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Molecular-dynamics simulations in systems of rare gases using Axilrod-Teller and exchange three-atom interactions

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Molecular-dynamics simulations on cluster formation in compressed argon and xenon gases were performed, with use of a Lennard-Jones (6,12) potential together with Axilrod-Teller three-atom interactions and those of exchange type, applying results of a recent analysis of these three-body potentials [Phys. Rev. A **30**, 1593 (1984)]. Selective stabilization of clusters Ar_{19}, Xe_{13}, and Xe_{19} (possibly also Xe_{25}) was established, predominantly as a result of the three-atom exchange potential. It is conjectured that these exchange contributions, in combination with selective stability due to cluster ionization, explain the phenomena observed in time-of-flight mass spectroscopy experiments on rare-gas-atom clusters.

I. INTRODUCTION

The nature of rare-gas-atom clusters and the factors influencing their formation, stability, and other properties have been the subject of intensive research over the past few years.[1–20] At the time the first rare-gas-atom microclusters were experimentally identified by means of time-of-flight (TOF) mass spectroscopy[2] there was the tendency to believe that their properties could be ascribed to electrically *neutral* species.[2,4] This applies, in particular, to the observed maxima in cluster size distribution, corresponding to "magic numbers,"[10,21] i.e., to cluster sizes of particularly high stability with respect to their neighbors in size (or, alternatively, numbers marking the maximum intensity of clusters of high stability, followed by a drastic decrease in the distribution). It has generally been felt that no *two-atom* (pairwise additive) potential will reproduce such magic numbers, although no definitive proof can be given. Calculations by two of us[15,16] including, in addition to a Lennard-Jones (6,12) pair potential, also three-atom dispersion forces, indicated clearly that selectively stable cluster of 13 atoms could be formed in xenon under the influence of a three-atom potential. However, since in TOF experiments the identification of clusters is carried out after the neutral clusters have been ionized, the question was posed whether these clusters were not products of fragmentation of ionized entities. A model was proposed by Haberland,[18] in which it was assumed that singly charged dimers were formed in the clusters directly after ionization, having a large excess of vibrational energy.[22] The transfer of this energy to the rest of the cluster would cause fragmentation, with the result that *ionized* clusters belonging to magic numbers are enriched and found to be most stable in cluster-size distributions. This model was recently tested by Soler *et al.*[19] and by Polymeropoulos and Brickmann,[20] using different approaches to the problem. The results indicate that ionized clusters are indeed more stable than neutral ones. Both of these studies were performed using Lennard-Jones pair potentials for neutral and ionized pairs, as well as charge-polarizability interactions. The depth of the potential well for the ionized pair was 1—2 orders of magnitude larger than that for the other interactions, whereas the Lennard-Jones parameter σ was reduced by approximately 40%. Full details are found in Refs. 19 and 20. No three-atom dispersion contributions were considered.

The fundamental question concerning possibly selective stability of atomic, ionic, or molecular clusters (sizes and geometries) reaches far beyond the specific subject of the influence of ionization processes in TOF mass-spectroscopic measurements on aggregates of rare-gas atoms (nucleation processes, catalytic activities of metal-atom clusters, etc.). The results of Refs. 15 and 16 indicated that detailed knowledge of interaction potentials is required in order to provide reliable answers. Pursuing these lines, we have recently[23] (Ref. 23 is henceforth denoted as I) performed detailed calculations on neutral clusters of rare-gas atoms in which the effect of the Axilrod-Teller (AT)[24,25] three-atom dispersion interactions was compared with that of a three-atom exchange (EX) potential[26,27] obtained from first- and second-order exchange Rayleigh-Schrödinger perturbation theory. Since, for different geometrical configurations of three argon or xenon atoms, the EX potential was found to be generally much more important than the AT contribution, we have undertaken a molecular-dynamics study on the formation of neutral clusters of such atoms, comparing the two three-atom potentials.

II. METHOD OF CALCULATION

The systems studied consist of 108 atoms under the usual cubic periodic boundary conditions; details of the molecular-dynamics calculation technique used have been

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published earlier.[16] In the present analysis, two types of calculation were performed: one at a fixed temperature of 120 K, and at reduced densities of 0.0553 and 0.0088, corresponding to number densities of 1.40×10^{21} and 1.27×10^{20} cm^{-3}, for argon and xenon, respectively, to compare the results with those of previous calculations[15,16] under the same conditions. Second, we performed a series of calculations at a reduced temperature of 0.793 (95 K for argon and 175 K for xenon) and a reduced density of 0.0553 (1.40×10^{21} cm^{-3} for Ar and 8.02×10^{20} cm^{-3} for Xe). For simulations using only the Lennard-Jones (6,12) potential, identical cluster distributions for argon and xenon result under the latter conditions.

Two types of interaction potential were used. First, a combination of a Lennard-Jones (6,12) (LJ) potential with[28] $\epsilon_{\rm Ar}/k=119.8$ K, $\sigma_{\rm Ar}=3.405$ Å, $\epsilon_{\rm Xe}/k=221$ K, $\sigma_{\rm Xe}=4.1$ Å, and an AT potential[24,25]

$$V_{\rm AT}(r_{ijk})=\nu(1+3\cos\theta_1\cos\theta_2\cos\theta_3)/r_{ij}^3r_{ik}^3r_{jk}^3 ,$$

in which $\nu=\frac{9}{16}I\alpha^3$, with I the first ionization potential of the atom and α its polarizability. The values of ν are 73.2×10^{-59} J m^9 for argon and 795.0×10^{-59} J m^9 for xenon. Further, r_{ij}, r_{ik}, and r_{jk} are the distances between the atoms i, j, and k, whereas θ_1, θ_2, and θ_3 are the interior angles of the triangle formed.

We recall here that the AT potential is straightforwardly obtained as the first term (triple dipole, thus *long-range*) of a multipole series for the interaction between spherically symmetric atoms in third order of Rayleigh-Schrödinger perturbation theory without exchange. In the present analysis it is *assumed* that it may still be applied at interatomic distances as small as the Lennard-Jones parameter σ. The validity of the AT potential should, therefore, be viewed with caution in the region of such small interatomic distances. The results of I show that the AT potential is competitive with the EX potential principally in the range of small interatomic distances. With this limitation in physical interpretation of the Axilrod-Teller expression in mind, we will continue using AT to denote this potential.

Second, we have used a combination of a LJ and an EX potential[26,27] obtained by applying first- and second-order exchange perturbation theory. Full details are found in I. Its expression is mathematically much more complex than the very simple AT potential, implying much longer computer times in large-scale molecular-dynamics calculations. For this reason, we have searched for an analytical fit to the EX potential which allowed us to perform calculations in a time not overly exceeding that needed to carry out the analysis with the AT potential. The expression we have used is of the following form: with $V(r_{ijk})$ denoting the total potential for a triplet (ijk), we write (dropping indices) $V=V_{\rm LJ}+V_{\rm EX}\equiv V_{\rm LJ}(1+F_{\rm EX}^{\rm fit})$, and obtain

$$F_{\rm EX}^{\rm fit}=L_1F_1+L_2(\cos\theta_1-A_4)(\cos\theta_2-A_4)(\cos\theta_3-A_4)F_2 ,$$

where

$$F_1=[(\beta r_{ij})^{A_2}+(\beta r_{ik})^{A_2}+(\beta r_{jk})^{A_2}]\times\exp[-(E_1+E_2+E_3)] ,$$

with

$$E_1=A_1(\beta r_{ij}-\beta r_{ik})^2 ,$$
$$E_2=A_1(\beta r_{ij}-\beta r_{jk})^2 ,$$
$$E_3=A_1(\beta r_{ik}-\beta r_{jk})^2 ,$$

and

$$F_2=(\beta r_{ij}+\beta r_{ik})^{A_3}+(\beta r_{ij}+\beta r_{jk})^{A_3}+(\beta r_{ik}+\beta r_{jk})^{A_3} .$$

In the above expressions, the angles θ_1, θ_2, and θ_3 are again those of the triangle formed by the three atoms at distances r_{ij}, r_{ik}, and r_{jk} from each other. The (Gaussian) parameter β characterizes the extension of the electronic charge distribution of the atom (see also I); its values are 0.623 and 0.454 Å^{-1} for argon and xenon, respectively.[27] The constants L_1, L_2, and A_1–A_4 have the following values:

$$L_1=-0.079\,651 ,\quad L_2=-6.943\,733 ,$$
$$A_1=0.635\,672 ,\quad A_2=-0.199\,994 ,$$
$$A_3=-3.136\,486 ,\quad A_4=0.195\,736 .$$

The product of $F_{\rm EX}^{\rm fit}$ and $V_{\rm LJ}$ reproduces the properties of the three-atom exchange potential with good accuracy for angles θ between 40° and 180°, and for interatomic distances as large as[29] 7 Å.

As before,[15,16] a cluster is defined as an aggregate in which each atom is not farther away than a distance 2.0σ from at least one other atom (regarding the effect of variations of this limit, see Ref. 15). In addition, the restriction was imposed that this condition has to be fulfilled for a time interval of a complete period of oscillation of a two-atom cluster. The frequency of an oscillation with a maximum internuclear distance of 2.0σ is 0.73 and 0.30 ps^{-1} for argon and xenon, respectively.[16] Again, two types of cluster size distribution were monitored: one in which all clusters formed were counted, and one in which clusters of the same atoms formed more than once during the simulation were counted only once. The average lifetime of clusters of a given size was obtained by dividing the first distribution by the second one.

Each calculation was performed three times, starting from different random initial conditions. These calculations are very time consuming and it is thus not possible to carry out a sufficient number of simulations in order to do an exact statistical analysis. However, the results shown in Figs. 1 and 2 are typical insofar as the relative intensities of the various size clusters are independent of the random initial conditions although the absolute intensities may differ somewhat from run to run. Results were collected over 30 000 integration steps, with a time interval of 20×10^{-16} s. Test calculations over 60 000 steps did not appreciably change the density distribution of the clusters. Since in a single integration step particles move only a small distance compared with interatomic distances, we averaged their position coordinates over 100 steps and used these average coordinates for the cluster identification procedure.

III. RESULTS AND DISCUSSION

In Fig. 1 we show the cluster densities versus cluster size distributions and the average lifetimes of clusters at 120 K and reduced densities of 0.0553 and 0.0088 for argon and xenon, respectively. Clusters made up of the same atoms at subsequent sampling steps of the simulation are counted only once, thus giving a distribution of unique cluster sizes. Results obtained for the two different potentials are plotted side by side for each cluster size. Black columns represent results obtained with a LJ-plus-AT potential, whereas white columns refer to calculations carried out with a LJ-plus-EX potential. These calculations were performed, as mentioned earlier, to compare the effect of the two potentials under the same conditions as in earlier analyses.[15,16]

The general observation from this figure is that the LJ-plus-EX potential leads (in most cases) to more stable clusters than the LJ-plus-AT potential. This is, in particular, reflected in the relative densities of clusters corresponding to magic numbers compared to the densities of their immediate neighbors. In the case of argon, no clusters corresponding to Ar_{19} were obtained with the LJ-plus-AT potential, and it was previously concluded[16] that, even for xenon, no reasonable-size calculation with this potential would provide information on this particular cluster size. On the other hand, the LJ-plus-EX potential does give a (small) peak at Ar_{19} without other peaks in its vicinity, indicating increased stability of this cluster in comparison to its neighboring clusters. The same is observed for the average lifetime which, although rather short, is longer than the period of oscillation of an Ar_2 cluster.

For xenon the same general observations can be made. The LJ-plus-AT potential yields slightly more stable Xe_{13} clusters than the LJ-plus-EX potential both regarding density and average lifetime. On closer inspection one sees that the relative density and average lifetime of Xe_{13} with respect to its neighbors are much more pronounced for the LJ-plus-EX potential. This implies high selective stability for Xe_{13} clusters formed under the effect of this interaction. For Xe_{19}, again, a stabilizing effect produced by the exchange potential is observed if one considers the density of Xe_{19} relative to its neighbors. It should be noted that no such effects regarding selective stability (*magic numbers*) were observed with the use of the LJ potential alone.[15,16]

Figure 2 presents the cluster density and average lifetimes versus cluster size distributions of argon and xenon clusters at a reduced temperature of 0.793 and a reduced

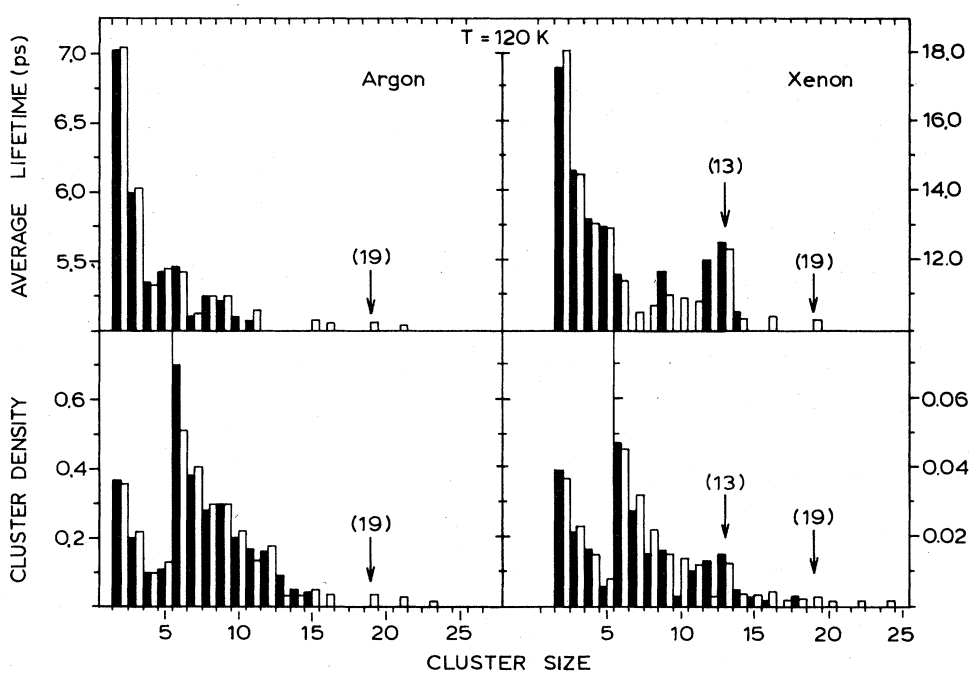

FIG. 1. Cluster density vs cluster size distribution (bottom) and average lifetimes (top) at a temperature of $T = 120$ K and reduced densities of 0.0553 and 0.0088 for Ar and Xe, respectively. Cluster configurations made up of the same atoms at different times of the simulation are counted only once. Density of clusters 2—5 and the average lifetimes for Ar clusters are given on the left-hand side while the density of clusters larger than 5 and average lifetimes for Xe clusters are given on the right-hand side of the figure. Dark columns represent clusters being built under the influence of a LJ-plus-AT potential; light columns represent clusters being built under the influence of a LJ-plus-EX potential. Average cluster lifetimes equal to or less than one period of oscillation of Ar_2 clusters (~ 5 ps) or of Xe_2 clusters (~ 10 ps) are not shown in the figure.

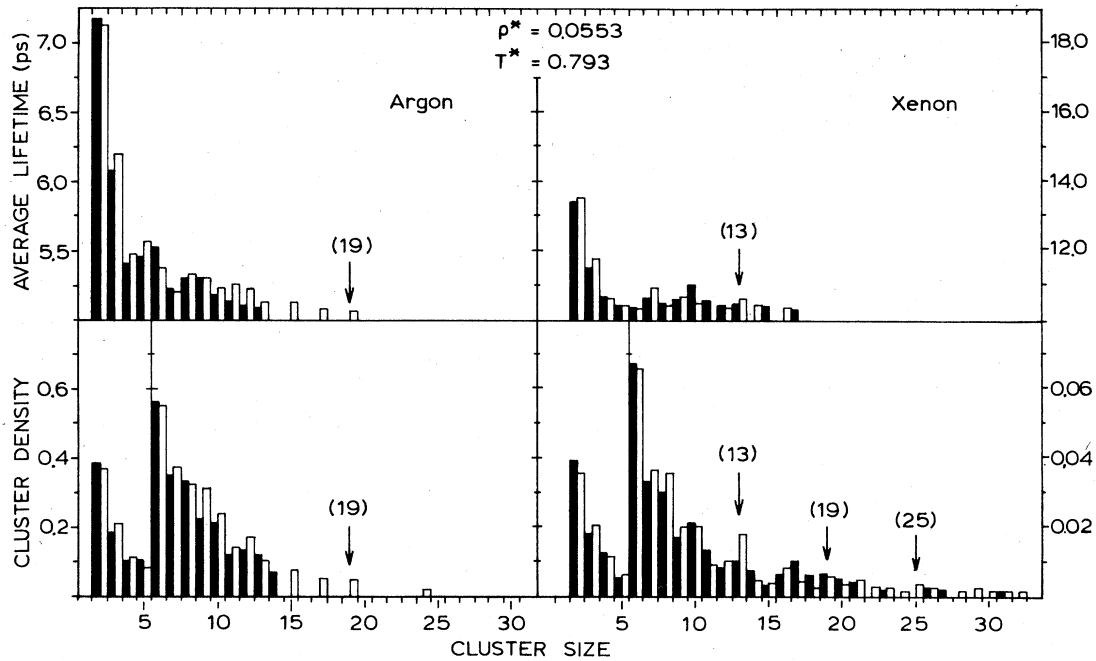

FIG. 2. Cluster density vs cluster size (bottom) and average lifetimes (top) as described in Fig. 1 for Ar and Xe clusters at a reduced density $\rho^* = 0.0553$ and a reduced temperature $T^* = 0.793$.

density of 0.0553. This calculation at corresponding states provides a direct comparison of the influence of three-atom interactions in different gases. Under these conditions, the cluster size distribution for xenon shows more structure than that for argon. The average lifetimes for xenon clusters are, however, shorter than in the case of Fig. 1. This behavior is due to the increased density of the xenon gas and, thus, the more frequent collisions between the atoms.

For these gases, the same observations regarding selective stability of Ar_{19}, Xe_{13}, and Xe_{19} as made for the previous case (Fig. 1) hold. In addition, some Xe_{25} clusters are found, with the LJ-plus-EX potential, with a higher density than their neighbors, but with a lifetime shorter than 10 ps.

The results presented in this analysis are in agreement with the qualitative predictions of I, in which we compare the AT with the EX potential for different arrangements of three argon and three xenon atoms. In particular, it is apparent that the influence of the exchange potential is more pronounced for xenon than for argon.

The results of this analysis confirm our previous[15,16] standpoint that three-atom interactions play an important role for stability of rare-gas clusters and should be included in molecular-dynamics simulations on such systems. As found previously,[20] ionization also contributes to the stabilization of clusters of certain sizes. At the present time, it cannot be decided which one of the two effects plays the more important role for a given cluster size. We are presently performing calculations to test the influence of the exchange potential on the dissociation temperature of both neutral and ionized clusters.

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[29]Potential energy surface diagrams of the exact EX potential and of the function $F_{\mathrm{EX}}^{\mathrm{fit}}$ may be obtained upon request.