The Stability of Rare Gas Clusters by Ionization

E. E. Polymeropoulos, S. Löffler, and J. Brickmann
Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Darmstadt

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Computer simulations of the dissociation dynamics of argon and xenon neutral and singly charged clusters with 5 – 20 atoms were performed. It is shown that the stability of clusters with 'magic numbers' of atoms ($n = 19$ for argon, and $n = 13, 19$ for xenon) as found in TOF mass spectra, is more enhanced by ionization than that of their neighbours, indicating the importance of the ionization for the cluster size distribution found in experiments.

I. Introduction

An increasing interest in rare gas cluster research is related to the occurence and the nature of stable clusters with 'magic numbers' of atoms. The existence of such aggregates has been proposed by Hoare [1] who used sphere packing rules to show that certain clusters are more stable than others. However, the experimental difficulties involved in generating and detecting small neutral clusters [2] have lead to a controversy concerning the nature of rare gas clusters in general, and of 'magic number' clusters in particular, since in most experiments detection takes place after neutral clusters have been ionized. The controversy is focussed on the question whether 'magic numbers' in cluster size distributions are related to properties of the neutral clusters or whether the ionization process plays the dominant role for the observed stability maxima. The available experimental evidence is still non-conclusive [2 – 10] although lately there is a tendency to accept a process that infers fragmentation of clusters after ionization which in turn favours more stable structures [7 – 10].

In this work the results of molecular dynamics simulations on neutral and ionized argon and xenon clusters with 5 – 20 atoms are presented. The calculations were performed in order to find out the differences in the stability of neutral and charged clusters and so to contribute to a solution of the controversy mentioned above.

Some information concerning the stability of rare gas clusters has already been supplied by computer simulations [11 – 15] but most of these calculations were performed with neutral clusters which were then compared with mass spectra of ionized clusters. To our best knowledge there have been only two simulations on ionic rare gas clusters.

In the work of Gay and Berne [14] the coulomb explosion of doubly charged xenon clusters is studied while Soler et al. [15] investigated the stepwise decay of a large singly charged cluster as a function of time.

II. Model Approach

In this paper the results of two series of calculations for neutral and ionic clusters are reported. In the first series (series A) neutral clusters with 5 – 20 atoms were studied. The interatomic interactions were modelled by Lennard-Jones (12, 6) potentials with parameters $\sigma_{Ar} = 3.405$ Å, $\varepsilon_{Ar} = 119.8$ K and $\sigma_{Xe} = 4.1$ Å, $\varepsilon_{Xe} = 221$ K [16] for argon and xenon, respectively. For each cluster size 20 independent simulations were carried out in which the temperature (as calculated from the average kinetic energy of the particles) was "adiabatically" raised (by scaling of the momenta) at a constant rate of $3 \cdot 10^{-5}$ K per time step (corresponding to $\Delta T/\Delta t = 1.5 \cdot 10^{10}$ K/s) from $T \approx 10$ K up to dissociation. In all simulations (of neutral and ionic clusters) only single particle dissociation was observed. It was also found in any case that the particles remaining in the cluster formed a very compact (sphere like) structure. The dissociation point was defined as the point when the dissociating atom had a distance from the center of mass that is twice the maximum atomic distance from the center in the initial low temperature structure and at the same time had a distance from any other atom of the cluster that exceeds 5 σ. The corresponding temperatures T_{diss} for individual runs were determined from a linear fit of T vs. time at the desintegration point $t = \tau_{diss}$. The dissociation temperatures determined in

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Reprint requests to Prof. Dr. J. Brickmann, Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstr. 20, D-6100 Darmstadt.

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this way are systematically too high. The systematic error depends on the heating rate $\Delta T/\Delta t$ (and so on the calculated desintegration time τ_{diss}). The exact dissociation temperature T_{D} could be obtained by a limiting procedure from $T_{\text{diss}} \to T_{\text{D}}$ as $\tau_{\text{diss}} \to \infty$. However, this procedure could not be realized because of the drastic increase of computer time. On the other hand such a procedure is not necessary to study the relative stability of neutral and charged clusters of the same size. Since both types of clusters desintegrate in the same manner (single particle dissociation and remaining compact cluster) we assume that the systematic error of the T_{diss}-values is the same for both, the neutral and the charged clusters. This assumption is confirmed by a few sets of calculations with a slower heating rate: The dissociation temperature are decreased smoothly in both cases but the data are insufficient for the limiting procedure mentioned above.

The T_{diss}-values for neutral argon and xenon clusters averaged over 20 simulations as a function of the cluster size are shown in Figure 1. The average deviation of the T_{diss} values does not exceed 3 percent for clusters with more than 14 atoms and decreases with increasing cluster size. The average fluctuation for the desintegration time τ_{diss} is higher (7.5 percent for Xe_{16}) as a consequence of different initial conditions (and temperatures) for the individual runs.

The T_{diss} values of Fig. 1 cannot be related in a simple manner to the binding energy of an atom to the cluster as a consequence of the systematic error mentioned above. This is clearly seen by considering the average ratio $T_{\text{diss}}(\text{Xe})/T_{\text{diss}}(\text{Ar}) = 2.03$ for clusters with more than ten atoms while a ratio of $\varepsilon_{\text{Xe}}/\varepsilon_{\text{Ar}} = 1.85$ for the dissociation energies results from the law of corresponding states [1]. A second systematic error is related to the omission of three body interactions in our calculations. Additional three body interactions lead to a weak stabilization of a neutral cluster with the magic number 13 for xenon, as was recently demonstrated by two of the present authors [12, 13], but do not qualitatively change the results for argon. The three body interactions are much weaker than the charge-polarizability interactions which are expected in the ionized cluster.

In our study of the stability enhancement of neutral clusters by ionization the three body interactions are, therefore, not included in both series of simulations.

The simulations on charged clusters (series B) were performed following a model approach of Haberland [9], i.e. it was assumed that directly after ionization an Ar_2^+ or a Xe_2^+ complex, respectively, is formed in the cluster. Again 20 simulation runs per cluster size were performed, each one starting with the actual position- and momentum coordinates of the corresponding neutral clusters of series A at the simulation temperature of about 10 K. The pair of neighbouring atoms with the largest distance from the center of mass was chosen to build the initial charged dimer complex. The interaction potential for the atoms of the ionic pair was again modelled by a Lennard-Jones potential with parameter $\sigma_{\text{Ar}_2^+} = 0.6 \cdot \sigma_{\text{Ar}}$, $\varepsilon_{\text{Ar}_2^+} = 50 \cdot \varepsilon_{\text{Ar}}$, and $\sigma_{\text{Xe}_2^+} = 0.7 \cdot \sigma_{\text{Xe}}$, $\varepsilon_{\text{Xe}_2^+} = 30 \cdot \varepsilon_{\text{Xe}}$ [17, 18] for argon and xenon, respectively, approximately reflecting the potential for a covalent bond in these dimers. For computational convenience the Lennard-Jones potentials we have used are not as deep as the ones given in [17] and [18] but demonstrate well the difference in potential depth between neutral and ionic clusters. The non-ionic interaction between atoms of the dimer

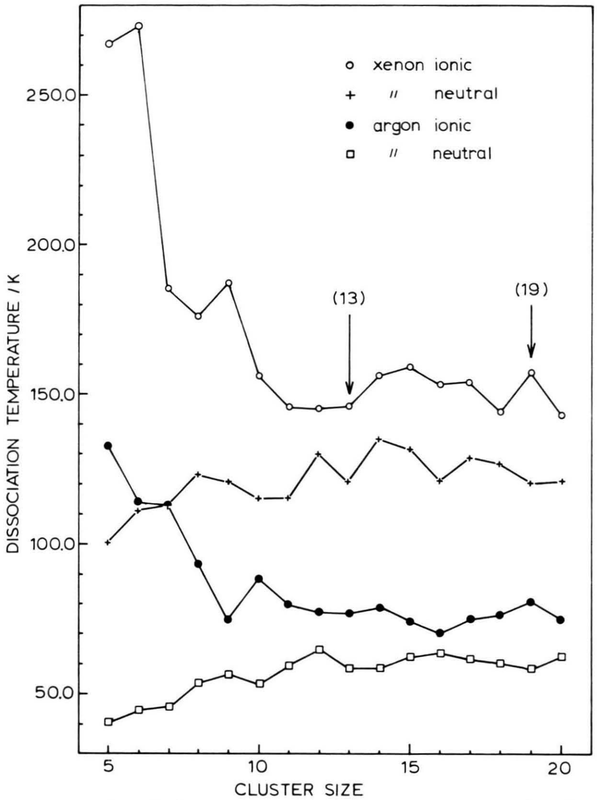

Fig. 1. Dissociation temperature T_{diss} vs. cluster size for ionic (○ xenon, ● argon) and neutral (+ xenon, □ argon) clusters.

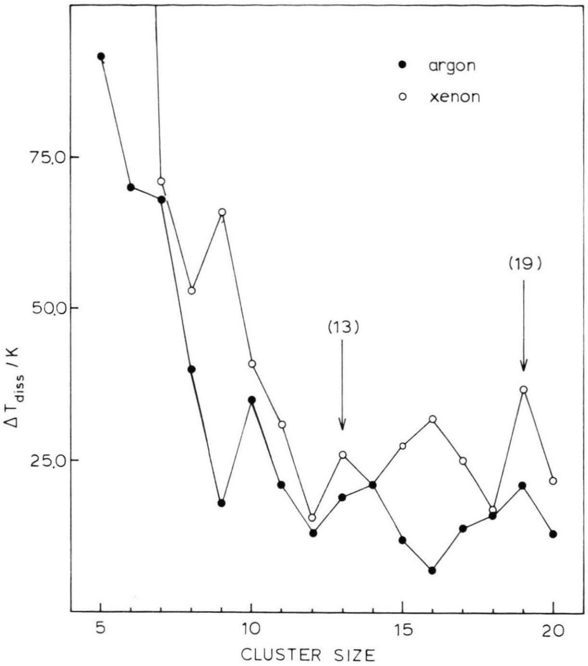

Fig. 2. Difference in dissociation temperature ΔT_{diss} between ionic and neutral clusters vs. cluster size for xenon (○) and argon (●).

and other atoms of the cluster was taken to be the same as in neutral clusters. Additional potential terms occur from the charge-polarizability interaction (proportional to r^{-4}) where each atom of the ion pair was assumed to carry one half of the positive charge, and the neutral argon and xenon atoms had the standard polarizabilities of $\alpha_{\mathrm{Ar}} = 1.63$ Å^3, and $\alpha_{\mathrm{Xe}} = 4.0$ Å^3, respectively. The sudden creation of charged dimers in the clusters generates a large amount of vibrational excess energy. This excess energy may lead to a dissociation of the cluster after having been transferred to the other vibrational degrees of freedom. There are two mechanisms for such an energy transfer. The first one, corresponding to a direct v-v transfer, is very slow ($\sim 10^{-9}$ s) as a consequence of the difference between the "intramolecular" vibrational frequency of the charged dimer and the van der Waals modes of the cluster. This process was simulated, as in series A, by an "adiabatic" heating of the cluster at a constant rate. This heating was necessary also here because the total integration times of the order of 10^{-10} s for a single run are too short to observe a complete v-v-energy transfer from the ionic pair to the van-der-Waals modes. A second energy relaxation process is related to charge-migration in the cluster. This process was simulated by a Monte-Carlo scheme following each integration step, based on a Landau-Zener type transition between different energy surfaces which are accidentally degenerate. For this reason the total potential energy was calculated after each integration step for the actual location of the ion pair, and for all the cases where the charge on one of the dimer atoms was moved to a neighbouring atom, so forming a charged dimer which differs by one atom from the original one. If the two potential values were approximately equal the quantum transition probability for a hopping between the crossing energy surfaces was calculated with the aid of a simplified Landau-Zener approach [19, 20], i.e. it was assumed that this probability can be given as $P = 1 - \exp(-\lambda \Delta V^2)$, where ΔV is the splitting of two energy surfaces at the crossing point, and that ΔV decreases exponentially with the distance between the neutral atom to which the charge is transferred and the nearest atom in the original ion pair. The parameter λ and the decrease of ΔV with interparticle distance d were determined according to the splitting of the bonding and antibonding energy values in the ion dimer as a function of the atomic distance in the ion pair [17].

With the model approach the charge was transferred frequently in the initial phase of the individual simulations. After this initial time ($\approx 10^{-12}$ s) charge transfer occurred seldom, suggesting localisation. The dissociation temperature for the ionized clusters was calculated as in series A from the kinetic energy of the system excluding the relative kinetic energy of the ion atoms.

The latter was excluded from the temperature calculation because the vibrational temperature of the dimer ion was usually found to be much higher than the cluster temperature during the simulation time (of the order of $10^{-10} - 10^{-9}$ s), a consequence of the slow direct vibrational energy transfer ($\tau \approx 10^{-9}$ s) from the dimer to the cluster. Moreover, the actual vibrational energy of the ionic dimer (and so the corresponding temperature) has no direct influence on the single atom dissociation from the cluster.

III. Results and Discussion

The average dissociation temperature T_{diss} for the ionized clusters as a function of the cluster size is also shown in Figure 1. Again, the T_{diss}-values contain the systematic errors related to the determination procedure and the omission of three body interactions. It is seen that the T_{diss}-values of the ionic clusters are higher than those for the neutrals, demonstrating higher stability. Moreover, these curves show much more structure than the corresponding ones for the neutral aggregates. For both argon and xenon the values for ionic and neutral clusters show a tendency to approach comparable values with increasing cluster size, as expected. The distribution for Xe_n^+ shows maxima at $n = 9$, 15, and 19, and the one for Ar_n^+ at $n = 10$, 14, and 19.

These maxima are not necessarily reflecting the absolute stability of the clusters because of the systematic errors mentioned above. These errors may not be monotonous functions of the cluster size. However, assuming the same additive systematic error for the dissociation temperatures of a neutral and an ionized cluster of the same size and formed by the same kind of atoms, the comparison of the T_{diss}-values of the ionic with that of the neutral cluster gives information on the enhancement of the stability caused by ionization. This enhancement can be seen from the difference of the ionization temperatures $\Delta T_{\mathrm{diss}} = T_{\mathrm{diss}}\,(\mathrm{ionic}) - T_{\mathrm{diss}}\,(\mathrm{neutral})$ which is plotted in Figure 2. In these plots there are maxima for Xe_n^+ at $n = 9$, 13, 16, and 19 and for Ar_n^+ at $n = 10$, 14, and 19. The Xe-values reproduce rather well the mass spectrum of xenon [2], particularly the 'magic numbers' 13 and 19 show much larger ΔT_{diss}-values than their neighbours. The available experimental results on argon clusters [5, 10, 21, 22] show partly different stability patterns than the T_{diss}-values but agree for the magic number 19. Our results indicate that ionization enhances the relative stability of some magic number clusters and may thus be, at least partly, responsible for the experimentally found size distribution.

Our simulations demonstrate that there is indeed a connection between ionization and stability of rare gas clusters. The question whether fragmentation after ionization enriches certain stable clusters can be answered at this point. Recent experiments [22] on water clusters suggest that dissociation takes place during the first four microseconds after ionization. This time, however, is out of the possible time scale of MD-calculations.

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[1] M. R. Hoare, Adv. Chem. Phys. **40,** 49 (1979).
[2] J. Farges, M. F. de Ferrandy, B. Raoult, and G. Torchet, J. Chem. Phys. **78,** 5067 (1983).
[3] O. Echt, A. Reyes Flotte, M. Knapp, K. Sattler, and E. Recknagel, Ber. Bunsenges. Phys. Chem. **86,** 860 (1982).
[4] E. Recknagel, Ber. Bunsenges. Phys. Chem. **89,** 201 (1984).
[5] A. Ding and J. Hesslich, Chem. Phys. Lett. **94,** 54 (1983).
[6] L. Friedman and R. J. Beuhler, J. Chem. Phys. **78,** 4669 (1983).
[7] U. Buck and H. Meyer, Phys. Rev. Lett. **52,** 109 (1984).
[8] T. D. Märk and C. W. Castleman, Jr., in "Advances in Atomic and Molecular Physics", edited by D. R. Bates and B. Bederson, Academic Press, New York 1984, Vol. 20.
[9] H. Haberland, in "13th International Conference of Electronic and Ionic Collisions, Berlin 1983, Book of Invited Lectures", edited by J. Eichler, I. Hertel, and N. Stolterfoht, North-Holland, Amsterdam 1984.
[10] H. P. Birkhofer, H. Haberland, M. Winterer, and D. R. Worsnop, Ber. Bunsenges. Phys. Chem. **88,** 207 (1984).
[11] E. E. Polymeropoulos and J. Brickmann, Chem. Phys. Lett. **92,** 59 (1982); **96,** 273 (1983).
[12] E. E. Polymeropoulos and J. Brickmann, Ber. Bunsenges. Phys. Chem. **87,** 1190 (1983).
[13] J. M. Soler and N. Garcia, Phys. Rev. **A 27,** 3307 (1983).
[14] J. G. Gay and B. Berne, Phys. Rev. Lett. **49,** 194 (1982).
[15] J. M. Soler, J. J. Saenz, N. Garcia, and O. Echt, Chem. Phys. Lett. **109,** 71 (1984).
[16] J. A. Barker, in "Rare Gas Solids", edited by M. L. Klein and J. A. Venables, Academic Press, London 1976, Vol. 1, Chapt. 4, pp. 212–264.
[17] W. R. Wadt, J. Chem. Phys. **68,** 402 (1978).
[18] W. C. Ermler, Y. S. Lee, and K. S. Pitzer, J. Chem. Phys. **69,** 976 (1978).
[19] L. D. Landau and E. M. Lifshitz, Quantum Mechanics, Pergamon Press, London 1958, p. 309.
[20] C. Zener, Proc. Roy. Soc. London **A 137,** 696 (1932).
[21] A. J. Stace, J. Phys. Chem. **87,** 2286 (1983).
[22] A. J. Stace and C. Moore, Chem. Phys. Lett. **96,** 80 (1983).