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Free Carboxylate Stretching Modes

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We report the first IR spectroscopic observation of carboxylate stretching modes in free space, i.e., in the complete absence of solvent or counterions. Gas-phase spectra of a series of benzoate anions have been recorded and compared to condensed-phase spectra, revealing the profound influence of the environment on the symmetric and antisymmetric carboxylate stretch modes.

C═O stretching bands are among the most distinctive infrared features of organic molecules. The exact frequency of the carbonyl stretch is very sensitive to its chemical environment and hence amide C═O stretching bands are for instance excellent probes of the H-bonding interactions in peptides and proteins. Upon deprotonation of a carboxylic acid, a carboxylate moiety (COO^-) is formed and its infrared signature is also well-known, for instance, from carboxylate salts and their solutions.[1,2] In these spectra, the symmetric and antisymmetric carboxylate stretching modes are typically found in the 1400 and 1600 cm^{-1} ranges, respectively. The splitting between the two bands, $\Delta\nu_{a-s}$, is often used to determine the geometry and strength of counterion binding.[3] The $\Delta\nu_{a-s}$ values are commonly compared to “free” ion spectra, where free means unbound to a counterion such as in dilute solution. However, the condensed environment will inevitably influence the vibrational frequencies, and most notably those of the COO^- moiety, because of its more diffuse electron density. Although this is not a problem for comparison of the band separation with and without the counterion, it leaves one wondering where the bands are in a “truly” free ion, i.e., in the gas phase. Such values could be used to directly evaluate the influence of the solvent on the carboxylate vibrational frequencies.

With the use of several action spectroscopy methods, ever more gas-phase ion spectra have been reported in recent years. Most studies have, however, focused on cationic species and gas-phase IR anion spectra have received not nearly as much attention.[4] Gas-phase carboxylate stretch modes have been reported in the search for zwitterionic amino acids in the gas phase.[5,6] However, in these systems the negative charge on the carboxylate group is necessarily stabilized by the presence of a positive charge[5] or dipole interactions.[6] Hence, the reported values for the carboxylate stretching modes are again influenced by the presence of (partial) positive charges, though perhaps to a lesser extent than in condensed-phase environments. In fact, this influence could be investigated by comparison to gas-phase spectra of uncomplexed, i.e., free, carboxylate species. Here, we present the first gas-phase IR spectra of the carboxylate stretching modes in free space, in particular of the benzoate anion and some of its monofluoro and amino derivatives.

Carboxylate anions are generated by electrospray ionization using a solution of the corresponding carboxylic acid (typically 1 mM in 50/50 MeOH/H_2O) and a Micromass Z-Spray source with a needle voltage of around −2.2 kV.[7] Benzoate anions are thus generated from a solution of benzoic acid and mass-selectively stored in the Penning trap of a Fourier transform ion cyclotron resonance mass spectrometer (FTICR-MS), where they are exposed to the tunable IR radiation of the free electron laser FELIX.[8] If the wavelength is in resonance with an absorption in the anion, IR multiple photon dissociation (IRMPD) occurs, resulting in the loss of CO_2, yielding an anionic fragment at mass 77. Recording the photofragment yield as a function of laser wavelength gives an IR action spectrum that generally reproduces the true absorption spectrum very well.[9]

Figure 1 shows the IRMPD spectrum of the benzoate anion compared to the gas-phase absorption spectrum of benzoic acid. Deprotonation of the carboxylic acid causes a formal reduction of the CO bond order from 2 to 3/2 and is observed to induce a red shift of the stretching vibration of approximately 140 cm^{-1}, yielding an antisymmetric carboxylate stretch mode at 1626 cm^{-1}. The next strongest absorption in the benzoate anion spectrum corresponds to the symmetric carboxylate stretch mode, which is observed at 1311 cm^{-1}, approximately 100 cm^{-1} lower than typical condensed-phase values of around 1400 cm^{-1}. This gives a $\Delta\nu_{a-s}$ value of 315 cm^{-1} for the free benzoate anion. Finally, the bands around 700 and 800 cm^{-1} are the CH out-of-plane bending and carboxylate scissoring bands, respectively; the latter also contains some C−C stretching character.

Observed frequencies are in good agreement with Gaussian03 anharmonic frequency calculations[10] using the B3LYP density functional, if diffuse functions are included in the basis set, as seen from the comparison between the 6-31G** and the 6-31+G** calculations (see also Table 1). Of the various vibrational modes, the antisymmetric carboxylate stretch frequency is particularly sensitive to inclusion of diffuse functions, indicating that, as expected, the electronic wavefunction is more diffuse around the carboxylate moiety. We further verified that scaled (0.98) harmonic frequency calculations give an equally acceptable result, as shown in the bottom panel of Figure 1. The best match for the carboxylate modes is obtained using the largest basis set employed in this study (aug-cc-pVDZ),

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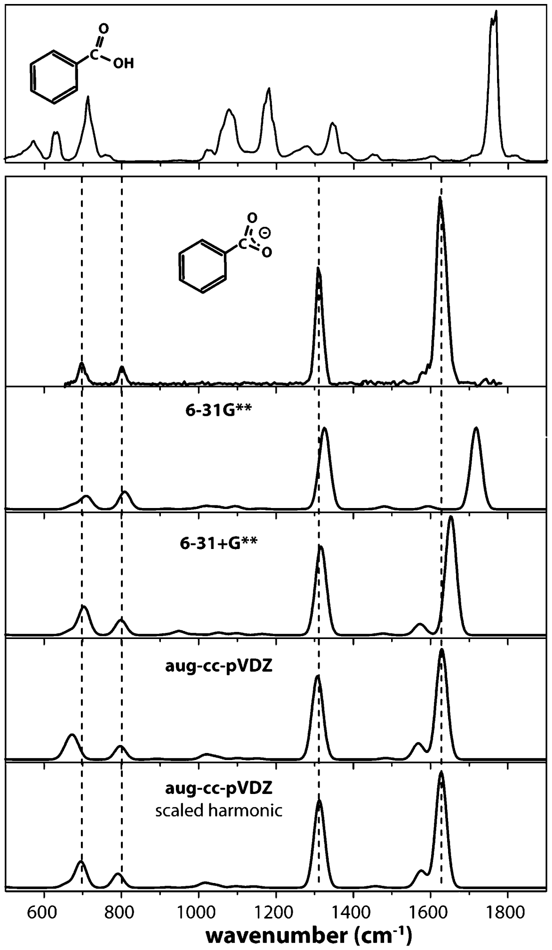

Figure 1. Infrared spectrum of the benzoate anion compared to anharmonic frequency calculations using the B3LYP functional and different basis sets. The gas-phase spectrum of neutral benzoic acid (taken from the NIST Chemistry Webbook) is shown for comparison in the top panel.

TABLE 1: Experimental and Computed (B3LYP) Anharmonic Vibrational Frequencies of the Benzoate Anion (All Values in cm^{-1})

mode	exp	6-31G**	6-31+G**	aug-cc-pVDZ	harm[a]
COO^- asym str	1626	1718	1653	1629	1627
Ring CC stretch	∼1582	1593	1572	1568	1574
COO^- sym str	1311	1325	1316	1307	1311
C−C str, OCO bend	804	809	799	797	790
CH oop bend	699	711	703	660/679	692/698

[a] Harmonic B3LYP/aug-cc-pVDZ scaled by 0.98.

although the CH out-of-plane bending mode near 700 cm^{-1} is curiously far off for this basis set compared to smaller ones. In contrast to the calculations using the 6-31G basis sets, aug-cc-pVDZ predicts two almost equally intense out-of-plane CH bending modes (see Table 1 and Supporting Information). The experiment shows no evidence for a double peak structure. Comparison of harmonic and anharmonic frequencies computed using aug-cc-pVDZ further suggests that calculation of the anharmonicity is inaccurate for this mode.

IRMPD spectra of the three isomers of the mono-fluoro-substituted benzoate anion are shown in Figure 2 along with scaled harmonic frequency calculations at the B3LYP/aug-cc-pVDZ level of theory, which adequately reproduce the main features in the spectra. The calculation for the ortho isomer predicts a nonplanar structure in which the carboxylate group is twisted[2b,11] by about 55° relative to the aromatic plane. The antisymmetric COO^- stretch mode is found at a slightly higher frequency than for the unsubstituted benzoate anion, in agreement with Spinner's finding that electron-withdrawing groups blue shift the antisymmetric COO^- stretch.[2b] The blue shift is smaller for the *p*-aminobenzoate anion,[12] again in agreement with the solid-state spectra[2b] and with the higher electrophilicity of the F atom compared to the amino group.

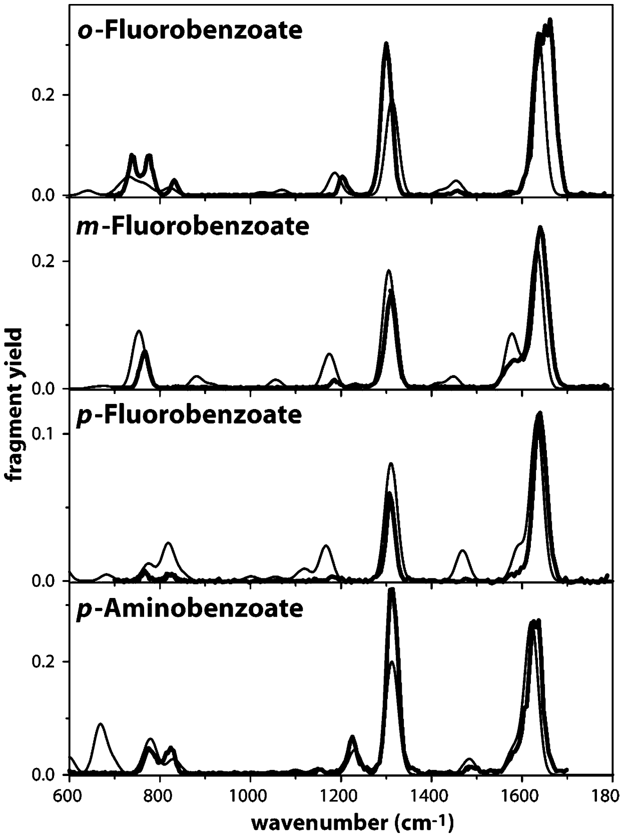

Figure 2. IRMPD spectra for the three isomers of the monofluorobenzoate anion and the *p*-aminobenzoate anion (thick) compared to scaled (0.98) harmonic frequency calculations at the B3LYP/aug-cc-pVDZ level of theory (thin).

TABLE 2: Symmetric and Antisymmetric CO Stretch Frequencies (in cm^{-1}): Condensed vs Gas Phase

	solid state[a]		gas phase[b]	
	COO^- asym	COO^- sym	COO^- asym	COO^- sym
benzoate	1553	1410	1626	1311
o-fluorobenzoate	1599	1396	∼1650	1300
m-fluorobenzoate	1565	1408	1641	1311
p-fluorobenzoate	1550	1413	1639	1309
p-aminobenzoate	1540/1546	1408/1390	1628	1307

[a] As sodium salt. Values from ref 2b. [b] This work.

Contrary to the solid-state spectra of ref 2b, however, the frequency of the antisymmetric COO^- stretch band remains relatively unchanged with the position of the F-atom in the ring. (The slightly broader band for the ortho isomer is possibly caused by the nonplanar structure and the steric hindrance and/or electrostatic repulsion between the fluoro and carboxylate groups.) The solid-state spectra[2b] showed a shift of ∼50 cm^{-1} going from the ortho to the para isomer (Table 2), whereas the shift in the gas phase is only ∼10 cm^{-1}. It appears thus as if the shift reported by Spinner is not a purely through-bond, inductive effect but is strongly enhanced by the environment.

In fact, in his 1967 paper, Spinner already hinted at this possibility by stating that[2b] “a separation of inductive and direct-field effects is hardly ever possible.”

In conclusion, we have presented the first gas-phase IR spectra of the free carboxylate stretching modes. The splitting between the symmetric and antisymmetric carboxylate stretch modes of around 315 cm^{-1} is much larger than for any benzoate salt. The splitting increases for electrophilic ring substitution, but is only marginally dependent on the substitution position in the ring.

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Supporting Information Available: Optimized structures and frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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