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# Proton Tunneling in Heterodimers of Carboxylic Acids: A Rotational Study of the Benzoic Acid–Formic Acid Bimolecule

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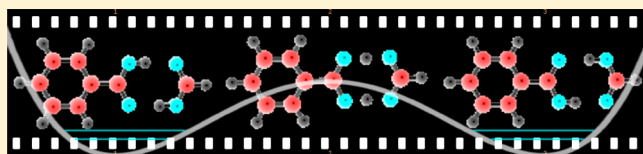
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## Supporting Information

**ABSTRACT:** Tunneling effects have been measured in the pulsed jet Fourier transform microwave spectra of two isotopologues of the benzoic acid–formic acid bimolecule. The tunneling splittings are originated by the concerted proton transfer of the two carboxylic hydrogens. From the values of these splittings for the OH–OH and OD–OD species, it has been possible to model/size the barrier to the concerted double proton transfer.

**SECTION:** Spectroscopy, Photochemistry, and Excited States

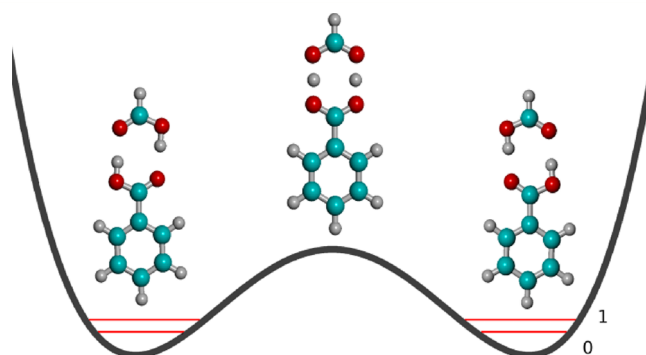


Molecular systems with two equivalent configurations that can interconvert upon proton exchange are particularly suitable to investigate the rate of such a process and the corresponding potential energy surface. High-resolution spectroscopy, such as microwave (MW) spectroscopy, has provided considerable information on this kind of problem for a single proton transfer, for classical systems such as malonaldehyde (MA),<sup>1</sup> 2-methyl-MA,<sup>2</sup> 2-nitro-MA,<sup>3</sup> and tropolone.<sup>4</sup> In all cases, two equivalent structures with a  $C_s$  symmetry are connected by proton exchange through a transition state with a  $C_{2v}$  symmetry. Extensive ab initio predictions for MA, including vibrational properties and a proton tunneling barrier of 13.8 kJ/mol, were found to be consistent with experimental data.<sup>5</sup>

A similar proton transfer takes place in pairs of carboxylic acids, but in this case, a double concerted proton transfer is required. The nature of such a kind of molecular system is depicted in Figure 1 for the bimolecule benzoic acid–formic acid (BA–FA). The two units are bound cooperatively together, since both act as proton donor and acceptor, forming a large eight-membered ring containing two hydrogen bonds. Such a kind of hydrogen bonding is the strongest one found within neutral species, with the monomers held together by more than 60 kJ/mol. Gilli et al. explain such a “strong” interaction in terms of a resonance-assisted hydrogen bond model.<sup>6</sup>

Also for this kind of complex, MW spectroscopy can supply tunneling splittings.

So far, interesting spectroscopic results have been obtained on the homodimers of carboxylic acids mainly with other high-resolution techniques. Among them, a rotationally resolved



**Figure 1.** Proton tunneling and potential energy profile to the concerted double proton transfer in carboxylic acid bimolecules.

laser-induced fluorescence (LIF) investigation of the dimer of benzoic acid<sup>7</sup> allowed for the tunneling effects to be revealed.

LIF methods generally require a chromophore group, restricting such studies to systems containing such a tag, so that the homodimers of simpler carboxylic acids have been investigated with other high-resolution methods such as femtosecond degenerate four-wave mixing and Raman spectroscopy.

These methods supplied information, such as tunneling splittings in the ground and vibrationally excited states, on

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formic acid<sup>8–14</sup> and acetic acid<sup>15</sup> homodimers, but rather large uncertainties are associated with the measured values.

MW investigations provide the most accurate vision of the molecular structure and can supply tunnelling splittings and, hence, information on the dynamics and on the potential energy surfaces. Carboxylic acid dimers were early observed with low-resolution MW spectroscopic methods by Costain in 1961<sup>16</sup> and Bellot and Wilson in 1975.<sup>17</sup> Then Bauder and co-workers provided detailed supersonic-jet FTMW analyses for some carboxylic acid bimolecules: the structures of CF<sub>3</sub>COOH...HCOOH and CF<sub>3</sub>COOH...CH<sub>3</sub>COOH have been determined through the analyses of the rotational spectra of several isotopologues.<sup>18</sup> For the latter complex, also the *V*<sub>3</sub> barrier to internal rotation of the methyl group was determined. Antolinez et al. reported the MW spectrum of the trifluoroacetic acid–cyclopropanecarboxylic acid bimolecule.<sup>19</sup> In none of these cases is doubling of the rotational transitions attributable to a double proton transfer tunneling observed. The proton transfer would have required, indeed, a simultaneous internal rotation of the heavy CF<sub>3</sub> top to reach an equivalent potential energy minimum. The resulting large reduced masses of the motion quench the tunneling effects.

Only recently has doubling related to the proton transfer been observed on the FTMW spectra of the formic acid–propionic acid dimer,<sup>20</sup> and of the formic acid–acetic acid bimolecule.<sup>21</sup> In the first case, the proton tunneling was measured for two species. In the second case, the double proton transfer motion was coupled—in order to reach an equivalent minimum—with a 60° internal rotation of the methyl group. The problem is similar to that encountered in the case of proton transfer in methylmalonaldehyde.<sup>2</sup> Howard conducted a superb analysis of the two-dimensional problem, but its complexity made it difficult to obtain from the determined splittings a precise and unique value of the barrier to the proton transfer.

In the case of dimers without additional motion with respect to the coupled proton transfer, and which offer the possibility to measure the tunneling splittings also for the OD deuterated species, it would be more direct to estimate the potential energy surface. Interesting results have already been obtained from MW data for a homodimer, the dimer of acrylic acid.<sup>22</sup>

We decided to obtain similar results for a hetero dimer of carboxylic acids, and here we report the rotational spectrum of the bimolecule BA–FA (shown in Figure 1).

The investigation of the spectrum was supplemented with theoretical electronic structure calculations, the details of which are given in the appropriate section. The MP2 calculations provide a considerably distorted shape with respect to planarity, which we will see to be in contrast with the experimental evidence. The obtained results, concerning the spectroscopic constants and the dissociation energy, are shown in Table 1.

Guided by the theoretical calculations presented above, the rotational spectrum of benzoic–formic acid heterodimer was assigned for  $\mu_a$ -type transitions. Each transition was split into two lines due to the proton tunnelling, and each of them appeared as a doublet according to the Doppler effect. All transitions have been fitted simultaneously with a coupled Hamiltonian using the Pickett's SPFIT program<sup>23</sup> with *I*-representation of Waltson's *S* reduction.<sup>24</sup> The following expression was used:

$$H = \sum_i H_i^R + H^{CD} + H^{\text{int}}, \quad \text{with } i = 0, 1 \quad (1)$$

**Table 1.** Calculated (6-311++G(d,p) Basis Set) Values of Relative Energies, Dissociation Energies, Spectroscopic Constants, and Dipole Moment Components of the BA–FA Dimer<sup>a</sup>

	B3LYP	MP2
<i>A</i> /MHz	2914.9	2891.4
<i>B</i> /MHz	392.6	392.0
<i>C</i> /MHz	346.0	345.9
$\Delta_c/\text{uÅ}^2$	0.000	−2.938
<i>D</i> <sub>J</sub> /Hz		7.9
<i>D</i> <sub>JK</sub> /Hz		32.4
<i>D</i> <sub>K</sub> /Hz		189.4
<i>d</i> <sub>1</sub> /Hz		−1.0
<i>d</i> <sub>2</sub> /Hz		−0.1
$\mu_a$ /D	−1.90	−1.55
$\mu_b$ /D	0.09	−0.07
<i>D</i> <sub>e</sub> /kJmol <sup>−1</sup>		65.5
<i>D</i> <sub>e,CP</sub> /kJmol <sup>−1</sup>		51.4
<i>D</i> <sub>0</sub> /kJmol <sup>−1</sup>		60.3

<sup>a</sup>*D*<sub>e</sub>, *D*<sub>e,CP</sub>, and *D*<sub>0</sub> are the equilibrium, counterpoise-corrected, and zero-point dissociation energies, respectively. Absolute values of the MP2 energies, counterpoise-corrected energies, and zero-point energies are −609.1691816, −609.1637953, and −609.0180900 *E*<sub>h</sub>, respectively.

and

$$H^{\text{int}} = \Delta E_{01} + F_{ab} \times (P_a P_b + P_b P_a) \quad (2)$$

with *i* = 0, 1 and where *H*<sup>*R*</sup> represents the rotational Hamiltonian and *H*<sup>*CD*</sup> accounts for the centrifugal distortion constants.  $\Delta E_{01}$  is the vibrational tunnelling splitting energy between the 0<sup>+</sup> and 0<sup>−</sup> substates of the vibrational ground state (labeled as 0 and 1 through the text), and *F*<sub>ab</sub> is the vibration–rotation interaction parameters. The spectroscopic parameters are reported in the left column of Table 2.

In order to check the contribution of the skeletal motion to the proton tunnelling, we also investigated the spectra of DH, HD, and DD oxygen-deuterated species. In the analysis of the monodeuterated species, we notice that the single isotopic substitution breaks down the symmetry of the complex, annihilating the tunnelling splitting and originating two different isotopologues (BA–D and FA–D, depending on the position of the D atom). The tunnelling splitting is observable, however, in the double DD substituted species. Since its  $\Delta E_{01}$  splitting is quite smaller than the HH species, it was difficult to simultaneously fit  $\Delta E_{01}$  and the *F*<sub>ab</sub> Coriolis coupling constants. For this case, according to Pickett,<sup>25</sup> we obtain the *F*<sub>ab</sub> value from the rotation of the principal axes system to the reduced Eckart axes system.<sup>26</sup> The results of these last fittings are reported in the right columns of Table 2.

The inertial defects ( $\Delta_c$ ) of the various isotopologues are also given in Table 2. Their values are close to zero for the OH–OH and OD–OD species. However, the effective inertial defects of the BA(OD)–FA and BA–FA(OD) are much higher (negative), because the fittings do not include the *F*<sub>ab</sub> Coriolis coupling constant; then the proton vibrational effects are accounted for in the effective rotational constants.

Within a low barrier to proton exchange, the BA–FA molecular complexes can be assigned to the *C*<sub>2v</sub> point group symmetry. A  $\pi$  rotation around the *a*-principal axis exchanges three pairs of equivalent protons, which are fermions with *I* = 1/2. Then, the complex obeys the Fermi–Dirac statistics, which

**Table 2. Experimental Spectroscopic Constants of the Observed Isotopologues of the BA–FA Bimolecule (S-Reduction, I<sup>r</sup> Representation)**

	OH–OH	OD–OD	BA(OD)-FA	BA-FA(OD)
$A_0/\text{MHz}$	2913.893(8) <sup>a</sup>	2869.731(4)	2891.11(1)	2893.20(1)
$B_0/\text{MHz}$	396.0645(2)	392.14402(2)	394.34623(4)	393.14467(4)
$C_0/\text{MHz}$	348.72660(6)	345.00654(5)	347.28813(4)	346.38684(4)
$A_1/\text{MHz}$	2913.900(8)	2869.728(4)		
$B_1/\text{MHz}$	396.0616(2)	392.14393(2)		
$C_1/\text{MHz}$	348.72424(5)	345.00653(5)		
$D_J/\text{Hz}$	7.44(6)	7.16(2)	6.69(9)	
$D_{JK}/\text{kHz}$	0.033(2)	[0.033] <sup>b</sup>		
$d_1/\text{Hz}$	−0.88(7)	[−0.88]		
$\Delta E_{01}/\text{MHz}$	548.72(6)	8.3(3)		
$F_{ab}/\text{MHz}$	26.978(7)	{29.4} <sup>c</sup>		
$\Delta_c/\text{uÅ}^2$	−0.229(1)	−0.027(1)	−1.151(2)	−1.155(2)
$\sigma/\text{kHz}^d$	1	4	2	
$N^e$	84	120	22	22

<sup>a</sup>Error in parentheses in units of the last digit. <sup>b</sup>Values in brackets fixed to the values of the most abundant isotopic species. <sup>c</sup>Evaluated according to Pickett; see text. <sup>d</sup>Root-mean-square deviation of the fit. <sup>e</sup>Number of lines in the fit.

require the total wave function to be antisymmetric upon such an exchange, that is,

$$\Psi_{\text{TOT}} = \Psi_e \Psi_v \Psi_r \Psi_s = A \quad (3)$$

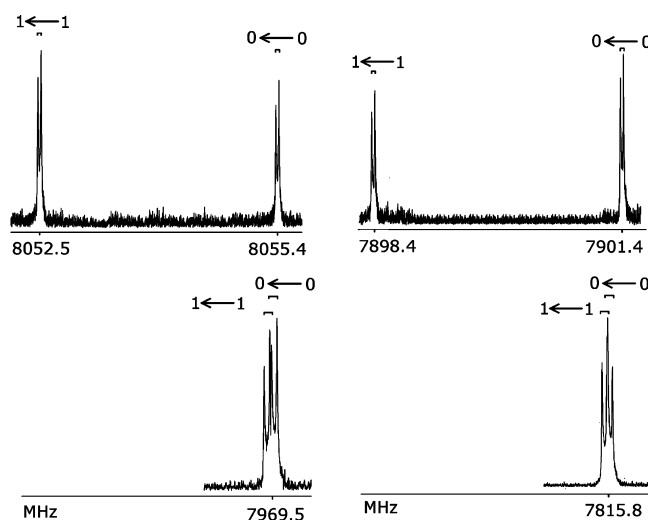
where  $\Psi_e$ ,  $\Psi_v$ ,  $\Psi_r$ , and  $\Psi_s$  are the electronic, vibrational, rotational, and spin wave functions, respectively.

$\Psi_e$  is symmetric for the ground electronic state, while  $\Psi_v$  is symmetric, upon double proton exchange, for  $\nu = 0$ , and antisymmetric for  $\nu = 1$ . For three pairs of protons, there are 36 symmetric spin functions (S) and 28 antisymmetric spin functions (A), while the rotational wave functions are symmetric or antisymmetric, upon a  $\pi$  rotation around the  $a$ -principal axis, for  $K_a$  even or odd, respectively. As a result,  $\mu_a$ -type lines, which connect the same tunnelling level states ( $\nu$ :  $0 \rightarrow 0$  or  $1 \rightarrow 1$ ), will have a statistical weight of 9:7 in favor of the  $\nu = 0$  or of the  $\nu = 1$  component line for  $K_a$  even or odd, respectively.

Such an effect is observed in the spectrum and shown in Figure 2 for the  $11_{0,11} \leftarrow 10_{0,10}$  and  $11_{1,11} \leftarrow 10_{1,10}$  transitions.

In the DD complex, the  $\pi$  rotation around the  $a$ -principal axis inverts only two pairs of fermions and one pair of bosons, and the total wave function must be symmetric. The 36/28 statistical weight of the OH–OH species becomes 66/78 for the OD–OD isotopologue.

The determination of the barrier from the measured tunneling splittings is less straightforward than, for instance, that in most cases of internal rotation. Proton transfer is strongly coupled with cooperative structural rearrangements, and these affect the splittings to a large extent. A simple flexible model representing the rearrangements as functions of the transfer coordinate is inadequate and actually has failed in the present type of system. The reason is adiabatic decoupling of the fast motion of the protons as light particles in deep and narrow potential wells from the slow motions dominated by heavy atom displacements. A more realistic model should allow for additional degrees of freedom for the heavy atom modes. In the case of MA, a  $(3N - 6)$ -dimensional model based on a large amount of properties obtained ab initio has been found to reproduce the experimental data for the vibrational ground state.<sup>5</sup> Some theoretical approaches to interpret the proton tunneling splittings in the dimer of formic acid are also available.<sup>27,28</sup>



**Figure 2.** The inversion splittings are shown above for the  $11_{0,11} \leftarrow 10_{0,10}$  (left) and  $11_{1,11} \leftarrow 10_{1,10}$  (right) transitions of the OH–OH (top) and OD–OD (bottom) species. One can observe the 9/7 statistical weight (see text) for the normal species.

Here we use a general purpose simpler three-dimensional (3D) model (see ref 29 for the one- (1D) and two-dimensional (2D) versions), based on quantum chemical results for the stationary points of the potential energy surface (equilibrium and saddle point configurations), as recently applied to a hydrogen-bonded dimer of acrylic acid.<sup>22</sup> Using reduced coordinates,  $x$  for the double proton transfer and  $y_1$  and  $y_2$  for other changes of structure, we set  $(x, y_1, y_2) = (0, 0, 0)$  at the  $C_{2v}$  symmetric saddle point configuration and  $(x, y_1, y_2) = (\pm 1, \pm 1, 1)$  at equilibrium. Then the changes of structural parameters obtained ab initio when going from the saddle point to equilibrium are separated into components of symmetry type  $B_1$  associated with  $y_1$  and of type  $A_1$  associated with  $y_2$ . The minimum energy path (MEP) is then assumed to be given by interpolation:  $y_1 = x$ ,  $y_2 = x^2$ . The potential energy function is assumed as



$$V(x, y_1, y_2) = s(x)\{B_2(1 - x^2)^2 + [f_1/s(1)](y_1 - x)^2 + [f_2/s(1)](y_2 - x^2)^2\} \quad (4)$$

Along the MEP it reduces to the double minimum profile given by the first term,  $s(x) B_2(1 - x^2)^2$ , where  $B_2$  is the barrier height and

$$s(x) = 1/[1 + w_b(B_2/D_0)^{1/2}x^2 + (B_2/D_0)x^4] \quad (5)$$

a shape factor designed to yield an asymptotic approach to the dissociation energy  $D_0$ . The factor also contains a parameter  $w_b$  that allows one to manipulate the barrier width. Displacements of  $y_1$  and  $y_2$  from the MEP lead to an increase in potential energy controlled by force constant factors  $f_1 = k_1/2$  and  $f_2 = k_2/2$  to be treated as parameters associated with the two  $y$  modes. These are chosen as derived from the quantum chemical results and used as hypothetical representatives of the vibrational modes that interact with the proton transfer.

The calculation outlined in a recent paper<sup>22</sup> uses an adiabatic approximation separating the fast  $x$  motion from the two  $y$  motions. Accordingly, we calculate wave functions for the proton transfer ( $x$ ) at fixed values of  $y_1$  and  $y_2$  and obtain energies  $E(y_1, y_2)$  as potential energy surfaces for the  $y$  modes. Since for a double minimum tunneling system in the vibrational ground state there are two such surfaces that avoid crossing, we use a localized representation yielding crossing surfaces and an (off-diagonal) tunneling interaction. When neglecting kinetic energy interactions between the three variables, it is sufficient to calculate wave functions in one of the three dimensions at a time.

The wave functions for the parent species HH as well as for the DD species are symmetric or antisymmetric with respect to the substitution  $(x, y_1, y_2) \rightarrow (-x, -y_1, y_2)$ , and the corresponding energy levels for the vibrational ground state are spaced by the tunnel splitting  $\Delta E_{01}$ . No such symmetry relation applies in the case of the DH species where a proton with a short bond to either the benzoic or the formic acid moiety is replaced by a deuteron. For an interpretation of the two observable tunnel splittings for HH and DD, assumptions have to be made for the five model parameters. For the dissociation energy, we assume  $D_0 = 5040 \text{ cm}^{-1}$  as obtained ab initio, and the barrier height  $B_2$  is expected between the ab initio values  $2338 \text{ cm}^{-1}$  (B3LYP) and  $2830 \text{ cm}^{-1}$  (MP2). After trying various values for the force constant factors  $f_1$  and  $f_2$  and adjusting the parameters  $B_2$  and  $w_b$ , we arrived at the interpretation shown in Table 3.

With the parameters shown in Table 3, the local vibrational ground states of the HH species were  $737 \text{ cm}^{-1}$  above the potential energy minima, and the fundamental frequencies for the representative modes  $y_1$  and  $y_2$  were obtained as  $121 \text{ cm}^{-1}$

**Table 3. Results of a Model Calculation**

tunnelling splittings		
	obs	calc
$\Delta E_{01}(\text{HH})/\text{MHz}$	548.72(6) <sup>a</sup>	547.8
$\Delta E_{01}(\text{DD})/\text{MHz}$	8.3(3)	8.1
parameters		
$B_2/\text{cm}^{-1} = 2442(150)$	$w_b = -0.80^b$	
$f_1/\text{cm}^{-1} = 270^c$	$f_2/\text{cm}^{-1} = 60^c$	

<sup>a</sup>Errors in parentheses are expressed in units of the last digit. <sup>b</sup>Shape function parameter. <sup>c</sup>Assumed; see text.

and  $42 \text{ cm}^{-1}$ , respectively. The DH species with the deuteron on the formate side was found to be more stable by  $18 \text{ cm}^{-1}$  than that with the deuteron on the benzoate side. Further sets of model parameters and calculated properties are given in Table 3S of the Supporting Information.

The barrier to proton transfer appears to be consistent with the theoretical values given eight lines before of Table 3, but quite lower than the tentative values calculated from the spectroscopic data in some cases (see Table 4).

**Table 4. Barriers to Proton Tunneling as Estimated from the Experimental Spectroscopic Data for Some Carboxylic Acid Bimolecules**

	$\Delta E_{01}/\text{MHz}$	$B_2/\text{cm}^{-1}$	ref
$(\text{C}_6\text{H}_5\text{COOH})_2$	1114.0(10) <sup>a</sup>	6220	7
$(\text{HCOOH})_2$	474(12) <sup>b</sup>	4232 <sup>c</sup>	11, 12
$\text{HCOOH}-\text{HC}_2\text{COOH}$	291.428(5)	8000	20
$\text{HCOOH}-\text{CH}_3\text{COOH}$	250.44(1) <sup>d</sup>	8000	21
acrylic acid dimer	880.6(6)	2485(150)	22
BA-FA	548.72(6)	2442(150)	this work

<sup>a</sup>Errors in parentheses are expressed in units of the last digit. <sup>b</sup>This splitting is from ref 11. The barrier estimation is for  $(\text{DCOOH})_2$  from ref 12. <sup>c</sup>This splitting is for the A state of the internal rotation. A meaningless value of  $-136.167(3) \text{ MHz}$  is reported for the E state.

In summary, we have assigned the rotational spectra of four isotopologues of the BA-FA bimolecule. We measured the tunneling splittings for the HH and DD species. The ratio between the two splittings is the key parameter to estimate the contribution of the skeletal structural relaxation to the proton transfer motion. The observed double proton transfer properties have been interpreted by a simplified 3D model involving two representative heavy atom motions derived from quantum chemical results.

## COMPUTATIONAL AND EXPERIMENTAL SECTION

Different theoretical methods and basis sets were used during the course of this work, as implemented in the Gaussian 03 suite of programs.<sup>30</sup> Initially, DFT theory (B3LYP) was used for the 6-311++G(d,p) basis set. Additionally, the structure of the stable conformer of dimer was reoptimized using the MP2 method with the same basis set. Harmonic frequency calculations confirmed that the predicted conformers are true minima at this level of theory. Moreover, the calculations were performed to estimate the binding energy, and also the counterpoise correction<sup>31</sup> was included in calculations to help remove the basis set superposition error.

The 4–18 GHz Balle-Flygare Fourier-Transform Microwave (FT-MW) spectrometer<sup>32,33</sup> built at the Universidad del País Vasco (UPV-EHU) has been described elsewhere,<sup>34</sup> so only relevant details will be reported here. Commercial samples of solid benzoic (or benzoic-OD) acid were vaporized by a resistive heater at 353 K wrapped around a customized nozzle and diluted in flowing carrier gas combination (1% of formic acid in Ne). The mixture was expanded through a 0.8 mm diameter nozzle in a high vacuum chamber evacuated by a rotary and a diffusion pump. The stagnation pressure was 0.2 MPa, and the effective rotational temperature produced in the expansion is estimated to be  $\approx 2 \text{ K}$ . As a result of the pulsed supersonic expansion ( $\sim 250 \text{ ms}$ ), molecules cool down their internal degrees of freedom, reaching very low rovibrational temperatures. No decomposition products were noticeable.

The molecules are excited inside a Fabry–Perot resonator by a sequence of 1  $\mu$ s low-power (<150 mW) MW pulses, detecting the molecular spontaneous emission in the time domain. Finally, the frequency spectra are obtained by Fourier transforming the time-dependent signal. All transitions appear to be split due to the coaxial arrangement of the jet and resonator axis. The accuracy of frequency measurements is better than 3 kHz, and resolvable transitions are obtained for lines separated less than ca. 10 kHz.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

(1) Complete ref 30; (2) tables of transition frequencies; (3) table with B3LYP/6-311++G\*\* optimized geometry of the complex; (4) table with alternative flexible model fittings. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) (a) Rowe, W. F.; Duerst, R. W.; Wilson, E. B. The Intramolecular Hydrogen Bond in Malonaldehyde. *J. Am. Chem. Soc.* **1976**, *98*, 4021–4023. (b) Baughcum, S. L.; Duerst, R. W.; Rowe, W. F.; Smith, Z.; Wilson, E. B. Microwave Spectroscopy Study of Malonaldehyde (3-Hydroxy-2-propenal). 2. Structure, Dipole Moment, and Tunneling. *J. Am. Chem. Soc.* **1981**, *103*, 6296–6303. (c) Baughcum, S. L.; Smith, Z.; Wilson, E. B.; Duerst, R. W. Microwave Spectroscopy Study of Malonaldehyde. 3. Vibration–Rotation Interaction and One-Dimensional Model for Proton Tunneling. *J. Am. Chem. Soc.* **1984**, *106*, 2260–2265. (d) Turner, P.; Baughcum, S. L.; Coy, S. L.; Smith, Z. Microwave Spectroscopy Study of Malonaldehyde. 4. Vibration–Rotation Interaction in Parent Species. *J. Am. Chem. Soc.* **1984**, *106*, 2265–2267.
- (2) (a) Sanders, N. D. Vibration–Torsion Interaction in the Microwave Spectrum of Internally Hydrogen-Bonded Methylmalonaldehyde. *J. Mol. Spectrosc.* **1981**, *86*, 27–42. (b) Ilyushin, V. V.; Alekseev, E. A.; Chou, Y. C.; Hsu, Y. C.; Hougen, J. T.; Lovas, F. J.; Picraux, L. B. Reinvestigation of the Microwave Spectrum of 2-Methylmalonaldehyde. *J. Mol. Spectrosc.* **2008**, *251*, 56–63 and references therein.
- (3) Caminati, W. Proton Tunneling and Nitro-Group Torsion in 2-Nitro-malonaldehyde. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 825–838.
- (4) Keske, J. C.; Lin, W.; Pringle, W. C.; Novick, S. E.; Blake, T. A.; Plusquellic, D. F. High-Resolution Studies of Tropolone in the  $S_0$  and  $S_1$  Electronic States: Isotope Driven Dynamics in the Zero-Point Energy Levels. *J. Chem. Phys.* **2006**, *124*, 074309.
- (5) Meyer, R.; Ha, T.-K. Quantum States of Hydrogen Transfer and Vibration in Malonaldehyde. *Mol. Phys.* **2003**, *101*, 3263–3276; Rotational Constants of Malonaldehyde and Isotopic Species Derived from Ab-Initio Results. *Mol. Phys.* **2005**, *103*, 2687–2698.
- (6) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. Evidence of Intramolecular N–H...O Resonance-Assisted Hydrogen Bonding in  $\beta$ -Enaminones and Related Heterodienes. A Combined Crystal-Structural, IR and NMR Spectroscopic, and Quantum-Mechanical Investigation. *J. Am. Chem. Soc.* **2000**, *122*, 10405–10417.
- (7) Kalkman, I.; Vu, C.; Schmitt, M.; Meerts, W. L. Tunneling Splittings in the  $S_0$  and  $S_1$  States of the Benzoic Acid Dimer Determined by High-Resolution UV Spectroscopy. *ChemPhysChem* **2008**, *9*, 1788–1797.
- (8) Matylytsky, V. V.; Riehn, C.; Gelin, M. F.; Brutschy, B. The Formic Acid Dimer (HCOOH)<sub>2</sub> Probed by Time-Resolved Structure Selective Spectroscopy. *J. Chem. Phys.* **2003**, *119*, 10553–10562.
- (9) Georges, R.; Freytes, M.; Hurtmans, D.; Kleiner, I.; Auwera, J. V.; Herman, M. Jet-Cooled and Room Temperature FTIR Spectra of the Dimer of Formic Acid in the Gas Phase. *Chem. Phys.* **2004**, *305*, 187–196.
- (10) Xue, Z.; Suhm, M. A. Probing the Stiffness of the Simplest Double Hydrogen Bond: The Symmetric Hydrogen Bond Modes of Jet-Cooled Formic Acid Dimer. *J. Chem. Phys.* **2009**, *131* (054301), 1–14.
- (11) Madeja, F.; Havenith, M. High Resolution Spectroscopy of Carboxylic Acid in the Gas Phase: Observation of Proton Transfer in (DCOOH)<sub>2</sub>. *J. Chem. Phys.* **2002**, *117*, 7162–7168.
- (12) Ortlieb, M.; Havenith, M. Proton Transfer in (HCOOH)<sub>2</sub>: An IR High-Resolution Spectroscopy Study of the Antisymmetric C–O Stretch. *J. Phys. Chem. A* **2007**, *111*, 7355–7363.
- (13) Gutberlet, A.; Schwaab, G. W.; Havenith, M. High Resolution IR Spectroscopy of the Carbonyl Stretch of (DCOOD)<sub>2</sub>. *Chem. Phys.* **2008**, *343*, 158–167.
- (14) Birner, O.; Havenith, M. High-Resolution Infrared Spectroscopy of the Formic Acid Dimer. *Annu. Rev. Phys. Chem.* **2009**, *60*, 263–275.
- (15) Riehn, C.; Matylytsky, V. V.; Gelin, M. F.; Brutschy, B. Double Hydrogen Bonding of Acetic Acid Studied by Femtosecond Degenerate Four-Wave Mixing. *Mol. Phys.* **2005**, *103*, 1615–1623.
- (16) Costain, C. C.; Srivastava, G. P. Study of Hydrogen Bonding. The Microwave Rotational Spectrum of CF<sub>3</sub>COOH–HCOOH. *J. Chem. Phys.* **1961**, *35*, 1903–1904.
- (17) Bellott, E. M., Jr.; Wilson, E. B. Hydrogen Bonded Bimolecular Complexes of Carboxylic Acids in the Vapor Phase: Observation and Characterization by Low Resolution Microwave Spectroscopy. *Tetrahedron* **1975**, *31*, 2896–2898.
- (18) Martinache, L.; Kresa, W.; Wegener, M.; Vonmont, U.; Bauder, A. Microwave Spectra and Partial Substitution Structure of Carboxylic Acid Bimolecules. *Chem. Phys.* **1990**, *148*, 129–140.
- (19) Antolinez, S.; Dreizler, H.; Storm, V.; Sutter, D. H.; Alonso, J. L. The Microwave Spectrum of the Bimolecule Trifluoroacetic Acid... Cyclopropanecarboxylic Acid. *Z. Naturforsch.* **1997**, *52a*, 803–806.
- (20) (a) Daly, A. M.; Bunker, P. R.; Kukolich, S. G. Communications: Evidence of Proton Tunneling from the Microwave Spectrum of the Formic Acid–Propiolic Acid Dimer. *J. Chem. Phys.* **2010**, *132* (201101), 1–3. (b) Daly, A. M.; Douglass, K. O.; Sarkozy, L. C.; Neill, J. L.; Muckle, M. T.; Zaleski, D. P.; Pate, B. H.; Kukolich, S. G. Microwave Measurements of Proton Tunneling and Structural Parameters for the Propiolic Acid–Formic Acid Dimer. *J. Chem. Phys.* **2011**, *135* (154304), 1–12.
- (21) Tayler, M. C. D.; Ouyang, B.; Howard, B. J. Unraveling the Spectroscopy of Coupled Intramolecular Tunneling Modes: A Study of Double Proton Transfer in the Formic–Acetic Acid Complex. *J. Chem. Phys.* **2011**, *134* (054316), 1–9.
- (22) Feng, G.; Favero, L. B.; Maris, A.; Vigorito, A.; Caminati, W.; Meyer, R. Proton Transfer in Homodimer of Carboxylic Acids: The

Rotational Spectrum of the Dimer of Acrylic Acid. *J. Am. Chem. Soc.* **2012**, *134*, 19281–19286.

(23) Pickett, H. M. The Fitting and Prediction of Vibration–Rotation Spectra with Spin Interactions. *J. Mol. Spectrosc.* **1991**, *148*, 371–377. Current versions are described and available from <http://spec.jpl.nasa.gov>.

(24) Watson, J. K. G. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: New York/Amsterdam, 1977; Vol. 6, pp 1–89.

(25) Pickett, H. M. Vibration–Rotation Interactions and the Choice of Rotating Axes for Polyatomic Molecules. *J. Chem. Phys.* **1972**, *56*, 1715–1723.

(26) Eckart, C. Some Studies Concerning Rotating Axes and Polyatomic Molecules. *Phys. Rev.* **1935**, *47*, 552–558.

(27) Shida, N.; Barbara, P. F.; Almlöf, J. A Reaction Surface Hamiltonian Treatment of the Double Proton Transfer of Formic Acid Dimer. *J. Chem. Phys.* **1991**, *94*, 3633–3643.

(28) Barnes, G. L.; Sibert, E. L., III. The Effects of Asymmetric Motions on the Tunneling Splittings in Formic Acid Dimers. *J. Chem. Phys.* **2008**, *129* (164317), 1–9.

(29) Meyer, R. Flexible Models for Intramolecular Motions, a Versatile Treatment and Its Application to Glyoxal. *J. Mol. Spectrosc.* **1979**, *76*, 266–300.

(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; et al. *Gaussian 03*, revision B.01; Gaussian Inc.: Pittsburgh, PA, 2003.

(31) Boys, S. F.; Bernardi, F. The Calculations of Small Molecular Interactions by the Differences of Separate Total Energies. Some Procedures with Reduced Errors. *Mol. Phys.* **1970**, *19*, 553–566.

(32) Balle, T. J.; Flygare, W. H. Fabry–Perot Cavity Pulsed Fourier Transform Microwave Spectrometer with a Pulsed Nozzle Particle Source. *Rev. Sci. Instrum.* **1981**, *52*, 33–45.

(33) (a) Grabow, J.-U.; Stahl, W. A Pulsed Beam Microwave Fourier Transform Spectrometer With Parallel Molecular Beam and Resonator Axes. *Z. Naturforsch. A.* **1990**, *45*, 1043–1044. (b) Grabow, J.-U. Doctoral Thesis, Christian-Albrechts-Universität zu Kiel, Kiel, Germany, 1992. (c) Grabow, J.-U.; Stahl, W.; Dreizler, H. A Multioctave Coaxially Oriented Beam-Resonator Arrangement Fourier-Transform Microwave Spectrometer. *Rev. Sci. Instrum.* **1996**, *67*, 4072–4084.

(34) Cocinero, E. J.; Lesarri, A.; Eciija, P.; Grabow, J.-U.; Fernandez, J. A.; Castaño, F. Conformational Equilibria in Vanillin and Ethylvanillin. *Phys. Chem. Chem. Phys.* **2010**, *12*, 12486–12493.