

VIII-W Electronic Structure and Collision Dynamics of Atoms and Molecules Studied by Electron Impact near the Bethe Ridge

Binary ($e,2e$) or electron momentum spectroscopy (EMS), based on the so-called electron Compton scattering, is a high-energy electron-impact ionization experiment in which kinematics of all the electrons are fully determined by coincident detection of the two outgoing electrons. The ability to measure electron momentum distribution for each molecular orbital, square modulus of the momentum-space wavefunction, is a remarkable feature of this technique. Since momentum-space and position-space are uniquely related to each other by Fourier transformation, electron momentum distribution is highly sensitive to diffuse parts of the position-space wavefunction that are important in chemical reaction and molecular recognition. However, the potential of EMS has not been fully achieved as yet, due mainly to the extremely small cross sections involved. For these reasons, together with various improvements to spectrometers we are aiming at developing next-generation EMS for chemistry, which would give quite unique and versatile information on electronic structure of molecules.

VIII-W-1 A High Sensitivity Electron Momentum Spectrometer with Simultaneous Detection in Energy and Momentum

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A new apparatus for electron-electron coincidence experiments has been developed to examine molecular orbital patterns quantitatively by electron momentum spectroscopy. Using a spherical analyzer and position-sensitive detectors, it enables one to measure energy and angular correlations between the two outgoing electrons simultaneously. The design and performance of the apparatus is reported together with results on Ar to show extensive improvements in coincidence count rates and statistical precision, covering a wide range of binding energies and momenta.

VIII-W-2 The Impact Energy Dependence of Momentum Profiles of Glyoxal and Biacetyl and Comparison with Theory at Their High-Energy Limits

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[*J. Phys. B: At., Mol. Opt. Phys.* **36**, 2539 (2003)]

We report an electron momentum spectroscopy study of the two outermost orbitals of dicarbonyls, glyoxal and biacetyl. The experiments were performed at impact energies of 800, 1200 and 1600 eV by using a recently developed multichannel ($e,2e$) spectrometer. The experimental momentum profiles clearly show remarkable variations in the low momentum region with increase in impact energy. Furthermore, it has been found that the two molecules reach their high-energy limits at different impact energies, indicating that the range of the validity of the plane-wave impulse approximation (PWIA) largely depends on the target in

question. The results at 1600 eV are employed for comparisons with PWIA calculations using Hartree-Fock and density functional theory (DFT). While the DFT calculations reproduce well the observations for glyoxal, considerable discrepancies between experiment and theory exist in biacetyl.

VIII-W-3 ($e,2e$) Ionization-Excitation of H₂

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[*Phys. Rev. A* in press]

Binary ($e,2e$) measurements are reported for simultaneous ionization-excitation processes of H₂. The experiments were performed at impact energies of 1200, 1600 and 2000 eV using an energy- and momentum-dispersive spectrometer. Momentum profiles for transitions to the $2s\sigma_g$ and $2p\sigma_u$ excited final ion states are presented as normalized intensities relative to the cross section of the primary ionization to the $1s\sigma_g$ ground ion state. The results are compared with theoretical calculations of Lermer *et al.* [*Phys. Rev. A* **56**, 1393 (1997)] using the first-order plane-wave impulse approximation. Certain features of the discrepancies between experiment and theory can be explained by incorporating contributions from the second-order two-step mechanisms into the ($e,2e$) cross sections. Furthermore, the present results suggest that $2s\sigma_g$ and $2p\sigma_u$ cross sections approach their high-energy limits in different ways.

VIII-W-4 Electron Momentum Spectroscopy of N₂O

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[*J. Electron Spectrosc.* in press]

An electron momentum spectroscopy study of the outer valence orbitals of N₂O is reported. The experi-

ments were performed at impact energies of 1000, 1200, 1600 and 1800 eV by using a recently developed multichannel ($e,2e$) spectrometer. The experimental momentum profiles are compared with each other to examine their impact energy dependence. The results are used for comparisons with Hartree-Fock (HF) and density functional theory (DFT) calculations using various basis sets. The DFT and HF calculations with large basis sets are in good agreement with the measured electron momentum profiles, with the exception of that of the 6σ orbital for which the HF method underestimates the cross sections in the low momentum region.

VIII-W-5 A High Sensitivity Electron Momentum Spectrometer with Two-Dimensional Detectors and Electron Momentum Distributions of Several Simple Molecules

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[*J. Electron Spectrosc.* submitted]

Electron momentum spectroscopy (EMS) makes it possible to examine orbital patterns of individual molecular orbitals in momentum space. A new spectrometer for electron-electron coincidence experiments for EMS has been developed to obtain orbital patterns quantitatively. Using a spherical analyzer and position-sensitive two-dimensional detectors combined with fast electronics, simultaneous measurements of energy and angular correlations between the two outgoing electrons can be made. This spectrometer features high sensitivity and an ease of changing impact energies. Details of the apparatus are described and impact energy dependence of electron momentum distributions of the HOMO of H₂ and biacetyl are compared.

VIII-W-6 Electron-Impact Double Ionization Mechanisms in the Impulsive Regime

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[*Phys. Rev. Lett.* submitted]

Five-fold differential cross sections (5DCS) for the electron-impact double ionization of the $3s$ electrons of magnesium have been measured in a high-impact-energy, high-momentum-transfer regime within the ionization mechanisms can be accurately described by simple models in which the ionization processes and the initial-state atomic properties can be separated. In the unique experimental geometry, the form of the measured cross sections provides strong evidence for impulsive two-collision ionization mechanisms. Second Born calculations are in agreement with the experimental data providing further evidence for the mechanisms. The implications for the measurement of two-electron densities are discussed.

VIII-W-7 Second Born Approximation Calculations of Double Ionization of Mg

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Electron impact double ionization, also called the ($e,3e$) reaction, can provide direct information on correlated motion of atomic electrons, provided that the collision mechanism is known. Possible mechanisms for the ($e,3e$) reaction include shake-off (SO), two-step 1 (TS1), and two-step 2 (TS2). The SO and TS1 are of the first order in the projectile-target interaction, while the TS2 is a second-order process. In this study we theoretically examine contributions from TS2 in the scattering geometry chosen for the ($e,3e$) experiments of the Maryland group, which investigate correlated motion of the $3s$ electrons in the magnesium atom. It has been found that dominant contribution from the Second Born term is involved in the observed ($e,3e$) cross sections of Mg. Electron correlation effects in the initial target state are also studied using a configuration interaction wave function.

VIII-W-8 Orbital Momentum Profiles and Binding Energy Spectra for the Complete Valence Shell of CO

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Electron momentum profiles and binding energy spectra for the complete valence shell of CO have been measured using an energy- and momentum-dispersive ($e,2e$) spectrometer at an impact energy of 1600 eV. It has been found that shapes of the orbital momentum profiles are well reproduced by Hartree-Fock calculations. Binding energy spectra and momentum profiles in the satellite region beyond 22 eV binding energy of CO are studied in detail, determining pole strength distributions of the molecule. Comparisons are made for the pole strength distributions with theoretical predictions of Ehara and Nakatsuji using the SAC-CI general-R method. The agreement between experiment and theory is generally good, but some discrepancies remain for ionization transitions with small pole strength lower than about 0.1.

VIII-W-9 ($e,2e$) Study on Ionization-Excitation and Double Ionization of He

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A binary ($e,2e$) study has been carried out for He at an impact energy of 2000 eV using a recently developed energy- and momentum-dispersive spectrometer. Binding energy and momentum ranges up to about 100 eV and 4 au were then covered. Momentum distributions of the individual ionization-excitation transitions, converging to the double ionization threshold, have been compared with first-order plane-wave impulse

calculations of Mitroy *et al.* [*J. Phys. B* **18**, 4149 (1985)]. For the primary ionization that leaves the residual He^+ ion in the $n = 1$ ground state, agreement between experiment and theory is satisfactory. On the other hand, for ionization-excitation that leads to change of state of both the two target electrons the experiments always exhibit larger intensity than theory, suggesting noticeable contributions from the second-order two step mechanisms.

VIII-W-10 Development of a Triple Coincidence Spectrometer for a Complete Three-Dimensional Mapping of Electron Momentum Densities in Gaseous Molecules

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Electron momentum spectroscopy has been developed as a powerful means for the investigation of electronic structure and electron correlation. In particular, the ability to measure electron momentum distribution for each molecular orbital, square modulus of the momentum-space wavefunction, is a remarkable feature of this technique. It is unfortunate, however, that experimentally observable electron momentum distribution is spherically averaged due to random orientation of gaseous targets, smearing out details of electronic structure inherently involved in the experiments.

To overcome the experimental difficulty a new apparatus has been developed for a complete three-dimensional mapping of electron momentum densities in gaseous molecules. Based on the axial recoil, measurements of vector correlations among the two outgoing electrons and fragment ion correspond to $(e,2e)$ experiments with oriented molecules. Dissociation of molecular ions perpendicular to the incident electron momentum vector are detected with seven independent channeltrons, while the two outgoing electrons are detected with a pair of position-sensitive detectors. A schematic diagram of the kinematics of our experiments is shown in Figure 1.

Although there are substantial backgrounds due to a huge number of fragment ions produced by forward scattering of electron projectile, we have successfully measured genuine triple coincidence signals for the first time. Figure 2 shows an example of the results, which plots directional electron momentum densities obtained

for the $2\sigma_g$ ionization of O_2 . While the statistics of the data is not satisfactory, we can clearly see anisotropy of electron momentum densities. For establishing this method developments in detection of the outgoing electrons in the momentum dispersive plane around full 2π azimuth are now in progress to increase sensitivity of two additional orders of magnitude.

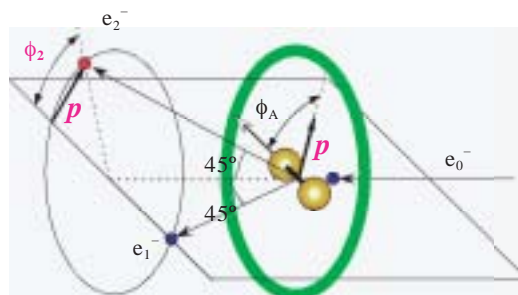


Figure 1. Schematic diagram of the kinematics of the $(e,2e)$ directional momentum density experiment. The spectrometer records only the component of momentum perpendicular to the scattering plane. When dissociation takes place in the perpendicular plane, the channeltron detectors will record the arrival of the dissociation products.

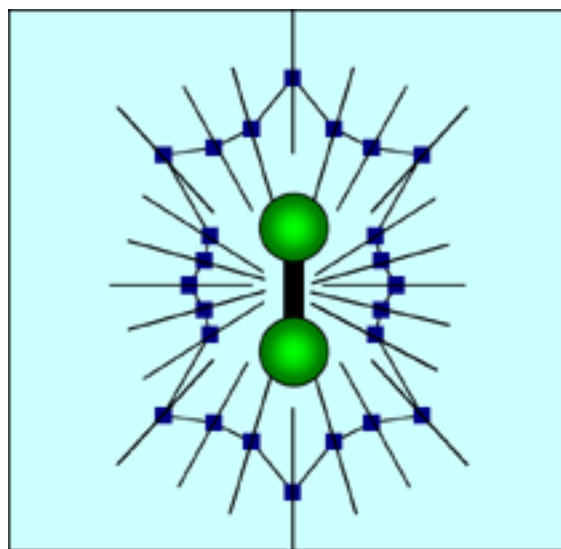


Figure 2. Directional electron momentum densities for the $2\sigma_g$ orbital ionization of O_2 .

VIII-X 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.

VIII-X-1 Multilayer Polarizers for the Use of He-I and He-II Resonance Lines

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[*Surf. Rev. Lett.* **9**, 587 (2002)]

Multilayer polarizers for the use of He resonance lines have been developed. Si/Mg and SiC/Mg multilayers were designed and fabricated for the He-I and He-II resonance lines, respectively. The performance was checked by the use of synchrotron radiation. The polarizance and *s*-reflectance of the He-II polarizer measured at an angle of incidence of 40° were 0.98 and 41%, respectively. The polarizance of the He-I polarizer measured at an angle of incidence of 31.5° was 0.96.

VIII-X-2 Polarization Measurements of Laboratory VUV Light: A First Comparison between Multilayer Polarizers and Photoelectron Angular Distributions

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[*J. Electron Spectrosc.* **130**, 79 (2003)]

The use of photoelectron angular distributions to determine the linear polarization of VUV light over a wide range of photon energies is demonstrated. Light at wavelengths from 25.6 to 73.6 nm, partially polarized by large angle reflections in a toroidal grating monochromator and at a refocus mirror, has been analyzed. The results are validated by comparison measurements at spot wavelengths using multilayer polarizers.

VIII-X-3 Carbon K-Shell Photoelectron Angular Distribution from Fixed-in-Space CO₂ Molecules

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[*J. Phys. B: At., Mol. Opt. Phys.* **36**, L25 (2003)]

Measurements of photoelectron angular distributions for carbon *K*-shell ionization of fixed-in-space CO₂ molecules with the molecular axis oriented along, perpendicular and at 45° to the electric vector of the light are reported. The major features of these measured

spectra are fairly well reproduced by calculations employing a relaxed-core Hartree-Fock approach. In contrast to the angular distribution for *K*-shell ionization of N₂, which exhibits a rich structure dominated by the *f*-wave (*l* = 3) at the shape resonance, the angular distribution for carbon *K*-shell photoionization of CO₂ is quite unstructured over the entire observed range across the shape resonance.

VIII-X-4 N 1s Photoionization Cross Sections of the NO Molecules in the Shape Resonance Region

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[*J. Phys. B: At., Mol. Opt. Phys.* in press]

The N 1s partial photoionization cross sections of NO leading for the ³Π and ¹Π ionic states have been measured in the shape resonance region for the first time. The twin local maxima in the cross sections have been tentatively assigned, based on the simple models for the photoabsorption intensities and for the branching ratio of the ³Π and ¹Π ionic states from the σ* shape resonance state.

VIII-X-5 Multiplet-Specific N 1s Photoelectron Angular Distributions from the Fixed-in-Space NO Molecules

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[*Phys. Rev. Lett.* submitted]

Angular distributions of multiplet-specific N 1s photoelectrons from the fixed-in-space NO molecules have been measured for the first time. The dynamics of the σ* shape resonance appeared in the channel leading to the ³Π and ¹Π ionic states has been made clear from the analyses of the angular distributions. Multiplet-specific multichannel calculations have reproduced the observed angular distributions fairly well.

VIII-X-6 Shape-Resonance-Enhanced Vibrational Effects in the Angular Distributions of C 1s Photoelectrons from Fixed-in-Space CO Molecules

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[*Phys. Rev. Lett.* in press]

Angular distributions of C1s photoelectrons from fixed-in-space CO molecules have been measured with

vibrational resolution. A strong dependence of the angular distributions on the vibrational states of the residual molecular ion has been found for the first time in the region of the shape resonance. Calculations in the relaxed core Hartree-Fock approximation have reproduced the angular distributions fairly well in the general shapes of the angular distributions due to the correct description of nuclear motion as an average of the internuclear-distance-dependent dipole amplitudes.

VIII-X-7 Angular Distributions of Vibrationally Resolved C 1s Photoelectrons from Fixed-in-Space CO Molecules: Vibrational Effect in the Shape-Resonant C 1s Photoionization of CO

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[*J. Electron Spectrosc.* submitted]

We have measured molecular-frame photoelectron angular distributions (MF-PAD) for the vibrationally resolved C1s photoelectron from CO molecule in the s shape resonance region. The MF-PAD's for the $v_f = 0, 1$, and 2 levels in the C1s $\rightarrow \epsilon l\sigma$ channel are apparently different each other at each incident photon energy. These MF-PAD's agree with the present theoretical results from the averaging the nuclear distance dependent dipole matrix elements with the relaxed core Hartree-Fock calculations. The present results show that the internuclear distance dependences of the phase and of the magnitude of the dipole matrix element play a crucial role in the C1s photoionization of CO.

VIII-X-8 Coulomb Hole in N₂, CO and O₂ Deduced from X-Ray Scattering Cross Sections

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Total (elastic + inelastic) x-ray scattering cross sections $\sigma_{ee}(q)$ are very sensitive to electron correlation effects, since they are related to the Fourier transform of the radial electron-electron pair distribution function $P(r_{12})$.¹⁾ X-ray scattering experiments can hence provide a crucial check of whether or not a theoretical wave function takes electron correlation properly into consideration.

In this study, accurate $\sigma_{ee}(q)$ of N₂, CO and O₂ were measured by the use of the energy dispersive method up to a momentum transfer of $q = 12$ a.u. $P(r_{12})$ was extracted from the cross sections. The Coulomb hole, defined as the difference between the exact $P(r_{12})$ and the corresponding function evaluated at Hartree-Fock limit, has been derived from experimental data. Comparison with configuration interaction calculations shows small but systematic differences between the theoretical and experimental results.

Reference

1) N. Watanabe *et al.*, *Review of Modern Quantum Chemistry*, K. D. Sen, Ed., World Scientific; Singapore, 553 (2002).

VIII-X-9 Absolute Surface Coverage Measurement Using a Vibrational Overtone

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Sub-monolayer absolute surface number densities are obtained by cavity ring-down spectroscopy (CRDS) for trichloroethylene, cis-dichloroethylene, and trans-dichloroethylene adsorbed on silica using the first C-H stretching overtones, which are probed with the idler of a seeded optical parametric amplifier having a 0.075 cm⁻¹ line width. The absolute surface number densities are found by invoking conservation of the integrated band intensity with adsorption together with knowledge of the transition moment orientation as derived from the adsorbate polarization anisotropy. The evanescent wave CRDS (EW-CRDS) measurements employ a fused-silica monolithic folded resonator with a peak finesse of $\approx 28,500$ at 1650 nm. The absolute coverage of trichloroethylene on SiO₂ is also obtained by a mass-spectrometer-based surface-uptake technique, which is briefly contrasted with the EW-CRDS method. The sensitivity of EW-CRDS for trichloroethylene detection with an unclad resonator is found to be comparable to that obtained with a long-effective-path-length waveguide having a trichloroethylene-enriching polysiloxane coating.