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Communication: Frequency shifts of an intramolecular hydrogen bond as a measure of intermolecular hydrogen bond strengths

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Infrared-ultraviolet double resonance spectroscopy has been applied to study the infrared spectra of the supersonically cooled gas phase complexes of formic acid, acetic acid, propionic acid, formamide, and water with 9-hydroxy-9-fluorene carboxylic acid (9HFCA), an analog of glycolic acid. In these complexes each binding partner to 9HFCA can function as both proton donor and acceptor. Relative to its frequency in free 9HFCA, the 9-hydroxy (9OH) stretch is blue shifted in complexes with formic, acetic, and propionic acids, but is red shifted in the complexes with formamide and water. Density functional calculations on complexes of 9HFCA to a variety of H bonding partners with differing proton donor and acceptor abilities reveal that the quantitative frequency shift of the 9OH can be attributed to the balance struck between two competing intermolecular H bonds. More extensive calculations on complexes of glycolic acid show excellent consistency with the experimental frequency shifts. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4752246>]

One of the most important non-covalent¹ molecular interactions is hydrogen bonding.^{2,3} It is of inherent and general interest in physics, chemistry, and biology. Hydrogen bonding has been extensively characterized by experiment and computation, especially on small water clusters⁴ but also for clusters of carboxylic acids.^{5,6} The most familiar effect is a substantial redshift in the frequency of the OH stretching mode for a hydroxyl involved in H-bonding.⁷ The redshift can be attributed to a charge transfer from the proton acceptor to the σ^* OH local molecular orbital and thus a weakening of the OH bond. (The occasional “anomalous blueshift” as in trifluoromethanol complexes requires special explanation,⁸ referring to participation by other MOs.^{9,10}) H-bonding may involve one or more partners in a complex or may be intramolecular as in the case of hydroxy acids such as glycolic acid HO-CH₂-COOH. For this species there is a substantial interaction between the carboxyl group’s carbonyl oxygen and what we shall call the “exo” OH reflecting the fact that it is not part of the carboxyl group. An experimental estimate¹¹ of the alcoholic and carboxyl OH stretches in glycolic acid places them at about 3585 cm⁻¹. The almost complete overlap of the transitions makes distinguishing the carboxylic OH stretch from the exo OH stretch difficult but inspection of Fig. 1 of Ref. 11 suggests values of 3575 cm⁻¹ for the exo OH stretch and 3590 cm⁻¹ for the carboxyl OH stretch. Computed values¹¹ of the anharmonic stretching frequencies obtained by fitting a two-dimensional grid of B3LYP/6-311++G(2d,2p) energies are 3582 cm⁻¹ and 3561 cm⁻¹, respectively. These and the reported OH stretching value of 3585 cm⁻¹ lie far to the red of the OH stretch in, e.g., gas phase ethanol,¹² 3682 cm⁻¹ and 3667 cm⁻¹ for *anti* and *gauche* conformers, respectively, or methanol,¹³ 3684 cm⁻¹. This can be attributed to internal OH...O = hydrogen bonding.

Here we report our spectroscopic study of a hydroxy acid, 9-hydroxy-9-fluorene carboxylic acid (9HFCA) and its complexes with partners, which may be carboxylic acids, formamide, or one or two waters. Our measurement is capable of resolving the carboxylic OH stretch at 3579 cm⁻¹ from the 9-hydroxyl (9OH) stretch at 3538 cm⁻¹ in 9HFCA. Owing to intramolecular H bonding as already described, the hydroxy acid’s exo OH stretching frequency was red shifted relative to the OH stretch of alcohols by more than 100 cm⁻¹. Our study focuses on the further frequency shifts of the exo OH stretch attending complex formation.

9HFCA contains an aromatic segment, fluorene. As a chromophore, it is useful for electronic spectroscopy studies.¹⁴ We do not expect the fluorene to affect the H-bonding seriously; the carboxylic acid group is not extensively conjugated with the fluorene π system, and neither are the complex bonding partners. This is supported by the fact that both hydroxyl stretches are very similar to those of glycolic acid. Extensive calculations have also shown¹⁵ that the binding energies for 9HFCA and glycolic acid with water are very similar.

The experimental set-up and methodology used is similar to that applied in previous work on 9-fluorene methanol and its clusters.¹⁶ The 9HFCA and its 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. Solvents were 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. The measurement of the ground state IR spectrum is via an IR-UV double

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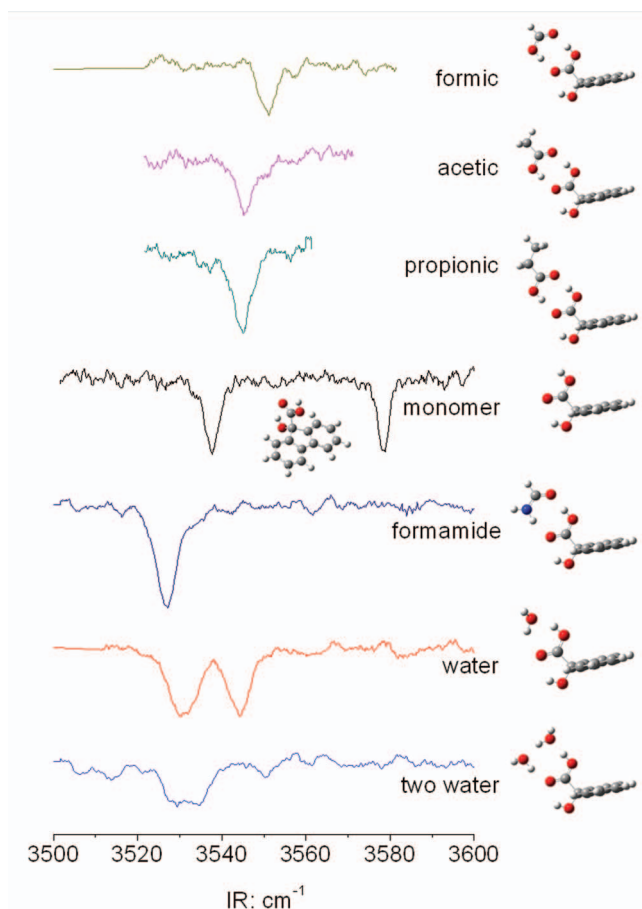


FIG. 1. The IR spectra of the shifts of the 9OH stretch in the monomer and its complexes.

resonance technique. The UV laser was generated with a frequency doubled Nd:YAG laser (Quanta-Ray DCR-3), pumping a Lumonics Hyper-dye laser followed by frequency doubling. Tunable IR in the OH stretching region 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 by difference frequency generation in lithium niobate (Spectra Physics IR-WEX). The IR was approximately 0.5 mJ/pulse over the spectral range studied. To obtain the IR spectrum the UV laser was fixed to the electronic origin transition of interest (monomer or cluster) and the ion signal due to the resonance ionization 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, would deplete the ground state population leading to a depletion of the ion 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 –20 laser shots with IR off.

Figure 1 shows the IR spectra over the range 3500–3600 cm^{-1} for the gas phase monomer 9HFCA and 1:1 complexes of 9HFCA with formic, acetic, and propionic acids; formamide; and water, as well as a 1:2 complex of 9HFCA with water. The monomer 9HFCA displays peaks at 3538 and

3579 cm^{-1} . We assign the first peak as the 9OH stretch and the second as the carboxylic acid OH stretch. For comparison, the OH stretch in formic acid monomer is 3570 cm^{-1} while the transition broadens and shifts to about 3110 cm^{-1} for the dimer.⁷ Each complex is an analog of formic acid dimer in that (1) the 9HFCA is bonded to its partner through two intermolecular hydrogen bonds which are nearly parallel to each other and (2) the acids in each complex act as both proton donor and acceptor. The peak at 3579 cm^{-1} in 9HFCA (i.e., the free carboxyl OH stretch) is drastically red shifted in the complexes, and moves out of the recorded spectral range. Figure 1 shows that the 9OH stretching frequency is blue shifted by 13 cm^{-1} for the complex with formic acid and 7 cm^{-1} for both acetic and propionic acids, but red shifted by 11 cm^{-1} in formamide.

Figure 1 also shows the IR spectra for complexes with one and two water clusters. There are two peaks in the observed region for the 9HFCA- H_2O complex, at 3531 cm^{-1} (“red”) and at 3544 cm^{-1} (“blue”). In the 1:2 complex 9HFCA- $(\text{H}_2\text{O})_2$ the red band remains unchanged and the blue band is not observed. One would expect 9OH would not be shifted much in one and two water complexes, so we assign the peak at 3531 cm^{-1} as 9OH and 3544 cm^{-1} as water symmetric OH stretch.

We optimized structures and simulated the vibrational spectra of the glycolic acid model for 9HFCA monomer and its complexes with carboxylic acids, formamide, acetaldehyde, water, thioformic acid, and ammonia using B3LYP and M06-2X density functionals and the many-body MP2 method. We also conducted M06-2X and B3LYP calculations for complexes of 9HFCA (MP2 calculations were beyond our reach for this large system). All calculations used GAUSSIAN 09 software.¹⁷ The results of the computations are presented in Table I. The consensus of this array of calculations is that the OH stretch at issue is blue shifted in complexes of 9HFCA or its glycolic acid model with carboxylic acids, HCl and HF acids, and red shifted for complexes with formamide, ammonia, acetaldehyde, and one or two waters.

The geometries of the H bonds detailed in Figure 2 provide a simple guide to the source of frequency shifts. The intermolecular bond lengths and harmonic frequency shift values quoted in the following summary are from B3LYP/6-311++G(d,p) calculations. The distances from the carboxyl –OH of the hydroxy acid to the partner’s carbonyl oxygen vary over a narrow interval, (1.64 to 1.77 Å) and the 9OH distance to the carboxyl carbonyl oxygen is almost unchanged for the entire series of complexes, ranging from 1.98 to 2.00 Å. In contrast the distances between the carbonyl =O of the hydroxy acid to the partner’s –OH, –CH, –NH, or –SH vary over a much wider range, from 1.70 to 2.67 Å. We assume that $\text{H}\cdots\text{X}$ ($\text{X}=\text{O}, \text{N}, \text{S}$ or C) distances correlate with H bonding strength. Hydrogen bonds between 9HFCA’s hydroxyl proton donor and partners’ proton acceptors are of familiar strength and structure. Then the salient differences among the H-bonded complexes can only be traced to variation in the partners’ H-donation effectiveness. As we show in the following discussion, effective H-bonding donation from the partner to the hydroxyl acid’s carboxyl carbonyl oxygen is associated

TABLE I. Computed intramolecular bond OH shifts in complexes of 9HFCA and glycolic acid compared to the uncomplexed acids.

Methods	The shift (cm^{-1}) of intra OH in the clusters										
	NH ₃	CH ₃ CHO	HCONH ₂	HCOSH	H ₂ O	(H ₂ O) ₂	CH ₃ COOH	CH ₃ CH ₂ COOH	HCOOH	HCl	HF
B3LYP/6-311++G(d,p) ^a	-23	-15	-8	-2	-5	-5	1	1	5	11	18
B3LYP/aug-cc-pVDZ ^a	-23	-16	-4	1	-1	0	8	7	12	18	23
M06-2X/aug-cc-pVDZ ^a	-16	-7	1	1	-5	0	9	9	13	-6	17
MP2/aug-cc-pVDZ ^a	-21	-15	-5	-1	-3	-3	4	4	5	12	17
M06-2X/6-311++G(d,p) ^b	-23	-11	-7	-2	-7	0	5	3	11	17	15
B3LYP/6-311++G(d,p) ^b	-30	-21	-9	-4	-4	-3	4	4	9	15	25
Experiments ^b	N/A	N/A	-11	N/A	-7	-7	7	7	13	N/A	N/A

^aIn glycolic acid clusters.^bIn 9HFCA clusters.

with blueshifts, while ineffective donation is associated with red shifts.

The computed exo OH bond lengths optimized in B3LYP/6-311++G(d,p) reflect the computed and observed shifts in OH stretching frequency. For isolated 9HFCA the exo OH distance is 0.96963 Å. In the complex with formic acid, the exo OH bond length is 0.96910 Å, shorter than the bond in glycolic acid and consistent with the observed and computed blueshift. For the complex of 9HFCA with formamide, the exo OH bond length is 0.97002 Å, longer than the bond in 9HFCA and consistent with a redshift. For the complexes of 9HFCA with acetaldehyde and ammonia the exo OH bond lengthens further (0.97056 and 0.97120 Å, respectively) consistent with the increasing redshift. The linear correlation between optimized bond length and computed frequency shift is excellent as seen in upper panel of Figure 3. This is also the case for the modeling of the glycolic acid systems.

Weinhold's natural bond orbital (NBO) analysis¹⁸ addresses this question directly. To avoid eccentric behavior in the analysis we used a smaller basis: B3LYP/6-31G(d,p) calculations are the source of the OH σ^* populations quoted here. For isolated 9HFCA, the OH σ^* population is 0.0248 electron. For the blue-shifted formic acid–9HFCA complex the OH σ^* population is 0.0240 electron; the reduction in antibonding is consistent with a blueshift in the stretching vibration. For the red-shifted formamide–9HFCA complex the OH σ^* population is 0.0295 electron; the increase in antibonding

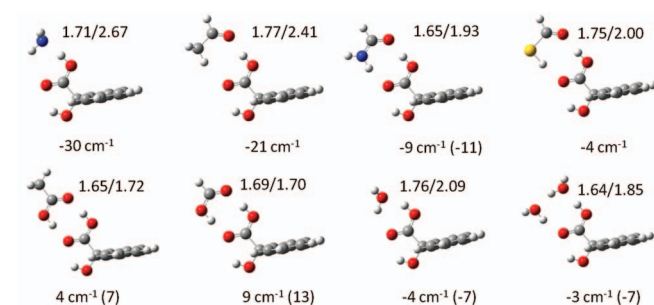


FIG. 2. Computed H-bonding structures of 9HFCA complexing with several binding partners. The notation R1/R2 refers to distance from the 9OH to the partner's acceptor (R1) and the distance from the 9HFCA carbonyl to the partner's H donor (R2). The computed 9OH shifts relative to monomer are listed; experimental values appear in brackets.

is consistent with a redshift. The computed frequency shifts again correlate greatly with the NBO population in the OH σ^* MO as seen in lower panel of Figure 3. This is also the case for the modeling of the glycolic acid systems.

We can offer a rationale for the red- and blueshifts based on the H donor effectiveness. If the partner donates H which engages the carbonyl oxygen of the hydroxy acid's carboxyl group in H-bonding, then internal H bonding between the carbonyl oxygen and the exo OH is weakened. The red-shift associated with internal H-bonding is reduced, so the OH frequency shifts toward the free alcohol value – a blueshift. How can a (further) redshift in the exo OH stretch occur? In the limiting case, the partner does not interact at all with the hydroxyl acid's carboxyl carbonyl oxygen, but H-bonds strongly to the hydroxy acid's carboxyl OH. We picture the weakening of that OH band as the result of charge transfer to the carboxyl OH σ^* local MO. Consequent charge transfer through the bonds linking the carboxyl group to the exo OH can then populate the exo OH's σ^* local MO weakening that bond and

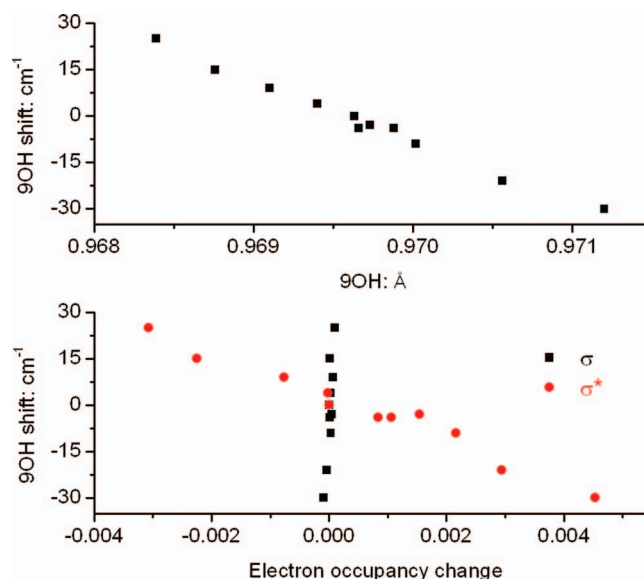


FIG. 3. Dependence of 9OH frequency shifts on bond distances and population of the σ and σ^* natural bond orbitals (NBOs) for the complexes listed in Table I. Populations are relative to values for the uncomplexed 9HFCA, 1.986 for the bond, and 0.02498 for the antibond. Note the σ bond orbital electron occupancy is almost unchanged and σ^* population correlates well with the 9OH shift.

effecting a (further) redshift. In short, we expect that a redshift of the exo-OH stretches would be accompanied by a greater population in the OH σ^* local MO and a blueshift would be attended by a lesser population in the OH σ^* local MO.

The above analysis provides a sensitive test of the molecular orbital approach to hydrogen bond description. The correlation between bond length, bond frequency and NBO populations are consistent with the summary of hydrogen bond parameters in the recent review article by Weinhold and Klein.¹⁹ Cluster studies on a number of related systems with donor and acceptor sites, such as formanilide,²⁰ have shown the possible interaction of donor and acceptor hydrogen bonds. The measured frequency of the intramolecular H bond in the current study provides a more subtle probe of the donor and acceptor influence of the intermolecular H bonds. The subtle interactions of multiple intramolecular and intermolecular hydrogen bonds are revealed which may be useful in the characterization of gas phase complexes such as peptides and nucleic acid bases which are the subject of numerous recent papers.^{21,22}

In conclusion, we have measured, by IR spectroscopy, the shifts in the hydroxyl OH stretching frequency associated with the formation of gas phase H-bonding complexes between 9HFCA and a variety of partners including carboxylic acids, formamide, and water. DFT calculations of shifts in harmonic frequencies show excellent agreement with the experimental observations, and predict more dramatic shifts in complexes still to be explored experimentally. The computations illustrate the relation between OH stretching frequencies and the geometry of the complexes. The sign of the frequency shifts results from a balance struck between the competing effects of proton donation from 9HFCA and donation from the partner in the complex. A semi-quantitative model explains the shifts by reference to natural bond orbital analysis, specifically the population of the σ^* MO associated with the hydroxyl OH. More extensive calculations on glycolic acid and its complexes show similar phenomena and may be rationalized in a similar way. Our results and analysis suggest that the vibrational spectrum of a nearby functional group can serve

as a reporter diagnosing details of the H-bonding in a complex. This can be the basis for understanding the as yet little explored interactions of multiple hydrogen bonds.

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