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Articles

Negative Hyperconjugation versus Electronegativity: Vibrational Spectra of Free Fluorinated Alkoxide Ions in the Gas Phase

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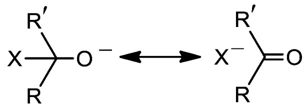
CO stretching frequencies of free, gaseous, fluorinated alkoxide ions shift substantially to the blue, relative to those of corresponding alcohols complexed with ammonia. Free α-fluorinated ions, pentafluoroethoxide and heptafluoroisopropoxide anions, display further blue shifts relative to cases with only β-fluorination, providing experimental evidence for fluorine negative hyperconjugation. DFT analysis with the atoms in molecules (AIM) method confirms an increase in CO bond order for the α-fluorinated ions, demonstrating an increase in carbonyl character for the free ions.

Highly fluorinated alcohols have fascinated chemists for decades, ever since the preparation of trifluoroethanol was first described more than 80 years ago.[1] They possess greater acidity than the analogous alcohols derived from hydrocarbons, but geminally fluorinated alcohols larger than CF_3OH tend to be unstable, owing to spontaneous expulsion of hydrogen fluoride. Preparation and the ^{13}C NMR spectra of heptafluoroisopropanol have been reported only recently,[2] but many salts of geminally fluorinated alcohols have been described, especially those of pentafluoroethanol and heptafluoroisopropanol[3] (whose conjugate bases are drawn as **1** and **2** in Scheme 1 below). Ion pairing of cations with these anions limits the ability to observe the vibrational spectra of the alkoxides in condensed phases and shifts the stretching frequencies of the substituents attached to the same carbon as the negatively charged oxygen. Here, we report IR action spectra of negative ions **1** and **2** isolated in the gas phase, compare them with the spectra of ions **3**–**6** recorded under the same conditions, and discuss possible implications with respect to fluorine negative hyperconjugation.

$CF_3CF_2O^-$ $(CF_3)_2CFO^-$ $CF_3CH_2O^-$
1 **2** **3**

$(CF_3)_2CHO^-$ $(CF_3)_2CH_3CO^-$ $(CF_3)_3CO^-$
4 **5** **6**

Scheme 1. Free alkoxide ions examined in this study.



Scheme 2. Negative-ion hyperconjugation in an alkoxide ions.

Scheme 2 illustrates the concept of hyperconjugation, which was introduced by Mulliken in 1939, as it applies to the anions under investigation. A recent report regarding the acidities of fluorinated hydrocarbons discounts negative β-hyperconjugation in the most acidic examples, but gives it a role in stabilizing more basic carbanions.[4] Given the complicated nature of fluorine negative hyperconjugation with respect to carbon acidities, it seems appropriate to explore the effect on alkoxide ions. Hyperconjugation predicts that increasing the negative charge on oxygen (for example, in an isolated alkoxide versus its salt) should weaken the C–X bond. It also implies (as tested here experimentally) that the C–O bond in the isolated anion ought to develop increased carbonyl character as X changes from H to F. The experimental data presented here confirm that expectation.

The technique used for these investigations was infrared multiple-photon dissociation (IRMPD) spectroscopy. In these experiments, isolation of ions of a given m/z value in an ion cyclotron resonance (ICR) cell is followed by infrared photolysis, using a tunable free-electron laser operating in the 500–1800 cm^{-1} domain. Frequencies that induce ion dissociation correspond to resonant IR absorptions.[5,6]

For negative ions, two types of dissociation can occur: electron detachment (in which case the parent ion disappears without any fragments observed) or decomposition to smaller anions through the expulsion of neutral species. In the present study, ion **1** dissociates primarily through the first pathway, whereas the other ions dissociate through the second route.

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Figure 1 depicts the IRMPD spectra of ions **1**–**6** as silhouettes with the calculated DFT (B3LYP/aug-cc-pVTZ harmonic frequencies scaled by 0.97) IR harmonic spectra in red, and the predicted anharmonic spectra superimposed for ions **1**–**4**. This level of anharmonic calculation has been shown to give good fits to IRMPD spectra for small ions.[9] The band positions and relative intensities are matched, confirming the identification of the ion structures. Table 1 compares the scaled normal-mode CO stretching frequencies with our IRMPD measurements, as well as calculated C–O bond lengths, Hooke's Law stretching spring constants (κ), and AIM bond orders (n). The Supporting Information summarizes the bond dissociation energies and calculated AIM bond critical point electron densities,[8] from which the bond orders were determined.

Table 1. Calculated Hooke's Law spring constants (κ), CO bond lengths (r), harmonic CO stretch frequencies, experimental CO stretch frequencies, and bond orders (n) calculated by using the AIM method.[7,8]

Ion	κ[a,b] (N m^{-1})	Calcd r_{CO}[a] [Å]	Calcd CO stretch[a,c]	Observed CO stretch[d]	Calcd n[e]
1	1027	1.222	1577	1578	1.84
2	784	1.244	1488	1496	1.72
3	609	1.321	1185	1188	1.41
4	635	1.307	1219	1236	1.47
5	620	1.310	1232	1243	1.46
6	734	1.290	1276	1299	1.54

[a] Calculated at B3LYP/aug-cc-pVTZ. [b] Calculated harmonic spring constants based on ±5 and ±10 pm displacements. [c] Normal-mode frequencies scaled by 0.97. [d] IRMPD experimental values (±3 cm^{-1}). [e] AIM bond orders; see text.

Anharmonicity of the vibrations leads to small red shifts and broadening of IR transitions when they are monitored by IRMPD spectroscopy.[5,6] The magnitude of the redshift can be gauged by comparing the experimental spectra (silhouettes) with the predicted anharmonic frequencies (dashed lines) in Figure 1. In each case, the IRMPD band corresponding to the C–O stretch is slightly lower than the calculated fundamental, but the discrepancy is <35 cm^{-1}. As the absolute frequencies measured by IRMPD spectroscopy have this deviation, the conclusions from this work are based on the differences between the C–O stretching bands observed for ions **1** and **2** (listed in Table 1) versus those for ions **3–6**.

DFT calculations reveal some unexpected features of gaseous alkoxide ions. Although the experimental IR absorptions in the CH stretching regions of trifluoroethoxide on a copper surface (2950 cm^{-1})[10] and of sodium hexafluoroisopropoxide in a KBr pellet (2834 cm^{-1})[11] match the calculated frequencies for cuprous trifluoroethoxide and sodium hexafluoroisopropoxide in the gas phase, respectively, we find that the CH stretches predicted for free gaseous alkoxides shift substantially to lower frequencies, that is, 2481 and 2392 cm^{-1} for isolated ethoxide, 2424 cm^{-1} for isolated isopropoxide, 2476 and 2541 cm^{-1} for isolated $CF_3CH_2O^-$, and 2543 cm^{-1} for isolated $(CF_3)_2CHO^-$. The apparent weakening of the C–H bond adjacent to negatively charged oxygen is consistent with negative

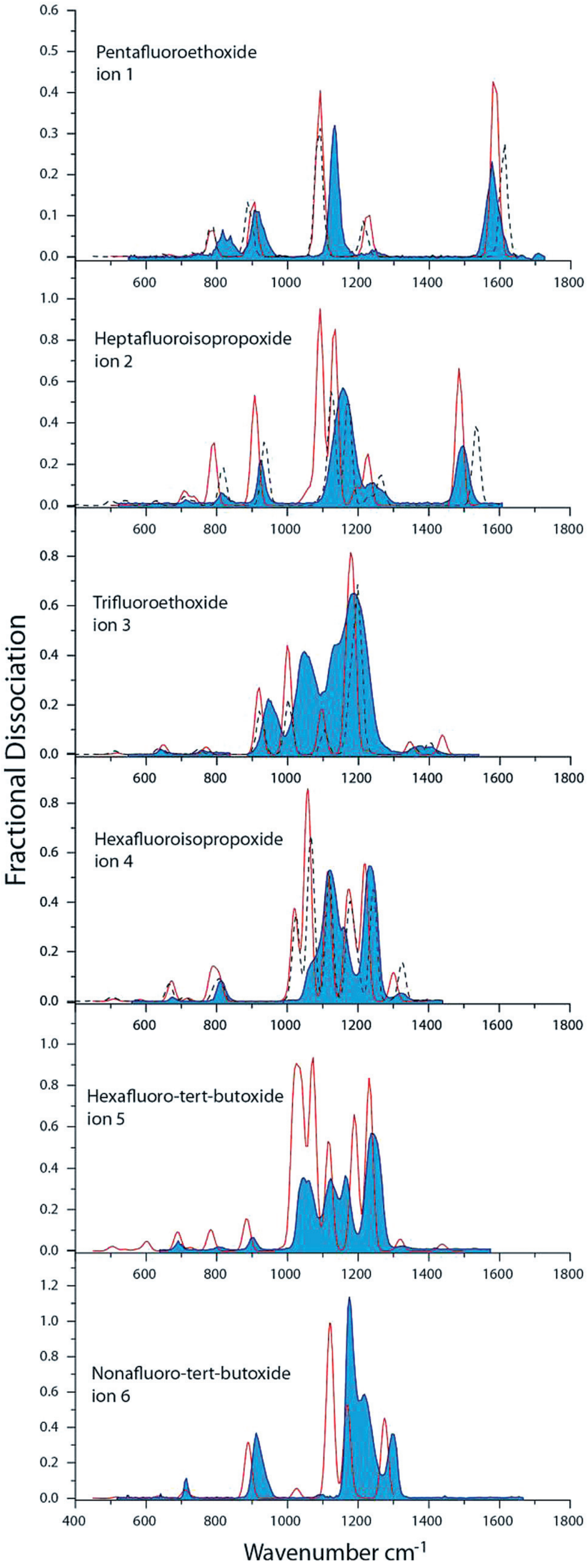


Figure 1. Experimental IRMPD spectra (silhouettes) of the free alkoxide ions with superimposed scaled normal-mode frequencies (solid red curves) and unscaled anharmonic frequencies (dashed black curves using harmonic intensities for ions **1**–**4**) predicted by B3LYP/aug-cc-pVTZ calculations.

hyperconjugation, as depicted in Scheme 2, where X = H. Unfortunately, that particular domain of the IR spectrum is difficult of access for the lasers that are currently available to perform gas-phase IRMPD spectroscopy; hence, only theoretical predictions are available at this time. However, the CO stretches occur in an easily probed region and show pronounced differences between perfluorinated anions **1** and **2** and those having only CF_3 groups (**3**–**6**). As noted above, this progression also behaves in a fashion consistent with Scheme 2, when X is varied from H to F.

Animating the DFT normal modes shows that the C–O stretches of free alkoxide ions stand apart from other vibrations and do not exhibit extensive mixing with motions of other atoms. C–O stretching frequencies of the gaseous ammonia complexes of trifluoroethanol, hexafluoroisopropanol, and nonafluoro-*tert*-butanol have been reported at 1103, 1143, and 1179 cm^{-1}, respectively,[12] whereas the IR absorption spectrum of the sodium salt of **4** displays a strong band at 1277 cm^{-1} and weaker bands at 1250 and 1231 cm^{-1}.[11] These values can be compared with the spectra reproduced in Figure 1 and summarized in Table 1. By contrast, the gaseous ammonia complexes exhibit C–O stretches with a redshift of 85–120 cm^{-1} from the free ions.

Hyperconjugation also causes the CF bonds geminal to oxygen to lengthen. Table 2 summarizes a comparison between those CF bonds and the CF bonds in the trifluoromethyl groups (as predicted by our DFT calculations). Although CF stretches cannot be easily isolated from one another experimentally, computational results show elongation and loosening of the CF bond geminal to oxygen in terms of calculated bond lengths, as well as in terms of Hooke's Law spring constants (κ) and values of the bond critical-point electron densities (ρ_{bcp}),[8] which (as described below) provide a measure of the bond order. The lengths of all C–F bonds in the CF_3 groups of the free alkoxides are between 1.343 and 1.381 Å. Table 2 selects the longest and one of the shortest bonds for comparison with the CF bonds geminal to oxygen.

Table 2. Calculated (B3LYP/aug-cc-pVTZ) CF bond lengths, corresponding Hooke's Law harmonic spring constants (κ), and bond critical point electron densities (ρ_{bcp}) calculated by using the AIM method.[8]

Ion	CF position	CF bond length	κ_{CF} [$N\,m^{-1}$]	CF ρ_{bcp}
1	C1	1.471	193	0.2132
2	C2	1.540	141	0.1809
3	C2 longest	1.381	415	0.2565
4	C1 shortest	1.352	471	0.2766
$(CF_3)_2CFONa$	C2	1.426	315	0.2327

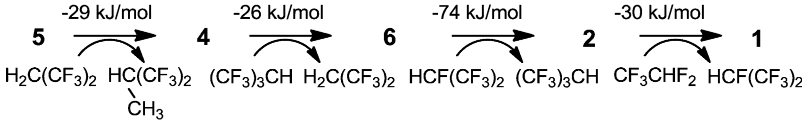
Comparison of ion **2** with its gaseous, neutral sodium salt (also listed in Table 2), both of which possess a plane of symmetry, shows a substantial effect from diminishing the negative charge on oxygen; the central CF bond becomes 0.045 Å shorter in the salt, whereas the values of the CF κ and ρ_{bcp} values become greater. The CF spring constant of the salt is more than twice as large as for ion **2**, as summarized in Table 2.

The CO stretch of the gaseous sodium salt of ion **2** contributes the highest frequency vibration, with only slight motions of the other atoms, and has a predicted (scaled) harmonic value of 1349 cm^{-1}, which is more than 100 cm^{-1} lower than the CO stretch of the free alkoxide. Hence, the presence of the full negative charge on the oxygen of ion **2** increases the κ constant for the CO stretch at the same time as it diminishes the κ constant for the geminal CF bond. Unfortunately, salts of ion **1** are unsymmetrical, so similar calculations for them become more complicated and are not reported here.

What is the difference between electronegativity and hyperconjugation? The energetic effects of a substituent can be subdivided into a cylindrically symmetric part and a less symmetrical part, which depends upon the orientation. The former is as a consequence of electronegativity, whereas the latter comprises hyperconjugation. For a diatomic or a linear polyatomic, only electronegativity plays a role, because of symmetry. For ions **1**--**5**, the lack of any rotational symmetry of the carbon attached to oxygen introduces anisotropy. Although it is not yet possible to quantitate electronegativity and hyperconjugation separately, the theory of atoms in molecules (AIM) conveys a semiquantitative measure by using the AIM bond order, *n*. This is given by the expression $n = e^{-AB}(e^{A\rho}-1)$, where ρ (or, more precisely, ρ_{bcp} for the CO bond) stands for the electron density at the bond critical point of the CO bond.[7] This expression is slightly modified from the one originally proposed by Bader,[8] so as to give a bond order of zero when $\rho_{bcp} = 0$.

To what extent can the increase in the C–O stretching frequency be ascribed to the effects of fluorine negative hyperconjugation? As the experimental bands for the C–O stretching frequencies match the scaled normal modes within 25 cm^{-1}, theoretical comparisons seem justified. The calculated Hooke's law spring constants (κ) confirm the trend observed experimentally, as does the sequence of calculated bond lengths, in addition to the sequence of isodesmic reactions summarized in Scheme 3, which shows a large jump between the ions containing hydrogen and the perfluorinated ions.

Our efforts to dissect the effects of negative hyperconjugation from those of electronegativity become complicated by the fact that the progression from ions **3**–**6** to **2** to **1** also follows the electronegativity increase of the attached groups. If one accepts that the electronegativity of a CF_3 group is less than that of a fluorine substituent (as inferred from core bind-



Scheme 3. Sequence of calculated (B3LYP/aug-cc-pVTZ) isodesmic reactions showing the unusual stability of ions **1** and **2**.

ing energies),[13] then the aforementioned trends might simply result from increasing electron-withdrawing character. As mentioned above, AIM analysis shows a marked increase in CO bond order that appears to confirm hyperconjugation.

Choosing bond orders of $n = 2$ for acetyl fluoride and $n = 1$ for ethanol, the AIM bond order of acetaldehyde shifts by $\Delta n = -0.16$ relative to acetyl fluoride, based on ρ_{bcp} for the CO bond. This seems consistent with the change in going from ion **3** to ion **6**, $\Delta n = 0.13$, as shown in Table 1. By attributing those changes in n wholly to the electronegativity difference between the hydrogen and fluorinated substituents, we surmise that an even greater change must arise from an additional effect. As Table 1 summarizes, the change in going from ion **4** to ion **2** is $\Delta n = 0.25$, which is in support of hyperconjugation. If we naively suppose that bond order should change by twice as much in going from ion **3** to ion **1** (i.e. $\Delta n = 0.32$), owing to electronegativity alone, the calculated change, $\Delta n = 0.43$, again supports the inference of hyperconjugation.

Theory thus buttresses experiment, attributing the observed increase in CO stretching frequencies of ions **1** and **2** to combined effects of electronegativity and of hyperconjugation.

Experimental Section

Ions **3**–**6** are readily formed through the electrospray ionization (ESI) of 1:1 solutions of water/methanol containing 1–5 mM of the corresponding alcohols (which are commercially available). IRMPD of ions **3** and **4** produces CF_3^- exclusively through the expulsion of the corresponding neutral carbonyl compounds. IRMPD of ion **5** produces both m/z 111, which is assigned to the structure of the enolate of trifluoroacetone, and CF_3^- as fragment ions.

IR irradiation of ion **6** yields four different fragments, CF_3^- and $C_3F_7^-$ as minor products and ions **1** and **2** as major products. $C_3F_7^-$ arises from expulsion of neutral CF_2O, whereas ion **1** comes from loss of neutral CF_2 and **2** comes from loss of two CF_2 neutral species. IR irradiation of ion **2**, which produces **1** as well as a small amount of CF_3^-, confirms the latter pathway. Although neutral CF_2 is a carbene, many ion decompositions of highly fluorinated ions in the gas phase proceed through CF_2 expulsion.[14]

Assignment of CO stretching bands was based upon comparisons between experiment and theory. For ions **1**, **2**, and **6**, the CO stretch contributes the highest frequency band. For ions **3**–**5**, the CO stretch contributes the most intense absorption between 1150 and 2550 cm^{-1}, both theoretically and experimentally.

DFT calculations were performed by using the aug-cc-pVTZ basis set with the B3LYP and the M062X functionals. Both give comparable results, and the B3LYP results are presented herein. Hooke's Law κ values corresponding to 5 and 10 pm deviations from the equilibrium geometry were calculated by using an ultrafine grid for 5 points for each alkoxide calculated at B3LYP/aug-cc-pVTZ with the bond (CO or CF) constrained to be 5 or 10 pm shorter than the equilibrium geometry (x and x'), at the equilibrium geometry (y), and constrained to be 5 or 10 pm longer than the equilibrium geometry (z and z'). Parabolic potentials representing the best symmetrical fits to the points $2[(x+z)/2-y]/(5\times10^{-12})^2$ and $2[(x'+z')/2-y]/(1\times10^{-11})^2$ and passing through the origin were fitted. The tabulated values of κ thus represent mean values for a symmetric (harmonic) fit to the asymmetric calculated potentials.

Bond-order calculations were based on the AIM approach by using wavefunctions computed with an ultrafine grid, using acetyl fluoride as the standard for a C=O double bond ($\rho_{bcp} = 0.4543$) and ethanol as the standard for a C–O single bond ($\rho_{bcp} = 0.2550$), giving the values $A = 1.096$ and $B = -1.032$. By using these parameters, the CO bond order of acetaldehyde was calculated to be 1.84. Table 1 lists the AIM CO bond orders for the free anions under investigation. The isolated sodium salts have calculated AIM CO bond orders roughly $\Delta n = 0.1$ smaller than the corresponding free ions. As there is no reference for a carbon–fluorine double bond, Table 2 reports only the values of ρ_{bcp} for the selected CF bonds. Table S3 (in the Supporting Information) compares observed CO stretching frequencies with anharmonic calculations.

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Keywords: difluorocarbene · electron detachment · infrared multiple photon dissociation · ion cyclotron resonance · photolysis

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