Librational control of reactions in large clusters

Pavel Jungwirth

J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 18223 Prague 8, Czech Republic

Abstract

A new way to control of the yield of reactions in clusters is presented and demonstrated on the formation of the Cl_2 molecule from a photodissociated HCl molecule trapped on a $Cl(Ar)_{12}$ cluster using molecular dynamics simulations. The key to the method is the large amplitude librational motion of the hydrogen atom prior to photolysis. Starting from the ground librational state practically no product is formed. On the other hand, turning on the control mechanism by optical or thermal preexcitation of the system to the first excited librational state leads to a 70% Cl_2 product yield.

Inert clusters represent a unique medium for studying solvent effects on the reactivity of chemical species deposited in or on them. Recent experiments dealing with several reactions on large argon clusters [1] have demonstrated the feasibility of the new cluster isolation technique which is in many aspects complementary to traditional matrix isolation reactivity studies. In clusters, effects connected with the mutual separation and orientation of the reactants become crucial since they can have an enormous effect on the reaction yield. This also opens the possibility of an efficient control of the outcome of the reaction provided one can influence e.g., optically the spatial characteristics of the reactants.

The principal goal of the present paper is to outline a new strategy for photochemical reaction yield control in cryogenic clusters. The method is tailored to the following experimental setup. First, one of the reactants (radical, ion, or a small molecule) is embedded in an inert cluster e.g, by coexpansion into the vacuum [2–6]. In the next step, the second reactant which is a diatomics containing hydrogen and one heavy atom (e.g, a hydrogen halide) is deposited on the cluster using a pick-up technique [1,7]. After the preparation of the mixed cluster, the control mechanism consists in preexciting the strongly delocalized librational mode of the hydrogen atom by a microwave (far-IR) radiation or thermally, before the UV photolysis of the hydrogen halide. As will be discussed in detail in next paragraphs, the preexcitation of the hydrogenic librational mode results in a favorable orientation of the photodissociating heavy atom for the reaction with the cluster embedded reactant. We note, that together with other investigators studying this type of systems we use the term libration [8], while different authors employ the term hindered rotation [9] for a motion the amplitude of which is too large for a normal vibrational mode.

Mixed systems consisting of one HCl molecule and one to tens of argon atoms have been extensively studied as prototypes of heterogeneous clusters both experimentally using microwave and IR spectroscopy and theoretically [2–6,9–18]. From the perspective of the present study two points are most important. First, the structures and interatomic potentials of the two smallest clusters HClAr and $HCl(Ar)_2$ are very well known today together with the shapes of the ground and first excited hydrogenic librational wavefunctions [9–11]. Second, it has been shown that for all studied cluster sizes the most stable ground state structure consists of the HCl molecule deposited on the argon cluster with the hydrogen atom strongly delocalized but still pointing towards the rare gas cluster [11].

In this work we demonstrate the performance of the new control mechanism for the process of formation of the Cl_2 molecule from a photolyzed HCl molecule deposited on a $Cl(Ar)_{12}$ cluster. In the light of the previous studies the system investigated here can be viewed as a HCl molecule trapped on a 'magic' size (completed first solvation layer) Ar_{13} cluster, where the central argon is replaced by a chlorine atom. The $Cl(Ar)_{12}$ cluster has been studied recently in the context of cluster melting and reaction collisions with hydrogen [19,20]. Since the Cl-Ar interaction, the weak anisotropy of which is being neglected, has practically the same range and is slightly stronger than the Ar-Ar potential, the $Cl(Ar)_{12}$ cluster has similar icosahedral shape as the Ar_{13} system with the argon atoms forming a complete shell around the central chlorine [19,20].

We apply to the process under study an empirical rule stating that a satisfactory description of photochemical processes is usually achieved using classical trajectories, provided the initial quantum state of the system is properly sampled [21]. Indeed, during photodissociation the hydrogen atom acquires a large amount of kinetic energy which brings it close to the classical limit. The other atoms remain much colder but they are also significantly heavier which makes again classical approach plausible. On the other hand, prior to photolysis the light and cold hydrogen atom moving with a large amplitude in a very shallow potential well is a strongly quantal object, the non-classical nature of which has to be taken into account. Here, we solve this problem by propagating a swarm of trajectories the initial coordinates of which sample properly the delocalized hydrogenic librational wavefunction. At very low temperatures (few Kelvins) typical for these processes the initial classical momenta of all particles can be approximately set to zero and the trajectories of the heavy atoms are initiated from their equilibrium positions.

The molecular dynamics simulations are preceded by a structure optimization of the $Cl(Ar)_{12}HCl$ complex in its ground electronic state using previously employed empirical interatomic potentials [20], assuming that the weak interaction between the two chlorine atoms is similar to the Ar-Ar van der Waals interaction. The optimal structure corresponds to an icosahedral argon shell surrounding the chlorine atom with the HCl molecule weakly bound to the icosahedron with the Cl molecule lying on its C_3 axis (see Figs. 1-2). As a next step, the initial positions of the hydrogen atom for classical trajectories are sampled using the quantum mechanical librational wavefunction. It is beyond the means of current computational methods to solve the vibrational Schrödinger equation for the whole cluster. Luckily, the HCl molecule has only three argon atoms as nearest neighbors with which it forms a pyramidal structure, and one can safely neglect the influence of the remaining much more distant argons and of the central chlorine atom on the shape of the librational wavefunction. Unfortunately, the solution of the quantum vibrational problem for the pentaatomic $HCl(Ar)_3$ system is still computationally rather demanding and has not been accomplished yet. On the other hand, ground and first excited librational functions (called Σ bend, in-plane Π bend and out-of-plane Π bend) have already been evaluated for a smaller $HCl(Ar)_2$ cluster [9,10]. Except that the two Π bends become degenerate in the $HCl(Ar)_3$ cluster, the situation is expected to be very similar in the two systems [22]. Especially, there is a very good correspondence between the Σ-type bends in the two clusters, therefore we assumed the Σ-type bend as the crucial librational mode in the investigated $Cl(Ar)_{12}HCl$. Classical trajectories started with different orientations of the HCl molecule, i.e. with different initial H-Cl(of the HCl molecule)-Cl(solvated) angles θ, were then weighted by the square of the ground or first excited librational (Σ bend) wavefunction at the given value of the angle θ as calculated for the $HCl(Ar)_2$ system [10], multiplied by $sin\theta$. Since in these wavefunctions the large amplitude hydrogenic motions are very well separated from the heavy atom motions we assumed for all trajectories the same optimized initial positions of argon and chlorine atoms. Finally, the photoexcitation of the HCl molecule by a short UV laser puls was modeled in the present simulations by switching, at t=0, from the ground electronic state of HCl to the repulsive first exited potential of this molecule [14]. At the same time, an attractive potential between the two chlorine atoms, corresponding to the ground electronic state of the Cl_2 molecule was turned on [23] together with the attractive ground state HCl potential between the hydrogen and the solvated chlorine atom [20]. All classical trajectories were propagated using a standard fourth order Gear algorithm [24] for 20 ps with a timestep of 0.25 fs.

In all simulated trajectories with the angle θ sampling the whole interval $(0^o, 180^o)$, the hydrogen atom acquires a large portion of kinetic energy and flies within several femtoseconds away, either directly for large values of the angle θ, or after a collision with the $Cl(Ar)_{12}$ system if the initial angle θ is small. For very small values of the angle θ hydrogen can even penetrate into the cluster but since it cannot get fast enough rid of the large excess energy it is scattered away and consequently no formation of a new stable HCl molecule is observed. This is in accord with previous studies, where an extremely low HCl yield for a highly energetic hydrogen in the $HCl(Ar)_{13}$ system is described [12,19,20]. At the same time the chlorine atom from the photolyzed HCl molecule acquires an energy of 0.09 eV, which is 1/36 (the H:Cl mass ratio is 1:35 for the most abundant Cl isotope) of the excess energy, and a recoil in the opposite direction than the hydrogen atom. The crucial parameter which decides whether the reaction leading to the formation of the Cl_2 molecule takes place or not is the direction in which the photodissociating Cl atom is being pushed. It turns out that classical trajectories started with different values of the angle θ sharply fall into two categories - non-reactive and reactive, the critical angle being 80^o. In other words, if the initial angle θ is smaller than 80^o no trajectory is reactive, while for $\theta \geq 80^o$ all trajectories lead to the formation of the Cl_2 molecule.

A typical non-reactive trajectory ($\theta = 45^o$) is depicted in Fig. 1, while Fig. 2 shows a typical reactive trajectory ($\theta = 135^o$). The difference between the two simulations is enormous. In the first, non-reactive case both atoms of the former HCl molecule fly away with the $Cl(Ar)_{12}$ cluster remaining practically intact. This is due to the fact, that the heavy chlorine atom is being pushed out of the cluster with enough kinetic energy to overcome the attraction to the other Cl atom and the argons. At the same time the collision of the hydrogen atom with the cluster is energetically very inefficient due to the large difference in masses of the colliding partners. Thus, the compact $Cl(Ar)_{12}$ cluster only slowly rolls away. In the second, reactive case the hydrogen freely flies away while the photodissociating Cl atom is recoiled towards the $Cl(Ar)_{12}$ cluster. This time, the collision is energetically very efficient due to similar masses of chlorine and argon, and this is even enhanced by the arising strong attractive force between the two chlorine atoms. As a result a Cl_2 molecule is formed and stabilized by heating and partially disintegrating the cluster. Indeed, within 20 ps the argon cluster is completely melted and several argon atoms are ejected from it.

A more quantitative analysis of the stabilization of the newly formed Cl_2 molecule is based on Fig. 3, which depicts the time evolution of the Cl-Cl bond distance for a reactive trajectory with the initial angle θ equal to 180^o, a borderlying reactive trajectory with $\theta = 80^o$, and a borderlying non-reactive trajectory with $\theta = 75^o$. In the first case, the chlorine atoms start to approach each other from the very beginning, efficiently transfering part of their kinetic energy to the argons during the first few picoseconds, after which the Cl_2 molecule becomes stabilized in a highly excited vibrational state. Further relaxation and energy transfer to the melted argon cluster is much less efficient and is only partially covered by the present simulation. The employed Morse Cl-Cl potential [23] supports 104 bound vibrational states. At the end of our simulation the energy of the Cl_2 vibration corresponds to v=70, which is 0.37 eV below the dissociation limit. In the two other cases, the photodissociating chlorine atom moves initially out of the $Cl(Ar)_{12}$ cluster. For $\theta = 75^o$ this motion continues and consequently no reaction occurs, while in the case of $\theta = 80^o$ the attraction between the chlorine atoms is just strong enough to revert around 1.5 ps the direction of the motion of the photodissociating chlorine atom and bring the partners together. Subsequently, the Cl_2 molecule stabilizes by energy transfer to the argons and after 4 ps its motion becomes similar to the case with $\theta = 180^o$, except that for angles different from 180^o a non-negligible rotational excitation of the Cl_2 species takes place, too. Detailed analysis of the dynamics of the product molecule and the rest of the system, together with an approximative construction of the librational states directly for the $Cl(Ar)_{12}HCl$ cluster are in the focus of an ongoing separate study [25].

In order to evaluate the efficiency of the proposed librational control scheme it is necessary to know how large part of the librational wavepacket lies in the reactive region $80^o \leq \theta \leq 180^o$. As discussed earlier, for this we used the calculated ground and first excited wavepacket corresponding to the Σ bend in the $HCl(Ar)_2$ complex [9]. While in the ground librational state with the H atom delocalized but still pointing essentially towards the cluster small values of the angle θ are sampled and only 2% of the wavepacket lie in the reactive region, for the first excited state which is much more delocalized with the preferential hydrogen orientation being out of the cluster, this number reaches 70%. In other words, the quantum yield of the formation of the Cl_2 molecule by HCl photolysis in the $Cl(Ar)_{12}HCl$ cluster is, when the librational control mechanism is switched off, only 2%, while by turning on the control scheme the quantum yield grows by a factor of 35. This is a very efficient control mechanism, which can be realised either directly by microwave (far-IR) radiation [2–5] or by means of heating the cluster. Indeed, since the energy difference between the ground and first excited librational state is 39.55 cm^{-1} [3], at the helium temperature of 4 K only a fraction of 7×10^{-7} of the $Cl(Ar)_{12}HCl$ clusters is in the excited librational state and the quantum yield for the process under study practically does not rise above 2%. On the other hand, at 35 K which is just below the melting temperature of the $Cl(Ar)_{12}$ cluster [19,20] the fraction of thermally librationally excited clusters rises to 0.17 resulting in a 14% total quantum yield of the formation of the Cl_2 molecule.

In conclusion, we outlined in this paper a novel and efficient scheme for the control of reactions in large clusters. The method consists in the preexcitation of the librational motion of a hydrogen halide molecule deposited on a large inert cluster seeded by an atomic radical, prior to the photolysis of the diatomics. Classical molecular dynamics simulations which take into account the quantum nature of the initial hydrogenic librational state show that in the $Cl(Ar)_{12}HCl$ cluster this control mechanism qualitatively enhances the quantum yield of the formation of the Cl_2 molecule from 2% to 70%. From the perspective of a possible future experiment it is important to stress that the reported computer simulations mimic a very realistic experimental setup.

We would like to thank J. M. Hutson and B. Schmidt for valuable comments. Support from the Granting agency of the Academy of Sciences of the Czech Republic via a grant No. A4040706 is gratefully acknowledged.

REFERENCES

[1] C. Gee, M. A. Gaveau, O. Sublemontier, J. M. Mestdagh, and J.-P. Visticot, J. Chem. Phys. 107 (1997) 4194.

[2] T. D. Klots, C. Chuang, R. S. Ruoff, T. Emilsson, and H. S. Gutowsky, J. Chem. Phys. 86 (1987) 5315.

[3] M. J. Elrod, D. W. Steyert, and R. J. Saykally, J. Chem. Phys. 94 (1991) 58.

[4] M. J. Elrod, D. W. Steyert, and R. J. Saykally, J. Chem. Phys. 95 (1991) 3182.

[5] M. J. Elrod, J. G. Loeser, and R. J. Saykally, J. Chem. Phys. 98 (1993) 5352.

[6] L. Oudejans, K. Nauta, and R. E. Miller, J. Chem. Phys. 105 (1996) 10410.

[7] T. E. Gough, M. Mengel, P. A. Rowntree, and G. Scoles, J. Chem. Phys. 83 (1985)4958.

[8] S. Hennig, A. Cenian, and H. Gabriel, Chem. Phys. Lett. 205 (1993) 354.

[9] A. Ernesti and J. M. Hutson, J. Chem. Phys. 106 (1997) 6288.

[10] A. R. Cooper and J. M. Hutson, J. Chem. Phys. 98 (1993) 5337.

[11] D. T. Anderson, S. Davis, and D. J. Nesbitt, J. Chem. Phys. 107 (1997) 1115.

[12] M. Y. Niv, A. I. Krylov, and R. B. Gerber, Faraday Disc., in press.

[13] A. Garcia-Vela and R. B. Gerber, J. Chem. Phys. 103 (1995) 3463.

[14] A. Garcia-Vela, R. B. Gerber, and U. Buck, J. Phys. Chem. 98 (1994) 3518.

[15] A. Garcia-Vela, R. B. Gerber, D. G. Imre, and J. J. Valentini, Phys. Rev. Lett. 71 (1993) 931.

[16] T. Schroder, R. Schinke, and Z. Bacic, Chem. Phys. Lett. 235 (1995) 316.

[17] Z. Bacic and R. E. Miller, J. Phys. Chem. 100 (1996) 12945.

[18] P. Jungwirth and B. Schmidt, Chem. Phys. Lett. 259 (1996) 62.

[19] B. Schmidt and R. B. Gerber, Phys. Rev. Lett. 72 (1994) 2490.

[20] B. Schmidt and R. B. Gerber, J. Chem. Phys. 101 (1994) 343.

[21] R. B. Gerber, A. B. McCoy, and A. Garcia-Vela, Ann. Rev. Phys. Chem. 45 (1994) 275.

[22] J. M. Hutson (private communication).

[23] A. A. Buchachenko and N. F. Stepanov, Chem. Phys. Lett. 261 (1996) 591.

[24] M. P. Allen and D. J. Tildesley, Computer simulations of liquids (Clarendon, Oxford, 1987), p. 82.

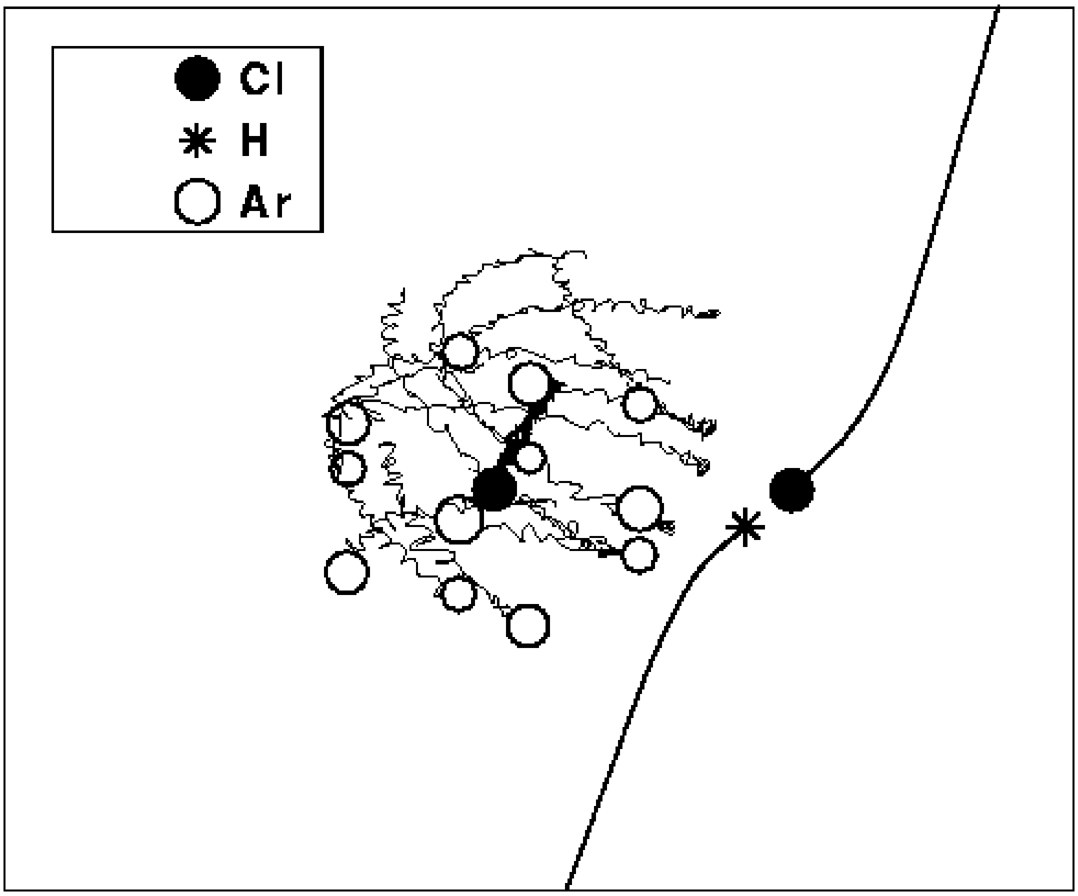
[25] P. Zdanska, P. Jungwirth, and B. Schmidt, in preparation.

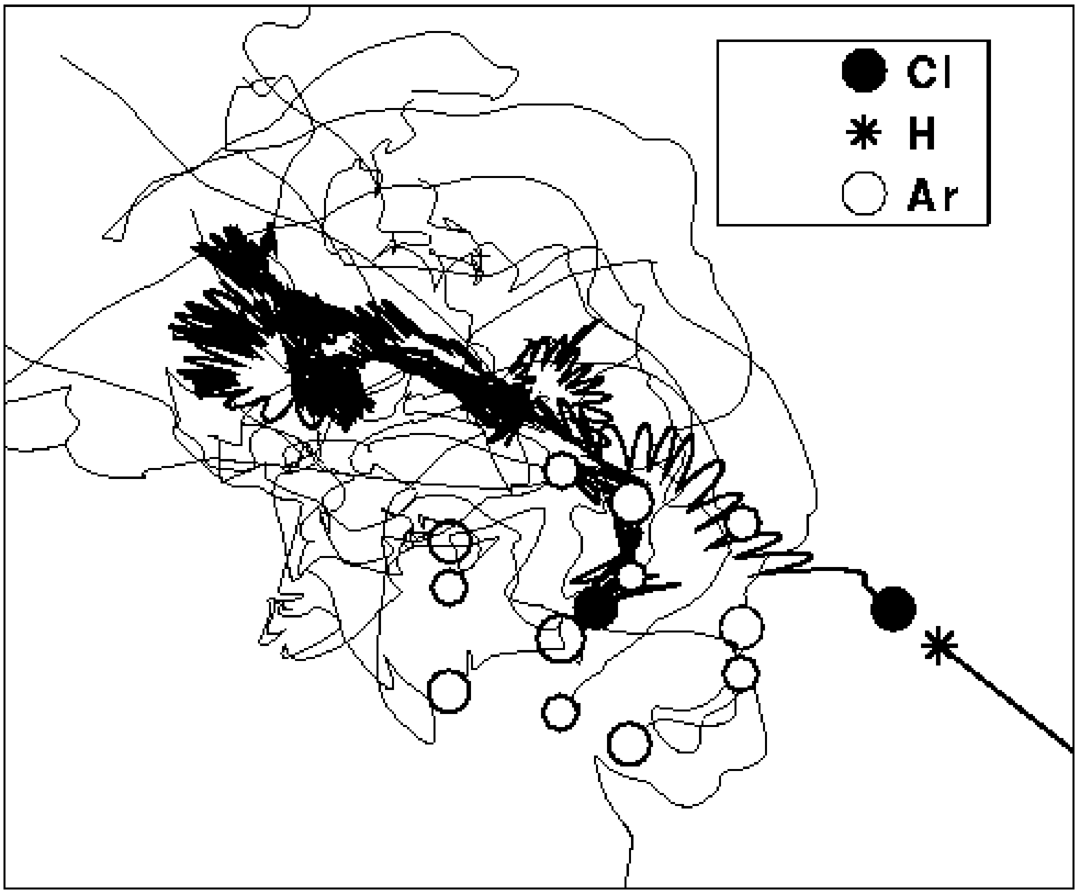
FIGURES

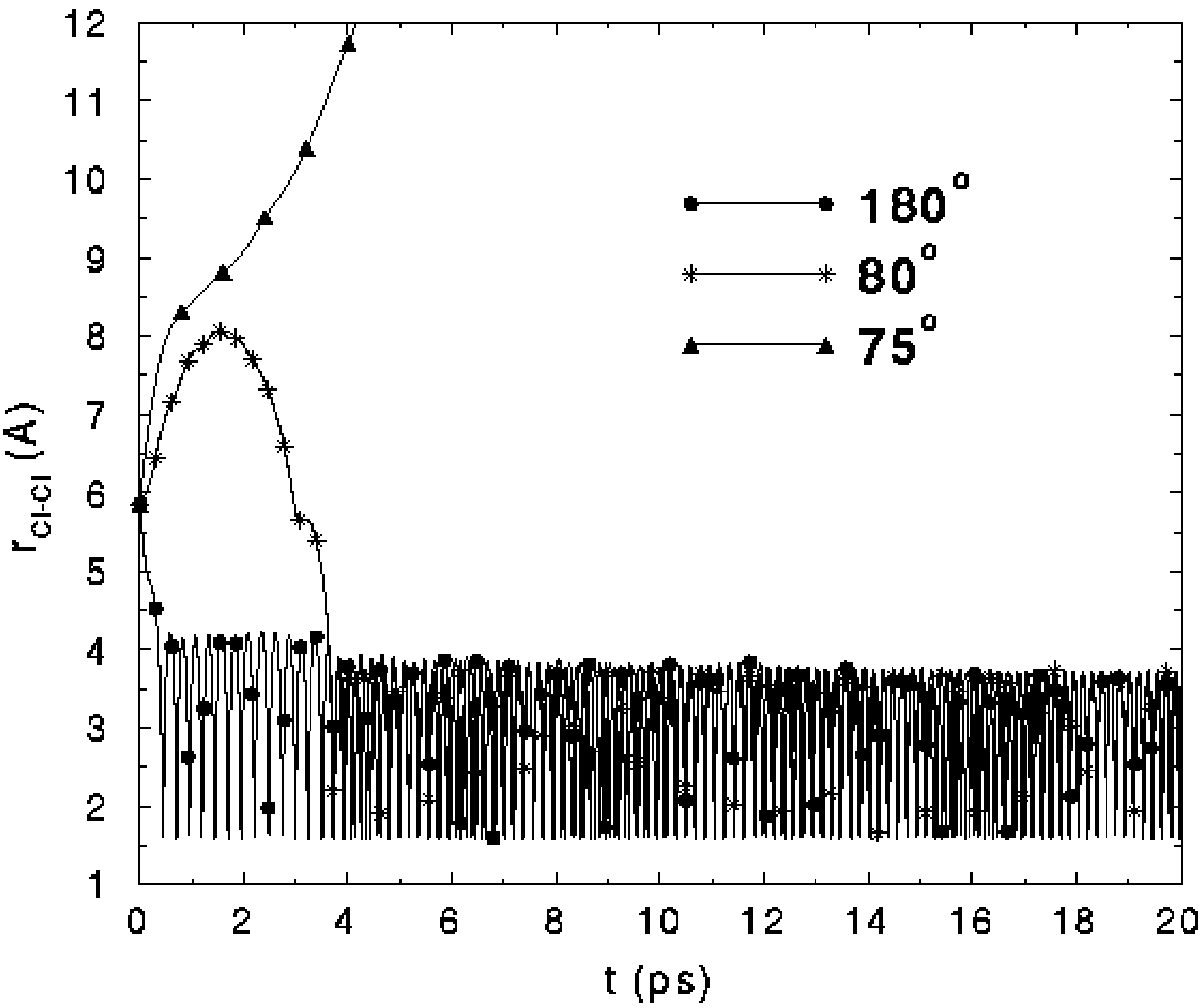
FIG. 1. A non-reactive event ($\theta = 45^o$). Filled and empty circles and a star depict initial positions of the individual atoms while lines represent 20 ps trajectories. The HCl molecule nearly freely photodissociates and the rest of the cluster slowly rolls away preserving its icosahedral shape.

FIG. 2. A reactive event ($\theta = 135^o$). Filled and empty circles and a star depict initial positions of the individual atoms and lines represent 20 ps trajectories. A Cl_2 molecule is formed while the hydrogen atom flies away. The argon cluster is melted and partially disintegrated.

FIG. 3. Time evolution of the Cl-Cl distance for a reactive trajectory ($\theta = 180^o$), a borderlying reactive trajectory ($\theta = 80^o$), and a borderlying non-reactive trajectory ($\theta = 75^o$). In the non-reactive event, the photodissociating chlorine atom flies away, while for the reactive encounters it is trapped by the second chlorine and the Cl_2 product is stabilized by heating and evaporating argon atoms.


Cl
H
Ar


Cl
H
Ar


180°
80°
75°
$r_{Cl\text{-}Cl}$ (A)
t (ps)
0
2
4
6
8
10
12
14
16
18
20
1
2
3
4
5
6
7
8
9
10
11
12