Electron Diffraction of Trapped Cluster Ions

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Introduction

First results of electron diffraction from C_{60}^{+} ions stored in an rf Paul trap are reported. Gas-phase electron diffraction (GED) has been applied[1] over the past several decades to the study of cluster structures by scattering electrons from cluster beams formed within a supersonic expansion. In this case the relatively broad distributions of cluster size and temperature prevents detailed measurements of structural properties as a function of cluster size under well determined thermodynamic conditions. The application of rf Paul trap techniques both to store mass selected cluster ions and to control their internal energy[2], provides the possibility to apply GED methods to study the size dependence of cluster structure and structural dynamics. This paper introduces the first measurements of trapped ion electron diffraction (TIED).

The experimental apparatus is composed of an electron gun, an ion trap, a multichannel plate detector and a CCD camera assembled on a common axis to maintain alignment. In GED, the orientationally averaged scattering from the molecular structure produces a ring pattern superimposed on a smooth background resulting from the atomic scattering. GED from a neutral C60 beam was used to calibrate and develope this technique with a well defined species whose GED spectrum has been studied previously[3] and to evaluate the constraints imposed by background scattering, detector saturation and rf field perturbations.

Primary effort during the development of the TIED technique was directed towards controlling the background electron scattering, optimizing trap conditions for elastic scattering and evaluating the inelastic electron scattering. We have successfully obtained diffraction patterns from ~ 10^4 trapped C_{60}^{+} ions. The dominant inelastic channels have been identified as primarily due to the formation of multicharged C_{60}^{z+} ions. No evidence of C_{60}^{+} ion fragmentation has been observed.

Diffraction from Trapped Ions

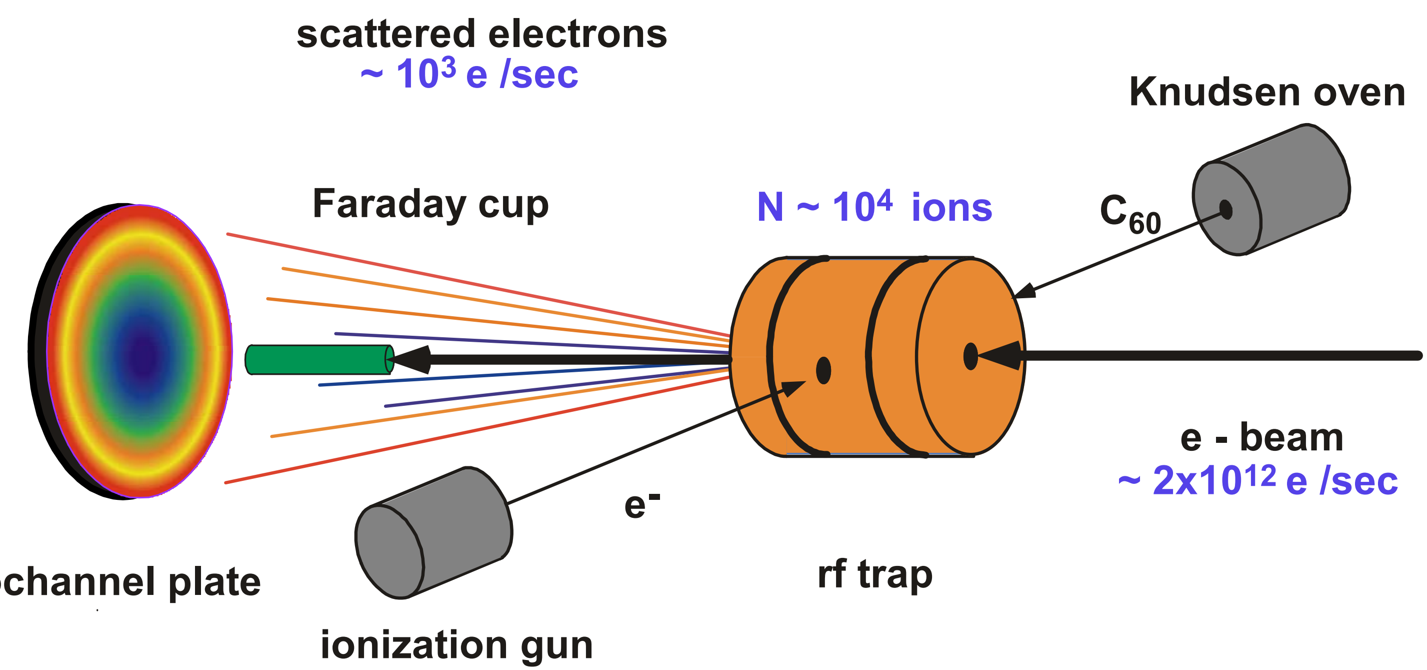


Fig. 1. The overall experimental concept for obtaining diffraction patterns from trapped cluster ions is shown. Cluster ions can be stored in an rf Paul trap by in-situ ionization of an effusive beam emitted by an oven. The trapped ions are then exposed to a high energy electron beam to obtain a diffraction pattern with adeqate S/N to derive structural information. As a result of the orientational and spatial disorder of the trapped cluster ions, the diffraction pattern will be in the form of Debye-Scherrer rings similiar to powder diffraction. The primary issue is the small number (10^2- 10^5) and density (10^6-10^8 cm^{-3}) of trapped cluster ions which leads to a low rate of elastic scattering relative to the incident electron beam. In this situation, it is essential to minimize the electron background scattering within the confined trap volume and the backscattering of high energy electrons from the Faraday cup.

Experimental Setup

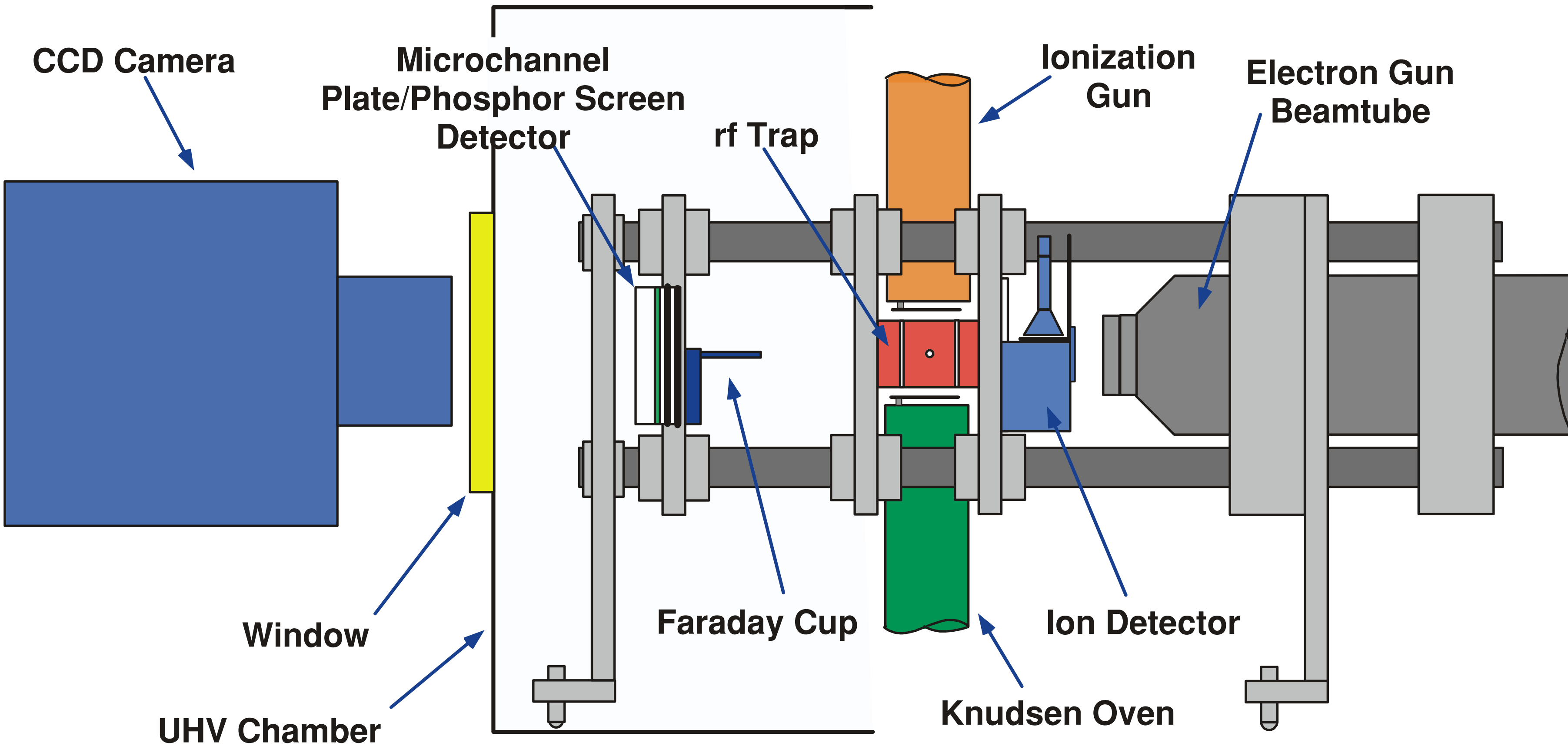


Fig. 2. The experimental setup includes an alignment structure on which the individual components are mounted. The structure maintains a cylindrical symmetry around the electron beam axis and aligns the rf trap, Faraday cup and microchannel plate (MCP) detector along this axis. The CCD camera is mounted external to the UHV chamber and images the phosphor screen within the MCP assembly which displays the diffraction pattern. The vacuum chamber achieves a base pressure of ~10^{-9} Torr and during data taking the pressure is ~10^{-8} Torr. Diffraction data is obtained for e-beam energy of 40 keV and beam current of ~0.4 μA.

Electron Background with Faraday Cup Electron Trap

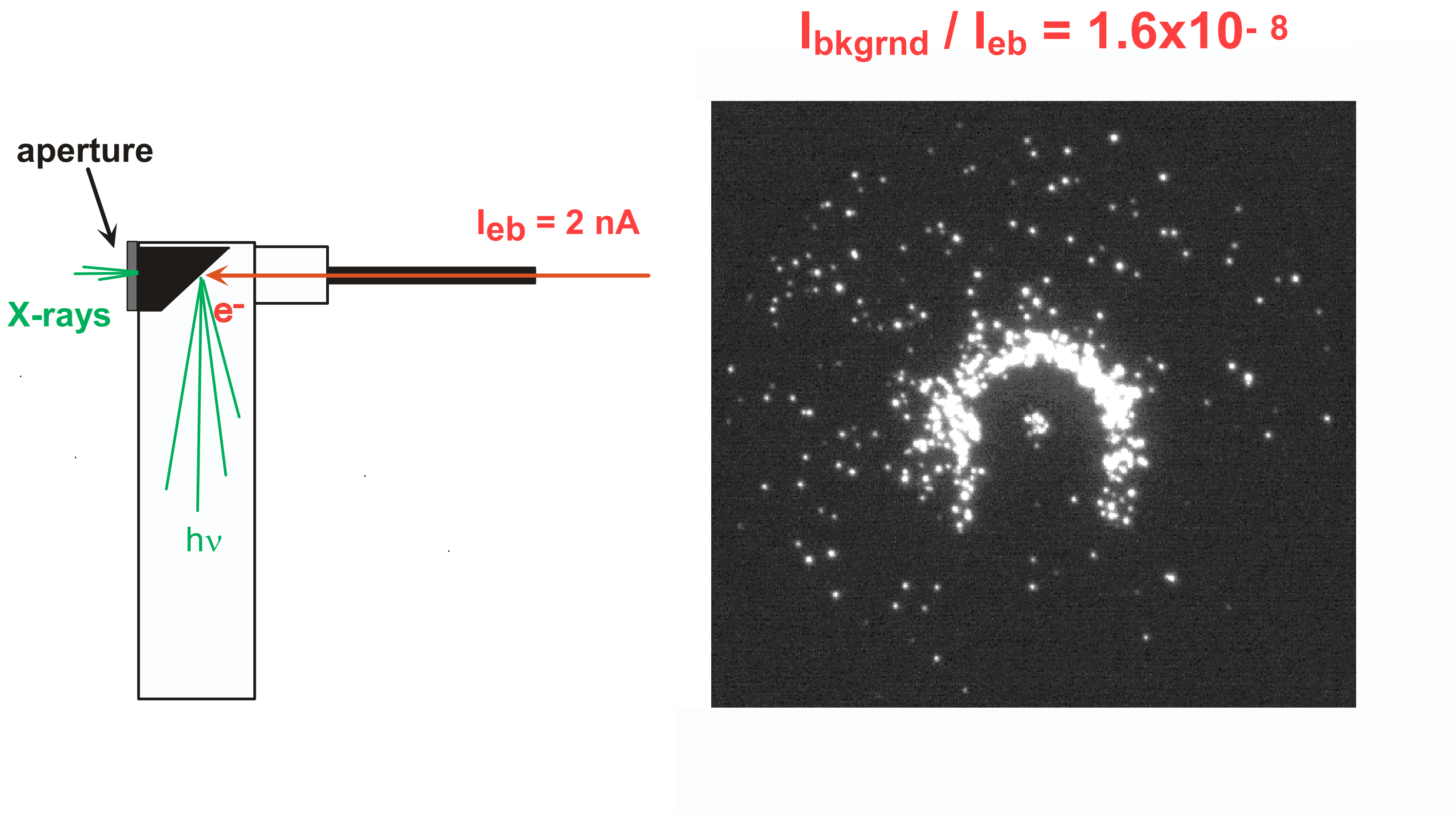
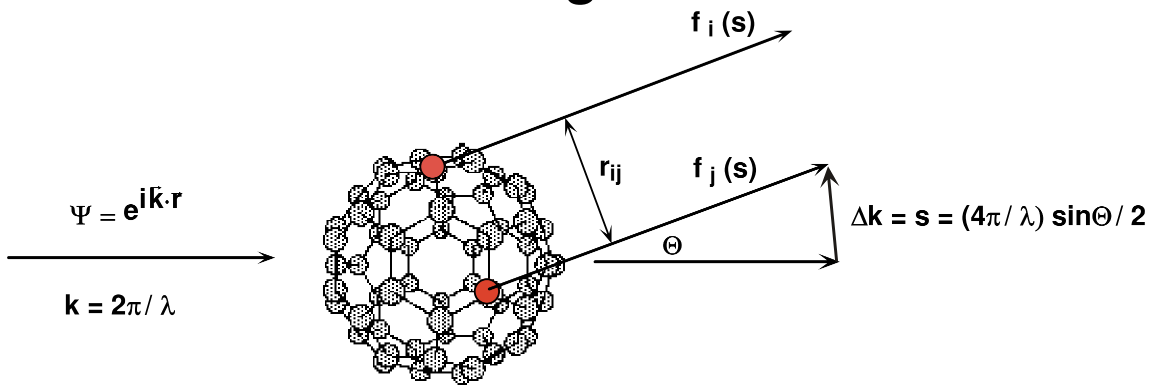


Fig. 3. The background electron scattering was measured by counting the rate of single electron events detected by the MCP at low incident electron beam current (~2nA) in the absence of cluster ions and at the chamber base pressure. The low background level shown above was achieved for a Faraday cup designed as an electron trap which provided asymmetric entry and escape solid angles. In addition the cup was constructed to maximize the conversion of high energy electrons to x-rays which were then absorbed in the walls.

Electron Scattering in Molecules



$$I_{elastic} = \sum_i I_{atom}(s) + \sum_{i,j}' I_{molec}(s) \propto \sum_i |f_i(s)|^2 + \sum_{i,j}' f_i(s)\, f_j^*(s) \frac{\sin(s r_{ij})}{s r_{ij}}\, e^{-l_{ij}^2 s^2 / 2}$$

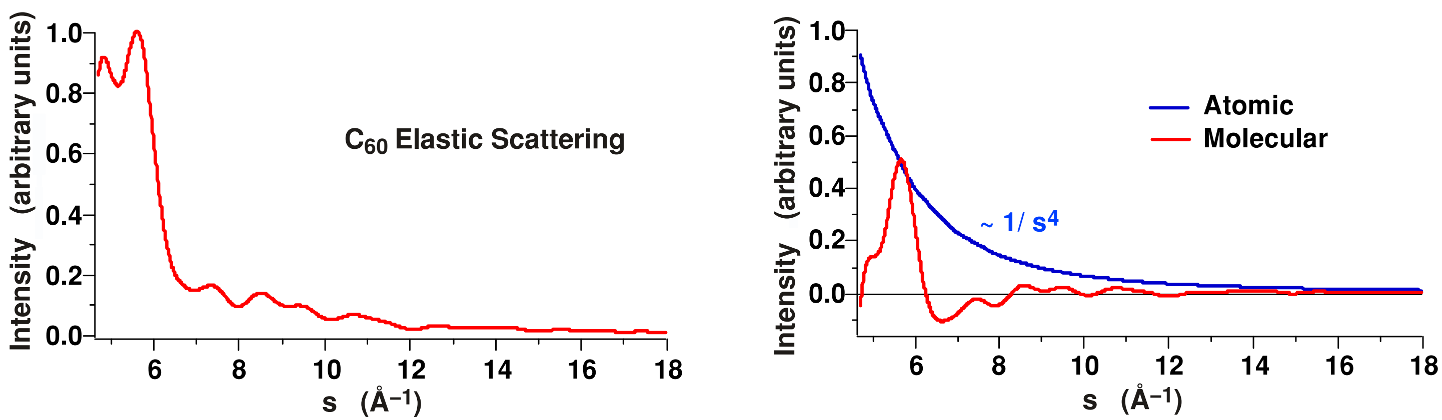


Fig. 4. Gas phase electron scattering in molecules is composed of (a) elastic scattering from individual atoms, (b) the interference of waves scattered from atoms separated by distances characteristic of the molecular structure, and (c) inelastic scattering characteristic of the molecular electron energy states. The orientationally averaged elastic contributions are expressed above in terms of the atomic scattering amplitudes f_{ij} , the atomic separations r_{ij} and the vibrational mean amplitudes l_{ij} . The total elastic scattering intensity distribution is shown on the left as a function of s and the separate contributions of the atomic and molecular scattering are displayed on the right.

BeamData Sequence

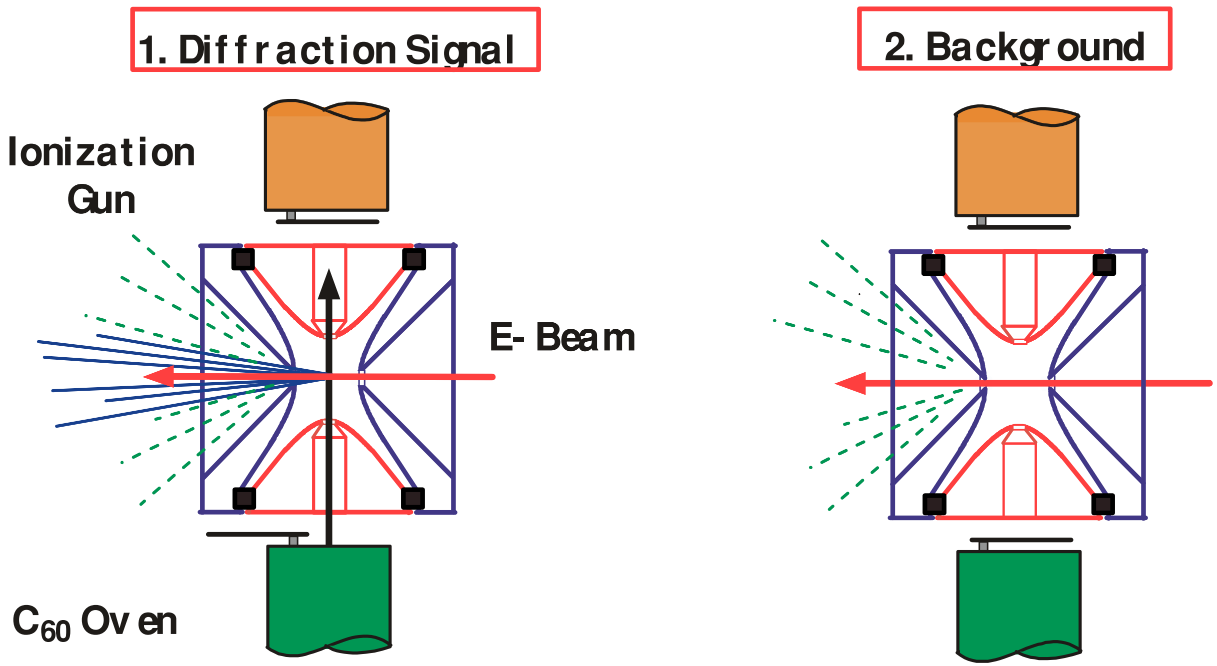


Fig. 5. Diffraction data was obtained first from a neutral beam of C_{60} emitted by the oven source shown in Fig. 2 as it passed through the trap in the absence of rf voltage. In the beam data sequence, the diffraction signal is obtained for a period of time determined by the CCD pixel saturation and then an electron background signal is obtained under identical conditions but with the C_{60} oven shutter closed. This data sequence is repeated over a total experimental runtime of ~2.5 h at an e-beam current of 50 nA and an oven temperature of ~800 K. Using the C_{60} vapor pressure, the number of molecules in the volume defined by the intersection of the molecular and electron beams is estimated to be ~5×10^5.

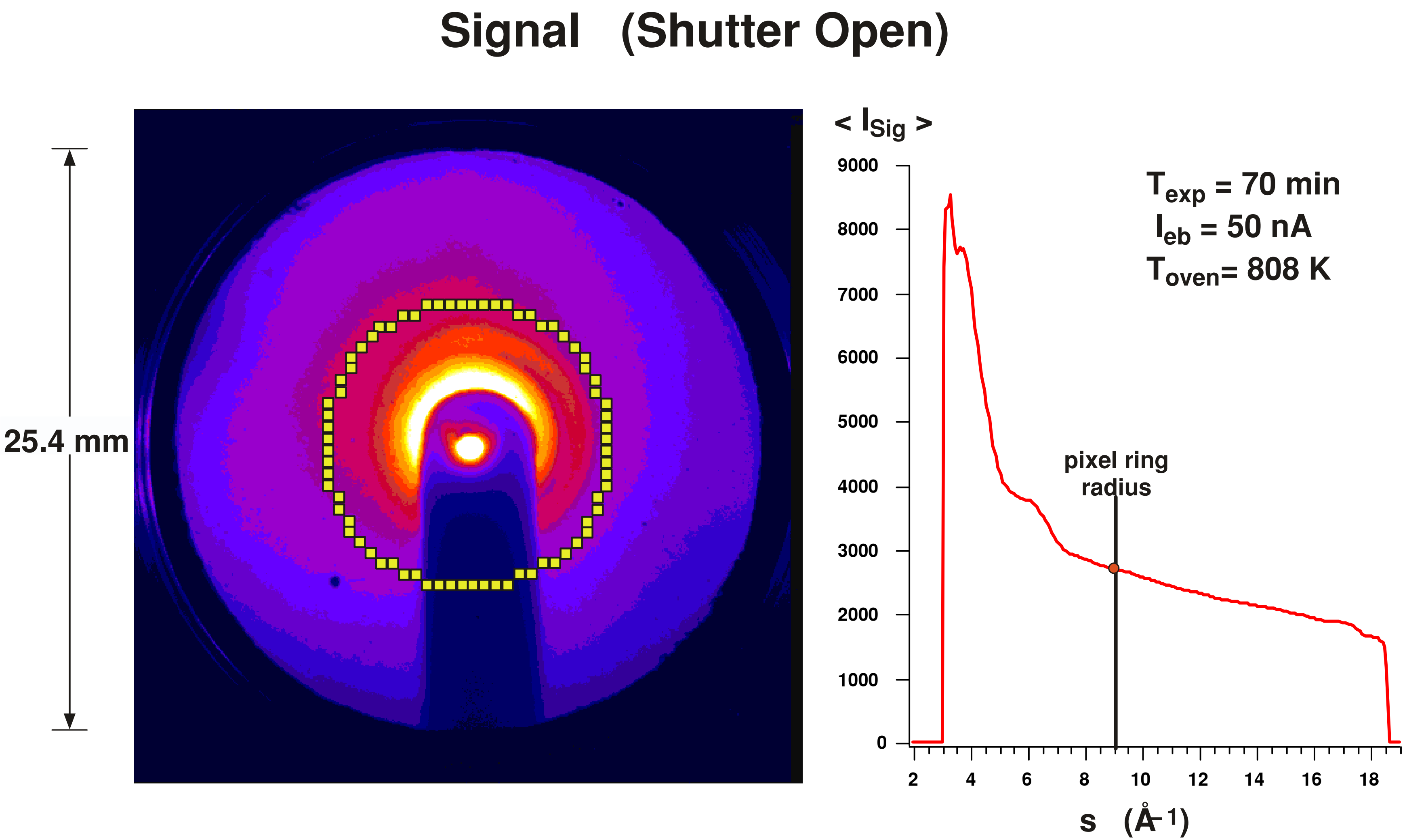


Fig. 6. The pseudocolor image displays the CCD data obtained with the oven shutter open for a total exposure time of 70 min. The MCP diameter of 25.4 mm is indicated. The width of the Faraday cup mount of ~ 7 mm shadows the pattern and the central spot is produced by X-ray emission from an aperture in the cup as shown in Fig. 3. The plot of average signal intensity vs s ($Å^{-1}$) is obtained by averaging the CCD pixels forming a circle around the electron beam axis neglecting pixels shadowed by the Faraday cup. The radius of the circle is related to s through the scattering angle as defined in Fig. 4.

Background (Shutter Closed)

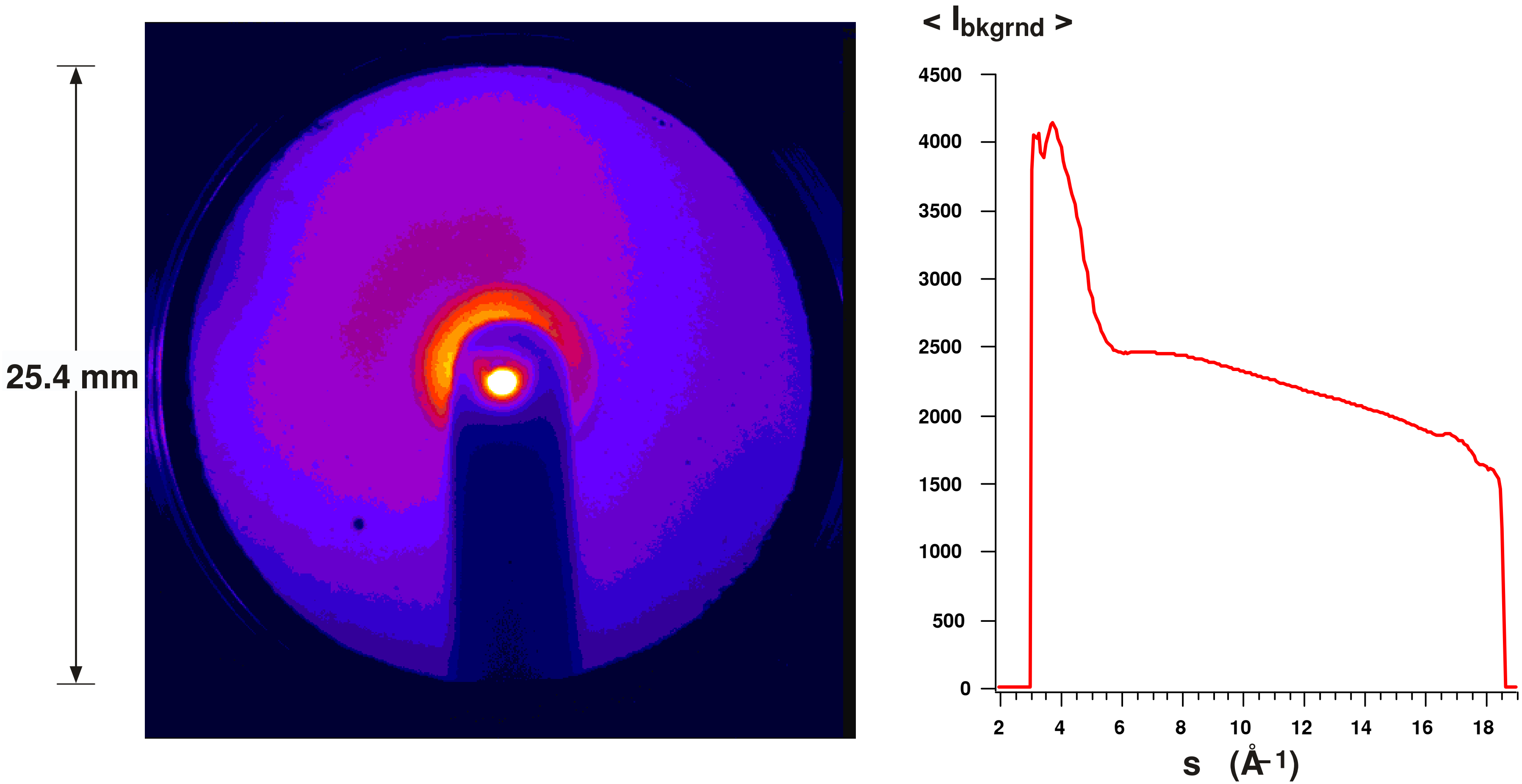


Fig. 7. The pseudocolor image displays the background CCD data obtained with the oven shutter closed for total exposure time of 70 min. The plot of average background intensity vs s ($Å^{-1}$) is obtained by averaging the CCD pixels forming a circle similiar to Fig. 6.

Difference = Signal – Background

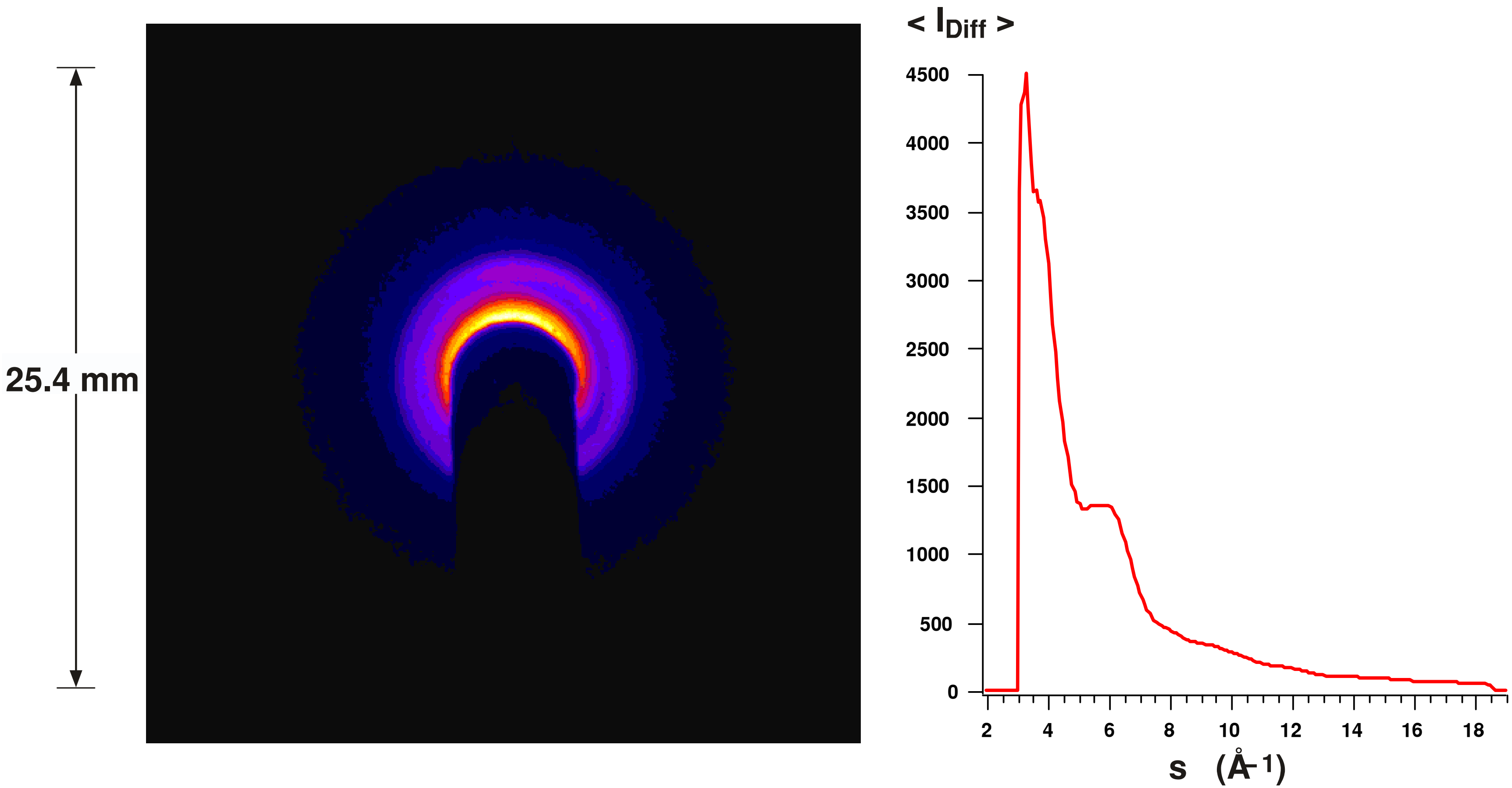
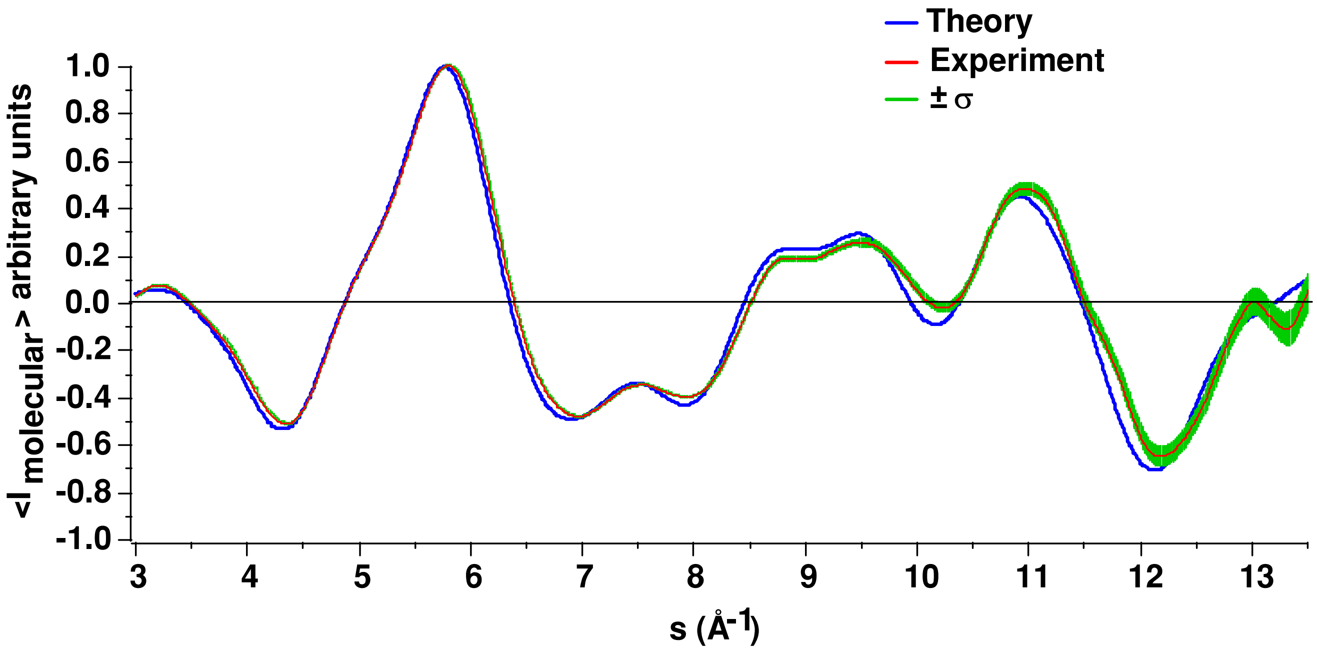
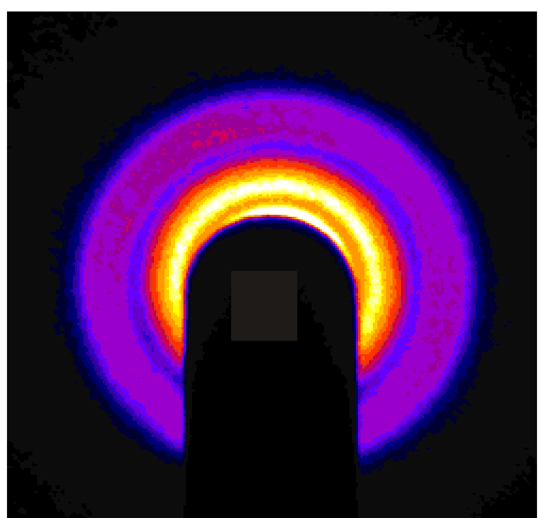


Fig. 8. The pseudocolor image displays the CCD diffraction data obtained by subtracting each background pixel intensity from the corresponding signal pixel intensity and averaging this difference over all sets taken during the 70 min exposure. The plot of average difference intensity vs s ($Å^{-1}$) is obtained by averaging the CCD pixels forming a circle around the electron beam axis similiar to Fig. 6. Note the emerging ring pattern obtained after the background is removed. Also note that except for the region near s=3 $Å^{-1}$ the background intensity exceeds the corresponding diffraction intensity.

C_{60} Neutral Beam Diffraction





i_{eb} = 410 nA

t_{exp} = 0.5 h

T_{oven} = 525 °C

Trap rf Field Effects

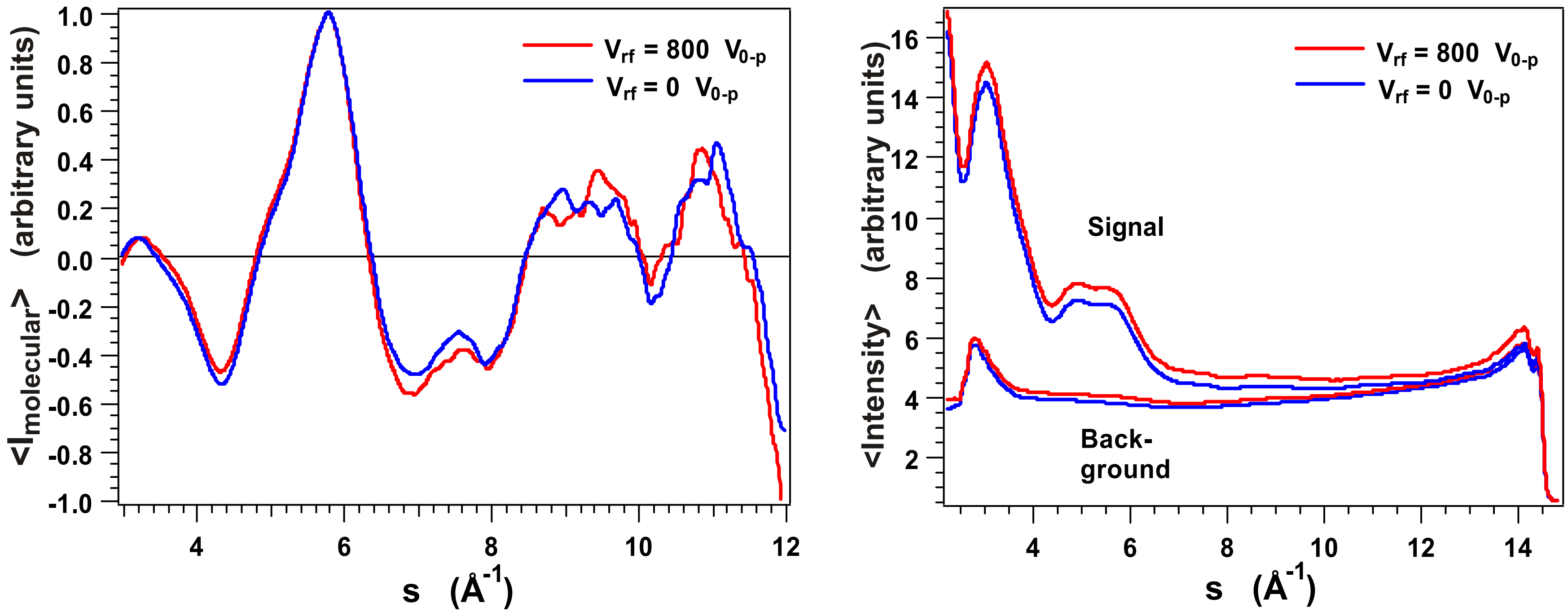


Fig. 10. The possible effects of the trap rf field on the scattered electrons was studied by comparing diffraction data produced by e-beam scattering from a neutral C_{60} beam passing through trap center with the rf field on, with data obtained with the rf field off. The diffraction data shown on the left indicates that V_{rf}=800 V_{0-p} produces no appreciable effect on the diffraction pattern. This is consistent with estimates of the field perturbations of the scattering angle and the electron energy. Plots of the signal and background electron scattering obtained for the C_{60} beam are shown on the right. These indicate that the electron scattering background is slightly increased by the presence of the rf fields. Apparently, electrons derived from ionization events and beam scattering from aperatures are swept out of the trap by the rf fields and increase the measured CCD signals almost uniformly across the detector. The degree to which this might constrain the rf voltage amplitude will depend on the diffracting species.

Trap Data Sequence

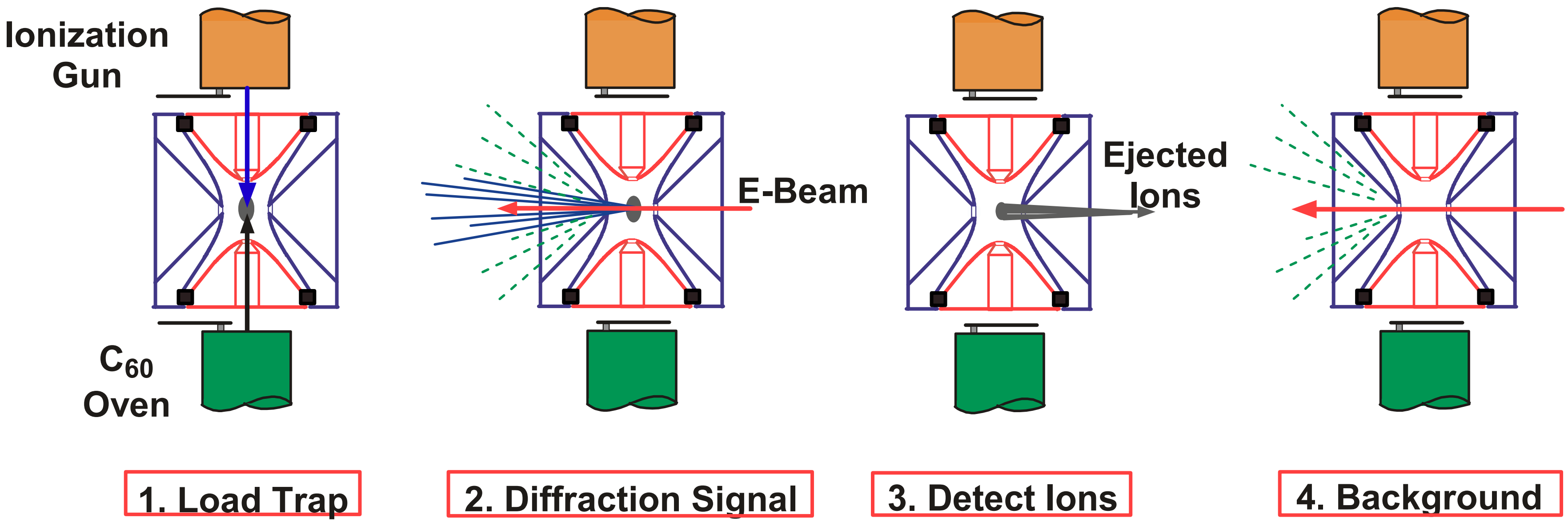


Fig. 11. Diffraction data was obtained from trapped C_{60}^+ by multiple trap loadings. The total experimental runtime is composed of repetitions of the data sequence shown above. After the trap is loaded with ions by in-situ ionization of the C_{60} beam, the C_{60}^+ ion species is isolated by resonantly ejecting all other m/z ions. The C_{60}^+ internal energy is then relaxed using a He gas pulse. The UHV chamber is then evacuated to $\leq 10^{-8}$ Torr and the ions are exposed to the 40 keV e-beam for 45 s to obtain their diffraction signal. After the exposure, the ions are resonantly ejected into an ion detector to observe the mass spectrum. This provides a continuous observation of the inelastic scattering channels as well as a measure of the initial ion number. The background signal is obtained after the ejection of the ions from the trap.

Mass Selection and Detection

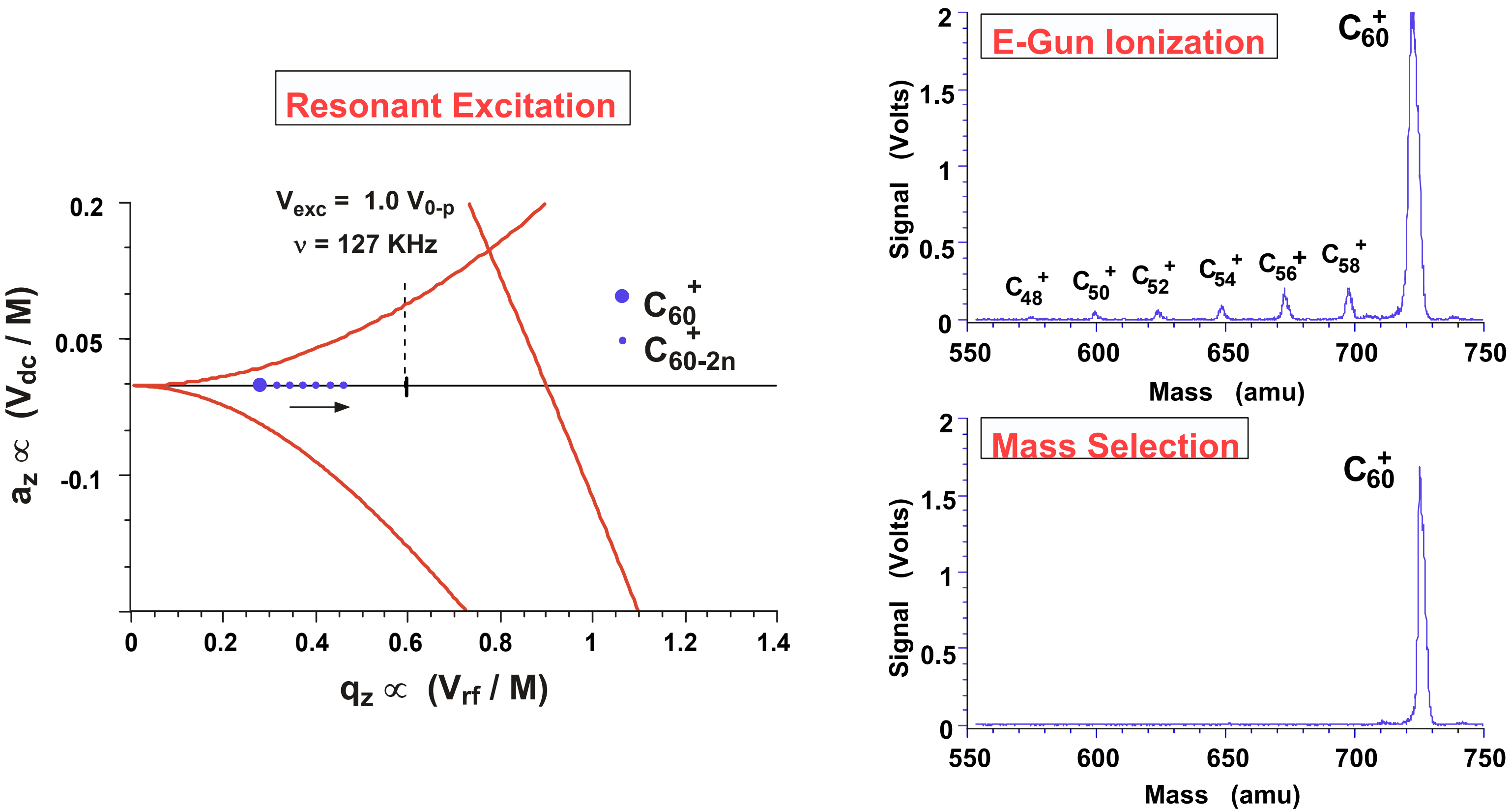
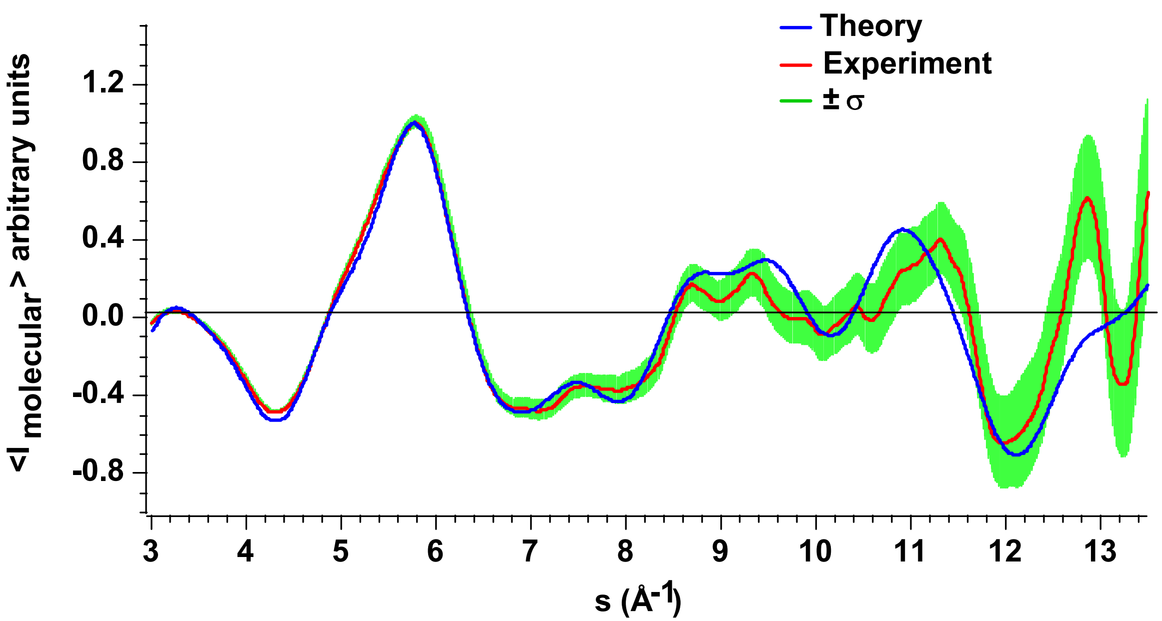
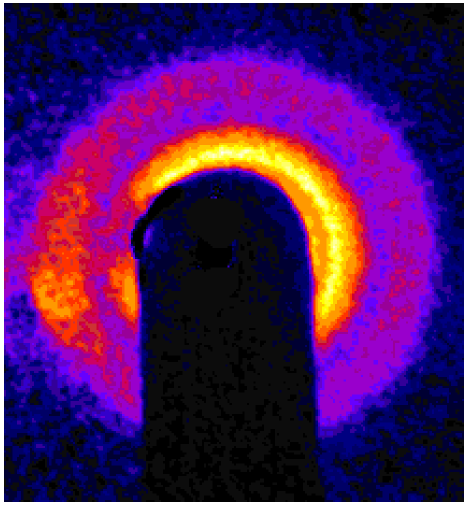


Fig. 12. The trap stability diagram on the left defines the parameter space (a_z, q_z) associated with stable ion trajectories. In these experiments, operating points in this space lie along the line a_z=0 as shown. Mass spectra of ions stored in the trap after in-situ ionization of C_{60} include C_{60}^+ and fragmented fullerenes C_{60-2n}^+, as displayed in the plot at the top right. This spectrum was obtained by varying the rf drive voltage V_{rf} to sweep each specific ion of mass m and charge z sequentially through resonance with an external rf voltage V_{exc}. These excited ions are ejected through the trap endcap aperture and impinge upon the external dynode of an electron multiplier. This resonant excitation is used to isolate C_{60}^+ in these diffraction experiments as shown in the bottom right mass spectrum This resonant ejection process is also applied after the ions are exposed to the 40 keV e-beam to detect the products of inelastic scattering.

C_{60}^{+} Trapped Ion Diffraction





i_{eb} = 400 nA

t_{exp} = 4.5 h

N_{ion} ~ 2×10^4 ions

Inelastic Electron Scattering

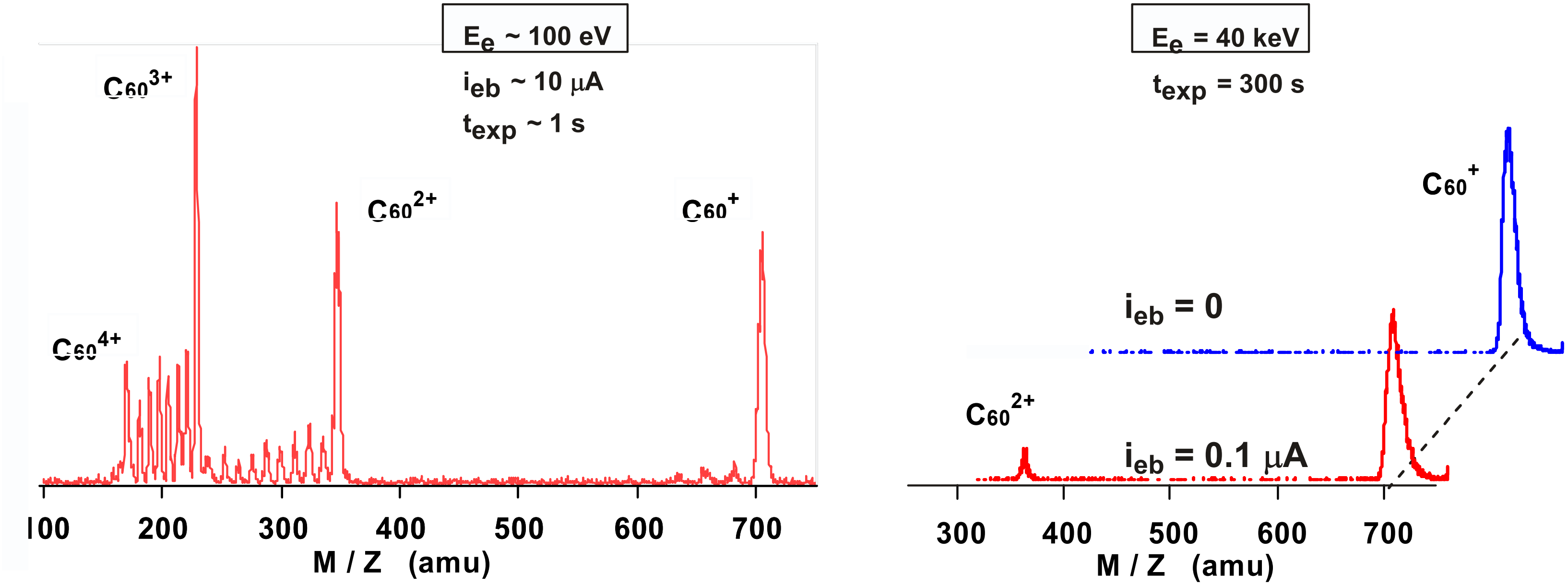


Fig. 14. Inelastic scattering data is shown which compares the mass spectra resulting from exposure of C_{60}^+ ions to low and high energy electrons. The spectrum on the left was obtained by resonant ejection of the trapped ions after ~1 s exposure to the beam of the ionization electron gun having an energy of ~100 eV at a current of ~10 μA. In addition to fragmentation products C_{60-2n}^+, a significant number of multiply charged ions C_{60}^{z+} and C_{60-2n}^{z+} are also produced. The mass spectrum on the right (red curve) was obtained by exposing the trapped ions for 5 min to the 0.1 μA beam of 40 keV electrons used for the diffraction experiments. The blue curve shows the mass spectrum obtained after 5 min without exposure. Note that exposure to the 40 keV beam results in only a slight decrease in the number of C_{60}^+ ions. The dominant inelastic scattering channel observed at these high energies is the production of multiply charged ions; however, in sharp contrast, to low energy electrons, no fragmentation is observed. This is consistent with previous measurements[4] of excitation of gas phase C_{60} by high energy electrons and photons which identified the surface plasmon excitation near 20 eV as the autoionization channel. Since the ionization of C_{60}^+ requires ~12 eV, such an ionization process leaves ~8 eV in internal energy which is not expected to produce significant fragmentation. The trap operating point was chosen so that ions with z >1 were unstable, so that the trapped species was predominantly C_{60}^+ during the 45 s exposure of the diffraction measurements.

Mass Scaling

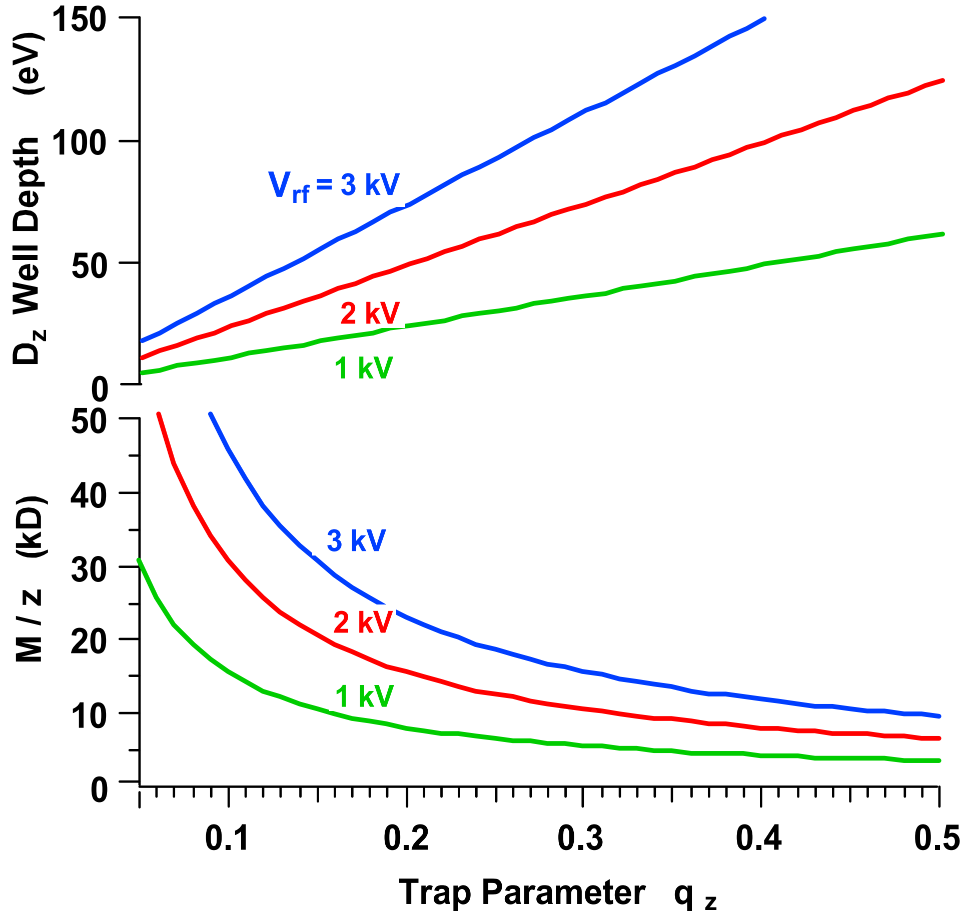


Fig. 15. It is useful to estimate the cluster mass range which could be stored in a given trap geometry considering the rf voltage as a limiting parameter. The mass scaling plot above has been calculated for a trap frequency of 600 kHz and endcap separation z_0=0.3 cm with r_0=Ã2 z_0. These parameters represent a reasonable compromise to reach heavier mass limits with minimum rf voltage. The ion mass and charge which can be trapped at a specific trap stability parameter q_z is shown above. In general lower values of q_z require less rf voltage for a given ion mass. Plots of m/z ion vs q_z and the related trapped ion well depth are shown for several rf drive voltages.

Summary and Discussion

This poster has introduced a new technique to measure electron diffraction from trapped ions (TIED) and has demonstrated the technique by measuring diffraction patterns from ~10^4 C_{60}^+ ions stored within an rf Paul trap. These measurements required a 4.5 h exposure to the ~400 nA current of a 40 keV e-beam corresponding to a total runtime of ~12 h. In this respect, diffraction from C_{60}^+ is an exceptionally severe test of the technique. The experimental system has been designed to integrate a high energy electron gun, an ion trap, a multichannel plate detector and a CCD camera so that diffraction data can be acquired reproducibly over multiple hour exposure times involving hundreds of trap loading cycles. The Faraday cup and the alignment structure have been designed to reduce background electron scattering rates to 10^{-8} of the primary e-beam current. In these first measurements, the diffraction patterns exhibited S/N~10 --2 over the range of momentum transfer s ~3 -11 A^{-1} respectively. The dominant noise contributions were from high energy background electrons, residual neutral gas electron scattering and lower energy electrons ejected from the trap by the rf field. The saturation of the CCD detector by this electron background currently places upper limits on the e-beam current of ~400 nA and on the duration of an exposure cycle of ~45 s. The cloud density was not optimized in these measurements since elastic scattering from He at the pressures (>10^{-6} Torr) required to relax the ion kinetic energy introduces excessive background scattering.

The inelastic scattering channels will always be an important part of these measurements. Monitoring these channels is routinely performed by resonant ejection of the trap contents into an electron multiplier after an exposure cycle. The dominant inelastic channels have been identified as primarily due to the formation of multicharged ions C_{60}^{z+}. No evidence of C_{60}^+ ion fragmentation has been observed. This is consistent with past observations in high energy electron scattering experiments[4] which indicated that the C_{60}^+ surface plasmon excitation with ensuing second ionization dominated the interaction. Since the trap stability of multicharged species is easily manipulated, these higher z ions do not contribute to the diffraction pattern but only lead to a decrease in the number of the parent species.

References

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