Finally, the capacity of NCS-Chrom to generate bistranded lesions with an abasic site (1′ or 4′ chemistry) on one strand and a direct strand break (5′ chemistry) two nucleotides to the 3′-side on the complementary strand results in an unprecedented type of premutagenic lesion.[43] The mutagenicity of the abasic site is probably significantly enhanced by the break on the opposite strand. Because of the loss of the duplex character of the DNA at the lesion site, cellular apurinic/apyrimidinic endonucleases appear to be less effective in removing the abasic lesion,[42a] so that repair of the strand break likely occurs first. This process results in the insertion of a wrong base opposite the noncoding abasic site. With the reestablishment of the duplex structure, the abasic site is removed but replaced by a base determined by the mutagenized lesion on the complementary strand. Uniquely, mutagenesis occurs entirely during the repair process in the absence of DNA replication.

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Fusion Reactions in Dense Hot Atom Assemblies Generated by Cluster Impact[†]

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The nuclear physics of D-D fusion reactions is well understood. The reaction products and the energy liberated have been well characterized. Rates of reaction have been shown to depend on rates of tunneling through the coulomb barrier between the reactant deuteron nuclei. The reactions under consideration are

$$\mathrm{D} + \mathrm{D} = {}^{3}\mathrm{He} + \mathrm{n} + 3.3\ \mathrm{MeV}$$

and

$$\mathrm{D} + \mathrm{D} = \mathrm{T} + \mathrm{P} + 4.0\ \mathrm{MeV}$$

The problem of finding conditions suitable for the practical production of energy from thermonuclear fusion processes has, with the exception of uncontrolled reactions in thermonuclear weapons, so far not been solved. Extensive efforts to develop techniques of magnetic or inertial confinement of dense energetic assemblies of fuel atoms have demonstrated the need for much more research. Additional information is needed in the area of condensed matter science for the solution of the fusion energy problem. An understanding must be developed of the properties of dense systems of atoms capable of sustaining fusion reactions in burning processes analogous to chemical combustion processes. To achieve the energy density and particle density required for ignition of the fusion burning process, matter must be compressed and heated to densities and "temperatures" orders of magnitude larger than those required for chemical combustion.

To appreciate the difficulty of igniting controlled fusion reactions, one should consider the magnitude of the energy and particle densities needed. The power density required for inertially confined fusion is estimated at about 2×10^{14} W/cm^2.[1] But the delivery of energy to an assembly of fuel atoms is not a sufficient condition for the ignition of thermonuclear reactions. The atoms must be in a state of high density, and most of the available energy must be in atomic motion or in the form of translational energy. The "microbombs" needed for the controlled release of fusion energy are of limited size and lifetime and may not survive long enough to establish thermodynamic equilibrium. Consequently deposition of energy into electronic degrees of freedom rather than atomic translations can be very inefficient. With inertial confinement, the efficiency of energy transfer to fuel atoms can be optimized,[1] if energy is delivered to heat surface elements of a pellet containing the fusion fuel to a temperature of approximately 200 eV (approximately 2×10^6 K). If beams of heavy ions were used to directly heat and compress an inertially confined assembly of fuel atoms, then current pulses of the order of 2×10^{12} A/cm^2 would be needed. Space charge limitations[2] prohibit the generation of atomic ion beams with 200 eV kinetic energy and this magnitude of current density.

The mutual repulsion of similarly charged ions moving with relatively low velocities has been a major obstacle to efforts to ignite inertially confined systems of fusion fuel atoms. Winterberg[3] suggested the use of

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macroions as projectiles to overcome this problem. He proposed the use of particles that would require very large accelerators capable of energizing superheavy ions. His ideas did not stimulate experimental effort, in part because of the expense involved and because of the novel technology required.

What was clearly needed was basic research on the problem of generating atomic assemblies with high energy density and high particle density. To this end, we considered the use of cluster ions as projectiles that could directly and efficiently deposit translational energy into a target. The idea was to use particles much smaller than those imagined by Winterberg, but which could be accelerated to sufficiently high velocities with small accelerators. The observation of fusion reactions was not considered likely, but the production of small assemblies of atoms with energy densities and particle densities approaching fusion conditions was considered a distinct possibility.

A cluster containing 100 water molecules accelerated to an energy of a few hundred kiloelectronvolts will impact an area on a target of about 10^{-14} cm^2 in a time of roughly 10^{-14} s. The atomic ion current density needed to deposit energy in the same surface element of the target at the same rate is of the order of 10^{11} A/cm^2. Current densities of this magnitude with particle kinetic energy of a few hundred electronvolts/atomic mass unit cannot be generated because of space charge limitations. Low particle energy (velocity less than 10^8 cm/s) is necessary to insure that most of the energy deposited in the target produces translationally hot atoms rather than electronic excitation. In spite of the fact that heavy water clusters are capable of depositing power at the rate of roughly 10^{13} W/cm^2, cross sections for D–D fusion reactions of deuterons with several hundred volts of energy are too small (less than 10^{-50} cm^2 for 500-V deuterons) to permit experimental observation of fusion events with available cluster beam intensities. But if the impact process generates an assembly of atoms with a fraction of this assembly heated to much higher than average energies, then there might be a chance for experimental detection of fusion products.

Lifetimes of inertially confined atomic assemblies with energy densities of more than a few hundred electronvolts/atom are determined by the size of the assembly. With cluster projectiles of a few hundred atoms generating assemblies of less than a few thousand atoms in the target, formation of Maxwellian energy distributions is not expected. The possibility of alternative mechanisms for the generation of small numbers of "high energy" fuel atoms resulting from the shock waves generated by cluster impact was an area that we thought merited investigation. The search for cluster fusion was in fact a search for "exotic" energy amplification mechanisms in atomic systems subjected to the shock waves associated with cluster impact. These would be processes that would take the energy of a small number of fuel atoms in the dense assembly from values of hundreds of electronvolts/atom to a few kiloelectronvolts/atom.

The idea of an "exotic" energy amplification mechanism was stimulated by consideration of energy amplification processes taking place with shaped charges or in the impact of macroscopic projectiles on solid targets.[4] The impact of a cluster on a solid surface differs significantly from atomic ion impacts in that the simultaneous interaction of n cluster atoms with m atoms in the surface of the solid target establishes a mechanism for target and cluster compression that is unique to the interaction of many-body systems with solids in impact processes. By contrast, an atomic ion is a "point projectile" that penetrates the solid with very little compression of the solid target. Very crude estimates of the magnitude of the energy lost from cluster atoms during the penetration of the target suggest pressures in excess of 50 megabars exerted on the target by clusters made up of atoms carrying kinetic energy of about 1 keV/atom. The properties of matter subjected to transient pressures of this magnitude are not well understood nor are the details of the energy-transfer processes in cluster impact. If cluster impact proceeds via mechanisms similar to those observed with macroscopic projectiles, a cavity surrounded by a sheath of energetic atoms is formed and the shock wave generated with the collapse of the cavity produces an energy amplification.[4] If a fraction of fuel atoms in the projectile–target assembly can be heated to energies much larger than the projectile-atom energy, the possibility for observation of fusion reactions may exist. The recognition of our ignorance of the details of energy-transfer processes in cluster impacts stimulated experiments to search for high energy density assemblies using the D–D reaction as a diagnostic tool.

Discussion of Cluster Fusion Experiments

The apparatus used in our cluster fusion experiments[5,6] is shown schematically in Figure 1. It consists of a differentially pumped cluster ion source, a quadrupole mass analyzer, a Cockcroft–Walton accelerator, and a target chamber containing a target loaded with deuterium (titanium deuteride, zirconium deuteride, or perdeuteriopolyethylene) and a solid-state detector. Two Cockcroft–Walton accelerators have been used, one with voltage up to 325 kV and the second up to 600 kV. With the expectation of relatively low rates of fusion in these experiments it was necessary to maximize the intensity of the cluster ion beams. But the ion beams must also be free of deuterium-containing impurities of low molecular weight which, when accelerated to high velocity, can generate fusion events. The generation of heavy water cluster ions from a mixture of He and D_2O in a corona discharge in the ion source with a large ratio of neutral water molecules to ions served to eliminate deuterium-containing ions of low molecular weight in the ion source. Collisions of ions with neutral water molecules during the expansion of the gas through the source nozzle and skimmer provided additional scavenging of lower molecular weight ions with the formation of a distribution of cluster ions subsequently mass filtered by the quadrupole mass analyzer. Low-resolution mass analysis effectively removes any possible atomic or molecular deuterium ion derivatives and water cluster ions of low molecular weight. The

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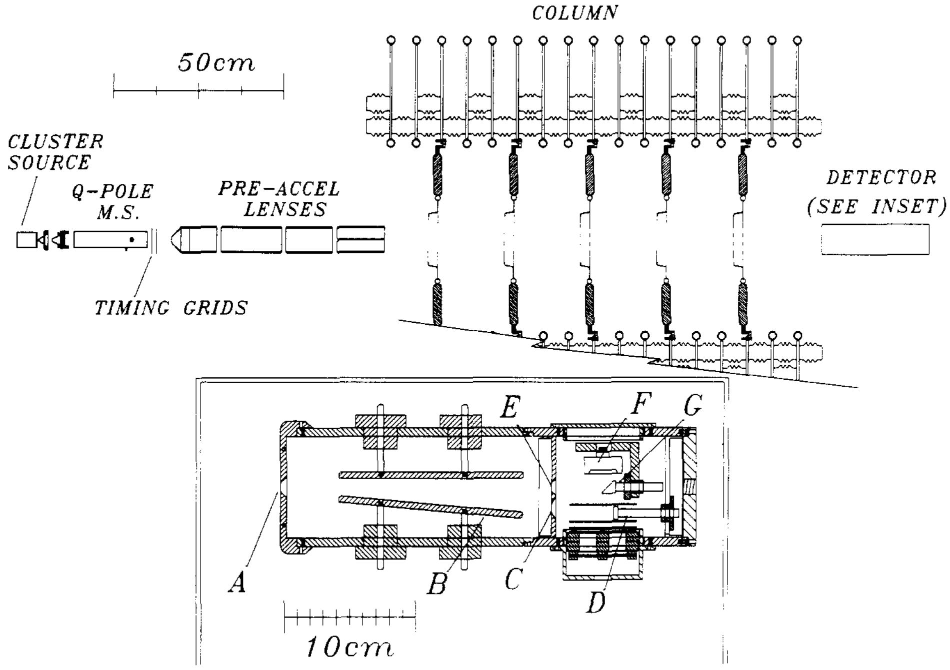

Figure 1. Schematic diagram of the apparatus. A mixture of D_2O and He gas is ionized in a corona discharge in the ion source. The weakly ionized plasma is expanded through a supersonic nozzle in the ion source into a differentially pumped region between the nozzle and the skimmer. Cluster ions are extracted from the skimmer with the drawout lens and mass analyzed in the quadrupole mass spectrometer. A low-frequency (292-kHz) quadrupole power supply capable of mass analysis up to an m/e of about 200 000 was used. The ions are then focused and injected into a Cockcroft–Walton accelerating column. After acceleration the beam passes through aperture A and then between two electrostatic deflection plates B. If no voltage is applied to B, the beam passes through aperture E and strikes a deuterated target G. The charged particles produced by D–D fusions in G are detected in the solid-state detector F. With appropriate voltage applied to the plates B, the beam is deflected so as to pass through aperture C to the copper probe and electron-multiplier assembly D for secondary electron distribution measurements. For time-of-flight experiments the beam is pulsed by the pair of timing grids at the exit of the quadrupole mass analyzer.

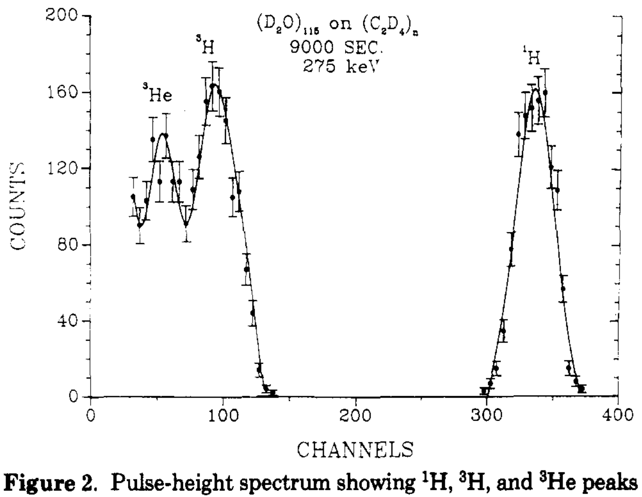

Figure 2. Pulse-height spectrum showing ^{1}H, ^{3}H, and ^{3}He peaks produced by cluster ion impact on a perdeuteriopolyethylene target.

mass-filtered ion beam was then introduced into the acceleration column and focused onto the target. Beam intensities were measured with a 70% transmission copper grid. The ion current measurements, made with a picoammeter, were corrected for secondary electron yields ejected by cluster impacts on the monitor grid; independently determined data on secondary electron yields produced by clusters on copper targets[7] were used to make these corrections.

Secondary electron yields were independently measured with attenuated beams using channel plate electron multipliers. These measurements were necessary to establish the integrity of the cluster beams reaching the target. Individual cluster impacts produce electron pulses that are directly proportional to the number of atoms in the cluster; secondary electron yields can easily reach between 50 and 150 electrons/impact, depending on cluster velocity and the atomic number of the constituent atoms. Degraded cluster beams which are formed by grazing lens or slit elements or by gas-phase collisions under marginal vacuum conditions can be distinguished from beams of much higher molecular weight parent species by observation of secondary electron pulse spectra. Breakup of high-energy clusters into small ion fragments can frequently give stronger current signals on picoammeter detectors but can readily be recognized because the secondary electron pulses produced typically contain fewer than 10 electrons/impact.

D–D fusion protons have approximately 3 MeV of kinetic energy and are easily detected using an energy-sensitive charged-particle solid-state detector. The solid-state detector was mounted in a geometry that collected about 10% of the fusion protons generated in the target. Proof that the charged particles with kinetic energy of 3 MeV were indeed protons was established by use of a 4.8 mg/cm^2 aluminum absorber placed between the target and the detector. This absorber shifted the fusion tritons detected originally at about 1 MeV into the X-ray background and shifted the 3-MeV peak by about 0.30 MeV, an energy loss that identifies the peak as due to protons. With careful X-ray shielding and the use of perdeuteriopolyethylene targets ^{3}He fusion products could be observed as well as fusion protons and tritons. Typical experimental

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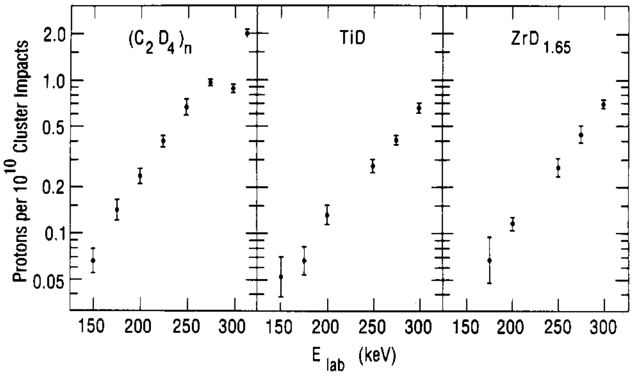

Figure 3. Energy dependence of proton yields (corrected for detector geometry) from D–D reactions produced by impact of 100-molecule cluster ions on the respective targets. Data were obtained with low-resolution mass distributions containing clusters ranging from 50 to 150 water molecules with about 84 and 116 water molecules at the distribution half-height.

results are presented in Figure 2. The ^{3}H and ^{3}He yields were approximately equal, as expected from the known, nearly equal cross sections for the two branches of the D–D reaction. The direct observation of three of the four products of D–D fusion reactions clearly establishes evidence for fusion reactions.

The ability to initiate these reactions with deuterons in clusters moving with relatively low velocities (deuterons with no more than 150 eV/amu center of mass energy) was viewed with considerable skepticism.[8] The initial reaction to these observations was that there must be a small fraction of impurity ions of low molecular weight in the beam, accelerated to velocities sufficient to react with high cross sections. This view was stimulated by our observation of fusion rates that appeared to be more than 20 orders of magnitude larger than rates calculated for 0.3-keV deuterons.

Experiments were carried out to determine rates of fusion as a function of cluster energy. Results are presented in Figure 3. The energy dependence studies clearly eliminate the possibility that beam contamination with fully accelerated (200–300-keV) deuterons was responsible for the observed fusion events. The cross section for D–D reaction in this range changes by less than 50% while the observed fusion rates increase by nearly a factor of 10 in the same energy range. The possibility remained, however, that monomer water ions or derivatives, e.g., OD^+ or D_3O^+, would be accelerated to velocities that would enable constituent deuterons to drive fusion reactions with an energy dependence similar to that observed in our experiments. A variety of experiments were carried out to explore this possibility.[6] All of them led to the conclusion that the observed fusion events are not caused by artifacts or beam contamination. The most conclusive evidence supporting the interpretation that the fusions observed in our experiments were indeed the result of low velocity cluster impacts was obtained in an as yet unpublished time of flight (TOF) analysis of the cluster ion beam and the correlation of fusion events with arrival times of clusters in studies with pulsed cluster beams.[9] In these experiments the beam was pulsed by means of grids prior to entry into the acceleration column (see Figure 1). A calculation of the level of monomer beam needed to account for the observed fusion events at 350 keV gave values roughly 2 orders of magnitude larger than the limits set from the TOF spectra. These results were supported with results obtained in a study of the correlation of the times that elapse between opening the grid gates and observation of fusion protons. More than 90% of the fusion events are correlated with the time required for transit of the clusters from the grid to the target. If fast deuterons or fast water molecule ions were generating fusion protons, they would appear in the first 10% of the times in the respective spectra unless these fast species were generated by decomposition processes in or close to the acceleration column. The direct analysis of beam composition using TOF spectroscopy eliminates this possibility.

The TOF studies appear to be conclusive in establishing a mechanism of energy transfer in cluster-impact processes that produces the energy and particle densities required for D–D fusion at rates much faster than predicted with very simple models. It is difficult at this point to conclude whether the process is driven by a very high compression bringing reactant deuterons into close proximity to increase rates of tunneling through the coulomb barrier or there is an energy amplification mechanism that produces a small fraction of very high energy fuel atoms or both. We noted above that results obtained in macroscopic impact processes suggest a mechanism for the generation of very high energy densities. The use of shaped charges has been exploited for nearly 200 years to produce high-velocity jets with great penetration power.[4] For example, jets of steel with roughly 10 times the velocity of the detonation wave driving them have been observed.[4] The idea of the hollow charge or shaped charge provides a mechanism of focusing the energy of a detonation wave on to a small fraction of material in the apex of a collapsing cone at the center of the shaped charge. There is no problem with energy conservation because only a small fraction of the atoms in the shock wave are heated to high energy densities. Birkhoff et al.[4] have considered the hypothetical case of the collapsing cone with a conical wave front moving perpendicularly to the surface of a conical liner so that it strikes all surfaces at the same instant. The velocity of the jet is given by

$$V_j = (V/\sin\alpha)(1 + \cos\alpha)$$

where α is the angle between the walls of the cone and the perpendicular to the base and V is the detonation velocity. With wave fronts of this sort the velocity of the jet can be increased indefinitely by decreasing the cone angle. But as this angle approaches 0, the mass of the jet also approaches 0 so that there are practical limits for heating finite amounts of material in a collapsing cone. Nevertheless, the model can easily account for an increase of more than 1 order of magnitude in the kinetic energy of atoms in the jet over that in the detonating shock wave.

The fundamental question that remains unanswered is whether it is possible to reproduce, on the microscopic scale of hundreds of atoms, the shaped-charge phenomenon observed with macroscopic projectiles. Research on the impacts of accelerated "micrometeorites" (iron particles much larger than cluster ions used in fusion studies)[10] showed interesting craters generated

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in targets by the impact process. With metal targets, craters containing evidence of jet formation were observed. Studies with larger, more energetic clusters may shed some light on this point.

So far the phenomenon of cluster fusion has been confirmed in one other laboratory.[11] The experimental evidence tends to support the conclusion that dynamic energy focusing that generates high-velocity deuterons can occur in cluster impacts on solids. In another study[12] an attempt was made to produce D-D fusion with D_2 clusters impacting on deuterated surfaces. No fusions were observed. These results can be interpreted as evidence for the need for heavier atoms to establish an energy amplification mechanism. The Lyon group[12] used beam intensities an order of magnitude smaller than ours and did not establish the integrity of the cluster beam at the target with secondary electron analysis. The failure to use beam diagnostics at the target and the sensitivity of cluster fusion reactions to possible target contamination not completely removed in experiments with low beam intensities could possibly account for failure to observe fusion reactions. In our experiments the observation of cluster fusion events depended on maintaining beam intensities above some critical level that would minimize contamination of the target surface. With beams of more than about 0.5 nA, the fusion yields scaled linearly with beam intensity. At lower beam intensities, fusion yields decreased faster than beam currents when the current was varied. Our studies with targets coated with thin gold films[6] also revealed a very high degree of sensitivity of cluster fusion reactions to target surface contamination.

The results obtained in cluster fusion studies are remarkable in that they suggest that the collective interaction of atoms in large molecular projectiles with target atoms can generate "unexpected" energy distributions. The observation of fusion events has so far not been explained by model calculations. Models employing a "Fermi shuttle" in which a pair of deuterons is compressed between a pair of heavy atoms have been proposed.[13-15] This model provides for some energy amplification in a fraction of the hot atoms generated by the cluster impact. Little or no evidence could be found for significant energy amplification with computer simulations that were based on two-body interactions.[8] But so far computer simulations with acceleration of light particles by repeated scattering between heavy beam particles still fail to explain the experimental results. The original discrepancies, as large as 80 orders of magnitude with larger clusters, are reduced to discrepancies ranging from 8 to 18 orders of magnitude. We conclude that the experiments have uncovered an energy amplification mechanism that is operative on a microscopic scale and that is possibly similar to energy-amplification mechanisms observed with macroscopic shaped-charge phenomena.

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Ligand-Coupling Reactions of Hypervalent Species

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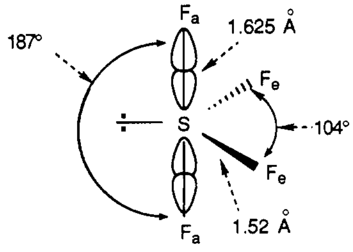
A typical example of a three-center, four-electron bond, called a hypervalent bond by Musher,[1] can be found in the structure of SF_4, as demonstrated by X-ray crystallographic analysis by Rundle et al.[2] and Pimentel.[3] The central atom in a hypervalent species is valence-shell-expanded and tends to extrude one pair of electrons to assume the normal valency of an octet. There are three conceivable ways for hypervalent



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