Electronic Decay

DOI: 10.1002/anie.201004446

Using pH Value To Control Intermolecular Electronic Decay**

Nikolai V. Kryzhevoi and Lorenz S. Cederbaum**

The way in which an ionized, isolated molecule releases its stress depends on the vacancy created. Having lost an outer-valence electron, the molecule changes its geometry to adjust to a new charge distribution. If a deeper, inner-valence electron is removed, the system may also relax through emitting a photon. Ionization of a core electron is usually followed by fast Auger decay. The presence of a chemical environment around the ionized system modifies these relaxation processes. Particularly large changes may occur after ionization from an inner-valence shell when a relaxation pathway much faster than photon emission may become operative, namely intermolecular Coulombic decay (ICD).[1] ICD is an electronic decay in which the energy released upon refilling the initial inner-valence vacancy by an outer-valence electron from the same molecule is transferred efficiently, typically on a femtosecond [10^{-15} s] timescale, to the surrounding environment causing its ionization (see Figure 1). Because of its intermolecular character, ICD represents a very sensitive tool to probe the environment.[2,3] Controllability through environmental changes can make this process even more valuable. The ability to enhance ICD in a controlled manner, to quench competing mechanisms, or to reduce it and even switch it off on demand to avoid possible negative consequences might be of great importance, especially in chemical and biological processes. For example, as a process feasible in water,[4] ICD brings a certain threat for hydrated substances, specifically for biomolecules, which can be damaged by low-energy electrons or water radical cations produced in this electronic decay[5–7] so that a regulation of ICD could be essential in this case. Herein we show that protonation or deprotonation of the system under study exerts a profound impact on ICD and suggest changes in the environmental pH value as an appropriate means to control this decay process.

We consider ammonia dimers and trimers as well as their protonated and deprotonated counterparts as proof-of-principle systems. The convenience of such small clusters is that the effect of protons is sharply defined. The trimers give valuable insight into how electronic decay pathways change with increasing cluster size. Furthermore, the trimers can be considered as prototype systems in which a solute molecule has normal and protonated/deprotonated solvent molecules simultaneously in its neighborhood. What also counts is that dimers and trimers allow for an accurate theoretical treatment and an experimental verification of our findings should not involve difficulties.[8] Ammonia is chosen for two reasons. Curiosity is one of them. Ammonia has very unusual properties giving rise to interesting chemistry and as a solvent, it is perhaps more versatile than water (see for example, the Review, Ref. [9]). In spite of the widely recognized significance of ammonia, ICD in this system has never been studied. The second, more important reason is the possibility to protonate/deprotonate ammonia clusters to allow investigating, theoretically and experimentally, the response of ICD to changes of pH value.

After a removal of an inner-valence electron, an isolated NH_3 molecule, like many other molecules, cannot relax by emitting another electron for energetic reasons. In contrast, both the H-donor and H-acceptor molecules in the ammonia dimer can decay electronically after inner-valence ionization. This possibility can be inferred from the middle panel of Figure 2 showing that the respective singly ionized states lie

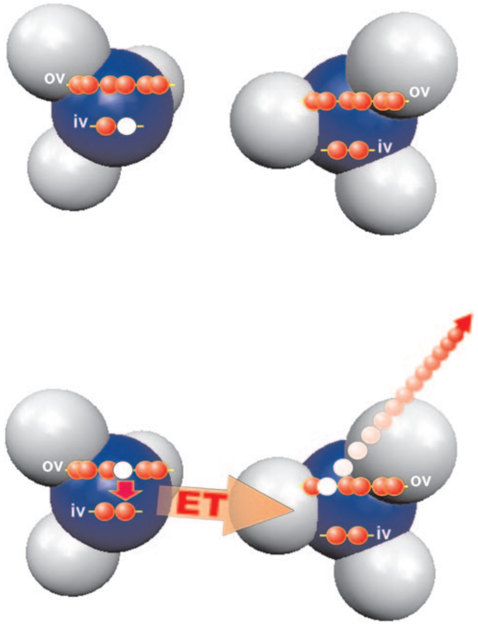

Figure 1. Schematic representation of intermolecular Coulombic decay. After ionization of an inner-valence electron (top), the created vacancy is filled by an outer-valence electron of the same molecule. The energy released is transferred to a neighboring molecule causing the ionization of its outer-valence electron (bottom). The autoionization of the initially ionized molecule by the released energy (intramolecular electronic decay) is forbidden energetically. ov denotes outer-valence, iv inner-valence, and ET energy transfer.

---

[*] Dr. N. V. Kryzhevoi, Prof. Dr. L. S. Cederbaum
Theoretische Chemie, Physikalisch-Chemisches Institut
Universität Heidelberg
Im Neuenheimer Feld 229, 69120 Heidelberg (Germany)
Fax: (+49) 6221-54-5221
E-mail: nikolai.kryzhevoi@pci.uni-heidelberg.de
lorenz.cederbaum@pci.uni-heidelberg.de

[**] We are grateful to the European Research Council (ERC Advanced Investigator Grant no. 227597) and to the Deutsche Forschungsgemeinschaft for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201004446.

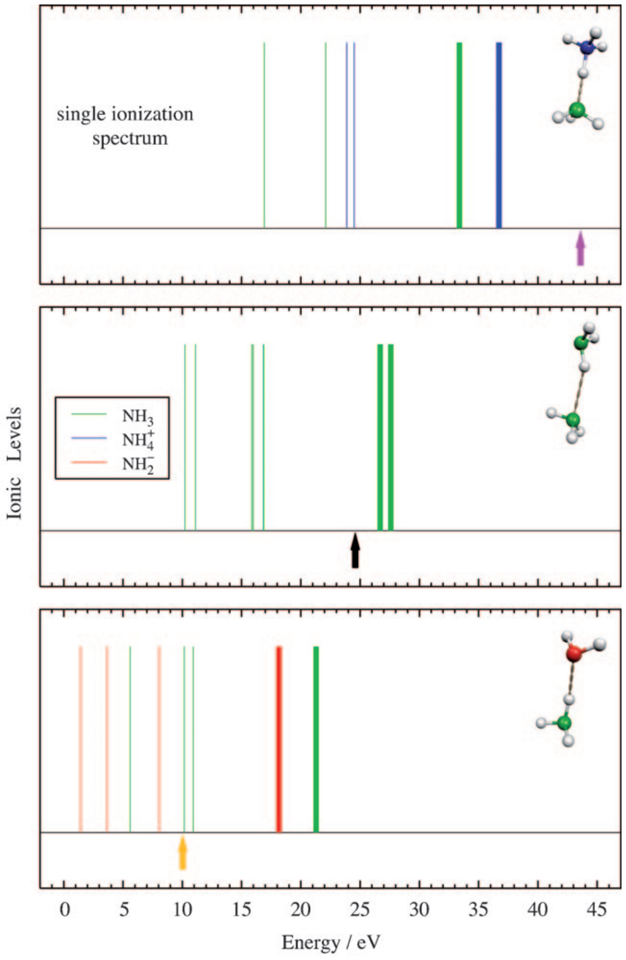

Figure 2. Calculated single-ionization potentials (vertical lines in the upper part of each panel) and the double-ionization thresholds (the arrow in the lower part of each panel) of the protonated (top), normal (middle), and deprotonated (bottom) ammonia dimers. The thin vertical lines at low energies correspond to ionization out of the outer-valence molecular orbitals. The thick vertical lines at higher energies describe ionization out of the inner-valence molecular orbitals. Colors of the vertical lines correspond to the types of the molecules in the dimers (see inset molecular structures, gray H, blue, green, or red N). Colors of the arrows specify different distributions of the two holes in the double-ionization thresholds: one hole on the ammonia molecule and one on the amide anion (yellow), two holes on different ammonia molecules (black), one hole on the ammonia molecule and one on the ammonium cation (magenta). Note the effect of protonation and deprotonation on the absolute and relative energies of the singly ionized states and double-ionization thresholds.

more than 2 eV above the double ionization threshold. The onset of double ionization starts with the nearly degenerate singlet and triplet dicationic states where two outer-valence $3a_1$ electrons are removed, each from a different ammonia molecule. The population of these states through electronic decay is possible only by the ICD mechanism, namely an inner-valence $2a_1$ vacancy is occupied by a $3a_1$ electron from the same molecule and a $3a_1$ electron of the neighboring molecule is ionized. Note that the above two dicationic states are the only ones which are energetically below the inner-valence single-ionization potentials (see Supporting Information). Note that the ammonia dimer is a "floppy" system and has several low energy isomers. We have checked that ICD operates in these isomers as well.

A similar picture holds for the ammonia trimer. All its three nearly degenerate inner-valence ionized main states can undergo intermolecular electronic decay as seen from the middle panel of Figure 3. Because each ammonia molecule now has two neighbors, the number of available ICD channels for each inner-valence vacancy doubles and the respective ICD rate is roughly twice as large as the ICD rate of either monomer in the ammonia dimer.[10]

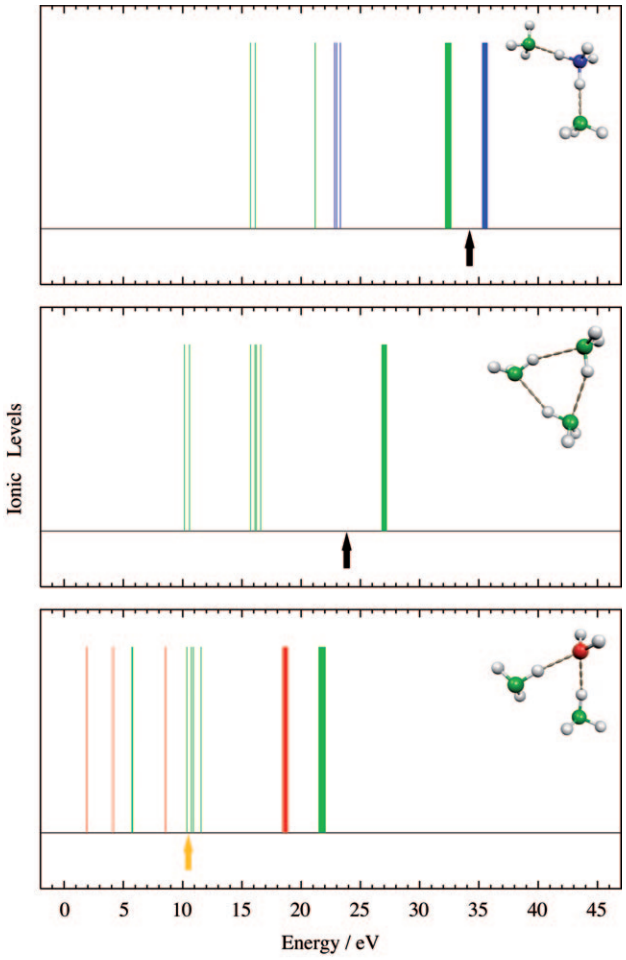

Figure 3. The same as in Figure 2 but for the ammonia trimers. Note that ICD is not possible in the protonated trimer (see text).

Much less effort is needed to detach electrons from the deprotonated systems. As seen from the bottom panels in Figure 2 and Figure 3, the single- and double-ionization potentials of the deprotonated dimers and trimers are noticeably lower than those of the normal clusters. Remarkably, the inner-valence vacancy of any ammonia molecule in the deprotonated clusters now has plenty of new open decay channels at its disposal (see Supporting Information) so that electronic decay of this vacancy speeds up considerably compared to the normal clusters.

Deprotonation has another, and perhaps the most striking consequence. Owing to the unique electronic structure of the deprotonated ammonia clusters, ICD can start in them by applying a rather low energy. Actually, this process can even be initiated by the withdrawal of an outer-valence $1e$ electron from NH_3 (see the states slightly above 10 eV in Figure 2 and 3), making the deprotonated ammonia clusters the first systems for which the feasibility of ICD in the outer-valence regime has been discovered. In contrast to ICD after inner-valence ionization, the outer-valence type ICD found in this case is rather sensitive to geometry changes, because the double-ionization threshold is relatively close to the outer-valence $1e$ ionization energy, in particular, it is no longer operative in a Zundel-type deprotonated dimer with a shorter intermolecular distance. Note that the ionization of the $1e$ orbital in an isolated NH_3 molecule is most likely to be followed by a very fast internal conversion which brings the system into the ground cationic state through a conical intersection.[11] The appearance of the outer-valence type ICD as a competing process in the deprotonated ammonia clusters makes the whole story of ionizing ammonia even more intriguing.

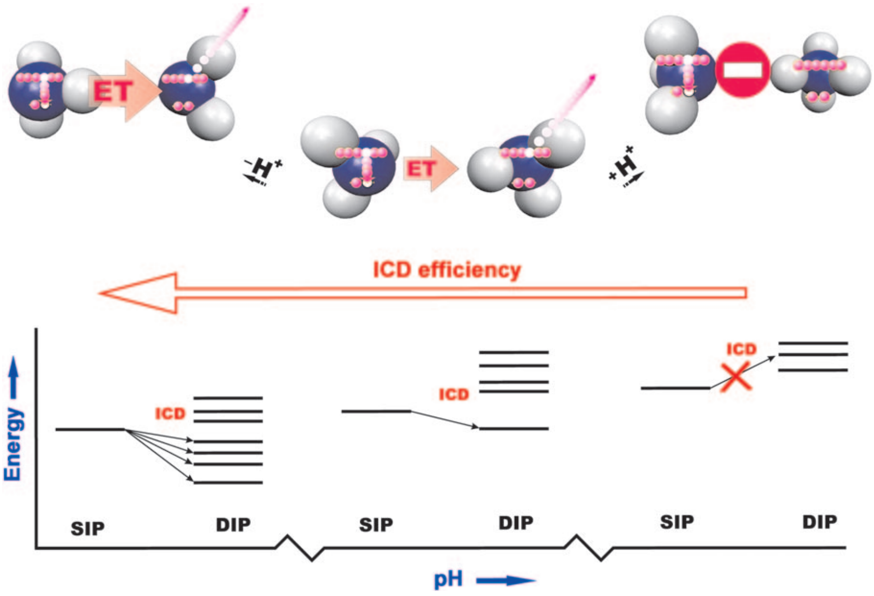

Figure 4. Impact of protonation/deprotonation on the intermolecular Coulombic decay (ICD). Bottom: schematic representation of single-ionization potentials (SIP) and double-ionization potentials (DIP) of a deprotonated (left), normal (center), and protonated cluster (right). The SIPs and DIPs of the deprotonated cluster are noticeably smaller than those of the normal cluster. The appearance of additional decay channels in the deprotonated cluster enhances the ICD efficiency. The SIPs and DIPs are largest in the protonated cluster. If the double-ionization onset happens to lie above the SIP, then ICD terminates. Top: not only the ICD efficiency but also the energy transferred (ET) from one molecule to another in the course of ICD as well as the kinetic energy of the outgoing ICD electron are strongly influenced by pH value. Both these energies have larger values at lower pH values. At higher pH values, when ICD is terminated, no energy transfer can occur, as indicated by the "no entry" symbol between the molecules after protonation.

Protonation has the opposite effect on the ammonia clusters than deprotonation. As seen from the top panels of Figure 2 and Figure 3, the single- and double-ionization potentials of the protonated clusters are remarkably higher than those of the normal ones. The double-ionization threshold of the dimer is subject to a particularly strong energy enhancement. Apparently, neither the ammonia molecule nor the ammonium cation in the dimer can undergo ICD after inner-valence ionization. Protonation switches ICD off!

Although the increase of the double ionization threshold in the trimer as a result of protonation is not as significant as in the dimer, protonation prohibits ICD in the trimer as well. Figure 3 suggests however that the inner-valence ionized ammonium cation in the trimer can, in principle relax, as its energy is above the double-ionization threshold. This threshold corresponds to the two outer-valence ionized neighboring ammonia molecules and thus the process in question is not ICD. It is rather the so-called electron-transfer mediated decay (ETMD)[12] which is associated with an intermolecular electron transfer and as such is much less efficient than ICD and not of central relevance in the present context. The schematic representation of the ETMD process is shown in Figure S3 of the Supporting Information.

In conclusion, we have demonstrated that deprotonation and protonation have a great impact on the intermolecular Coulombic decay. A proton withdrawal accelerates ICD while adding a proton inhibits this decay process substantially, sometimes up to its complete termination, as depicted in Figure 4. The discovered sensitivity of ICD is of importance since it makes ICD controllable through one of the most convenient environmental factors, namely pH value.

Experimental Section

Methods: The geometries of the clusters have been optimized using the second-order Møller–Plesset theory. Computations of the single- and double-ionization spectra have been performed using propagator methods within the so-called algebraic diagrammatic construction (ADC) schemes.[13,14] The non-Dyson third-order ADC scheme (nD-ADC(3))[15] developed for the one-particle propagator were employed to calculate the ionization potentials and intensities of the singly ionized states while the double-ionization potentials and intensities of the doubly ionized states were calculated by means of the second-order ADC(2)[14,16] method developed for the particle-particle propagator. The augmented cc-pVTZ basis sets[17] were used in all the computations.

Received: July 20, 2010
Revised: October 27, 2010
Published online: January 5, 2011

Keywords: ab initio calculations · ammonia clusters · electronic decay · ionization potentials · protonation

[1] L. S. Cederbaum, J. Zobeley, F. Tarantelli, *Phys. Rev. Lett.* **1997**, *79*, 4778.

[2] E. F. Aziz, N. Ottosson, M. Faubel, I. V. Hertel, B. Winter, *Nature* **2008**, *455*, 89.

[3] N. Sisourat, N. V. Kryzhevoi, P. Kolorenč, S. Scheit, T. Jahnke, L. S. Cederbaum, *Nat. Phys.* **2010**, *6*, 508.

[4] I. B. Müller, L. S. Cederbaum, *J. Chem. Phys.* **2006**, *125*, 204305.

[5] T. Jahnke, H. Sann, T. Havermeier, K. Kreidi, C. Stuck, M. Meckel, M. Schöffler, N. Neumann, R. Wallauer, S. Voss, A. Czasch, O. Jagutzki, A. Malakzadeh, F. Afaneh, Th. Weber, H. Schmidt-Böcking, R. Dörner, *Nat. Phys.* **2010**, *6*, 139.

[6] M. Mucke, M. Braune, S. Barth, M. Förstel, T. Lischke, V. Ulrich, T. Arion, U. Becker, A. Bradshaw, U. Hergenhahn, *Nat. Phys.* **2010**, *6*, 143.

[7] O. Vendrell, S. D. Stoychev, L. S. Cederbaum, *ChemPhysChem* **2010**, *11*, 1006.

[8] a) P. Farmanara, H.-H. Ritze, V. Stert, W. Radloff, I. V. Hertel, *J. Chem. Phys.* **2002**, *116*, 1443; b) J. T. Snodgrass, J. V. Coe, C. B. Freidhoff, K. M. McHugh, S. T. Arnold, K. H. Bowen, *J. Phys. Chem.* **1995**, *99*, 9675.

[9] J. J. Lagowski, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2007**, 37, 115.

[10] R. Santra, J. Zobeley, L. S. Cederbaum, *Phys. Rev. B* **2001**, *64*, 245104.

[11] C. Woywod, S. Scharfe, R. Krawczyk, W. Domcke, H. Köppel, *J. Chem. Phys.* **2003**, *118*, 5880.

[12] J. Zobeley, R. Santra, L. S. Cederbaum, *J. Chem. Phys.* **2001**, *115*, 5076.

[13] J. Schirmer, L. S. Cederbaum, O. Walter, *Phys. Rev. A* **1983**, *28*, 1237.

[14] J. Schirmer, A. Barth, *Z. Phys. A* **1984**, *317*, 267.

[15] J. Schirmer, A. B. Trofimov, G. Stelter, *J. Chem. Phys.* **1998**, *109*, 4734.

[16] F. Tarantelli, *Chem. Phys.* **2006**, *329*, 11.

[17] R. A. Kendall, T. H. Dunning, R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796.