IX-R Electronic Structure and Collision Dynamics of Atoms and Molecules Studied by Electron Impact at Large Momentum Transfer

Binary (*e*,2*e*) or electron momentum spectroscopy (EMS) is a high-energy electron-impact ionization experiment at large momentum transfer. The method involves coincident detection of the two outgoing electrons, allowing one to measure electron momentum densities for individual transitions or to look at molecular orbitals in momentum space. For molecular targets, however, EMS has long been plagued by the fact that the conventional (*e*,2*e*) experiments measure averages over all orientations of gaseous targets; the spherical averaging results in enormous loss of versatile information on the target electronic structure, anisotropy of the target wavefunction in particular. To overcome the historical experimental difficulty, we have proposed the (*e*,2*e*+M) method based on axial recoil fragmentation of the residual molecular ion and molecular frame (*e*,2*e*) cross sections have been successfully measured for the first time. Further attempts along this line are now in progress, opening the door for detailed studies of bound electronic wavefunctions of molecules as well as of stereodynamics of electron-molecule collisions.

IX-R-1 Development and Use of a Multichannel (*e*,2*e*) Spectrometer for Electron Momentum Densities of Molecules

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[*J. Phys. Chem. Solids* **65**, 2055–2059 (2004)]

We have developed an (*e*,2*e*) spectrometer with the introduction of modern multiparameter techniques. In particular, the high sensitivity achieved by simultaneous detection in energy and momentum is remarkable, opening up the possibilities of more precise and more advanced studies on the electronic structure of atoms and molecules. To illustrate some of the features, an overview of our recent results is presented. Highlights are applications to collision dynamics of H_2 and development of a method for a complete three-dimensional mapping of electron momentum densities in gaseous molecules. Both of these studies are based on the high sensitivity of the spectrometer.

IX-R-2 Observation of Molecular Frame (*e*,2*e*) Cross Section Using an Electron-Electron-Fragment Ion Triple Coincidence Apparatus

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[*J. Electron Spectrosc. Relat. Phenom.* **141**, 83–93 (2004)]

An apparatus for electron-electron-fragment ion triple coincidence experiments has been developed to examine binary (*e*,2*e*) scattering reaction in the molecular frame. In the axial recoil limit of fragmentation of the residual ion, measurements of vector correlations among the three charged particles are equivalent to (*e*,2*e*) experiments with fixed-in-space molecules. Details and performance of the apparatus are reported, together with preliminary result of collision dynamics study on ionization-excitation processes of fixed-in-space H_2 molecules. We believe that this is the first observation of molecular frame (*e*,2*e*) cross sections.

IX-R-3 (*e*,3*e*) Collisions on Mg in the Impulsive Regime Studied by Second Born Approximation

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[*J. Phys. B: At., Mol. Opt. Phys.* **37**, 4551–4560 (2004)]

Five-fold differential cross sections for electron-impact double ionization of the 3s electrons of magnesium have been calculated in the second Born approximation in the impulsive regime. Comparing these results with calculations carried out in the first Born approximation demonstrates the dominant contribution of the second Born term. The second Born calculation shows that contribution of the two-step 2 (TS2) process becomes large under the condition where sequential binary collisions on the Bethe ridge can occur. The effect of electron correlation in the initial target state is also examined by using a configuration interaction wavefunction.

IX-R-4 Electron Momentum Spectroscopy of Valence Satellites of Neon

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[*J. Electron Spectrosc. Relat. Phenom.* **142**, 325–334 (2005)]

Electron momentum spectroscopy (EMS) study of the neon valence satellites is reported. The experiments were performed at impact energies of 1250, 1450 and 1670 eV using a multichannel spectrometer that features high sensitivity. Binding energy spectra up to 100 eV and momentum profiles for the $2p^{-1}$ and $2s^{-1}$ primary transitions as well as the satellites are presented. The results are used to examine impact energy dependence of the relative intensities and shapes of the satellite momentum profiles. The results are also used to determine symmetries and spectroscopic factors of the satellites, and are compared with the previous experiments by EMS and photoelectron spectroscopy and sophisticated theoretical calculations. The present study has largely resolved controversies in the previous studies.

IX-R-5 Theoretical Fine Spectroscopy with Symmetry-Adapted-Cluster Configuration-Interaction Method: Outer- and Inner-Valence Ionization Spectra of Furan, Pyrrole, and Thiophene

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[*J. Chem. Phys.* **122**, 234319 (10 pages) (2005)]

Theoretical fine spectroscopy has been performed for the valence ionization spectra of furan, pyrrole, and thiophene with the symemtry-adapted-cluster configuration-interaction general-*R* method. The present method desribed that the π^1 state interacts with the $\pi_3^{-2}\pi^*$, $\pi_2^{-2}\pi^*$, and $\pi_2^{-1}\pi_3^{-1}\pi^*$ shake-up states provoding the split peaks and the outer-valence satellites, both of which are in agreement with the experiments. The intensity distributions were analyzed in detail for the inner-valence-region. In particular, for furan, theoretical intensities were successfully compared with the intensity measured by the electron momentum spectroscopy. The interactions of the $3b_2$ and $5a_1$ states with the shake-up states were remarkable for furan and pyrrole, while the $4b_2$ state of thiophene had relatively large intensity.

IX-R-6 Observation of a Molecular Frame (*e*,2*e*) Cross Section: An (*e*,2*e*+M) Triple Coincidence Study on H_2

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[*Phys. Rev. Lett.* **94**, 213202 (4 pages) (2005)]

We report the first experimental results showing transition-specific anisotropy of molecular frame (*e*,2*e*) cross sections. Vector correlations between the two outgoing electrons and the fragment ion have been measured for specific ionization-excitation processes of H_2. The results enable us to obtain molecular frame (*e*,2*e*) cross sections for transitions to the $2s\sigma_g$ and $2p\sigma_u$ excited states of H_2^+, thereby making stereodynamics of the electron-molecule collisions directly visible.

IX-R-7 (*e*,2*e*) and (*e*,3–1*e*) Studies on Double Processes of He at Large Momentum Transfer

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[*Phys. Rev. A* **72**, 32705 (11 pages) (2005)]

The double processes of He in electron-impact ionization, single-ionization with simultaneous excitation and double-ionization, have been studied at large momentum transfer using an energy- and momentum-dispersive binary (*e*,2*e*) spectrometer. The experiment has been performed at an impact energy of 2080 eV in the symmetric noncoplanar geometry. In this way we have achieved a large momentum transfer of 9 a.u., a value that has never been realized so far for the study on double-ionization. The measured (*e*,2*e*) and (*e*,3–1*e*) cross sections for transitions to the $n = 2$ excited state of He^+ and to doubly ionized He^{2+} are presented as normalized intensities relative to that to the $n = 1$ ground state of He^+. The results are compared with first-order plane-wave impulse approximation (PWIA) calculations using various He ground-state wavefunctions. It is shown that shapes of the momentum-dependent (*e*,2*e*) and (*e*,3–1*e*) cross sections are well reproduced by the PWIA calculations only when highly correlated wavefunctions are employed. However, noticeable discrepancies between experiment and theory remain in magnitude for both the double processes, suggesting importance of higher-order effects under the experimental conditions examined as well as of acquiring more complete knowledge of electron correlation in the target.

IX-R-8 Electron Momentum Spectroscopy of the HOMO of Acetone

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[*J. Photochem. Photobiol.* in press]

Electron momentum profiles of the HOMO of acetone have been measured under experimental conditions where a use of the plane-wave impulse approximation is justified. A double peak is observed in the experimental profile and it was found that calculated profiles by the use of the standard basis set always underestimate the magnitude of the low momentum peak. Possible origins of the discrepancies between the calculated and measured profiles are examined, leading to an improved agreement by modifying the exponents of diffuse functions employed.

IX-R-9 (*e*,3–1*e*) Reactions at Large Momentum Transfer: The Plane-Wave Second Born Approximation

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[*Phys. Rev. A* to be submitted]

We consider theoretically symmetric (*e*,3–1*e*) reactions of He atom at large momentum transfer. For evaluating the corresponding four-fold differential cross sections, a theory based on the re-normalized plane-wave second Born approximation (SBA) is developed. The numerical SBA calculations for both coplanar and non-coplanar symmetric geometries are performed and compared with experiments.

IX-R-10 Binary (*e*,2*e*) Study on Xe: Momentum Profile for the 4d Orbital Revisited

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[*J. Phys. B: At. Mol. Opt. Phys.* to be submitted]

Binary (*e*,2*e*) cross sections have been measured for Xe using an energy- and momentum-dispersive multichannel spectrometer at impact energy of 2055 eV. Assuming that the Xe 5p ionization process can be described by the distorted-wave Born approximation (DWBA), the experimental momentum profile for the 4d orbital was placed on an absolute scale. The absolute-scale Xe 4d experiment has been compared with DWBA calculations using the Hartree-Fock and Dirac-Fock wavefunctions, in order to exploit relativistic effects in both shape and intensity of momentum profile. Although DWBA/DF has been found to give better description than DWBA/HF, noticeable discrepancies between experiment and theory still remain.

IX-R-11 Binary (*e*,2*e*) Study on Inner Shell Orbitals of Ar and Xe

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[*J. Phys. B: At. Mol. Opt. Phys.* to be submitted]

Binary (*e*,2*e*) experiments were performed on Xe 4p, 4s and Ar 2p, 2s orbitals. The results are compared with distorted-wave Born approximation calculations using the Hartree-Fock and Dirac-Fock wavefunctions, in order to exploit relativistic effects in momentum profile. Furthermore, for Xe the experiments have revealed a broad band at around 100 eV, which has not been found by photoelectron spectroscopy. The band has been assigned as giant resonance of Xe 4d in the sequential two collisions of the projectile with the target electrons.

IX-R-12 Construction of a New (*e*,2*e*+M) Apparatus for Complete Imaging of Molecular Orbitals

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We have constructed a new electron-electron-fragment ion triple coincidence apparatus for complete imaging of molecular orbitals. The major sections of the apparatus are a chamber equipped with a 2300 L/s turbo molecular pump, an electron gun, a spherical analyzer followed by a hexagonal delay-line position-sensitive detector which covers the full 2π azimuth of the two outgoing electrons emerging at the scattering angle of 45°, a velocity imaging system to detect all of parent and fragment ions from the 4π solid angle, and data gathering electronics. The electron gun and spherical analyzer have been developed at the machine shop of the Tohoku University, while the chamber and the data gathering electronics have been developed at the equipment development center of IMS. This project aims at fully extending our preliminary (*e*,2*e*+M) studies [M. Takahashi *et al.*, *J. Phys. Chem. Solids* **65**, 2055 (2004); *J. Electron Spectrosc. Relat. Phenom.* **141**, 83 (2004); *Phys. Rev. Lett.* **94**, 213202 (2005)], which have made it possible to perform molecular frame (*e*,2*e*) spectroscopy for the first time.

IX-S Electronic Structure and Collision Dynamics of Atoms and Molecules Studied by Photon Impact

The group takes another, photon-impact, approach to issues of electronic structure and collision dynamics, since photon-impact and electron-impact or photoelectric effects and Compton scattering are complementary to each other.

IX-S-1 Inner-Shell Photoelectron Angular Distributions from Fixed-in-Space OCS Molecules

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[*J. Phys. B: At. Mol. Opt. Phys.* **38**, L63–L68 (2005)]

The photoelectron angular distributions (PADs) for the OCS O 1s, C 1s and S $2p_{1/2}$, $2p_{3/2}$ ionization have been measured in the shape resonance region. The experimental results have been compared with multiple scattering Xα calculations. It is found that the position of an ionized atom plays a significant role. For a central position (C 1s ionization) the PAD is relatively symmetric. In the case of S 2p and O 1s ionization, electrons are emitted highly preferentially in a solid cone directed from the molecular centre to the respective S or O atom. For the OCS O 1s ionization the S–C fragment plays a very effective role as a 'scatterer' in the shape resonance region nearly all intensity in PAD is concentrated in the lobe between θ = 50° and 80°, but not along the molecular axis.

IX-S-2 Coincidence Velocity Imaging Apparatus for the Study of Angular Correlations between Photoelectrons and Photofragments

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[*J. Electron Spectrosc. Relat. Phenom.* submitted]

A new apparatus of coincidence velocity mapping has been developed for studies on inner-shell photoionization dynamics of molecules. It achieves velocity imaging for electrons and ions simultaneously, and keeps the time focusing. To demonstrate the performance of the new apparatus, some examples, photoelectron angular distributions from Ne atoms and randomly oriented NO molecules, photoion angular distributions from CO molecules, and photoelectron angular distributions form fixed-in-space CO and NO molecules, are reported.

IX-S-3 Non-Dipole Effects in the Angular Distribution of Photoelectrons from the K-Shell of N_2 Molecule

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[*J. Phys. B: At. Mol. Opt. Phys.* submitted]

Measurements and calculations of contribution of the non-dipole terms in the angular distribution of photoelectrons from the K-shell of randomly oriented N_2 molecules are reported. The angular distributions have been measured in the plane containing the photon polarization and the photon momentum vectors of linearly polarized radiation. Calculations have been performed in the relaxed core Hartree-Fock approximation with a fractional charge, and many-electron correlations were taken into account in the random phase approximation. Both theory and experiment show that the non-dipole terms are rather small in the photon energy region from the ionization threshold of the K-shell up to about 70 eV above it. From the theory it follows that the non-dipole terms for the individual shells of $1\sigma_g$ and $1\sigma_u$ are considerably large, therefore measurements resolving the contributions of the $1\sigma_g$ and $1\sigma_u$ shells are desirable.

IX-S-4 Direct Observation of a Symmetry Lowering in Core-Electron Ionization for Highly Symmetric Molecules

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The symmetry lowering occurs quite often in the ionization of a core electron of equivalent constituent-atoms for highly symmetric molecules since the core-hole states of those molecules are generally quasi-degenerate and therefore couple over non-totally symmetric vibrational modes. Such couplings, referred as quasi-Jahn-Teller couplings, have been clearly investigated for the most basic example of CO_2; the relation between the symmetry lowering and core-hole localization has been proved. The symmetry lowering which removes the equivalence of two oxygen atoms causes a fundamental quantum mechanical question; is it possible to decide whether the core hole is localized on the right oxygen atom or on the left? Here we report the direct observation of the symmetry lowering of the CO_2 induced by O1s photoionization.