

Dissociation dynamics of diatomic molecules embedded in impact heated rare gas clusters

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Molecular dynamics simulations demonstrate facile dissociation of halogen molecules embedded in rare gas clusters upon impact at a surface at collision velocities up to 10 km/s. Two pathways are discerned: a heterogeneous dissociation of the molecule on the surface and a homogeneous mechanism where rare gas atoms which have rebounded from the surface cause the translational–vibrational coupling. The total yield of dissociation of the clustered molecule can reach up to 100%, whereas the yield of dissociation of the bare, vibrationally cold molecule saturates below 40%. A systematic study of the role of different conditions is made possible by not accounting for the atomic structure of the surface. The role of dissipation at the surface is found, however, to be quite important and is allowed for. Larger clusters, clusters of the heavier rare gases and a more rigid surface, all favor the homogeneous mechanism. Evidence for a shock front which, upon the initial impact, propagates into the cluster; the binary nature of the homogeneous dissociation process; and the absence of a dominant cage effect are discussed. A quantitative functional form of the velocity dependence of the yield of dissociation, which accounts for the size of the cluster, the rigidity of the surface and other attributes, is used to represent the data. The physics of the processes within the cluster is dominated by the novel dynamical features made possible when the duration of the atom–molecule collisions is short compared to the vibrational period. This “sudden” regime is sudden with respect to all modes of the nuclear motion and provides a hitherto unavailable tool for examination of reaction dynamics under extreme conditions.

I. INTRODUCTION

Dissociation of diatomic molecules (and halogens, in particular) in shock waves has been studied extensively.¹ A lingering intriguing problem has been the unexpectedly low Arrhenius activation energy of such processes or, equivalently, the negative activation energy of the reverse reaction (i.e., a third body assisted recombination).² Among the factors that have been considered as contributing to the observed kinetic behavior have been the enhancement of the rate of collisional dissociation by internal excitation of the diatomic molecules and the possible role of “multiquantum” transitions in which the molecule gains several vibrational quanta per collision.^{1,3} The report⁴ of exceedingly high interatomic velocities following impact of a homogeneous rare gas cluster on a surface suggests that such dissociation processes can readily take place when a diatomic molecule is embedded inside the cluster. The present paper presents a computational study aimed at elucidating the dynamics of such dissociation processes. The important generalization that emerges from our study is that cluster impact provides a hitherto not well-characterized physicochemical regime, where the intermolecular coupling is comparable or faster

than all intramolecular motions. At ordinary velocities, only the rotations are in this “sudden” regime. Indeed the rates for rotational–translational energy transfer are rather high.⁵ During cluster impact, the rates for translational to vibrational energy transfer reach comparable values. It is possible that the reported^{6,7} efficient electronic excitation in cluster impact is also due to this novel coupling regime.

The preceding paper⁸ presents the results of a detailed molecular dynamics simulation of an impact induced dissociation on a realistic metallic surface. *Inter alia* it points out the importance of dissociation following the impact of the diatomic molecule itself on the surface. The corresponding process for the bare molecule has been thoroughly studied previously,⁹ both experimentally¹⁰ and by molecular dynamics simulations.^{11,12} In a preliminary study, we have verified that an isolated cold halogen molecule will dissociate in a single collision with a single rare gas atom at the relative velocities typical of the systems of interest.¹³ There is therefore evidence that two pathways to dissociation are available—a homogeneous one, taking place inside the cluster, and a heterogeneous one, which requires an impact of the molecule on the surface. One of the purposes of the present paper is to examine the relative importance of the two

mechanisms for dissociation and the factors that affect them. It will, of course, be the case that the "homogeneous" process is more typical of larger clusters, but several additional considerations (e.g., the halogen to rare gas mass ratio) are also relevant. It is the very dependence of the yield of dissociation on the nature of the rare gas, as seen also in the single collision study,¹³ that provides a simple indication of the role of the homogeneous process. Quantitative considerations will be given in Sec. III C below.

The local density of the cold cluster is quite high and it is further compressed upon impact. One could therefore expect that the homogeneous dissociation processes can involve more than one rare gas atom and, as such, can give rise to "many body" effects. We have looked for such collective effects both because they can give rise to novel modes of behavior, not seen in binary collisions, and because these serve as probes for any "shock front" following the impact of the cluster on the surface.^{8,14} In Sec. III F, we discuss why the chemistry in the rare gas clusters is essentially binary and consider suitable, alternative, systems to examine for such effects. On the other hand, using the vibrational energy of the initially cold halogen molecule as a thermometer, we find that there is a shock front. The evidence for the presence of a front is a localization, in time, of the vibrational-translational coupling. However, the atoms in the front appear to act largely independently of one another. In a similar way, we do not find a dominant role of a "cage effect."¹⁵⁻¹⁷ Any halogen molecule which acquired sufficient energy to dissociate is observed to proceed to do so, with hardly any hindrance by the surrounding cluster. We provide a possible explanation of this observation, an explanation which depends on the atypically high velocities characteristic of the system. In Sec. III G, we also suggest where cage effects may become more noticeable.

An important caveat about the present work, as well as all the background computational studies that were cited, is that the motion of the atoms is computed for a given potential. This means that the role of excitation of the electronic degrees of freedom of neither the surface nor that of the cluster is taken into consideration. After the atoms in the "face" of the cluster have rebounded from the surface while the bulk of the cluster is still moving forward, the relative velocities can reach high values. This is the case even "on the average" since the kinetic energy which is initially that of the center of mass motion is either dissipated by the surface or converted to energy of relative motion. At such cluster velocities that can be readily experimentally realized [1–10 km/s (Refs. 4, 7, and 18–20)], pair energies exceeding several electron volts are quite probable. (At a velocity of 1 km/s, the kinetic energies of rare gas atoms are 4.8 and 15.7 kcal/mol for Ar and Xe respectively.) It is therefore not quite realistic to neglect the possible electronic excitation of the halogen atoms and further work in this direction is in progress.

The high relative velocities (tens of Angstroms per picosecond) of the constituents of the cluster means that the entire course of the dissociation runs for at most a few hundred femtoseconds. At the end of this period, the cluster fragments^{4,21} and collisional processes cease. However, at

the relevant densities, the time scale is sufficient for quite a few collisions so that sequential processes are possible. Indeed we shall present both trajectory time histories and other quantitative evidence that the halogen molecule suffers more than one collision prior to its dissociation.

The numerical methodology we chose was dictated by the need to perform a wide survey of the possible physicochemical processes of the halogen molecule embedded in the rare gas cluster. This is achieved by adopting an approximate description of the surface, while treating exactly the (classical) dynamics of the constituents of the cluster. The results are validated by comparison to the exact (classical) dynamics of both the cluster and the layered surface as presented in the preceding paper. The scaling laws, discussed in Sec. III D provide further support for our approach. Specifically, we used three different approximations. The simplest was the rigid surface. This surface reflects any incident atom or molecule. *Inter alia*, the rigid surface seriously overestimates the velocity of those rare gas atoms that are the earliest to be reflected from the surface and thereby overestimates the efficiency of the homogeneous dissociation process which typically involves one such atom colliding with a halogen molecule that is still moving towards the surface. Even the rigid surface results are not unphysical and they can be scaled to give a more realistic dependence on the initial velocity (cf. Sec. III D below). However, at a minor increase in computational time, one can allow for the role of dissipation of energy by the surface by including a frictional force in the dynamics. By taking the friction to decrease exponentially as one recedes from the surface, it is possible to mimic a quite realistic behavior. Besides friction, one can, of course, also include conservative potentials (with or without attractive wells) between the incident atoms and/or molecules and the surface. An alternative approach, and one that allows us to readily examine the role of surface temperature, is the "hard cube" model,²² which has been tested for scattering of rare gas atoms from metallic surfaces.²³ Here the incident particle strikes a hard cube, moving with a thermal velocity distribution at the temperature of the surface. The mass M of the hard cube is the parameter of the model. The higher is M the more rigid is the surface. We are able to mimic the results of the preceding paper⁸ by taking the hard cube mass to be heavier than the mass of the (Pt) surface atom. Of course, none of these models takes into account the effects of surface corrugation. A less important limitation is our failure to account for subsurface layers. It has been shown that at high impact energies, clusters can deform and even penetrate the surface.²⁴ We estimate that the time scale for these deformations to couple back to the cluster and influence the chemistry within is too long to be important for the homogeneous processes which are over in far less than 1 ps after the impact.

The essence of the methodology is outlined in Sec. II and more details can be found in the preceding paper.⁸ The results are presented in Sec. III, organized according to the physicochemical question rather than by system. The majority of our results are for either Cl₂ or for I₂ in Ar or Xe clusters of different sizes (from the bare molecule to 550 rare gas atoms). Collision velocities are up to 10 km/s. We are

TABLE I. Potential parameters used in the molecular dynamics simulations. (A) Lennard-Jones parameters; (B) Morse parameters.

		ϵ (kJ/mol)	σ (Å)	
(A)	Ar-Ar	0.996	3.41	
	Ar-Cl	1.198	3.38	
	Ar-I	2.508	3.74	
	Xe-Xe	1.903	4.06	
	Xe-Cl	1.657	3.71	
	Xe-I	3.468	3.92	
		D_e (kJ/mol)	β_e (Å ⁻¹)	r_e (Å)
(B)	Cl-Cl	242.5	2.0024	1.987
	I-I	150.1	1.8750	2.656

able to account, quantitatively, for the entire variations seen within the range of systems/conditions that were examined. It is, in part, for this reason that the results are presented and discussed for all the systems together.

II. METHODOLOGY

The initial condition for each trajectory was a cold ($T = 50$ K) X_2Rg_n cluster moving towards the surface with a specified center of mass velocity, where X and Rg are a halogen and rare gas atoms, respectively. The initial coordinates and momenta of the cluster atoms were obtained by equilibrating a trial set of values, using a standard molecular dynamics procedure.²⁵ Equilibration runs of 3 ps were found sufficient, as judged by monitoring the time evolution of the isolated cluster. No evaporation of atoms from the cluster during the equilibration procedure was detected. At the beginning of the run, the halogen molecule was placed in the center of the cluster, with a random orientation. The molecule did not move far from its central location during the equilibration run. Even increasing the temperature of the cluster to 80 K did not cause the molecule to wander to the surface of the cluster. The initial equilibration of the cluster is the most computer time consuming step in our computation. Typically, an ensemble of 100 different initial cluster conditions was used as this brings the sampling error in the (high) yield of dissociation down to an acceptable value. However, and as will be discussed below, the hard cube model of the surface, which requires a longer integration time for the collision trajectories, can achieve a better statistical accuracy of the results with the same number of initial cluster configurations. For an entire ensemble of trajectories, the hard cube model is, therefore, least demanding in terms of computer time.

The potential energy of the cluster is a sum of atom-atom potentials as used in earlier simulations of reactions of halogens in rare gas liquids and clusters.²⁶⁻²⁹ The X-X potential was approximated by a Morse-type functional form and the X-Rg and Rg-Rg potentials were of a Lennard-Jones 12-6 functional form of range σ and depth ϵ . The parameters necessary to specify the potentials are collected together in Table I. The potential between a single rare gas atom and the halogen molecule is thus of a "dumb bell"³⁰ type and one may worry that it is too anisotropic for this

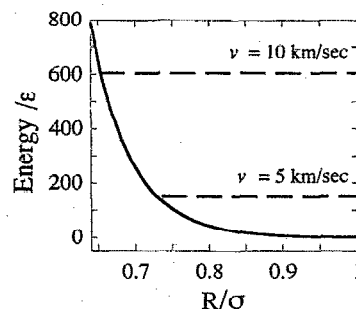


FIG. 1. The Lennard-Jones 12-6 potential between Ar and I atoms, in units of the well depth ϵ vs the atom-atom distance, in units of the range parameter σ . The turning point is shown for two high energy collisions at the indicated velocities. (At a relative velocity of 10 km/s, the relative kinetic energy of Ar and I atoms is about 365 kcal/mol.) At these high energies, the turning point is so much in that the point on the abscissa where $R = \sigma$ is at the end of the scale and the well region is further to the right.

system. In a preliminary study,¹³ we have compared the dissociation dynamics in a $Rg-X_2$ collision for a dumb bell potential as used here with that for a more realistic London, Eyring, Polanyi, and Sato (LEPS) type functional form,⁵ which includes three body forces. At the high collision velocities (tens of Angstroms per picosecond) of interest, the only potential parameter that appeared to have a role was the radius of the hard core surrounding each atom. A comment about this "hard" core is in order. One typically describes the short range part of a Lennard-Jones 12-6 potential as "steeply repulsive." The conventional measure of the repulsion is the force, in reduced units, where energy is measured in units of the well depth. We are, however, in the unfamiliar regime where the magnitude of the $Rg-X_2$ collision energy is tens or even hundreds in units of the well depth of the $Rg-X$ potential. In this regime, the distance of closest approach is significantly below the value of the range parameter σ of the Lennard-Jones potential (Fig. 1). The observation that the atoms are, effectively, only about half as large as we are used to thinking about them will be invoked below to account for the absence of any strong cage effect.

The trajectory is propagated in time using classical dynamics and a Gear five value predictor-corrector integration method. After the impact, the trajectory is followed in time for another picosecond. The molecule is taken to have dissociated if, at the end of the trajectory, the interatomic distance exceeds five times the equilibrium bond distance R_e . As will be discussed in detail in Sec. III G, past the dissociation, the two halogen atoms recede very rapidly. The simultaneous expansion of the cluster and the near absence of a cage effect all ensure that there is no ambiguity in the criterion for dissociation.

The interaction of the cluster with the surface is described by one of three procedures. As discussed in the Introduction, all three are but a caricature of the actual dynamics of the impact. The essential point is that, for our purpose, the results are realistic enough. This will turn out to be the case because what really matters is the magnitude (and the angular spread) of the velocity with which the atoms recede from the surface. There are, of course, other features of the

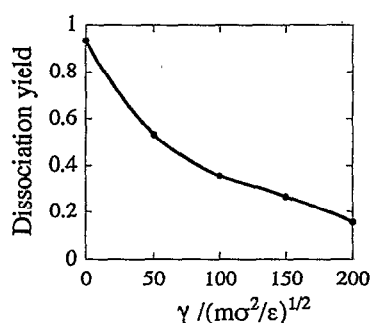


FIG. 2. The yield of dissociation of Cl_2 following impact of a relatively slow ($v=3$ km/s) $\text{Ar}_{125}\text{Cl}_2$ cluster vs the reduced friction parameter $\gamma^* = \gamma(m\sigma^2/\epsilon)^{1/2}$. In this figure, as in all other figures below, the initial velocity is in the direction of the normal to the surface. The range of γ values is from a rigid surface to an energy loss of more than 60% (cf. Fig. 11).

problem for which our approach is wholly unsuitable. On the other hand, the comparison to the results⁸ obtained using a realistic description of the surface indicates that the dissociation dynamics on a chemically inert surface appears to be governed primarily by the rigidity of the surface and is otherwise not very sensitive to details.

The simplest model to implement is the rigid surface approximation. Upon impact, the component of the velocity perpendicular to the surface is reversed with the other two components remaining the same. In other words, the atoms are reflected from the surface without any dissipation of their kinetic energy. In particular, and unlike the experimental²³ reality or the other two models that we will use, in the rigid surface limit, the reflected atoms retrace their path and hence move right back into the cluster. As is only to be expected, the dissociation is most efficient on a rigid surface (Fig. 2). The other two procedures do allow for energy dissipation by the surface.

Rather than a hard wall repulsion to the surface, one can introduce a more realistic atom-surface potential, dependent on the distance from the surface. We included not only a conservative force, but also a frictional force proportional to the velocity. The dependence of the frictional force on the distance of the atom from the surface was taken either proportional to the conservative force or to decrease exponentially with the distance with a range parameter L : force $= v\gamma m \exp(-x/L)$. The magnitude of the friction is measured, as usual, by a coefficient γ (dimensions 1/time, so that the reduced γ is in units of $(m\sigma^2/\epsilon)^{1/2}$). As long as the motion is not overdamped, the energy loss is an exponentially decreasing function of γ and so is the yield of dissociation (Fig. 2).

A more intuitive description of the energy loss is provided by the hard cube model.²² An incident cluster atom collides with a hard cube of mass M whose position is located at the surface. The magnitude and direction of the velocity of the hard cube are sampled from a one dimensional thermal distribution at the temperature of the surface. It is this sampling which can be used to generate distinct trajectories for any given set of initial conditions for the cluster and thereby improve the statistics. The velocity v' of the

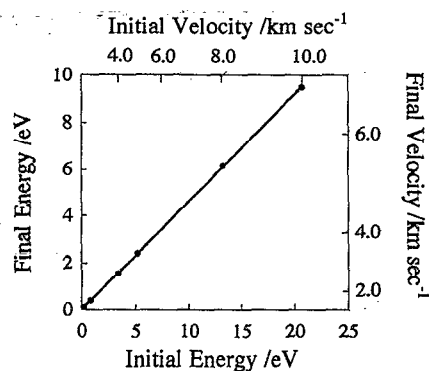


FIG. 3. The final kinetic energy of Ar atoms scattered from a realistic Pt surface (Ref. 8) at 300 K vs the initial kinetic energy. The dots are an average over ten trajectories, with an initial velocity in the direction of the normal to the surface. The linear dependence, shown as a solid line, is the result of the hard cube model (Ref. 22) and corresponds to a 54% energy loss. The mass of the cube (207 amu or $\mu=0.19$) is computed from the slope of the line. There is a finite intercept (about 0.04 eV), which is not seen on the scale of the plot. For convenience of interpretation of the other figures, the corresponding velocity scale is also shown.

rebounding atom is expressed in terms of the reduced mass parameter μ which equals the ratio of the mass m of the incident atom to the mass M of the hard cube. Only the velocity component in the direction normal to the surface undergoes a change according to

$$v'_\perp = \left(\frac{\mu-1}{\mu+1} \right) v_\perp + \left(\frac{2}{\mu+1} \right) u. \quad (2.1)$$

Here u is the velocity of the hard cube which has a one dimensional thermal distribution. Smaller values of μ correspond to a more rigid surface.

In the energy range of interest, the energy loss observed in simulations using a realistic surface model⁸ can be very well fitted by the hard cube model (Fig. 3). We have determined the value of M , for impact of an Ar atom to equal 1.06 the mass of a Pt atom (or 207 amu), from the slope of Fig. 3. Thus, while the second term in Eq. (2.1) is, for our conditions, essentially negligible, a realistic value for $[(\mu-1)/(\mu+1)]$ is below unity. This not only reduces the magnitude of the velocity of the atoms that collided with the surface, but also changes the direction of the velocity vector, leading to an angular divergence of the rebounding rare gas atoms and hence to a decrease in the local density of the cluster.

In the hard cube model, and like the case of a reflecting surface, the change in velocity of the incident atom is instantaneous. It is possible to incorporate in the hard cube model an attraction to the surface.²² Sample computations did not suggest that this makes a significant difference for our collision energies which are well in excess of a reasonable well depth. A more chemically reactive surface can, however, influence the subsequent dynamics.

As we shall show in quantitative terms in Sec. III C, an important role of the inelastic collisions with the surface is that the rebounding rare gas atoms fan out due to a spread in their velocities. In general, this causes the ultimate divergence of the constituents of the cluster. To see the specific

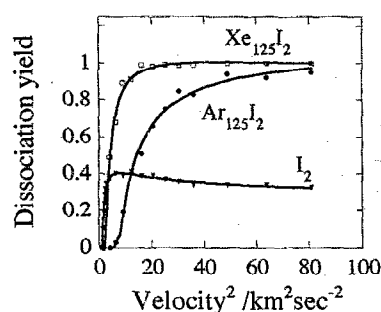


FIG. 4. The yield of dissociation vs the squared velocity of impact for a bare molecule and for a molecule embedded in a cluster of 125 atoms of Ar and in a cluster of 125 atoms of Xe. The impact is on a rigid surface. In this and the other plots of the yield, each point is obtained by running 100 trajectories and, where appropriate, the statistical error due to the finite sample size is indicated. The solid lines are a fit to Eq. (3.2), where it is assumed that two mechanisms contribute to the yield. A heterogeneous one where the molecule reaches the surface and dissociates on it and a homogeneous mechanism where the molecule dissociates within the cluster, before reaching the surface. For the heavier rare gas, the homogeneous process is more probable.

implication for our problem, consider the very first rare gas atoms that reached and receded from the surface. Due to their diverging trajectories, not all these atoms reach the molecule that is still moving towards the surface. The energy dissipation at the surface is important not only because less energy is available, but also because fewer atoms are available for the molecule to collide with.

III. THE DYNAMICS OF DISSOCIATION

The presentation of the results puts an emphasis on the nature of the possible processes and their quantitative description. We begin with the functional form for the velocity dependence of the yield of dissociation and its representation in terms of the two mechanisms—the homogeneous one, occurring within the cluster, and the heterogeneous one. Section III B examines the role of the cluster size and this discussion continues into Sec. III C, where the branching ratio is determined. The increasing importance of the homogeneous mechanism for more rigid surfaces is cast in quantitative terms in Sec. III D. The evidence that the first atoms which are reflected from the surface constitute a shock front which propagates into the cluster is discussed in Sec. III E. The dynamics of the very dissociation process and the cage effect are discussed in Secs. III F and III G, respectively. Section III H is a summary of our conclusions regarding the efficiency of the homogeneous mechanism.

A. The yield of dissociation

The yield of dissociation of halogen molecules embedded in a cluster has a threshold energy. Above the threshold, it is a rapidly increasing function of the collision velocity and can reach 100% (Fig. 4). This is unlike the surface impact induced dissociation of unclustered vibrationally cold halogen molecules, where the yield reaches a plateau below 40%.⁹ The higher yield for dissociation of the clustered molecules correlates with the evidence provided by examination

of individual trajectories. Molecules can dissociate homogeneously within the cluster, without reaching the surface. A third item of indirect evidence is that, at a given collision velocity, the dissociation yield in a Xe cluster is far higher than that in an Ar cluster (Fig. 4).

A quantitative summary of these conclusions is obtained by expressing the overall yield as a sum of two terms. The first represents the yield of dissociation of molecules on the surface. We take its functional velocity dependence to be that of an unclustered molecule. The functional form for the yield of homogeneous dissociation is adapted from the velocity dependence of the cross section for collision induced dissociation by a single rare gas atom.¹³ For either term ($i=1,2$), we use the form

$$\text{Yield}_i \propto (v^2 - v_{0e,i}^2)^{m_i} / v^2. \quad (3.1)$$

Here v is the velocity and v_{0e} is the effective threshold value. For the moment, we regard v_{0e} as a free parameter, to be determined by a fit to the computed yield. The subscript e denotes “effective” values, i.e., values which can depend on the cluster size, etc. Below we shall find it possible to use constant values, when we shall drop the subscript e . The value of the thresholds $v_{0e,i}$ is found to increase with the size of the cluster (and with the binding energy of the diatomic), but to decrease for heavier rare gases and/or for a more rigid surface. We continue the analysis of the threshold energies in Sec. III B. The exponents m_i in Eq. (3.1) are not varied, but are kept at the values $m_1=0.85$ found from a fit to the yield of dissociation of the isolated, vibrationally cold molecules and $m_2=1.2$ from a fit to the isolated atom–molecule process in the gas phase.¹³

The velocity dependence of the computed yield, as determined for an ensemble of trajectories, is represented as a sum of the contributions of the two alternative pathways

$$\text{Yield} = C_{e,1} \frac{(v^2 - v_{0e,1}^2)^{m_1}}{v^2} + C_{e,2} \frac{(v^2 - v_{0e,2}^2)^{m_2}}{v^2}, \quad (3.2)$$

where the two C 's are numerical prefactors. The functional form (3.2) provides a fit of the computed yield, to within its statistical uncertainty, for the entire range of collision velocities and systems studied. It does equally well for all models of the surface including the realistic one discussed in the preceding paper.⁸ There are four effective parameters in the fit: the values of the two thresholds, $v_{0e,i}$, $i=1,2$, and the prefactors of the two terms. (The two exponents are taken from that of the unclustered molecule and from the isolated gas phase collision.¹³ They are not used as fitting parameters.) Below we shall propose a quantitative interpretation of the values of the four “effective” parameters. Only then will we be able to identify the branching ratio of the two mechanisms.

An indication for the importance of a homogeneous mechanism is the dependence of the yield of dissociation on the identity of the rare gas atom. In the preliminary study¹³ of the isolated Rg–X₂ collision in the gas phase, we have pointed out that this is primarily a mass effect, as expected,⁵ for vibrational energy transfer in the impulsive, hard sphere limit. What this also means is that the gas phase results for the collision induced dissociation with all rare gases can be

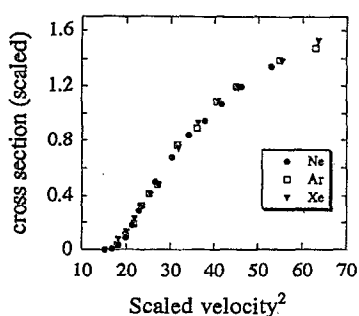


FIG. 5. A reduced representation of the yield of dissociation when an isolated Cl_2 molecule collides, at a high velocity, with a single rare gas atom. By scaling the cross section by an area characteristic of the rare gas atom and similarly for the velocity, the earlier results (Ref. 13) can be made to fall on a common functional form. (The velocity for Xe is unscaled and is in kilometers per seconds.)

put on a common reduced plot (Fig. 5). It follows that the functional dependence of the dissociation cross section {scaled by d^2 , where d is the range parameter of the cross section for the isolated collision¹³ [Eq. (11)]} on the (scaled, by the reduced mass) velocity can be expressed in a manner which is independent of the identity of the rare gas. We shall make extensive use of such scaling in the discussion that follows.

B. The size of the cluster

The qualitative result of the computations conforms to our intuitive expectations: the larger the cluster, the more important is the homogeneous process. To make this conclusion quantitative, we need a functional form for the yield of dissociation where the dependence on the cluster size is explicit. The parametrization proposed in Sec. III A was able to collapse the entire role of the size of the cluster into two factors. The first was a numerical prefactor that is presumably related to the branching fraction. The other is the effective value of the threshold v_{0e} . For either the heterogeneous or the homogeneous process, the value of v_{0e} is found to increase with the size of the cluster. For a given initial velocity, the energy per rare gas atom is independent of the size of the cluster, so why does the threshold increase?

Figure 6 shows a typical trajectory during the early stages, just before and shortly after the front atoms of the cluster reach the surface. As can be seen, the halogen molecule is slowed down by glancing collisions with those rare gas atoms which have already been reflected from the surface. Say that this halogen molecule reaches the surface. Its velocity normal to the surface will be lower than the nominal initial velocity of the cluster. It is a characteristic of higher energy, nearly hard sphere, collisions that the fractional energy loss is nearly constant (cf. Fig. 3). Since the initial kinetic energy of the center of mass of the halogen molecule is quite high, the actual loss in kinetic energy can be quite high. (A center of mass velocity of the halogen molecule of 1 km/s is equivalent to 8.5 and 30.4 kcal/mol for chlorine and iodine, respectively.) Lower impact parameter collisions can also transfer energy to the vibration of the initially cold mol-

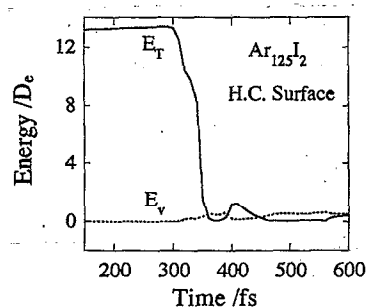


FIG. 6. The kinetic energy (E_T) of the motion, in the direction normal to the surface, of the center of mass of an I_2 molecule and the vibrational energy (E_v) during the approach to the surface. The molecule is embedded in a cluster of 125 Ar atoms and the role of the surface is described by the hard cube model. The figure also shows that vibrational excitation of the halogen molecule can occur prior to the ultimate collision that leads to dissociation.

ecule. As a result, the molecule can either dissociate, in which case it does not reach the surface intact or it can remain bound and reach the surface. Any vibrational excitation will enhance the dissociation on the surface, but the gain in vibrational energy of a molecule which remains bound is typically much smaller than the loss of center of mass kinetic energy. Hence, while vibrational excitation is more effective than translation in inducing dissociation, the gain in one is small compared to the loss of the other and the net result is that collisions en route to the surface will be detrimental for the yield of dissociation.

On route to the surface, the incident halogen molecule tends to lose far more translational energy than to gain vibrational energy, that should not, however, make one overlook the translational–vibrational coupling. In Sec. III E below, we shall show that it serves as a sensitive probe for the microscopic shock front in the cluster. It also means that the first homogeneous collision that transfers energy to the vibration is not necessarily the one that will lead to dissociation. Molecules can be first vibrationally excited not all the way to dissociation. In this respect, the caveat already noted is relevant. The very same collision that provided some vibrational excitation typically also removed a larger amount of center of mass translational energy.

The other route to dissociation is for the molecule to gain enough energy by a lower impact parameter collision with a rare gas atom. The relative velocity in such a collision will be lower than what it would nominally be. (As discussed above, the downward moving molecule has been slowed down. The rare gas atom which has rebounded from the surface has also been slowed down, but by collisions with other rare gas atoms which are still moving towards the surface.) In summary, the bigger the cluster, the lower the effectively available energy due to intracuster collisions.

A simple quantitative representation of the decrease of the initial velocity is by a “mean free path” correction, whereby the nominal velocity v is multiplied by $\exp(-n/\bar{n})$, where n is the number of cluster atoms. We find that for a given cluster, the same value of \bar{n} is needed for both the heterogeneous and the homogeneous processes. Another way of making the same point is to say that the effective thresh-

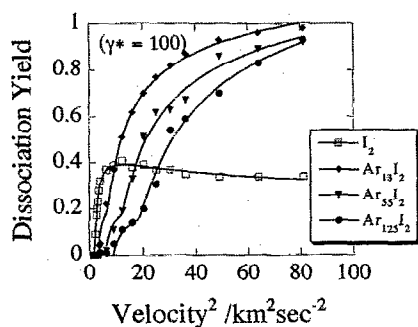


FIG. 7. The computed yield of dissociation vs the initial velocity for clusters of increasing size, where friction is used to describe the energy dissipation at the surface. See the text for details of the fit.

old v_{0e} has the same n dependence in both terms of Eq. (3.2). It follows that if, in Eq. (3.2), we replace the velocity variable v by $v \exp(-n/\tilde{n})$, then one can fit the computed yield using a common value v_0 of the threshold energy, a value which is independent of the cluster size (Fig. 7). (The threshold energy v_0 is still dependent, of course, on the identity of the halogen molecule, etc...) For the heterogeneous mechanism, the threshold is that found for the bare, vibrationally cold molecule. For the homogeneous mechanism, the value of the common threshold is determined by the fit. Both thresholds do, however, depend on the rigidity of the surface and we return to this point in Sec. III D below.

C. The branching ratio

The discussion in Sec. III B determined how the cross section for each process varies with the size of the cluster. The effect can be represented by replacing the nominal velocity v by the effective velocity $v_e = v \exp(-n/\tilde{n})$, but keeping a threshold value v_0 , which is independent of the cluster size. One can now rewrite Eq. (3.2) as

$$\text{Yield} = (1-p)C_1 \frac{(v_e^2 - v_{0,1}^2)^{m_1}}{v_e^2} + pC_2 \frac{(v_e^2 - v_{0,2}^2)^{m_2}}{v_e^2}, \quad (3.3)$$

where p is the branching fraction of those collisions that proceed by the homogeneous mechanism. For a given surface and cluster composition, the functional dependence (3.3) recovers the dependence on velocity for all the cluster sizes we examined ($n=0-550$). Typical results are shown in Fig. 7. Elsewhere we shall provide an independent determination of the branching ratio, which corroborates the conclusions based on the fit to Eq. (3.3).

As expected, the homogeneous mechanism increases in importance with increasing cluster size (Fig. 8). We tend to think of the branching ratio $p/(1-p)$ as the effective area of the surface as seen by those rare gas atoms that rebound towards the halogen molecule (and cause it to dissociate) vs the area as seen by a halogen molecule that does dissociate on the surface. The latter should be nearly energy independent because the energetic aspects are taken care of by the factors that multiply $(1-p)$ in Eq. (3.3). The former should increase with increasing cluster size, but should ultimately

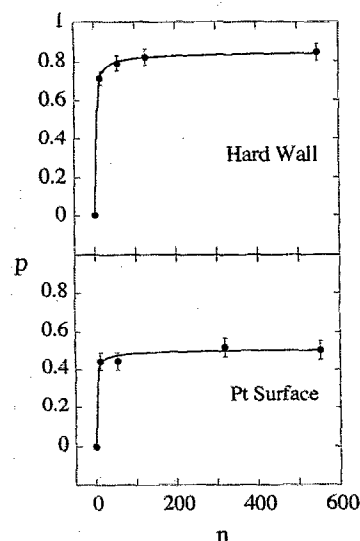


FIG. 8. The branching fraction p for homogeneous dissociation plotted vs the number n of Ar atoms in the cluster. The results are shown for a rigid surface model and for a realistic model (Ref. 8) of a Pt surface. The solid curve is a fit to Eq. (3.4).

saturate. There have been extensive discussions of the scaling of cluster properties with size.³¹ A simple empirical form that conforms to both our intuition and to the data (Fig. 8) is

$$p/(1-p) = s_\infty [1 - (n_0/n)^{1/3}] / s_0, \quad (3.4)$$

where n_0 is the threshold value of the cluster size, below which the homogeneous mechanism ceases to operate $p=0$; s_∞ is the area in the limit of a large cluster; and s_0 is the area for a halogen molecule. The ratio s_∞/s_0 is large for a more rigid surface (where the atoms are reflected from the surface into a narrower cone), but is of the order of unity for surfaces where the dissipation of energy to the surface is not small, including the realistic model discussed in the preceding paper.⁸ This ratio is also higher for the heavier rare gases.

D. The role of the surface

In this paper, the primary attribute of the surface is its rigidity, which determines the extent of energy loss upon collision. Other parameters that one can control are the surface temperature and the attraction/repulsion with the surface atoms. At the high velocities of interest, the role of the thermal energy is very small, (cf. Fig. 3) nor could we identify novel features due to the interaction of the halogen atoms with the surface. The reason for the absence of surface-specific effects in our computation is that those halogen molecules which do reach the surface either dissociate or escape without further effects. That the interesting dynamics cease past the time point when the molecule impacts the surface is due to the local density of rare gas atoms having already gone down at that point. Therefore, very seldom do the reflected but undissociated molecules encounter a rare gas atom and dissociate in the bulk. (In this connection, see also the discussion of the cage effect below.) In terms of the branching between the two processes, it therefore does not

matter if the halogen atoms are or are not very much attracted to the surface. (Of course, such an attraction does affect the energetics of the dissociation process on the surface.) What will have a far larger effect on the homogeneous process is any strong attraction of the clustering atoms (or molecules) with the surface. This is for the same reason which governs the effects of surface rigidity, to which we now turn.

Only for the rigid surface do the atoms regain their full initial velocity upon reflection. In either the simulations using a realistic model of the surface or for the more approximate models, the dissipation is well described as a constant fractional energy loss (cf. Fig. 3). This will no longer be the case at far higher temperatures, but is a good approximation for our conditions. It follows that the velocity of a rebounding atom is fractionally lower than the initial velocity of the cluster. It is the velocity after reflection from the surface that is needed for dissociation. This is the case for either type of process. Consider first the dissociation on the surface. As the first halogen atom impinges on the surface, its velocity, which before the collision was essentially parallel to that of the second halogen atom, is now essentially antiparallel to it. Kinetic energy of the center of mass motion has thereby been converted to internal excitation of the molecule. The lower the magnitude of the velocity of the rebounding halogen atom, the less the energy available for internal excitation. The essence of the argument remains unchanged if one allows the second halogen atom to also strike the surface. It follows that the threshold energy for dissociation on any given surface is a constant (i.e., independent of cluster size) fraction of the threshold velocity for a rigid, hard surface. Rather than using a threshold velocity which is a decreasing function of the surface rigidity, we can introduce a threshold value which is the same for all values and reduce the effective velocity v_e (Sec. III C) by a constant factor α , which is higher the greater is the energy dissipation by the surface. The theoretical value of α is determined by Eq. (2.1). At lower surface temperatures, when the role of the thermal motion of the surface atoms is negligible as compared to the high velocities of incidence, $\alpha = (\mu + 1)/(\mu - 1)$.

Figure 9 (upper panel) shows such a reduced plot for the dissociation of I_2 computed using the hard cube model of the surface. It is seen that to a good approximation, there is indeed a universal behavior. The range of parameters shown in the plot spans an order of magnitude variation in surface rigidity, but the more rigid the surface, (the lower is the value of μ), the better is the scaling and the rigid surface results fall on the same plot as the results shown for finite values of μ .

Also shown in Fig. 9, in the lower panel, is a scaled plot for a cluster of 125 Ar atoms. There is a shade more scatter than for the upper panel, but overall the result is very clear. By appropriate scaling of the velocity, one can account for the role of dissipation of energy by the surface. (For both mechanisms, we use the same value for the scaling factor α .) What this means is that the same functional form can account not only for the yield of dissociation for clusters of different sizes on a given surface, but also for a variety of surfaces. We emphasize that this result is due primarily to the

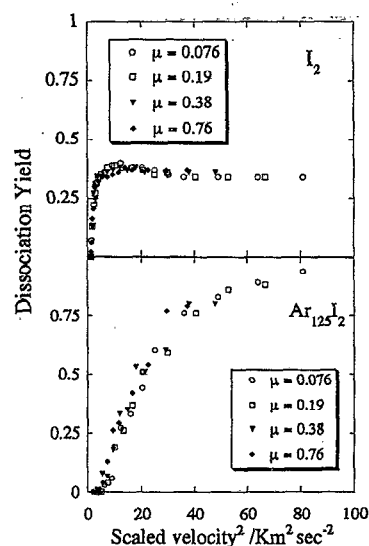


FIG. 9. A scaled plot for dissociation on surfaces of differing rigidity. The velocity of incidence is scaled by a factor α which varies with the reduced mass parameter μ of the hard cube model. The values of μ are given in the inset and correspond to an order of magnitude variation in the surface rigidity. (Upper panel) The bare I_2 molecule. (Lower panel) A cluster of I_2 embedded in 125 Ar atoms. The fit to the functional form (3.3) is not shown for reasons of clarity.

relatively high velocities of impact. It is for such conditions that simple models of surface rigidity can capture the essence of the problem, namely, that the atoms rebound from the surface with a fractional reduction in their initial velocity. While our discussion emphasized the hard cube model, one needs to note that the model invoking friction leads to a similar prediction. Indeed a comparison of Fig. 7 with Fig. 15 shows that the dynamics are also very similar for the two models. We expect, however, that for much softer surfaces (where the energy loss exceeds 80%), the scaling argument will break down. Strong attractive forces to the surface will also affect the validity of our considerations.

An important special case of the scaling argument is the result that the yield of dissociation, as computed for a realistic surface, can be well represented by the functional form (3.4). The fit is shown in Fig. 5.

To examine the effect of surface rigidity on the branching ratio, consider Eq. (3.3). To derive a universal behavior for the finite size cluster (lower panel of Fig. 9), we scaled the velocity down by a factor α . (α increases towards unity the more rigid is the surface.) Since after this scaling the results for different surfaces closely fit on the same curve, it follows that the change of the branching ratio p with α is compensated by the change of the two individual terms in Eq. (3.3) due to the scaling of the velocity. The yield of dissociation on the surface is readily shown to vary as $(\alpha^2)^{-0.15}$, where the numerical exponent is the exponent m_1 in Eq. (3.1) minus unity. This term is multiplied by $(1-p)$. For the product to remain invariant, $(1-p)$ should vary as $\alpha^{0.3}$. The yield of homogeneous dissociation scales as $(\alpha^2)^{0.2}$. This factor is multiplied by P . Invariance of the product requires that P should decrease with α as $\alpha^{-0.4}$. The two

expectations are not quite quantitatively consistent, which accounts for the slight scatter in the lower panel of Fig. 9. On the other hand, the trend is quite clear: The homogeneous mechanism is favored by a more rigid surface. The direct determination of p by fitting the velocity dependence of the overall yield of dissociation (cf. Fig. 8) results in values which are consistent with the expected trend.

The essentially unimportant role of the surface temperature is most easily discussed in terms of the hard cube model. We were able to account for both the cluster size effect and the role of surface rigidity by assuming that the velocity with which the rare gas atoms depart from the surface scales as the velocity of incidence. This is only true if the thermal velocity is small compared to the initial velocity. (This will also not be the case if there is a strong interaction with the surface.) For our conditions, the scaling assumption is an excellent approximation for the realistic surface (cf. Fig. 3), and it can be understood on the basis of the hard cube approximation. At far higher temperatures, it will no longer hold.

An important aspect, not explicitly considered in our work, is the role of the vibrational frequency spectrum of the solid. One expects that the surface mass density provides a useful measure for the rigidity.³²

E. The shock front

For a cluster where one can expect several shells of rare gas atoms (say $n^{1/3} > 4$), the first atoms to hit the surface will do so at about the same time. The more rigid the surface, the more these atoms rebound back into the cluster with comparable velocity vectors. The result is that the downcoming atoms or molecule will, at about the same time, experience collisions with these oppositely moving atoms. The width of such a front, in time, is less than σ/v , where σ is the range of the interatomic potentials. At the velocities used here, which are lower than 0.1 \AA/fs , this front should last for 50 fs or longer.

There are three ways that the molecule can discern the rare gas atoms. The longest range is the coupling to the motion of its center of mass (Fig. 6). Of somewhat shorter range is the coupling to the rotation. The expected tens of femtoseconds duration of the shock front is shorter than the rotational period, and therefore⁵ just of the right magnitude to be probed by the rotational motion of the diatomic molecule. (The vibrational periods are 59 and 155 fs for Cl_2 and I_2 , respectively. The rotational period increases with the rotational quantum number. At 50 K, it is about 1 and 2.4 ps, respectively.) Moreover, the range of the anisotropy of the atom-molecule potential means that the translational-rotational coupling will begin to occur at much longer atom-molecule separation than those for effective translational-vibrational coupling. (The latter requires close-in collisions.¹³) It follows that of the two internal energies, the rotational motion will be coupled to the shock front before the vibrational motion and will remain coupled to it after the vibrational motion is already *de facto* isolated (Fig. 10). It is therefore the vibrational motion of the halogen molecule which provides the more sensitive test for the "arrival time" of the shock front.

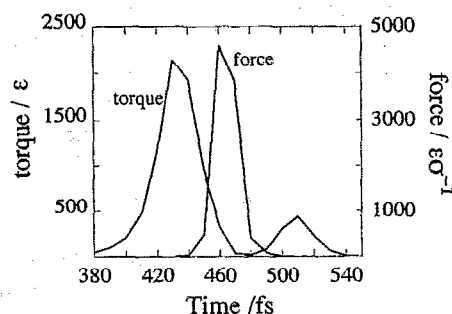


FIG. 10. The sequential coupling of the internal energies of the molecule to the shock front. Due to the longer range of the anisotropy of the potential, the rotational motion is the first to be coupled to the atoms reflected back from the surface. The effective coupling to the vibration requires a closer approach of the rare gas atom and hence is somewhat delayed. Shown is the torque on the molecule and the force along the bond direction vs time. Computed for I_2 , at an initial velocity of 5 km/s, for a cluster of 125 Ar atoms impacting on a hard cube surface.

Figure 11 shows a time profile of the vibrational energy of a Cl_2 molecule, embedded in an Ar_{125} cluster, for a time interval after the leading atoms of the cluster have reached the surface. Examination of the trajectories establishes that for both cases shown, the molecule has not yet reached the surface. A clear spike is evident in the vibrational energy. We have moreover verified that the inverse relation between velocity and the period of the shock front remains valid up to impact velocities of 15 km/s. In the larger clusters and provided the surface is rigid, a second, often more diffuse, front

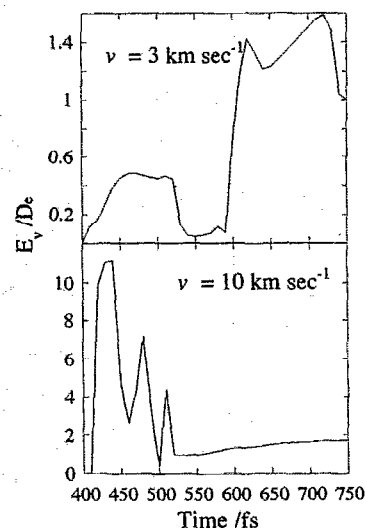


FIG. 11. The vibrational energy of the halogen molecule as a probe for a shock front. Shown is the vibrational energy of Cl_2 , in units of its dissociation energy D_e vs time embedded in a cluster of 125 Ar atoms. Examination of the trajectories shows that the molecule is moving down and has not yet reached the surface. It is excited by collisions with rare gas atoms which were at the front of the cluster and have already reflected, from the rigid surface, back into the cluster. (Upper panel) A low velocity. (Lower panel) A high velocity. We emphasize that these results were obtained for impact of the cluster on a rigid wall. A softer surface will cause both a spatial and a temporal dispersion of the front.

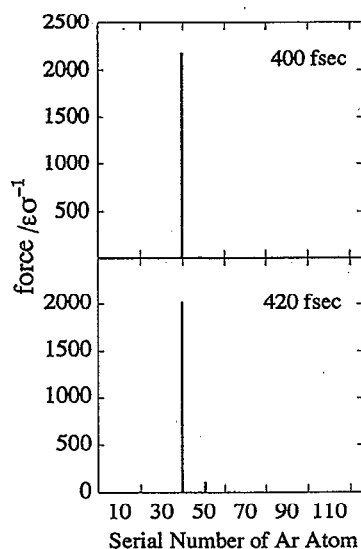


FIG. 12. The force (in reduced units) along the bond of the halogen I_2 molecule applied by the different rare gas atoms after impact at $t=340$ fs at a velocity of $v=5$ km/s on a surface described by the hard cube model. Forty femtoseconds after the impact, the rebounding rare gas atoms begin to reach the molecule and couple to the rotation. By 400 fs the coupling to the vibration is also strong, as shown.

can also be discerned due to the second wave of atoms reflected from the surface. Both the duration of the translational–vibrational coupling and the spacing between the fronts are as expected for the two velocities shown in Fig. 11. On the other hand, for a softer surface, the variation in magnitude and direction of the atoms which rebounds from the surface tends to average out the sharper front which is characteristic of a hard, rigid surface.

F. Details of the dynamics

The picture of a microscopic shock front propagating into the cluster suggests that collective, many body, effects can be important. For the chemistry of interest to us in this paper, such effects are not dominant. This is not unexpected since the primary event of interest is an efficient translation–vibration energy transfer. For a rare gas atom–halogen molecule collision, this will only occur for close-in collisions,¹³ which at the velocities of interest (cf. Fig. 1) means distances of less than two-thirds of the range of the Lennard-Jones Rg–X potential. Examination of individual trajectories verifies that at any given time, it is only one, or sometimes two, rare gas atoms that exercise a significant force along the interatomic axis of the halogen molecule (Fig. 12). Another dynamical reason why fewer rare gas atoms can couple to the vibration at any given moment in time is a steric one. Vibrational excitation requires a force with a large component along the direction of the interhalogen bond. The repulsion between the rare gas atoms means that not more than two atoms can easily do so. In other words, there is a limited “cone of acceptance”⁵ for vibrational excitation. On the other hand, any rare gas atom in the first shell around the molecule can exercise a torque.

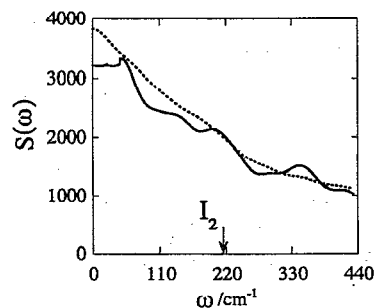


FIG. 13. The power spectrum of the force acting along the bond of the I_2 molecule vs frequency. The vibrational frequency of I_2 is indicated as a reference. Computed for an initial velocity of 3 km/s and as an average over an ensemble of 20 trajectories. (Solid line) The power spectrum of the molecule embedded in 125 Ar atom cluster. (Dashed line) The same power spectrum, but computed as an incoherent sum of contributions of individual rare gas atoms.

The absence of “many body” vibrational excitation can also be seen in the frequency domain. This is most readily examined using the Fourier transform of the time correlation function of the force along the interhalogen bond. This correlation function has been extensively discussed^{33–35} in connection with the validity of the binary collision model³⁶ of vibrational excitation of diatomics in solution.

The time correlation function is computed, by appeal to the ergodic theorem,³⁷ as the power spectrum of the force. Specifically, we compute

$$S(\omega) = \left\langle \left| \int_0^T \sum_{j=1}^n f_j(t) e^{i\omega t} \right|^2 \right\rangle, \quad (3.5)$$

where $f_j(t)$ is the force along the molecular axis due to atom j of the rare gas at time t . The result is shown in Fig. 13 for I_2 in a cluster of 125 Ar atoms at a initial velocity of 3 km/s. Also shown in Fig. 13 is the power spectrum for the case when the different atoms act independently of one another. This is computed just as in Eq. (3.5), except that it is a sum of uncorrelated terms

$$S_{\text{unc}}(\omega) = \left\langle \sum_{j=1}^n \left| \int_0^T f_j(t) e^{i\omega t} \right|^2 \right\rangle. \quad (3.6)$$

It is clear that while the two results are not identical, there is hardly any compelling evidence for many body effects.

The magnitude of the Fourier transform of the time correlation function is also of interest because it provides a useful measure of the efficiency of transfer of translational energy into vibrational excitation at the frequency ω .^{5,33} The rather short duration, (Fig. 11) of the impulsive collisions typical of the velocity range of interest¹³ means that the Fourier transform, as shown in Fig. 13, extends to quite high frequencies. In this respect, we note that the Fourier transform relation between the time and the frequency response is as valid in classical as in quantum mechanics. Hence, while the dynamics in the simulation is classical, the wide range of frequencies that can be excited by the unusually short intermolecular coupling is accounted for.

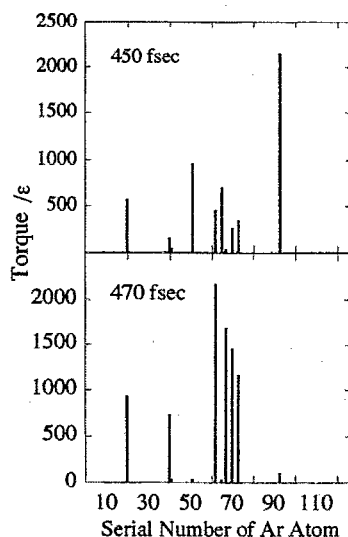


FIG. 14. The torque (in reduced units) acting on the halogen molecule. Other details are the same as in Fig. 12, which is for the force acting on the vibration.

The evidence from the power spectrum is that cluster impact provides a practical route to vibrational excitation of molecules more rigid than the halogens. In terms of the adiabaticity parameter ξ , the vibrational excitation appears to be in the sudden limit.⁵

The anisotropy of the rare gas atom–halogen molecule potential extends to a far longer range than the force on the vibrational motion. It is therefore only to be expected that rotational excitation of the halogen may be more many body in nature. Figure 14 shows the number of rare gas atoms that exercise a significant torque on the halogen molecule for two time instants in a 125 atom cluster, just past the initial impact with the surface. Several atoms are simultaneously active. It should, however, be borne in mind that the “dumb-bell” atom–atom type potential used to represent the rare gas–halogen molecule interaction is possibly too anisotropic and consequently may overestimate the collective nature of the rotational excitation.

The significantly longer range of the anisotropy of the potential as compared to the range of the potential for vibrational excitation is also manifested in the duration of the collision (Fig. 10). Whereas the duration of the impulsive vibrational energy transfer is 10–30 fs, the anisotropic coupling acts for many more tens of femtoseconds, i.e., essentially for the entire passage of the “shock front.” There is therefore a difference between vibrational and rotational excitation. The dynamics of the former is the same as in an isolated binary collision, whereas in the cluster, rotational–translational coupling can last for much longer and several rare gas atoms can take part.

For a larger cluster, a halogen molecule can undergo several impulsive translational–vibrational couplings with (different) rare gas atoms. These are typically uncorrelated and well separated in time. It is quite common, however, for the coupling to the rotation to persist for the entire time

interval between these independent impulsive events.

The longest range interaction is to the center of mass motion of the halogen molecule. Up to a dozen rare gas atoms can engage in slowing down the halogen molecule at any given moment. This coupling, which can considerably slow down the molecule (cf. Fig. 6) is a dominant factor in determining the role of the size of the cluster. In Sec. III B, we allowed for it by the introduction of an effective velocity which is dependent on the number n of rare gas atoms in the cluster.

Discussions of third-body-assisted recombination of halogen atoms^{2(b),38} invoke, as a possible step, the formation of a Rg–X intermediate. Microscopic reversibility would then suggest that the dissociation process will also proceed by a similar route. This may be the case in the immediate post threshold energy region, but otherwise this species will dissociate within a few vibrational periods. One could argue that the longer times over which the rare gas atom is coupled to the molecule by the anisotropic forces are a signature of such a complex. Even then, the collision lasts for less than the X_2 vibrational period. It requires a much deeper well for this, so-called, chaperon mechanism to be relevant under the present conditions. The ultimate extreme of this limit is when the atoms (or molecules) of the medium can have a long range chemical interaction with the substrate molecule. In this case, vibrational excitation would be far more efficient³⁹ and its cone of acceptance would be much wider, particularly so since at such higher energies an “insertion” type approach can also be effective.^{40–42}

All of the above is not to say that significant collective effects are necessarily absent. The lessons from simulations of activated chemical reactions in solution⁴³ are very relevant to us. In rare gas solvents, it is typically one or, at most, a few solvent atoms that strongly couple to a nonpolar solute at any given moment.⁴⁴ Not so for reactions of polar molecules in associated solvents such as water. As the system moves to cross the activation barrier, at a given time point, many water molecules engage in helping it along.⁴⁵ Impact of homogeneous clusters of polar molecules (e.g., water and sulfur dioxide)⁷ have already been studied. It would therefore be of particular interest to examine the dynamics of high energy chemical processes taking place within such clusters or in molecular or ionic clusters.

G. The cage effect

Experimental results^{16,28,46–49} and simulations^{15,17,28} of dissociation of molecules in clusters can manifest quite dramatic cage effects. In particular, the yield of photodissociation can decrease to almost zero as the cluster size increases and one or more “solvation shells” are enveloping the molecule. Examination of simulations verifies the intuitive expectation that the role of the surrounding medium is to slow down the dissociation fragments and ultimately to detain them so that they can recombine.

No such strong cage effects are seen in the present simulations. Once the halogen molecule has dissociated, the two atoms are found to recede with hardly any noticeable hindrance. We consider that at least two factors, both unique to the special conditions in impact-heated clusters, contribute to

this behavior. The first, and, to our mind, the primary, factor is the unusually high velocities at which the halogen atoms separate after the dissociation. Consider the homogeneous mechanism. As for the isolated Rg-X₂ collision in the gas phase, here too the yield of dissociation has a *de facto* threshold which is higher than the bond energy of X₂ (cf. Fig. 3 of Ref. 13). It follows that even just past the threshold, the halogen atoms recede with a finite kinetic energy. The molecular level interpretation of this observation is that already mentioned, namely, that the dissociation occurs upon a hard sphere collision between a rare gas and a halogen atoms. If we think of the rare gas atom as a photon whose role is to provide the necessary energy, we can make an analogy with the case of optical excitation and say that here the dissociation starts with a rather compressed diatomic molecule. Of course, the photodissociation occurs from a repulsive excited electronic state, but here too, the initial energy of the unbound molecule is largely potential. The excess potential energy of the two close-in atoms is converted to kinetic energy of the separated atoms. At the high kinetic energies of the receding halogen atoms and of the rare gas atoms that surround them, the atoms are "smaller" than we normally tend to consider them (cf. Fig. 1 above). This fact alone tends to reduce the local density of the cluster by a factor of 2 or more. Beyond that, the high velocities of the rare gas atoms also mean that the cage is a very shaky one, with large fluctuations in the rare gas atoms interatomic distances. Both the size of the atoms is smaller and the probability of any but a glancing collision is smaller.

The second consideration is that by the time homogeneous dissociation of the molecule took place, the cluster already begins to expand. The expansion is most noticeable in the direction parallel to the surface,^{7,8} and it too acts so as to reduce the local density.

In the original discussion of the cage effect,⁵⁰ an analogy was made with the motion of a collection of hard spheres on a vibrating tray. To a certain extent, this analogy can be used here too. Two modifications are necessary. The first is that the tray is large and that the collection of molecules initially occupies a localized and small area on the surface of the tray. The other is that the tray is really shaking. Perhaps a more current day analogy is to a pair of dancers who happen to separate on the floor of a fashionable disco.

H. Summary

Section III sought to interpret the role of the molecule itself, of the surrounding medium, and of the surface in the impact induced dissociation, with special reference to the hitherto unexplored homogeneous process. Necessarily, our conclusions are limited in the scope of their validity. First and foremost, we have neglected any electronic excitations. Next, our surface was chemically inert and, in this paper, lacked any structure. Within these simplifying assumptions, we found a very systematic dependence on such factors as the identity of the rare gas (the heavier, the better), the size of the cluster (larger clusters favor homogeneous dissociation), the dissociating molecule, and the rigidity of the surface. While the qualitative trends were all in the intuitively expected direction, it was also possible to incorporate the

trends, in a quantitative fashion, into a functional form for the velocity dependence of the yield of dissociation. This represented the yield as a sum of two contributions—that of a heterogeneous and a homogeneous process. The detailed dynamics of the dissociation is essentially governed by the fast scale of the motion. At such impact velocities that dissociation is possible, it takes less than 100 fs to cover a distance comparable to the range of the long range forces. It takes 10 fs or less to cover the scale of the short range repulsions which are responsible for the vibrational excitation. The interatomic motion is thus comparable or, typically, faster than the intramolecular vibrations and is much faster than molecular rotation. Cluster impact provides us therefore with a new regime (hitherto only accessible in such circumstances as the chemistry in front of the cone during the re-entry of a satellite⁵¹ or that of translationally very hot atoms⁵² produced in nuclear recoil and, possibly, in sonochemistry),⁵³ where the intermolecular coupling acts on a scale fast compared to that of all intramolecular motions.

IV. CONCLUDING REMARKS

The dissociation process in impact heated clusters appears to be dominated by those rare gas atoms that are first to rebound from the surface. As they counterpropagate into the main body of the cluster, these atoms significantly slow down the halogen molecule which is moving towards the surface. The heavier the rare gas, the more effective is this process, which can, for a lighter halogen molecule in a heavier rare gas, reverse the direction of motion. The collisions also cause vibrational excitation, often sufficient to dissociate the molecule. However, it is not necessarily the very first collision between the halogen molecule and a returning rare gas atom which will cause the molecule to dissociate. The molecules which are still bound when they reach the surface will, at all but the lower initial velocities, dissociate on the surface. The result is that in the post-threshold regime, the total yield of dissociation will exceed the yield of the heterogeneous process and can reach up to 100% (Fig. 15). On the other hand, in the low energy region, increasing the dissipation of energy at the surface will considerably reduce the yield (Fig. 2). There is no third-body assisted recombination of the halogen atoms because the forces are weak compared to the velocities with which the atoms move and because of the low local density of the rare gas atoms. In future studies, we intend to examine the dynamics in more strongly bound clusters.

The role of the surface appears to be primarily a dissipative one. Some, or much, of the kinetic energy of impact is removed and is thereby not available on the time scale of interest (Fig. 2). The other, related, aspect is the angular dispersion of those rare gas atoms that rebound from the surface. The fewer such atoms that are reflected back into the cluster, the lower is the local density of hot atoms so the lower is the rate of energetic intracluster collisions (Fig. 7). The bigger the cluster, the less important is the reduction in density. The role of surface specific effects and of surface structure sensitivity remains to be elucidated. The very preliminary indications are that at the high velocities in ques-

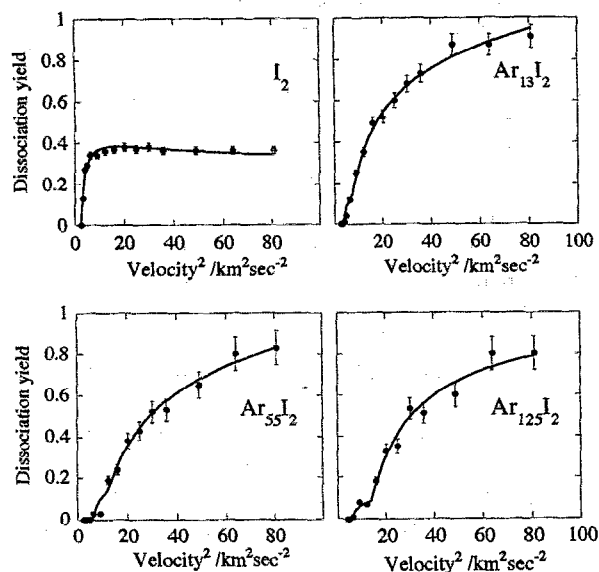


FIG. 15. The yield of dissociation of clusters of different sizes. I₂ in Ar_n clusters $n=0, 13, 55,$ and 125 vs the initial velocity for impact on a surface described by the hard cube model. The fit is to Eq. (3.3) with a common value of the threshold. (The effective energy thresholds for the clusters are larger by 1.45, 2.4, and 2.7, respectively.) The error bars are the estimated statistical noise for an ensemble of 100 trajectories.

tion, such effects would primarily result from local deformations and bulk penetration effects.

The sequence of events inside the cluster is primarily governed by the high velocities in question. At center of mass velocities higher than a few kilometers per second, intermolecular motions are as fast or faster than intramolecular ones. The collisional perturbations are then rather sudden-like, and what distinguishes the different internal modes is not their unperturbed frequencies, but rather the range of forces that couple them to the translational motion. As a rare gas atom approaches the halogen molecule, a sequential hierarchy of couplings is manifested and this ordering governs the resulting dynamics. First, in terms of its range, is the translation-translation transfer. This slows down the halogen molecule and thereby requires a higher initial velocity than might otherwise suffice. The bigger the cluster, the more important are these collisions (Fig. 7). As the rare gas atom approaches closer to the molecule, it is coupled to the rotation by the long range anisotropy of the potential. The torque on the molecule can be quite high and several atoms can simultaneously exercise such a torque (Fig. 14). Even closer in, the short range atom-atom repulsion induces efficient vibrational excitation. The magnitude of the force along the direction of the bond is commensurate (cf. Fig. 10 with the magnitude of the torque on the bond). However, to apply an effective coupling, the rare gas atom needs to approach as much as possible along the bond axis, so that only one or two rare gas atoms couple effectively to the vibration, at any given instant (Fig. 12). Unlike the case of the rotation, only hot rare gas atoms can induce significant vibrational excitation. (The rotational period of the halogen molecule is so long, that even quite slow atoms will be in the sudden regime

with respect to it.) The selectivity of the vibration as a thermometer for hot atoms was used (Fig. 11) to monitor the progress of the shock front through the cluster. An important aspect, not addressed in this study, is the possibility of translational to electronic coupling.

The physics described above could be phrased in a quantitative fashion and thereby provide a systematic account of the dependence of the yield of dissociation on such factors as the size of the cluster or the rigidity of the surface. Figure 15 is a summary of the computed yield of dissociation on the initial velocity for a variety of cluster sizes impacting a surface described by a hard cube model. There is a systematic variation in the thresholds, etc. The fit shown uses a common value of the threshold which is independent of the cluster size (or, cf. Fig. 9, of the rigidity of the surface). It assumes that two mechanisms contribute to the yield—a heterogeneous one, which is identical in all respects to the dissociation of an isolated molecule on the surface, and a homogeneous route in which one rare gas atom transfers enough vibrational energy to the molecule to break the bond. The tightness of the fit provides further evidence that in these rare gas clusters, the dissociation events are essentially binary in nature.

The combined evidence strongly suggests that the extreme conditions which prevail for the very few hundreds of femtoseconds after the cluster impact provide not only an opportunity for new and creative chemistry, but also offer the theoretician a window into a new coupling regime, that of thermally induced femtochemistry.⁵⁴

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