4-31G	6-31G	6-31G**	Ref. 2	Ref. 3	Ref.4
$f_{C=O,C=O}$	−0.183	−0.090	−0.104	−0.152	−0.191	−0.192	−0.1	−0.404	−0.555
$f_{C-O,C=O}$	−0.107	−0.063	−0.051	−0.043	−0.071	−0.114	−0.1	0.056	−0.200
$f_{C=O,C-O}$	0.170	0.096	0.100	0.170	0.212	0.237	0.1	0.128	0.0

[a]Dipole—dipole coupling calculated with dipole moment derivatives obtained for the FA monomer (I) and dimer (II) (cf. Table 1).

constants are the same in all sets, even though the magnitudes vary widely. We may also compare our results with the ab initio force constants of Bosi et al. [8] and Karpfen [10]. The former derived $f_{C=O,C=O}$ to be −0.3 mdyn Å^{-1}, but did not calculate the other two interaction terms; Karpfen's values for these three terms are −0.050, −0.161, and 0.146 mdyn Å^{-1}, respectively. The signs agree with ours, though again, the problem of different definitions of the non-redundant coordinates exists. Karpfen's results agree with ours in showing that $f_{C=O,C-O}$ has a large magnitude. Our normal mode calculations show that this interaction has as much effect on the splitting as the $f_{C=O,C=O}$ term.

We now discuss the C=O str splitting. Table 4 shows in the first column the splitting, $\nu(B_u)-\nu(A_g)$, calculated directly from the SCF energy gradient by displacing the dimer along the zero-order normal coordinates Q_g and Q_u. Our 4-31G value of 42 cm^{-1} compares well with that found by Hayashi et al. [9] (44 cm^{-1}) even though these authors computed the full force field ab initio, whereas we used empirical intramonomer force constants [4]. Similarly, the splitting of 56 cm^{-1} given by the larger split-valence basis

TABLE 4

Calculated splitting $\nu(B_u)-\nu(A_g)$ of the C=O stretch frequencies of the formic acid dimer (in cm^{-1})

	SCF energy gradient along Q_g and Q_u	Dipole—dipole[a,b]	Charge—charge[b]
4-31G	42	30	40
6-31G	56	32	53
6-31G**	c	33	56

[a]Based on derivatives for the monomer. [b]Calculated using eqns. (3), (6), and (10). [c]Not calculated.

agrees with the value of 58 cm^{-1} derived by Karpfen [10] from a complete ab initio force field using a double-zeta basis.

Table 4 also shows the splittings given by the dipole—dipole and charge—charge models obtained using eqns. (3), (6) and (10). We see that the dipole—dipole model gives a splitting of at least 30 cm^{-1} and is therefore not negligible, as Bosi et al. [7, 8] had concluded. The larger splittings obtained with the charge—charge model indicate that higher-order multipole terms are necessary. Whereas the dipole—dipole splittings are somewhat insensitive to basis set, the splittings derived from the charge—charge model increase significantly on going from the 4-31G to the 6-31G and 6-31G** bases. At both the 4-31G and 6-31G levels, the charge—charge model gives essentially the full splitting found from the SCF energy gradient. Because the charges and charge derivatives were computed for the monomer, this result implies that intermonomer charge redistribution, i.e. polarization and charge-transfer, do not contribute markedly to the C=O str mode splitting. Analysis of the separate contributions to the splitting again shows the charge-flux terms in eqn. (6) to be essential: the $(\partial q^A / \partial Q^A)(\partial q^B / \partial Q^B)$ term accounts for 45 cm^{-1} of the total of 56 cm^{-1} at the 6-31G** level, and the FPC term is small and of the wrong sign. A closer examination of each atom—atom term in eqn. (6) reveals that the principal contributions to the splitting come from the atom—atom interactions within each O$\cdots$H—O hydrogen bond. While the interaction between the two carbonyl oxygens across the ring is the largest in magnitude, it has the wrong sign; it is primarily because of the presence of two O$\cdots$H—O groups that the net splitting is in the correct direction.

Electrostatic interaction models, therefore, can explain a large part of the splitting of the carbonyl stretch mode in the dimer. The largest splitting calculated is 56 cm^{-1} using the charge—charge model, compared to the observed [1] value of 74 cm^{-1}. We think that an additional contribution to the splitting can be attributed to a difference in anharmonicity of the A_g and B_u modes. If we consider only the diagonal cubic anharmonic force constant $\partial^3 V / \partial Q^3$, we see that by symmetry this term is zero for the B_u mode. A lowering of the A_g mode due to this anharmonic term would therefore contribute entirely to the splitting. (Other anharmonic terms are expected to have smaller effects, and are likely to lead to a smaller differential shift of the A_g and B_u modes.)

To see whether the shift of the A_g mode is indeed of the proper magnitude, we computed the cubic force constants, $\partial^3 V / \partial Q_g^3$ and $\partial^3 V / \partial Q_u^3$, with the 4-31G basis by displacing the dimer along Q_g and Q_u by ± 0.4 Å u$^{1/2}$. The values, obtained by three-point differentiation [21] of the energy gradient, are (in mdyn Å^{-2} u$^{-3/2}$): -2.682 (A_g) and 0.000 (B_u). The B_u diagonal cubic anharmonicity is zero, as expected. Using well-known expressions [31] relating anharmonic force constants to anharmonicity coefficients, we find the shift of the A_g mode due to this cubic anharmonicity to be -13 cm^{-1}. In this derivation we used, for consistency, a harmonic

frequency of 1831 cm^{-1} as computed from the quadratic force constant $\partial^2 V/\partial Q_g^2$. A similar calculation with the 6-31G basis also gives a shift of -13 cm^{-1}. By comparison, Bock et al. [32] found, with the 4-31G basis, a shift of -27 cm^{-1} in the C=O str mode of *trans*-FA monomer due to cubic and quartic internal coordinate force constants. Thus, anharmonicity can indeed account for most of the discrepancy between the observed splitting and that calculated using the charge—charge interaction model. (The potentials (1) and (5) are, of course, anharmonic, but to derive cubic force constants from them would require higher derivatives of the dipole moment and charges.)

Thus, the large g—u splitting of the C=O str mode in carboxylic acid dimers seems to be mainly a consequence of their structure: the closeness and relative orientation of the monomers brought about by the cyclic hydrogen bonding configuration result in large electrostatic vibrational interactions, and the particular symmetry of the structure leads to a difference in anharmonicity of the g and u modes that adds to the observed splitting. A similar explanation probably applies to the g—u C=O str mode splitting in crystalline diketopiperazine [5, 20].

CONCLUSIONS

We have demonstrated that simple electrostatic models can account for most of the observed splitting in the carbonyl stretch mode of the formic acid dimer. While electron-correlation effects, not included in our Hartree—Fock calculations, may well be important, we have shown that anharmonicity can explain most of the remaining discrepancy; these effects are therefore likely to be small.

Our results show that a proper application of the dipole—dipole coupling model does give a large splitting, contrary to previous conclusions [7], and thus indicate the physical origin of at least part of the observed splitting.

The good results obtained with the charge—charge interaction model show the feasibility of using dynamical partial charges from ab initio calculations to study molecular interactions and properties. It remains to be seen whether charge fluxes such as $\partial q/\partial S_i$ can be transferred between similar molecules, as dipole derivatives $\partial \vec{\mu}/\partial S_i$ seem to be [33].

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