Can super-excited molecules survive fragmentation?

A. Nath,* M. J. Prushan, J. G. Gilbert

Chemistry Department, Drexel University, Philadelphia, PA 19104, USA

An Auger event triggered by electron-capture (EC) decay of ^{57}Co incorporated in a chelate molecule results in the loss of an average of 5 electrons. During subsequent charge neutralization, the molecule acquires >50 eV of excitation energy. Only molecules having a large π-electron system were found to escape fragmentation. The fate of the molecule was followed by the 14.4 keV Mössbauer emission which occurs 10^{-7} second after the EC event. For a conjugated molecule to survive fragmentation, it should be able to disperse its energy in a time interval shorter than the period of atomic vibrations. We had proposed earlier that p-electrons undergo collective excitation and that the plasmon decays in $<10^{-14}$ second accompanied by ejection of an electron leaving the molecule unscathed. Intermolecular energy transfer is not important and even an isolated molecule of ^{57}Co(II) phthalocyanine encapsulated in a zeolite supercage escapes fragmentation following an Auger event. Our model for rapid disposal of large excitation energy receives additional support from recent reports of single or mulitphoton plasmon excitation (~20 eV) in an isolated C_{60} and C_{70} fullerene molecule followed by ejection of a single energetic electron leaving the molecule intact.

One can deposit several tens of electron volt energy on a molecule either by an intense laser beam or by charge neutralization of a highly ionized molecule. A highly charged molecule can be obtained via an Auger event. Auger ionization in an atom can be triggered by the creation of a hole in the core shell. The hole can be created through radioactive decay, for instance by orbital electron-capture where the nucleus absorbs an electron most probably from the K-shell, or by internal conversion of a gamma-ray during isomeric transition in a nucleus. An electron from a less tightly bound shell hops in to fill the core vacancy, while the excess energy goes to eject another electron. These two vacancies are in turn filled by electrons from the next outer shell or sub-shell. Thus the vacancy cascade traverses to the valence shell, resulting in a multiply charged ion; the atom having lost several electrons (Fig. 1). The multiply charged ion is rapidly neutralized by transfer of electrons from neighboring atoms in the molecule. The positive charges are driven to the extremities of the molecule due to electrostatic repulsion. This redistribution of charges occurs within 10^{-16} to 10^{-15} second and hence without any change in the relative positions of the individual constituent nuclei. In the gas phase, a Coulombic explosion follows with formation of several positive ions with high kinetic energy (Fig. 2). For instance, mass spectrometric studies of the internal transition of the isomeric decay of ^{80m}Br in CCl_3^{80m}Br results in formation of Br, Cl, and C cations with maximum charges of +13, +7 and +3, respectively.[1] Coulomb explosion has also been exploited for obtaining geometrical images of small molecules.[2] The large Coulomb repulsion of the nuclei within molecules

rapidly stripped of their electrons make them move in directions determined by the stereochemistry. For bigger molecules, the Coulomb explosion model should be used with caution.

However, in solids, the situation is more complicated. Emission Mössbauer studies of Auger after-effects in cobalt complexes indicate that all compounds, except those having a high degree of conjugation i.e., molecules with a large number of delocalized π-electrons, undergo fragmentation.[3,4] The electron-capture decay of a ^{57}Co atom triggers, an Auger event resulting in the loss of 4–6 electrons from the molecule in which it is incorporated. The 14.4 keV Mössbauer emission conveys information regarding the chemical form(s) in which the daughter ^{57}Fe is stabilized within 10^{-7} second following the electron-capture. Fragmentation of a molecule was identified by the detection of degraded ionic species ^{57}Fe^{2+} and ^{57}Fe^{3+} in the emission Mössbauer spectra. If the emission spectrum corresponds to that of the parent complex, then that indicates that the molecules have escaped fragmentation. The question arises as to how does the Auger event lead to fragmentation of a molecule in the solid state? First, a few soft electrons are emitted during the Auger ionization, some of their energy can be deposited in the parent molecule leading to partial degradation of the molecule.[5] Second, the parent molecule can undergo Coulombic explosion if one assumes that the rate of flow of electrons from neighboring molecules to the highly charged parent molecule is not fast enough. It is rather unlikely; however Coulombic fragmentation of small molecules or rupture of a single bond connecting the highly charged atom to the rest of the molecule cannot be ruled out.[3,6]

* E-mail: amar.nath@drexel.edu

The possible role of Coulombic explosion has also been considered for latent track formation induced by heavy-ions in dielectric solids.[7,8] Third, and most importantly, rapid charge neutralization occurs when electrons from neighboring molecules including some of the soft electrons produced by Auger electrons floating nearby flow to the highly charged parent molecule. During charge neutralization, a very large amount of electronic excitation energy (>50 eV) is deposited on the molecule (Fig. 3). Most of them succumb to this super-excitation and fragment. However, we find surprisingly that molecules possessing large number of delocalized π-electrons like $^{57}Co(II)$ phthalocyanine, vitamin B_{12}, and $^{57}Co(III)(phen)_3(ClO_4)_3$ survive and do not fragment. One should be surprised not because a large number of complexes undergo fragmentation but because some complexes having a high degree of conjugation do not. They apparently have at their disposal a special mechanism whereby large amounts of energy is dissipated very rapidly ($<10^{-14}$ s) and efficiently from the epicenter, and the molecule remains unscathed. The conventional mode by which a large molecule in a solid can lose its energy is via radiationless transitions, whereby the electronic excitation energy is degraded into vibrational energy, and lost as heat to the surrounding molecules. A molecule with tens of eV energy would take longer than 10^{-12} second to dispose off its energy via this mode. To eliminate possible Förster type mechanisms involving rapid intermolecular energy transfer, it is desirable to look at the Auger after-effects in "matrix isolated molecules". In hemoglobin, each of the four sub-units contain a heme which is completely surrounded by peptide chain making only loose contacts with the former. Mössbauer spectrum of hemoglobin with heme ring incorporating ^{57}Co instead of Fe, showed no signs of fragmentation.[9] Similarly, $^{57}Co(II)$ phthalocyanine encapsulated in a supercage of zeolite-Y showed the same spectrum as that observed for the iron analog in absorption Mössbauer spectroscopy.[10] In short, even a single isolated molecule if protected by delocalized electrons can survive fragmentation. We proposed[4,6] that during charge neutralization following an Auger event, the loosely bound π-electrons can undergo collective excitation and then the plasmon can decay losing all its energy to a single electron which is ejected. The decay time of a plasmon is less than 10^{-14} second.[11] The huge amount of electronic excitation energy can thus be disposed off in a neat fashion leaving the molecule intact. The proposed mechanism receives strong support from the recent photoemission studies of C_{60} and C_{70}.[12,13] The photo-ion yield is dominated by a strong resonance at about 20 eV. The results have been interpreted as collective excitation of π-electrons either by a single or a high intensity multi-photon process. The

plasmon is strongly coupled to single electron continuum states, and the plasmon decay is associated with an ejection of an electron which overshadows the direct photoionization process. We submit that the strong coupling is not confined to C_{60} and C_{70} as alluded by the authors, but all molecules with a large number of delocalized electrons would exhibit this novel mode of self-protection.
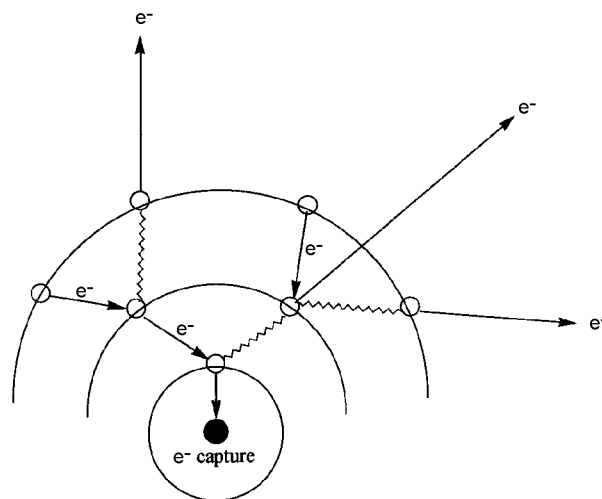

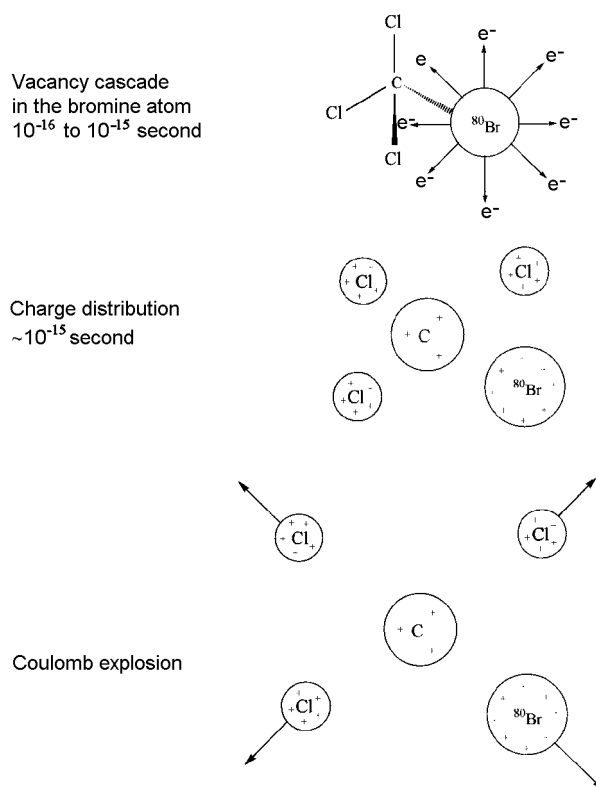Fig. 1. Auger cascade following electron-capture decay

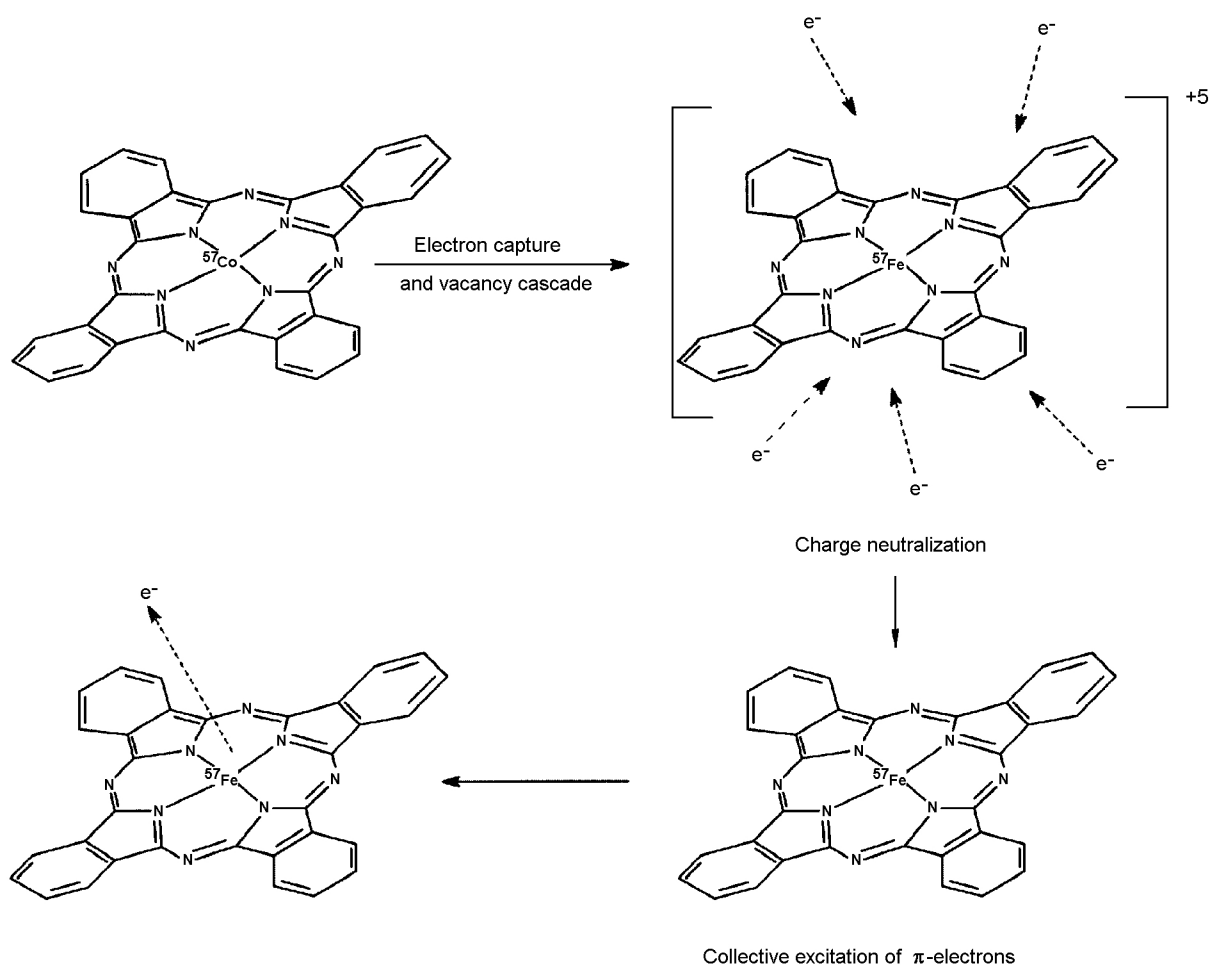Fig. 2. Coulomb explosion of gaseous $CCl_3{}^{80m}Br$

Fig. 3. Collective excitation of π-electrons following charge neutralization of multiply ionized ^{57}Co phthalocyanine as a result of Auger event

References

1. S. WEXLER, Science, 156 (1967) 901.
2. Z. VAGER, R. NAAMAN, E. P. KANTER, Science, 244 (1989) 426.
3. A. NATH, M. P. KLEIN, W. KÜNDIG, D. LICHTENSTEIN, Radiat. Effects, 2 (1970) 211.
4. M. B. MISROCH, C. J. SCHRAMM, A. NATH, J. Chem. Phys., 65 (1976) 1982.
5. A. HALPERN, in: Handbook of Hot Atom Chemistry, T. MATSUURA (Ed.), Kodansha Publ., Tokyo, 1992.
6. A. NATH, Ch. SAUER, A. HALPERN, J. Chem. Phys., 78 (1983) 5125.
7. T. A. TOMBRELLO, Intern. J. Mass Spectrom. Ion Process, 126 (1993) 11.

8. D. A. YOUNG, Radiat. Measur., 27 (1997) 575.
9. T. S. SRIVASTAVA, S. TYAGI, A. NATH, Proc. Natl. Acad. Sci. USA, 74 (1977) 4996.
10. A. NATH, C. HEANEY, J. STELMACH, S. NAGY, unpublished result.
11. W. BRANDT, R. H. RITCHIE, in: Proc. Conf. Physical Mechanism in Radiation Biology, 1974, R. D. COOPER, R. W. WOOD (Eds), Technical Information Center, US. AEC, 1974, p. 20.
12. I. V. HERTEL, H. STEGER, J. DE VRIES, B. WEISSER, C. MENZEL, B. KAMKE, W. KAMKE, Phys. Rev. Lett., 68 (1992) 784.
13. S. HUNSCHE, T. STARCZEWSKI, A. l' HUILLIER, A. PERSSON, C.-G. WAHLSTRÖM, B. VAN LINDEN VAN DEN HEUVELL, S. SVANBERG, Phys. Rev. Lett., 77 (1996) 1966.