

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

Binary (e,2e) or electron momentum spectroscopy (EMS) 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 method enables us to look at individual molecular orbitals in momentum space, based on the so-called electron Compton scattering. However, EMS has long been plagued by the fact that the present experiments measure averages over all orientations of gaseous targets. The spherical averaging results in enormous loss of versatile information on electronic structure, in particular that on anisotropy of the target wavefunction. Consequently, one must be content to use EMS only as a stringent test for the target wavefunction model employed. Under these historical circumstances, we have successfully developed an electron-electron-fragment ion triple coincidence apparatus that makes it possible to carry out molecular frame EMS experiments for the first time, opening up the possibilities for detailed studies of bound electronic wavefunctions of molecules.

IX-U-1 (e,2e) Ionization-Excitation of H₂

**TAKAHASHI, Masahiko¹; KHAJURIA, Yugal;
UDAGAWA, Yasuo²**

(¹IMS and Tohoku Univ.; ²Tohoku Univ.)

[*Phys. Rev. A* **68**, 042710 (7 pages) (2003)]

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 σ_g and 2p σ_u excited final ion states are presented as normalized intensities relative to the cross section of the primary ionization to the 1s σ_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 σ_g and 2p σ_u cross sections approach their high-energy limits in different ways.

IX-U-2 Electron Momentum Spectroscopy of N₂O

**KHAJURIA, Yugal; TAKAHASHI, Masahiko¹;
UDAGAWA, Yasuo²**

(¹IMS and Tohoku Univ.; ²Tohoku Univ.)

[*J. Electron Spectrosc. Relat. Phenom.* **133**, 113–121 (2003)]

An electron momentum spectroscopy study of the outer valence orbitals of N₂O is reported. The experiments were performed at impact energies of 1000, 1200, 1600 and 1800 eV by using a recently developed multi-channel (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 func-

tional 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 6s orbital for which the HF method underestimates the cross sections in the low momentum region.

IX-U-3 Triple Differential Cross-Section of Ne(2s²) in Coplanar to Perpendicular Plane Geometry

**CHEN, Li Q.¹; KAHJRIA, Yugal; CHEN, Xian J.¹;
XU, Ka Z.¹**

(¹USTC)

[*Eur. Phys. J. D* **26**, 141–146 (2003)]

The distorted wave Born approximation (DWBA) with spin average static exchange potential has been used to calculate the triple differential cross sections (TDCSs) for Ne(2s²) ionization by electron impact in the coplanar to perpendicular plane geometry at 110.5 eV incident energy. The present theoretical results at gun angles $\Psi = 0^\circ$ (coplanar symmetric geometry) and $\Psi = 90^\circ$ (perpendicular plane geometry) are in satisfactory agreement with the available experimental data. A deep interference minimum appears in the TDCS in the coplanar symmetric geometry and a strong peak at a scattering angle $\xi = 90^\circ$ caused by the single collision mechanism has been observed in the perpendicular plane geometry. The TDCSs at the gun angles $\Psi = 30^\circ$, and $\Psi = 60^\circ$ are predicted.

IX-U-4 A High Sensitivity Electron Momentum Spectrometer with Two-Dimensional Detectors and Electron Momentum Distributions of Several Simple Molecules

TAKAHASHI, Masahiko¹; UDAGAWA, Yasuo²
(¹IMS and Tohoku Univ.; ²Tohoku Univ.)

[*J. Electron Spectrosc. Relat. Phenom.* **137-40**, 387–391 (2004)]

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.

IX-U-5 Practical Means for the Study of Electron Correlation in Atoms

VAN BOEYEN, Roger W.¹; WATANABE, Noboru²; DOERING, John P.¹; MOORE, John H.³; COPLAN, Michael A.³
(¹Johns Hopkins Univ.; ²IMS and Tohoku Univ.; ³Univ. Maryland)

[*Phys. Rev. Lett.* **92**, 223202 (4 pages) (2004)]

Electron correlation is basic to the understanding of a diverse range of physical and chemical phenomena, yet, there have been no direct measurements of the correlated motion of electrons. Measurement of the correlated momenta of atomic electrons is possible via electron-impact double ionization provided that the ionizing collisions are both impulsive and binary, and the three-body scattering mechanism is known. The results reported here satisfy these conditions, and a practical means for the study of atomic electron correlation through measurement of two-electron momentum densities is presented.

IX-U-6 Development and Use of a Multichannel (e,2e) Spectrometer for Electron Momentum Densities of Molecules

TAKAHASHI, Masahiko¹; UDAGAWA, Yasuo²
(¹IMS and Tohoku Univ.; ²Tohoku Univ.)

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

We have developed an (e,2e) 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 H₂ 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-U-7 Electron Momentum Spectroscopy of Valence Satellites of Neon

WATANABE, Noboru¹; KHAJURIA, Yugal;
TAKAHASHI, Masahiko¹; UDAGAWA, Yasuo²
(¹IMS and Tohoku Univ.; ²Tohoku Univ.)

[*J. Electron Spectrosc. Relat. Phenom.* in press]

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-U-8 Observation of Molecular Frame (e,2e) Cross Section Using an Electron-Electron-Fragment Ion Triple Coincidence Apparatus

TAKAHASHI, Masahiko¹; WATANABE, Noboru¹; KHAJURIA, Yugal; NAKAYAMA, Kazuya²; UDAGAWA, Yasuo²; ELAND, John H. D.³
(¹IMS and Tohoku Univ.; ²Tohoku Univ.; ³IMS and Oxford Univ.)

[*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,2e) 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,2e) 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 H₂ molecules. We believe that this is the first observation of molecular frame (e,2e) cross sections.

IX-U-9 (e,3e) Collisions on Mg in the Impulsive Regime Studied by Second Born Approximation

WATANABE, Noboru¹; COOPER, John W.²; VAN BOEYEN, Roger W.³; DOERING, John P.³; MOORE, John H.²; COPLAN, Michael A.²
(¹IMS and Tohoku Univ.; ²Univ. Maryland; ³Johns Hopkins Univ.)

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

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-U-10 Molecular Frame (e,2e) Cross Sections Observed for Ionization-Excitation Processes of H₂

TAKAHASHI, Masahiko¹; WATANABE, Noboru¹; KHAJURIA, Yugal; UDAGAWA, Yasuo²; ELAND, John H. D.³
(¹IMS and Tohoku Univ.; ²Tohoku Univ.; ³IMS and Oxford Univ.)

[*Phys. Rev. Lett.* submitted]

We report on first kinematically complete experiment of (e,2e) scattering by molecules using the electron-electron-fragment ion triple coincidence technique. Vector correlations among the two outgoing electrons and the fragment ion have been measured for ionization-excitation processes of H₂. The results are used to obtain (e,2e) cross section in the molecular frame and to observe the collision stereodynamics, the phenomenon that has never been explored so far.

IX-U-11 Double Ionization of He by (e,3-1e) at Large Momentum Transfer

KHAJURIA, Yugal; WATANABE, Noboru¹; TAKAHASHI, Masahiko¹; UDAGAWA, Yasuo²; POPOV, Yuri V.³; KOZAKOV, Konstantin A.³; VINITSKY, Pavel S.³; CHULUUNBAATAR, Ochbadrakh⁴
(¹IMS and Tohoku Univ.; ²Tohoku Univ.; ³Moscow State Univ.; ⁴JINR)

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

The present (e,3-1e) experiment aims at investigating double ionization at large momentum transfer that would provide direct information on electron correlation in the target initial state. The (e,3-1e) method involves coincident detection of the two fast outgoing electrons while keeping the slow outgoing electron undetected. It has been found from comparison between experiment and theory that (e,3-1e) momentum profile is very sensitive to the target electron correlation, as expected. In fact, the experimental profile shape is reproduced

well by first Born calculations using highly correlated wavefunctions. However, there is noticeable intensity difference between experiment and theory. The calculation underestimates the experimental cross sections significantly by a few times of magnitude, suggesting need of incorporating higher Born terms and/or more accurate description of correlated electron pair in helium.

IX-U-12 (e,2e) Study on Distorted Wave Effects in the Xe 4d⁻¹ Ionization Process

KHAJURIA, Yugal; WATANABE, Noboru¹; YOSHINO, Tae²; SAKAI, Yasuhiro²; TAKAHASHI, Masahiko¹; UDAGAWA, Yasuo³
(¹IMS and Tohoku Univ.; ²Toho Univ.; ³Tohoku Univ.)

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

Momentum profiles for the Xe 4d⁻¹ ionization process have been studied by means of binary (e,2e) at various impact energies. The results are found to exhibit considerable intensity near the momentum origin that the plane-wave impulse approximation (PWIA) theory can not predict. The discrepancy from PWIA is substantially reduced by distorted-wave theory. Furthermore, momentum profiles for the core 4d_{3/2} and 4d_{5/2} orbitals of Xe are compared with associated theoretical momentum profiles generated using Dirac-Fock wavefunctions to investigate relativistic effects in the ionization process.

IX-U-13 The Impact Energy Dependence of Momentum Profile of Acetone and Comparison with Theory at Its High-Energy Limit

CHO, Tegyon¹; KHAJURIA, Yugal; WATANABE, Noboru²; TAKAHASHI, Masahiko²; UDAGAWA, Yasuo¹
(¹Tohoku Univ.; ²IMS and Tohoku Univ.)

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

We report an electron momentum spectroscopy study of the outermost orbital of acetone. The experiments were performed at impact energies of 800, 1200, 1600 and 2000 eV by using a recently developed multichannel (e,2e) spectrometer. The results at 2000 eV are compared with plane-wave impulse approximation calculations using Hartree-Fock (HF) and density functional theory (DFT). While the DFT calculations reproduce the observations better than HF, noticeable discrepancy between experiment and theory still remains.

IX-V 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-V-1 N 1s Photoionization Cross Sections of the NO Molecules in the Shape Resonance Region

HOSAKA, Kouichi¹; ADACHI, Junichi^{1,2};
TAKAHASHI, Masahiko³; YAGISHITA, Akira^{1,2}
(¹Univ. Tokyo; ²KEK-PF; ³IMS and Tohoku Univ.)

[*J. Phys. B: At., Mol. Opt. Phys.* **36**, 4617–4629 (2003)]

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.

IX-V-2 Shape-Resonance-Enhanced Vibrational Effects in the Angular Distributions of C 1s Photoelectrons from Fixed-in-Space CO Molecules

ADACHI, Junichi^{1,2}; HOSAKA, Kouichi¹;
FURUYA, Shuusaku³; SOEJIMA, Kouich³;
TAKAHASHI, Masahiko⁴; YAGISHITA, Akira^{1,2};
SEMENOV, Sergei K.⁵; CHEREPKOV, Nikolai A.⁵
(¹Univ. Tokyo; ²KEK-PF; ³Niigata Univ.; ⁴IMS and Tohoku Univ.; ⁵State Univ. Aerospace Instrum.)

[*Phys. Rev. Lett.* **91**, 163001 (4pages) (2003)]

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.

IX-V-3 Photoelectron-Photoion-Photoion Coincidence in Ar Dimers

FANIS, Albert De^{1,2}; OURA, Masaki³; SAITO, Norio⁴; MACHIDA, Masatake^{3,5}; NAGOSHI, Mitsuru⁵; KNAPP, Alexandra⁶; NICKLES, Jurgen⁶; CZASCH, Achim⁶; DÖRNER, Reinhard⁶; TAMENORI, Yusuke¹; CHIBA, Hisashi⁷; TAKAHASHI, Masahiko⁷; ELAND, John H. D.⁸;

UEDA, Kiyoshi²

(¹JASRI; ²Tohoku Univ.; ³RIKEN; ⁴Natl. Metrology Inst.; ⁵Himeji Inst. Tech.; ⁶Univ. Frankfurt; ⁷IMS and Tohoku Univ.; ⁸Oxford Univ.)

[*J. Phys. B: At., Mol. Opt. Phys.* **37**, L1–L8 (2004)]

Photoelectron-photoion-photoion coincidence momentum imaging was applied to study 2p photoemission from Ar dimers. We present measurements of the kinetic energy released in fragmentation of Ar₂⁺⁺, angular distributions of energetic fragments, angular distributions of photoelectrons in the laboratory frame and in the molecular frame. The mean kinetic energy of fragment Ar⁺ ions, 2.2 eV, is larger than the value estimated from the Coulomb explosion model with the equilibrium Ar–Ar distance. No significant differences between the photoelectron angular distributions of monomers and dimers can be found in the laboratory frame. The photoelectron angular distributions of dimers in the molecular frame show a minimum for electron emission along the dimer axis at low energies (1.2 and 3.4 eV) and become isotropic at higher kinetic energies.

IX-V-4 Multiplet-Specific N 1s Photoelectron Angular Distributions from the Fixed-in-Space NO Molecules

HOSAKA, Kouichi¹; ADACHI, Junichi^{1,2};
TAKAHASHI, Masahiko³; YAGISHITA, Akira^{1,2};
LIN, Ping⁴; LUCCHESI, Robert R.⁴
(¹Univ. Tokyo; ²KEK-PF; ³IMS and Tohoku Univ.; ⁴Texas A&M Univ.)

[*J. Phys. B: At., Mol. Opt. Phys.* **37**, L49–L55 (2004)]

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.

IX-V-5 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

ADACHI, Junichi^{1,2}; HOSAKA, Kouichi¹;
FURUYA, Shuusaku³; SOEJIMA, Kouich³;
TAKAHASHI, Masahiko⁴; YAGISHITA, Akira^{1,2};

SEMENOV, Sergei K.⁵; CHEREPKOV, Nikolai A.⁵
(¹Tokyo Univ.; ²KEK-PF; ³Niigata Univ.; ⁴IMS and
Tohoku Univ.; ⁵State Univ. Aerospace Instrum.)

[*J. Electron Spectrosc. Relat. Phenom.* **137-40**, 243–248
(2004)]

We have measured molecular-frame photoelectron angular distributions (MF-PAD) for the vibrationally resolved C1s photoelectron from CO molecule in the σ shape resonance region. The MF-PAD's for the $v_f = 0, 1,$ and 2 levels in the C1s $\rightarrow \epsilon\ell\sigma$ 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.

IX-V-6 Coulomb Hole in N₂, CO and O₂ Deduced from X-Ray Scattering Cross Sections

**WATANABE, Noboru¹; KAMATA, Yohei²;
YAMAUCHI, Kota²; UDAGAWA, Yasuo²;
MÜLLER, Thomas³**
(¹IMS and Tohoku Univ.; ²Tohoku Univ.; ³Res. Cent.
Jülich)

[*Mol. Phys.* **102**, 649–657 (2004)]

Accurate total (elastic + inelastic) x-ray scattering cross sections $\sigma_{ee}(q)$ 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. The radial electron pair distribution function $P(r_{12})$ 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 for the first time. Comparison of multi reference configuration interaction (MRCI) and averaged quadratic coupled cluster (MR-AQCC) calculations indicate substantial shortcomings of MRCI due to the lack of size extensivity. The overall agreement with experiment is good but some differences between the theoretical and experimental results remain.

IX-V-7 Absolute Surface Coverage Measurement Using a Vibrational Overtone

**PIPINO, Andrew C. R.¹; HOEFNAGELS, Johan P.
M.²; WATANABE, Noboru³**
(¹Natl. Inst. Standards Tech.; ²Eindhoven Univ. Tech.;
³IMS and Tohoku Univ.)

[*J. Chem. Phys.* **120**, 2879–2888 (2004)]

Determination of absolute surface coverage with sub-monolayer sensitivity is demonstrated using evanescent-wave cavity ring-down spectroscopy (EW-CRDS) and conventional CRDS by employing conservation of the absolute integrated absorption intensity between gas

and adsorbed phases. The first C–H stretching overtones of trichloroethylene (TCE), *cis*-dichloroethylene, and *trans*-dichloroethylene are probed using the idler of a seeded optical parametric amplifier having a 0.075 cm⁻¹ line width. Polarized absolute adsorbate spectra are obtained by EW-CRDS using a fused-silica monolithic folded resonator having a finesse of 28500 at 6050 cm⁻¹, while absolute absorption cross sections for the gas-phase species are determined by conventional CRDS. A measure of the average transition moment orientation on the surface, which is utilized for the coverage determination, is derived from the polarization anisotropy of the surface spectra. Coverage measurement by EW-CRDS is compared to a mass-spectrometer-based surface-uptake technique, which we also employ for coverage measurements of TCE on thermally grown SiO₂ surfaces. To assess the potential for environmental sensing, we also compare EW-CRDS to optical waveguide techniques developed previously for TCE detection.

IX-V-8 Direct Observation of a Symmetry Lowering in Core-Electron Ionization for Highly Symmetric Molecules

**HOSAKA, Kouichi¹; ADACHI, Junichi^{1,2};
GOLOVIN, Alexander V.²; TAKAHASHI,
Masahiko³; TERAMOTO, Takahiro¹;
WATANABE, Noboru³; YAGISHITA, Akira^{1,2}**
(¹Tokyo Univ.; ²KEK-PF; ³IMS and Tohoku Univ.)

(Nature to be submitted)

The Jahn-Teller theorem governs stable structures of crystalline solids and molecules with an element of symmetry. This is because electro-vibrational (vibronic) coupling splits degenerate adiabatic-states by lowering the symmetry. 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 CO₂; 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 CO₂ induced by O1s photoionization.