

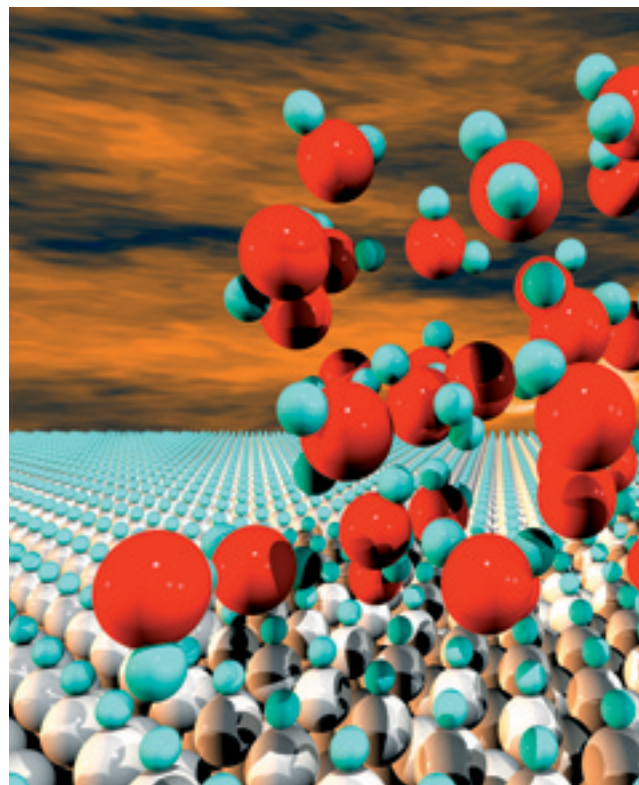
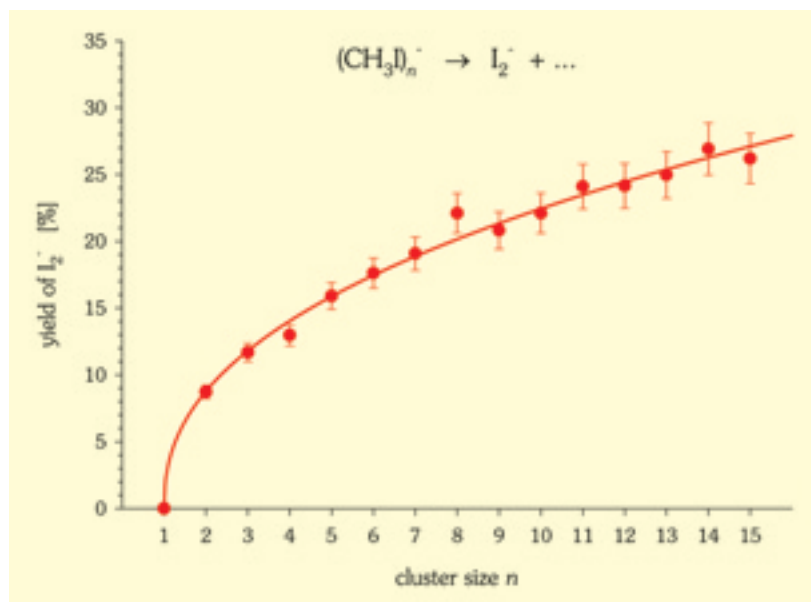
## Collision-Induced Reactions of Molecular Clusters

Due to their importance for heterogeneous catalysis and materials science the interactions of gas-phase particles with solid surfaces have attracted enormous interest. Most investigations however deal with thermal energies and isolated particles, while very little is known about the chemical reactivity at large energy- and particle densities. An exciting, cross-disciplinary approach for the experimental elucidation of chemical and physical processes under such unusual conditions involves the use of molecular reactants embedded in a cluster that is impacted on a solid surface at hypersonic velocities, providing a perfectly defined system on a nanometre scale. These investigations reveal a variety of relevant fundamental mechanisms, including energy transfer, charge transfer, and chemical reactions under (momentarily)

**extreme conditions of pressure and temperature.**

Chemical reactions in extreme environments with conditions beyond common temperatures and pressures play a central role both in basic and applied research. The generation of controlled extreme conditions thus is a primary goal for chemical science – and a challenge for experiment and theory [1]. Prominent examples are the collision-induced synthesis of organic molecules by high-velocity molecular collisions between interstellar clouds as a possible explanation for the »origin of life«, or high-threshold reactions that are relevant e.g. in the commercial production of fertilizers (NO synthesis) or future energy sources (methanol synthesis). Due to their high activation energies, such reactions do not take place regularly under ambient conditions. Because dissociation would precede, they cannot be initiated by conventional heating. One possible approach to overcome this problem is an energy

**Fig. 2**  
Reaction yield of the collision-induced synthesis of molecular iodine  $I_2^*$ , due to the surface-impact of iodomethane cluster ions  $(CH_3I)_n^+$ , as a function of the cluster size  $n$ .



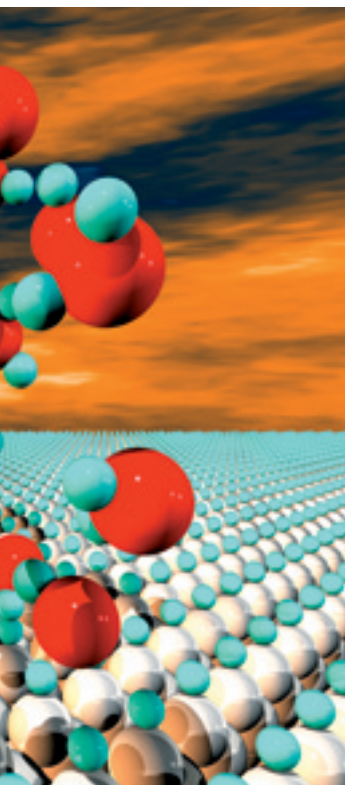
**Fig. 1**  
Simulation of a cluster of 32 water molecules prior to its impact on a hydrogen-terminated diamond crystal.

deposition that is faster than the energy redistribution, realised for example by femtosecond laser pulses or high-velocity collisions. For investigating chemical reactions taking place under such extreme conditions, aggregates with only a few molecules are ideally suited model systems. These perfectly defined midjet liquid-like drops are called clusters.

Thus our experimental approach to explore chemical and physical processes at extraordinarily high pressures and temperatures on a nanometre scale is to impact a molecular cluster, moving at a hypersonic velocity (about ten times the velocity of the molecules at room temperature, 1–10 km/s, or 0.1 Å/fs), on a solid surface, see Fig. 1. The intuitive view provided by molecular dynamics simulations [2–4] is that on impact the cluster is compressed in the direction nor-

### Materie bei hohen Energie- und Teilchendichten

Mit einer neuartigen experimentellen Methode untersuchen wir chemische Reaktionsabläufe bei (kurzzeitig) außergewöhnlich hohen Energie- und Teilchendichten. Die Verwendung von Molekülclustern mit exakt definierter Teilchenzahl unter wohldefinierten Ultrahochvakuum-Bedingungen ermöglicht – in Kombination mit molekular-dynamischen Simulationen – ein Verständnis der ablaufenden Prozesse auf molekularer Ebene. Die gewonnenen Erkenntnisse sind für Astrophysik, Plasma-Wand-Wechselwirkung, Materialwissenschaften und chemische Prozesstechnologien von herausragender Bedeutung.



mal to the surface, because the leading molecules already reach and rebound from the surface, while the rest of the cluster is still moving forward. This sudden increase in particle density, lasting for a few ten to hundred femtoseconds, provides enough time for several collisions to take place, allowing for sufficient energy transfer from translation to vibration. Due to the collisions

within the cluster and between the cluster and the solid surface, the initially directed velocity of the cluster will be rapidly redistributed. The resulting energy content is controllable via the initial collision velocity. Shortly after the impact, the cluster will disintegrate into fragments, a process that can be regarded as advantageous as it serves to isolate the nascent reaction products from further collisions.

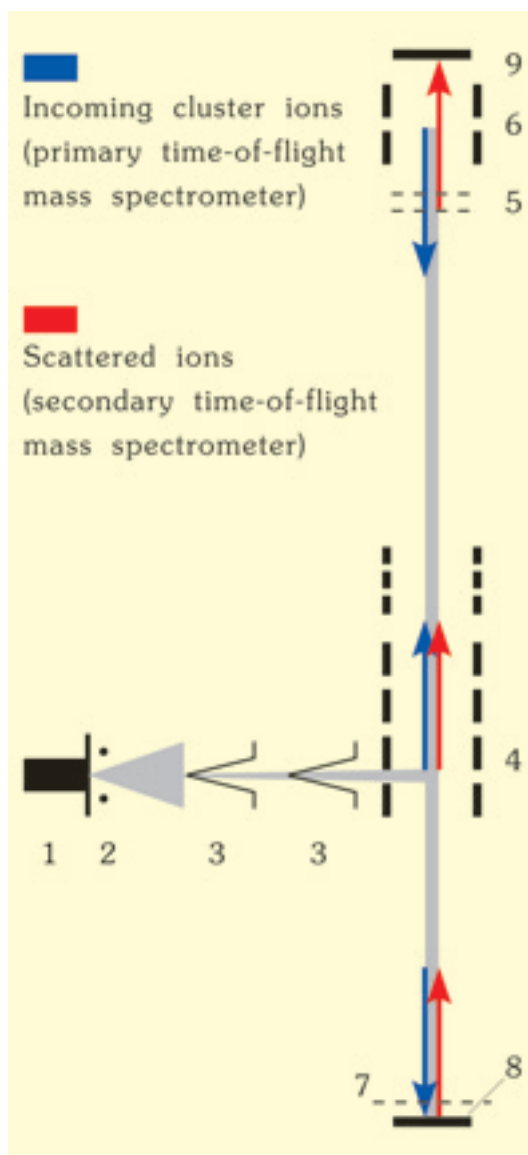
While both simulations and experiments have shown that bond *dissociation* can occur within a cluster compressed by the impact on a solid surface, initially it was much less obvious whether bond *formation* is also possible in the very short time between cluster impact and subsequent cluster fragmentation. This question has been experimentally answered only recently [5,6] by the demonstration of the collision-induced reaction of iodomethane cluster ions  $(\text{CH}_3\text{I})_n^-$  to molecular iodine  $\text{I}_2^-$ . Four-centre collisions, involving the switching of covalent bonds, such as  $\text{CH}_3\text{I} + \text{CH}_3\text{I} \rightarrow \text{I}_2 + \text{CH}_3\text{CH}_3$ , are nominally »forbidden« because of an unfavourable orbital correlation [7] with a high barrier

along the reaction coordinate, requiring vibrational excitation of the reactants. Beside the non-linear cluster-size dependence, a very remarkable result is the surprisingly large reaction yield, shown in Fig. 2.

Our experimental configuration is depicted in Fig. 3 and consists of a pulsed cluster-ion source, a primary time-of-flight mass spectrometer including a pulsed mass-gate, and the UHV (Ultra High Vacuum) target collision chamber containing a secondary time-of-flight mass spectrometer for product-ion analysis. The most important experimentally accessible parameters are the available kinetic energy and the size of the cluster, because in such small systems chemical and physical properties strongly depend on size. From a

**Fig. 3**

*Sketch of the experimental setup: Molecular cluster ions are generated efficiently by pulsed, supersonic expansion (1) of the gaseous substance diluted in a carrier gas and subsequent ionisation by electrons emitted from a pulsed filament (2). The expanding jet is collimated by two consecutive conical skimmers (3) and passed to the primary time-of-flight mass spectrometer (4). Here ions are extracted perpendicular to the axis of the neutral beam, accelerated to kinetic energies of about 6 keV, and mass-selected by a pulsed mass-gate (5). After reflection (6), they are guided towards the target (8) and decelerated to the desired collision energy by the use of a strong retarding field between a grounded mesh (7) and the target surface, to which a high voltage is applied. Ions leaving the target are reaccelerated, allowing a mass analysis through their time-of-flight from the target to the detector (9).*





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chemical point of view, the energy range from 0.1 eV/molecule to about 10 eV/molecule is especially interesting, as it allows fragmenting the cluster, dissociating the molecules within the cluster, and forming new chemical bonds without destroying the solid substrate. Because the target surface is mostly used as energy converter, it is chosen to be chemically inert, focussing on intra-cluster reactions.

To summarise, key features of the novel method of collision-induced reactions of molecular clusters are the

- exceptionally fast activation, allowing for a very efficient redistribution of the initially directed kinetic energy of the cluster into internal excitations of the molecules
- short-term compression of the cluster, enabling frequent simultaneous collisions of several molecules, that significantly should ease three- and four-centre reactions
- locally high energy density, enabling to surmount even very high activation energies
- sterically suitable solution of the reactants within the cluster, facilitating high reaction cross sections as compared to the gas phase
- perfectly defined and freely adjustable composition of the reactants within the cluster with the precision of a single molecule.

No other experimental technique is available to provide this unique combination of unusual parameters: cluster-surface collisions thus allow the systematic investigation of ultra fast processes under exceptionally high energy- and particle densities under well-defined conditions.

In particular, one goal of our studies is to explore the possibility of influencing the outcome of collision-induced reactions, e.g. by employing inert solvent molecules such as argon or xenon. During impact, they will act as collision partners, possibly affecting the reaction mechanism.

Other central questions include: Given a reaction with two product channels, will the yield be thermodynamically controlled, and what are the parameters affecting the branching ratio? How does the cluster size influence the reaction yield? Do all molecules within the cluster contribute equally or is there a preference for molecules within the cluster, or for molecules on

the cluster surface? Is it possible to detect collective effects such as shock waves?

We are therefore keen to advance the new experimental method allowing us to explore the exciting opportunities of chemical reactions in extreme environments.

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