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Chemical reactions induced by cluster impact

I. $(CH_3I)_n^- \rightarrow I_2^-$

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Abstract. This contribution addresses the reactive scattering of iodomethane cluster anions off a diamond-coated silicon surface in the kinetic energy range of 1–100 eV/molecule. We report the experimental result of an impact-induced and cluster-specific chemical reaction. The measured yield for the reaction $(CH_3I)_n^- \rightarrow I_2^-$ is surprisingly high. Even for the small cluster-anions investigated here, $n < 15$, a relative reaction yield of more than 15% I_2^- molecules per I^- fragment could be observed.

PACS. 34.50.Lf Chemical reactions, energy disposal, and angular distribution, as studied by atomic and molecular beams – 36.40.Jn Reactivity of clusters – 61.46.+w Clusters, nanoparticles, and nanocrystalline materials – 82.40.-g Chemical kinetics and reactions: special regimes and techniques

1 Introduction

In recent years there has been increasing research interest in the interaction of (large) molecular ions with solid surfaces. At hyperthermal energies, molecular ions mostly dissociate upon surface impact, revealing rich chemistry in their fragmentation and reaction pattern. Cluster-ion–solid-surface collisions [1–36] are thought [34–72] to have unique characteristics due to the temporary buildup of high particle densities and the ultrafast dissipation and redistribution of significant amounts of energy within a very localized region.

While collision-induced dissociation reactions are well known from surface scattering of individual molecules, the most demanding challenge for cluster–solid-target collisions are cluster-specific, collective phenomena, such as the formation of new chemical bonds [68–74]. Previous work in our lab [35, 36] has focused on the mechanism and the time scale of cluster fragmentation. We have been able to show that the time needed for the complete fragmentation of protonated ammonia cluster cations upon surface impact is much faster than a sequential loss process such as metastable cluster dissociation. This ultrafast dissipation of energy within the impact-heated cluster suggests that this energy will be available to activate reactants in the cluster, and also implies that the products of any chemical reaction will be kinetically stable, because the cluster rapidly disintegrates after its impact and thus will not be able to confine or relax the products.

This article experimentally examines the inelastic interaction of negatively charged clusters of a simple organic molecule, methyliodid, with a solid, nonreactive diamond surface in the kinetic energy range of 1–100 eV/molecule, presenting a collision-induced and cluster-specific chemical reaction.

2 Experimental setup

The basic setup of the experimental apparatus has been described in detail elsewhere [36]. Here we give only a brief description of the features relevant to the present study.

The instrument used for our investigations consists mainly of a pulsed cluster-ion source, a primary time-of-flight mass spectrometer, a pulsed ion-mirror serving as a mass-gate, and an ultrahigh vacuum target collision chamber containing a secondary time-of-flight mass spectrometer for product analysis.

Cluster ions are efficiently generated by the supersonic expansion of gaseous methyliodid diluted in a mixture of 70% neon and 30% helium as carrier gas, and the subsequent ionization by electrons emitted from a pulsed filament. The jet source consists of a home-built pulsed valve with a 0.5 mm conical orifice [75]. Operation conditions are $\simeq 100\,\mu$s pulse width, 10 Hz repetition rate, 120 kPa stagnation pressure and 330 K stagnation temperature. Electrons are emitted from a circular, shielded, glowing thori-

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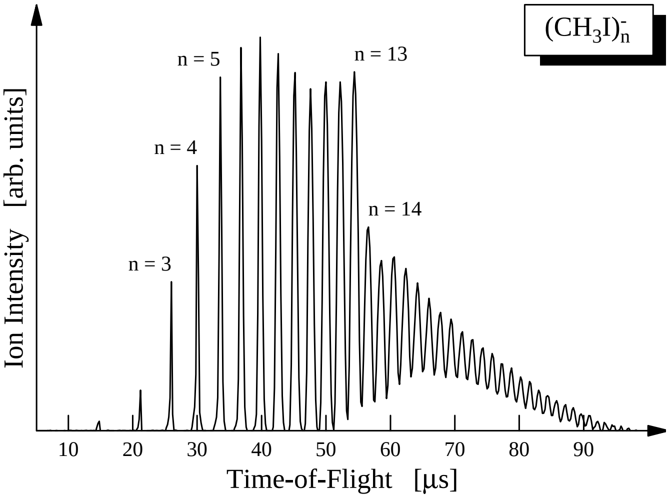

Fig. 1. Primary time-of-flight mass spectrum of iodomethane cluster anions $(CH_3I)_n^-$, measured with the ion mirror acting as a Faraday cup.

ated tungsten filament, located $\simeq 2$ mm from the nozzle, and are accelerated to 70–120 eV by a 4–10 μs voltage pulse. The expanding jet is collimated and passed to the primary time-of-flight mass spectrometer. Here ions are extracted perpendicular to the axis of the neutral beam and accelerated to a kinetic energy of about 2 keV. Mass selection of the beam is achieved by pulsing the high voltage applied at a planar ion mirror, at the correct timing, deflecting a single cluster size by 90° into the UHV scattering chamber. Incident cluster ions are perpendicular to a silicon target, which is coated with a $\simeq 10\,\mu$m thick p-type diamond film [76] and heated to about 400 K. This target shows several important characteristics: (a) it is electrically conductive ($\simeq 80\,\Omega\,\mathrm{cm}^{-1}$) with a high secondary-electron emission; (b) the possible presence of adsorbates can be detected with high sensitivity [36]; and (c) its high Debye temperature allows for a small loss of kinetic energy of the cluster ions to the target [28,36]. Prior to impact, cluster ions are decelerated to the desired collision energy by the use of a strong retarding field between a grounded mesh and the target surface, to which a high voltage is applied. The same high field ($\simeq 10^6\,\mathrm{V\,m}^{-1}$) that decelerates the incoming cluster ions is also used to efficiently collect and reaccelerate scattered ions. It allows a mass analysis of fragment ions through their time-of-flight from the target to the detector. The temporal zero in these secondary time-of-flight mass spectra is accurately defined by secondary electrons emitted from the target as a result of the impacting cluster anions. The second time-of-flight mass spectrometer is equipped with a retarding field energy analyzer in front of the ion detector to determine the kinetic energy distribution of ions. This measurement is accomplished by a mass-specific integration of transmitted ions as a function of the retarding voltage of the analyzer. As has been shown previously [36], the measured data can be fitted accurately to an error function, which corresponds to a Gaussian energy distribution of the beam. The Gaussian maximum is taken as the mean kinetic energy of the ions. The energy spread of the primary cluster beam is less than 1% of the kinetic energy.

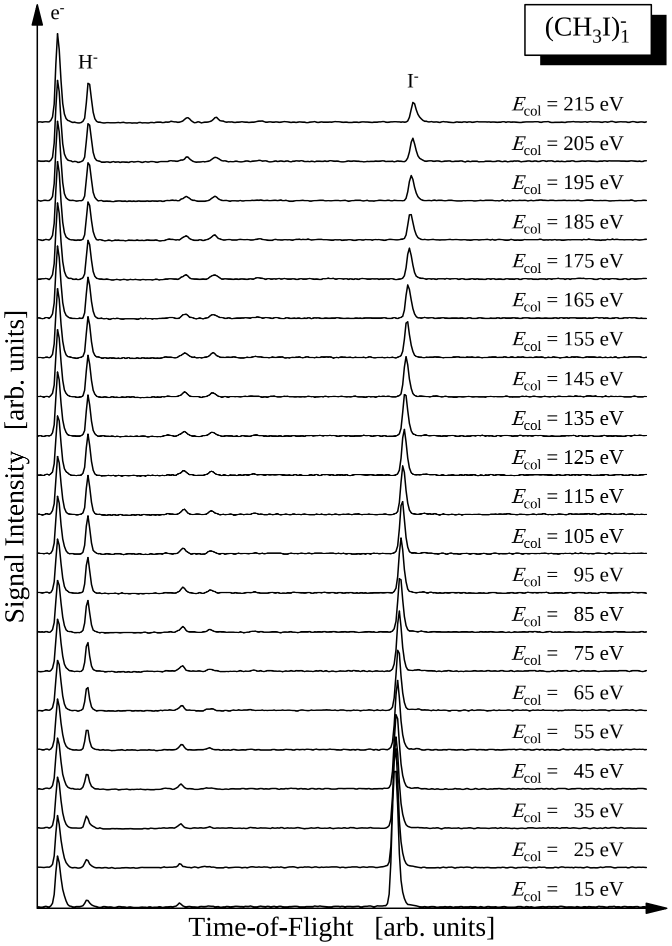

Fig. 2. Secondary time-of-flight mass spectra due to the impact of molecular anions CH_3I^- on the diamond target. The emission of secondary electrons from the target surface reflects the temporal shape of the impacting ion beam and allows an accurate mass analysis.

3 Results and discussion

Our first example of a chemical reaction induced by cluster ions colliding with a solid surface is the reaction of iodomethane cluster anions $(CH_3I)_n^-$ to molecular iodine I_2^-. Figure 1 presents a primary time-of-flight spectrum of the $(CH_3I)_n^-$ cluster beam. Two features are of interest here: First, the pronounced change in intensity from $(CH_3I)_{13}^-$ to $(CH_3I)_{14}^-$ cluster ions is due to the first solvation shell. Second, contrary to other experiments [77–79], expansion conditions can be chosen where neither ionization-induced fragment anions (such as methyl groups or atomic or molecular iodine) nor the $I^-{\cdot}CH_3I$ ion-dipole complex can be detected. Possible explanations might be the very early ionization process or that smaller clus-

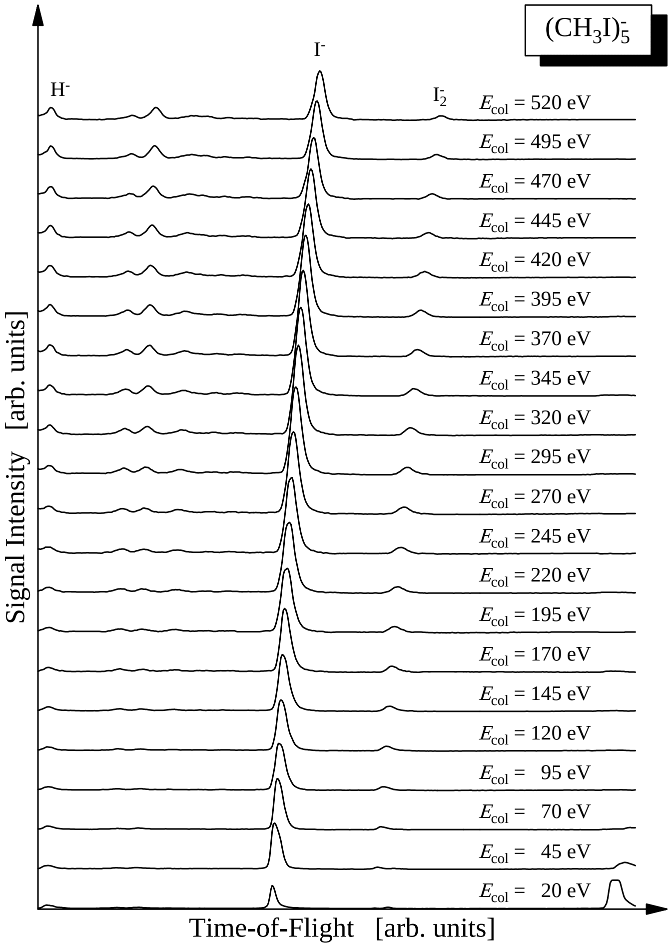

Fig. 3. Secondary time-of-flight mass spectra of anions scattered off the diamond target surface after the impact of iodomethane cluster anions $(CH_3I)_5^-$.

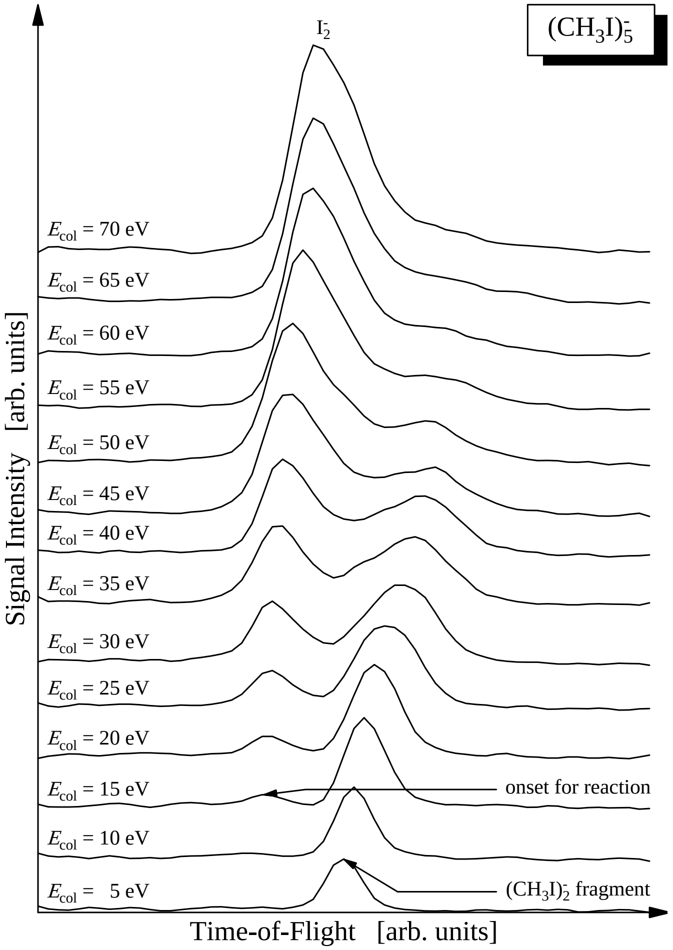

Fig. 4. High-resolution secondary time-of-flight mass spectra due to the impact of $(CH_3I)_5^-$ cluster anions, demonstrating the transition from cluster fragmentation to cluster reaction as a function of the collision energy E_{col}. The energy threshold for detecting the molecular iodine ion is approximately 15 eV.

ter ions (including the monomer) result from fragmented, larger clusters only.

Scattering molecular anions off the diamond surface results in secondary time-of-flight spectra, as shown in Fig. 2 for impact energies $E_{col} = 15$–$215\,eV$. The most abundant collision products are secondary electrons, hydrogen anions H^-, and the atomic iodine fragment anion I^-. Within our sensitivity, no molecular iodine anions I_2^- can be detected.

Secondary time-of-flight spectra of colliding cluster anions are presented in Fig. 3 for the iodomethane pentamer $(CH_3I)_5^-$: For all collision energies investigated, the atomic iodine fragment ion is the dominating mass peak, whereas the yield of secondary hydrogen anions is much smaller than in the case of CH_3I^-. Other small ions such as $C_2H_2^-$ can be detected as well. In this case, however, it is not possible to safely distinguish between cluster fragments and sputtered target molecules as the origin of these mass peaks. At fairly low collision energies, $E_{col} < 45\,eV$, some surviving parent cluster anions $(CH_3I)_5^-$, as well as a few iodomethane dimer fragment ions $(CH_3I)_2^-$, can be observed. Whereas the dimer anions gradually cease to exist for higher impact energies, a new peak due to molecular iodine I_2^- evolves for collision energies $E_{col} \gtrsim 15\,eV$. It reaches its maximum intensity at $E_{col} \simeq 200\,eV$ where it saturates. This transition from cluster impact-induced fragmentation to cluster impact-induced reaction as a function of the collision energy is shown in more detail in Fig. 4. These measurements allow an estimate of the energy threshold for the detection of the molecular iodine anion I_2^-.

A quantitative evaluation and the comparison of yields of scattered ions is made possible by a mass-specific integration of the secondary ion signals, depicted in Fig. 5, as a function of the collision energy E_{col}: At very low collision energies $E_{col} \lesssim 20\,eV$, some of the impinging ions recoil intact from the target surface, while for impact energies $E_{col} \gtrsim 50\,eV$, only very few intact parent ions are left, with the simultaneous appearance of small ionic fragments. The absence of any fragment ions with intermediate sizes or sizes close to the parent cluster ion is quite remarkable. This *shattering* has been equally observed for hydrogen-bonded cluster cations such as protonated ammonia, methanol, and water [28, 34–36] and has been pre-

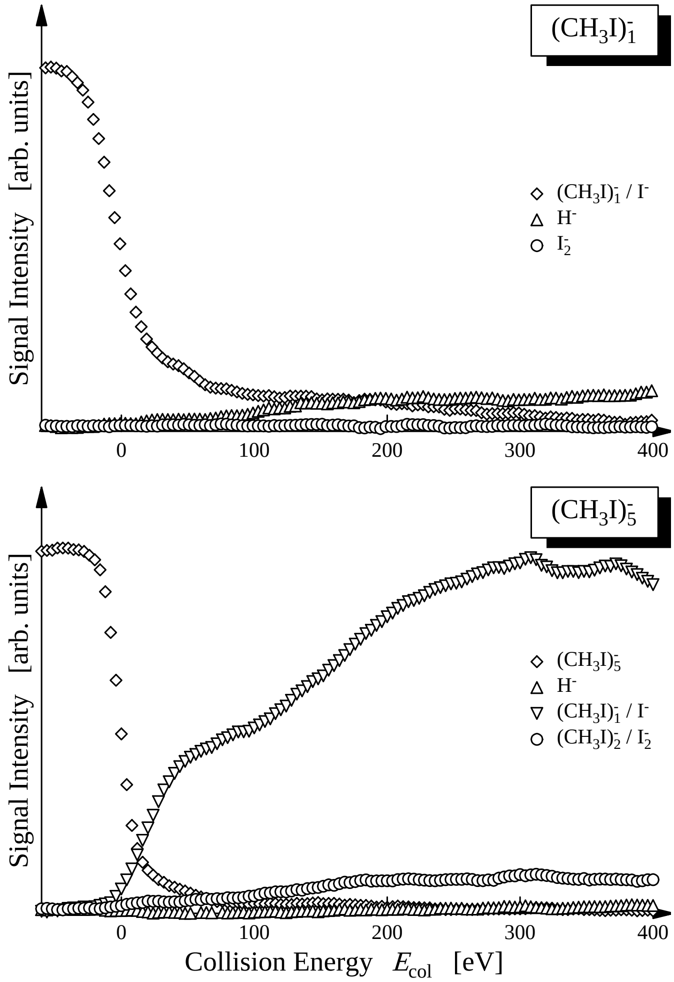

Fig. 5. Fragmentation pattern of iodomethane anions resulting from the collision with the diamond surface. The measured signal of scattered ions (cf. Figs. 1 and 2) is integrated for several mass ranges and plotted as a function of the collision energy E_{col}. Data points to the left of $E_{\mathrm{col}} = 0$ eV represent reflected ions. Top: impact of molecular iodomethane ions $(\mathrm{CH_3I})_1^-$. Bottom: impact of iodomethane cluster ions $(\mathrm{CH_3I})_5^-$.

dicted previously [50, 56]. Because in the present setup only negatively charged particles are measured, the large dip in the total ion yield can be attributed to the neutralization of ions during the scattering event. However, the possibility of ions reacting with or adsorbing at the target cannot be excluded completely.

The cluster size dependence of the reaction yield $Y(\mathrm{I}_2^-)$ is shown in Fig. 6 (top). It has been normalized to the yield of atomic iodine fragment anions $Y(\mathrm{I}^-)$ so that a quantitative comparison of ion intensities in the wide mass range of 144–2160 amu can be made without worrying about anion production and detection efficiencies. This ratio is best described by a fit of the functional form $Y(\mathrm{I}_2^-)/Y(\mathrm{I}^-) \propto \sqrt{n-1}$. The cluster size dependence for the nucleophilic association reaction to iodine molecules I_2^- is significantly different from the process leading to atomic hydrogen anions; see Fig. 6 (bottom). Its size dependence

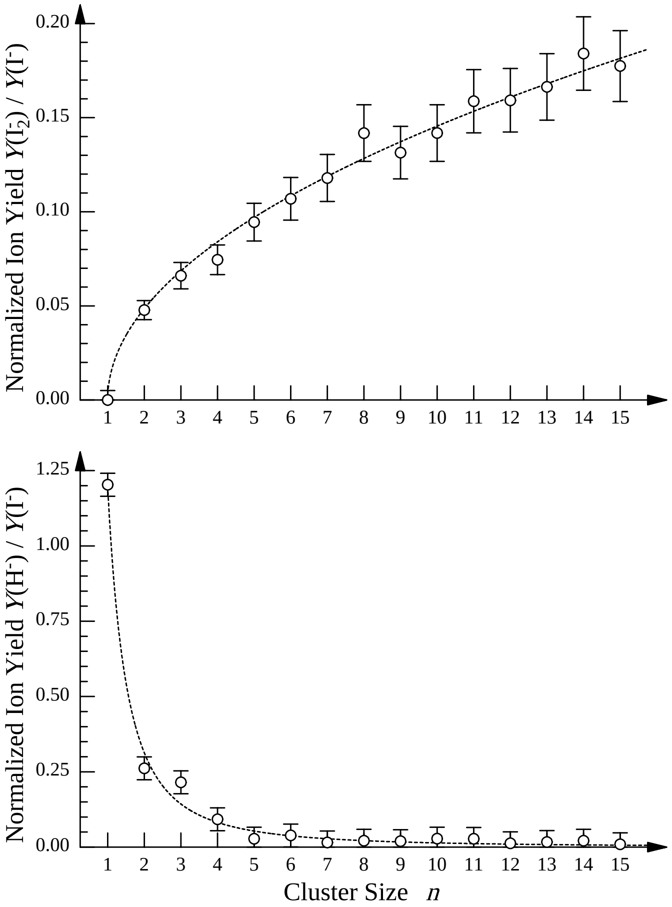

Fig. 6. Reaction yield of molecular iodine I_2^- (top) and yield of atomic hydrogen H^- (bottom), normalized to the yield of atomic iodine fragments I^-, as a function of the size n of the impacting iodomethane cluster anions $(\mathrm{CH_3I})_n^-$. The ratio is evaluated at the collision energy yielding the largest ion signal. The dotted lines are fits to the data points; see text.

is best described by $Y(\mathrm{H}^-)/Y(\mathrm{I}^-) \propto n^{-2}$. We do not have a model for the reaction mechanism to explain this relation. Additional experiments exploring the effect of the solvent on the reactivity have been published elsewhere [28].

Some characteristics of the above results deserve emphasis: The first one is the existence of an energy threshold of about 3 eV/molecule for the detection of the collision-induced reaction of iodomethane pentamer anions to molecular iodine ions, as depicted in Fig. 4. The second aspect is the remarkable cluster size dependence of the reaction yield: While no reaction can be detected for the single molecular anion, the normalized reaction yield rises monotonically, and exceeds 15% for cluster ions consisting of 15 iodomethane molecules. Also, within the accuracy of the data, no effect caused by the filling of the first solvation shell can be observed. Finally, the low flux of approximately 10^6 cluster ions per second impinging on the target surface should be mentioned; even assuming a sticking factor of 1, the probability for a significant contribution to the molecular bond formation via a recombinative desorption mechanism can be safely neglected.

4 Summary

We have presented experimental results showing that the scattering of molecular ion clusters from a solid surface can be used to efficiently break and form new chemical bonds. The reaction $(CH_3I)_n^- \rightarrow I_2^-$, induced by cluster impact, exhibits a pronounced cluster size dependence. Even for the small $(CH_3I)_n^-$ cluster ions investigated here, $n < 15$, a surprisingly large relative reaction yield of more than 15% I_2^- molecules per I^- fragment could be observed.

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