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Resonant soft X-ray photofragmentation of propane

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Abstract

A comparison was made between the mass spectra of propane ($\text{CH}_3\text{CH}_2\text{CH}_3$) for resonant soft X-ray photofragmentation and for electron-impact ionization. The soft X-ray photon energy was tuned to 287.7 eV to promote Auger relaxations from the C–H bonds ($1s \rightarrow \text{C-H } \sigma^*$ transition). It was hypothesized that this would lead to proton loss without C–C chain fragmentation. Compared to traditional 70 eV electron-impact ionization, photoionization does bias the mass spectrum toward proton loss; however, residual vibrational energy in the room temperature propane leads to a non-trivial amount of C–C bond scission. The resonant soft X-ray photofragmentation is dominated by three-carbon ions between 38 and 40 u created by the loss of hydrogen while the electron-impact ionization is dominated by a major peak at 29 u corresponding to the two-carbon ion C_2H_5^+ . Within each envelope of three-, two-, or single-carbon ions the core-level photoionization spectrum showed a bias toward enhanced multiple hydrogen removal compared to the electron-stimulated spectrum.

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1. Introduction

Polyethylene and polypropylene dominate the synthetic polymer commercial market. Their dominance is spurred on by new developments in metallocene catalysts that provide an unprecedented level of synthetic control [1]. A polymer's molecular mass and molecular-mass distribution are critical in determining its performance properties. Mass spectrometry [2] is currently the most promising method for obtaining accurate molecular mass and absolute molecular mass distributions [3]. Molecular mass determination by mass spectrometry requires the

formation of intact macromolecular ions in the gas phase. This is typically accomplished by the gas-phase association of metal cations (e.g. Na^+ , K^+ , Cu^+ , Ag^+) with polar or polarizable functional groups on the polymer. Polymers that lack such functional groups (such as the polyolefins named above) have not been amenable to mass spectrometric characterization and cannot be analyzed for molecular mass distribution using existing techniques of metal cationization. Toward this end we have studied resonant soft X-ray photofragmentation [4] as an alternative method of creating intact gas-phase alkane ions, that is, ions where there may be hydrogen loss but no C–C bond rupture. The method has the advantage over matrix-assisted laser desorption/ionization (MALDI) or electrospray ionization in that no metal cation is required to charge the

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molecule. Moreover, core-level photoionization, as compared to valence-level photoionization, offers the possibility of highly-selective molecular structure measurement (e.g. branching) that is critical in the determination of synthetic polymer properties. Core-level photoionization has the advantage over valence-level photoionization [5] in that it offers the possibility of chemical or structural specificity. This is not as important for *n*-alkanes, which lack heteroatoms or a complex molecular structure, but may be useful in the case where molecular structure is more important, such as branching or with molecules cyclic structures [6–8]. To simplify the introduction of the analyte into the gas phase, we use propane as an analog to polyethylene.

The study of site-selective resonant soft X-ray photofragmentation was initiated in 1983 by Eberhardt and co-workers on carbon monoxide [9], acetone [9], and nitrogen [10]. What was most enticing about this work was their ability to fragment acetone ($(\text{CH}_3)_2\text{C}=\text{O}$) at either the C=O or C–C bonds shown by the appearance of either C^+ and O^+ ($\text{C}1s \rightarrow \pi^*$) or CH_3^+ and H^+ ($\text{C}1s \rightarrow \sigma^*$) as a function of photon energy. More recently Ibuki et al. [11] found that for oxygen and nitrogen resonant soft X-ray excitations of methyl cyanofornate ($\text{CH}_3\text{O}=\text{COC}\equiv\text{N}$) and methyl cyanoacetate ($\text{CH}_3\text{O}=\text{COCH}_2\text{C}\equiv\text{N}$) site-selective fragmentation was found in the latter molecule but not for the former. They concluded that the degree of localization of the molecular orbital that releases the Auger electron plays a critical role in determining the predominant fragmentation channel. Senba et al. [12] performed similar experiments on acetonitrile ($(\text{CH}_3)\text{C}\equiv\text{N}$) using the $\text{N}1s \rightarrow \pi^*$ transition and showed that in this case the fragmentation was *not* localized on the $\text{C}\equiv\text{N}$ bond due to the delocalized nature of the unoccupied molecular orbitals. Thomas et al. [13] studied the core excitations of carbon and oxygen for the isomers of propanol. They found that for iso-propanol neither carbon nor oxygen excitation result in localized fragmentation. However, for *n*-propanol localization was observed for the C–C bond adjacent to the oxygen. Clearly site-selective resonant soft X-ray photofragmentation has many subtle aspects that remain unexplained.

Here we explore the use of carbon resonant soft X-ray core-level excitation in propane in an effort to

create an intact molecular ion with only the loss of a hydrogen atom, that is, ions where there has been no C–C bond rupture. The ability to do this would open up a new avenue for polyolefin mass spectrometry, in particular, the determination of the molecular mass distribution of saturated hydrocarbon materials. As a guide we used the theoretical calculations of Kelber and Jennison [14] on localized Auger final states in *n*-alkanes and polyethylene (effectively an infinite length *n*-alkane). Their work indicated that the dominant feature in the Auger spectrum of alkanes is due to strongly localized states involving holes in the CH_2 and CH_3 p-like orbitals which reside predominantly on the C–H bonds, thus we chose the C–H σ^* transition. This localization effect was seen to increase with increasing chain length indicating that polyethylene should have transitions that are more local in character than gas-phase alkanes. We believe this observation can be exploited in resonant soft X-ray photoionization/photofragmentation studies and ultimately be applied to macromolecular mass spectrometry. Lastly, excitation to the C–C antibonding orbital was not chosen because it has a very low cross-section compared to the C–H antibonding cross-section (by about an order of magnitude), and because it sits above the core-level ionization threshold for propane. This last feature makes the separation of autoionization processes from direct ionization processes difficult without using coincidence counting techniques.

2. Experimental

The experiments were carried out on the U7A NIST/Dow Chemical Materials Characterization end-station at the National Synchrotron Light Source (Brookhaven National Laboratory, Upton, NY). A description of the beamline has been given elsewhere [15]. The monochromator energy resolution (≈ 150 meV) and photon energy were calibrated by comparing the transmission spectrum from gaseous carbon dioxide with electron energy-loss reference data. The photon energy was set to 287.7 eV to stimulate $1s \rightarrow \text{C-H } \sigma^*$ transitions in the propane [16]. High-purity propane was introduced to the system via an ultrahigh vacuum leak valve. From a base pressure of 1.3×10^{-5} Pa (1×10^{-7} Torr) the chamber pres-

sure was raised to 1.3×10^{-3} Pa (1×10^{-5} Torr) by the introduction of the propane. An energy-tunable photon beam with cross sectional dimensions of 2×2 mm was directed through the ion source of a bellows-mounted quadrupole mass spectrometer. Care was taken to avoid having the photon beam impact the repeller cage, the filaments, or the grid. Floating each element and checking for changes in bias away from ground potential resulting from photoemission accomplished this. Furthermore, the photon beam intensity was measured by a photodiode with and without the mass spectrometer in place to insure that the beam was not occluded. The quadrupole mass spectrometer was run alternately in high resolution and in high sensitivity modes. High resolution was used for positive peak identification; however, these scans suffered from poor signal intensity. The mass spectrometer when run in high sensitivity mode did not suffer from signal intensity problems; however, the resolution was below 1 u making peak identification difficult, thus the need to take data in both modes under otherwise identical experimental conditions. The high sensitivity mode also has the beneficial feature that it will pass all ions with (almost) equal probability [17,18]. The high-resolution mode strongly discriminates against higher mass ions making absolute intensity comparisons within a spectrum invalid. This reinforces the need for taking data in both modes.

3. Results

Shown in Fig. 1 is the high-resolution mass spectrum of propane ionized by 70 eV electrons and by resonant 287.7 eV photons. The photon-stimulated spectrum shows poor signal-to-noise due to the low detection efficiency of the quadrupole mass analyzer run in the high-resolution mode. Fig. 2 shows the corresponding normalized data. Apparent peaks at masses greater than the 44 u parent radical cation in Fig. 2 are attributed to a non-zero baseline in the original spectrum of Fig. 1. To normalize, the mass axis was coalesced into integer-mass-unit-wide bins and the signal intensity scaled to unity for the major ('base') peak. This way of displaying the data is typical for low-mass quadrupole spectra and facilitates rapid comparison between spectra as well as to

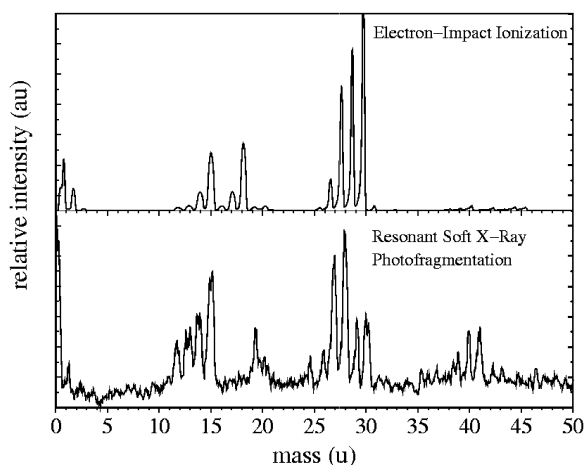


Fig. 1. Propane mass spectra obtained by using 70 eV electrons (top) and resonant 287.7 eV photons (bottom) as the ionization mechanism. Quadrupole mass selection was performed with the instrument set to its highest resolution.

spectra found in reference databases. The electron-stimulated spectrum shows dominant peaks in the range 29–25 u corresponding to $C_2H_5^+$ down to C_2H^+ . These clearly involve C–C chain scission, as does the complementary single-carbon series that ranges from 15 u down to 12 u. In the 43–39 u range are found the ions that have been dehydrogenated (lower mass peaks multiple times) but have not undergone C–C scission. It is these ions (or more

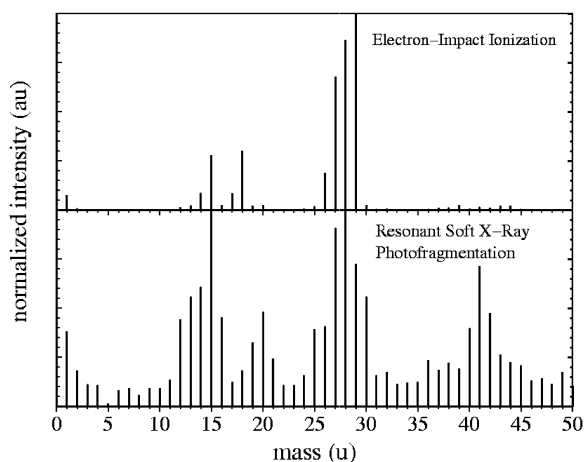


Fig. 2. The same data as shown in Fig. 1 normalized on the mass axis by coalescing the signal into integer-mass-unit-wide bins and scaling the signal intensity to unity for the major ('base') peak.

particularly their macromolecular analogs) that are most important to polyethylene molecular mass distribution measurement. Finally, the series of peaks from 18 to 16 u are for residual water in the chamber, and those at 20 and 19 u are for doubly-ionized three-carbon species ($C_3H_n^{+2}$, $n < 8$).

The high-resolution resonant photon-stimulated spectra in Figs. 1 and 2 retain the fundamental features of the electron-stimulated with the exception of the relative differences in intensity: there is an enhancement of the three-carbon singly-charged ions compared to the two-carbon and single-carbon singly-charged ions. Furthermore, within each three-, two-, or single-carbon ion cluster there is a bias toward lower mass indicative of an enhanced hydrogen loss for each ion type. In addition the intensity of the double-ionized peaks at 19 and 20 u is increased compared to the electron-stimulated ionization (Notice that there are no peaks in the 18–16 u mass range: the 287.7 eV photons are unable to ionize the residual water in the vacuum chamber, as expected).

Shown in Figs. 3 and 4 are spectra taken under the same conditions and processed in the same manner except that now the quadrupole mass spectrometer was optimized for high sensitivity rather than high resolution. In this case specific peak identification becomes difficult; however, a better accounting of

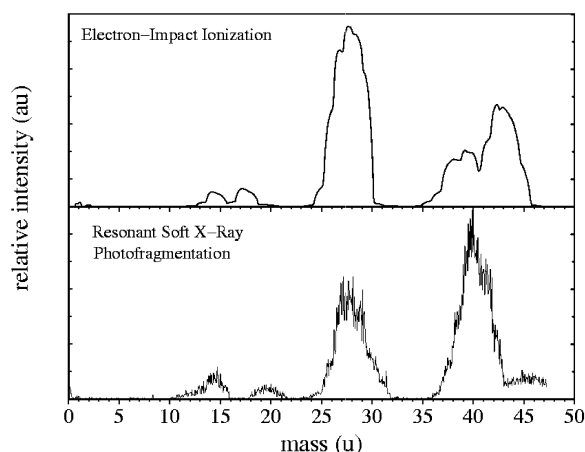


Fig. 3. Propane mass spectra obtained by using 70 eV electrons (top) and resonant 287.7 eV photons (bottom) as the ionization mechanism. Quadrupole mass selection was performed with the instrument set to its highest sensitivity.

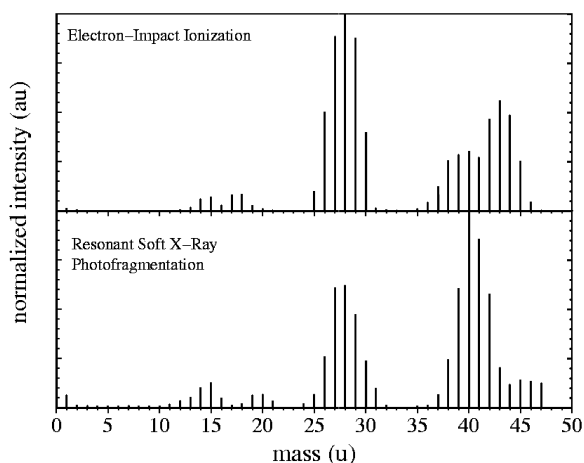


Fig. 4. The same data as shown in Fig. 3 normalized on the mass axis by coalescing the signal into integer-mass-unit-wide bins and scaling the signal intensity to unity for the major ('base') peak.

the absolute abundances of ions can be made since now the mass spectrometer will have almost equal sensitivity across its mass range. Here it becomes clear that the resonant photon-stimulated spectrum compared to the electron-stimulated spectrum is biased toward three-carbon ions at the expense of two-carbon and single-carbon ions but is not entirely devoid of the lower-mass ions. Note that in the normalized data the binning procedure yields intensity at masses where no ions are possible (e.g. 31, 45 u). This is a result of the low resolution of the spectrum and does not affect the relative intensity of three-carbon versus two-carbon and single-carbon ions since these groups of ions are widely separated in mass. Here the biasing toward hydrogen removal in the three-carbon ions is clearly seen in the resonant photon-stimulated ionization spectrum.

By integration of the raw data the ratio of three-carbon to two-carbon ions for the resonant photon-stimulated spectrum was 1.51 while for the electron-stimulated spectrum it was 0.81. This indicates a clear bias toward dehydrogenation in the resonant photon-stimulated case compared to the electron-stimulated data; nevertheless, there is clearly a significant amount of undesired C–C chain scission occurring.

It should be noted that below the ionization threshold no mass spectrum was detected in accord with the low cross sections expected for valence

level photoionization and the low intensity of second harmonic light from the synchrotron beam. The 2s valence cross section is about one order of magnitude lower, and the 2p valence cross section about two orders of magnitude lower, than the 1s (core level) cross section [19] at 287.7 eV. As for the second harmonic light, it is only 5% of the total beam intensity and its cross section is only about half that of the 1s resonant cross-section.

4. Discussion

These results can be interpreted by considering the example of Miron et al. [20] on bromochloromethane (ClCH₂Br). When they excited the either the Cl2p or Br3d core levels to just above the binding energies of the lone pairs in Cl and Br, respectively, they induced site-specific fragmentation at that atom yielding the molecular ions CH_xCl⁺ and CH_xBr⁺, respectively. The final two-hole state of the Auger process showed a ‘memory’ of the initial photoelectron state due to the localization of the lone pairs. The addition of slightly more energy to above the Cl2p and Br3d ionization thresholds elicits Cl⁺, Br⁺, and CH_x⁺ ions but no molecular ions: the site-specific nature of the fragmentation was been lost. The molecule fragments due to its internal vibrational energy according to the thermodynamic strengths of its component bonds. Finally, when they excited the C(1s)VV transition they see the same non-site-specific phenomenon: the high-energy C 1s excitation left the molecule with sufficient internal energy to fragment into atomic but not molecular ions. For propane considered in this work the localization of the C–H unoccupied orbitals is not sufficient to insure only C–H bond scission.

Next consider the work of Kukuk et al. [21] on deuteromethane. Non-resonant ejection of one carbon 1s electron at 350 eV (resulting in an Auger relaxation leaving two holes in the valence levels) produced more CD₂⁺, CD⁺, C⁺ ions than CD₃⁺ or CD₄⁺ ions. Also observed were small amounts of D⁺ and D₂⁺. The trace amount of CD₄⁺ produced comes from direct valence ionization. The fact that only a trace amount of D⁺ was observed indicates that ultra-fast decomposition of the C–D bond is a low-probability event. These observations are reflected in

the propane studied here. Even though the propane was ionized on resonance the resultant mass spectrum showed not only multiple hydrogen loss but C–C bond scission as well. The self-consistent-field calculations of Kukuk et al. [21] showed that after removal of a deuteron from the double-ionized deuteromethane (CD₄⁺²→CD₃⁺+D⁺) there remains more than 10 eV of translational and vibrational energy in the CD₃⁺ fragment. This in turn causes secondary fragmentation. Much the same must occur in the propane experiments presented here.

5. Conclusion

A comparison was made between the mass spectra of propane for resonant soft X-ray photofragmentation and electron-impact ionization. The soft X-ray photon energy was tuned to 287.7 eV to promote Auger relaxations from the 1s→C–H σ* transition. The core-level photoionization is dominated by three-carbon ions between 38 and 40 u created by the loss of hydrogen while the electron-impact ionization is dominated by a major peak at 29 u corresponding to the two-carbon ion C₂H₅⁺. Within each envelope of three-, two-, or single-carbon ions the core-level photoionization spectrum showed a bias toward enhanced multiple hydrogen removal compared to the electron-stimulated spectrum. These results can be explained by consideration of the internal vibrational energy of the room temperature propane and its ion fragments that rapidly distributes energy from the excited C–H bond throughout the molecule.

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