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Interaction-induced absorption in argon-krypton mixture clusters: Molecular-dynamics study

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Molecular-dynamics (MD) simulations have been used to calculate the many-body time-correlation functions and interaction-induced absorption spectra for the small clusters composed of binary argon (Ar)-krypton (Kr) mixtures. The liquid state phase of $\mathrm{Ar}_k\mathrm{Kr}_{13-k}$ $(0<k<13)$ clusters has been studied, and considerable differences between the interaction-induced absorption of the clusters and bulk matter are observed.
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I. INTRODUCTION AND SIMULATION DETAILS

When two dissimilar rare-gas atoms interact, a dipole moment is generated, due to mutual distortion of the atomic charge clouds. The corresponding absorption spectrum lies in the far infrared, typically in the range $0-250\ \mathrm{cm}^{-1}$. The far-infrared absorption by *bulk* rare-gas mixtures, both in the gas and the liquid phase, has been one of the most explored interaction-induced processes in the last 30 years [1].

The finite-size clusters are currently being intensively studied because their properties are significantly modified from those of bulk materials. By studying clusters, we can also better understand the origins of collective behavior in bulk systems. One would like to know whether and how the peculiarities of atomic dynamics in a very small system influence the interaction-induced spectra. Very recently, the phenomenon of depolarized (Rayleigh) light scattering from the Ar_{13} cluster has been studied [2]. A distinct difference between the depolarized Rayleigh spectrum of a small argon cluster and its counterpart of bulk argon was reported. However, to the best of our knowledge there has been no report on the interaction-induced absorption for the matter in its embryonic state, namely, for small clusters. This is the subject of our computer experiments. Particularly, we examine here the $\mathrm{Ar}_k\mathrm{Kr}_{13-k}$ $(0<k<13)$ clusters with the ''magic'' total number of atoms $N=13$.

The interatomic potential between atoms is taken to be the usual Lennard-Jones potential of the form $V(r_{ij})=4\varepsilon[(\sigma/r_{ij})^{12}-(\sigma/r_{ij})^6]$, where r_{ij} is the distance between the atoms i and j, $-\varepsilon$ is the minimum of the potential at a distance $2^{1/6}\sigma$. For the values of ε and σ for pure argon and krypton atoms see [3]. The potential parameters between unlike atoms α and β are given by Lorentz-Berthelot rules $\sigma_{\alpha\beta}=(\sigma_\alpha+\sigma_\beta)/2$ and $\varepsilon_{\alpha\beta}=(\varepsilon_\alpha\varepsilon_\beta)^{1/2}$. More sophisticated potentials exists for the rare-gas atoms' interaction. However, at the present stage we do not make a comparison with experimental data so the detailed form of the potential is not crucial in this context. The classical equations of motion are integrated up to 10 ns by the velocity Verlet algorithm. The integration time step used is 0.25 fs, which ensures that the total energy is conserved to within 0.01%. The appropriate correlation functions were averaged over 10^3 time origins. The origins were separated by a time interval equal to 10 integration time steps. Our calculations were carried out for a constant energy ensemble for zero total linear and angular momentum of the whole system and the clusters were equilibrated for 2×10^5 molecular dynamics (MD) steps. The average energy can be adjusted as desired by a process of adiabatic heating (or cooling), wherein the velocities are scaled by a factor slightly exceeding (or less than) 1, for a limited time interval at a sufficiently slow rate.

II. RESULTS

The interaction-induced spectrum is related to the Fourier transform of the time correlation function $C(t)$,

$$C(t)=\sum\ \langle\mu_{ij}(t)\cdot\mu_{kl}(0)\rangle,\tag{1}$$

where μ_{ij} is the dipole moments induced in a pair of dissimilar atoms and the sum is over all pairs of unlike atoms in the mixture containing N_A and N_B atoms of type A and B, $N_A+N_B=N$. The correlation function $C(t)$ of the total dipole moment $\mu=\Sigma_{i,j}\mu_{ij}$ can be decomposed into pair, triplet, and quadruplet contributions [1]

$$C(t)=C_2(t)+C_{3a}(t)+C_{3b}(t)+C_4(t),\tag{2}$$

$$C_2(t)=\sum_{i\in N_A,i'\in N_B}\langle\mu_{ii'}(t)\cdot\mu_{ii'}(0)\rangle,\tag{3}$$

$$C_{3a}(t)=\sum_{i\in N_A,i'\neq j'\in N_B}\langle\mu_{ii'}(t)\cdot\mu_{ij'}(0)\rangle,\tag{4}$$

$$C_{3b}(t)=\sum\ \langle\mu_{ii'}(t)\cdot\mu_{ji'}(0)\rangle,\tag{5}$$

TABLE I. Parameters for the Ar-Kr induced dipole, taken from [8].

μ_0 (10^{-31} C m)	r_0 (10^{-10} m)	α (10^{-10} m^{-1})	β (10^{-10} m^{-1})	D_7 (10^{-31} C m)
0.741	3.468	2.961	0.984	−615.854

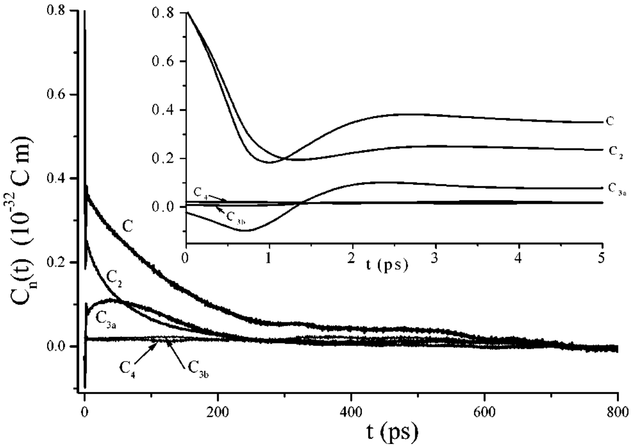

FIG. 1. Correlation functions $C(t)$ for a liquid $Ar_{11}Kr_2$ cluster at $T=40$ K.

$$C_4(t)=\sum_{i\neq j\in N_A,i'\neq j'\in N_B}\langle \mu_{ii'}(t)\cdot\mu_{jj'}(0)\rangle, \tag{6}$$

where eventual irreducible three-body dipole moments have been neglected. In the following, the two-body dipole moments μ_{ij} are identified with dipole functions available in the literature [4,5]

$$\mu_{ij}=\mu(r_{ij})\mathbf{n}_{ij}, \tag{7}$$

$$\mu(r)=\mu_0 e^{-\alpha r-\beta(r-r_0)^2}+D_7/r, \tag{8}$$

where μ_0, α, β, r_0 are parameters evaluated for different rare-gas pairs. The values of these parameters for the Ar-Kr induced dipole, taken from [5], are given in Table I.

Although in the dense fluid phase the measured interaction-induced spectrum is not directly related to any one of the component correlation functions $C_n(t)$ $(n=2,3a,3b,4)$, this decomposition helps to analyze the line shape of the interaction-induced absorption spectrum of bulk materials [6]. We applied a similar approach to the study of the interaction-induced absorption in clusters.

The n-body correlation functions $C_n(t)$ and $C(t)$ of three Ar_kKr_{13-k} clusters $(k=2,6,11)$ in the liquid state at the temperature $T=40$ K have been calculated *via* MD method. The quantum corrections to $C(t)$ are expected to be small in case of Ar-Kr mixture [5] and have been neglected. As an example, the functions $C_n(t)$ and $C(t)$ of $Ar_{11}Kr_2$ cluster are presented in Fig. 1. The correlation functions $C_4(t)$ and $C_{3b}(t)$ appear to be the small positive constants and have no discernible effect on the course of $C(t)$. The only negative function is $C_{3a}(t)$ for $t\leqslant 1.5$ ps, becoming positive and flat later on. Note a market, broad dip in the short-time region of $C_{3a}(t)$. The positive correlation function $C_2(t)$ decays fast for $t\leqslant 1$ ps and has substantially higher amplitude than $C_{3a}(t)$. Hence the cancellation effect, which results in the negative portion of $C(t)$ for the bulk mixtures [5–8] is moderate in the case of clusters. Consequently, after a rapid decay $(t\leqslant 1.2$ ps), the total correlation function $C(t)$ remains non-negative and exhibits a very long-time tail lasting for several hundred picoseconds. One should remember that $C(t)$ for the bulk mixtures of argon-krypton decays to zero after a few ps [5].

Figure 2 shows the plots of the normalized correlation function $\hat{C}(t)=C(t)/C(0)$ of Ar_kKr_{13-k} clusters at $T=40$ K for $k=2$, 6, and 11. The very short time dynamics

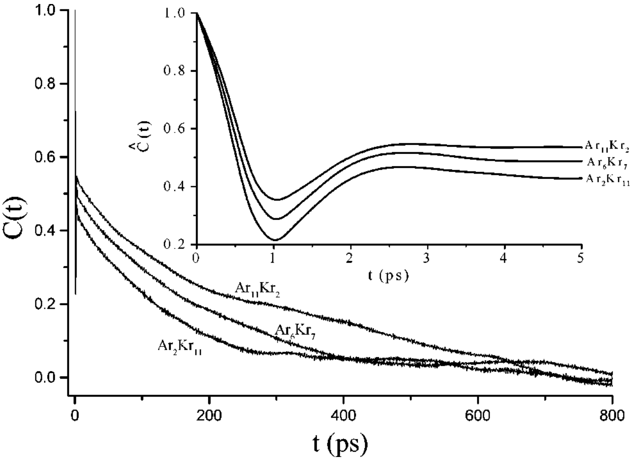

FIG. 2. Correlation functions $\hat{C}(t)$ of Ar_kKr_{13-k} $(k=2,6,11)$ clusters at $T=40$ K.

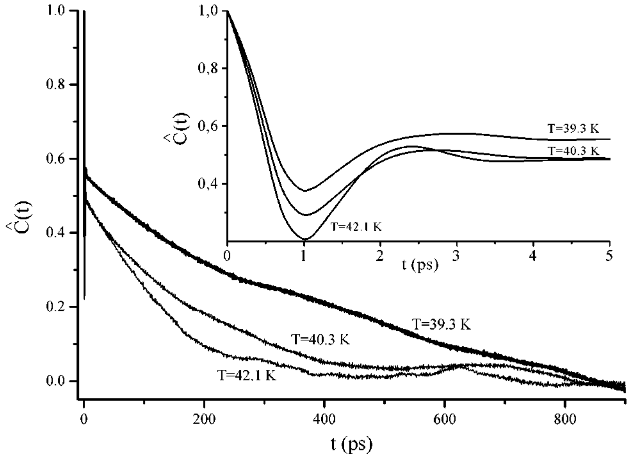

FIG. 3. Temperature dependence of the correlation function $\hat{C}(t)$ of the liquid Ar_6Kr_7 cluster.

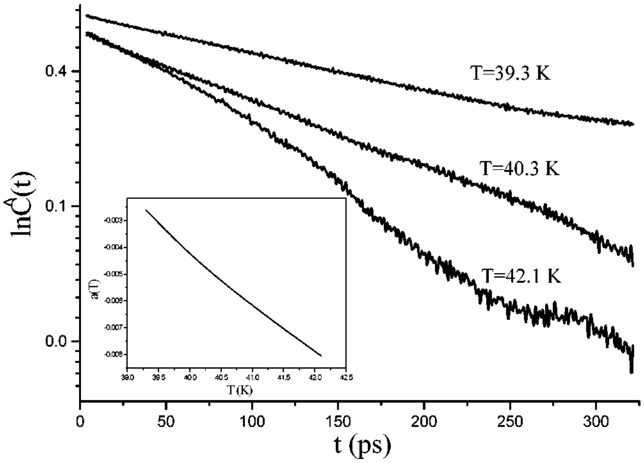

FIG. 4. Temperature dependence of the long-time tail of $\hat{C}(t)$ for the liquid Ar_6Kr_7 cluster (logarithmic plot).

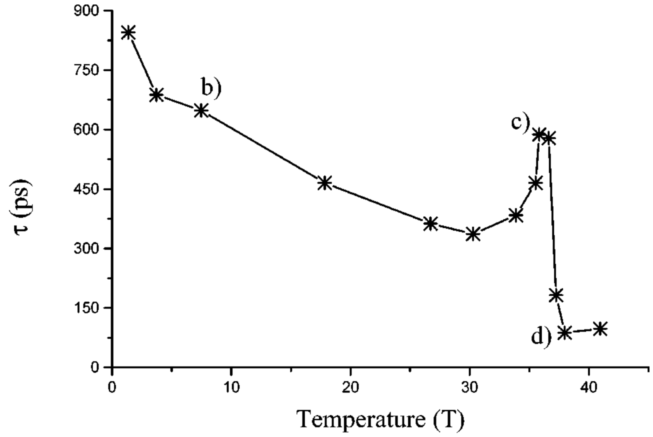

FIG. 5. Temperature dependence of the total correlation time $\tau=I(0)=\int_0^\infty dt\hat{C}(t)$ for the Ar_6Kr_7 cluster.

(ballistic region, $t<0.3$ ps) hardly depends on the concentration changes. However, the region around a minimum of $\hat{C}(t)$ and later on is quite sensitive to the variation of k; as the fraction of Ar atoms in the cluster increases, the dip in $\hat{C}(t)$ systematically fills in. We have seen before (Fig. 1) that this minimum is the result of cancellation of $C_n(t)$ components of $C(t)$, particularly important is the ratio between $C_{3a}(t)$ and $C_{3b}(t)$ since $C_2(t)$ is always positive and $C_4(t)$ negligible. Apparently, the reciprocal relations between $C_n(t)$ (cancellation effect) strongly depends on the cluster's composition.

We have also examined the temperature dependence of $\hat{C}(t)$ for an Ar_6Kr_7 cluster in the liquid phase and this is presented in Fig. 3. $\hat{C}(t)$ is a surprisingly sensitive function of the cluster's temperature T; there are two changes that occur as T varies. The most evident change is the filling in the short time dip of $\hat{C}(t)$; lowering the temperature by as little as 2 K fills in about 50% of the dip. However, the position of the dip, i.e., the minimum of $\hat{C}(t)$ remains stable. The other change is substantial, increasing of the amplitude of the long-time tail of $\hat{C}(t)$, as temperature is lowered. Observing the decay of the long-time tail of $\hat{C}(t)$ in Fig. 3, one may recognize that it approximately follows an exponential low behavior $\hat{C}(t)\propto\exp[-a(T)t]$ for large t. The confirmation of this is given in Fig. 4, where $\ln\hat{C}(t)$ is plotted. We have also found that the coefficient $a(T)$ linearly depends on the temperature, as shown in the inset of Fig. 4. We would like to point out that the interaction-induced absorption measurements can be used as a quite sensitive indicator of phase transition in mixed clusters. In Fig. 5 we show how the total correlation time $\tau=\int_0^\infty dt\hat{C}(t)$ depends on the temperature—a dramatic increase of τ is observed once the melting point of the Ar_6Kr_7 cluster is approached. We did not attempt to make simulations in the narrow temperature region very close to phase transition, where the fluctuations become larger and larger. To complete our paper we also present in Fig. 6 the Fourier transforms of $\hat{C}(t)$ for three different temperatures.

The present work is mainly of theoretical interest since the intensity of the interaction-induced absorption of small clusters is very weak. The natural, low-temperature environment where the atomic or molecular mixture clusters could exist is the interstellar space so these studies can be linked to the discussion on the spectrum of cosmic dust [2].

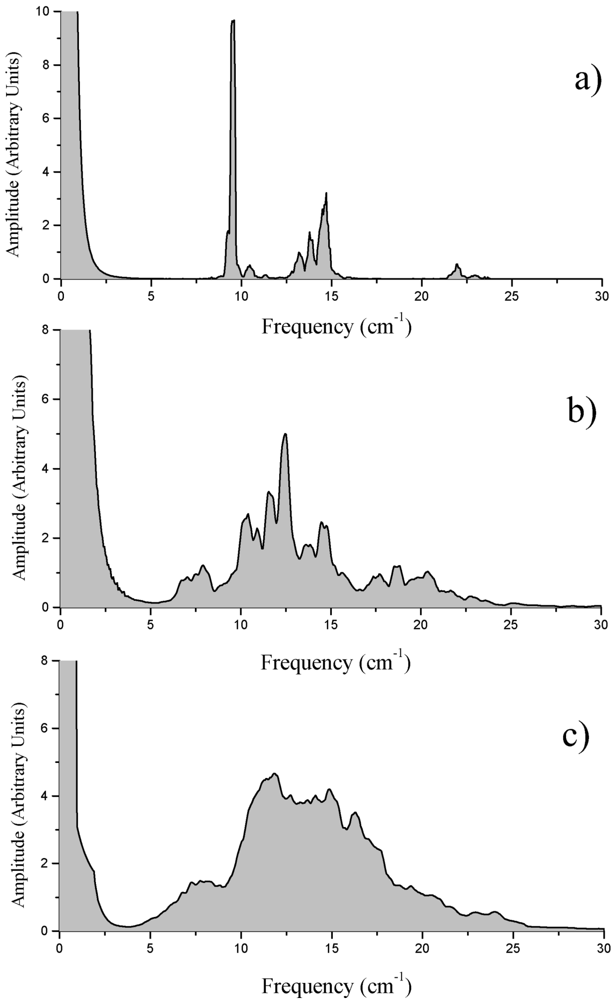

FIG. 6. Frequency transforms $I(\nu)=\int_0^\infty dt\hat{C}(t)\cos(2\pi\nu)$ at three temperatures: (a) $T=7.48$ K, Ar_6Kr_7, (b) $T=35.84$ K, and (c) $T=37.95$ K.

In conclusion, we made a reconnaissance study of the interaction-induced absorption in small argon-krypton clusters using *classical* MD simulations. The deficiencies of this approach are (i) application of very simple Lennard-Jones potential, (ii) neglecting the quantum mechanical effects and, (iii) the possible contributions coming from irreducible three-body terms in the induced dipole and in the interaction potential [1], (iv) use of the phenomenological form of the induced dipole moment. All these more or less questionable assumptions may be ruled out by performing in the future *ab initio* or *first principles* [9] MD simulations. The phenomena of interaction-induced absorption or light scattering seem to be a good ''battle field'' for testing the efficiency and reliability of the *first principle* MD technique.

ACKNOWLEDGMENT

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