Theoretical modeling of the OH stretch infrared spectrum of carboxylic acid dimers based on first-principles anharmonic couplings

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Carboxylic acid dimers serve as prototypical systems for modeling the unusual spectral behavior of the hydride stretch fundamental. Large anharmonic effects associated with the pair of cooperatively strengthened OH⋯O=C hydrogen bonds produces complicated infrared spectra in which the OH stretch oscillator strength is spread over hundreds of wave numbers, resulting in a complicated band sub-structure. In this work cubic anharmonic constants are computed along internal coordinates associated with the intramolecular OH stretch, intermolecular stretch, and OH bend internal coordinates for the formic acid and benzoic acid dimers. These are then projected onto the normal coordinates to produce mixed states that are used in computing the OH stretch infrared spectrum. For the benzoic acid dimer the calculations accurately reproduce for three deuterated isotopomers the overall breadth and much of the vibrational sub-structure in the observed spectra. For the formic acid dimer, the spectrum is calculated using a model employing a subset of the cubic force constants as well as using the full cubic force field. The spectra calculated for the formic acid dimer are sparser and somewhat more sensitive to the exact positions of the anharmonically coupled states than that of the benzoic acid dimer. Again semiquantitative agreement with experiment is obtained.


I. INTRODUCTION

The hydride stretch region of infrared spectra has long been used to diagnose the presence and strength of hydrogen bonds involving the XH group.1 When an XH group forms a hydrogen bond, the XH stretch fundamental undergoes a large frequency shift, the magnitude of which reflects the strength of the hydrogen bond formed. Accompanying this frequency shift is a corresponding broadening and increase in the infrared intensity of the XH fundamental. The infrared (IR) spectra of the carboxylic acid dimers manifest all of these effects. These species are particularly interesting because they are held together by two cooperatively strengthened OH⋯O=C hydrogen bonds. In symmetric carboxylic acid dimers, such as the formic acid,2–4 acetic acid,5 or benzoic acid6 homodimers shown below, the OH stretch bands are spread over more than 500 cm⁻¹, and exhibit a rich sub-structure that reflects the presence of strong anharmonic couplings.

Formic acid dimer Acetic acid dimer Benzoic acid dimer

Much past theoretical work on these species has sought to determine the most important sources of the broadening and sub-structure in the OH stretch region of the spectra. Here, we return to these issues, motivated by new infrared spectra obtained under supersonic jet conditions of the formic acid dimer,2,3 the acetic acid dimer,5 and three isotopomers of the benzoic acid dimer.6 The cooling under these conditions collapses the population entirely into the zero-point vibrational level (which can be split by tunneling). Furthermore, in the case of the benzoic acid dimer, the double resonance scheme employed (fluorescence-dip infrared spectroscopy) ensures that the observed spectral absorptions are uncontaminated by hot bands, but instead arise purely from the zero-point level, with a rotational distribution in the 3–5 Kelvin temperature range.5 Such conditions resolve sub-structure that would be obscured in the presence of hot bands. Furthermore, the selectivity of the double resonance scheme also enables the acquisition of infrared spectra from individual deuterated isotopomers free from interference from one another.

In a recent paper we presented initial results of a theoretical model which sought to account quantitatively for the structure observed in the OH stretch spectrum of the benzoic acid dimer.6 This model was able to account for the overall breadth of the spectrum as well as for the major sub-structure observed. The present paper provides a full account of the model, building on the initial results in several ways.
In Sec. II the relationship of the current work to prior theoretical approaches to the vibrational spectra of H-bonded dimers is briefly reviewed. Section III develops the theoretical model used in this work. Section IV provides computational results that serve as input for the theory. These involve an extensive set of electronic structure calculations of the geometries, harmonic vibrational frequencies, and key anharmonic constants for the formic acid dimer (FAD) and for the benzoic acid dimer (BAD). The ability of the simple physical model, employing only a subset of the anharmonic couplings, to capture the important physics is established by carrying out for FAD a calculation of the spectrum using the full cubic force field. Finally, in Sec. V, the model is applied to formic acid dimer and three isotopomers of benzoic acid dimer. We shall see that much of the sub-structure in the IR spectra of these dimers can be accounted for by a single cubic anharmonic term coupling the OH stretch and OH bend internal coordinates.

II. BACKGROUND MATERIAL

The goal of the present study is to generate vibrational spectra of FAD and BAD in the region of the OH fundamental, allowing for cubic couplings. There is a considerable body of previous theoretical work in this area starting with the early studies of Bratos and Hadzi and Sheppard. For a recent review, the reader is referred to the work of Chamma and Henri-Rousseau. In cyclic H-bonded dimers the main couplings appear to be Davydov coupling between the two localized OH stretch vibrations, Fermi coupling between the OH stretch and nearly resonant combination bands, and coupling between OH stretch and interdimer H-bond vibrations.

Maréchal and Witkowski have modeled the complex structure of the acetic acid dimer using an adiabatic treatment that describes the coupling of the high frequency X-H and low frequency X-Y vibrations. This model, using empirically determined coupling constants, provided good agreement with experiment. Wójcik et al. used instead ab initio methods to calculate the relevant cubic potential couplings and concluded that the coupling between the OH stretch and intermolecular H-bond vibrations does not account for the observed spectrum. However, because the calculations were at the Hartree–Fock level and employed the small 4-31G basis set, the results should be considered qualitative at best.

Subsequently Maréchal reanalyzed the IR spectra of carboxylic acid dimers in the gas phase, highlighting the role of the so-called “parasitic” Fermi resonances. From his perspective, Fermi resonances complicate the analysis of the IR spectra, hiding the more interesting, temperature-dependent effects of the coupling of the OH stretch with the lower frequency modes. Using an elegant deconvolution procedure, Maréchal removed the effects of the Fermi resonances, obtaining spectra, with relatively narrow full width at half maximum (FWHM), and which, in principle, include effects due to coupling with the low frequency modes only. To the best of our knowledge, there has been no attempt to verify these results by comparing with spectra calculated using ab initio values of the coupling constants.

Very recently, Ito and Nakanaga have obtained high-resolution jet-cooled infrared spectra of FAD by cavity ring down spectroscopy. These low temperature spectra are much less congested than the earlier room temperature spectra, as expected if coupling to low-frequency modes were the dominant contributors to the width of the spectra in the latter and supporting the conclusions of Maréchal.

III. THEORETICAL MODEL

This section describes the calculation of potential couplings and the theoretical models used to calculate the vibrational spectra of BAD and FAD. For BAD only a limited set of potential couplings are calculated, with the choice of couplings being motivated by the prior studies described above. In particular, we incorporate the cubic force constants that couple the OH stretch to the OH bending and to the intermolecular H-bond stretching degrees of freedom. In order to test the appropriateness of this truncated cubic force field approach, it was also applied to FAD, for which spectra are also calculated using the full cubic force field.

We first describe the truncated force field model, as applied to BAD. However, other than the labeling of the coordinates, and the need to account also for the CH stretch vibrations, the model is also applicable to FAD. The calculation of the IR spectra proceeds via a three-stage process. We first choose local internal coordinates that are linear combinations of the normal coordinates. Although there is no fundamental reason for the internal coordinates to be linearly related to the normal coordinates, this choice simplifies the transformation between the two coordinate systems. We then obtain using electronic structure methods a restricted cubic force field as a function of the internal coordinates. The resulting force field is then re-expanded as a function of the normal coordinates. The vibrational spectrum is obtained by diagonalizing the resulting Hamiltonian in a basis set that consists of states that are directly coupled to the OH fundamental, and, as such, the resulting spectrum includes all possible coupling mechanisms considered in earlier research. The remainder of this section describes these steps in more detail.

A. Choice of coordinates

The standard approach for determining the relation between internal coordinates, \( \mathbf{R} \), and Cartesian coordinates, \( \mathbf{x} \), is to construct the \( \mathbf{B} \)-matrix of Wilson, Decius, and Cross

\[
\mathbf{R} = \mathbf{Bx}. \tag{1}
\]

The Cartesian coordinates, in turn, are linearly related to the normal coordinates \( \mathbf{Q} \) via the \( \ell \)-matrix as

\[
\mathbf{x} = \ell \mathbf{Q}, \tag{2}
\]

which itself is the output of a normal mode calculation. Combining Eqs. (1) and (2), we obtain the transformation between internal and normal coordinates

\[
\mathbf{R} = \mathbf{BQ} = \ell \mathbf{Q}. \tag{3}
\]

For the set of \( \mathbf{R} \) coordinates to be linearly related to the normal coordinates, the elements of the \( \mathbf{B} \)-matrix must be
The OH stretch infrared spectrum of carboxylic acid dimers

B. Choice of cubic coupling terms

In the truncated cubic force field, the key coupling terms involving the OH stretch fundamentals are divided into two contributions:

\[ V = V_{sb} + V_{ss} \]

where \( V_{sb} \) is the OH stretch–bend force field which takes the form

\[ V_{sb} = f_{345} R_3 R_4 R_5 + \frac{1}{2} f_{122} R_1 R_2 R_5 + \frac{1}{2} f_{244} R_2 R_4 R_5, \]

and \( V_{ss} \) is the OH stretch-H-bond stretch force field which is of the form

\[ V_{ss} = \frac{1}{2} f_{122} R_1 R_2 R_3 + \frac{1}{2} f_{133} R_1 R_3 R_3. \]

C. Calculation of spectra

To calculate the spectra, the potential given by Eqs. (5)–(7) is re-expressed in terms of the normal coordinates using Eq. (4). This yields the cubic force field

\[ V(Q) = \frac{1}{6} \sum_i \sum_j \sum_k F_i,j,k Q_i Q_j Q_k. \]

This is tantamount to projecting the potential couplings involving the OH stretch modes onto the normal coordinates of the molecule. The largest contributions to the potential of Eq. (8) can be separated into stretch–stretch and stretch–bend components as in Eq. (5). For \( h6-h6 \) BAD this is straightforward, since the antisymmetric OH stretch character and the interdimer stretch character are both contained primarily in one normal coordinate (\( Q_{12} \), \( Q_{77} \), respectively). (The numbering scheme for the normal modes of BAD is defined in Table III, below.) The coupling terms involving the symmetric OH stretch normal coordinate have been omitted since this mode is infrared inactive, but these terms are necessary when considering the partially deuterated BAD isomers. With this in mind, Eq. (8) reduces in the case of BAD to

\[ V(Q) = \frac{1}{2} \sum_i \sum_j F_{i,j,12} Q_i Q_j Q_{12} + \frac{1}{2} F_{77,12,12} Q_{77} Q_{12} Q_{12}. \]

The first term includes the stretch–bend coupling that leads to Fermi resonances, and the second term corresponds to the stretch–stretch coupling that leads to progressions in the interdimer mode. It is important to note that the term involving the sum over \( i \) and \( j \) also includes coupling to normal modes other than the COH bends. This is a consequence of the bend local modes having sizable projections onto several normal modes.

The cubic force field is combined with the standard normal-mode Hamiltonian, and the spectrum calculated by diagonalizing the resulting Hamiltonian matrix in a basis set that includes the ground state, the IR active OH stretch fundamental, all combination states that are directly (Fermi) coupled to this fundamental and that have energies within 600 cm\(^{-1}\) of the fundamental. In addition, the basis includes progressions built on these vibrational states (including the zero-point level) involving the low-frequency interdimer nor-
TABLE I. The key geometrical parameters [cf. Fig. 1(b)] of the formic and benzoic acid monomer and dimers.

<table>
<thead>
<tr>
<th></th>
<th>Formic acid</th>
<th>Benzoic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B3LYP</td>
<td>MP2</td>
</tr>
<tr>
<td></td>
<td>6-31+G(d)</td>
<td>6-311+G(2d,p)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>r_1 (Å)</td>
<td>1.202±0.003</td>
<td>1.205</td>
</tr>
<tr>
<td>r_2 (Å)</td>
<td>1.343±0.003</td>
<td>1.345</td>
</tr>
<tr>
<td>r_3 (Å)</td>
<td>1.097±0.021</td>
<td>1.097</td>
</tr>
<tr>
<td>r_4 (Å)</td>
<td>0.972±0.017</td>
<td>0.978</td>
</tr>
<tr>
<td>(\Theta_1) (deg)</td>
<td>124.6±0.5</td>
<td>125.1</td>
</tr>
<tr>
<td>(\Theta_2) (deg)</td>
<td>124.1±3.1</td>
<td>125.3</td>
</tr>
<tr>
<td>(\Theta_3) (deg)</td>
<td>106.3±0.4</td>
<td>107.8</td>
</tr>
</tbody>
</table>

aReferences 19 and 20.

bThe experimental geometrical parameters for the benzoic acid dimer are from x-ray diffraction measurements (Ref. 27).

bB3LYP/6-31+G(2d,2p)/6-31+G(d) (see text).

cAssumed in refinement of electron diffraction data.

Analysis of vibrational spectra was performed using the cubic force field. An interesting observation is that the calculated frequencies for the monomer and dimer are nearly identical with these two basis sets, as are the harmonic frequencies close to the MP2 values, these results provide strong evidence that the B3LYP method does not provide a quantitatively correct description of this aspect of the H-bonding in the FAD dimer. For BAD, the B3LYP procedure was used for optimizing the geometry, calculating the harmonic frequencies and normal modes, and for calculating the cubic force field of molecules of this size. In this case, the geometry was optimized using the cubic force field, and the MP2 calculations give shifts in the OH stretch frequencies in going from FA to FAD, about 116 cm\(^{-1}\) smaller than those obtained from the B3LYP calculations. Since quadratic CI with single and double excitations (QCISD) calculations (results not tabulated) give harmonic frequencies close to the MP2 values, these results provide strong evidence that the B3LYP method does not provide a quantitatively correct description of this aspect of the hydrogen bonding.

For BAD, the B3LYP procedure was used for optimizing the geometry, calculating the harmonic frequencies and normal modes, and for calculating the cubic force field of the benzoic acid dimer. In this case, the geometry was optimized using the cubic force field, and the MP2 calculations give shifts in the OH stretch frequencies in going from FA to FAD, about 116 cm\(^{-1}\) smaller than those obtained from the B3LYP calculations. Since quadratic CI with single and double excitations (QCISD) calculations (results not tabulated) give harmonic frequencies close to the MP2 values, these results provide strong evidence that the B3LYP method does not provide a quantitatively correct description of this aspect of the hydrogen bonding.
cal parameters and harmonic frequencies of BAD as well as the monomer.

Although Ref. 29 assigned a band at 1450 cm$^{-1}$ to this fundamental, we omit it because it does not show up in high-resolution gas-phase spectra (Ref. 31). This assignment was also rejected in Ref. 21.

The cubic anharmonicity constants of FAD were calculated using the B3LYP and MP2 methods, in both cases, employing the 6-31+G(2d,p) basis set, whereas those for BAD were calculated using the B3LYP/mixed basis set approach. Table IV summarizes the most important anharmonicity constants from these calculations. For FAD, the B3LYP and MP2 procedures are found to give similar anharmonicity constants, with the MP2 values generally being only about 3%–5% larger than the B3LYP values. This close agreement justifies the use of the B3LYP method for evaluating these constants.

Table V compares for FAD the Fermi resonance coupling terms calculated using the restricted and full force fields. In those cases that the couplings are large in magnitude, the B3LYP and MP2 coupling terms agree to within 30%. The agreement between the coupling constants calculated using the truncated and full cubic force fields (both using the B3LYP method) is less satisfactory. However, even so, the coupling constants calculated using the truncated force field agree to within a factor of 2 (and generally much better) with those from the full force field in all cases that the latter are greater than 30 cm$^{-1}$ in magnitude. This agreement suggests that the main source of the Fermi coupling is via the $f_{345}$ stretch-bend coupling. Table V also reports the empirical frequencies and couplings used by Marechal. Given that this was a restricted empirical fit, one cannot expect more than the rough qualitative agreement that is observed.
TABLE III. Calculated harmonic and experimental frequencies (cm$^{-1}$) of benzoic acid monomer and dimer.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Monomer B3LYP</th>
<th>Dimer B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>COOH modes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu$OH</td>
<td>A'</td>
<td>3567</td>
</tr>
<tr>
<td>$\nu$(C==O)</td>
<td>A''</td>
<td>1752</td>
</tr>
<tr>
<td>$\nu$(C–O)</td>
<td>A'</td>
<td>1347</td>
</tr>
<tr>
<td>$\delta$OH</td>
<td>A'</td>
<td>1169</td>
</tr>
<tr>
<td>$\pi$OH</td>
<td>A''</td>
<td>628</td>
</tr>
<tr>
<td>$\delta$CO$_2$</td>
<td>A'</td>
<td>384</td>
</tr>
<tr>
<td>Rock</td>
<td>A'</td>
<td>216</td>
</tr>
<tr>
<td>Wag</td>
<td>A''</td>
<td>160</td>
</tr>
<tr>
<td>Twisting</td>
<td>A''</td>
<td>71</td>
</tr>
</tbody>
</table>

Intermolecular modes

<table>
<thead>
<tr>
<th>Mode</th>
<th>Monomer B3LYP</th>
<th>Dimer B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-bond stretch</td>
<td>A'</td>
<td>77</td>
</tr>
<tr>
<td>H-bond shearing</td>
<td>A'</td>
<td>78</td>
</tr>
<tr>
<td>Tilting</td>
<td>A'</td>
<td>81</td>
</tr>
<tr>
<td>Cogwheel</td>
<td>A'</td>
<td>82</td>
</tr>
<tr>
<td>Torsion</td>
<td>A'</td>
<td>83</td>
</tr>
<tr>
<td>Butterfly</td>
<td>A'</td>
<td>84</td>
</tr>
</tbody>
</table>

*The characterization of the atomic displacements corresponding to the normal modes of BA/BAD are taken from Ref. 32.

V. COMPARISON WITH EXPERIMENT

A. Benzoic acid dimer isotopomers

Figure 2 presents stick spectra for the fully protonated [d$_{0}$-d$_{0}$, Fig. 2(a)], ring-deuterated [d$_{5}$-d$_{5}$, Fig. 2(b)], and ring-deuterated–H/O–D [d$_{5}$-d$_{6}$, Fig. 2(c)] BA dimers, computed using the cubic anharmonic constants and, with the exception of the IR active OH stretch vibration, fundamental frequencies obtained using the B3LYP/mixed basis set calculations. The OH stretch fundamental was assigned a frequency of 2950 cm$^{-1}$. The experimental spectra presented directly above the calculated spectra have been reported previously. This earlier study also reported a spectrum calculated using the force field described in Eq. (8) and using B3LYP force constants, but with the 6-31+G* basis set on all atoms.

The over-all width and major substructure of the observed bands of the three isotopomers of BAD are remarkably well reproduced by the calculated spectra, particularly in the low-frequency region of the spectrum. For all three isotopomers, the high-frequency region above 2950 cm$^{-1}$ is much more congested in the experimental spectrum than in that calculated using the truncated cubic force field. The calculations reveal that most of the combination bands that gain intensity from coupling to the O–H stretch also have contributions from the C–O stretch (in combination with a vibration that contains some O–H bend character). The cubic anharmonic constants used in the present model (Table V) do not include cubic couplings involving the C–O stretch local mode, which might be anticipated to be coupled to the O–H stretch, since the two groups are H-bonded to one another. It is anticipated that refinement of the model to include this coupling would fill in much of the structure missing in the calculated spectrum.

As our earlier study led us to believe, in all three BAD...
isotopomers, it is the coupling via $f_{345}$ of the $B_u$ O–H stretch with the $B_u$ symmetry combination bands involving the O–H bend that dominates the spectrum. In fact, the O–H stretch/intermolecular stretch coupling ($f_{133}$), which has often been invoked to explain the appearance of the O–H stretch spectrum in strongly H-bonded dimers, appears not to be important in the spectra of the carboxylic acid dimers. These results are consistent with the conclusion of Marechal. In a series of test calculations we have found that the magnitude of $f_{133}$ would have to be increased from its calculated value by a factor of 5 or more for the structure from the intermolecular stretch to significantly contribute to the breadth and spectral congestion of the spectrum.

**B. Formic acid dimer**

Figure 3 compares the experimental cavity ringdown spectrum of Ito and Nakanoaga [Fig. 3(a)] with the stick spectrum computed using the restricted force field analogous to that used for BAD [Fig. 3(b)]. The cubic force constants used in the model are from B3LYP/6-311+G(2d,p) calculations as are the frequencies, with the exception of the asymmetric OH stretch fundamental which was set to 2950 cm$^{-1}$, the same value as was chosen for BAD.

The poor agreement of the calculated spectrum with experiment is disappointing, with the simple model predicting a spectrum dominated by just two strong IR transitions, whereas the observed spectrum is far more complicated. This raises the question why the reduced cubic force field model works so much better for BAD than FAD.

One possible explanation for the greater success of the reduced model for BAD than for FAD is the larger number of near resonant states in the former. In particular, in FAD the OH local bend modes involve contributions from only the

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**TABLE V.** Cubic coupling constants (cm$^{-1}$) in dimensionless normal coordinates for the formic acid dimer.

| Energy$^a$ | Coupling$^b$ | Coupling$^c$ | Coupling$^d$ | Energy$^e$ | | Assignment |
|-----------|-------------|-------------|-------------|-----------|----------|
| 1960      | -16.80      | -16.06      | -19.61      | 2420      | 70       | $\delta_{C-O}(Ag)$ $\delta_{C-O}(Bu)$ |
| 2148      | -10.59      | -10.34      | -7.68       | 2520      | 70       | $\delta_{C-O}(Bu)$ $\delta_{C-O}(Ag)$ |
| 2341      | 15.71       | 12.74       | 39.81       | 2640      | 95       | $\delta_{C-H}(Bu)$ $\delta_{C-H}(Ag)$ |
| 2756      | -22.00      | -13.82      | -19.20      | 2860      | 45       | $\delta_{C-H}(Bu)$ $\delta_{C-H}(Ag)$ |
| 2592      | -11.09      | -6.54       | -2.29       | 2976      | 95       | $\delta_{C-H}(Ag)$ $\delta_{C-H}(Bu)$ |
| 2654      | -29.86      | -30.00      | -55.72      | 2996      | 55       | $\delta_{C-H}(Ag)$ $\delta_{C-H}(Bu)$ |
| 2664      | -38.15      | -35.04      | -58.59      | 2630      | 95       | $\delta_{C-H}(Ag)$ $\delta_{C-H}(Bu)$ |
| 2737      | 15.46       | 7.09        | -15.01      | 2810      | 40       | $\delta_{C-H}(Ag)$ $\delta_{C-H}(Bu)$ |
| 2797      | 20.98       | 15.40       | 15.59       | 2810      | 40       | $\delta_{C-H}(Ag)$ $\delta_{C-H}(Bu)$ |
| 2809      | 53.32       | 38.01       | 28.22       | 2765      | 45       | $\delta_{C-H}(Ag)$ $\delta_{C-H}(Bu)$ |
| 2869      | 72.35       | 82.54       | 70.94       | 2850      | 55       | $\delta_{C-H}(Ag)$ $\delta_{C-H}(Bu)$ |
| 2887      | -13.95      | -12.80      | -30.91      | 2930      | 45       | $\delta_{C-H}(Ag)$ $\delta_{C-H}(Bu)$ |
| 2955      | -6.56       | -5.81       | -15.14      | 2930      | 45       | $\delta_{C-H}(Ag)$ $\delta_{C-H}(Bu)$ |
| 3032      | 19.54       | 13.88       | 20.66       | 3025      | 65       | $\delta_{C-H}(Ag)$ $\delta_{C-H}(Bu)$ |
| 3092      | 26.52       | 30.15       | 31.06       | 3085      | 70       | $\delta_{C-H}(Ag)$ $\delta_{C-H}(Bu)$ |
| 3116      | 4.62        | 2.98        | 9.39        | 3165      | 25       | $\delta_{C-H}(Ag)$ $\delta_{C-H}(Bu)$ |
| 3188      | 15.91       | 15.98       | 16.67       | 3165      | 25       | $\delta_{C-H}(Ag)$ $\delta_{C-H}(Bu)$ |

$^a$Transition frequencies calculated using experimental fundamental frequencies of Bertie and Michaelin (Ref. 19) with the exception of the $\delta_{C-H}(Bu)$ and $\delta_{C-H}(Ag)$ modes whose frequencies were taken to be 1447 and 1422 cm$^{-1}$, respectively.

$^b$Couplings calculated with MP2/6-311+G(2d,p) using Eq. (8).

$^c$Couplings calculated with B3LYP/6-311+G(2d,p) using Eq. (8).

$^d$DFT results for full cubic force field.

$^e$Results of Marechal (Ref. 12).
an aside, it should be noted that this motion corresponds to double proton transfer, which our potential model does not describe even qualitatively. The work of Vener et al. suggests that one quantum of excitation of this mode is sufficient to surmount the barrier to tunneling.

The intense peak observed at 2937.7 cm\(^{-1}\) in the IR spectrum of FAD is due to the CH stretch as has been clearly demonstrated by the isotopic substitution study of Ito and Nakanaga. To obtain a theoretical peak of similar intensity in the calculated spectrum displayed in Fig. 3(c) it was necessary to increase the B3LYP dipole moment derivative for the CH stretch by a factor of 1.4. The surprisingly large intensity of this peak is due to the fact that the CH and OH stretch normal modes are admixtures of the CH and OH stretch local modes; hence the CH stretch vibration borrows its intensity from the OH stretch. Thus, it appears that the B3LYP calculations underestimate the extent of mixing of the OH and CH stretches. With the adjustment of the CH dipole moment derivative, the theoretical spectrum calculated using the full cubic force field and experimental fundamentals is in qualitative agreement with experiment, especially in regard to the broad spectral width and the major contributions to the sub-structure.

Given the striking dissimilarity between the spectra reported in Figs. 3(b) and 3(c), obtained using the truncated and full cubic force fields, respectively, it is worthwhile examining in detail the differences between the two calculations. Figure 4 presents a series of calculated spectra that test the full cubic results against the restricted analysis, with various terms selectively removed or adjusted. Figures 4(a) and 4(b) examine the sensitivity of the calculated spectrum to the choice of the fundamental frequencies for the OH bend vibrations. This test was carried out because there is an ambiguity in the experimental value of the frequency of the \(B_u\) OH bend vibration. Although Bertie and Michaelian attributed a very weak feature observed near 1450 cm\(^{-1}\) to the \(B_u\) OH bend vibration, this is in disagreement with force field and electronic structure calculations that place the frequency of the \(B_u\) OH bend about 25 cm\(^{-1}\) below that of the \(A_g\) OH bend vibration. This has led Qian and Krimm to reject the assignment of the weak 1450 cm\(^{-1}\) feature to the \(B_u\) OH bend vibration. On the other hand, there appears to be a consensus that the fundamental frequency of the symmetric \((A_g)\) OH bend vibration is 1415 cm\(^{-1}\).

The theoretical spectrum reported in Fig. 4(a) was obtained with the choice of 1447 and 1422 cm\(^{-1}\) for the frequencies of the \(A_g\) and \(B_u\) OH bend fundamentals, respectively, with this state ordering and splitting being chosen to be consistent with the MP2 calculations. While this choice places the \(A_g\) vibration 32 cm\(^{-1}\) higher than experiment, this may simply be a reflection of the need to include higher frequency fundamentals and higher-order couplings. For comparison, Fig. 4(b) retains the Bertie and Michaelian assignments of 1415 and 1450 cm\(^{-1}\) for the \(A_g\) and \(B_u\) OH bends. As such, this figure is the same as Fig. 4(c) with the exception that here we have used the \(ab\ initio\) dipole derivatives, with the result that the line corresponding to the CH stretch is less intense. The reversal in ordering of the \(A_g\) and \(B_u\) bend modes (compared to the Bertie and Michaelian as-

\[ S(\omega) \]

\[ \omega \]

FIG. 3. Comparison of (a) jet-cooled infrared spectrum of the formic acid dimer obtained by Ito and Nakanaga using cavity ring down (CRD) spectroscopy and (b) and (c) \(T=0\) K theoretical stick spectra. The spectrum in (b) assumes a restricted cubic force field that couples harmonic modes whose frequencies are obtained using DFT; (c) is calculated using the full cubic force field that couples harmonic oscillators whose frequencies are obtained from experiment and includes contributions from the CH stretch bright state. Also shown are the results of spectral broadening with a Gaussian line shape. See text for details.

OH bend and C==O stretch normal modes, whereas in BAD the CH bends are important as well. The two major peaks in the calculated spectrum of FAD shown in Fig. 3(b) are due to the strong Fermi resonance interaction between the OH bend combination state \(v_1 + v_8\) (1488 + 1454 = 2942 cm\(^{-1}\)) and the OH stretch \(v_1\). The \(v_5 + v_7\) (1765 + 1488 = 3253 cm\(^{-1}\)) and \(v_6 + v_9\) (1691 + 1454 = 3145 cm\(^{-1}\)) combination states involving OH bends and C==O stretches, are far enough out of resonance to be much less important borrowers of intensity.

For FAD, calculation of the vibrational spectrum using the full \(ab\ initio\) or density-functional theory (DFT) cubic force fields is possible. Figure 3(c) shows the stick spectrum of FAD computed using the full B3LYP/6-311+G(2d,p) cubic force field and experimental values for the fundamental frequencies, with the exception of the \(A_g\) OH stretch fundamental, which has not yet been observed. The frequency of the \(A_g\) OH stretch fundamental was estimated by assuming a splitting of 110 cm\(^{-1}\), close to that obtained in the MP2 calculations, between the two OH stretch fundamentals. This places the \(A_g\) OH stretch fundamental at 3000 cm\(^{-1}\). The calculated spectrum is relatively insensitive to this value.
are results of spectral broadening with a Gaussian line shape.

The removal of the anharmonic terms produces a second-order effect on the spectrum in which the overall width is retained, but the splittings of several bands on the high-frequency end of the spectrum are lost. In Fig. 4(d), all coupling terms involving the intermolecular stretching modes \( Q_{21} \) and \( Q_{23} \) have been removed from the spectrum. Again, the overall width of the spectrum is retained. Table VI indicates which combination states are involved in the spectrum reported in Fig. 4(d) and how they contribute to the intensity sharing. These results thereby confirm the dominant role of the stretch-bend coupling term in determining the width of the spectrum of FAD, as it was for that of BAD.

Figure 4(e) results from using the restricted cubic force field, which includes the low frequency modes. The spectrum of Fig. 4(e) has an appearance very similar to that of Fig. 4(d) above it. This visual comparison makes clear the major difference between the full and restricted cubic anharmonic analyses of FAD; namely, that the calculations with the restricted cubic force field predict very little coupling with the low-frequency modes of the dimer. In general, we find that the restricted analysis significantly underestimates the couplings to the low frequency modes. This is expected to also be the case for BAD. However, as these couplings only make minor contributions to the overall spectral width of the low-temperature spectra of BAD, this is not a serious shortcoming. A second, smaller difference is that in contrast to Fig. 4 there is no peak at 3259 cm\(^{-1}\) in the spectrum reported in Fig. 4(e). The 3259 cm\(^{-1}\) peak is due to the combination band \( v_4 + v_1 \) (3000 + 248 = 3248 cm\(^{-1}\)). Here the symmetric and antisymmetric OH stretches are coupled via an antisymmetric dimer stretching mode. This interaction was not included in the restricted model, since only coupling of the OH stretches to the symmetric dimer stretch modes was considered in Eq. (7). To include coupling to antisymmetric dimer stretches, one would need to extend the restricted model by including terms of the form \( R_2 R_3 R_4 \), where \( R_4 \) is the dimer stretch mode of \( B_u \) symmetry. One would also need a more realistic treatment of the very anharmonic OH symmetric stretch such as that of Vener et al.\(^{18}\)

The results shown in Fig. 4 indicate that state-by-state agreement with experiment is beyond the scope of the present theoretical calculations because the spectral details are very sensitive to the energies of the combination bands. Nonetheless the central features of the spectrum, in particu-
lar, its width, and the mechanisms responsible for these features have been elucidated and understood with our models.

C. Comparing FAD and BAD

The most notable similarity between the FAD and BAD spectra is that they are very broad (300–550 cm$^{-1}$), with the width being due to strong Fermi resonance interactions with background states involving excitation of the OH bends and C$\equiv$O stretches. The low-frequency modes make only minor contributions to the overall width, but they do contribute to the congestion. An important difference between the spectra of these two dimers is that in BAD many additional resonance interactions are possible in the lower frequency region of the spectrum. This is a consequence of the fact that normal mode OH bend vibrations of BAD have contributions from both the OH and CH bends. This leads to a sharing of intensities over many states, which fills in the lower frequency region of the spectrum for BAD. In FAD, the lower frequency portion of the spectra is relatively sparse. A second important difference is that the OH and CH stretch local modes of FAD mix when forming the normal modes. This greatly enhances the intensity of the CH asymmetric stretch of the spectrum. This is a consequence of the fact that normal mode OH bend vibrations of BAD have contributions from both the OH and CH bends. This leads to a sharing of intensities over many states, which fills in the lower frequency region of the spectrum for BAD. In FAD, the lower frequency portion of the spectra is relatively sparse. A second important difference is that the OH and CH stretch local modes of FAD mix when forming the normal modes.

In either case, the remarkable breadth of the OH stretch absorption in the IR spectra of FAD and BAD can be accounted for by the $f_{345}$ term, which is unusually large in these systems. If we were to freeze all the internal coordinates except those described by the $R_1$-$R_3$ coordinates of Eq. (4), then the $f_{345}$ Force constant maps onto a single cubic coupling term in the normal-mode approximation. In dimensionless coordinates, this coupling constant has a magnitude of 370 cm$^{-1}$. This means that two states that were exactly degenerate in the absence of coupling would be split by $\Delta E = 2(370)/\sqrt{8} = 260$ cm$^{-1}$. Gelussus and Thiel have compiled CH stretch–bend coupling parameters for a number of halocarbons. These are typically between 40 and 100 cm$^{-1}$, although they do approach 300 cm$^{-1}$ in CHBr$_3$ and CHI$_3$. The analogous OH stretch–bend anharmonic term of H$_2$O is 134 cm$^{-1}$.

VI. CONCLUSIONS

The present work provides a simple physical picture of the dominant cause for the unusual breadth and sub-structure of the O–H stretch infrared spectrum of carboxylic acid dimers. Cubic anharmonic constants were calculated for FAD and BAD using a set of five key internal coordinates that are closely related to the O–H stretch ($B_6$ and $A_4$), O–H bend ($B_6$ and $A_4$), and intermolecular stretch ($A_4$) vibrational modes. It is found that a single cubic anharmonic coupling term ($f_{345}$), which couples the O–H stretch with appropriate symmetry combination bands accounts for the overall breadth and the dominant sub-structure of the experimental spectra. This term dominates over the $f_{133}$ term that couples the O–H stretch with the intermolecular stretch. A single cubic anharmonicity ($f_{345}$) can have such a profound effect largely because the “pure” O–H bending coordinate included in the model maps onto several normal modes that are spread over several hundred wave numbers. In other words, the component of the O–H bend in several normal modes takes a single (1+1):1 Fermi resonance with the O–H stretch and spreads it over many levels in the 2600–3100 cm$^{-1}$ region consistent with the 500 cm$^{-1}$ width observed experimentally.

While it is satisfying that a single anharmonic constant can account for much of the observed spectra, it is clear that further refinements to the model involving “second tier couplings” would further improve the fit. We have already noted that the high frequency end of the spectrum, which involves C$\equiv$O stretch/O–H bend combination bands, has too little intensity relative to experiment. This points to the need for inclusion of anharmonic terms involving the C$\equiv$O stretch, which have not been taken into account in the present model.

The present study also shows that B3LYP density functional calculations, when used with a suitably flexible basis set, are able to account in a qualitatively correct manner for the cubic anharmonic coupling constants. Although there are indications from the calculations on FAD, that the MP2 procedure is somewhat more reliable for describing the interactions between the monomers of carboxylic acid dimers, given the other approximations, namely, the truncation in the vibrational basis set and the truncation of the force field at cubic terms, it seems justifiable to adopt the B3LYP procedure for obtaining the harmonic frequencies and the cubic force constants needed for calculating the vibrational spectrum.

Finally, it will be important to extend this model and its refinements to a wider range of strongly H-bonded homo- and heterodimers. Recent experimental data on the 2-pyridone dimer (with its two N–H···O=C H-bonds)$^{25}$ and the mixed 2-pyridone/2-hydroxypyridine dimer (with its one N–H···O=C and one OH···N H-bond)$^{26}$ would benefit from a similar analysis. Predictions of the spectra for the DNA base pairs and other very strong single XH···Y H-bonded complexes will also stimulate further experiment and a reassessment of existing spectral data in light of the model.

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APPENDIX: COORDINATE TRANSFORMATIONS

The internal coordinates are given in Eq. (4). In addition to these coordinates we introduce the constraint for overall rotation [cf. Eq. (A1)] and center of mass translation [cf. Eqs. (A2) and (A3)].

$$R_\text{R} = \sum_{i=1}^{N} m_i (x_i z_i - z_i x_i),$$  \hspace{1cm} (A1)
The order of the internal coordinates is chosen so that the transformation matrix allows us to calculate the internal force constants 

\[
\begin{align*}
R_x &= \sum_{i=1}^{N} m_i x_i, \\
R_y &= \sum_{i=1}^{N} m_i y_i, \\
R_z &= \sum_{i=1}^{N} m_i z_i.
\end{align*}
\]  

For benzoic acid there are \( N = 30 \) atoms. Given that we treat the RCOO groups as rigid bodies that are not allowed to rotate and that we are only allowing in-plane motions, the \( x \) and \( z \) coordinates of atoms 3 and 4 serve to define the values of all the coordinates of these groups. As a result, the above Eqs. (A1)–(A3) reduce to 

\[
R_x = \alpha (x_3 - x_4) + \beta (x_1 - x_2) - \gamma (z_3 - z_4) - \delta (z_1 - z_2),
\]

\[
R_y = m_H (x_3 + x_4) + m_M (x_1 + x_2),
\]

\[
R_z = m_H (z_3 + z_4) + m_M (z_1 + z_2).
\]  

The last two summations are over all the atoms in the left, rigid monomer. Rewriting Eq. (4) and Eqs. (A4)–(A6) in matrix form one obtains

\[
\begin{pmatrix}
R_1 \\
R_2 \\
R_4 \\
R_5 \\
R_6 \\
R_{TX}
\end{pmatrix} = \begin{pmatrix}
\alpha & -\beta & -\gamma & -\delta \\
-1 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & 1 \\
0 & 0 & 0 & 0 & 0 & -1 \\
0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix} \begin{pmatrix}
x_1 - x_2 \\
x_3 - x_4 \\
z_1 - z_2 \\
z_3 - z_4 \\
x_1 + x_2 \\
z_1 + z_2
\end{pmatrix}.
\]

The order of the internal coordinates is chosen so that the transformation matrix \( \mathbf{B} \) is block diagonal. Inverting \( \mathbf{B} \) we find

\[
\mathbf{B}^{-1} = \begin{pmatrix}
f & \gamma g & -ag & g & 0 & 0 & 0 & 0 \\
f & \gamma g & \beta g & g & 0 & 0 & 0 & 0 \\
-1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -m_H / M & 1/M & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1/M & 0 & 0 \\
0 & 0 & 0 & 0 & -m_M / M & 1/M & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1/M & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/M
\end{pmatrix},
\]

where \( M = m_H + m_M \), \( g = 1/(\alpha + \beta) \), and \( f = - (\gamma + \delta) g \).

The \( \mathbf{B}^{-1} \) matrix allows us to calculate the internal force constants \textit{ab initio} using finite difference methods, since we can arbitrarily extend any one of the above internal coordinates and calculate the corresponding values of the Cartesian displacement coordinates.

17. The harmonic frequencies for the \textit{H}_5-\textit{H}_5 and \textit{D}_5-\textit{D}_6 dimers are 3150 and 3100 \textit{cm}^{-1}, respectively. The choice of 2950 \textit{cm}^{-1} for the OH stretch fundamental corrects for the large anharmonicity anticipated for this vi-
bration, and places the fundamental in its approximately correct position
by comparison with experiment.
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