Probing the stiffness of the simplest double hydrogen bond: The symmetric hydrogen bond modes of jet-cooled formic acid dimer

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Formic acid dimer is held together and kept planar by two strong hydrogen bonds, which give rise to intermolecular vibrations. Raman active fundamentals, overtones, and combination bands involving out-of-plane bending and stretching vibrations of the hydrogen bonds are recorded under jet-cooled, vacuum-isolated conditions between 100 and 750 cm\(^{-1}\) and assigned with the help of isotopic substitution. Individual anharmonicity effects are shown to be very small \((\chi_{ij} = -(1 \pm 2) \text{ cm}^{-1})\), where they are accessible by experiment. However, they may accumulate to substantial differences between harmonic and anharmonic fundamental excitations. Preliminary experimental evidence for the most elusive fundamental vibration of formic acid dimer, symmetric OH torsion, is presented. A rigorous experimental reference frame for existing and future high level quantum chemical and dynamical treatments of this important prototype system is provided. The effects of clustering beyond the dimer on the low frequency dynamics are found to be small, whereas argon coating gives rise to blueshifts. © 2009 American Institute of Physics.

I. INTRODUCTION

Two hallmarks of the hydrogen bond are its directional- ity and its cooperativity. The former is a key to molecular recognition, whereas the latter has consequences for fundamental dynamical processes such as concerted hydrogen transfer. Both aspects are of paramount importance in biology but they also need to be characterized at a structurally more elementary level in order to advance a quantum description of biomolecular processes.

The dimer of formic acid is among the most elementary systems which exhibit accentuated hydrogen bond directionality and some degree of cooperativity. It is a distinctly planar complex with hydrogen bond-mediated restoring forces toward all kinds of tilting. It involves periodic chemical bond breaking and making on the nanosecond time scale even at 0 K due to facile concerted hydrogen transfer through high barriers along the equivalent hydrogen bonds. These features come with the rare property that this dimer can be prepared and studied in the room temperature gas phase (GP) at high abundance.

Therefore, formic acid dimer (FAD) has been well studied by a range of experimental techniques in particular, by vibrational spectroscopy. The centrosymmetry turns infrared and Raman techniques into perfectly complementary approaches. Structural studies by microwave spectroscopy are difficult due to the inversion symmetry, but alternatives exist. In view of the elementary character of FAD, it is not surprising that the number of theoretical approaches outnumbers the experimental ones (see, e.g., Refs. 12–17 and references cited therein). Some of these theoretical studies carry the quantum dynamical description to fairly accurate and high-dimensional levels, thus allowing for rigorous comparison to spectroscopic data.

Despite these intense experimental and theoretical studies, important experimental data are still missing. Such gaps slow down theoretical progress. Among them, the lack of anharmonicity information in the hydrogen bond modes is quite prominent. The spectroscopy of vibrational fundamentals itself is already challenging, with the last missing van der Waals mode eluding discovery until 2007. The direct study of such van der Waals modes can supply very sensitive information on the hydrogen bond dynamics. However, fundamental excitations only provide insights into the shape of the potential energy hypersurface close to the minimum structure, which is furthermore indirect because of anharmonicity. Larger excursions can be realized by overtone and combination transitions, which are not easily accessible in a system without low-lying electronic states. Action spectra have nevertheless been obtained using selective photodissociation and have yielded anharmonic coupling constants. However, these anharmonic studies concentrate on intramolecular modes. An indirect approach to hydrogen bond modes via combinations with hydride stretching vibrations fails in this case because carboxylic acid dimers exhibit a very complex dynamics in these hydrogen-bound stretching states. The spectroscopy of higher-lying minima typically probes small excursions from those, rather than large excursions from the global minimum. Both aspects are important for the hydrogen bond dissociation kinetics and in the condensed phase, but for a reliable force field of cyclic FAD, information in between is currently most needed.

The present work takes a direct hydrogen bond mode spectroscopy approach. It exploits the capability of Raman
scattering to access the low wave number region of the vibrational dynamics at high sensitivity and it makes use of the recent progress in combining spontaneous Raman scattering with supersonic expansions of hydrogen-bonded systems. It is a continuation of our previous effort to characterize the hydrogen bond fundamentals and it is an essential step on the way to fully characterize the low temperature vibrational dynamics of FAD. It does not provide access to the subtle dependence of hydrogen transfer tunneling processes on vibrational excitation at the nanosecond scale at the current stage. This is because the available spectral resolution only allows for the probing of subnanosecond dynamics.

FAD has 24 fundamental modes which may be classified according to their $C_{2v}$ point group symmetry behavior and which correspond to 13 different kinds of vibrational motion. While the intermolecular twisting mode $\nu_{16}$ [in Herzberg notation, adopting, however, the representation sequence $A_{g}, B_{g}, A_{u}, B_{u}$ (Ref. 39)] is only IR active and the intermolecular stretching mode $\nu_3$ is only Raman active, the other 11 vibrations occur in Davydov pairs of IR active and Raman active modes, which are split in a mode- and isotope-dependent way.

Many of them have been characterized a long time ago in the GP for dimers close to room temperature in thermodynamic equilibrium with the monomers. Infrared and Raman spectroscopy have been applied and isotope substitution was used to assign the assignments. The out-of-plane (o.o.p.) bending potential has occasionally been severely underestimated but apart from some assignment gaps, a satisfactory description of the harmonic force field has emerged toward the end of the last century. Nevertheless, the thermal excitation in regular GP spectra results in significant band shape distortions because much less than 10% of the molecules are in the vibrational ground state at room temperature. This makes an accurate estimate of the band center difficult unless high resolution spectroscopy reveals the hot band structure. The latter is difficult in the Raman case and at low wave number in the infrared.

One way of reducing thermal excitation is the application of matrix isolation techniques. It also gives access to less stable isomers but may suffer from site splittings. Very recently, matrix isolation also became possible for Raman probing. The spectral simplification offered by this technique comes at the price of matrix shifts, which are sometimes difficult to predict and can lead to changes in resonance patterns.

Therefore, more effort has been invested in infrared supersonic jet approaches over the last decade. These range from low resolution studies using mostly cavity ringdown techniques over medium resolution Fourier transform infrared (FTIR) spectra and action spectra to very high resolution analyses including tunneling splittings. Typically, the focus was on the C–H/O–H/C=O/C–O valence vibrations and on some of their isotopic variants. The O–H stretching dynamics turned out to be particularly challenging due to interactions with combination bands from the lower frequency range. So far, such jet techniques have not been applied to the far infrared (FIR) range, although this would be technically possible. The Raman active half of the fundamentals is only beginning to be explored in the jet-cooled regime.

A bottom-up approach which starts with a combined IR/Raman characterization of the lowest frequency modes, where regular dynamics prevails, and systematically progresses toward higher state densities appears indispensable for an in-depth understanding of the complex and irregular hydride stretch dynamics. To minimize ambiguities, it is essential to know the extent of anharmonicity expected in the combination bands. This extent is particularly uncertain for the large amplitude van der Waals modes.

Fortunately, all six intermolecular modes fall below 300 cm$^{-1}$ and thus all their two-quantum overtones and combination bands are well separated from the lowest intramolecular modes, which start above 600 cm$^{-1}$. The IR coverage of unperturbed intermolecular fundamentals is limited to room temperature GP studies, whereas the Raman active fundamentals have been studied in the jet and were recently confirmed in matrix isolation.

The interest in intermolecular combination bands is amplified by several quantum studies including anharmonic contributions. These studies indicate surprisingly small anharmonic constants, typically well below the accuracy limit of room temperature GP band centers. Therefore, an experimental investigation of some of these excited vibrational states appears particularly timely. In the present work, we report for the first time on four weak Raman active overtones, which could be unambiguously assigned with the help of systematic isotope substitution. In addition, we tentatively assign a further overtone and very weak intermolecular combination bands. Furthermore, we analyze some previously observed IR-active intermolecular fundamental and combination bands of FAD. Finally, the lowest intramolecular bands between 600 and 750 cm$^{-1}$ are characterized and a weak fundamental is tentatively assigned a band center for the first time.

II. METHODS

The spontaneous Raman scattering spectrometer used in this work is a modified version of the one described previously. Pure helium (Air Liquide, 99.996%) and, in some cases, also pure argon (Air Liquide, 99.999%) were used as a carrier gas flowing through a thermostated glass saturator which contained the studied compounds (HCOOH, Sigma-Aldrich, >98%; partially and fully deuterated isotopomers with 98%D, Cambridge Isotope Laboratory, 95% chemical purity). In Fig. 2 (see below), all four isotopomers were measured at a saturator temperature of 289 K. The resulting formic acid concentration in the gas mixture was estimated at 3% by assuming near saturation of the 1.5 bar helium flow in the saturator. The gas mixture was collected in a 67 L stainless steel reservoir and expanded through a hombuilt 8.0 $\times$ 0.05 mm$^2$ slit nozzle into an aluminum chamber with dimensions 60 $\times$ 60 $\times$ 40 cm$^2$. The stagnation pressure in the reservoir was set to 1 bar for formic acid and...
to 500 mbar for the three deuterium isotopomers. The chamber was evacuated by a 250 m³/h Roots pump backed by a 100 m³/h rotary vane pump.

Further measurements at higher and lower concentrations led to slightly different band shapes due to varying contributions by aggregates of dimers. However, the changes in band maxima were less than the spectral resolution of the setup (see Fig. 4 later on), although larger clusters are undoubtedly present at the highest concentrations. During the measurements of the spectra in Figs. 3–5, the gas mixture was collected in a 4.7 L teflon-coated reservoir and expanded through a homebuilt 4.0 × 0.15 mm² slit nozzle into the chamber with the stagnation pressure set to 700 mbar. In these cases, a 500 m³/h Roots pump was added to further extend the zone of silence in the expansion chamber.

A frequency doubled continuous Nd:YVO₄ laser (532 nm, Coherent Verdi V18, P = 18 W) serving as light source was focused on the jet expansion at a distance of 0.4 or 1 mm (in some cases also 3 mm) from the nozzle exit. At these nozzle distances, the expansion is still dominated by isolated FAD. The 90° scattered light was filtered by a Raman edge filter (L.O.T., φ = 25 mm, OD6.0, T > 90%, 535.4–1200 nm), dispersed by a McPherson Model 2051 monochromator (f/8.6, f = 1000 mm) and detected by a back-illuminated liquid N₂ cooled charge coupled device (CCD) camera (PI Acton, Spec-10: 400 B/LN, 1340 × 400 pixel). The spectra represent averages over four to six 200–300 s jet measurements. Cosmic ray signals were removed iteratively by comparing these measurement blocks. Typically, no background correction was carried out on the CCD readout because the jet expansion displaces any residual air impurities in the chamber. In some cases, neat He expansions were used as a reference without inelastic scattering for checking purposes.

Depolarization measurements were carried out by rotating the exciting laser from its perpendicular polarization relative to the scattering plane into a parallel orientation using a λ/2 retardation plate (Edmund, E43-695). Bands that are reduced in intensity by more than a factor of 6/7 are due to totally symmetric vibrations.

Harmonic quantum chemical calculations were carried out with the help of the GAUSSIAN03 program suite to assist the isotope analysis. Calculations using the B3LYP hybrid functional and MP2 perturbation theory with different basis sets for the fundamental vibrational modes of FAD and other isotopomers are compared to some previously reported MP2 calculations. Where literature calculations had to be repeated for Raman intensity information, the fundamental wave numbers typically agreed within a few cm⁻¹.

Anharmonic force field calculations and a subsequent perturbation analysis, as implemented in the GAUSSIAN package, were carried out to assess the influence of anharmonicity on the fundamentals and to calculate individual anharmonicity constants.

III. RESULTS AND DISCUSSION

A. Experimental spectra

The cyclic FAD has six intermolecular vibrational modes (see Fig. 1), three of which are IR active. The lowest one, ν₁₆(A₁₆) near 69 cm⁻¹, corresponds to the intermolecular twisting vibration. The others represent in-plane (i.p.) (ν₂₄,B₄) as well as o.o.p. bending motions (ν₁₅,A₁₅). Their fundamental wave numbers have been reported in early low resolution IR GP work and were recently reinvestigated. In this context, the band center of ν₁₅ was located reliably at 168.47 cm⁻¹ using high resolution spectroscopy, whereas a substantial discrepancy was observed for ν₂₄ (248–268 cm⁻¹) vide infra. IR active combination bands have also been found early on and were summarized and assigned in Ref. A combination band previously reported at 307 cm⁻¹ was relocated at 311 cm⁻¹. Apart from a lack of jet-cooled data and some inconsistencies in the low resolution band positions, a satisfactory knowledge on the IR-active hydrogen bond mode manifold may thus be diagnosed. However, it typically does not reach a level at which anharmonicity effects in these modes may be derived in a reliable way. We will come back to this issue in the following.

The other three intermolecular modes are Raman active. They represent intermonomer stretching motion ν₃(A₁⁴) and symmetric i.p. ν₃(A₁₄) as well as o.o.p. bending vibrations ν₁₂(B₂⁴) and ν₁₁(B₂⁴) vide infra. The jet-cooled fundamental band positions have already been reported in a previous article and were recently confirmed by matrix isolation Raman spectroscopy with moderate matrix shifts. These results are summarized in Table I for comparison with the band positions of the present

![Schematic drawings and experimental wave numbers (in cm⁻¹) of the six intermonomer fundamentals in the low frequency region.](image-url)
TABLE I. Band maxima (in cm$^{-1}$) and assignments of Raman active low frequency modes of (HCOOH)$_2$ and its isotopomers. The isotope redshifts (in cm$^{-1}$) relative to (HCOOH)$_2$ observed in the present work are listed in parentheses.

<table>
<thead>
<tr>
<th>(HCOOH)$_2$</th>
<th>(DCOOH)$_2$</th>
<th>(HCOOD)$_2$</th>
<th>(DCOOD)$_2$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jet$^a$</td>
<td>Jet$^b$</td>
<td>Matrix$^c$</td>
<td>Jet$^a$</td>
<td>Jet$^b$</td>
</tr>
<tr>
<td>139</td>
<td>n.o.</td>
<td>n.o.</td>
<td>139 (0)</td>
<td>n.o.</td>
</tr>
<tr>
<td>161</td>
<td>165</td>
<td>165</td>
<td>159 (2)</td>
<td>162</td>
</tr>
<tr>
<td>194</td>
<td>194</td>
<td>196</td>
<td>193 (1)</td>
<td>192</td>
</tr>
<tr>
<td>242</td>
<td>242</td>
<td>251$^d$</td>
<td>212 (30)</td>
<td>212$^e$</td>
</tr>
<tr>
<td>319$^f$</td>
<td>n.o.</td>
<td>n.o.</td>
<td>n.o.</td>
<td>n.o.</td>
</tr>
<tr>
<td>336</td>
<td>n.o.</td>
<td>n.o.</td>
<td>289 (47)</td>
<td>n.o.</td>
</tr>
<tr>
<td>386</td>
<td>n.o.</td>
<td>n.o.</td>
<td>n.o.</td>
<td>n.o.</td>
</tr>
<tr>
<td>400</td>
<td>n.o.</td>
<td>n.o.</td>
<td>n.o.</td>
<td>n.o.</td>
</tr>
<tr>
<td>435$^f$</td>
<td>n.o.</td>
<td>n.o.</td>
<td>n.o.</td>
<td>n.o.</td>
</tr>
<tr>
<td>482</td>
<td>n.o.</td>
<td>n.o.</td>
<td>423 (59)</td>
<td>n.o.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$This work.  
$^b$Reference 4.  
$^c$Reference 48 (argon matrix, 19 K).  
$^d$A band at 243 cm$^{-1}$ was also assigned to $\nu_{15}$.  
$^e$Typographical error in Ref. 4 (222 instead of 212 cm$^{-1}$), see also Ref. 57.

reinvestigation. In addition, four weakly Raman active overtone transitions are assigned based on Fig. 2 and their band maxima are also listed in Table I. Only the overtone of the IR-active vibration $\nu_{15}$ had been previously reported in the Raman GP spectra, 39,40 5% below the jet-cooled position. The 5% redshift may be explained by thermal weakening of the hydrogen bond at room temperature. A very weak band at 598.8 ± 1.9 cm$^{-1}$ mentioned for (HCOOH)$_2$ in the room temperature GP spectrum 39 could not be confirmed in the present work. Other Raman active overtone/combination bands have not been reported in the literature.

We shall start with the discussion of slight wave number differences between the earlier jet work 4 and the present one in Table I. Most differences are within 1 cm$^{-1}$ and may be explained by integer rounding errors, calibration uncertainties, and slight shifts due to cluster contributions beyond the dimer. The only systematic differences of 1–4 cm$^{-1}$ refer to the lowest frequency mode in the previous study, the i.p. bending fundamental $\nu_6$. Here, the earlier determination of the band maximum was affected by a spectral drift in the holographic notch filter used in Ref. 4 (Kaiser Optical Systems, $\phi$=62 mm, 532.0–2.5 nm) and the associated efficiency drop upon aging. In the present work, a more stable Raman edge filter with cutoff closer to the Rayleigh line (see Sec. II) was employed and allows for a more reliable determination of the band maximum in this broad band in Fig. 2.

When comparing the present jet data to the recent matrix isolation spectra, the $\nu_{12}$ fundamental deserves detailed discussion. In the jet spectra, the quoted band center estimate is actually midway between two peaks separated by ≈5 cm$^{-1}$. The symmetry of the vibration, the similar shape and height of the two components, and the invariance with respect to isotope substitution in all three cases led us to an assignment of these two subbands as $\Delta f \neq 0$ transitions. Their separation is consistent with an expected rotational temperature of ≈50 K at a distance of ≈8 nozzle diameters. This is significantly higher than the temperature obtained in an IR cavity-ringdown study 49 because the expansion is probed so close to the nozzle exit for the Raman spectrum. With the improved signal-to-noise ratio of the present spectra, we have no reason to question this original assignment, 4 although a band shape simulation using Raman intensities and rigid rotor rotational constants would be desirable. Surprisingly, the matrix isolation spectra also contain two bands, 48 although rotation is certainly suppressed in the Ar host. One band matches the jet value quite closely, whereas the other stron-
The dominant \( \nu_{12} \) band at 257 cm\(^{-1} \) under strongly Ar-coating conditions (3 mm nozzle distance) indeed supports the existence of a second transition on its low-wave number wing. This might be the \( \nu_{16} + \nu_{15} \) combination band proposed before,\(^4\) but its intensity would be unusually large.

Site splittings are less likely for the amorphous Ar arrangements around the molecule. The substantial Ar shifts underscore the importance of vacuum-isolated spectra in the comparison of experimental and quantum-chemical data. Ar nanocoating in the jet clearly offers a way to better understand bulk Ar matrix spectra. One may speculate that the new features in the Ar expansion arise from a polar dimer, which is not present in the He expansion. However, our current understanding of the Ar coating process is that it happens downstream of the acid dimerization and will not lead to isomerization. This is different from the He droplet behavior.\(^30\)

As in our previous work,\(^4\) we have used isotope substitution to corroborate the mode assignment of the Raman active hydrogen bond fundamentals (see Table I). The \( \nu_9 \) mode shows a weak isotope dependence, which is also tabulated directly in parentheses. The isotope pattern of \( \nu_9 \) is also weakly pronounced, but it contains a counterintuitive trend, which has been explained in part by off-diagonal anharmonicity contributions.\(^4\) The \( \nu_{12} \) mode is particularly sensitive to C deuteration, as one might expect from Fig. 1.

### B. Comparison with harmonic predictions

While the assignment of the three Raman-active fundamentals based on isotope substitution patterns is beyond doubt,\(^4\) it is instructive to compare the experimental anharmonic transitions to harmonic predictions at different levels of quantum-chemical approximation. Table II contains such a comparison using inexpensive methods and basis sets which leave room for a systematic sampling of the multidimensional potential energy hypersurface.\(^18–20\) Already for the three Raman active fundamentals, it is obvious that the simple MP2/6-31+G* level shows the best agreement in this comparison. The deviations are on the order of 1\% except for the intermolecular stretching mode, where the prediction is 5\% too high. The latter finding is not too surprising because isotope effects had revealed a substantial off-diagonal anharmonicity contribution in this mode,\(^9\) which has the effect of reducing the effective stretching force constant for light hydrogen bonds compared to heavier deuterium bonds. The proper comparison between experiment and theory at the force constant level would involve an infinitely heavy hydrogen atom and the true harmonic wave number of (HCOOH)\(_2\) is thus likely to be somewhat closer to 200 cm\(^{-1} \) than to the experimental anharmonic fundamental of 194 cm\(^{-1} \). Nevertheless, the double hydrogen bond is probably slightly weaker than predicted at MP2/6-31+G* level.

At the B3LYP/aug-cc-pVTZ level, all Raman active fundamentals are systematically overestimated by up to 10\%. This is also the case for the MP2/aug-cc-pVTZ level, whereas the MP2/6-311+G* calculations severely underestimate the stiffness of the FAD plane. By fortuitous error cancellation, the MP2/6-31+G* level may therefore be
viewed as a surprisingly accurate zeroth order description of the Raman active hydrogen bond fundamentals. This remains true when the best available values for the IR active van der Waals modes are included in the analysis (see Table II). Again, the B3LYP/aug-cc-pVTZ potential hypersurface appears to be too stiff, whereas the MP2/6-311+G* hypersurface is far too soft, in particular, in the o.o.p. modes. The surprising fidelity of the MP2/6-31+G* description of the FAD fundamentals carries over to all isotopomers (Table III) and even the largest relative error in the $v_r$ mode decreases with deuteration as it should. While we will not focus on Raman scattering strengths in this work, it may be mentioned that the predicted intensity ratio is about 1:10:50 for $v_8$: $v_{12}$ in fairly good agreement with the experiment.

There is IR information that requires further discussion. The $v_{24}$ fundamental was recently located at 268 cm$^{-1}$, revising earlier assignments near 248 cm$^{-1}$. The earlier value fits the calculated harmonic MP2/6-31+G* prediction much better, whereas the new proposal is more in line with MP2/aug-cc-pVTZ predictions, which failed for the o.o.p. bending mode (Table II). A rotationally resolved or jet measurement of this band could resolve the discrepancy, but we note that the reduced transmission of the beam splitter caused excessive noise around 250 cm$^{-1}$ in Ref. 21 and may have complicated the assignment. Currently, we slightly favor the earlier assignment at 248 cm$^{-1}$ for the band maximum but the 0 K value is likely to fall in between the two values.

At this stage, one must concede that the good agreement between experiment and MP2/6-31+G* calculations rests on a comparison between harmonic and harmonic values. Overtones and combination bands are needed to judge whether it also holds at the purely harmonic level. For this purpose, the 6 to 7 new weak bands observed in this study turn out to be valuable. Their isotope patterns (where available, see Table I and Fig. 2) and band positions suggest straightforward assignments. The lowest one must be the overtone of the IR-active twisting mode $2v_{15}$. It coincides with potential absorptions from air impurities, but the absence of other rotational transitions of O$_2$ and N$_2$ in the vicinity rules out a major distortion of the band profile. The highest transition correlates nicely with twice the dominant Raman active fundamental wave number (Fig. 2, o.o.p. bending) and is thus assigned to $2v_{12}$. Its photon count is about 100 times lower than for the fundamental. The weakest sharp band (see Fig. 4 below) corresponds to the overtone of the stretching fundamental $2v_8$. It scatters about 200 times less photons than the fundamental. The strongest nonfundamental transition has no consistent Raman active combination counterpart, but it matches the isotope pattern of the infrared o.o.p. bending fundamental and is thus assigned to $2v_{15}$.

This means that three out of the four Raman-active overtone transitions correspond to twisting or bending motions of FAD out of its planar minimum structure. Together with the corresponding fundamentals, these overtones of $v_{16}$, $v_{15}$, and $v_{12}$ span a systematic data set for the characterization of anharmonicity in these distortions. Note that the overtone of the i.p. rocking mode $v_9$, which shows some promise in promoting the hydrogen exchange tunneling, could not be safely identified in the regular Raman spectrum at the present signal-to-noise ratio. Its scattering strength must be a factor of 10 weaker than that of the neighboring $2v_{15}$ state at least. As shown below, a polarization experiment can at least provide tentative evidence for it by removing the depolarized fraction of the $2v_{15}$ band.

Table III lists the harmonic predictions for the proposed bending and stretching overtones for all four symmetric isotopomers, taking simply twice the calculated harmonic fundamental wave number. Isotope shifts are given in parentheses. They vary between nearly 0 and almost 70 cm$^{-1}$. Both

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**Table II.** Comparison of calculated harmonic FAD low frequency fundamentals using different quantum chemical methods and basis sets with experimental (anharmonic) values (in cm$^{-1}$).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Experiment</th>
<th>B3LYP</th>
<th>MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_{16}$</td>
<td>68$^a$, 69.2$^c$</td>
<td>76.1</td>
<td>69.3</td>
</tr>
<tr>
<td>$v_9$</td>
<td>161$^d$</td>
<td>176.4</td>
<td>169.1</td>
</tr>
<tr>
<td>$v_{15}$</td>
<td>168.5$^e$</td>
<td>184.4</td>
<td>192.7</td>
</tr>
<tr>
<td>$v_8$</td>
<td>194$^f$</td>
<td>212.2</td>
<td>212.3</td>
</tr>
<tr>
<td>$v_{12}$</td>
<td>242$^g$</td>
<td>260.2</td>
<td>260.0</td>
</tr>
<tr>
<td>$v_{24}$</td>
<td>248$^h$, 268$^i$</td>
<td>282.8</td>
<td>281.2</td>
</tr>
</tbody>
</table>

$^a$Reference 57, similar values were obtained before (Ref. 14).
$^b$References 43 and 55 (FIR spectrum in GP).
$^c$Reference 21 (high resolution FIR spectrum in GP).
$^d$This work (Raman supersonic jet spectrum).
$^e$Reference 21, see text for discussion.

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**Table III.** Calculated harmonic wave numbers (in cm$^{-1}$) for FAD low frequency modes at the MP2/6-31+G* level. The calculated wave number shifts (in cm$^{-1}$) between (HCOOH)$_2$ and its three isotopomers are listed in parentheses.

<table>
<thead>
<tr>
<th>Mode</th>
<th>(HCOOH)$_2$</th>
<th>(DCOOH)$_2$</th>
<th>(HCOOD)$_2$</th>
<th>(DCOOD)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2v_{16}$</td>
<td>137.6</td>
<td>136.6(1.0)</td>
<td>137.4(0.2)</td>
<td>136.6(1.0)</td>
</tr>
<tr>
<td>$v_9$</td>
<td>162.1</td>
<td>161.3(0.8)</td>
<td>158.3(3.8)</td>
<td>157.7(4.4)</td>
</tr>
<tr>
<td>$v_8$</td>
<td>202.9</td>
<td>200.4(2.5)</td>
<td>201.7(1.2)</td>
<td>199.3(3.6)</td>
</tr>
<tr>
<td>$v_{12}$</td>
<td>242.3</td>
<td>212.2(30.1)</td>
<td>236.9(5.4)</td>
<td>208.5(33.8)</td>
</tr>
<tr>
<td>$2v_{15}$</td>
<td>338.0</td>
<td>290.2(47.8)</td>
<td>323.0(15.0)</td>
<td>279.8(58.2)</td>
</tr>
<tr>
<td>$2v_{12}$</td>
<td>484.6</td>
<td>424.4(60.2)</td>
<td>473.8(10.8)</td>
<td>417.0(67.6)</td>
</tr>
</tbody>
</table>

$^a$Twice the calculated fundamental wave numbers.
the observed band positions and the wave number shifts between FAD and its isotopically substituted counterparts in the present work match the calculated ones very well, rendering the assignments given in Table I straightforward.

The \( \nu_{16} \) and \( \nu_{12} \) overtones which we find in this work had not been assigned before. The overtone band of \( \nu_{15} \) had been reported in previous Raman room temperature GP spectra with wave numbers of \( 317.7 \pm 1.4 \text{ cm}^{-1} \) for (HCOOH)\(_2\),\(^{39} \) \( 275 \pm 2 \text{ cm}^{-1} \) for (DCOOH)\(_2\),\(^{40} \) \( 305 \pm 3 \text{ cm}^{-1} \) for (HCOOD)\(_2\),\(^{40} \) as well as \( 266.2 \pm 1.3 \text{ cm}^{-1} \) for (DCOOD)\(_2\).\(^{39} \) The systematic redshifts in the GP spectra compared to the jet spectra are mostly due to thermal bond weakening effects in the former. This is also seen in the GP trace shown in Fig. 4. The thermal shifts are between 4\% and 5\% and are capable of masking any anharmonicity effect in FAD. This clearly shows that jet-cooled spectra are indispensable for a straightforward anharmonicity analysis, as it will be carried out in the following.

C. Anharmonicity analysis

For two modes \( \nu_1 \) and \( \nu_2 \), the term values \( G \) as a function of quantum numbers \( \nu_1 \) and \( \nu_2 \) may be written as\(^{38} \)

\[
G(\nu_1, \nu_2) = \omega_1 (\nu_1 + \frac{1}{2}) + \omega_2 (\nu_2 + \frac{1}{2}) + x_{1,1} (\nu_1 + \frac{1}{2})^2 + x_{2,2} (\nu_2 + \frac{1}{2})^2 + x_{1,2} (\nu_1 + \frac{1}{2})(\nu_2 + \frac{1}{2}).
\]

It follows that

\[
\nu_1 = G(1,0) - G(0,0) = \omega_1 + 2x_{1,1} + \frac{1}{2}x_{1,2},
\]

\[
2\nu_1 = G(2,0) - G(0,0) = 2\omega_1 + 6x_{1,1} + x_{1,2},
\]

\[
\nu_1 + \nu_2 = G(1,1) - G(0,0) = \omega_1 + \omega_2 + 2x_{1,1} + 2x_{2,2} + 2x_{1,2},
\]

and the relevant anharmonicity constants \( x_{1,1} \) and \( x_{1,2} \) can be extracted from

\[
x_{1,1} = \frac{1}{2}(2\nu_1 - \nu_1 \times 2),
\]

\[
x_{1,2} = (\nu_1 + \nu_2) - \nu_1 - \nu_2.
\]

From the jet Raman overtones and fundamentals, one obtains for the \( \nu_{12} \) mode of the different isotopomers an average diagonal anharmonicity constant \( x_{12,12} \) of \(-1 \pm 1 \text{ cm}^{-1} \) (see Table IV). This persistently negative value is just slightly larger than the error bar due to calibration and residual band center uncertainties from the band profile. We conclude that a jet measurement is essential for its detection because thermal shifts in the room temperature GP are an order of magnitude larger and matrix isolation shifts are difficult to predict.

For the \( \nu_{15} \) mode, the infrared fundamental band center for the main isotopomer is available from a rotationally resolved measurement\(^{21} \) in good agreement with earlier GP work.\(^{43,55} \) Therefore, an anharmonic analysis based on the Raman overtone is also possible and yields \( x_{15,15} = -0.5 \text{ cm}^{-1} \). For isotopomers, no reliable experimental IR fundamentals are available, but if we take the calculated harmonic fundamental band positions in Table III as an approximate reference validated by the HCOOH result, the \( x_{15,15} \) are all slightly negative and probably do not exceed 1 or 2 cm\(^{-1} \) in magnitude (see Table IV).

The same is true for the very weak first overtone of the dimer stretching mode \( \nu_8 \) (Fig. 4), which features an anhar-
mononicity constant $x_{8,8} = -1$ cm$^{-1}$. The fact that this overtone band has a width of less than 2 cm$^{-1}$ puts a loose upper bound on the hydrogen transfer tunneling splitting in the excited state. The assignment of $2\nu_3$ is further confirmed by a depolarization measurement because the dimer stretching mode is predicted to give rise to a strongly polarized band. Figure 5 shows a comparison of the spectrum recorded with perpendicular polarization of the excitation laser and the polarized component alone (bottom). The latter is estimated by subtracting the spectrum with parallel laser polarization, multiplied by $7/6$, from the spectrum with perpendicular laser polarization. One can see that the band at 385 cm$^{-1}$ persists quite strongly as does $\nu_8$. The persistence of signal at $\nu_{12}$ is in part a consequence of its strong scattering intensity, which reacts sensitively to concentration variations, but may also reflect an overlapping $A_4$ band, as speculated above. Furthermore, the polarized spectrum reveals a very weak band at 319 cm$^{-1}$ (marked with an arrow), which we tentatively assign to $2\nu_3$, again consistent with a very small diagonal anharmonicity constant of $\approx 1.5$ cm$^{-1}$. It is more than 200 times weaker than the fundamental.

A larger uncertainty exists for the analysis of diagonal anharmonicity in $\nu_{16}$ because the IR fundamental has not been analyzed at rotational resolution and the Raman overtone is weak and possibly affected by nearby air impurity absorptions. However, there is satisfactory agreement between different lower resolution studies of the fundamental. Within these uncertainties, the anharmonicity constant $x_{16,16}$ is negligible.

Raman active combination bands are found to be ex-

![FIG. 5. Spectrum of FAD in He (\textasciitilde 0.7\%) with the excitation laser perpendicular to the scattering plane (top trace) and residual after subtracting \textasciitilde 7/6 of the spectrum obtained with the excitation laser parallel to the scattering plane. $A_4$ bands with a small depolarization ratio $\rho_{A_4}$ persist most.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Dimer & Mode & Anharmonic calculation & Experiment \\
\hline
(HCOOH)$_2$ & $2\nu_{13}(A_4)$ & (141.6$\times 71.3$) & 0.5 \quad (139$\times 69.2$) \\
 & $2\nu_{13}(A_4)$ & (326.5$\times 163.9$) & 0.7 \quad (319$\times 161.3$) \\
 & $2\nu_{13}(A_4)$ & (346.7$\times 174.4$) & 1.1 \quad (336$\times 168.5$) \\
 & $2\nu_{13}(A_4)$ & (376.5$\times 190.2$) & 1.9 \quad (386$\times 194.2$) \\
 & $2\nu_{13}(A_4)$ & (490.1$\times 246.0$) & 2.0 \quad (482$\times 242.2$) \\
 & $\nu_{12}+\nu_{13}(B_4)$ & 407.9$\times 246.0$, 163.9 & 2.0 \quad 400$\times 242.2$, 161.3 \\
 & $\nu_{13}(B_4)$ & 433.2$\times 246.0$, 190.2 & 3.0 \quad 435$\times 242.2$, 194.1 \\
 & $\nu_{12}+\nu_{13}(B_4)$ & 315.9$\times 246.0$, 71.3 & 1.4 \quad 311$\times 242.2$, 69.2 \\
 & $\nu_{13}(B_4)$ & 336.4$\times 163.9$, 174.4 & 1.0 \quad 329$\times 161.3$, 168.5 \\
 & $\nu_{12}+\nu_{13}(B_4)$ & 417.3$\times 246.0$, 174.4 & 3.1 \quad 395$\times 242.2$, 168.5 \\
 & $\nu_{13}(B_4)$ & 425.1$\times 163.9$, 264.6 & 3.4 \quad 395$\times 161.3$, 253.7 \\
(DCOOH)$_2$ & $2\nu_{13}(A_4)$ & (141.5$\times 71.3$) & 0.6 \quad (139$\times 68.3$) \\
 & $2\nu_{13}(A_4)$ & (297.2$\times 149.2$) & 0.6 \quad (289$\times 145.1$) \\
 & $2\nu_{13}(A_4)$ & (429.4$\times 215.4$) & 0.7 \quad (423$\times 212.4$) \\
 & $2\nu_{13}(A_4)$ & (484.7$\times 243.5$) & 1.2 \quad (473$\times 238.2$) \\
 & $\nu_{12}+\nu_{13}(B_4)$ & 313.4$\times 243.5$, 71.5 & 1.6 \quad 299$\times 238.2$, 68.7 \\
 & $\nu_{13}(B_4)$ & 408.6$\times 243.5$, 168.2 & 3.1 \quad 390$\times 238$161.5 \\
 & $\nu_{12}+\nu_{13}(B_4)$ & 413.3$\times 160.6$, 256.0 & 3.3 \quad 390$\times 157.7$, 248.1 \\
 & $\nu_{13}(B_4)$ & 313.4$\times 71.4$ & 0.5 \quad (139$\times 68.3$) \\
(DCOOD)$_2$ & $2\nu_{13}(A_4)$ & (141.4$\times 71.4$) & 0.7 \quad (139$\times 68.3$) \\
 & $2\nu_{13}(A_4)$ & (289.1$\times 145.2$) & 0.7 \quad (278$\times 139.9$) \\
 & $2\nu_{13}(A_4)$ & (425.5$\times 213.5$) & 0.8 \quad (417$\times 210.2$) \\
 & $\nu_{12}+\nu_{13}(B_4)$ & 283.9$\times 213.5$, 71.4 & 1.0 \quad 277$\times 210.2$, 68.3 \\
\hline

\end{tabular}
\caption{Comparison of calculated B3LYP/6-31+G(2d, 2p) anharmonic constants derived from intermolecular overtone and combination bands of FAD and its isotomers with experimentally derived constants using experimental jet and GP data as well as theoretical isotope extrapolation. Rigorous experimental values are given in boldface, whereas combinations relying on unresolved GP bands are given in parentheses.}
\end{table}
TABLE V. Tentative assignment of some IR active combination bands of FAD and its isotopomers observed in earlier FIR GP work (Refs. 21, 43, and 55). Predictions are made based on the calculated band positions of IR active fundamental modes at MP2/6-31+G* level (slanted) and the jet Raman data of this work, neglecting mixed anharmonicity contributions. Assignments in parentheses for (HCOOD)$_2$ were not proposed in Ref. 39.

<table>
<thead>
<tr>
<th>Experiment (cm$^{-1}$)</th>
<th>Dimer</th>
<th>Assignment</th>
<th>Prediction (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>311$^a$, 307$^{34}$</td>
<td>(HCOOH)$_2$</td>
<td>$v_{16}+v_{12}$, $v_{15}+v_{12}$</td>
<td>68.8+242=310.8</td>
</tr>
<tr>
<td>299$^b$</td>
<td>(HCOOD)$_2$</td>
<td>$v_{16}+v_{9}$, $v_{15}+v_{9}$</td>
<td>169.0+161=330.0</td>
</tr>
<tr>
<td>277$^c$</td>
<td>(DCOOD)$_2$</td>
<td>$v_{16}+v_{12}$, $v_{15}+v_{12}$</td>
<td>68.7+238=306.7</td>
</tr>
<tr>
<td>329$^b$</td>
<td>(HCOOH)$_2$</td>
<td>$v_{15}+v_{9}$</td>
<td>161.5+157=318.5</td>
</tr>
<tr>
<td>395$^b$</td>
<td>(HCOOH)$_2$</td>
<td>$v_{15}+v_{12}$, $v_{15}+v_{12}$</td>
<td>68.3+210=278.3</td>
</tr>
<tr>
<td>300$^b$</td>
<td>(HCOOD)$_2$</td>
<td>$v_{15}+v_{9}$, $v_{24}+v_{9}$</td>
<td>139.9+157=296.9</td>
</tr>
<tr>
<td>390$^b$</td>
<td>(HCOOD)$_2$</td>
<td>$v_{15}+v_{12}$, $v_{24}+v_{12}$</td>
<td>253.7+161=414.7</td>
</tr>
<tr>
<td>325$^b$</td>
<td>(HCOOH)$_2$</td>
<td>$v_{25}$</td>
<td>248.1+157=405.1</td>
</tr>
</tbody>
</table>

$^a$Reference 21 (high resolution FIR GP spectrum).
$^b$Reference 43 (FIR GP spectrum).
$^c$Reference 55 (FIR GP spectrum).

The Raman insights obtained for the fundamentals, overtones, and combination bands may be used to reanalyze some IR work in this spectral range. Three IR active van der Waals combination bands of FAD and some corresponding isotopomer bands were reported in earlier work$^{21,39,43,55}$ (see Table V and Fig. 6). The lowest frequency one of (HCOOH)$_2$ was observed from 307 (Refs. 43 and 55) to 311 cm$^{-1}$ (Ref. 21). Related band positions for (HCOOD)$_2$((DCOOD)$_2$) were reported$^{33}$ at 299 cm$^{-1}$ (277 cm$^{-1}$ in Ref. 55). Two higher energy IR active combination bands at 329 and 395 cm$^{-1}$ were detected in Ref. 43. Bertie and Michaelian$^{39}$ assigned the nondeuterated and fully deuterated bands in the room temperature GP spectra, neglecting anharmonic contributions.

Because of the band center uncertainties associated with thermal excitation, we have followed a slightly different prediction strategy, combining our jet-cooled Raman fundamentals with harmonic MP2/6-31+G* predictions for the IR fundamentals. The predicted combination band positions neglecting mixed anharmonicity are listed in Table V. Some experimental data for (HCOOD)$_2$ are included as well.

We exemplify the situation for the band observed at 307/311 cm$^{-1}$. Based on the addition of IR and Raman GP fundamental values, two combination band assignments were proposed, namely, $v_{15}+v_9$ or $v_{16}+v_{12}$.$^{39}$ Both combinations give a wave number sum close to 300 cm$^{-1}$(163+137,68 +230) when constructed from the thermal GP data. By combining our accurate Raman jet band positions with MP2/6-31+G* IR predictions (or in this case equivalently the best available IR experimental data) instead, the wave number sum is 330 cm$^{-1}$(169+161) or 311 cm$^{-1}$(69+242).

FIG. 6. Comparison of the predicted and experimental band positions of FAD below 500 cm$^{-1}$ up to two vibrational quanta. The Raman active bands are marked with black solid lines while the IR active ones are shown as red dotted lines. The experimental data (center, Raman transitions from this work and Ref. 4, IR transitions from Refs. 21, 43, and 55) are flanked by columns of harmonic MP2/6-31+G* predictions building on a given o.o.p. or i.p. bending, stretching, or twisting fundamental. See also Tables II and V.
It is tempting to favor the latter assignment in this case, i.e., $\nu_{16} + \nu_{12}$, although the GP combination band maximum may be thermally shifted from the band center. However, a thermal shift of $\approx 20$ cm$^{-1}$ (or more if anharmonicity effects are taken into account) appears less likely. The predicted isotopic substitution pattern follows the experimental one quite well in both cases and cannot be used as an assignment aid in this case. On the other hand, the harmonic simulated band position of $\nu_{15} + \nu_9$ is in good agreement with the observed band at 329 cm$^{-1}$, which was not assigned in Ref. 39. Unfortunately the isotopomer bands are not observed, leaving some room for confirmation.

If we settle for the assignment of the 311 cm$^{-1}$ band to $\nu_{16} + \nu_{12}$ and of the 329 cm$^{-1}$ band to $\nu_{15} + \nu_9$, the mixed anharmonicity appears to be negligible in these cases as well. A firm statement has to await a jet-cooled IR measurement of these two combination bands. However, there is already some evidence from an analysis of hot band structure in these two fundamental may be somewhat too high in energy $\nu_{15}$ is very sensitive to C–H deuteration. For an assessment of anharmonicity, IR jet spectra will be indispensable.

If we assume $\nu_{15} + \nu_{12}$ as the correct assignment of the IR active band at 395 cm$^{-1}$, it is interesting to see that only the two o.o.p. IR active fundamental bands are available for strong combinations and only the overtone bands of these two are detected with substantial intensity in our Raman jet study. The Raman o.o.p. bending mode $\nu_{12}$ is the only one of the three Raman active fundamental modes whose overtone is observed with significant intensity. One may speculate that o.o.p. motion also couples strongly to other modes and that it should be preferentially considered for the assignment of combination bands in higher frequency regions.

The most important finding is that all intermolecular modes of FAD for which combinations and overtones were observed have very small diagonal and off-diagonal anharmonicity constants on the order of $-1 \pm 2$ cm$^{-1}$. This is in line with reduced-dimensionality anharmonic calculations$^{16,17}$ and appears to convey a surprisingly harmonic picture of the hydrogen bond modes in this hydrogen bond prototype. As we will show in Sec. III D, this impression can be deceiving.

D. Anharmonic perturbation theory

In the recent Raman matrix isolation study, the standard second order perturbation theory approach implemented in the GAUSSIAN program suite was applied to $\nu_{12}$ and yielded an anharmonic wave number of 245 cm$^{-1}$ at B3LYP/6-311+G(2d,2p) level in satisfactory agreement with the experimental jet value of 242 cm$^{-1}$. The corresponding harmonic wave number of 261 cm$^{-1}$ for this mode is in much poorer agreement with the experiment. This can be rationalized when considering the relationship (in the absence of anharmonic resonances)

$$\nu_{12} = \omega_{12} + 2x_{12,12} + \frac{1}{2} \sum_{j \neq 12} x_{12,j}. $$

The diagonal anharmonicity correction is only $-2$ cm$^{-1}$, whereas the five off-diagonal contributions from the other hydrogen bond modes accumulate to $-7$ cm$^{-1}$. Three of these are largely confirmed by experiment in the present work, the others would require FIR jet spectroscopy. The remaining gap between the harmonic and anharmonic $\nu_{12}$ fundamental of about $-10$ cm$^{-1}$ is the net effect of positive and negative intra/intermolecular couplings. This underscores the need for an extensive experimental study of combination bands in the higher frequency range because the validity of the perturbation approach also requires testing.

Table IV summarizes the anharmonic predictions of the B3LYP/6-311+G(2d,2p) perturbational analysis and compares the effective anharmonicity constants $\omega_{ij}$ to those derived from experiment. In the case of $\omega_{38,8}$, i.e., the anharmonicity constant of the dimer stretching mode, reaction surface variational results (at B3LYP/6-31+G$^*$ level where the fundamental may be somewhat too high in energy) are also available. They are sensitive to the variational basis set, but the largest basis set yields a value of $-1.1$ cm$^{-1}$ in excellent agreement with experiment and reasonable agreement with perturbation theory.

Not surprisingly, an anharmonic perturbation theory analysis at the MP2/6-31+G$^*$ level reveals that the close agreement of the harmonic predictions with experiment is a consequence of fortuitous error cancellation. The (approximate) anharmonic predictions for the hydrogen bond fundamentals are now significantly lower than our experimental data.

Figure 7 plots the two anharmonic predictions and the harmonic MP2/6-31+G$^*$ prediction against the experimental band centers derived in this work. The most consistent performance is found for the anharmonic B3LYP approach (circles). The harmonic MP2/6-31+G$^*$ results (squares), which are shifted by 50 cm$^{-1}$ for clarity, show a perfect correlation for all but the stretching fundamental and only slight overestimates for the two-quantum transitions. When corrected for anharmonicity effects, all band positions are seen to be systematically underestimated at MP2/6-31+G$^*$ level as expected (triangles).

In this context we wish to point out a recent quantum chemical study including anharmonicity at the MP2/6-311+G(d,p) level. Comparison with the present experimental data shows that a full counterpoise (CP) correction during optimization and force field evaluation is needed to obtain qualitatively reasonable results for anharmonic constants. For example, $\nu_{12} - \omega_{12}$ is predicted at $+1.4$ cm$^{-1}$ without CP correction. With correction, it is predicted at $-17$ cm$^{-1}$ in good agreement with the less basis set-sensitive B3LYP result of $-16$ cm$^{-1}$ (6-311++G(2d,2p)). On the other hand, the absolute predictions at CP-corrected MP2/6-311...
The intermolecular transitions of FAD are framed on their lower end by rotational transitions, which are difficult to access in our instrument because of the Rayleigh edge filter, and on the high wave number end by the lowest intramolecular mode of the HCOOH dimer. This is the \( A_g \)-symmetric OCO bending mode \( \nu_7 \), which has already been discussed in detail in Ref. 4. It is blueshifted relative to the corresponding vibrations in formic acid monomer and its isotopomers (also denoted as \( \nu_7 \)), which may be seen as weak sharp bands in the spectra of the dimer-dominated expansion [marked as M in Fig. 2 (Refs. 39, 40, and 57)]. They are easily identified by comparison with GP spectra (not shown) and by their different concentration dependence. Furthermore, they match quite closely the harmonic MP2/aug-cc-pVTZ predictions (see Table VI), whereas the fortuitously good performance of the MP2/6-31+G* approach breaks down for this and other intramolecular modes. The band in the HCOOH expansion is particularly weak because the spectrum was recorded at a stagnation pressure of 1 bar instead of 0.5 bar for the deuterated isotopomers. Therefore, the clustering extent is higher.

Table VI lists some weak dimer bands near the lowest intramolecular FAD vibration \( \nu_7 \), which are marked with different labels in Fig. 2. It is unlikely that they arise from water impurities in the formic acid samples, although such impurities are always an issue in this chemically unstable compound. The bands at 692 cm\(^{-1} \) (label \( A \)) and 637 cm\(^{-1} \) (label \( B \)) in the jet spectrum of \( \text{DCOOH} \) are instead assigned as the intramolecular OCO bending modes of the unsymmetrically isotope-substituted \( \text{DCOOH–DCOOD} \) dimer. Such mixed dimers can arise from partial isotope exchange at the container walls and the presence of about 10% \( \text{DCOOD} \) is indeed also evidenced by a small \( \text{DCOOH} \) monomer peak marked in Fig. 2. Weaker evidence of isotope exchange is also seen in the \( \text{DCOOD} \) and \( \text{HCOOD} \) spectra, but not in the HCOOH spectra, which were measured before introducing deuterated compounds into the apparatus. The lower frequency band at 637 cm\(^{-1} \) in the DCOOH spectrum is unusually strong, indicating that there might be another contribution underneath, e.g., from \( 3\nu_{12} \).

Both mixed dimer bands \((A,B)\) are shifted by about 15 cm\(^{-1} \) to higher wave number relative to their symmetric dimer \( \nu_7 \) counterparts (see Table VI). This blueshift is underestimated by the calculations, but the assignment is still...
hindered internal rotation or torsion of the OH group relative to actually not the lowest fundamental. Instead, the strongly Raman active o.o.p. hydrogen bond bending vibrations of HCOOH and band of the dimer. The harmonic predictions for this mode show a wide variation in agreement with the observation. Interestingly, the C–H/C–D isotope effect is relatively stable and in good agreement if one takes into account some negative anharmonicity contribution x11,11 which will almost certainly exist for this large amplitude vibration. A doublet band characteristic for Bg symmetry in the nondeuterated HCOOH dimer spectrum at 911 cm−1 (not shown) is also consistent with a ν11 assignment and will be discussed in detail in a future systematic investigation of the intramolecular Raman active modes of FAD. We note that it has recently been assigned in the room temperature GP at 922.0 ± 1.5 cm−1 confirming an earlier assignment. A thermal shift of 11 cm−1 is not unusual for such an intramolecular vibration, but the direction of the shift is surprising. Normally, one would expect a shift toward the corresponding monomer fundamental, which is found at much lower wave number. Even in the case of the less hydrogen bond affected ν7 vibration, the thermal GP band maximum is significantly redshifted. Therefore, one should not dismiss other explanations for the GP band such as ν7 + ν12 at this stage.

### IV. CONCLUSIONS

The present work advances the characterization of hindered rotor o.o.p. modes in FAD and its deuterium isotopomers in several important directions:

(i) It presents the first overtone measurement of the only Raman active o.o.p. hydrogen bond bending vibration. Its almost negligible diagonal anharmonicity points at a rather linear restoring force in this double hydrogen bridge.

(ii) It presents overtone measurements of the two IR active o.o.p. hydrogen bond bending and twisting modes, thus providing the first jet-cooled characterization of these modes, eliminating thermal or matrix perturbations. Although the evidence is more indirect in this case, the results also point at rather small diagonal anharmonicity contributions.

(iii) It presents new, still preliminary evidence for the symmetric o.o.p. OD torsional mode in FADs, the last dimer mode which had remained unassigned in the literature until very recently, if one discounts the strongly coupled and spectrally delocalized OH stretching mode.

---

**Table VI. Assignment of some intramolecular Raman active modes of (HCOOH)2 and its isotopomers between 600 and 750 cm−1.** Experimental band maxima (in cm−1) are compared with the calculated harmonic band positions (in cm−1) using the MP2 method with different basis sets. The blueshifts (in cm−1) from ν7 of isotopically mixed dimers relative to the corresponding symmetric dimer modes are listed in parentheses.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Dimer</th>
<th>Label</th>
<th>Calculation (MP2)</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(HCOOH)2</td>
<td>...</td>
<td>aug-cc-pVTZ^a</td>
<td>630.8</td>
</tr>
<tr>
<td></td>
<td>(DCOOH)2</td>
<td>...</td>
<td>698 cm−1</td>
<td>628</td>
</tr>
<tr>
<td></td>
<td>(HCOOD)2</td>
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<td>675.5</td>
</tr>
<tr>
<td></td>
<td>(DCOOH)2</td>
<td>...</td>
<td>628</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DCOOH-DCOOOH A</td>
<td>...</td>
<td>674(9.5)</td>
<td>692(16)</td>
</tr>
<tr>
<td></td>
<td>DCOOH-DCOOOH B</td>
<td>...</td>
<td>622(9.3)</td>
<td>637(13)</td>
</tr>
<tr>
<td></td>
<td>HCOOH-HCOOD C</td>
<td>...</td>
<td>680(9.8)</td>
<td>698(16)</td>
</tr>
<tr>
<td></td>
<td>HCOOH-HCOOD D</td>
<td>...</td>
<td>627(9.5)</td>
<td>641(13)</td>
</tr>
<tr>
<td>ν11(Bg)</td>
<td>(HCOOH)2</td>
<td>...</td>
<td>979.4</td>
<td>934.3</td>
</tr>
<tr>
<td></td>
<td>(DCOOH)2</td>
<td>...</td>
<td>990.7</td>
<td>946.3</td>
</tr>
<tr>
<td></td>
<td>(HCOOD)2 E</td>
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<td>721.8</td>
<td>693.5</td>
</tr>
<tr>
<td></td>
<td>(DCOOH)2 F</td>
<td>...</td>
<td>719.5</td>
<td>690.1</td>
</tr>
</tbody>
</table>

^aReference 57.

^bTo be published in detail.
(iv) The spectra include the first overtone assignment of the symmetric hydrogen bond stretching mode, again very close to twice the fundamental frequency and without any evidence for accelerated hydrogen exchange tunneling at the available spectral resolution. More tentatively, the overtone of the i.p. bending fundamental is detected. Very weak signatures of intermolecular combination bands are also discussed. It would be desirable to have reliable intensity predictions for these two-quantum transitions, which are found to be two to three orders of magnitude weaker than their one-quantum counterparts.

(v) The effect of Ar condensation on FAD is illustrated, leading to significant blueshifts of the intermolecular fundamentals and helping to interpret the recent matrix isolation spectra. 48

The small anharmonicity effects in the van der Waals modes tend to support reaction path Hamiltonian approaches which treat bath modes harmonically. 17,19-20 However, the cumulative effect of small anharmonicity contributions on the fundamental frequencies can be rather large, as anharmonic perturbation calculations indicate. Basically, all spectral features down to the noise level can be attributed to symmetric dimers and monomers of formic acid, supporting the expectation that isomeric forms of the dimer are not present in significant amounts.

Taken together, these new experimental results advance our understanding of the low frequency FAD dynamics quite substantially, as summarized in Fig. 6. They will also promote the assignment of the extremely complex spectra 17,49 above 2000 cm\(^{-1}\). An important intermediate step will be a jet study of the intramolecular Raman spectra below 2000 cm\(^{-1}\), which is currently under way in our laboratory and which will complement selected IR jet data. 11,21 Even more so than in the monomers, 64 this region will involve a number of vibrational resonances in the dimers, which need to be unraveled with the help of isotope substitution. 22,23

A largely improved experimental setup will be needed to resolve FAD tunneling splittings as a function of vibrational excitation because these splittings are exceedingly small. 5,19 However, the symmetric modes which Raman spectroscopy is able to probe are particularly promising in this context because they are expected to show the largest enhancements. 20 Tunneling will be further slowed down in homologs of FAD such as the dimer of acetic acid, 26,65,66 where methyl group rotation must be synchronized to hydrogen transfer. The study of its low frequency modes may provide additional insights into the o.o.p. dynamics of the carboxylic acid dimer subunit.

A further exploration of unsymmetric dimers, either by isotope exchange as in this work or by chemical substitution, 26,65,66 is indicated as soon as the symmetric dimers are fully understood because this can provide alternative insights into the hydrogen bond-mediated coupling strengths. Furthermore, the transition from concerted to stepwise double proton transfer can be investigated in such systems. 68 Ultimately, a detailed experimental anharmonic force field 14 of these prototype systems for double hydrogen bonding should be reachable by a combination of IR and Raman spectroscopy in supersonic jets. Such force fields appear to be a prerequisite for accurate tunneling splitting predictions. 16,18,19

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