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Unimolecular dissociation kinetics of rare gas clusters: A comparison of molecular simulation results with dissociation rate theories

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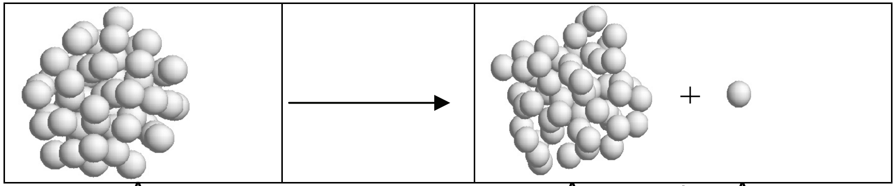
A molecular dynamics simulation was carried out to model unimolecular dissociation reaction of Ar_{54}, Ar_{55} and Ar_{56} clusters. Mass spectra of Ar_n clusters indicate that Ar_{13}, Ar_{55} like clusters are relatively stable compared to their neighbours. Those stable clusters which possess closed packed icosahedral structure are identified as "magic clusters" or "magic numbers".



$Ar_{55} \longrightarrow Ar_{54} + Ar$

Dissociation rate constants, k(E) and distribution of the release of kinetic energy due to dissociation, P(E,□$_{tr}$), as a function of internal energy, (E), of the above mentioned three clusters were calculated. The dissociation rate constants, "*computer experimental data*", were then compared with classical RRK theory for unimolecular dissociation. Simulation and theory rate constants show the same trend, that is $k^{56}(E) > k^{54}(E) >> k^{55}(E)$, the lowest dissociation rate constant for the most stable cluster (Ar_{55}). However qualitative agreement was very poor.

Further, least square fitting procedure was applied to fit simulation data to RRK theory expression by taking the two parameters, namely, frequency factor, □, and degrees of freedom, (s-1), as adjustable parameters. Obviously, the rate constants were in a good agreement (since the fitting procedure), and further the adjusted parameters indicate the higher dynamical stability of Ar_{55} clusters, in accord with the mass spectrum of Ar_n clusters.

Kinetic energy release distribution from molecular simulation gave a maximum at lower energy region with a long tail at higher energy region, while RRK theory showed exponential decay shape. However at higher kinetic energy releases both simulation and theory data showed a very good agreement. Instead of one frequency factor, one can use ratio of densities of state of product and the reactant as in RRKM theory. In this aspect, works are in progress to calculate classical density of states of rare gas clusters.

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