

Reactive Collisions as a Signature for Meltinglike Transitions in Clusters

Burkhard Schmidt* and R. Benny Gerber

Fritz Haber Research Center for Molecular Dynamics and Department of Physical Chemistry,

The Hebrew University of Jerusalem, Jerusalem 91904, Israel

and Department of Chemistry, University of California, Irvine, California 92717

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The formation of HCl molecules in collisions of H atoms with $\text{Cl}(\text{Ar})_{12}$ clusters is studied by classical trajectory calculations as a function of the cluster temperature. At sufficiently low impact energy ($E = 10$ kJ/mol) a pronounced threshold effect with temperature is observed: In the solidlike regime of the cluster ($T \leq 40$ K) there is strong screening of the Cl atom by the icosahedral Ar solvation shell preventing H+Cl association. In the liquidlike phase of the aggregate ($T \approx 45$ K) a sharp onset of reactivity is found with a reactive cross section of 11.4×10^{-20} m².

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There has been intensive interest in recent years in structural transitions in finite systems, focusing on their relation to phase transitions in condensed matter. Because of their relatively simple and well-characterized van der Waals interaction, rare gas clusters have been frequently studied as model systems in theoretical work. Monte Carlo (MC) and molecular dynamics (MD) simulations predicted a relatively sharp meltinglike transition even for small clusters in the range of 13–147 particles [1–6]. One interesting finding is the existence of a small difference between the melting and freezing temperature, and a range of coexistence of solidlike and liquidlike behavior for these systems [3]. Other interesting results are the phenomenon of surface melting for larger Ar clusters [5] and the occurrence of a hierarchy of different structural transitions for certain heteroclusters [7].

One possible experimental approach to the study of structural transitions is to embed in these systems a molecular impurity that can serve as a chromophore. Vibrational spectroscopy of infrared-active molecules [8] and electronic spectroscopy of aromatic molecules [7,9,10] in Ar clusters have contributed to our knowledge of the structure and dynamics of "microsolvation," especially when supported by MC or MD simulations [7,11–13]. However, experimental indications of phase transitions in all these studies are still rather indirect and hampered by many difficulties. There is a strong need for new experimental signatures for the meltinglike transition in clusters.

The present work suggests a novel approach to observing structural transitions. By doping rare gas aggregates with a radical, certain properties of the cluster can be investigated by monitoring the occurrence of association reactions in collisions with another radical. These types of atom-cluster reactions are also of considerable chemical interest as a model framework for solvation effects in chemical reactions [14,15]. These effects have been studied also in the framework of rare gas microclusters, where the well-defined size and structure of the solvation offer unique advantages in understanding the reaction dynamics [16–19].

The present article builds on the sensitivity of reactions in clusters to the state (solidlike or liquidlike) of the cluster. The study focuses on the system $\text{H}+\text{Cl}(\text{Ar})_{12}$ and, in particular, on the dependence of the reactivity of the H+Cl association on the cluster temperature. One reason for the choice of this model system is the similar range and strength of the Ar-Ar and Ar-Cl interaction. The icosahedral minimum energy configuration of $\text{Cl}(\text{Ar})_{12}$ with twelve Ar atoms forming a complete shell around the Cl atom in the center [20] is similar to pure rare gas clusters. In contrast to the fcc packing of solid Ar, icosahedral growth sequences of clusters are well established both experimentally [21] and theoretically [22,23] up to a cluster size of approximately 1600 particles [24]. Our choice of H atoms as a collision partner stems from three reasons. First, their small size allows penetration of an Ar shell already at moderate energies; second, the energy transferred in collisions with the heavier rare gas or halogen atoms is very limited; third, the energy released upon adsorption of H on the cluster surface is very small. For all these reasons, the internal state of the cluster is not disturbed substantially by the collision prior to the event of H+Cl recombination. Therefore, the association reaction with an H atom is a much more sensitive probe for phase changes than heavy atom recombination.

As a first stage of our study of the $\text{H}+\text{Cl}(\text{Ar})_{12}$ system, a series of constant energy MD simulations to characterize the thermodynamics of the cluster was carried out. Assuming ergodicity of the trajectories, a number of different structural and dynamical properties were obtained by calculating various averages over trajectories of a length of 10 ns (1 ns for $T = 42$ – 46 K). The simulations were started from a cluster configuration of I_h symmetry with the Cl in the center. It is noted that apart from this global minimum of the potential surface (-53.9 kJ/mol) there is a local minimum (-52.7 kJ/mol) corresponding to a structure with the Cl at one of the corners of the cluster which was not used in the simulations presented here. One basic statistical property is the caloric equation of state. It is defined as the depen-

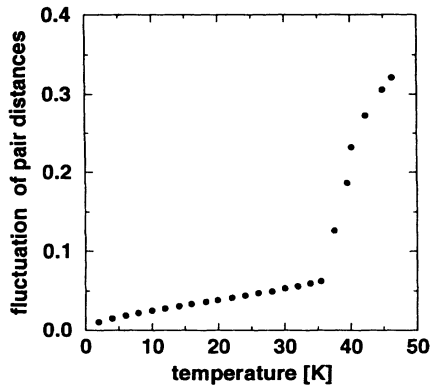


FIG. 1. Relative rms fluctuation of the atom-atom distances of $\text{Cl}(\text{Ar})_{12}$ as a function of the cluster temperature.

dence of the mean total energy on the temperature T , related to the mean kinetic energy $\langle E_{\text{kin}} \rangle$ of an N particle system by

$$T = \frac{2}{3N-6} \frac{\langle E_{\text{kin}} \rangle}{k_B}, \quad (1)$$

where k_B is the Boltzmann constant. Up to a temperature of 36 K it is a nearly linear function, which corresponds to a constant heat capacity. Above this temperature we find a discontinuity in the slope and an onset of larger fluctuations. For $T > 46$ K evaporation of atoms from the cluster is frequent and prevents such simulations. In order to characterize the transition in more detail, we calculate the relative root mean square (rms) fluctuation of the atom-atom distances, defined by

$$\delta = \frac{2}{N(N-1)} \sum_{i < j} \frac{(\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2)^{1/2}}{\langle r_{ij} \rangle}, \quad (2)$$

where $\langle r_{ij} \rangle$ is the average of the distance between atoms i and j and where the summation extends over all pairs of atoms in the cluster. As can be seen in Fig. 1, there is a slow, steady increase of δ up to $\delta = 0.06$ at $T = 36$ K, indicating the thermal expansion of the solidlike cluster. The sudden rise of δ beyond this temperature which extends up to $\delta = 0.32$ at $T = 46$ K reflects a largely increased mobility of the particles. This further supports the idea of a structural transition of the $\text{Cl}(\text{Ar})_{12}$. As another criterion, we calculate radial distribution functions of the distances of the particles from the center of mass of the cluster. Figure 2 shows these distributions as separate curves for Cl and Ar for three different temperatures. The upper panel [Fig. 2(a)] gives the low temperature limit for the example of $T = 10$ K. The Cl atom is located in the center and the Ar atoms are restricted to a well-defined icosahedral shell at $r = 0.37$ nm. Even at $T = 40$ K the picture basically remains unchanged [see Fig. 2(b)]. The peaks are slightly broader and shifted to marginally higher radii. However, the high value of the fluctuation of the atom-atom distances ($\delta = 0.23$) indicates that there are large amplitude thermal motions of

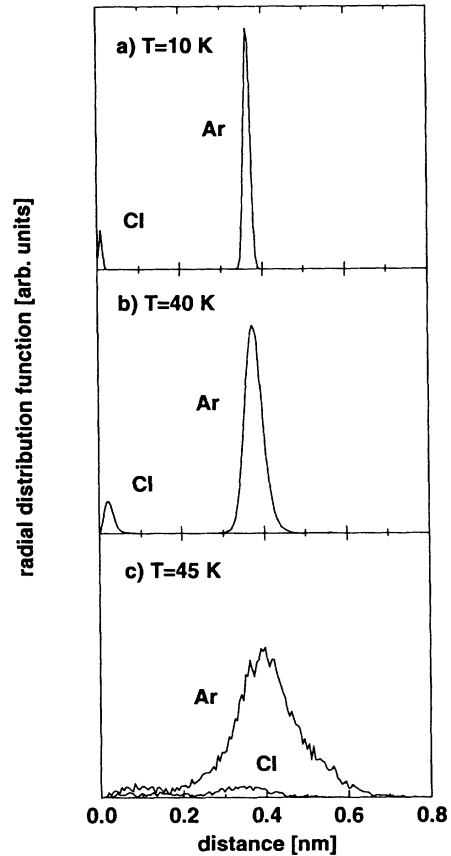


FIG. 2. Radial distribution function of the distances of Cl and Ar from the center of mass of $\text{Cl}(\text{Ar})_{12}$ for different cluster temperatures.

the atoms. These can be attributed to angular motion of the Ar atoms only, which account for the liquidlike properties at this temperature, notwithstanding that the Ar atoms are confined to the region of the solvation shell, which explains why these fluctuations are not reflected by the radial distributions. The basic icosahedral structure of the cluster remains intact and the cluster is still solidlike at $T = 40$ K. This is in contrast with the situation at $T = 45$ K. As can be seen in Fig. 2(c), the radial distributions of the atoms are dramatically changed. Various types of nonsymmetric cluster configurations are realized. There is finite probability of finding the Ar in the center and Cl in the first shell. In addition to this kind of rearrangement there are "floaters," i.e., Ar atoms leaving this shell [5]. This free mobility of the atoms is a clear indication of a liquidlike phase. From all these criteria we can conclude that there is a phase change of the $\text{Cl}(\text{Ar})_{12}$ cluster which corresponds to the melting transition of bulk matter. The transition temperature is confined to the region between $T = 40$ and 45 K. Note that this is considerably below the triple point temperature of bulk Ar at $T = 84$ K which is in accord with earlier findings [1-6].

Next, the reactivity of the atom-cluster scattering pro-

cess is calculated. We make use of standard techniques commonly used in calculations of reaction dynamics [25]. The atoms are treated as classical particles moving on a single potential surface which is constructed from gas phase pair potential functions. Trajectories are obtained by numerically integrating Newton's equations of motion. In order to simulate the situation of a crossed beam experiment with a well-defined collision energy, we have to average over different initial conditions specified by impact parameter, orientation of the cluster, and its internal degrees of freedom. Typically, about 10^4 trajectories were required to obtain well-converged cross sections. More details of the calculations will be described in a forthcoming publication [26].

In the following we report the total reactive cross sections for the H+Cl association in H+Cl(Ar)₁₂ collisions calculated for a variety of cluster temperatures. The collision energy is defined as the kinetic energy associated with the relative translation in the center of mass system. At an energy of 10 kJ/mol, H atoms cannot penetrate the cage formed by the twelve Ar atoms surround the Cl atom if we assume the cluster to be at its minimum energy configuration ($T=0$ K). Figure 3(a) shows our results for finite temperatures. Up to a temperature of 40 K, where the cluster is still solidlike, the cage effect of the Ar basically remains valid. The widening of the "windows" caused by the thermal motion has no substantial effect. Only in extremely rare cases can the H penetrate the cage and recombine with Cl, while all other trajectories exhibit (nearly) elastic scattering of H from the cluster. The reactive cross section is negligibly small (only $0.43 \times 10^{-20} \text{ m}^2$ at $T=40$ K). In contrast, we find a high probability for H+Cl association in collisions with the Cl(Ar)₁₂ at $T=45$ K. At this temperature, the aggregate is liquidlike with high probability for the Cl to be at the surface of the cluster. This exposure of the reactant greatly contributes to the reactivity. The cross section is $11.4 \times 10^{-20} \text{ m}^2$ which exceeds the value for HCl formation in H+ClAr collisions at the same energy by about 50% [26]. This means that at low energies the van der Waals attraction between H and the larger Ar cluster enhances the capture rate of H and thereby the reactivity.

The picture of the temperature dependence of the reactivity changes at higher collision energies. As will be shown in detail in Ref. [26], there are "windows" for penetration of the rigid cluster ($T=0$ K) by H atoms opening up at 58 kJ/mol in the center of each of the triangles forming the icosaheder. They reach a size of roughly 10^{-20} m^2 at $E=100$ kJ/mol. The cross sections for this collision energy are shown in Fig. 3(b). Despite the appreciable size of the cage openings, no reactivity is found at $T=0$ K. This is because penetration through the windows is possible only for very close collisions and for specific orientations of the cluster, resulting in an extremely low statistical weight of such collisions. However, at finite temperatures but still in the solidlike regime, thermal motion of the atoms is sufficient to give some

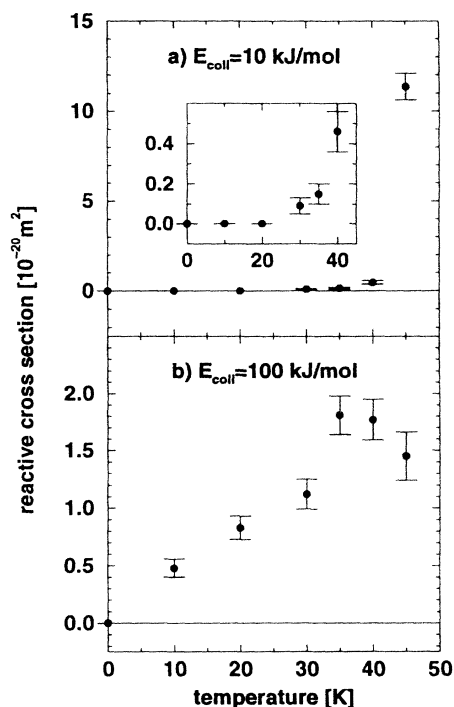


FIG. 3. Temperature dependence of the total reactive cross section for H+Cl(Ar)₁₂→HCl+12Ar association for two different collision energies. (a) $E=10$ kJ/mol. (b) $E=100$ kJ/mol.

reactivity. We find cross sections ranging from 0.5×10^{-20} to $(1.5-2) \times 10^{-20} \text{ m}^2$ at temperatures of 10 and 40 K, respectively. In contrast to our results for low impact energy, the melting transition does not lead to a further increase in reactivity. Instead, we find a slightly reduced cross section for H+Cl association in the liquid cluster at $T=45$ K. This drop is more pronounced at higher collision energies. At 200 kJ/mol there is a decrease from $0.9 \times 10^{-20} \text{ m}^2$ at $T=40$ K to $0.1 \times 10^{-20} \text{ m}^2$ at $T=45$ K.

The lower reactivity encountered for liquid clusters can be explained qualitatively as follows. The exposure of the Cl on the surface facilitates association with H atoms colliding from this side of the cluster. However, for H approaching the opposite side of the cluster, there are twelve Ar atoms shielding the Cl. Unlike the case for low energy, where trapping by the Cl(Ar)₁₂ contributes to the reactivity, this effect is of no importance at high energies because of the steep decrease of the capture rate with collision energy [19]. Therefore, the reaction probability is substantially reduced for collisions from the occluded side. At an energy of 100 kJ/mol these competing effects roughly cancel each other and the "melting" transition has almost no effect on the cross section. At even higher energies (200 kJ/mol) the capture rate of the H atoms is further decreased which leads to a reactive cross section that is considerably smaller than the one for the solidlike cluster.

In conclusion, our MD simulations of the $\text{Cl}(\text{Ar})_{12}$ cluster show a pronounced transition between $T=40$ K and $T=45$ K from a solidlike phase of icosahedral symmetry to a liquidlike phase with free mobility of the constituent atoms. This meltinglike transition has a strong effect on the $\text{H}+\text{Cl}$ associations in collisions with H atoms. Provided the impact energy is sufficiently low ($E=10$ kJ/mol), there is almost complete caging of the reactants by the Ar solvation shell for the solidlike cluster ($T \leq 40$ K), while at temperatures above the solid-liquid phase change ($T=45$ K) we find a high reaction probability. Thus, the reactivity of atom-cluster collisions offers a new exciting possibility of a very sensitive probe of the cluster and, in particular, of solid versus liquidlike states. Experimental observation of the melting temperature by this approach appears very interesting.

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*Present address: Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, D-37073 Göttingen, Germany.

- [1] C. L. Briant and J. J. Burton, *J. Chem. Phys.* **63**, 2045 (1975).
- [2] R. D. Etters and J. B. Kaelberer, *J. Chem. Phys.* **66**, 5112 (1977).
- [3] J. Jellinek, T. L. Beck, and R. S. Berry, *J. Chem. Phys.* **84**, 2783 (1986).
- [4] F. H. Stillinger and D. K. Stillinger, *J. Chem. Phys.* **93**, 6013 (1990).
- [5] R. E. Kunz and R. S. Berry, *Phys. Rev. Lett.* **71**, 3987 (1993).
- [6] H.-P. Cheng, X. Li, R. L. Whetten, and R. S. Berry, *Phys. Rev. A* **46**, 791 (1992).
- [7] S. Leutwyler and J. Bösiger, *Chem. Rev.* **90**, 489 (1990).
- [8] X. J. Gu, D. J. Levandier, B. Zhang, G. Scoles, and D. Zhuang, *J. Chem. Phys.* **93**, 4898 (1990).
- [9] M. Y. Hahn and R. L. Whetten, *Phys. Rev. Lett.* **61**, 1190 (1988).
- [10] U. Even, N. Ben-Horin, and J. Jortner, *Phys. Rev. Lett.* **62**, 140 (1989).
- [11] D. Eichenauer and R. J. LeRoy, *J. Chem. Phys.* **88**, 2898 (1988).
- [12] L. Perera and F. G. Amar, *J. Chem. Phys.* **93**, 4884 (1990).
- [13] G. Del Mistro and A. J. Stace, *Chem. Phys. Lett.* **196**, 67 (1992).
- [14] J. T. Hynes, *Annu. Rev. Phys. Chem.* **36**, 573 (1985).
- [15] J. Troe, *Annu. Rev. Phys. Chem.* **29**, 223 (1978).
- [16] R. Alimi and R. B. Gerber, *Phys. Rev. Lett.* **64**, 1453 (1990).
- [17] A. Garcia-Vela, R. B. Gerber, D. G. Imre, and J. J. Valentini, *Chem. Phys. Lett.* **202**, 473 (1993); *Phys. Rev. Lett.* **71**, 931 (1993); A. Garcia-Vela, R. B. Gerber, and U. Buck (to be published).
- [18] X. Hu and W. L. Hase, *J. Phys. Chem.* **96**, 7535 (1992).
- [19] X. Hu and C. C. Martens, *J. Chem. Phys.* **97**, 8805 (1992); **98**, 8551 (1993); **99**, 2654 (1993).
- [20] J. Siebers (private communication).
- [21] J. Farges, M. F. de Feraudy, B. Raoult, and G. Torchet, *J. Chem. Phys.* **78**, 5067 (1983); **84**, 3491 (1986).
- [22] A. L. Mackay, *Acta Crystallogr.* **15**, 916 (1962).
- [23] M. R. Hoare and P. Pal, *Adv. Phys.* **24**, 645 (1975).
- [24] B. Raoult, J. Farges, M. F. De Feraudy, and G. Torchet, *Z. Phys. D* **12**, 85 (1989).
- [25] R. N. Porter and L. M. Raff, in *Dynamics of Molecular Collisions*, edited by W. H. Miller, Modern Theoretical Chemistry (Plenum, New York, 1976), Pt. B, p. 1.
- [26] B. Schmidt and R. B. Gerber (to be published).