

A MOLECULAR PORTRAIT OF HYDROGEN CHLORIDE

DATA IN TWO DIMENSIONS PAINT A DETAILED PICTURE

The high brightness of the ALS makes it possible to generate data much more rapidly than at older synchrotron facilities. This capability certainly boosts scientific productivity by increasing the number of experiments that researchers can do in their time at the facility. But just as important is the ability to record much more detailed sets of data. The detail comes in several forms. It may be more closely spaced wavelength intervals in spectroscopy experiments (high spectral resolution); it may be small areas of a sample (high spatial resolution or imaging); or it may be two or more variables, such as wavelength and electron energy (two-dimensional measurements). The bottom line is that, with more data, researchers can paint a finer portrait of whatever physical, chemical, or biological process they are investigating.

TWO-DIMENSIONAL MAPS

A case in point is two-dimensional electron spectroscopy of the hydrogen chloride molecule (HCl). As a comparatively simple molecule with just two atoms, hydrogen (only one electron) and chlorine (17 electrons), HCl is a natural step up in complexity from atoms to molecules and therefore serves as a model system to investigate fundamental aspects of molecular behavior that ultimately affect chemical bonding in reactions. For example, researchers want to understand internal processes in which two or more electrons act in concert rather than independently (electron correlation and many-body effects). With the understanding gained from studies of simpler molecules, scientists can advance to larger, more complex assemblies of many atoms, which would otherwise be too difficult to address.

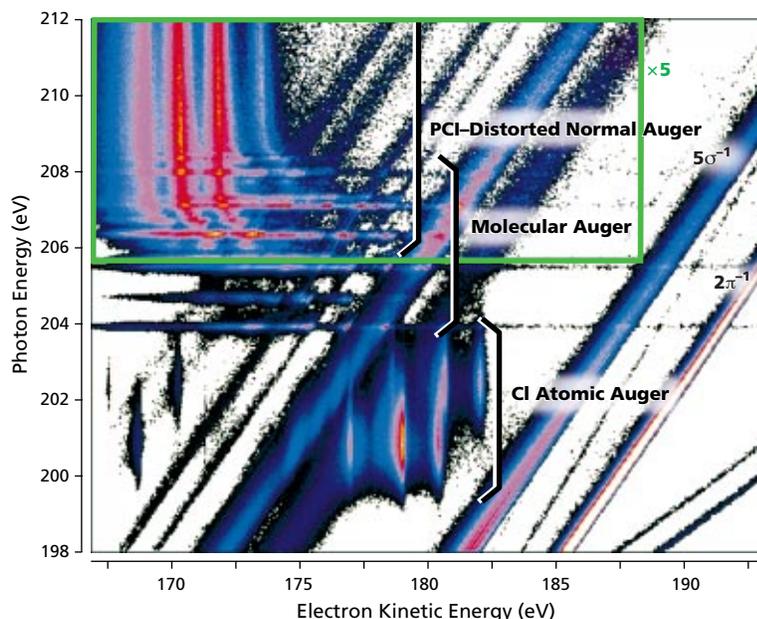
Absorption of an ultraviolet ray or x ray by a molecule usually results in the emission of one or more electrons (and sometimes molecular fragments) that provide the data for the experiment. The emit-

ted electrons have a spectrum of possible kinetic energies, with peaks at energies where a large number of electrons are detected. The energy spectrum reflects the behavior of the electrons in the molecule. The spectrum also depends on the wavelength of the x rays, since this determines how much energy is available to eject the electrons. Although much useful information comes from measurements at one or a few x-ray wavelengths, a more complete picture emerges from a two-dimensional map of peak positions and intensities with both electron kinetic energy and x-ray wavelength as axes. Measurement of the direction the emitted electrons take relative to the incoming x-ray beam provides still more detail.

INNER-SHELL IONIZATION

At the ALS, researchers have combined the high brightness of the ALS with advanced data-acquisition equipment and a rotatable experimental chamber to obtain two-dimensional electron spectra of HCl at several angles. In these experiments, HCl molecules absorb x rays with wavelengths blanketing an energy range above and below that sufficient to eject a tightly bound electron in an orbital associated mainly with the chlorine atom (ionization threshold). This absorption stimulates several processes that show up on the two-dimensional map. In general, the inner-shell chlorine electron (Cl 2p) can use the x-ray energy to move up into a less tightly bound molecular orbital or out of the molecule altogether (becoming a photoelectron). What happens next sheds light on other orbitals in the molecule, including those responsible for chemical bonding, and on the way the molecule reacts to a sudden increase in its energy.

After the initial x-ray absorption, another electron in a molecular orbital may “drop down” and fill the empty chlorine orbital. In so doing, it usually



Owing to the high brightness of the ALS and to advanced data-acquisition technology, researchers have been able to record two-dimensional electron spectra for the hydrogen chloride (HCl) molecule in the wavelength (photon energy) range near the threshold for ionization of a tightly bound inner-shell electron associated with the chlorine atom (Cl 2p). With the energy of the incoming photons and the kinetic energy of the ejected electrons as the two axes, the peak positions and their intensities identify numerous processes such as the chlorine atomic Auger, molecular resonant Auger, and normal Auger transitions distorted by post-collision interactions (PCI) labeled in the figure. (To make the latter more visible, the signal in the green box is shown at five times its actual value.) The diagonal lines, such as those labeled $5\sigma^{-1}$ and $2\pi^{-1}$, refer to the absorption of x rays by electrons in outer (valence) molecular orbitals rather than deep inside the chlorine atom, so that the electrons are ejected with high kinetic energy. Following these lines, one can study the interplay between the photoemission and Auger processes.

gives energy to a third electron, which then escapes from the molecule (molecular Auger electron). At some x-ray wavelengths, however, the chlorine electron jumps to an “antibonding” molecular orbital, which makes the molecule unstable, so that it dissociates into hydrogen and chlorine atoms. Auger electrons generated after the dissociation are then called atomic Auger electrons. These and other processes, such as slowing down or even recapture of electrons by the molecule (post-collision interactions),

have been accurately tracked at the ALS using the positions and intensities of electron peaks in the two-dimensional map.

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