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Communication: Spectroscopic measurement of the binding energy of a carboxylic acid-water dimer

Quanli Gu^{1,2} and J. L. Knee^{2,a)}

¹Chemistry Department, University of Virginia, Charlottesville, Virginia 22904, USA

²Chemistry Department, Wesleyan University, Middletown, Connecticut 06459, USA

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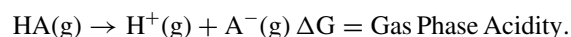
Infrared-ultraviolet two color pump-probe spectroscopy is used to measure the binding energy, D_0 , of a carboxylic acid-water dimer where the acid is 9-hydroxy-9-fluorenicarboxylic acid. The acid-water configuration presents a standard structure for the general acid-water interaction where the water bonds to the carboxylic acid group through two intermolecular hydrogen bonds. Photodissociation studies with product vibrational state resolution have enabled an accurate determination of the binding energy for this acid-water system to be $D_0 = 2975 \pm 30 \text{ cm}^{-1}$. Quantum chemical calculations are performed to compare with the experimental observations and a recent measurement on the water dimer ($D_0 = 1105 \pm 10 \text{ cm}^{-1}$). © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4711862>]

Hydrogen bonding has been of inherent interest to the scientific community and has been extensively studied in a number of contexts. In recent years there has been considerable attention on gas phase hydrogen bonding in small clusters from water dimer^{1,2} to biologically relevant molecules.³ A range of experimental methodologies have been applied but in particular molecular spectroscopy of various types has led to a great deal of information on the structure, potential surfaces and dynamics of these important species. One of the more difficult measurements to obtain spectroscopically is an accurate measurement of the binding energy, D_0 . Just recently a refined measurement of the water dimer binding energy was published by Reisler *et al.*¹ using resonance enhanced multiphoton ionization (REMPI) and velocity map imaging to determine the water dimer binding energy to be $1105 \pm 10 \text{ cm}^{-1}$. There are other examples of experimental binding energy measurements on hydrogen bonded systems⁴ but few with this level of accuracy and none previously on carboxylic acid-water dimers. Quantum chemical calculations have played an increasingly important role in these determinations as demonstrated by the excellent agreement of the calculated water dimer binding energy,² $1103 \pm 4 \text{ cm}^{-1}$, with the above mentioned experimental measurement. However, these computational accuracies become difficult if not impossible for larger systems.

An important class of hydrogen bonding interactions is that between molecular acids and water. These interactions play an important role in many chemical systems including atmospheric chemistry^{5,6} and biological systems where the acid-base interplay is critical for many functional groups. There have been calculations of the binding energy of a number of carboxylic acid-water dimers⁶⁻⁸ which vary significantly from 2500 to 3500 cm^{-1} with most of this variation being due to differences between computational methods.

Herein we report on an accurate experimental measurement of the gas phase binding energy of water to a carboxylic acid group measured by IR photodissociation spectroscopy. To our knowledge it represents the most accurate measurement of D_0 between water and a carboxylic acid group.

The particular carboxylic acid used in these measurements is 9-hydroxy-9-fluorenicarboxylic acid (9HFCA) shown as an insert in Figure 1. While this is a complicated molecular system the fluorene chromophore has been shown to be a useful chromophore for studies using electronic spectroscopy.⁹ The carboxylic acid group is not extensively conjugated with the π system and so the fluorene group is not expected to introduce any complications to the water interactions that would not be present in a wide range of organic acids. However, the 9-hydroxy (9OH) group is significant because, as seen in Figure 1, this group internally hydrogen bonds to the carbonyl oxygen. This configuration is similar to the simpler molecule glycolic acid.^{6,8} The acidity of these molecules¹⁰ is increased because the internal hydrogen bond stabilizes the anion product of the acid dissociation. For the current study what is of greater interest is the gas phase acidity which is defined as the free energy for the gas phase acid dissociation as follows:



The ΔG values are positive and a lower value indicates a stronger acid. The value for 9HFCA is not known but we have calculated it using thermodynamic values from a density functional theory calculation according to the prescription by Ho and Coote¹¹ using a B971 functional and a 6-311++g(d,p) basis set (all calculations performed with GAUSSIAN 09 (Ref. 12)). The result for 9HFCA is 317.4 kcal/mol . Calculations of other known acids show this method to be surprisingly accurate with a consistent overestimate of only several kcal/mol. The important point is that the internally bound hydroxyl group makes this a strong acid, for instance stronger than formic (338.4 kcal/mol) and glycolic

^{a)} Author to whom correspondence should be addressed. Electronic mail: jknee@wesleyan.edu.

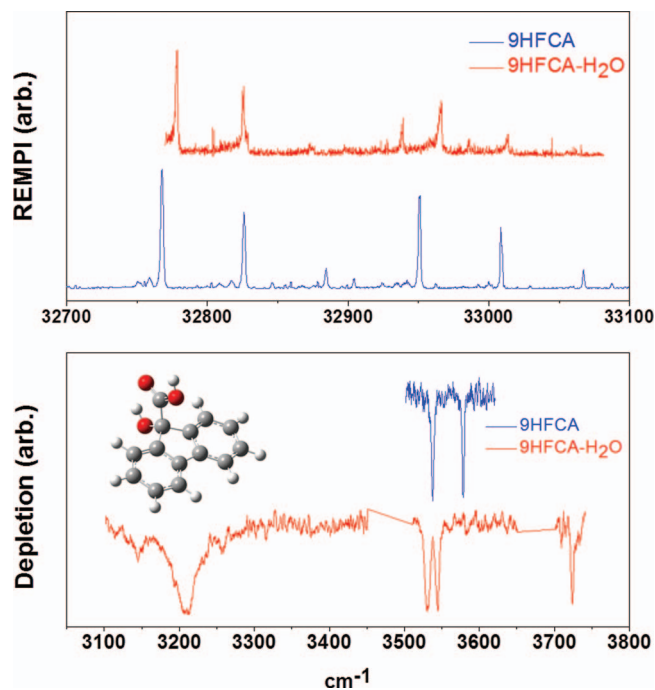


FIG. 1. (Top panel): Mass resolved REMPI spectra of 9HFCA and complex with water in the region of the S_1 origin. (Lower panel): IR spectra of monomer and water complex of 9HFCA in the OH stretching region. See text for peak assignments.

acid (327.8 kcal/mol) and comparable to trifluoroacetic acid (317.2 kcal/mole).¹⁰ Presumably, acid strength plays a role in the magnitude of the water binding energy so knowing this number for 9HFCA is useful for comparison of the binding energy measurements to other acids.

The bond strength measurements are based on an IR dissociation technique with measurement of the 9HFCA monomer product state subsequent to dissociation. The experimental setup and methodology used is similar to that applied in previous work on 9-fluorene-methanol and its clusters.¹³ The 9HFCA-water complexes were prepared in a pulsed supersonic expansion using 1 bar helium as a carrier gas. The 9HFCA (Aldrich) was placed in the body of the silicone coated pulsed valve (General Valve, series 9) which was heated to 120 °C to provide sufficient vapor pressure without any decomposition. Water was seeded in the helium via a variable flow controller and adjusted so that significant dimers were formed while limiting the formation of larger clusters. The pulsed beam (20 Hz) was skimmed and the spectroscopy was performed downstream in a second chamber at a distance of 10 cm from the nozzle.

Three types of spectroscopy are presented here. The first is REMPI using a single color UV pulse. This was generated with a frequency doubled Nd:YAG laser (Quanta-Ray DCR-3), pumping a Lumonics Hyper-dye laser, followed by frequency doubling to the desired UV wavelength. The $\sim 100 \mu\text{J}$ UV laser pulses were softly focused to intersect the molecular beam within the time-of-flight mass spectrometer. Appropriate extraction voltages were applied to direct the ions to a microchannel plate detector with subsequent detection via an HP 54510A oscilloscope and computer combination. The S_1 electronic state spectrum was obtained by scanning the UV

laser through the appropriate spectral region and recording the mass resolved ion signal, either the complex or monomer mass depending on the experiment. These REMPI spectra are displayed in the top panel of Figure 1 and show the S_1 origins and vibronic structure up to $\sim 300 \text{ cm}^{-1}$ excess energy.

The second and third types of experiments are closely related. The second is measurement of the ground state IR spectrum via an IR-UV double resonance technique. Tunable IR in the OH stretching region is generated by difference frequency generation in lithium niobate (Spectra Physics IR-WEX). The IR difference was generated between the Nd:YAG pump laser fundamental (Continuum NY-61) and a tunable dye laser (Lumonics HD500) operating in the 760–810 nm region. The IR was $\sim 0.5 \text{ mJ/pulse}$ over the spectral range studied. To obtain the IR spectrum the UV laser was tuned to the origin transition of interest (monomer or water cluster) and the ion signal was monitored. The IR laser was then introduced 20 ns earlier in time, softly focused and spatially aligned with the UV laser spot in a counter propagating geometry. IR absorption, when resonant, depletes the ground state population leading to a depletion of the REMPI signal. Depletions could typically reach as high as 80% and the sensitivity was further enhanced by taking the difference between 20 laser shots with IR on minus 20 laser shots with IR off.

The resulting IR spectra of the monomer and water complex are shown in the lower panel of Figure 1. The third experiment was similar but in this case the IR laser was fixed on one of the water complex bands and instead the UV laser was scanned in an attempt to measure any 9HFCA monomer products which may have been produced from IR dissociation of the complex. The resulting spectra are shown in Figure 2.

As mentioned above, Figure 1 displays the electronic ($32700\text{--}33100 \text{ cm}^{-1}$) and infrared spectra ($3100\text{--}3750 \text{ cm}^{-1}$) for 9HFCA and its water cluster. The monomer electronic origin band occurs at 32768 cm^{-1} and the 9HFCA- H_2O cluster origin is blueshifted by 10 cm^{-1} . The

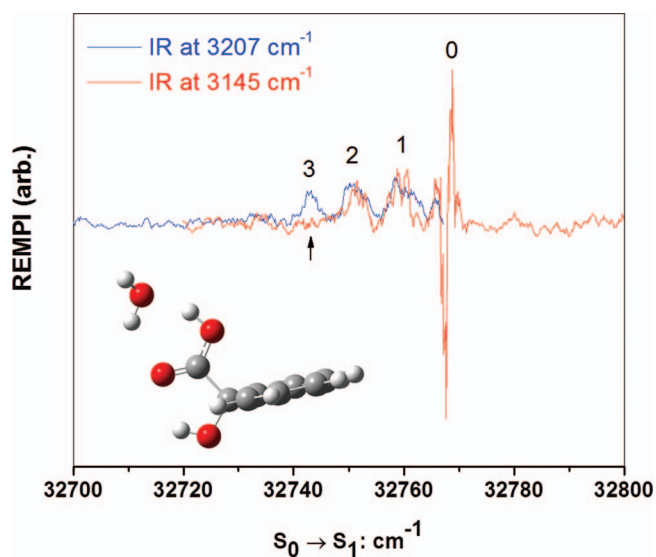


FIG. 2. IR on/off difference REMPI spectra of the 9HFCA monomer product comparing excitation of two different IR modes as indicated. The plots have been normalized to the $v = 1$ amplitudes. The arrow points out the missing $v = 3$ hot band when pumping the lower IR band at 3145 cm^{-1} .

monomer molecular geometry is C_s and the excited electronic state symmetry is A'' which is allowed via a long axis transition. Thus only totally symmetric vibrational modes are expected to be observed in the S_1 vibronic spectrum. Due to the insufficient vibrational cooling in the jet, there are three small equally spaced (9 cm^{-1}) hot bands to the red of S_1 origin of monomer. The identity of these bands is important to the determination of the binding energy. Due to the fact that $v = 3$ was observed it was assumed to be a relatively low frequency mode. The most likely choices were the carboxylic group torsional mode (a'' symmetry) calculated to have a fundamental frequency of 27 cm^{-1} (M06-2X/aug-cc-pVDZ), and a carboxylic group rocking motion perpendicular to the fluorene moiety (a' symmetry) with a calculated frequency of 68 cm^{-1} . Zero electron kinetic energy photoelectron spectroscopy conducted in another study (unpublished) was able to establish the hot band as being due to the acid group rocking motion, measured to be 67 cm^{-1} in the ground state (in perfect agreement with the calculated vibrational frequency). This mode is seen prominently in the S_1 spectrum, shifted to 58 cm^{-1} , thus the 9 cm^{-1} shift of the hot band from the origin is consistent with this assignment.

In the infrared spectra, 9HFCA displays two peaks at 3538 and 3579 cm^{-1} and we assign the first peak as the 9OH stretch (lowered in frequency due to the formation of the intramolecular hydrogen bond with the carbonyl group) and the second as carboxylic acid OH stretch. As expected 9HFCA- H_2O displays more peaks in the OH stretching region. The relatively broad peak at 3207 cm^{-1} is assigned as the carboxylic acid OH stretch redshifted by its bond to water, the peak at 3531 cm^{-1} as the 9OH stretch, the peak at 3544 cm^{-1} as the symmetric water OH stretch, and one at 3724 cm^{-1} as the water anti-symmetric stretch.

Photodissociation studies were then performed on the 9HFCA- H_2O cluster using IR-UV action spectroscopy as discussed above. The IR laser was tuned to a specific cluster absorption band and the UV laser scanned while monitoring the REMPI signal in the monomer channel to look for the production of monomer signal. As shown in Figure 2, when the IR laser was tuned to 3207 cm^{-1} , monomer product is observed as clearly seen in the appearance of three peaks assigned as the hot bands 32742 cm^{-1} ($v = 3$), 32751 cm^{-1} ($v = 2$), and 32759 cm^{-1} ($v = 1$). The cold monomer origin

is expected to be populated in the dissociation as well but it is not observed in the difference spectrum due to the large error in subtracting the huge background monomer signal (this explains the widely varying signal at $\sim 32768\text{ cm}^{-1}$). The IR was then tuned to the nearby 3145 cm^{-1} band and similarly the monomer product was observed in the probed REMPI spectrum but with a significant difference. Specifically the 32742 cm^{-1} ($v = 3$) band is now missing but the $v = 2$ and $v = 1$ bands are still clearly observed.

Based on this observation we can then confidently extract the binding energy D_0 as between 2944 cm^{-1} ($3145 - 67 \times 3$) and 3011 cm^{-1} ($3145 - 67 \times 2$). The fact that IR excitation at the slightly more energetic band at 3207 cm^{-1} produces the $v = 3$ product yields a slightly lower upper limit of 3006 cm^{-1} ($3207 - 67 \times 3$) providing additional confirmation that the above measurement of the dissociation threshold is correct. Based on these observations the binding energy is established as $D_0 = 2975 \pm 30\text{ cm}^{-1}$. To our knowledge this is the most accurate spectroscopic measurement on the binding energy for an acid-water dimer. This binding energy is substantially larger than the water dimer itself (1105 cm^{-1}) which is expected based on two bonds formed to water in the acid interaction.

An additional point worth noting is that when we excite at 3145 cm^{-1} we are above the threshold and the products appear within 20 ns. Dissociation experiments which identify the bond energy by scanning through the threshold often need to be concerned about the potential metastability of states at or slightly above threshold which do not dissociate on the experimental time scale, particularly important when determining the lower limit of D_0 . In this case we are relying on product state distributions to identify the threshold and so the time scale for dissociation is not a concern.

Quantum chemical calculations of the binding energy were performed to compare with the measured value and with previous calculations on similar acid-water complexes.⁶⁻⁸ The molecular systems and the various methodologies used in the calculations are summarized in Table I along with the results. These calculations all include zero-point energy and counterpoise corrections to the binding energy. There have been many published calculations of carboxylic acid-water binding energies with widely varying results. From our calculations, with limited computational resources for systems this size, it

TABLE I. Calculated D_0 (cm^{-1}) for dimers with water.

Method ^a	Water	9HFCA	Phenol	Glycolic	Formic	Acetic	Benzoic	Trifluoroacetic
B3LYP/6-311++g(d,p)	1045	2582	1620	2632	2484	2482	2542	2959
B3LYP/aug-cc-pVDZ	838	2483	1424	2465	2338	2367	2437	2765
MP2/6-311++g(d,p)	930	...	1013	2297	2114	2083	1573	2628
MP2/aug-cc-pVDZ	858	...	1628	2459	2299	2324	2421	2732
M06-2X/6-311++g(d,p)	1265	3268	2116	3263	3186	3149	3248	3631
M06-2X/aug-cc-pVDZ	1091	3076	1876	3103	2975	2985	3048	3384
Experiments	1105 ± 10^b	2975 ± 30^c	1916 ± 30^d					

^aFull optimization with zero point energy and basis set superposition error included.

^bReference 1.

^cThis work.

^dReference 15.

appears that the M06-2X density functional method¹⁴ with an aug-cc-pVDZ basis set gives the best agreement. This method also does well with the known water dimer binding energy. A number of other acid-water systems are also presented in the table for comparison and it is seen that generally binding energy does track the gas phase acidity, but not precisely. This is not surprising given some of the different properties which enter into the gas phase acidity, particularly anion product stability.

In conclusion for the first time we present an accurate spectroscopic measurement of the binding energy for an acid-water dimer using IR-UV action spectroscopy in a molecular beam. By analyzing the low frequency mode quantum number populations of the product after threshold dissociation, we are able to definitively determine the binding energy to be $D_0 = 2975 \pm 30 \text{ cm}^{-1}$. Comparison to quantum chemical calculations allows different methodologies to be assessed and indicates that substantial inaccuracies occur with widely used computational approaches. Our measurements and calculations strongly suggest that the D_0 of glycolic acid-water dimer is close to 3000 cm^{-1} and modestly higher than the D_0 of formic acid-water dimer.

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