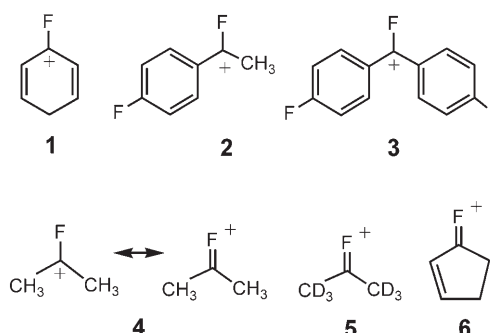# Communications

The Cationic C=F$^+$ Stretching Vibration in the Gas Phase**

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The carbonyl stretch has been recognized as the most distinctive vibration of polyatomic organic molecules, after Coblentz reported the infrared (IR) absorptions of aromatic aldehydes more than a century ago.[1] The present work explores the comparison between the C=O and C=F$^+$ bonds, which are isoelectronic and isolobal. Theory predicts that direct attachment of halogen (X) to a positively charged sp^2 carbon leads to CX bonding with lone-pair back donation, which is tighter than a single bond. IR spectroscopy has shown back donation for α-chlorocarbocations.[2] Natural bond orbital (NBO) analysis predicts that the cationic C−F bond possesses an even higher degree of π character than the cationic C−Cl bond, and is appropriately represented as C=F$^+$ in the absence of additional conjugative stabilization.[3]

Because carbocations are highly reactive, preparing them in media compatible with IR spectroscopy has demanded considerable ingenuity.[2,4] For this reason, determining IR absorptions of gaseous ions by means of their subsequent dissociation is a new and growing field. The wavelength dependence of resonant IR multiphoton dissociation (IRMPD) of gaseous ions, as measured with a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer, reveals their vibrational spectra.[5–7] To induce IRMPD, experiments described herein make use of the free electron laser FELIX as a source of intense and conveniently tunable IR radiation.[8] These measurements confirm the partial double bond between electron-deficient carbon and fluorine atoms.

Dopfer and co-workers[7] have examined resonant IRMPD spectra of protonated fluorobenzene. One of the isomers has a partial positive charge on the carbon to which fluorine is attached, as depicted by resonance structure **1**. These investigators correlated two in-plane vibrations of neutral fluorobenzene that have a high degree of C−F stretching character ($\tilde{\nu}_{7a} = 1239$ cm^{-1} and $\tilde{\nu}_{8a} = 1603$ cm^{-1}) with bands observed for **1** at 1308 and 1583 cm^{-1}. Coupling with other motions makes it difficult to assess more precisely

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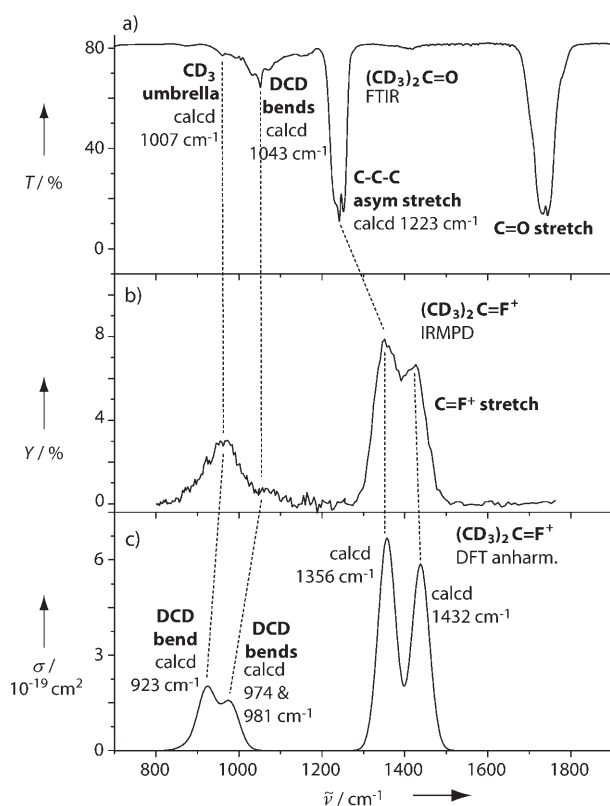Fax: (+1) 951-827-4713
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how much the stiffness of the C−F bond in the cation differs from that of the neutral molecule.

More recently, Reed and co-workers[4] have reported IR absorption spectra of crystalline salts of ions **2** and **3**. The reported bands for the cationic C−F stretch occur at 1175 and 1154 cm^{-1}. Theory predicts that the C=F$^+$ stretch in more highly saturated systems should occur at higher frequencies.

Among the simplest ions of this nature, the 2-fluoroisopropyl cation (**4**), was prepared in solution by Olah and co-workers,[9] but its vibrational spectra have not been published. This same ion has been created in the gas phase by Eyler, Lias, and Ausloos by the reaction of CF$_3^+$ ion with acetone, in which CF$_2$O is the uncharged byproduct.[10] Equation (1) illustrates this metathesis reaction schematically. The structure of ion **4** in the gas phase has been confirmed by collection and identification of the neutral products from its subsequent ion–molecule reactions.[11]

$$R^1R^2C=O \xrightarrow{CF_3^+} \left[\begin{array}{c} R^1R^2C-O-CF_3^+ \end{array} \right] \xrightarrow{-CF_2O} R^1R^2C=F^+ \qquad (1)$$
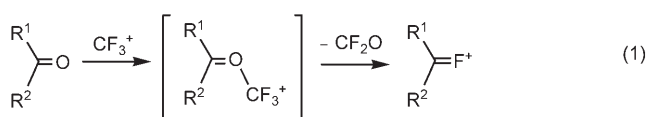
Because of the small number of atoms in **4**, resonant IRMPD on this ion in the gas phase presents a challenge. For that reason, we have examined the perdeuterated analogue **5**, for which the vibrational levels are more closely spaced. Following resonant absorption of one IR photon, the density of states of the isolated ion becomes sufficiently large for the probability of absorbing additional photons to increase substantially. Even if the additional photons no longer match this normal mode, the IR absorption cross section of the vibrationally excited ion becomes large enough for the ion to absorb more photons and acquire sufficient internal energy to expel neutral DF.

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Equation (1) constitutes a metathesis of F^+ for O, which are isoelectronic. Once formed, the ions react rapidly with the parent ketone to transfer a proton. To produce fluorinated cations in sufficient abundance for vibrational spectroscopy, it is necessary to make them under conditions in which the ketone starting material is present for only a short duration. CF_3^+ ions were produced by electron ionization of tetrafluoromethane in an external source, injected into an ICR cell where they were isolated by appropriate ejection pulses, and reacted with a pulse of helium seeded with the reactant ketone. Because Equation (1) is highly exothermic, its products are susceptible to skeletal rearrangements. For that reason, this study focuses on α-fluorocarbocations that represent global minima.

Ion **5** was produced by reaction of [D$_6$]acetone with CF_3^+. Its dissociation to $CD_3C\!=\!CD_2^+$ via DF loss has ample precedent in the metastable ion decompositions of **5**.[12] Figure 1 compares the resonant IRMPD spectrum of **5** in

The comparison with [D$_6$]acetone helps assign the observed bands. The lowest-frequency vibrations in Figure 1b, 1070 and 965 cm^{-1}, correspond to DCD bending modes, which correlate with the bending modes and CD$_3$ umbrella vibrations of [D$_6$]acetone.[14] The highest-frequency band in Figure 1b, 1425 cm^{-1}, is the $C\!=\!F^+$ stretch, which is lower than the $C\!=\!O$ stretch of the neutral ketone (1720 cm^{-1}). The 1355 cm^{-1} band for **5** exhibits a higher frequency than does the analogous deformation of [D$_6$]acetone. Table 1 compares the observed bands for **5** with the frequencies predicted by the anharmonic DFT calculations.

Table 1: DFT-calculated frequencies and harmonic intensities compared to observed band positions in the resonant IRMPD spectrum of ion **5**.[a]
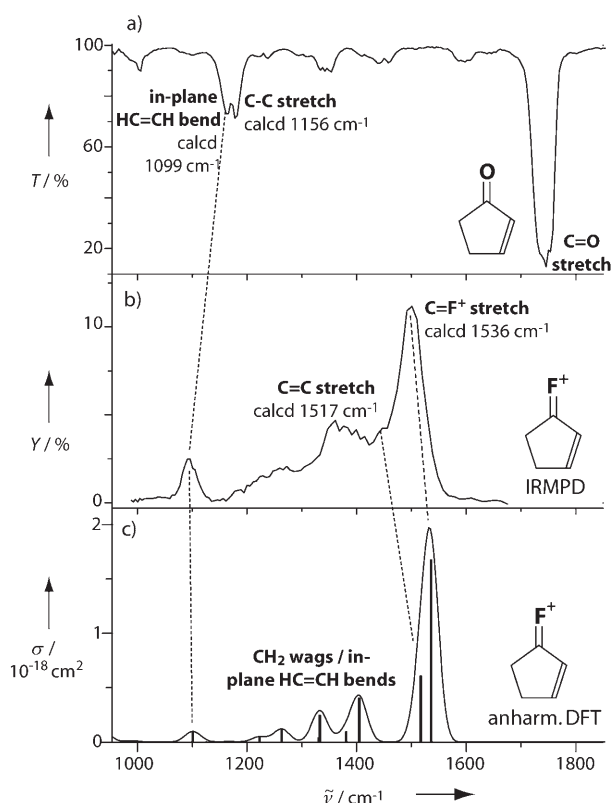
Assignment	$\tilde{\nu}_{calcd}$ [cm^{-1}][b]	I_{rel}	$\tilde{\nu}_{obs}$ [cm^{-1}]
$C\!=\!F^+$ stretch	1432	100	1425
CCC asym stretch	1356	114	1355
DCD bends	974, 981, 990,991	15, 7.1, 2.2, 2.5	1070
DCD bend	923	33	965

[a] See also Figure 1. [b] B3LYP/6-31G** with anharmonic corrections; ref. [13]. [c] Intensities I_{rel} relative to the $C\!=\!F^+$ stretch.

Figure 1. Comparison of b) the IRMPD spectrum of ion **5** (% fragment ion yield, Y) with c) an anharmonic frequency calculation, (harmonic absorption cross section σ at a 30 cm^{-1} full-width at half-maximum Gaussian lineshape; cf. Table 1), and with a) the gas-phase absorption spectrum of neutral perdeuterated acetone (% transmittance, T).

Assignments were confirmed by animating calculated normal modes. The excellent match between predicted and observed stretching frequencies, and relative intensities, suggests that animation provides a reliable guide. As anticipated, the $C\!=\!F^+$ stretch has a frequency nearly 300 cm^{-1} lower than a carbonyl stretch, although it stands apart from the other vibrations. The band at 1355 cm^{-1} observed for **5** correlates with a vibration at the same frequency seen in the gas-phase IRMPD of the $(CD_3)_2CD^+$ cation.[5] The shift of this C—C—C in-plane deformation relative to that of [D$_6$]acetone is consistent with the notion that hyperconjugation between methyl groups and a cationic sp^2 carbon makes C—C bonds stiffer.

Given the agreement between experiment and theory summarized by Figure 1 and Table 1, comparison of experiment with DFT can be extended to the more complicated problem of interpreting vibrations of a $C\!=\!F^+$ conjugated with a C=C double bond. Ion **6** readily forms from the reaction of 2-cyclopentenone with CF_3^+,[15] and possesses a sufficient density of states to be dissociated by resonant IRMPD via HF loss. DFT predicts structure **6** to be the most stable $C_5H_6F^+$ isomer. Figure 2 compares the published gas-phase IR spectrum of 2-cyclopentenone (a)[16] with the bands observed in the IRMPD of **6** (b) and the absorptions predicted by DFT for **6** (c).

Ion **6** displays more bands than does **5**. DFT predicts that the $C\!=\!F^+$ stretch, ν_{CF}, is coupled to the sp^2–sp^2 C—C single-bond stretch rather than to the C=C double-bond stretch, which is calculated to occur at a frequency that is lower by 19 cm^{-1} and with an intensity only about one-third as great as for ν_{CF}. This prediction contrasts to the IR absorption spectrum of neutral 2-cyclopentenone, in which the carbonyl and C=C stretches couple, and the sp^2–sp^2 C—C single-bond stretch occurs at 1175 cm^{-1}.

the 800–1800 cm^{-1} domain (b) with the spectrum predicted by density functional theory (DFT) at B3LYP/6-31G** using anharmonic corrections and harmonic relative intensities[13] (c), and also with the gas phase IR absorption spectrum of [D$_6$]acetone (a).

Figure 2. IRMPD spectrum of ion **6** (b) compared with an anharmonic DFT frequency calculation (c) and the gas-phase absorption spectrum of its neutral enone precursor (a).[16]

greater than that of **4**, 8.19 mdyne Å. As the higher frequency seen for the C=F$^+$ stretch in **6** does not reflect a bond with a stiffer spring constant, observed variations in ν_{CF} cannot naively be ascribed to differences in bond strength.

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Assuming that the shoulder at 1450 cm^{-1} in the resonant IRMPD spectrum of **6** represents a fundamental vibration, it must correspond to the C=C stretch. This assignment places it 50 cm^{-1} lower than the much more intense 1500 cm^{-1} band, which is assigned to ν_{CF}. Apart from this unanticipated degree of separation, there is good agreement between the calculated and observed spectra.

Hooke's Law constants for C=F$^+$ stretches can be gauged by DFT optimization of geometries in which the bond length is constrained to be slightly shorter and slightly longer (in the present case, 0.025 Å) than the equilibrium distances. These harmonic spring constants give an estimate of stiffness, and are not the same as the force constants for normal modes. The DFT spring constant for the C=F$^+$ of ion **4** has a value of 8.07 mdyne Å, which is a little more than 60% as large as the DFT spring constant for the C=O stretch of neutral acetone (12.8 mdyne Å). Ion **6** has a DFT spring constant very slightly