VOLUME 50, NUMBER 14 PHYSICAL REVIEW LETTERS 4 APRIL 1983

Site-Specific Fragmentation of Small Molecules Following Soft-X-Ray Excitation

W. Eberhardt[(a)]
Physics Department, Brookhaven National Laboratory, Upton, New York 11973

and

T. K. Sham and R. Carr
Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973

and

S. Krummacher
State University of New York at Stony Brook, Stony Brook, New York 11794

and

M. Strongin, S. L. Weng, and D. Wesner
Physics Department, Brookhaven National Laboratory, Upton, New York 11973

(Received 28 January 1983)

Soft–x-ray excitation involving C 1*s* electrons in CO and acetone, $(CH_3)_2CO$, is found to result in ionic fragmentation of the original molecule. The fragmentation pattern changes whether the C 1*s* electron gets ionized or excited into a Rydberg-line orbital or into an antibonding π^* molecular orbital. Moreover, the fragmentation occurs specifically around the site of the carbon atom where the optical excitation takes place. Based on these observations one might consider the use of tunable soft x rays to stimulate chemical reactions or to selectively break large organic molecules.

PACS numbers: 33.80.-b, 33.90.+h, 82.50.-m

Valence excitations by ultraviolet absorption in small molecules and the subsequent fragmentation has been studied extensively. Very little is known, however, about the processes following core (C 1*s*) excitations in these molecules. Carlson and Krause[1] have shown for a variety of small molecules that core ionization by x-ray line sources results in an abundance of ionic fragments. In light elements like C, N, and O a core hole created in the initial photoabsorption process decays preferentially via an Auger *KLL* transition rather than by x-ray emission, resulting in a highly charged molecule that is unstable and falls apart in a Coulombic explosion. In addition to these x-ray line studies well above threshold only *e*, (*e* + ion) coincidence data have been published dealing with the fragmentation of a few small molecules at several discrete electron energy losses around the C and N 1*s* edges.[2-4]

We here report the first studies of these fragmentation processes using continuously variable synchrotron radiation. We find that in the region of the C 1*s* absorption threshold organic molecules decompose into ionic fragments not only after direct core ionization but also following core to bound state (π^* or Rydberg) transitions. The fragmentation pattern, however, changes completely between these various types of excitation or ionization. Our data also demonstrate the even more important fact that in larger molecules like acetone $[(CH_3)_2CO]$ site-specific core to π^* excitations cause a break in the molecular structure at the site where the optical excitation occurred. Both the site-specific behavior and the modulation with photon energy of the fragmentation process could become important for a new area of x-ray–induced chemical reactions.

The experiments were performed at the uv ring of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory with use of a plane grating monochromator (PGM) described elsewhere.[5] The optical resolution in our experiments was about 1.3 eV at 290 eV as determined from the absorption spectra of molecules containing carbon atoms. The absorption spectra were taken by measuring the total ion current in an ionization chamber identical in design to the one used previously in similar experiments.[6] The ion chamber was operated in the proportional region such that the measured ion current was proportional to the number of photons absorbed in the gas. The light entered through a glass capillary array[7] with an optical transmission of 50% which has a gas leak rate of about 10^{-2} L/sec. With a 2000-L/sec pumping speed on the high-vacuum side of the array we achieved a pressure differential of 10^{-5}. This differential pumping stage was followed by a second aperture, again differentially pumped, and the exit slit of the monochromator which also is designed for differential pumping. No change in the total or partial pressure of the monochromator was observed in the course of these experiments.

At the end of the ion chamber the photon beam passed through the ionization region of a UTI 100 C mass spectrometer which was mounted with its axis perpendicular to the photon beam. For these experiments the filaments of the ion source were switched off while all grid voltages and the rf were operating. Since rather high-kinetic-energy fragments are produced in the Coulombic explosion we checked the collection efficiency by varying the grid and accelerating voltages in the ion source. No dramatic changes were found, however, so that we settled for one set of voltage parameters for all experiments. By increasing the high voltage on the multiplier we were able to actually count the individual ions rather than measure an amplified ion current.

Figure 1, curve *a* shows the absorption of CO as a function of photon energy in the region of the C 1*s* absorption threshold. We actually measured the total ion yield using the ion chamber. The first strong peak at 287.3 eV is due to the C 1*s* $\to \pi^*$ transition as reported earlier in electron energy-loss studies.[8,9] We used this peak to calibrate the energy of our monochromator. The weak structure at 293 eV corresponds to an excitation from the C 1*s* into a Rydberg-like orbital, presumably 3*p*.[8,9] The ionization energy for the C 1*s* electron is indicated in Fig. 1, curve *a* at 296.1 eV.[8-10]

Curves *b* through *g* in Fig. 1 show the yield of all possible single- and double-charge ionic fragments of CO versus excitation energy measured with the UTI mass spectrometer. The actual count rate was between 0.1 and 300 counts/sec depending on the various species and the current in the storage ring. All curves are normalized with respect to the monochromator output which was independently determined with use of Xe as probe in the ion chamber. Xe has a very slowly varying structureless cross section over the region of interest (270–310 eV).

All curves show a more or less developed peak at the C $1s \to 2\pi^*$ resonance. The relative strength of this peak varies for the different ionic species indicating changes in the branching ratio for ionic fragmentation. For example, at the π^* resonance 65% of all ions produced are C^+, whereas at 310-eV excitation energy, above the ionization limit for C 1*s* electrons, only 23% of all ions are C^+. Table I summarizes these branching ratios in greater detail. In this table the ion intensities have been normalized to 100 at 280 eV. We assume the transmission of the detector to be independent of the kinetic energy of the fragment since we observed no relative changes upon varying the potentials in the ionization region. Our data agree reasonably well with the electron-ion coincidence data at 280 eV.[3] The only real dis-

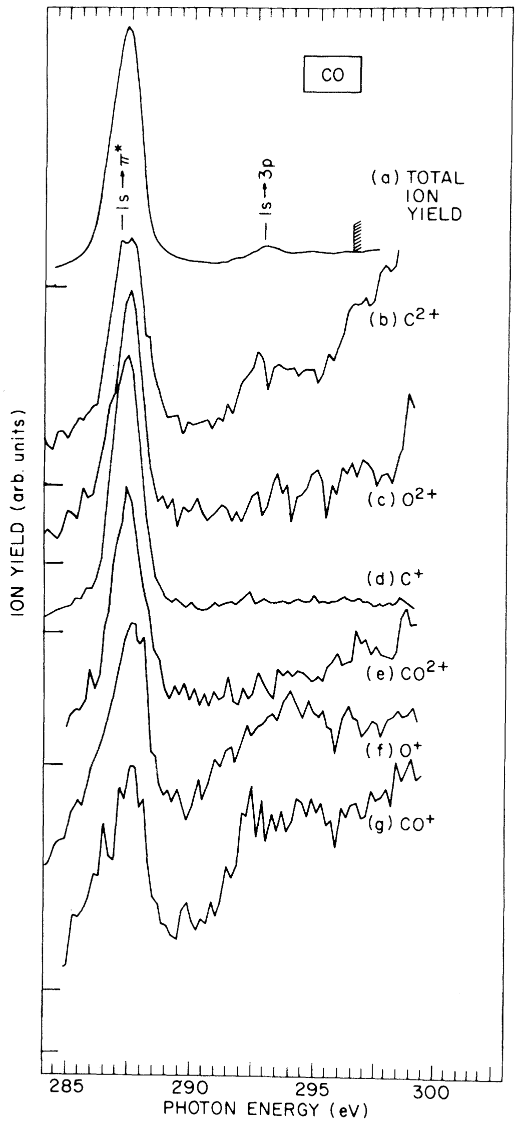

FIG. 1. Optical absorption (total ion yield) and fragment ion yields for CO in the energy region of the C 1s absorption threshold. The zero of each curve is indicated by a tick mark on the vertical scale and the relative intensities are summarized in Table I.

TABLE I. Relative ionic fragments of CO.

Ion	280 eV	287.3 eV ($C\,1s \rightarrow 2\pi^*$)	293 eV ($C\,1s \rightarrow 3p$)	310 eV	280 eV e^-, ion Ref. 3	Ion energy (eV) Ref. 3
C^{2+}	0.3	1.35	1.3	1.6	2	8
O^{2+}	0.1	0.85	0.3	0.8	1	16
C^+	19.7	255.0	27.9	31.6	22	8
CO^{2+}	1.1	7.4	3.3	4.2	2	thermal
O^+	7.0	15.3	11.7	12.2	26	6
CO^+	71.8	110.6	106.7	86.2	46	thermal
Sum	100	390.5	151.2	136.6	99	

agreement is in the ratio of O^+ and CO^+. We have no explanation for this discrepancy but want to note here that it cannot be related to the kinetic energy of the fragments as seen from the tabulated ion energies.

We can explain the strong variation in the ion production rate with excitation energy by studying the Auger decay of the C 1s core hole in CO. Moddeman *et al.*[11] have compared electron- and x-ray–excited Auger spectra and thus implicitly provide the Auger spectrum that follows from the decay of the $C\,1s \rightarrow 2\pi^*$ bound-state excitation. From Moddeman *et al.*[11] we find that the $2\pi^*$ excitation decays predominantly (49%) into the $5\sigma^{-1}1\pi^{-1}2\pi$ two-hole, one-electron, final-state configuration. 42% of the excited molecules end up in single-hole configurations ($5\sigma^{-1}$, $1\pi^{-1}$, or $4\sigma^{-1}$) whereas 9% finish in the $4\sigma^{-1}1\pi^{-1}2\pi$ configuration. This determination does not include the fraction of $3\sigma^{-1}$ and excited states of this configuration because these Auger lines overlap energetically with Auger lines following C 1s ionization and therefore their intensity is as yet unknown.

From the low-energy (10–60 eV) fragmentation studies of CO by Wight, van der Wiel, and Brion[12] we know that single-valence-hole configurations do not result in bond breaking whereas the $5\sigma^{-1}$-$1\pi^{-1}2\pi$ state decays exclusively into $C^+ + O$. The $4\sigma^{-1}1\pi^{-1}2\pi$ configuration decays into $C^+ + O$ and $C + O^+$ at the ratio of 54% to 46%. Combining all these numbers we expect the $C\,1s \rightarrow 2\pi^*$ excitation to produce C^+ and O^+ fragments in the ratio of 13:1. The experimentally observed ratio of 16.6:1 is not too far off from this crude estimate. On the other hand the previous electron energy-loss studies[3] find a ratio of 2:1 for these two fragments at the same excitation energy.

The same kind of analysis of the Auger spectrum following C 1s ionization finds the molecule predominantly in two-hole final states[11,13] ($5\sigma^{-1}$-$1\pi^{-1}$, $4\sigma^{-1}5\sigma^{-1}$, and $5\sigma^{-2}$). All three of these states are energetically high enough to lead to the simultaneous production of C^+ and O^+.[13,14] Whether they actually decay into the ionic fragments or remain stable as CO^{2+} depends on the actual shape of the potentials and possible potential curve crossings and is as yet not exactly determined. Because of these energetics and since after C 1s ionization there seem to be more Auger channels leading to $3\sigma^{-1}$ single- and multiple-hole state configurations, we conclude only qualitatively that the relative ratio between C^+ and O^+ should change in favor of O^+ as it does indeed according to the results listed in Table I. Clearly we need to study the ions produced in coincidence with Auger electrons to draw more quantitative conclusions.

Comparing gas-phase fragmentation with photon-stimulated desorption from surfaces[15] we might in the future be able to shed light on the important question of reneutralization, which is responsible for the low ion yields in the latter experiments.

Figure 2 shows the results of our fragmentation study of acetone [$(CH_3)_2CO$], a molecule containing inequivalent C atoms. The ionization threshold for the two different C atoms is indicated in Fig. 2, curve a. Only the carbon atom in the CO group gives rise to the π^* excitation observed at 288.5 eV. C atoms in saturated hydrocarbons do not display a π^* resonance in the core absorption.[6] Analogously we also expect the C atoms in the CH_3 groups of acetone to show only optical absorption for C 1s to Rydberg transitions which are generally one order of magnitude weaker than π^* excitations.[6] The most important conclusion

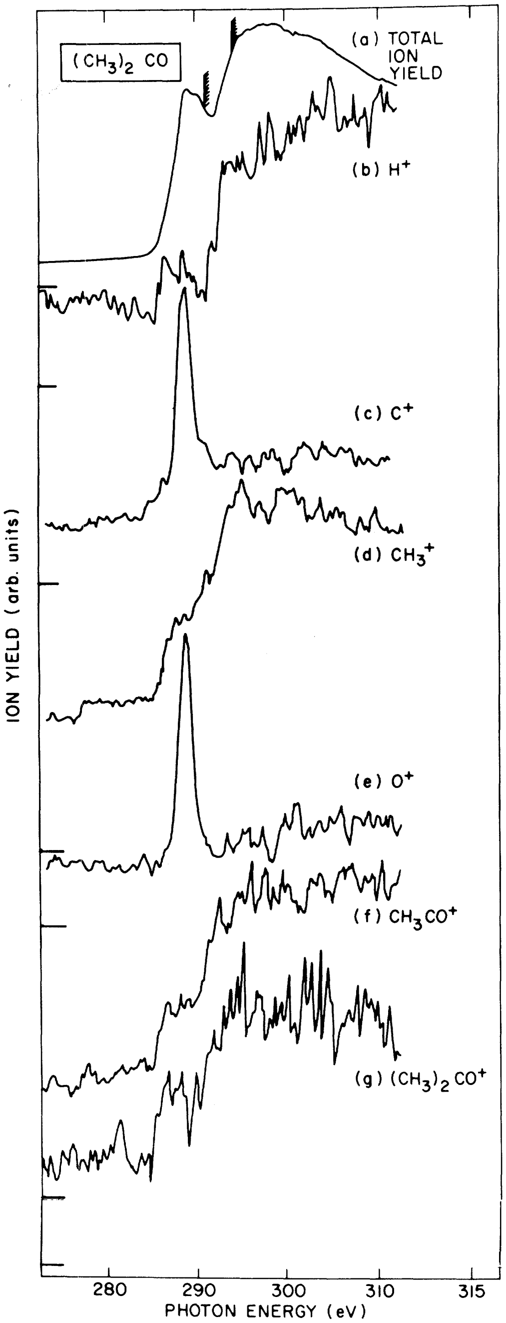

FIG. 2. Total ion yield and fragment ion yields of acetone around the C 1*s* absorption threshold. The zero of each curve is indicated by tick marks on the vertical scale. The ionization limit according to Ref. 10 for the two inequivalent C atoms is indicated on top of curve *a*.

drawn from the presence of the π^* resonance in the C^+ and O^+ yields but not in CH_3^+ or H^+ is that the π^* excitation causes the molecule to break locally around the CO group, producing C^+ and O^+ and presumably neutral CH_3 groups. This effect that the molecule breaks locally around the site of the carbon atom where the initial optical excitation took place might turn out to be very useful in the future. We foresee the use of tunable soft x rays as scalpel-like tools to break large organic molecules around certain selectable atoms (C, N, or O) within the molecule.

This work was performed at the uv ring of the NSLS. This work was supported in part by the Division of Materials Science and the Office of Basic Energy Science, U. S. Department of Energy, under Contract No. DE-AC02-76CH00016.

(a)Permanent address: Exxon Corporate Research Laboratory, P. O. Box 45, Linden, N.J. 07036.

[1] T. A. Carlson and M. O. Krause, J. Chem. Phys. 56, 3206 (1972).

[2] M. J. van der Wiel, Th. M. El-Sherbini, and C. E. Brion, Chem. Phys. Lett. 7, 161 (1970).

[3] R. B. Kay, P. E. van der Leeuw, and M. J. van der Wiel, J. Phys. B 10, 2521 (1977).

[4] A. P. Hitchcock, C. E. Brion, and M. J. van der Wiel, Chem. Phys. Lett. 66, 213 (1979).

[5] M. Howells, to be published.

[6] W. Eberhardt, R. P. Haelbich, M. Iwan, E. E. Koch, and C. Kunz, Chem. Phys. Lett. 40, 180 (1976).

[7] Galileo Electro Optics Corp., Sturbridge, Mass.

[8] M. Tronc, G. C. King, and F. H. Read, J. Phys. B 12, 137 (1979).

[9] A. P. Hitchcock and C. E. Brion, J. Electron. Spectrosc. 18, 1 (1980).

[10] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hedan, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969).

[11] W. E. Moddeman, T. A. Carlson, M. O. Krause, B. P. Pullen, W. E. Bull, and G. K. Schweitzer, J. Chem. Phys. 55, 2371 (1971).

[12] C. R. Wight, M. J. van der Wiel, and C. E. Brion, J. Phys. B 9, 675 (1976).

[13] H. Ågren and H. Siegbahn, Chem. Phys. Lett. 72, 498 (1980).

[14] D. E. Ramaker, to be published.

[15] R. Jaeger, J. Stöhr, R. Treichler, and K. Baberschke, Phys. Rev. Lett. 47, 1300 (1981).