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Aldehyde and Ketone Adducts of the Gaseous Trifluoromethyl Cation

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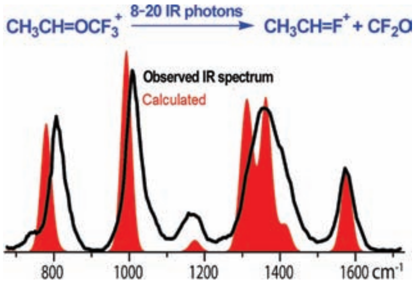
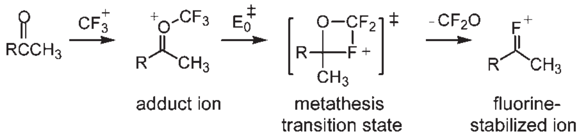
ABSTRACT



IR spectra of CF_3^+ adduct ions are reported for the first time using infrared multiple photon dissociation (IRMPD). Carbonyl stretches of ketone conjugate acids shift less than do those of ions containing $C{=}OCF_3^+$ groups. Carbonyl absorptions shift in proportion to the empirical softness of the corresponding neutrals. Anharmonic DFT fits band positions of $C{=}OCF_3^+$ stretches for aliphatic ions, but unscaled harmonic calculations match $O{-}CF_3$ stretches more closely. Calculated $O{-}CF_3$ bond orders increase with gas phase CF_3^+ affinities of the corresponding neutral carbonyl.

Recent interest in extending the scope for synthesizing fluorinated molecules has spurred exploration of reagents that donate electrophilic trifluoromethyl groups.[1] The trifluoromethyl cation (CF_3^+) represents the limit of such reactivity. The extreme Lewis acidity of the free CF_3^+ ion impedes its production in solution and has prevented its isolation in condensed media. CF_3^+ does form readily in the gas phase from electron ionization of CF_4, but its vigorous reactivity militates against the formation of Lewis acid–base adducts by direct attachment to nucleophiles.[2]

This communication describes action spectroscopy to look at vibrations of CF_3^+ adduct ions derived from simple aldehydes and ketones. Scanning the output of an IR free-electron laser[3] induces expulsion of CF_2O from gaseous adduct ions trapped in an FT-ICR (the last steps of eq 1). After excitation by a resonant photon, rapid absorption of nonresonant photons then promotes an ion to its dissociation threshold. Monitoring the wavelength dependence of fragmentation by mass spectrometry provides the IR spectrum of the parent ion.



(1)

CF_3^+ adduct ions have not previously been observed experimentally except by their *m*/*z* values in a mass spectrometer. IR multiple photon dissociation spectroscopy (IRMPD) allows an assessment of the extent to which a C═O stretch shifts as a function of the newly formed $O{-}CF_3$ bond.

As known from published experiments, CF_3^+ and other perfluorinated cations react with acetaldehyde and acetone

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(1) (a) Allen, A. E.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2010**, *132*, 4986–4987. (b) Wiehn, M. S.; Vinogradova, E. V.; Togni, A. *J. Fluorine Chem.* **2010**, *131*, 951–957. (c) Brand, J. P.; Fernandez, D.; Gonzalez, S. N.; Waser, J. *Chem. Commun.* **2011**, *47*, 102–115.

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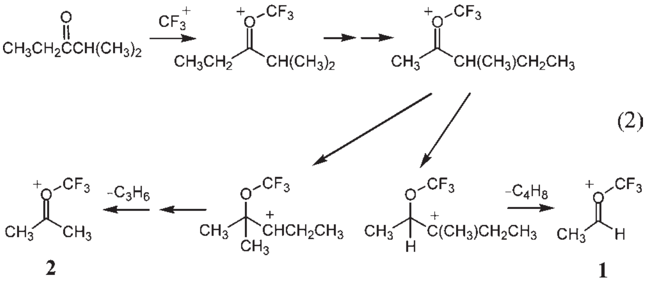
via metathesis (as eq 1 depicts)[3c,4] and do not yield simple adduct ions. The likely mechanism invokes electrophilic attack on the carbonyl oxygen. This attachment has such a high exothermicity ($\Delta H < -200$ kJ mol^{-1}) that it permits prompt access to four-membered cyclic transition states, surmounting the barrier $E_0^{\ddagger}$ and expelling carbonyl CF_2O to produce fluorine-stabilized carbocations.

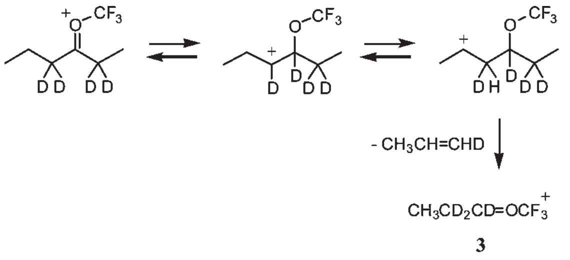


(2)

The experiments described here show that a gas-phase reaction of an aromatic ketone with CF_3^+ does yield an adduct ion as well as the fluoronium metathesis product. In contrast, as previously reported, many aliphatic ketones isomerize their carbon skeletons when CF_3^+ attaches.[5]

The ion–molecule reaction of propionaldehyde with CF_3^+ gives predominantly the rearranged metathesis product $Me_2C{=}F^+$.[4c] Aliphatic ketones larger than acetone give poor yields of fluoronium metathesis, preferring to undergo cationic rearrangements that lead to expulsion of neutral alkenes, as eq 2 illustrates.[5] The present study takes advantage of such rearrangements to produce CF_3^+ adducts of acetaldehyde, propionaldehyde, and acetone (which cannot be made by direct attachment to oxygen) and proves the distinct nature of the $C_3H_6OCF_3^+$ isomers.

In the gas phase, reaction of 2-methyl-3-pentanone with CF_3^+ leads to a sequence of cationic rearrangements by which propene or butene are expelled, creating a mixture



(3)

of the CF_3^+ adducts of acetaldehyde (**1**, *m*/*z* 113) and acetone (**2**, *m*/*z* 127), as eq 2 depicts.[5] An analogous rearrangement in the reaction of 3-hexanone-2,2,4,4-d_4 with CF_3^+ yields the adduct of propionaldehyde-1,2,2-d_3 (**3**, *m*/*z* 130), as eq 3 portrays. Deuteration in ion **3** serves to minimize any overlap with rearrangements that might produce CF_3^+ adducts of acetone. The results below show that the CF_3^+ adducts of propionaldehyde and acetone exhibit different carbonyl stretching frequencies, demonstrating that they exist as noninterconverting ions.

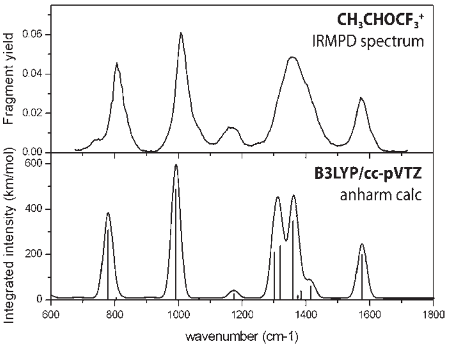


Figure 1. Comparison of the observed IRMPD spectrum of ion **1** (the CF_3^+ adduct of acetaldehyde) with the spectrum predicted by an anharmonic B3LYP/cc-pVTZ calculation using harmonic intensities (calculated peaks broadened by 30 cm^{-1}).

As Figure 1 illustrates, anharmonic DFT calculations[6] at B3LYP/cc-pVTZ match the experimentally observed band positions for the acetaldehyde adduct **1**. The highest frequency band in the figure warrants special attention, because it corresponds to the stretching mode of a C=O with CF_3^+ attached to it. While the carbonyl stretches of neutral acetaldehyde and propionaldehyde occur at 1746 cm^{-1} in the gas phase,[7] the band for the CF_3^+ adduct ion **1** has shifted 170 cm^{-1} to the red. Table 1 compares calculated frequencies with the observed band positions.

The C=O bands of other carbonyl compounds shift even more to the red upon attachment of CF_3^+. Figure 2 reproduces the IRMPD spectra of the adducts of acetone (**2**) and of propionaldehyde-1,2,2-d_3 (**3**). The adduct of propionaldehyde-d_3, **3**, moves 215 cm^{-1}, while the adduct of acetone, **2**, moves 230 cm^{-1}. These band positions agree with DFT anharmonic frequency predictions.

The most intense absorptions in both the calculated and the experimental spectra correspond to $O{-}CF_3$ stretches. These bands show the worst fits between experiment and theory. The observed bands occur at higher frequencies than anharmonic DFT predicts (e.g., 1030 cm^{-1} observed versus 997 cm^{-1} calculated for **3**). For these bands the harmonic frequencies (e.g., 1020 cm^{-1} for **3**) come closer to experiment than do the anharmonic frequencies.

Unlike aliphatic ketones, observable adduct ions form directly from attaching CF_3^+ to *p*-fluoroacetophenone. In

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Table 1. Experimental $\nu_{C=OCF_3^+}$ and ν_{OCF_3} Frequencies (cm^{-1} ±5) Compared with Anharmonic B3LYP/cc-pVTZ Values; Shifts Relative to Experimental C=O Stretches of Corresponding Neutral Carbonyl Compounds ($\nu_{C=O}$);[6] Bond Orders *n* As Described in Text; DFT Spring Constants κ for C=OCF$_3^+$ Bonds in N/m

	$\nu_{C=OCF_3}{}^+$				calcd *n*		
	calcd	obsd	shift	ν_{OCF_3} obsd	C=O	O–CF$_3$	calcd κ
$CH_3CH{=}OCF_3^+$ (**1**)	1576	1575	170	1010	1.602	0.844	931
$CH_3CD_2CD{=}OCF_3^+$ (**3**)	1522	1530	215	1030	1.576	0.873	904
$(CH_3)_2C{=}OCF_3^+$ (**2**)	1499	1500	230	1035	1.494	0.942	789
$4\text{-}FC_6H_4C(CD_3){=}OCF_3^+$ (**4**)	1364	1330	320	1075	1.311	1.087	630

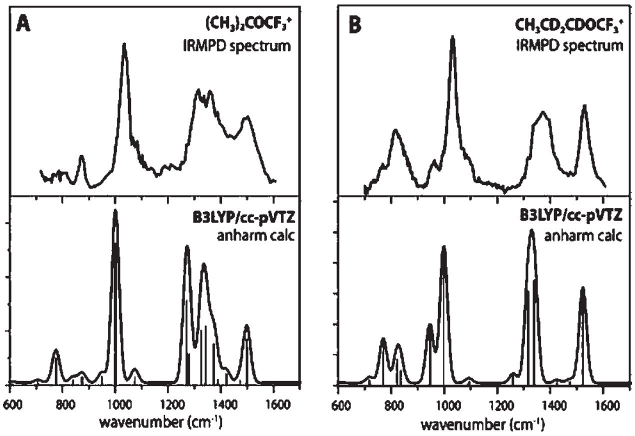

Figure 2. Comparison of the observed IRMPD spectra of ion **2** (**A**, the CF$_3^+$ adduct of acetone, *m*/*z* 127) and ion **3** (**B**, the CF$_3^+$ adduct of propionaldehyde-1,2,2-d_3, *m*/*z* 130) with the spectra predicted by anharmonic B3LYP/cc-pVTZ calculations using harmonic intensities (calculated peaks broadened by 30 cm^{-1}).

order to uncouple $\nu_{C=OCF_3}{}^+$ from other motions, the ion containing a trideuterated methyl group (**4**) was prepared, for which the carbonyl stretch clearly separates from bending vibrations of the methyl group. As Figure 3 portrays, anharmonic DFT calculations match most of the observed bands except for the very intense O–CF$_3$ stretch (1070 cm^{-1} observed versus 1047 cm^{-1} calculated for **4**) and $\nu_{C=OCF_3}{}^+$. As Table 1 summarizes, the $\nu_{C=OCF_3}{}^+$ band predicted by anharmonic DFT for **4** has an approximately 35 cm^{-1} higher frequency than seen by experiment.

A recent compendium of Lewis basicity scales[8] notes the correlations between frequency shifts in noncovalent complexes and the softness of the participating Lewis bases. O–CF$_3$ stretches couple to CH and CD motions on adjacent atoms, which stands in the way of looking at empirical relationships, but the shifts of observed C=O stretching frequencies do scale with an empirical measure of the softness of gaseous aldehydes and ketones.

Before looking at empirical relationships, predictions of theory warrant attention. As described in the literature, the theory of Atoms in Molecules (AIM) gives electron densities at bond critical points (ρ_{bcp}), from which bond orders (*n*) are

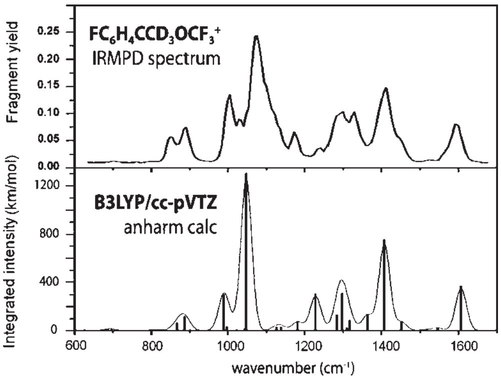

Figure 3. Comparison of the observed IRMPD spectrum of ion **4** (the CF$_3^+$ adduct of *para*-fluoroacetophenone-d_3, *m*/*z* 210) with the anharmonic B3LYP/cc-pVTZ spectrum using harmonic intensities (broadened by 30 cm^{-1}). The harmonic frequency for the O–CF$_3$ stretch (1078 cm^{-1}) gives a better fit to experiment.

gauged by the formula $n = e^{A(\rho_{bcp}-B)} - e^{-AB}$.[9] The constants *A* and *B* come from standards for single and double bonds (in this case isopropanol and acetone for carbon–oxygen bonds, which give $A = 2.09$ and $B = -0.166$). Table 1 lists representative values of *n*. The C=OCF$_3^+$ bond order for **4** is lower than that for the aliphatic ions.

As expected from the low anharmonic frequencies (relative to experiment) calculated for the O–CF$_3$ stretches, AIM underestimates bond orders for those single bonds, as the penultimate column of Table 1 lists. Nevertheless, the qualitative trend agrees with experiment: O–CF$_3$ bond order *n* increases as the C=OCF$_3^+$ stretching frequency $\nu_{C=OCF_3}{}^+$ decreases. With theoretical results compared with one another, the calculated CF$_3^+$ affinities in Table 2 give a linear plot versus O–CF$_3$ bond orders of the adduct ions.

The best known experimental enthalpy scales, H$^+$ affinity in the gas phase (proton affinity or PA) and BF$_3$

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Table 2. Proton Affinities (PA) and Experimental and Calculated Affinities for Lewis Acids (BF_3 and CF_3^+) with Selected Ketones and Aldehydes (kJ mol^{-1}); Reported Carbonyl Stretching Frequencies for BF_3 Adducts ($\nu_{C{=}OBF_3}$); and DFT Electronic Energy Barriers ($E_0^{\ddagger}$ in kJ mol^{-1}) for Fluoronium Metatheses

		BF_3 affinity				
	PA exptl[b]	exptl[c]	calcd[a,d]	$\nu_{C{=}OBF_3}$ (cm^{-1})	calcd CF_3^+ affinity[a]	calcd $E_0^{\ddagger a,e}$
$CH_3CH{=}O$	768	69.6	24.0	1663[f]	239	154
$CH_3CH_2CH{=}O$	786		25.8	1657[f]	253	158
$(CH_3)_2C{=}O$	812	76.0	27.1	1639,[g] 1624[h]	272	157
PhCH=O	834	74.9	30.9	1626[i]	318	210
4-F-PhCH=O	827	76.1	30.1	1627[i]	316	215
PhCMe=O	861	74.5	29.4	1568[j]	328	205
4-F-PhCMe=O	859		28.3		324	210

[a] Gas phase. [b] Value from webbook.nist.gov/Chemistry. [c] In CH_2Cl_2, ref 8. [d] B3LYP/cc-pVTZ (includes ZPE and counterpoise), this work. [e] B3LYP/cc-pVTZ electronic energy barrier for fluoronium metathesis, this work. [f] In CH_2Cl_2, ref 11a. [g] In CH_2Cl_2, ref 11b. [h] Solid, ref 11c. [i] In CH_2Cl_2, ref 11d. [j] In CH_2Cl_2, ref 11e.

affinity (in solution), differ from one another. As Table 2 summarizes, simple carbonyl compounds have a PA range >90 kJ mol^{-1}, while BF_3 affinities span <6 kJ mol^{-1}. Contrasts include *p*-fluorobenzaldehyde, which has a PA less than that of benzaldehyde, while its BF_3 affinity in CH_2Cl_2 is greater than that of benzaldehyde. Nor do shifts of the C=O stretch frequency ($\nu_{C{=}O} \rightarrow \nu_{C{=}OBF_3}$) scale with BF_3 affinity (cf. acetophenone vs *p*-fluorobenzaldehyde).

Owing to its high vertical ionization energy (IE), BF_3 is viewed as a hard electrophile. On the one hand, an empirical measure of electronegativity for Lewis acids, $^1/_2$(IE + EA), where EA denotes the electron affinity (or, for cations, the IE of the corresponding neutral radical), gives the ordering $CF_3^+ > CH_3^+ > BF_3$. On the other hand, empirical softness, 1/(IE − EA),[10] has a different ordering: $CF_3^+ \approx CH_3^+ > BF_3$ (see Supporting Information).

One might have anticipated that C=O stretches shift in proportion to the IE of the neutral aldehyde or ketone. As Figure 4 shows, a plot versus softness gives a better fit, with a slope of 11 000 eV cm^{-1} (1.38 eV^2). Had the *x*-axis of Figure 4 been IEs, the positions of the aliphatic compounds would remain the same, but the open circle shows where *p*-fluoroacetophenone would have fallen.

Attaching a fluorinated cation to a carbonyl group can be compared with protonation. Other workers have looked at protonated acetone in the gas phase.[12] Putting a proton on acetone weakens the carbonyl bond: $\nu_{C=OH^+}$ = 1580 cm^{-1} for $Me_2C{=}OH^+$ in the gas phase,[12] a shift of 150 cm^{-1} from the neutral ketone (anharmonic DFT predicts a shift to 1543 cm^{-1}). An experimental shift of greater magnitude (160 cm^{-1}) has been reported[13] from attachment of CHF_2^+ to CHF=O, in accord with the findings presented here.

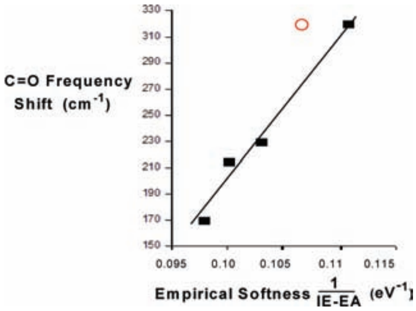

Figure 4. Shift in carbonyl stretching frequency (in cm^{-1}) as a function of the empirical softness[10] of the carbonyl compound ($[IE-EA]^{-1}$ in eV^{-1}). The open circle indicates the value for *p*-fluoroacetophenone if the *x*-axis were simply the vertical IE.

The present work has also examined the IRMPD of *O*-deuteronated *p*-fluoroacetophenone-d_3 (see Supporting Information). Theory matches the two bands with C=O stretch character (a strong band observed at 1430 cm^{-1} and a weak one at 1380 cm^{-1}). Comparing spring constants computed for $C=OH^+$ stretches with the DFT values of κ for $C{=}OCF_3^+$ stretches in Table 1 shows that protonated ketones (κ = 876 N/m for protonated acetone, κ = 730 N/m for *O*-protonated *p*-fluoroacetophenone) have stiffer C=O bonds than do the CF_3^+ adduct ions. This means that the larger shifts for the latter do not arise from differences in reduced mass. Appropriate levels of theory may provide a more detailed understanding of the correlation seen here.

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Supporting Information Available. DFT results and IRMPD of $p\text{-}FC_6H_4C(CD_3)OD^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Except where otherwise stated, IEs and EAs taken from www.webbook.nist.gov/chemistry. Chin and Harrison (*Org. Mass Spectrom.* 1969, *2*, 1073−1082) report that *p*-fluoroacetophenone has an IE only 0.04 eV higher than that of acetophenone, so the vertical IE of acetophenone (Kobayashi, T.; Nagakawa, *Bull. Soc. Jpn.* 1974, *47*, 2563−2572) is equated to that of *p*-fluoroacetophenone.