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Chemical Insights from High-Resolution X-ray Photoelectron Spectroscopy and ab Initio Theory: Propyne, Trifluoropropyne, and Ethynylsulfur Pentafluoride

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Abstract: High-resolution carbon 1s photoelectron spectroscopy of propyne ($HC{\equiv}CCH_3$) shows a spectrum in which the contributions from the three chemically inequivalent carbons are clearly resolved and marked by distinct vibrational structure. This structure is well accounted for by ab initio theory. For 3,3,3-trifluoropropyne ($HC{\equiv}CCF_3$) and ethynylsulfur pentafluoride ($HC{\equiv}CSF_5$), the ethynyl carbons show only a broad structure and have energies that differ only slightly from one another. The core-ionization energies can be qualitatively understood in terms of conventional resonance structures; the vibrational broadening for the fluorinated compounds can be understood in terms of the effects of the electronegative fluorines on the charge distribution. Combining the experimental results with gas-phase acidities and with ab initio calculations provides insights into the effects of initial-state charge distribution and final-state charge redistribution on ionization energies and acidities. In particular, these considerations make it possible to understand the apparent paradox that SF_5 and CF_3 have much larger electronegativity effects on acidity than they have on carbon 1s ionization energies.

Introduction

Over 30 years ago Siegbahn and co-workers[1] showed that inner-shell ionization energies depend on the chemical state of the atom from which the electron is ionized. The ionization energy increases with the oxidation state of the atom or with the electronegativity of the ligands attached to the atom. In addition, it is a local probe of the ability of the molecule to accept charge at a particular site. This close relationship between inner-shell ionization energies and fundamental chemical properties has led to numerous measurements of these energies. Correlations between core-ionization energies and other properties have been a rich source of insights into chemical phenomena.

Despite the successes that have been achieved, progress in the investigation of hydrocarbons has been slow. The differences in carbon 1s ionization energies in such molecules, even for chemically inequivalent atoms, are small compared to the experimental resolution that has been available until recently. A case in point is propyne, $HC{\equiv}CCH_3$, which is a prototype for the aliphatic alkynes. These reactive molecules have a rich and varied chemistry[2] and play an important role in organic synthesis. In propyne the three carbon atoms have quite different chemistry. The $HC{\equiv}$ unit is the site for electrophilic attack and is the most basic and possibly the most acidic end of the molecule. The central carbon, while susceptible to attack, is not as reactive as the $HC{\equiv}$ carbon. The CH_3 group is not highly reactive, but its acidity is only slightly different from that of the $HC{\equiv}$ group. The inner-shell photoelectron spectroscopy of this molecule provides a basis for a better understanding of its chemistry and, by extension, that of more complex molecules.

Measurements of the carbon 1s photoelectron spectrum of propyne by Cavell[3] showed only a single asymmetric peak. Although he analyzed this in terms of three components, each representing a contribution from one of the carbon atoms, Cavell expressed reservations about both the positions and the assignments of each component. It was, therefore, difficult to draw firm conclusions about the chemistry of the molecule from these measurements.

The development of high-brightness radiation sources at third-generation synchrotrons coupled with high-resolution spectrometers has allowed a striking change in the resolution of such experiments. Whereas Cavell worked with a resolution of about 1.1 eV, it is now possible to achieve an experimental resolution for carbon 1s photoelectron spectroscopy of less than 0.05 eV, or about half the natural line width (proportional to the inverse lifetime of the 1s hole). We present here the carbon 1s spectra

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of propyne, 3,3,3-trifluoropropyne, and ethynylsulfur pentafluoride ($HC\equiv CSF_5$) to illustrate the chemical information contained in such high-resolution spectra. In the propyne spectrum the contributions from the chemically inequivalent carbons are clearly resolved. Moreover, each peak in the spectrum has a distinctive pattern of vibrational structure associated with it. Comparison of these structures with those in model compounds and with predictions of ab initio electronic structure theory allows us to assign the peaks to the appropriate carbon atoms. With this information at hand, we are able to investigate the relationships between the ionization energies and the distinctive chemical properties of the different carbon atoms. The spectrum of trifluoropropyne shows not only the expected large shift in ionization energy of the carbon to which the fluorine atoms are attached but also significant modification of the positions and vibrational structure for the peaks associated with the ionization of the other two carbons. The spectrum of ethynylsulfur pentafluoride reflects the similarity of CF_3 and SF_5 as electronegative substituents. Also included are spectra of ethyne[4,5] and ethane,[6−8] which provide models for understanding the spectra of interest.

Methods

Experimental. Propyne and 3,3,3-trifluoropropyne were obtained from commercial sources. Ethynylsulfur pentafluoride was synthesized following the procedure described by Terjeson et al.[9]

The procedures for measuring the carbon 1s photoelectron spectra are the same as those we have used in other studies.[4,5,10,11] Photons of 320 and 330 eV were obtained from beamline 9.0.1 of the Advanced Light Source of the Lawrence Berkeley National Laboratory. The gas-phase photoelectron spectra were measured using a Scienta SES-200 electron spectrometer[12] (propyne and trifluoropropyne) or in a spherical-sector electrostatic analyzer (ethynylsulfur pentafluoride). The combined experimental resolution in the photoelectron spectra ranged from 45 meV for propyne and ethyne to 70 meV for the other molecules. The spectrum of CF_4 was measured simultaneously with each of the compounds of interest to provide an internal calibration; this allows us to align the spectra with a relative uncertainty of a few hundredths of an electronvolt. The carbon 1s ionization energy in CF_4 (301.898 meV[13]) provides an absolute calibration of the ionization-energy scale.

Computational. The intensity of vibrational lines in the photoelectron spectra were computed according to the Franck−Condon principle as described by Thomas et al.[6] For each site of ionization, this procedure uses the change in equilibrium geometry upon ionization, as well as the vibrational frequencies and normal modes for both initial and final states. These properties were computed from ab initio theory using the Gaussian-98[14] and MolCas-4[15] suites of programs. The procedure is implemented by a program, *g2fc*,[16] which uses the output of Gaussian-98 to calculate the changes in normal modes and the corresponding Franck−Condon factors for vibrational excitation.

In all cases, vibrational frequencies and normal modes were computed from second-order many-body perturbation theory (MP2),[17] using Dunning's correlation-consistent basis sets of triple-ζ quality, cc-pVTZ.[18] The core-ionized carbon atom was described by the carbon cc-pCVTZ set,[19] but without the core-correlating *d* function. The ionized core was represented by an effective core potential (ECP)[20] scaled to account for only one electron in the 1s shell.[21] The harmonic frequencies calculated in this way are slightly higher than the experimentally observed fundamental frequencies. In the case of ethyne, propyne and trifluoropropyne, we correct the frequencies by forming scaling factors from the ratios of observed[22] to computed ground-state frequencies and apply these to the computed frequencies of the core-ionized molecules. All scaling factors are in the range 0.95−1.00, with 0.98 being a typical value. For ethynylsulfur pentafluoride, experimental information on the fundamental frequencies is lacking, and all computed vibrational frequencies for this molecule were therefore scaled by a common factor of 0.98. Finally, in the case of propyne, the symmetric carbon−hydrogen stretching mode at the core-ionized methyl carbon atom was described using an anharmonic Morse potential, with parameters determined in our previous studies of methane.[21]

When computing structural changes upon ionization, we first applied the MP2/cc-pVTZ approach to the case of propyne. Comparison of results for methane and ethane obtained at this level with results from very accurate calculations[21,7] indicates that the MP2/cc-pVTZ method gives CH bond lengths for the core-ionized molecule that are too short by 0.2 pm. When the lengths of the methyl CH bonds in core-ionized propyne are increased by this amount, then this level of theory gives accurate vibrational profiles of the carbon 1s spectrum. For trifluoropropyne, however, the results obtained using the MP2/cc-pVTZ method are less than satisfactory. No correction factors were available for this molecule, and to resolve this situation, and also to identify where our theory fails, we have reoptimized the relevant structures at a higher level of theory. In this the core hole is explicitly included and variationally optimized,[21] and electron correlation is included in terms of configuration interaction (modified coupled pair functional, MCPF).[23] Atomic natural orbitals (ANO) were used as follows: H[3s2p], C, F[4s3p2d], and for core-ionized carbon, C*[7s5p3d].[24] The computed geometric changes provide an accurate description of the CF_3 part of the carbon 1s spectrum of trifluoroproyne; the acetylenic part of the spectrum has too little structure to serve as a test. The main flaw in

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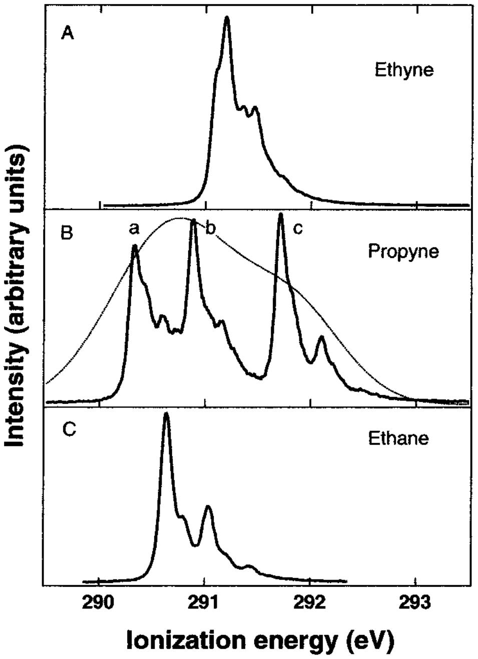

Figure 1. Experimental carbon 1s photoelectron spectra of ethyne, propyne, and ethane. The dotted curve in B shows the previously available data for propyne (ref 3).

the MP2 geometries turns out to be an exaggerated contraction of the carbon−carbon single bond, but only by 0.8 pm out of a net change of 7.2 pm. Still, an error of 11% in the bond contraction is enough to distort the spectrum significantly. Hence, our best geometries (MCPF/ANO) were used together with normal modes and frequencies from the MP2 calculation.

Shifts in vertical ionization energies as well as decomposition of ionization energies and acidities into the separate contributions from initial- and final-state effects were computed at the same level of theory as was used for the normal-mode analyses. It turns out that the computed shifts are quite sensitive to the choice of ground-state geometry, and the reported values were therefore obtained in the experimental ground-state geometries of propyne,[25] trifluropropyne,[26] and ethynylsulfur pentafluoride.[27]

Data Analysis. To model the spectra, we have assumed that each vibronic transition that appears in the spectra has a shape that results from combining the effects of the lifetime of the core hole, the resolution of the experiment, and the distortion of the spectrum that results from interaction of the photoelectron with the carbon KVV Auger electron. The instrumental resolution function is taken to be Gaussian with a full width at half-maximum of between 45 and 70 meV, as appropriate for the particular measurement. On the basis of our measurements on methane,[10] ethyne,[5] and tetrafluoromethane,[28] we have used an intrinsic width of 100 meV to account for the lifetime broadening for carbon atoms not attached to fluorine and 80 meV for carbon in the CF_3 group. The effects on the spectrum of interaction of the photoelectron and Auger electrons are modeled using the approach of van der Straten et al.[29]

Results

The spectra for the three hydrocarbons, propyne, ethyne, and ethane, are shown in Figure 1, with that of propyne in the center. Those of ethyne and ethane are above and below, to facilitate comparison. The spectra for the ethynyl groups of the fluorine-containing compounds are shown in Figure 2, with the spectrum of propyne repeated in Figure 2A for reference. Figure 3 shows the portion of the trifluoropropyne spectrum that is attributable to the CF_3 group. In Figures 2 and 3 the points represent the data, and the lines represent ab initio theoretical calculations of the vibrational structure. The calculated curves are discussed in more detail below.

Propyne. The spectrum of propyne shows three major peaks of about equal intensity, each from one of the three inequivalent carbon atoms. Each has associated with it a characteristic vibrational structure, and this structure provides an unambiguous means of assigning the peaks. For comparison, Cavell's spectrum[3] is indicated in Figure 1B by the dotted line; the additional structure that is revealed at higher resolution is striking.

Looking at the spectrum for ethane we see a pattern that arises primarily from excitation of the carbon−hydrogen stretching vibration accompanying core ionization.[6−8] The excitation of this vibration leads to the pronounced peak at an ionization energy about 400 meV greater than that of the main peak. The shoulder on the high-ionization energy side of the main peak is due to HCH bending.[6−8] Other features of this spectrum are due to additional excitations of these modes. Comparison with the spectrum of propyne shows a strong resemblance between the peak labeled "c" in propyne and that of ethane. We are therefore confident in assigning this peak to the CH_3 group in propyne. This assignment is also in accord with our theoretical calculations of both its shape (discussed below) and position (Table 1).

In ethyne, the 105-meV difference in energy between the *ungerade* and *gerade* carbon 1s orbitals[5,30] is noticeable in the spectrum, producing a shoulder on the low-ionization-energy side of the main peak and a double peak for the first vibrational satellite. This effect does not exist in propyne, where the carbons are inequivalent. On the other hand, there are contributions to the propyne spectrum from CC single-bond stretching as a shoulder on the high-ionization-energy side of the main peak; these are not present in ethyne. Allowing for these differences between ethyne and propyne, we can see that the vibrational pattern of peaks "a" and "b" are similar to what is observed for ethyne, and therefore we assign these two peaks to the acetylenic part of the molecule.

To assign the two acetylenic peaks to their respective carbon atoms we can rely on chemical intuition, theoretical calculations of the ionization energies, or theoretical calculations of the vibrational structure. We choose the last of these, since one of our goals has been to develop theoretical models that can be used to understand the vibrational structure that is apparent in X-ray photoelectron spectra of polyatomic molecules. The procedure, described in detail elsewhere,[6] provides intensities and energies for all significant vibrational excitations. Combining these with our knowledge of the instrumental resolution and intrinsic line shape, we construct the vibrational profile for each core-ionization. The three profiles for propyne are combined using least-squares fitting where the only adjustable parameters are a constant background and the overall height and position of each profile.

Figure 2A shows a comparison of the theoretical calculations (solid line) with the experimental data (circles). The calculation reproduces the essential features of the spectrum in a satisfactory

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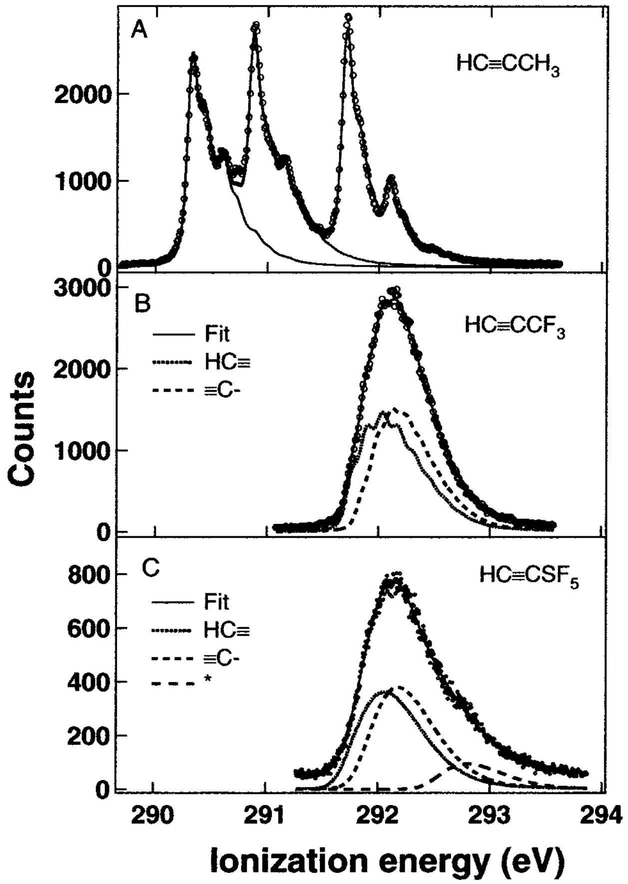


Figure 2. Carbon 1s photoelectron spectra for propyne and the ethynyl carbons in 3,3,3-trifluoropropyne and ethynylsulfur pentafluoride. The points show the experimental data, and the solid lines show the results of ab initio calculations of the vibrational profiles associated with the ionization of each carbon. In C, the line marked with an asterisk indicates the contribution of a possible impurity.

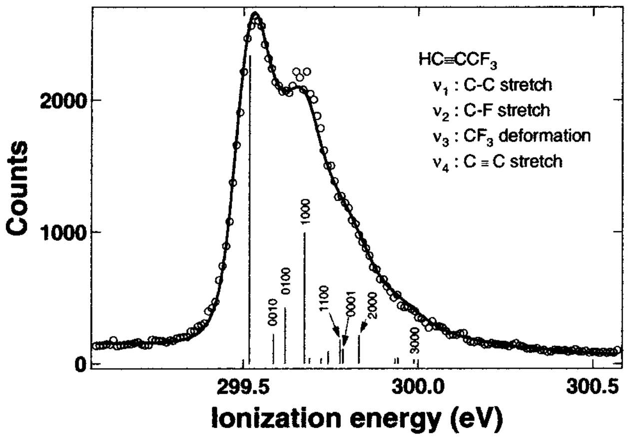


Figure 3. Carbon 1s photoelectron spectrum for the CF_3 group in 3,3,3-trifluoropropyne. The points show the experimental data, and the line shows the results of ab initio calculations of the vibrational profile. The vertical lines indicate the positions and relative intensities of the significant vibrational transitions. Each line is labeled with four vibrational quantum numbers to identify the particular modes that are excited.

way. For this fit, we have assigned peak "a" to the terminal HC≡ carbon, "b" to the central ≡C− carbon, and "c" to the $-CH_3$ carbon; the alternate choice for "a" and "b" produces a distinctly inferior fit. We can, therefore, conclude with confidence that the peaks should be assigned as indicated. This result shows the power of using good ab initio calculations in conjunction with a high-resolution spectrum to provide understanding that is not readily apparent from the data alone. It also indicates that similar calculations can be used to aid in the analysis of more complex, less resolved spectra.

3,3,3-Trifluoropropyne and Ethynylsulfur Pentafluoride. The spectrum for trifluoropropyne shows two major peaks. One, at high ionization energy, shown in Figure 3, is due to the CF_3 carbon. In keeping with the effects that are typically observed for fluorination, this peak is shifted by about 8 eV from the CH_3 peak in propyne. The solid line in Figure 3 shows the results of a theoretical calculation of the vibrational spectrum, adjusted in overall height and overall position by a least-squares fit to the data. The vertical lines show the relative intensities and positions of the main lines contributing to the spectrum. The theoretical result indicates that the major vibrational excitation involves the CC single-bond stretching mode and that there are weaker but significant contributions from CF-stretching and CCF-bending modes.

For the ethynyl carbons (Figure 2, B and C) both molecules show a single, broad, featureless peak. The two ethynyl peaks that are apparent in the propyne spectrum have both been shifted to higher ionization energies by the electronegative CF_3 and SF_5 groups. There is a greater shift for the terminal CH carbon than for the central carbon, with the result that the two peaks, which are well separated in propyne, are superimposed in the molecules with the electronegative substituents. The sharp vibrational structure seen in propyne is not apparent for these two compounds. The solid lines show the results of ab initio calculations of the vibrational structure, with the overall area and the positions for each contributing carbon adjusted by least-squares to give a best fit to the data. In these fits, the two contributing peaks are constrained to have the same area. In Figure 2, B and C, the peak with the lower ionization energy is that for ionization at the HC≡ carbon, and the peak with the higher ionization energy is that for ionization at the ≡C− carbon; the reverse ordering leads to an inferior fit for trifluoropropyne but a comparable fit for ethynylsulfur pentafluoride. Both the order shown in the figure and the magnitude of the splittings for the two molecules are in agreement with our theoretically calculated ionization energies. For ethynylsulfur pentafluoride, we were unable to fit the spectrum using only the calculated spectra. Other portions of the experimental carbon 1s spectrum as well as the sulfur 2p spectrum indicate the presence of a small impurity in the sample. As a result, we have included a third peak in this fit to represent the contribution from an impurity.

There is considerably more vibrational excitation in these molecules than in propyne. In Figure 2B each group contains more than 150 lines, whose relative intensities and positions are given by the theoretical calculations. In Figure 2C, more than 500 lines contribute to each group. For both molecules, the agreement between the observed and calculated spectra is quite good.

Ionization Energies. The fits shown in Figures 2 and 3, together with the calibration data, allow us to assign both adiabatic and vertical ionization energies to these molecules. The adiabatic ionization energy is the energy to produce the ion in its vibrational ground state. The vertical ionization energy corresponds to the ionization energy averaged over the vibrational manifold. These ionization energies, together with several others included for reference are given in Table 1. Also included in this table are the experimental and theoretical values of the vertical ionization energies relative to that of ethyne (average of $^2\Sigma_g^+$ and $^2\Sigma_u^+$).

Table 1. Carbon 1s Ionization Energies

molecule	atom	*I*, adiab. eV	*I*, vert. eV	Δ*I*, vert.[a] eV	Δ*I*, calc.[a] eV
ethyne	HC≡	291.128[b]	291.249[b]	0	0
ethane	$-CH_3$	290.545[b]	290.714[b]	−0.54	−0.52
methane	CH_4	290.689[b]	290.844[b]	−0.41	−0.41
propyne	HC≡	290.226	290.374	−0.88	−0.90
	≡C−	290.778	290.929	−0.32	−0.34
	$-CH_3$	291.610	291.755	0.51	0.52
trifluoropropyne	HC≡	291.689	292.025	0.78	0.71
	≡C−	291.789	292.144	0.89	0.79
	$-CF_3$	299.454	299.548	8.30	8.43
ethynylsulfur pentafluoride	HC≡	291.621	292.101	0.85	0.73
	≡C−	291.731	292.222	0.97	0.79

[a] Relative to ethyne (average of $^2\Sigma_g^+$ and $^2\Sigma_u^+$). [b] Reference 13.

For propyne, the vertical ionization energies are in close agreement with those reported by Cavell,[3] whereas those for trifluoropropyne are about 0.2 eV lower than those he reported. The close agreement for propyne is striking, considering the resolution of the earlier experiments.

Discussion

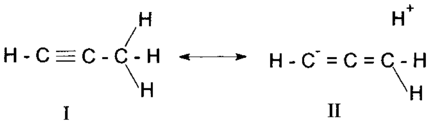
Once the peaks in the spectrum have been assigned, we turn to the chemical information that is contained in their positions and structures. We look first at the vibrational structure and then consider the vertical ionization energies.

Vibrational Structure. There is a striking contrast between the vibrational structure seen in propyne, ethane, and ethyne and that seen in trifluoropropyne and ethynylsulfur pentafluoride. In the hydrocarbons, the structure is characterized by features that are sharp within the limits set by the natural line width and the resolution, whereas in the fluoro compounds the vibrational structure is broad and featureless. This same contrast is seen in the differences between the adiabatic and vertical ionization energies, which reflect the average vibrational excitation that accompanies core ionization. For the first set of compounds these are typically about 150 meV, whereas for the second set the differences for the ethynyl carbons are about 400 meV. The immediate reason for this difference can be found in the calculated changes in equilibrium bond lengths and bond angles between the neutral and core-ionized molecules. For propyne, the typical change upon core ionization is a shrinkage of the bonds attached to the core-ionized atom, with a magnitude of 2−5 pm and a change in the CCH bond angle of 2° or less. For trifluoropropyne, on the other hand, the CC single bond *increases* in length by 6−10 pm upon core ionization of either of the ethynyl carbons; for ethynylsulfur pentafluoride, the corresponding increase is 13−15 pm. For both of these compounds, the change in CCF or CSF bond angle is 4−5°. These results suggest that core-ionization of either of the ethynyl carbons in these molecules leads to a considerable weakening of the CC single bond. Accompanying this is a softening of the potential along this coordinate and a lowering of the vibrational frequency in this mode. As a consequence, there is a large vibrational excitation spread over many levels and, correspondingly, a broad and featureless vibrational excitation pattern.

These differences can be understood in terms of the effects of the fluorines on the molecular charge distribution. Upon core ionization the valence orbitals on the core-ionized atom shrink toward the core hole, and this shrinkage is, in general, accompanied by a shortening of the bonds attached to this atom. In addition, there is a redistribution of the valence electrons to delocalize the positive charge. Thus each part of the ion can be considered to carry part of the net charge. For trifluoropropyne and ethynylsulfur pentafluoride the CF_3 and SF_5 groups are highly polar and have the positive end of their dipoles pointed toward the positively charged ethynyl group. Coulombic repulsion thus weakens the CC or CS single bonds, leading to the observed bond lengthening and pronounced vibrational structure. A similar effect is seen in the oxygen 1s ionization of CO_2, where the CO bond also lengthens upon core ionization[31] presumably for the same reason. In propyne, however, the negative end of the dipole of the CH_3 group points toward the ethynyl group, with the result that the CC single bond is strengthened by this interaction.

Ionization Energies. The agreement between the theoretical and experimental relative ionization energies for propyne is excellent, providing further confirmation of the quality of the calculations and the correctness of the peak assignments. For the hydrocarbons, the calculated shifts in ionization energy are within 0.03 eV of the experimental values. For the fluorinated compounds the discrepancies between experiment and theory are somewhat larger, as much as 0.15 eV. Despite this problem, theory and experiment agree as to the ordering of the ionization energies in trifluoropropyne.

The data for propyne show two striking results. The carbon 1s vertical ionization energy for the CH_3 group in propyne is 1.04 eV *higher* than it is in ethane, and for the CH group it is 0.88 eV *lower* than in ethyne. The simplest picture of core-ionization energy shifts is that they reflect the charge in the vicinity of the core-ionized atom. In this view, these results imply that the CH group in propyne is negative and that the CH_3 group is positive. This charge distribution can be understood in terms of two resonance structures:



I II

In II there has been transfer of electrons from the CH_3 group to the CH group. Corresponding to this charge distribution is a measured dipole moment of 0.784 D;[25] our theoretical calculations are in agreement with this and show that the direction is as indicated in II. Quantitatively, the transfer of about −0.05e from the CH_3 carbon to the CH carbon can account for both the dipole moment and the shifts in ionization energy. Thus, a small contribution from II produces a significant effect on the molecular properties.

Also contributing to the positive shift of the carbon 1s ionization energy of the CH_3 carbon in propyne relative to that in ethane is that in propyne this group is attached to an sp hybridized carbon, which is more electronegative than the sp^3 hybridized carbon in ethane. Transfer of electrons from the CH_3 group to the −C≡ carbon should be reflected in a decrease in the ionization energy for this carbon, and such a shift is seen, as indicated in Table 1. This shift is, however, only about one-third of the shift seen for the HC≡ carbon, suggesting that this effect is less important than the resonance effect. Moreover, we will see below that most of the shift for the −C≡ carbon is not due to the ground-state charge distribution but to charge rearrangement accompanying the core ionization.

For trifluoropropyne and ethynylsulfur pentafluoride, the two carbon peaks are shifted to higher ionization energy relative to

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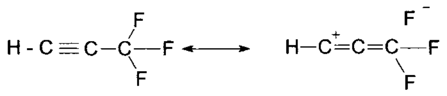
[31] (a) Clark, D. T.; Müller, J. *Chem. Phys.* **1977**, *23*, 429−436. (b) Domcke, W.; Cederbaum, L. S. *Chem. Phys.* **1977**, *25*, 189−196. (c) Kivimäki, A.; Kempgens, B.; Maier, K.; Köppe, H. M.; Piancastelli, M. N.; Neeb, M.; Bradshaw, A. M. *Phys. Rev. Lett.* **1997**, *79*, 998−1001. (d) Hahne, J. A.; Carroll, T. X.; Thomas, T. D. *Phys. Rev.* A **1998**, *57*, 4971−4973.

propyne, with the HC≡ carbon ionization energy being shifted much more than the −C≡ ionization energy. As a result, the two peaks overlap in the photoelectron spectra and can be disentangled only with the help of theory. The overall shift is expected and arises from the high electronegativity of the CF_3 and SF_5 groups. The differential shift can be understood in terms of resonance structures similar to II, but working in the opposite direction:



III IV

The ionization energies can be related to the basicity (reflected in the proton affinity) and the acidity (or deprotonation energy). Because both proton addition and core-electron removal produce a positive charge at a particular site, proton affinities and core-ionization energies are strongly correlated with one another. For protonation of oxygen and nitrogen in molecules where the sites of protonation and the geometric changes on protonation are similar, there are linear correlations with a slope of about −1.[32] These correlations have been valuable in assigning sites of protonation and in assessing the geometric changes that occur upon protonation. Until now, similar correlations have not been developed for protonation of hydrocarbons because of the difficulties of resolving closely spaced peaks in the carbon 1s photoelectron spectra. With high-resolution spectra we see the correlation in comparing propyne with ethyne. The proton affinity of propyne is 0.89 eV higher than that of ethyne,[33] and the ionization energy at the expected site of protonation, the CH carbon, is 0.88 eV less than in ethyne. (In this case, the geometric changes during protonation are not the same since the vinyl cation formed from protonating ethyne is thought to have a bridged structure.[33] However, the difference in energy between the bridged and classical structures is only about 0.2 eV.) On the basis of these numbers and the carbon 1s ionization energy of the HC≡ carbon in trifluoropropyne and ethynylsulfur pentafluoride, we can predict that the proton affinity for protonation at this carbon will be about 1 eV lower than in ethyne.

Looking at acidity, or deprotonation, we note that factors that tend to make an acidic site more negative will increase the deprotonation energy, and conversely, those that make a site more positive will decrease this energy. In propyne, as noted above, the ionization energy for the CH carbon is 0.88 eV less than in ethyne, suggesting that this carbon is more negatively charged in propyne than in ethyne. Nevertheless, the deprotonation energies of the two molecules are about the same. At the CH_3 carbon, the core-ionization energy is 1.04 eV greater than in ethane, and the gas-phase acidity is, in keeping with this, 1.6 eV less for propyne than for ethane.[22] There is an apparent contradiction in these observations. In both cases there is a shift of about 1 eV in ionization energy relative to that in an appropriate reference compound. For the CH end of the molecule, there is, however, almost no change in acidity, whereas for the CH_3 end there is a change much larger than 1 eV. Reasons for this difference are explored below.

In discussing such phenomena as core ionization, protonation, deprotonation, and electrophilic addition it has been useful to consider separately the effects of the initial-state charge distribution and the final-state redistribution of charge that occurs in response to the removal or addition of a proton or electron. Traditionally, acidities and proton affinities (basicities) have been explained in terms of the latter, often with emphasis on resonance effects.[34] In the last 15 years, however, it has become apparent that the initial-state charge distributions have a more important influence on relative acidities and basicities than has charge redistribution in the ion.[35−37] It is, therefore, of interest to assess the relative importance of these quantities in core ionization.

To a reasonable approximation, these effects can be expressed in terms of simple expressions:[35,38]

$$\Delta I = \Delta V_{\mathrm{I}} - \Delta R_{\mathrm{I}} \tag{1}$$

$$\Delta A = -\Delta V_{\mathrm{A}} - \Delta R_{\mathrm{A}} \tag{2}$$

$$\Delta P = -\Delta V_{\mathrm{P}} + \Delta R_{\mathrm{P}} \tag{3}$$

where ΔI is the difference in core-ionization energy for a given atom between one compound and another, ΔA is the difference in Brønsted acidity (deprotonation enthalpy[39]), and ΔP is the difference in proton affinity. The *V*s are the potential energies of a unit positive charge at either the nucleus from which the core electron is removed (V_{I}), the acidic proton (V_{A}), or the site of protonation (V_{P}). The *R*s represent the contribution of charge redistribution in the ion to the energy change for the process. A simplifying set of approximations is that

$$\Delta V_{\mathrm{I}} = \Delta V_{\mathrm{A}} = \Delta V_{\mathrm{P}} = \Delta V \tag{4}$$

and

$$\Delta R_{\mathrm{I}} = \Delta R_{\mathrm{A}} = \Delta R_{\mathrm{P}} = \Delta R \tag{5}$$

With these approximations, eqs 1 and 3 provide the basis for the negative correlation between core-ionization energies and proton affinities that has been mentioned above. Similarly, eqs 1 and 2 have provided a means for experimentally estimating ΔV and ΔR, since $\Delta I + \Delta A = -2\Delta R$ and $\Delta I - \Delta A = 2\Delta V$.[35,40] These quantities can also be obtained from theoretical calculations. The accuracy of our theoretically calculated values of the ionization-energy shifts indicates that this level of theory should also give reasonably accurate values of ΔV and ΔR.

For acidities the calculation of V_{A} and R_{A} presents no problems. The potential energy of the acidic proton, V_{A}, is easily calculated. Then R_{A} can be obtained from eq 2 and the

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[32] Brown, R. S.; Tse, A. *J. Am. Chem. Soc.* **1980**, *102*, 5222−5226. See also other references given in Sæthre, L. J.; Thomas. T. D.; Svensson, S. *J. Chem. Soc, Perkin Trans. 2* **1997**, 749−755.

[33] Aue, D. H. In *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; John Wiley and Sons: Chichester, 1997; pp 105−156.

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[37] (a) Solomons, T. W. G. *Organic Chemistry*, 5th ed.; John Wiley: New York, 1992; p 100. (b) Vollhardt, K. P. C.; Schore, N. E. *Organic Chemistry, Structure and Function*, 3rd ed.; Freeman: New York, 1999; p 832. (c) Jones, M. *Organic Chemistry*, 2nd ed.; Norton: New York, 2000; p 892.

[38] Davis, D. W.; Shirley, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 7898−7903.

[39] Gas-phase acidity is more conventionally defined as the Gibbs free energy of deprotonation. We have chosen to use enthalpy here, since the quantities that we are concerned with are more closely related to enthalpies than to free energies.

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Table 2. Acidities and Initial- and Final-state Contributions to Acidities from Theory

	acidity, A^a eV	ΔA eV	ΔV_A eV	ΔR_A eV
Shifts Relative to Ethyne				
ethyne, HC≡	16.38^b	0	0	0
propyne, HC≡	16.53^c	0.15	−0.39	0.24
trifluoropropyne, HC≡	15.40^b	−0.98	0.73	0.25
ethynylsulfide pentafluoride, HC≡	15.07^d	-1.31^d	0.91	0.40
Shifts Relative to Ethane				
ethane, CH_3−	18.22^b	0	0	0
propyne, CH_3−	16.58^c	−1.64	0.99	0.65

[a] ΔH_{298} for the deprotonation reaction, $RH \rightarrow R^- + H^+$ [b] Experimental value from ref 22. [c] Experimental value from ref 33. [d] Calculated using G3 methodology, ref 41.

Table 3. Initial- and Final-State Contributions to Carbon 1s Ionization Energies

molecule	atom	ΔI, vert eV	ΔV_I eV	$\Delta R_I{}^a$ eV
Relative to Ethyne				
propyne	HC≡	−0.88	−0.51	0.37
	≡C−	−0.32	−0.07	0.25
	$-CH_3$	0.51	0.62	0.11
trifluoropropyne	HC≡	0.78	0.99	0.21
	≡C−	0.89	0.91	0.02
	$-CF_3$	8.30	7.92	−0.38
ethynylsulfur pentafluoride	HC≡	0.85	1.18	0.33
	≡C−	0.97	1.16	0.19
Relative to Ethane				
propyne	$-CH_3$	1.04	1.02	−0.02

[a] $\Delta R_I = -\Delta I,\text{vert} + \Delta V_I$

Table 4. Comparison of Initial- and Final-State Contributions from Experimental Energies and from Theory

	$\Delta V_{\text{expt}}{}^a$ eV	ΔV_I eV	ΔV_A eV	$\Delta R_{\text{expt}}{}^b$ eV	ΔR_I eV	ΔR_A eV
Relative to Ethyne						
$\underline{HC}{\equiv}CCH_3$	−0.51	−0.51	−0.39	0.36	0.37	0.24
$\underline{HC}{\equiv}CCF_3$	0.88	0.99	0.73	0.10	0.21	0.25
$\underline{HC}{\equiv}CSF_5$	1.08	1.18	0.91	0.23	0.33	0.40
Relative to Ethane						
$HC{\equiv}C\underline{CH_3}$	1.34	1.02	0.99	0.30	−0.02	0.65

[a] $\Delta V_{\text{expt}} = (\Delta I,\text{vert} - \Delta A)/2$ [b] $\Delta R_{\text{expt}} = -(\Delta I,\text{vert} + \Delta A)/2$

experimental acidity.[22,33] Results obtained in this way are summarized in Table 2. (For ethynylsulfur pentafluoride no experimental value of the acidity is known. This we have calculated using the G3 method,[41] which reproduces the acidity of the other molecules within 0.07 eV (1.6 kcal/mol)).

For the core-ionization energies, the electric potential at the nucleus is only an approximation to the effect of the initial-state charge distribution on the core-ionization energy, as both the finite extent of the core orbital and valence-electron correlation need to be taken into account. Toward that end, we have developed an "extended Koopmans' theorem,"[42] which has been used to calculate the values of ΔV_I given in Table 3. From comparing results obtained at this level of theory with those calculated by a more rigorous approach[42] we estimate the uncertainty in these values to be about 0.1 eV. Values of ΔR_I, also given in this table, are obtained from the expression $\Delta I,\text{vert} = \Delta V_I - \Delta R_I$, where ΔI,vert is the experimentally measured shift in vertical ionization energy. We have chosen to use experimental values of ΔI rather than theoretical ones, because whereas the values of ΔV_I can be calculated fairly accurately from ground-state wave functions, theoretical values of ΔR_I depend on hole-state calculations of the ionization energies, which are less certain.

A comparison of values of ΔV and ΔR obtained from experiment and from theory is given in Table 4. Although the results from these different approaches differ in detail, they agree in the overall picture. For the HC≡ carbon a negative shift in potential is produced when the hydrogen in ethyne is replaced by a methyl group. A positive shift is produced by replacing the hydrogen with a CF_3 or SF_5 group, with a larger shift associated with the SF_5 group. The values of ΔR for this carbon are all positive by a few tenths of an eV relative to that for ethyne, reflecting the higher polarizability of the substituents, relative to that for hydrogen. A major disagreement is indicated in the last line of Table 4, which considers the methyl group in propyne relative to the methyl group in ethane. Here we see that the values of ΔR_I and ΔR_A differ significantly. About half of this difference arises from geometric relaxation. For most of the molecules considered here, the effect of geometric relaxation on the acidity is small and about the same for each molecule. However, the anion formed from deprotonation of the methyl group in propyne is the same as that formed by the deprotonation of allene, and there is a large change in structure from one having a single bond and a triple bond, as in I, to one having two double bonds, as in II. Despite this problem, the three methods agree that the potential at the methyl group in propyne is much more positive than in ethane.

To see an overall picture of the results of these calculations, we have plotted ΔV_A versus ΔV_I and ΔR_A versus ΔR_I in Figure 4. In both 4A and 4B, we have plotted the values for the HC≡ carbons relative to that for ethyne; in Figure 4A we have also included the values for the CH_3 carbon relative to that of ethane. The uncertainties shown for the points reflect the 0.1 eV uncertainty in the theoretical results, mentioned above. Also shown in Figure 4A is a least-squares fit of a straight line to the HC≡ points; this has a slope of 0.8. It is apparent that the values of ΔV_A and ΔV_I correlate well with one another and that eq 4 is a reasonable approximation. For ΔR, Figure 4B, the range of values is smaller than for ΔV, and the scatter in the results is more apparent. The straight line in this figure has unit slope and passes through the point for ethyne. The other data for the HC≡ group scatter around this line, indicating that eq 5 may provide a useful approximation but should be viewed with some caution for differences in ΔR of less than 0.1 eV.

For propyne, the values of ΔV indicate that the potential at the HC≡ end of the molecule is negative relative to what it is in ethyne. This effect can be attributed to resonance structure II. Similarly, the positive values of ΔR indicate that charge redistribution lowers the energy of the processes relative to that for ethyne. This effect can also be attributed to II, either enhancement of it for core ionization, or reversal of it for deprotonation. Because of the different sign of the ΔV term in eqs 1 and 2 the effects of potential and relaxation reinforce one another for core ionization and tend to cancel one another for deprotonation, leading to a large shift in ionization energy but to a small shift in acidity, as is observed. A similar effect is seen for carboxylic acids.[43] For the methyl end of propyne, the values of ΔV indicate that the principal difference in both ionization energy and acidity arises from the more positive potential at the CH_3 group in propyne relative to that in ethane.

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(42) Børve, K. J.; Thomas, T. D. *J. Electron Spectrosc. Relat. Phenom.* **2000**, 107, 155−161.

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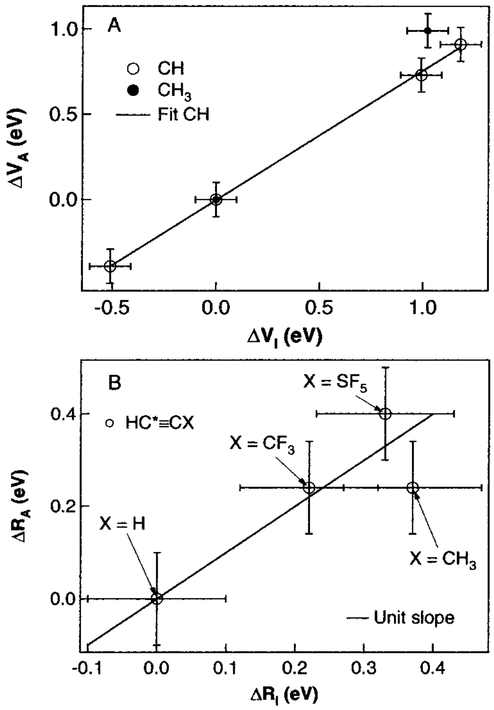

Figure 4. Correlations between theoretical values of ΔV_A and ΔV_I and between ΔR_A and ΔR_I. In A, results are shown for HC≡ relative to ethyne and for the CH_3 carbon in propyne relative to ethane. The straight line in A represents a linear fit to the HC≡ results. In B, only the HC≡ results are shown. The line has unit slope and passes through the point for ethyne.

For the −C≡ in propyne, ΔV is small, suggesting only small electron transfer between the methyl group and this carbon; most of the shift in ionization energy relative to that for ethyne is due to relaxation.

For trifluoropropyne and ethynylsulfur pentafluoride, the major influence on the core-ionization energies and the acidities is the initial-state charge distribution. However, for both of these molecules, the final-state charge redistribution plays an important role in determining the effects of the substituents. In both cases, ΔV_I and ΔR_I are positive; they tend to cancel each other in their effect on the ionization energy (eq 1) and to reinforce each other in their affect on acidity (eq 2). Both of these quantities are larger for SF_5 than for CF_3. For ionization energy, the larger ΔV_I for SF_5 is effectively canceled by the larger ΔR_I, with the result that ΔI is about the same for trifluoropropyne as it is for ethynylsulfur pentafluoride. On the other hand, the effect of SF_5 on acidity is much greater than that of CF_3, because of the larger value of both ΔV and ΔR.

Electronegativities. The pronounced shift in ionization energy of the CH_3 group in propyne relative to that for ethane reflects the electronegativity of the HC≡C group. On the basis of this shift, together with ionization energies of other CH_3X compounds, the electronegativity of this group falls between those of bromine (2.96) and iodine (2.66).[44] This is considerably smaller than the estimate (based on vibrational energies) of 3.3 for HC≡C given by Wells[45] or a value of 3.03 calculated by Bergmann and Hinze.[46] On the other hand, the average of the ionization energy and the electron affinity for this group,[22] which is the Mulliken definition of electronegativity,[46] gives an electronegativity of 2.24, and a correlation between methyl proton NMR shifts and electronegativities gives 2.5.[45]

For CF_3 and SF_5, the methods proposed by Bergmann and Hinze[46] give electronegativities of 3.36 and 3.65, respectively, both between chlorine and fluorine. This high electronegativity is reflected in the effects of both of these substituents on the carbon 1s ionization energies and the acidities of trifluoropropyne and ethynylsulfur pentafluoride. However, if we look at shifts in ionization energy for the carbon attached to these electronegative groups (0.89 eV for trifluoropropyne and 0.97 eV for ethynylsulfur pentafluoride, relative to ethyne), we find that they are much smaller than is found for a carbon atom attached to a single halogen (2.6 and 1.5 eV for fluorine and chlorine in fluoro- and chloroethene).[47] On the other hand, if we compare the acidities of trifluoropropyne and ethynylsulfur pentafluoride with those of fluoro- and chloroethyne (calculated using the G3 method[41]), we find that the effect of the single halogens (−0.2 and −0.4 eV, respectively, relative to that for ethyne) is much smaller than is seen for trifluoropropyne (−1.0 eV) and ethynylsulfur pentafluoride (−1.3 eV). Thus, one approach indicates electronegativities less than that of chlorine for these substituents and the other values greater than that of fluorine.

Measurements of the photoelectron spectra of $CF_3C{\equiv}CCF_3$ and $CF_3C{\equiv}CSF_5$ by Brant et al.[48] show a lower average carbon 1s ionization energy for the second compound than for the first. From this they concluded that the trifluoromethyl group is more electron-withdrawing than is the pentafluorosulfur group. This ordering of the carbon ionization energies is the reverse of what we have seen for trifluoropropyne and ethynylsulfur pentafluoride. However, in both cases, the differences in ionization energies are small and are influenced by relaxation energies as well as by the electron-withdrawing abilities of the substituents.

The preceding discussion illustrates the problems of relying on a single parameter such as electronegativity to describe electrical effects. We have already noted the differential influence of charge redistribution in the ion, which tends to lower the effect of an electronegative group on raising the ionization energy and to enhance its effect on decreasing the deprotonation energy. This influence is recognized by including the hardness, η, as well as the electronegativity in describing the electrical effect of a substituent,[46] or by three-[49] and four-parameter[50] descriptions of electrical effects. Qualitatively, hardness reflects the charge flow in response to a change in charge and is, therefore, closely related to the relaxation energy *R*. Specifically, the relaxation energy should be proportional to the polarizibility of the substituent, which, in turn, is expected to be proportional to the reciprocal of the hardness.[51] Thus, a small value of hardness implies a large relaxation energy. The hardness is often calculated using the principle of electronegativity equalization, and from the approach of Bergmann and Hinze,[46] we find that the values of η for CF_3 and SF_5 are considerably lower than those for fluorine and chlorine. Consequently, the effects of these substituents should be strongly modified by relaxation, as we have seen to be the case. Similar conclusions can be reached from a consideration of Charton's three-parameter treatment of electrical effects.[49]

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Conclusions and Summary

From an experimental point of view, we have seen that high-resolution inner-shell photoelectron spectroscopy provides a new level of detail in the carbon 1s photoelectron spectra of hydrocarbons and related compounds. For propyne, where only a single poorly resolved structure was seen previously, the spectrum shows clear resolution of the contributions from the three carbon atoms as well as the vibrational structure associated with each type of carbon 1s ionization. For trifluoropropyne and ethynylsulfur pentafluoride, the vibrational structure and the contributions from the chemically inequivalent carbons in the ethynyl group are not resolved. However, since the experimental resolution is quite good, we can be confident that this lack of resolution in the observed spectra is chemically significant. Ab initio calculations provide a basis for analyzing and interpreting these spectra.

Taking the core-ionization energies determined in these measurements together with experimental gas-phase acidities and theoretical calculations of the factors that influence these quantities, we are able to gain insight into the substituent effects of the methyl, ethynyl, trifluoromethyl, and pentafluorosulfur groups. In particular, the analysis shows that in the neutral molecule the ethynyl, trifluoromethyl, and pentafluorosulfur groups are strongly electron-withdrawing relative to hydrogen or methyl groups. This electron-withdrawing ability can be understood in terms of conventional resonance structures and the high electronegativity of fluorine. However, in assessing the effect of these groups upon a process such as electron or proton removal, it is also necessary to take into account both the initial-state charge distribution and the final-state charge redistribution. Moreover, the magnitude of the overall effect depends on the sign of the particle removed. For example, for core ionization, the initial-state and final-state effects may work in opposite directions, so that a substituent such as SF_5 has the initial-state influence strongly reduced by the final-state relaxation. By contrast, for acidity, the initial- and final-state effects for SF_5 are in the same direction, with the result that SF_5 has a very strong effect on acidity.

The striking difference between the sharp vibrational structure seen in propyne and the rather broad, featureless peaks seen in trifluoropropyne and ethynylsulfur pentafluoride also reflects the charge distribution in these molecules. For propyne, the intrinsic charge distribution of the methyl group leads to a relatively stable core-ionized molecule, whereas for the other two molecules, the highly polar nature of the CF_3 and SF_5 leads to considerable weakening and lengthening of the CC and CS single bonds upon core ionization, with a corresponding effect on the degree of vibrational excitation.

With high-resolution inner-shell spectroscopy and ab initio theoretical calculations, we have the possibility of probing the effect of substituents at all of the carbon atoms in a molecule. This ability holds promise for providing new insights into substituent effects.

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