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Driving High Threshold Chemical Reactions by Cluster-Surface Collisions: Molecular Dynamics Simulations for CH_3I Clusters

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Computational results for the surface impact of $(CH_3I)_n$ clusters are presented, and the dynamics of formation of molecular products is examined. The mechanism is compared to the high energy bimolecular CH_3I + CH_3I collision and to other reactions in impact-heated clusters, in particular, the burning of air. The results are discussed in reference to the experimentally observed formation of molecular iodine (as I_2^-) in surface collisions of $(CH_3I)_n^-$ clusters.

Introduction

Concerted four-center collisions such as

$$CH_3I + CH_3I \rightarrow I_2 + CH_3CH_3$$

are nominally "forbidden" because of an unfavorable orbital correlation.[1,2] In a more refined view there is a curve crossing so that the reactants do correlate to the products but with a high barrier along the reaction coordinate. This high barrier has been discussed, e.g., for $H_2 + H_2$ [3,4] and for HI + HI.[5−7] We[8−10] have suggested that such high barrier reactions could be thermally driven by cluster impact. In this approach, a cold, van der Waals bound cluster, in which the reactants are solvated, impacts a hard wall at a supersonic velocity.[11−15] Upon impact, a large fraction of the clusters have their (initially, directed) energy rapidly randomized, leading to ultrafast (tens of femtoseconds) heating. A rough estimate of the temperature rise within the hot and compressed cluster is provided by the equivalence of temperature to the random part of the kinetic energy. If, upon impact, the entire initially directed velocity of the cluster is rapidly randomized, the cluster temperature will reach a value that is V_0^2 times room temperature where V_0 is the initial velocity in units of the velocity of sound. A cluster impacting the surface at 4 km/s, which is about 10 Mach and is the velocity range of interest in this work, can therefore be rapidly heated to well over 10^4 K. Molecular dynamics simulations for a cluster of interacting but otherwise structureless particles verify this temperature range is accessible even when energy loss to the surface is allowed.[16] A short time after this practically instantaneous heating, the cluster fragments.[16−19] Reference 20 is a recent extensive review of our earlier work on cluster impact chemistry with special reference to N_2/O_2 clusters.

Computer simulations and experiments[21−25] show that bond dissociation can occur within an impact-heated cluster. It is less obvious that bond formation is also possible in the short available time. Time is short because the cluster rapidly fragments.[16,18] Computer simulations suggest that since there is time for 3−5 collisions, reactions are possible. This is true even for four-center reactions,[9] where vibrational excitation of the reactants is necessary for reaction. The origin of this requirement is the kinematic constraint that operates for four-center reactions.[26] The required vibrational excitation is possible when reactants are solvated by an inert cluster. Simulations clearly show that, prior to reaction, the cluster environment activates the reactants.[9] The motivation of this paper is the first reported experimental study of new bond formation under conditions of cluster impact.[21]

Dynamically, the most complex situation is when all the molecules of the cluster are potentially reactive. The reason is that many unsaturated species can be formed within the cluster so that the valence forces are many body. At the high initial compression that follows impact almost the entire cluster is electronically coupled. We have carried out simulations of impact heating of mixed N_2/O_2 clusters and noted high (up to 30% of the initial material) yield of formation of NO.[10] The "burning of air" reaction

$$N_2 + O_2 \rightarrow 2NO$$

has, so far, not been observed to occur by cluster impact. Christen and Even have recently reported[21] that a (singly negatively charged) cluster of CH_3I molecules, upon wall impact, leads to detectable formation of I_2^- molecules. Clusters of 2−15 molecules were studied as a function of the collision velocity. The yield is not high but is larger for larger clusters. In this work we report that molecular dynamics simulations of impact heating of CH_3I clusters leads to I_2 formation with a yield which is quantitatively similar to that observed, including the dependence on collision velocity and size of clusters, Figures 1 and 2.

The yield of formation of molecular products in the simulations is high at a collision velocity of about 4 km/s. This energy is above the threshold for electronic excitation. Yet Christen and Even report (private communication) that there is no light emission from the region of impact even at higher collision energies. We find the complete absence of evidence for electronic excitation not easy to understand. On the other hand, one expects a strong kinematic constraint against electronic

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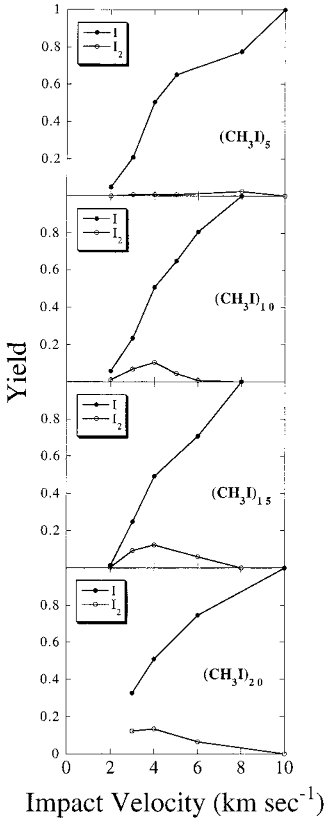

Figure 1. The yield (per CH$_3$I molecule) of molecular and atomic iodine, as indicated, vs the impact velocity normal to the surface for (CH$_3$I)$_n$ clusters of different sizes n. Note that the molecular product is more typical for the larger clusters and that it is confined to a fairly limited range in impact velocity.

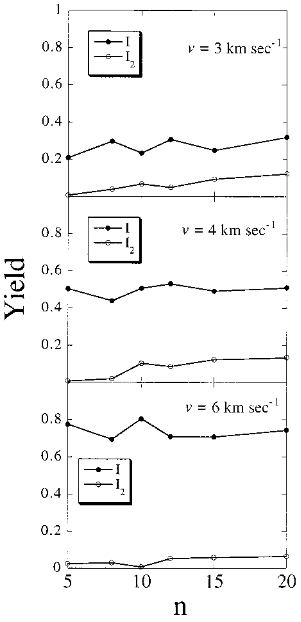

Figure 2. The yield (per CH$_3$I molecule) of molecular and atomic iodine, as indicated, for (CH$_3$I)$_n$ clusters of different sizes n at several values of the impact velocity at the surface.

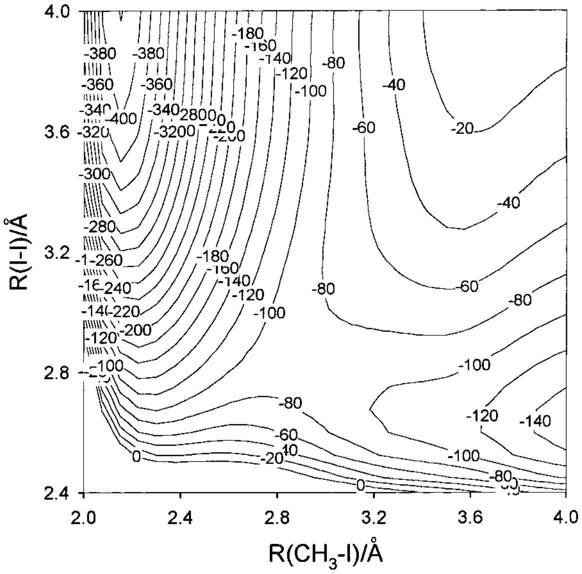

Figure 3. The contours of the potential energy between two CH$_3$I molecules held at an H configuration, as a function of the two bond distances. The potential energy contours are labeled by kJ/mol. The details of the potential are given in the appendix and the parameters are such that the resulting potential for two CH$_3$I molecules is very similar to that derived from the London equation as shown in reference 30. The reactants valley is at the upper left corner. The valley rises uphill and the barrier is quite late and high although not so high that it exceeds the dissociation energy to four atoms. The reaction coordinate in the barrier region is almost a pure CH$_3$—I elongation so that initial vibrational excitation is beneficial for crossing the barrier.

excitation at velocities of a few km/s.[27] The reason is that the crossing between the ground and lowest excited state is generally avoided so that there is an energy gap between them. The required energy has to be supplied by the kinetic energy of the nuclei and the heavy Iodine atom is strongly resistant to changes in its momentum.[28] Information theory estimates suggest about 10 km/s as the velocity for the onset of electronic nonadiabaticity, and recent detailed quantum mechanical computations[27] concur. It is therefore realistic to carry out classical molecular dynamics simulations at 4 km/s.

Potential. The results of a molecular dynamics simulation are only as physical as the potential that is used. There is no question that we do not have a realistic functional form of the potential for a system of many open shell species such as CH$_3$ and I. The problem is that chemical forces saturate. That is, the incipient formation of one bond weakens the other bonds. That is sometimes expressed as a “conservation of bond order” which means that a given atom can accommodate only so many bonds, and hence, in a concerted reaction, the new bond is being formed in concert with the breaking of the old bond. A functional form that describes this conservation was derived by London a long time ago.[29] The success of the London equation is that it allows empirical input on the different diatomics that represent the reactants and products. This not only means that the entire function is easily written down but also that its asymptotic behavior, that is, in the reactants and products regions, is guaranteed to be physically correct. Unfortunately, the London equation is only known for a tetratomic system (and for atoms in S states). We need a generalization, which, so far, is not available. What we do is to use a purely empirical form where the idea of conservation of bond order is imposed “by hand”. The details are given in an appendix, and Figure 3 shows a contour plot of equipotential lines for the approach of two CH$_3$I molecules in an H configuration.

Figure 3 shows equipotential contours as a function of the CH$_3$—I and I—I bond distances. The reactants valley is at the upper left corner. The valley rises completely uphill and the barrier is very late and high although not so high that it exceeds the dissociation energy to four atoms. The reaction coordinate in the barrier region is almost a pure CH$_3$—I elongation so that initial vibrational excitation is beneficial for crossing the barrier.

At the location of the barrier the I−I bond distance (2.85 Å) is stretched beyond its equilibrium value (2.65 Å) so that the newly formed I_2 will be vibrationally excited. These features of the potential are very similar to what is seen in the London potential for this system.[30] A new feature here is the presence of the van der Waals long-range attraction. These are hardly seen on the scale of Figure 3 except in the dissociation plateau where the contour at -20 kJ mol^{-1} actually encircles a well.

The energy requirements and energy disposal of the $CH_3I + CH_3I \rightarrow CH_3CH_3$ reaction, as judged from the potential, coincide from what one would conclude from a kinematic analysis.[26,30] In a kinematic model for AB + AB, the products separate with a velocity that is entirely provided by the A−B vibration and the relative velocity of the two atoms in the A−A or B−B products is provided by the approach velocity of the reactants. An exploratory study[30] examined the high-energy bimolecular $CH_3I + CH_3I$ collision for the London potential shown in Figure 3 and verified the expectations on the basis of topography of the potential.

The expected high vibrational excitation of the newly formed I−I bond and its low dissociation energy mean that many newly formed molecules dissociate so that the yield of molecular products after the cluster fragments is low.

It is instructive to compare the $CH_3I + CH_3I \rightarrow I_2 + CH_3CH_3$ potential used here, Figure 3, to the $N_2 + O_2 \rightarrow 2NO$ potential used in our earlier study on the burning of air.[10] Both potentials are of the same functional form, cf. Appendix, and as such are qualitatively similar. The quantitative differences are however quite significant. The two main differences are, first, that all the bonds are weaker and particularly so that of the CH_3^-−I reactant and the I−I product, cf. Table 1 below. This has two important observable implications. The weaker CH_3−I bond means that the barrier to reaction is lower so that chemical rearrangement should be possible at lower impact velocities and that the I_2 product is less stable so that its formation is restricted to a limited range of collision energies. The second difference in the potential is that the equilibrium bond distance in the two molecular products, I−I and CH_3−CH_3 are quite different. Since the I atom is by far bigger it tends to preclude a sufficiently close approach of the two methyl groups. The yield of CH_3CH_3 formation is consequently significantly lower than that of I_2.

The computed dynamics are not very sensitive to the details of the potential. Of course, the precise history of any particular trajectory is dependent on the details. But the meaningful results must be an average over a number (we use 50) of trajectories. The average is far less sensitive. Part of the reason is that we are dealing with a high-energy collision and so the results are most sensitive to the repulsive part of the potential, which is steep. So as long as the potential mimics the “size” of the atoms correctly, it will yield realistic results. Another reason is that the potential does not act against the kinematics. This is not impossible but it does not happen here. Finally, and as we pointed out before[9] and will further discuss below, in the cluster the reaction is not a simple bimolecular event. There is time for a few collisions so that details do get averaged out. This is particularly so in a cluster made up from reactants because, even for a single trajectory, if we ask not for its detailed history but for a more averaged question such as the yield of I_2, there is an inherent averaging over all the collisions in that cluster.

The simulations were carried for impact velocities in the range of up to 10 kms^{-1}, because beyond that range essentially only atomic iodine is formed. But the energetic threshold for the formation of electronically excited products is lower.[27] One can then question the use of only the ground electronic state potential. We therefore reiterate that in a separate, quantum mechanical, study of the high energy $CH_3I + CH_3I$ bimolecular collision we showed that the effective threshold for formation of electronically excited products is higher than 9 kms^{-1} for vibrationally cold molecules. This was shown to be due to the exponentially small transition probability due to the stringent Franck−Condon limitations on the heavy iodine atoms. Only for velocities well above the nominal threshold does the probability for nonadiabatic transitions become significant. Of course, this is due to the ground and excited surfaces being well separated over most of the range available for the motion of the nuclei and need not be the case for other systems.

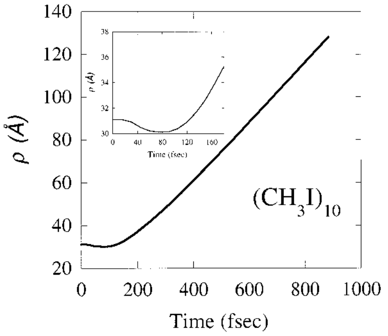

Figure 4. The hyper radius ρ, defined by eq 1, vs time for the impact of a $(CH_3I)_{10}$ cluster at the velocity of 4 kms^{-1}. The same impact is examined in detail in Figures 6−8. Note the rapid expansion of the cluster for times above 200 fs. The inset shows ρ for times immediately after the impact where it is seen that the cluster contracts first and expands only later.

Molecular Dynamics Simulations. The molecular dynamics simulations are standard.[31] A cluster of CH_3I molecules is first equilibrated at a low temperature. The long range van der Waals wells insure that the cluster packing is at the density of the liquid. Each atom of the cluster is then given the same additional velocity in the direction normal to the surface. This velocity of a few km/s is much higher than the thermal velocity so the cluster moves bodily towards the surface with this velocity as the velocity of its center of mass. From that instant, the equations of motion for the coordinates of each atom are being integrated with the forces being determined by the potential as discussed above. As the atoms of the cluster reach the surface, they instantaneously rebound, reversing the direction of their velocity component in the direction normal to the surface. An energy loss (likely) or energy gain (less likely) accompanies this reversal. The precise details are given by a hard cube model[32] as described in detail elsewhere.[9] The mean result of collisions with the surface is that 55% of the initially directed velocity is dissipated into the surface. This is consistent with the observed[21,33] time of flight spectra. Charge transfer to or from the surface is not allowed. The equations of motion are all the time being integrated.

Not all the atoms reach the surface. The atoms from the front of the cluster that are the first to rebound, deflect many of the incoming atoms. In larger clusters where there are several layers, one can see a propagation of a shock front.[24,34] Immediately after the impact with the surface, the cluster contracts because the back atoms are still moving in while the front atoms are moving out. After all atoms have undergone about one collision, the cluster begins to expand, as illustrated in Figure 4 for a $(CH_3I)_{10}$ cluster impacting at 4 kms^{-1}.

Shown in Figure 4 is the time dependence of the mean (RMS) radius of the cluster defined by

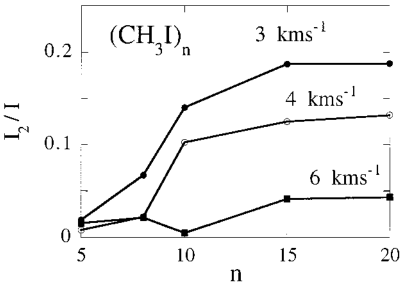

Figure 5. The yield of molecular iodine shown as a fraction of the yield of atomic iodine vs cluster size n for several impact velocities, as indicated.

$$\rho^2 \equiv \sum_{i=1}^{2n} m_i(\mathbf{r}_i - \mathbf{r}_{\mathrm{cm}})^2 / \sum_{i=1}^{2n} m_i \qquad (1)$$

Here m_i is the mass of the ith particle (I or CH_3), and $\mathbf{r}_i$ is its position at time t. The position of the center of mass of the cluster is $\mathbf{r}_{\mathrm{cm}} \equiv \sum_i m_i \mathbf{r}_i / \sum_i m_i$.

The time required for the cluster to expand is determined by its size. At 4 km/s the atoms move 0.04 Å/fs so that for a $(CH_3I)_{10}$ cluster, whose radius is about 30 Å, expansion is seen, Figure 4, to begin about 100 fs after the impact. The chemical identity of the species that exit from the impact is determined 900 fs after the impact. At this time the cluster has considerably expanded, Figure 4, but this long time is needed because highly vibrationally excited I_2 has a long vibrational period, cf. Figure 6 below, and one needs to wait and see if the molecule is bound or dissociated.

Figures 1 and 2 are the results of such simulations. Figure 5 plots the yield of molecular I_2 as a fraction of the yield of atomic Iodine, to conform to the manner of plotting of the experimental results.[21] The fractional yield is seen to increase as a function of cluster size, but it is low, being atmost about 10% that is, roughly from one I_2 molecule per cluster for the $n = 10$ clusters to two molecules at $n = 20$. The yield of I_2 is maximal for a collision velocity of 4 km/s and decreases at higher velocities. There are other molecular products. For example, some of the iodine remains bound to CH_3, but not necessarily to its original partner. Also, as mentioned, the yield of CH_3CH_3 is below that of molecular iodine. By about 8 km/s all the iodine exits in an atomic form. The decrease in the yield of molecular products is also seen[10] in the mixed N_2/O_2 clusters and for the same reason, the products dissociate. But in N_2/O_2 clusters this occurs at a higher collision velocity.

Discussion

During a 100 fs or more after the impact, the cluster is compressed. Examination of the trajectory shows that during this period each atom has several close neighbors. By a distance criterion the cluster consists of a number of small mixed polymers made up of CH_3 and I. As the cluster begins to expand, these polymers "dissociate". The distance criterion shows that molecular Iodine is not formed via a single four-center exchange.

During a 100 fs or more after the impact, the cluster is hot. Examination of the trajectory shows that during this period the relative velocities of neighboring atoms are high. By a kinetic energy criterion, the molecules in the hot cluster have dissociated. Of course, when the atoms are near, there is an attractive potential between them. This potential can keep a pair of atoms bound even if their kinetic energy is high. Why not use the total (kinetic plus potential) energy of a bond as a criterion? If the diatomic molecule is isolated, this is a correct criterion. But in the compressed cluster, and for the potential function that we use (cf. Appendix), the potential energy of a bond is very much a function of where the other atoms are. So much so, that by the energy criterion many bonds in the products result from what looks like a third (or even, many) body assisted recombination. In other words, a new bond is being formed between two Iodine atoms with lots of relative kinetic energy, when a nearby third atom departs while taking a fraction of the excess energy with it.

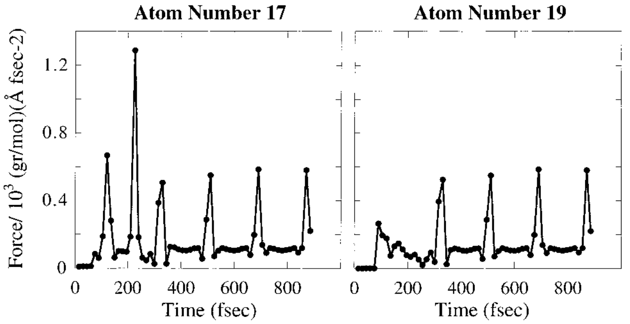

Figure 6. The force on Iodine atoms 17 (left part) and 19 (right part) vs time. Shown for the impact of a $(CH_3I)_{10}$ cluster at the velocity of 4 kms^{-1}. These two iodine atoms exit as a bound but vibrationally excited, molecule. The vibration of the nearly isolated molecule is seen for times above 300 fs when the cluster has, cf. Figure 4, considerably expanded.

In the gas phase dynamics of simple reactions, the distance or the energy criteria provides a reliable indication for the mechanism.[28] Even for reactions in liquids these criteria are still useful.[35,36] The conditions in the hot and compressed cluster are sufficiently different that an alternative probe is needed. Previously, we have used the force on an atom as a guide to the mechanism[9,10,24] and this turns out to be equally useful here.

We choose to discuss a $(CH_3I)_{10}$ cluster and the discussion will make reference to three Figures, Figures 6−8, which illustrate different aspects. Twenty "atoms" in the cluster are considered. The CH_3 groups are numbered 0−9, and the iodine atoms that are initially bound to them are numbered 10−19. For example, iodine atom number 17, which is an atom whose time history we will track, is initially bound to the CH_3 group whose number is 7. Our purpose is to trace how iodine atoms 17 and 19 ultimately emerge as a bound molecule.

Figure 6 shows the force vs time on the two iodine atoms of interest. The left part of Figure 6 shows that the first time a strong force was applied on either one was on atom 17 at 120 fs after impact. By checking on each one of the other 19 atoms of the cluster, it is found, Figure 7, left upper part, that the force was applied by a particular other atom, atom number 18. All the other atoms are not really involved. The collision at 120 fs, between two (heavy) iodine atoms, broke the bond between Iodine atom number 17 and its partner CH_3 group. This bond breaking is shown in the upper panel of Figure 8, where the relevant bond distance is plotted vs time. When iodine atom 17 is already receding from its CH_3 partner, iodine atom 19, whose original CH_3 group is number 9, is still bound to it, cf. Figure 7, left lower part. Form 120 fs on, lower part in Figure 8, iodine atoms 17 and 19 come closer. The heavier I atoms are slower moving and their interaction is realtively weak, and so, unlike the $N_2 + O_2$ reaction, it takes time until the I atoms come within their equilibrium bond distance.

The second major perturbation of Iodine atom 17 occurs at 225 fs, Figure 6, left part. It is a collision with a CH_3 group number 8 as shown in Figure 7, right upper part. This is a stabilizing collision, seen in many other cluster induced

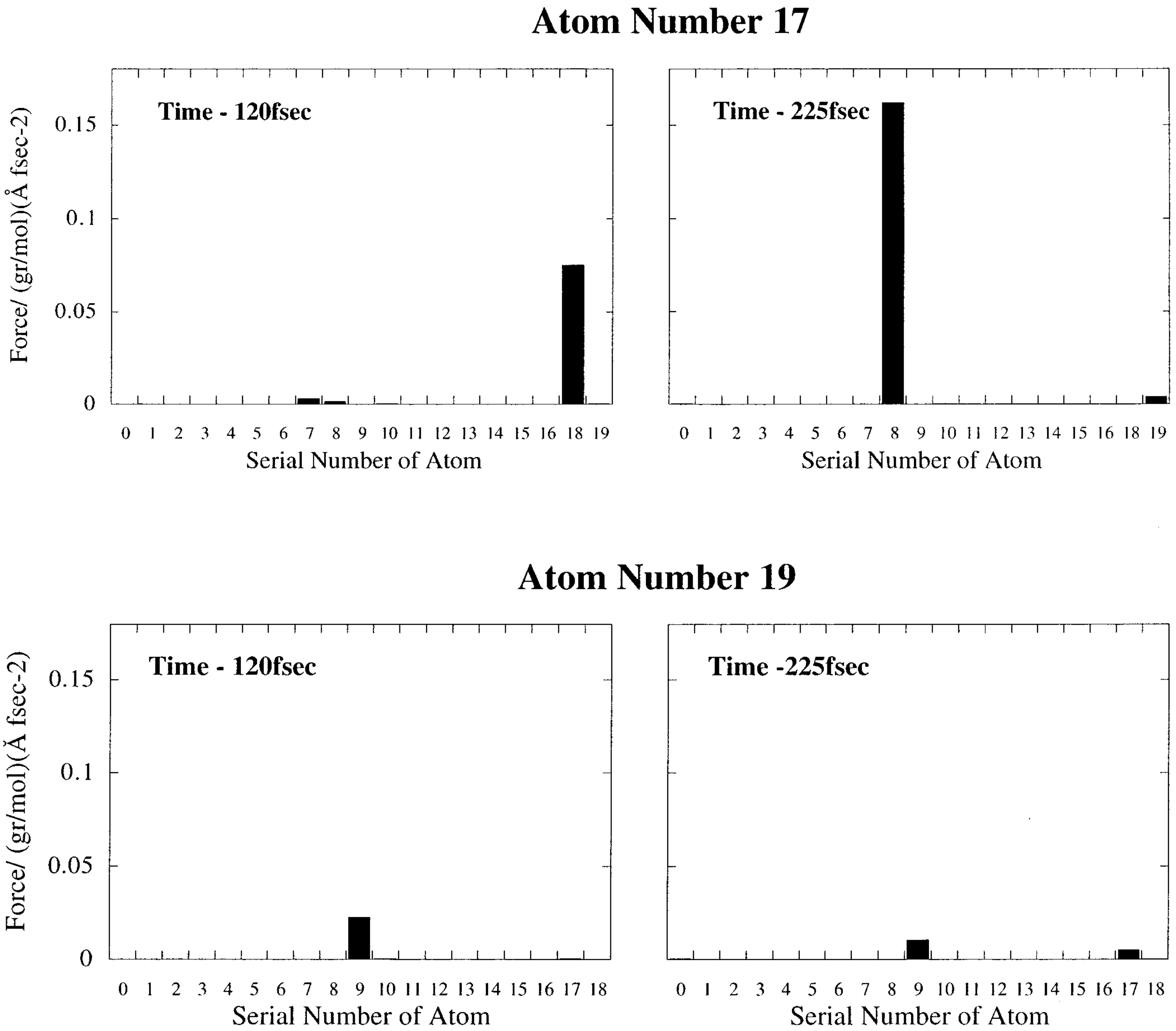

Figure 7. The force on Iodine atoms 17 (top row) and 19 (bottom row) resolved according to which of the other atoms of the cluster is exercising the force. The plots are for the two values of time at which there is a strong force applied on atom 17, cf. Figure 6.

processes.[9] At that point in time iodine atoms 17 and 19 are nearby, as shown by their bond distance in the lower part of Figure 8. Iodine atom 19 breaks its original bond with CH_3 group number 9 and from that time on, cf. lower part of Figure 8, remains bound to iodine atom 17. Figure 6 shows the time history of the force on the two atoms and Figure 8 their bond distance. The two iodine atoms are clearly bound, exercising equal and opposite forces on one another, with a period of less than 200 fs. This is a period one would expect for a vibrationally excited I_2 molecule. This excited bound I_2 molecule survives because beyond its time of formation the cluster rapidly expands.

How can one best describe the complicated choreography of the atoms as examined in Figures 6–8? The problem is that there are at least two, well separated in time, critical events. One is the collision at 225 fs that insures the I–I bond stabilization. Just prior to that event, an iodine atom, whose bond to its CH_3 partner is essentailly already broken, is approaching a still intact CH_3I molecule. Thus the second critical event is a fourth body (CH_3 group number 8) assisted Zeldovich mechanism, in which a radical, formed in a previous dissociation, is reacting with an undissociated molecule. The other critical event is at 120 fs when the first CH_3I molecule got a large kick which extended its bond. Overall therefore we have a cluster induced four-center reaction where, as always,[9] the role of the cluster is two-fold, to activate the reactants and to stabilize the products. We reiterate that these two actions by the cluster environment are well separated in time and so there is always a “history” rather than a single elementary event (i.e., a one time application of a force) that leads to the desired outcome.

For other trajectories, examination of atoms that form bound I_2 molecules shows that Figure 6 is typical. Sometimes an atom gets three kicks before an iodine molecule is formed. Sometimes just one. Occasionally the molecule is so vibrationally excited that its vibrational period is much higher, but the essence is as shown in Figure 6. Of course, only the minority of Iodine atoms exit as I_2 molecules. Mostly they exit as atoms or as CH_3I molecules. Then the history can be different. What remains true, irrespective of outcome, is that at a given point in time one or at most two atoms exercise a large force on a given atom. There is a well-defined sequence of hard kicks, which allows us to reconstruct the mechanism. The role of the other cluster atoms in delivering these kicks is what leads us to speak[8] of a “cluster catalyzed” reaction.

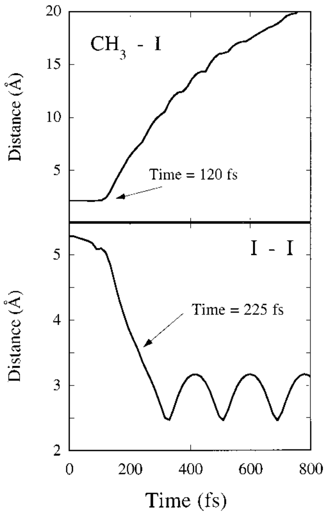

Figure 8. The CH_3—I (I atom number 17) and the I—I (atoms 17 and 19) bond distances vs time for the trajectory examined in Figures 6 and 7. Note how the CH_3—I (I atom number 17) bond is broken at the time of 120 fs when the strong force is applied on I atom 17, cf. Figure 6. The I—I (atoms 17 and 19) bond begins to form at 120 fs but the two Iodine atoms approach to within their equilibrium bond distance only later. The energy is drained out of the new bond by a strong collision with CH_3 group number 8, cf. Figure 7, at about 225 fs. The two panels show different slopes (≡velocities) but the reduced mass of the I—I motion is nearly five times as large as that for CH_3—I. Thus, as discussed in the text, the very same trajectory can be viewed as a fourth body assisted Zeldovich mechanism, referring to the CH_3 group number 8 assisted I approach to CH_3—I at 225 fs or as a cluster assisted four-center reaction, where the cluster environment intervened twice, activating at 120 fs and deactivating at 225 fs.

We have also examined the force on Iodine atoms that exit as atoms (not bound). The question is: Do they first react (to form I_2 or to change the CH_3 partner) and then the products dissociate or are the atoms formed by a hard collision of an initially bound CH_3I molecule which immediately dissociates? We find that both routes are possible.

That a mechanism can be established in terms of a sequence of binary or tertiary events was already seen for other processes within the hot cluster.[9] It is the hard nature of these kicks that make the outcome nearly independent of the details of the potential. These govern the "grass" seen in Figures 6 and 7. The "trees" are due to close in repulsive collisions, and what matters is the magnitude and direction of the impulse that is imparted. The impulse is the time integral of the force and so the integrand itself is not as important as the integral.

Finally we comment on the experimental observation[21] of the formation of molecular iodine (as I_2^-) in surface collisions of $(CH_3I)_n^-$ clusters. Strictly speaking, no comparison is possible because the clusters here are not charged. It is, however, not unreasonable to conclude from our work that it is the hard repulsive core of the atoms that determines the dynamics. If this is so, then the reported I_2^-/I^- ratio can be compared to our computed I_2/I ratio, both as a function of energy and as a function of cluster size, cf. Figure 5. For a cluster of n CH_3I molecules, an impact velocity of 1 kms^{-1} corresponds to an impact energy of roughly $3n/4$ eV. Our collision energies are therefore comparable to those used in the experiment. As in the experiment, the yield of the molecular Iodine decreases at higher energies. Similarly, the dependence of the yield ratio on the cluster size, while not exactly of the reported[21] $\sqrt{n-1}$ form, is quite similar. All of this is suggestive but definitely not conclusive. Experimentally, accelerating and detecting charged species is clearly easier. For the simulation, the presence of the charge creates a difficulty, particularly so for such systems where the negative charge can catalyze the four-center reaction. Since an extra electron on CH_3I will go into an antibonding orbital, this could be the case here and, if so, will invalidate the comparison. Possibly, the problem can be made into an advantage by selecting for future experimental study cases where the barrier to reaction is known to be significantly lowered by the presence of a charge. This will reduce the necessary impact energy, and therefore (for kinematic reasons as discussed above), will lower the internal excitation of the diatomic products and thereby enhance their chance for survival and detection.

Concluding Remarks

Molecular Iodine is formed, with a low yield (roughly 10% per parent CH_3I molecule) in a narrow supersonic velocity range about 10 Mach when clusters of CH_3I molecule impact a hard surface. The yield of molecular products does increase with cluster size. The high barrier to the four-center reaction or to dissociation means that there is a high threshold for formation of products, but with some excess energy, the nascent molecular Iodine product will dissociate. Details of the mechanism were examined in terms of the time history of the force on any given atom. It was shown that the mechanism is very well described as a sequence of hard binary collisions.

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Appendix

The Many-Atom Potential. The potential between the reactive atoms is one that has been used before in studies of many-atom systems.[37,38,39] It is of a form that allows for a weakening of a bond between a pair of atoms when one or more other reactive atoms are nearby. It also includes a long-range physical interaction that describes the packing in the cluster. With i,j, etc., being indices of atoms, the N atom potential is given as a sum over all pairs

$$V = \sum_{i=1}^{N}\sum_{j>1}^{N} V_{ij}$$

$$V_{ij} = V_{\mathrm{R}}(r_{ij}) - \tilde{b}_{ij}V_{\mathrm{A}}(r_{ij}) + V_{\mathrm{W}}(r_{ij}) \qquad \text{(A.1)}$$

Here V_{ij} is the chemical part of the atom—atom interaction. It is the sum of a repulsive short range potential V_{R} and a corresponding longer range attractive potential V_{A}

$$V_{\mathrm{R}}(r_{ij}) = 4\epsilon(\sigma/r_{ij})^{12}; \quad V_{\mathrm{A}}(r_{ij}) = 4\epsilon(\sigma/r_{ij})^{6} \qquad \text{(A.2)}$$

When $\bar{b}_{ij} = 1$, these two terms are the two-body potential of the diatomic molecule made up of atoms i and j. V_{W} is the long-range van der Waals potential:

$$V_{\mathrm{W}}(r_{ij}) = 10^{-4}[1.0 + 50.0\gamma + \gamma^2 + 10.0(\gamma - 1.0)b_{\mathrm{W}}]/a_{\mathrm{W}}$$

$$a_{\mathrm{W}} = \exp[\alpha_1(r_{ij} - r_{\mathrm{W}})] + \gamma\exp[-\alpha_1(r_{ij} - r_{\mathrm{W}})]$$

$$b_{\mathrm{W}} = \alpha\exp[\alpha_1(r_{ij} - r_{\mathrm{W}})] - \gamma\exp[-\alpha_1(r_{ij} - r_{\mathrm{W}})] \qquad \text{(A.3)}$$

The presence of the van der Waals term in the potential, eq A.1, means that even when no other atoms are nearby (so that $\bar{b}_{ij} = 1$), the long-range two-body potential has a shallow well

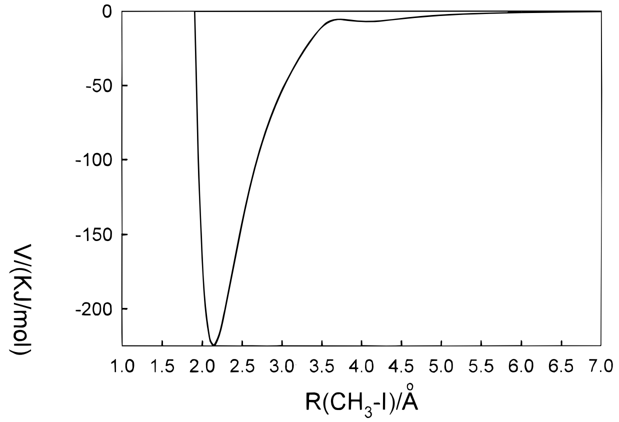

Figure 9. The two-body, CH_3−I potential including both the long-range van der Waals forces and the shorter range chemical forces. Parameters from the table. Note the small barrier between the shallow van der Waals well and the chemical well. The role of the barrier is to prevent chemical interaction between non bonded atoms in the cold cluster. In the hot cluster, the role of this barrier is negligible.

at about the van der Waals radius r_W. This is shown in Figure 9 for the CH_3−I potential. Note in this figure that there is a small barrier between the van der Waals and the chemical well. The role of the van der Waals well is to allow the cold cluster to form at the appropriate density. That is, when CH_3I molecules come near to one another, they feel the van der Waals forces between their atoms. We already noted the barrier to the left of the van der Waals region. Its role is to preclude any chemical forces between chemically unbounded atoms that have a low energy, as is the case in the cold cluster. After impact heating, the role of this barrier is negligible. To conclude, in the cold cluster an atom is either chemically bound to another, in which case these two atoms are nearby or the atom sees van der Waals forces with other atoms, in which case they are further apart. (Compare the values of σ and r_W in the table below).

The many-body character of the chemical interaction, (which means that V_{ij} can be a function not only of r_{ij} but also of the location of all the other reactive atoms), enters through $\tilde{b}_{ij}$ which is a coordination number which serves to reduce the strength of the attractive chemical potential between atoms i and j when other reactive atoms are nearby:

$$\bar{b}_{ij} = (b_{ij} + b_{ji})/2, \quad \bar{B} \equiv \sum_i \sum_{j \neq 1} b_{ij}$$

$$b_{ij} = 1/(1 + \sum_{k \neq i,j} f(r_{ik}) g(\theta_{ijk}) \exp((r_{ij} - r_{ij}^0)/a)) \quad \text{(A.4)}$$

and the superscript 0 designates an equilibrium value. $\bar{B}$ is the total coordination number. $f(r_{ik})$ is a cutoff function that turns off the influence of atom k when it is too far from atom i

$$f(r) = [1 - \tanh(\alpha_3(r - r^0))]/2 \quad \text{(A.5)}$$

g is similarly an angular cutoff function

$$g(\theta_{ijk}) = 1.0 + c/d - c/[d + (h - \cos\theta_{ijk})^2] \quad \text{(A.6)}$$

which insures that the angle made up by atoms i, j, k is not too acute. These definitions insure that $\bar{bij}$ is a monotonically decreasing function of the coordination number of atoms i and j. If there are no neighbors near the i,j pair then $\bar{b}_{ij} = 1$.

The parameters we used for the cluster of CH_3I molecules, treating the CH_3 group as an atom, are given in Table 1. For comparison, the parameters for the N_2/O_2 cluster are also given. Note in particular the very different bond strengths in the two systems. The lower yield of I_2 as compared to that of NO is directly attributed to the limited capacity of I_2 to accommodate vibrational excitation before the bond is broken. The lower impact velocity needed for reaction to occur for a cluster of CH_3I molecules is due to the lower CH_3−I bond dissociation energy which means that the barrier to reaction is lower, cf. Figure 3.

TABLE 1: Potential Parameters

	CH_3I	I_2	CH_3CH_3	N_2	O_2	NO
D_e (kJ/mol)	224.8	148.8	351.2	941.4	493.6	626.7
σ (Å)	1.906	2.376	1.368	0.9779	1.07578	1.0245
r_e (Å)	2.14	2.666	1.536	1.097	1.2075	1.15
r_W (Å)	3.6	4.2	2.9	3.72	3.31	3.51
α_1	2.8	3.0	1.7	3.0	3.0	3.0
γ	0.9	0.5	0.9	0.3	0.3	0.3
α_2	2.0	2.0	2.0	2.0	2.0	2.0
r^0 (Å)	2.7	2.7	2.7	1.3	1.3	1.3
α_3	1.7	1.7	1.7	3.0	3.0	3.0
c	25.0	25.0	25.0	25.0	25.0	25.0
d	4.0417	4.0417	4.0417	4.0417	4.0417	4.0417
h	0.0	0.0	0.0	0.0	0.0	0.0

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