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Medium and strong hydrogen bonds are common in biological systems. Here, they provide structural support and can act as proton transfer relays to drive electron and/or energy transfer. Infrared spectroscopy is a sensitive probe of molecular structure and hydrogen bond strength but strongly hydrogen-bonded structures often exhibit very broad and complex vibrational bands. As an example, strong hydrogen bonds between carboxylic acids and nitrogen-containing aromatic bases commonly display a 900 cm\(^{-1}\) broad feature with a remarkable double-hump structure. Although previous studies have assigned this feature to the OH, the exact origin of the shape and width of this unusual feature is not well understood. In this study, we present \textit{ab initio} calculations of the contributions of the OH stretch and bend vibrational modes to the vibrational spectrum of strongly hydrogen-bonded heterodimers of carboxylic acids and nitrogen-containing aromatic bases, taking the 7-azaindole—acetic acid and pyridine—acetic acid dimers as examples. Our calculations take into account coupling between the OH stretch and bend modes as well as how both of these modes are affected by lower frequency dimer stretch modes, which modulate the distance between the monomers. Our calculations reproduce the broadness and the double-hump structure of the OH vibrational feature. Where the spectral broadness is primarily caused by the dimer stretch modes strongly modulating the frequency of the OH stretch mode, the double-hump structure results from a Fermi resonance between the out of the plane OH bend and the OH stretch modes. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4914147]

I. INTRODUCTION

Hydrogen bonds are widely known to play important roles in many different biological and chemical systems. Because hydrogen-bonding gives rise to very anharmonic potential energy surfaces, vibrational spectroscopy is a highly sensitive tool for studying hydrogen-bonded systems. It is well known that the center frequency of an OH stretch mode is very sensitive to the presence and strength of the local hydrogen bond. As the strength of the hydrogen bond increases, the OH bond is weakened leading to a redshift of the OH stretching frequency.\(^{1,2}\) It is also known that the oscillator strength and width of the transition increases with the strength of the hydrogen bond.\(^{1,3,4}\) For weak and medium strength hydrogen bonds, both the frequency shift and width of the OH stretching vibration can be several hundred wavenumbers, but strong hydrogen bonds can lead to much broader spectral features with remarkable multi-hump structures.\(^{5-7}\)

Hydrogen-bonded dimers in nonpolar solvents form ideal model systems for studying the effect of the hydrogen-bonding strength on vibrational modes. Such dimers exhibit a number of unusual vibrational features. Some examples include: the homodimers of 7-azaindole and acetic acid, which exhibit vibrational spectra that include one broad spectral feature with a full width half maximum of approximately 500 cm\(^{-1}\) that contains underlying substructure;\(^{8-15}\) various phosphoric and phosphinic acids dimers, which display a triple-hump structure in their vibrational spectra spanning from 1000 to 3500 cm\(^{-1}\) (Refs. 5 and 7) and heterodimers of carboxylic acids and nitrogen-containing aromatic bases, which exhibit vibrational spectra that include a double-hump structure spanning from 1800 to 2700 cm\(^{-1}\).\(^{5,16-19}\)

A variety of different theoretical studies have been performed in order to understand the vibrational spectra of hydrogen-bonded dimers. These studies range from molecular dynamics simulations\(^{20}\) to \textit{ab initio} electronic structure calculations\(^{10,13,19,21-23}\) to deriving empirical models for the coupling between the relevant vibrational modes.\(^{24}\) One of the earlier \textit{ab initio} studies of the vibrational spectra of hydrogen bonded dimers was performed by Casteneda and co-workers.\(^{19}\) In this study, the vibrational frequencies of the 3,5-dimethylpyrazole—acetic acid dimer were calculated in the harmonic approximation using density functional theory (DFT). Like many other heterodimers between carboxylic acids and nitrogen-containing aromatic bases, the FTIR spectrum of this dimer contains a double-hump structure spanning from 1800 to 2700 cm\(^{-1}\). They reported an OH stretch frequency of 3148 cm\(^{-1}\).\(^{19}\) However, due to the strong hydrogen bonding present in this dimer, the use of the harmonic approximation to calculate the vibrational frequencies is questionable.

Many \textit{ab initio} studies have included the anharmonicity of the potential energy surface in their calculation of the vibrational spectra of hydrogen-bonded dimers.\(^{10,13,21-23}\) For example, Dreyer modeled the spectra of the homodimers of 7-azaindole and acetic acid using DFT and anharmonic force field calculations.\(^{10,13}\) These dimers exhibit bands with a full width half maximum of 500 cm\(^{-1}\) centered near 3000 cm\(^{-1}\) which are displayed in the bottom panel of Fig. 1. In these studies, the anharmonic force constants involving only one
mode were obtained by calculating the one dimensional potential energy surface and performing a least squares fit. For anharmonic force constants involving multiple modes, a finite difference procedure was used to calculate the anharmonic force constants from harmonic force constants at three points along each vibrational mode included in the calculation. Using this computational technique, Dreyer was able to incorporate several dimer stretch modes (low frequency modes that alter the distance between the monomers) and fingerprint modes into his calculations. These calculations demonstrated that the width and substructure of the NH and OH stretch peaks result from OH and NH stretches anharmonically coupling to dimer stretch modes and Fermi resonances of fingerprint modes.

In other studies of hydrogen-bonded systems, the anharmonic frequencies were computed using an explicitly calculated potential energy surface. This technique was used by Rheinecker and Bowman to compute the vibrational spectrum of Cl$_2$H$_2$O, and Elsaesser and co-workers to calculate the transition frequencies of the adenosine-thymidine base pair. In these studies, the potential energies at various points along the vibrational mode coordinate were computed, and a least squares fit was used to obtain the anharmonic force constants. In order to account for coupling between N vibrational modes with this technique, an N-dimensional potential energy surface must be computed. Although this technique provides a more robust understanding of the potential energy surface, it requires significantly more computational resources, which limits the number of modes and/or the size of the systems that can be studied.

Hanna and co-workers considered the three peaked structure of various phosphinic acid dimers. They created an empirical model that accounts for coupling between the OH stretches, OH bends, and dimer stretch modes. The model adiabatically separated the low-frequency dimer stretch mode from the high-frequency OH stretch and bend modes by modeling the OH stretch frequency as being linearly dependent on the dimer stretch mode coordinate. Using this model, they were able to successfully reproduce the three peaked structure of the phosphinic acids dimers.

Hydrogen-bonded structures in biological systems are often asymmetric (e.g., DNA base pairs). Consequently, hydrogen-bonded heterodimers are excellent model systems for biological hydrogen-bonded systems since they do not exhibit the symmetry of homodimers, which influences the vibrational modes of the system. In particular, dimers between carboxylic acids and nitrogen-containing aromatic bases provide excellent model systems due to their structural resemblance to DNA base pairs. In order to understand this class of heterodimers better, we chose to investigate vibrational spectrum of the 7-azaindole—acetic acid (7AI-Ac) and pyridine—acetic acid (Py-Ac) heterodimers.

As shown in the top two panels of Fig. 1, both the 7AI-Ac and Py-Ac dimers contain a double-hump structure in the 1800 to 2700 cm$^{-1}$ region of the vibrational spectrum. Because this feature is observed in both dimers' vibrational spectra, it has previously been assigned to the OH.$^{6,17}$ As can be seen by comparing the top and bottom panels of Fig. 1, the spectrum of the 7AI-Ac heterodimer has a completely different vibrational structure than either of the homodimers. The NH stretch forms a band that is about 250 cm$^{-1}$ broad peaked at 3250 cm$^{-1}$ while the OH forms the double-hump structure from 1800 to 2700 cm$^{-1}$. Similar double-hump structures have been observed in the vibrational spectra of many different heterodimers of carboxylic acids and nitrogen-containing aromatic bases.$^{6,16-18}$

The goal of our study is to explain both the shape and width of the OH feature in the infrared spectrum of heterodimers of carboxylic acids and nitrogen-containing aromatic bases employing the 7AI-Ac and Py-Ac heterodimers as model systems. In order to understand this vibrational structure, we utilized DFT to calculate the OH feature in the vibrational spectrum of these heterodimers. Since it has been shown that Fermi resonances of the OH bend modes give rise to the three-peaked structure of phosphinic acid dimers$^{24}$ and that low-frequency modes explain the spectral broadness of a variety of hydrogen bonded systems,$^{10,13,24,26}$ we chose to incorporate these vibrational modes into our calculation of the vibrational spectrum.

II. METHODS

In our approach, we included coupling between the dimer stretch, the OH bend, and the OH stretch modes. The coupling between the OH bend and stretch is treated by computing a two-dimensional potential energy surface and using it to construct a two-dimensional Hamiltonian. We adiabatically separated the OH stretch and bend modes from the order of magnitude slower dimer stretch mode by computing the vibrational frequencies and transition probabilities at 9 or 11 points along the dimer stretch coordinate. We used this information combined with the wavefunction of the dimer stretch to compute the vibrational spectrum.

All electronic structure calculations were performed using DFT with a 6-311+G(d,p) basis set and the Gaussian 09 software package.$^{27}$ Three different functionals (B3LYP, PBE, and M06-2X$^{28}$) were used to test the functional dependence
of the computed spectrum. B3LYP was chosen because Jens Dreyer demonstrated that it could be used to calculate the vibrational spectrum of the 7-azaindole$^{13}$ and acetic acid$^{10}$ homodimers. PBE and M06-2X were chosen because they have been reported to calculate the potential energy curve of hydrogen bonded dimers along the dimer dissociation coordinate significantly more accurately than B3LYP.$^{29}$ The effect of the CCl$_4$ solvent was incorporated at the dielectric continuum level using the Onsager model. The structures optimized using the B3LYP functional are displayed in Fig. 2.

The normal modes and harmonic frequencies were calculated using normal mode analysis in Gaussian 09. The normal mode analysis gives a matrix of eigenvectors $C_k$ which relate the mass-weighted Cartesian displacement atomic coordinates ($q_i$) to the normal mode displacement coordinates ($Q_k$) as shown in Eqs. (1) and (2).$^{30}$ In these equations, $m$ is the mass of the atom, $\Delta r_i$ is an individual atom’s displacement along a Cartesian coordinate, and $N$ is the number of atoms in the dimer,

$$q_i = \sqrt{m_i} \Delta r_i, \quad (1)$$

$$Q_k = \sum_{i=1}^{3N} C_{ki} q_i. \quad (2)$$

Since the potential energy surface is very sensitive to the length of the hydrogen bond, the dimer stretch modes that alter this distance are likely to modulate the OH stretch and bend modes strongly. Thus to calculate the infrared spectrum of the dimers, we incorporated dimer stretch modes that had a large impact on the hydrogen bond length. The modes chosen are displayed in Fig. 2. The calculated harmonic frequencies of these modes are 165 cm$^{-1}$ for Py-Ac and 140 cm$^{-1}$ for 7AI-Ac.

To demonstrate the effect of coupling between the OH stretch and bend modes, the vibrational spectrum was calculated first using the one-dimensional potential energy surfaces of the OH stretch coordinate only and then using two-dimensional potential energy surfaces, with the OH bend and stretch as coordinates. Dipole surfaces of the same dimensionality were constructed in order to calculate the transition dipole moments. The energy and dipole of 15 to 24 different points along the OH stretch and bend coordinates were calculated resulting in two-dimensional potential energy surfaces containing between 270 and 504 points. The potential energy surface covered all of the space in which the potential energy was less than 6400 cm$^{-1}$ above the equilibrium geometry. Convergence was tested by comparing the spectrum calculated using the entire potential energy surface with one calculated using a potential energy surface in which all of the points along the edge were removed.

In order to obtain transition frequencies that account for the anharmonicity of the potential energy surface, a variational calculation with a discrete variable representation$^{31}$ was performed. A more detailed description of the Hamiltonians can be found in the supplementary information.$^{32}$ Transition frequencies were calculated from the energy difference between the computed eigenstates. The transition probabilities were also computed using a discrete variable representation as shown for one dimension in Eqs. (3)–(5). Dipole operators $\langle \mu_{\sigma, mn} \rangle$ were constructed from the dipole surfaces $\langle \mu_{\sigma} | Q_n \rangle$ for each Cartesian coordinate. The transition dipole moments $\langle \mu_{\sigma} \rangle$ between initial state $i$ and final state $f$ were calculated from the dipole operators, and the transition probabilities $P_{if}$ were taken as being proportional to the magnitude of the transition dipole moment squared,

$$\mu_{\sigma, mn} = \delta_{mn} \mu_{\sigma} (Q_n), \text{ where } \sigma = x, y, \text{ or } z, \quad (3)$$

$$\mu_{if} = \langle \phi_f | \mu_x | \phi_i \rangle, \langle \phi_f | \mu_y | \phi_i \rangle, \langle \phi_f | \mu_z | \phi_i \rangle. \quad (4)$$

$$P_{if} \propto \left| \mu_{if} \right|^2. \quad (5)$$

To incorporate the effect of the dimer stretch mode, the potential energy surface calculation was repeated at 9 or 11 points along the dimer stretch coordinate. The points were selected to cover any region where the dimer stretch eigenstates with a significant population at room temperature have a substantial magnitude. The transition frequencies and transition dipole moment squared at different dimer stretch coordinate values were connected by a cubic spline fit in order to obtain these values as a smooth function of the dimer stretch coordinate. This treatment results in an effective adiabatic separation of the OH stretch and bend modes from the order of magnitude lower frequency dimer stretch mode.

In order to calculate the vibrational spectrum, 100 different geometries along the dimer stretch coordinate were sampled. These geometries were equally spaced and ranged from the minimum to the maximum computed values of the dimer stretch coordinate. Each geometry was modeled as contributing a Gaussian profile to the infrared spectrum. The height of each Gaussian was determined by the product of the square of the dimer stretch wavefunction amplitude (the probability of being in that geometry) and the transition dipole moment squared (the transition probability in that geometry). The full width half maximum of each Gaussian was set to 40 cm$^{-1}$ to account for homogeneous broadening and was centered at the calculated transition frequency of that geometry. By summing all of the Gaussians together, the infrared spectrum of a transition was calculated.
Several of the dimer stretch mode states are populated at room temperature (298 K). For example, the 165 cm\(^{-1}\) mode of the Py-Ac heterodimer has populations of 55%, 25%, 11%, and 5% for the four lowest energy states. The spectra of the 0 → 2 OH bend and 0 → 1 OH stretch transitions for each of the four lowest states of the dimer stretch mode were calculated, and the room temperature spectrum was obtained using a Boltzmann weighted sum of these spectra. The four states used in the Boltzmann weighted sum account for over 95% of the dimers. Consequently, higher energy dimer states were excluded from the calculation.

### III. RESULTS AND DISCUSSION

We begin by showing the results of Py-Ac dimer calculation using the B3LYP functional. We present the calculated spectrum both with and without the out of the plane OH bend to illustrate the effect of including this mode in the calculation. We will then examine the effects of changing the dimer stretch mode and OH bend mode. Finally, we examine the functional dependence and compare the results of the Py-Ac dimer to the 7AI-Ac dimer to study the structural sensitivity of the calculations.

Strongly hydrogen-bonded vibrations exhibit very anharmonic potentials that depend on the strength of the hydrogen bond. The low-frequency dimer stretch mode greatly modulates the hydrogen-bonding strength of the OH bond and correspondingly greatly affects the OH stretch vibrational frequency. This is illustrated in Fig. 3(a) which compares the one-dimensional potential of the OH stretch in the Py-Ac dimer at the equilibrium structure of the dimer stretch mode to that of the dimer at the classical turning point of the 2nd excited state of the dimer stretch mode. Due to strong hydrogen bonding, the potential energy surface of the equilibrium structure (plotted in blue) contains a large shoulder near the n = 2 level. At shorter distances between the monomers (plotted in green), the shoulder becomes less pronounced, and the potential becomes wider near the minimum. At longer distances between the monomers (plotted in red), a second higher energy minimum is formed, and the potential becomes narrower near the global minimum. To examine potential Fermi resonances between the OH stretch and bend modes, we calculated the two-dimensional potential energy surfaces as a function of the dimer stretch coordinate. Fig. 3(b) shows the potential energy surface of the OH stretch and out of the plane OH bend of the equilibrium structure. This figure shows that the OH out of the plane bend will result in a motion that changes the bond angle significantly more than the bond length since the lowest energy path along the OH bend coordinate corresponds to decreasing the OH stretch coordinate and either increasing or decreasing the OH bend coordinate. The anharmonicity caused by the hydrogen bond can be observed by the large shoulder present along the OH stretch coordinate at OH bend coordinate values near zero. The two-dimensional potential energy surfaces at the classical turning points of the 2nd excited dimer stretch state are displayed in Fig. S1 of the supplementary information. 32

The 0 → 1 OH stretch and 0 → 2 OH bend transition frequencies and probabilities were computed from the potential energy surfaces using the variational calculation described above. This calculation was repeated for several points along the dimer stretch coordinate to map out the effect of the dimer stretch mode on the OH stretch and bend modes. The results of the uncoupled OH stretch are given by the blue dashed lines in Fig. 4. At large distances between monomers (positive dimer stretch coordinate values), the OH stretch frequency is relatively high (nearly 3000 cm\(^{-1}\)) while at smaller distances between monomers, the frequency drops to about 2150 cm\(^{-1}\). This follows the expected dependence of the OH stretch frequency on the hydrogen-bonding strength. At large distances between the monomers, the hydrogen bond is weak and the OH stretch frequency is relatively high. As this distances decreases, the hydrogen bond becomes stronger resulting in lower vibrational frequencies. Also, as the hydrogen bond becomes stronger, the transition dipole moment increases dramatically indicating a large non-Condon effect. 3 The results of the coupled OH stretch and bend calculation are given by the solid blue and orange lines, respectively, in Fig. 4. At larger distances between the monomers, the OH stretch does not couple strongly to the OH bend. This is demonstrated by the close agreement between the coupled and uncoupled OH stretch transitions and the lack of any substantial transition dipole moment for the 0 → 2 transition of the OH bend. However, as the distance between the monomers decreases, coupling between these modes increases causing the frequency and the transition

![FIG. 3. Calculated potential energy surfaces of Py-Ac. The OH stretch and bend coordinates are defined by Eq. (2). (a) One-dimensional OH stretch potential energy curves at various points along the dimer stretch coordinate. The equilibrium structure is plotted in blue, the classical turning points of the 2nd excited state are plotted in red and green. Due to strong hydrogen bonding, the potential energy curves are very anharmonic. (b) Two-dimensional potential energy surface with the OH stretch and out of the plane bend as coordinates. Each contour corresponds to 3000 cm\(^{-1}\).](image-url)
dipole moment of the OH stretch to decrease, while the transition dipole moment of the OH bend overtone increases indicating a Fermi resonance between the two modes.

To compute the vibrational spectrum, we need the distribution of the geometries along the dimer stretch coordinate. The bottom panel of Fig. 4 shows the probability distribution of the four dimer stretch states included in the calculation. This illustrates the wide range of geometries along the dimer stretch coordinate that are sampled by each state of the low-frequency mode. The computed spectra of each of the dimer stretch eigenstates are displayed in Fig. S2 of the supplementary information. The computed spectrum of the OH stretch feature in the ground state of the dimer stretch mode has a full width half maximum of 200 cm\(^{-1}\) due to the zero point energy of the ground state of the dimer stretch. This indicates that even at low temperatures, these features are predicted to be quite broad. In order to obtain the room temperature spectrum, a Boltzmann weighted sum of these spectra was used. The calculated uncoupled and couple spectra at room temperature are displayed in Fig. 5. The uncoupled calculation reproduces the higher frequency peak quite well indicating that the higher frequency peak is due to the OH stretch. The calculated peak is remarkably broad, spanning over 600 cm\(^{-1}\). This demonstrates the importance of including anharmonicity in the calculation. Even though it does not extend to 1800 cm\(^{-1}\), the calculated peak is remarkably broad, spanning over 600 cm\(^{-1}\). This broadness arises from the large range of OH stretch frequencies sampled by the dimer stretch mode. However, the uncoupled OH spectrum fails to reproduce the double-hump structure of the spectrum, which shows that the OH stretch and dimer stretch modes alone cannot explain the lower frequency hump. Upon including the out of the plane OH bend, a lower frequency peak appears and the double-hump structure is reproduced. However, there are some noteworthy differences between the FTIR spectrum and the computed spectrum. The lower frequency peak is calculated to be taller and narrower than in the FTIR spectrum. Additionally, the FTIR spectrum does not have zero absorbance anywhere between the two humps, which contrasts with the calculated spectrum.

To test if other vibrational modes contribute to the spectrum, we repeated the calculation using different vibrational modes, as increasing the number of vibrational modes is computationally impractical at this level of theory. To investigate if the spectrum was highly dependent on the dimer stretch mode, another dimer stretch mode was examined. This mode twists the opposite way of the dimer stretch mode displayed in Fig. 2(a) and has a frequency of 119 cm\(^{-1}\). There are a number of vibrational modes that have OH bending character other than the out of the plane OH bend. To see how changing this mode impacted the calculation, three other bend modes were used: an out of the plane bend that includes the methyl group bending, an in the plane bend that includes the movement of the carbonyl and methyl groups, and the in the plane bend. They have harmonic frequencies: 1067, 1298, and 1504 cm\(^{-1}\), respectively. For comparison, the out of the plane bend has a harmonic frequency of 1061 cm\(^{-1}\). The spectra computed using these modes are displayed in Fig. 6. Movies of all of the vibrational modes are available in the supplementary information.

By comparing (a) and (b) in Fig. 6, one can see that changing the dimer stretch mode does not result in a significant change in the computed spectrum. Although the 165 cm\(^{-1}\) mode (b) provides a slightly more intense Fermi resonance than the 119 cm\(^{-1}\) mode (a), the spectra are nearly identical. This illustrates that the dimer stretch modes modulate the hydrogen bond length in an equivalent manner. On the other hand, the specific bending mode has a much larger impact on the computed spectrum. This is demonstrated by comparing (b), (c), (d), and (e) in Fig. 6. By far, the strongest Fermi resonance is the out of the plane bend (b). This is likely because the 1067 cm\(^{-1}\) mode (c) and the 1298 cm\(^{-1}\) mode (d)
include the motion of atoms other than the OH resulting in less coupling to the OH stretch and because the 1504 cm$^{-1}$ mode (e) is too high in frequency to significantly interact with the OH stretch. The FTIR spectrum shows many small lobes on the double-hump structure. This substructure is likely due to less intense Fermi resonances such as the ones displayed in (c) and (d). The small hump that is centered at 2940 cm$^{-1}$ in the FTIR spectrum may be the Fermi resonance with the in the plane bend (e); however, the dimer has a number of other vibrational modes with fundamental transition frequencies between 1350 and 1500 cm$^{-1}$ that contain some in the plane OH bending character. These modes along with the in the plane bend are likely contributing Fermi resonances that account for much of the intensity in the 2700–3000 cm$^{-1}$ region of the spectrum. These calculations indicate that the computed spectrum does not depend significantly on the dimer stretch mode selected and that the out of the plane OH bend gives rise to the most intense Fermi resonance.

Since calculations of Py-Ac showed that the OH out of the plane bend provides the largest Fermi resonance, the spectrum of 7AI-Ac was computed using the out of the plane bend. The calculated spectrum of 7AI-Ac is displayed in Fig. 7(b). For comparison, the calculation of Py-Ac is displayed in Fig. 7(a). Both calculations show that by including only the OH stretch and dimer stretch modes, one broad peak is calculated; and when the OH stretch, out of the plane OH bend and dimer stretch modes are included, a double-hump structure is obtained. However, the interpretation of the individual features within the double-hump structure differs between the dimers. In the case of Py-Ac, the double-hump structure consists of two non-overlapping peaks. The higher frequency peak is attributed to the OH stretch while the lower frequency peak is due to the overtone of the OH out of the plane bend indicating a conventional weakly coupled Fermi resonance. In the 7AI-Ac case, interpreting each feature of the double-hump is more complicated. Here, the vibrational structures from the OH stretch and the out of the plane OH bend are overlapping, indicating a very strongly coupled system. Consequently, the nature of the two humps in the calculated spectrum does not have a simple interpretation. It should be noted that the spectral density between the two humps does not go to zero for the 7AI-Ac dimer, which is in agreement with the FTIR spectrum of both dimers. Since the dimers have almost identical FTIR spectra in the double-hump region and are quite similar in structure, it seems unlikely that the two dimers would exhibit very different coupling strengths and resulting vibrational structure. The cause of the discrepancy between the calculated spectra is likely that the DFT calculations predict different hydrogen bonding strengths for the two geometries which in turn impacts the coupling between the OH bend and stretch modes.

To test if the difference in coupling strength between the two dimers could be dependent on the functional, we repeated the calculations with M06-2X and PBE functionals. The M06-2X and PBE functionals were chosen because both have been shown to reproduce energy curves along the hydrogen bond dissociation coordinate well. However, it is still unclear if these functionals are preferable for computing the anharmonic frequencies of the OH stretch and bend modes since these depend on the potential energy surface of the OH stretch and bend. The results from the different

FIG. 6. Calculated spectra of Py-Ac using different vibrational modes. The identity of each line follows the same convention as Fig. 5. (a) Dimer stretch mode changed to 119 cm$^{-1}$ mode. (b) The same spectra as displayed in Fig. 5 plotted for comparison. (c) Bend mode changed to 1067 cm$^{-1}$ mode. (d) Bend mode changed to 1298 cm$^{-1}$ mode. (e) Bend mode changed to 1504 cm$^{-1}$ mode.

FIG. 7. Functional dependence of the calculated spectra of 7AI-Ac and Py-Ac. The identity of each line follows the same convention as Fig. 5.
functionals are displayed in Fig. 7. In the case of Py-Ac, the M06-2X functional (c) is in near quantitative agreement with the B3LYP functional (a). This contrasts with 7AI-Ac calculations, where B3LYP (b) predicts overlapping OH stretch and bend features whereas M06-2X (d) predicts non-overlapping features similar to the Py-Ac case. Using the B3LYP functional, all calculations (including the OH stretch only calculations) predict significantly lower frequencies for the OH stretch, which means that PBE predicts stronger hydrogen-bonds than B3LYP and M06-2X. In the case of 7AI-Ac, PBE calculates the hydrogen-bonding interaction as being stronger than measured experimentally. The stronger hydrogen bonds resulting from the PBE calculations forces the features to be overlapping, since the transitions have the same frequencies at some populated point along the dimer stretch coordinate. Due to the functional dependence of the calculated spectra and the fact that other vibrational modes that contain OH bending motion are providing small Fermi resonances, better agreement between the experimental and calculated spectra would likely be obtained if more modes were included in the calculation and/or a functional that better describes the breadth of hydrogen bonding interactions were to be used. This improvement in agreement could be in the form of consistently predicting that the absorbance does not go to zero between the two humps or by predicting a broader OH bend feature that includes lower frequencies. Some of the calculations display these features in Fig. 7; however, none of the functionals consistently predict them for both molecules. Thus, it is unclear if better agreement is more likely to be achieved with a functional that is better designed to account for the hydrogen bonding interaction or by including more vibrational modes in the calculation.

Collectively, these calculations indicate that the exact assignments of individual features within the double-hump feature are very sensitive to both the functional used in the calculation and the dimer structure. As Fig. 7 shows, some of the calculations assign the higher frequency hump to the OH stretch and the lower frequency hump to the Fermi resonance of the out of the plane OH bend. The other calculations assign both humps to a combination of the OH stretch and the Fermi resonance of the out of the plane OH bend. Despite these differences, all six calculations are in qualitative agreement that the overall double-hump structure results from coupling between the OH stretch, out of the plane OH bend, and the dimer stretch modes. Quantitatively better agreement with experiment would likely be obtained by including more modes in the multidimensional potential energy surface calculation and using a functional that more accurately describes the hydrogen-bonding strength.

IV. CONCLUSION

We have presented an ab initio computational method for calculating the vibrational spectra of hydrogen-bonded dimers. This method accounts for coupling between the OH stretch and bend modes by computing their two-dimensional surfaces as well as an adiabatically separated dimer stretch mode that modulates the length of the hydrogen bond and correspondingly the vibrational frequency of the OH modes.

Unlike many of the previously used computational methods for calculating vibrational spectra, this method is able to explicitly incorporate the spectral broadness that results from low frequency modes modulating the frequency and transition probabilities of high frequency modes. We have used this method to explain the origin of the 900 cm$^{-1}$ broad double-hump in the vibrational spectrum of heterodimers of carboxylic acids and nitrogen-containing aromatic bases using Py-Ac and 7AI-Ac as models for these systems. The calculations show that the broadness of this feature can be reproduced by accounting for how a dimer stretch mode modulates the frequency and transition dipole moments of the out of the plane OH bend and OH stretch modes. The calculations predict that although the features of the double-hump will become spectrally narrower at lower temperatures, the OH stretch feature will retain a full width half maximum of at least 200 cm$^{-1}$ due to the zero point energy of the ground state of the dimer stretch. The origin of the double-hump is the coupling between the OH stretch and the out of the plane OH bend. Unlike the homodimers studied by Dreyer, fingerprint modes other than the out of the plane bend do not make large contributions to the vibrational spectrum of these heterodimers. Weaker Fermi resonances from various fingerprint modes which contain OH motion give rise to the substructure of the double-hump feature. The exact interpretation of the individual features within the double-hump structure varies with the dimer structure, and the functional used in the calculation as these variables impact the strength of the computed hydrogen bond. These variables determine if the calculated spectral features of the OH stretch and the Fermi resonance of the out of the plane OH bend are overlapping features. Despite this discrepancy, all of the calculations are in agreement that a double-hump structure is formed when coupling between the OH stretch, out of the plane OH bend, and dimer stretch modes are included.

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32. See supplementary material at http://dx.doi.org/10.1063/1.4914147 for details about how the Hamiltonians were constructed, two-dimensional potential energy surfaces of Py-Ac at different points along the dimer stretch mode, computed spectra for each of the dimer stretch eigenstates, OH stretch and bend transition frequencies and transition probabilities versus dimer stretch coordinate graphs for the spectra displayed in Figs. 6 and 7 as well as movies of all of the vibrational modes used in the study.