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Breathing Vibration of Ar Clusters Analyzed by Molecular Dynamics Calculation —Cluster-Shape Dependence of the Mode-Separation

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The vibrational motion of Ar clusters (Ar_n, n=20 and 30) having isomers in a variety of shapes was simulated by use of the molecular dynamics method and the mode-separation of the breathing vibration from the quadruple spheroidal vibration was investigated. It was found that these modes of highly spherical isomers were almost fully separated from each other, while coupling between these modes were significant in non-spherical isomers. The relation between the cluster shape and the mode-separation was elucidated.

KEYWORDS: Ar cluster, molecular dynamics, breathing vibration, shape-dependence

1. Introduction

Recently, the dynamics of clusters, e.g. phase change,[1)] fission[2,3)] and cluster impact fusion,[4,5)] have been actively investigated experimetally and theoretically. In these phenomena, large-amplitude low-frequency vibrations are expected to play an important role. There has been, however, little information on the vibrations of clusters probably because of the fact that the conventional normal-mode analysis is not effective on such vibrations.

In order to analyze the cluster vibrations, we have proposed a dense sphere model, in which a cluster is approximated by a dense sphere.[6–8)] The modes of the dense-sphere vibration are well studied in relation to the earth vibration.[9)] By use of the eigenfunctions of the dense-sphere vibration, it has been found that in nearly spherical clusters, the modes corresponding to the dense-sphere vibrations are approximately separated from one another.[8)] In addition, the shape of the cluster has been indicated to be closely related to the mode-separation and the coupling between the vibrational modes becomes stronger as the degree of sphericality decreases.[7)] This suggests that the strength of the coupling provides information on the cluster shape; the cluster has many metastable isomers in almost the same energy range and the structures of these isomers are slightly different from one another due to the isotropic property of the van der Waals bond.

In the present study, we produced isomers of Ar_{20} and Ar_{30} clusters having a variety of shapes by the molecular dynamics method and measured the relative strength of the mode coupling between the breathing and quadruple spheroidal vibrations (see Fig. 1) in each isomer. The strength of the mode coupling was plotted as a function of several parameters which were expected to represent the cluster shape. Thus the relation between the cluster shape and the mode-separation was elucidated.

2. Molecular Dynamics Calculation and Analysis

The metastable isomers of the clusters were generated from a 30 K liquid cluster. The icosahedral Ar_{13} cluster was adopted as a core, and addition of an Ar atom followed by optimization was repeated to produce the argon clusters, Ar_{20} and Ar_{30}. The cluster was then excited to about 30 K so that it melted and exhibited various shapes in the course of the molecular dynamics simulation. Then, the internal energy of the cluster was reduced gradually at a time interval of 20 ps. Forty four and forty eight different initial structures were thus produced for the Ar_{20} and Ar_{30} clusters, respectively, and the isomers were subjected to the mode analysis by use of the dense sphere model.[7,8)]

One of the isomers was chosen, and was elongated in the x-, y- and z-direction in the same proportion so that the breathing vibration was excited the most efficiently. The molecular dynamics method was again used to trace the time evolution of Ar atoms in the isomer. The Ar atoms in the isomer were allowed to move during about 40 ps; the average distance, $\bar{r}$, of the Ar atoms from the center of mass of the isomer,

$$\bar{r} = \frac{1}{n}\sum_{i=1}^{n} r_i \qquad (1)$$

was calculated and stored at an interval of 0.04 ps, where r_i is the distance for the i-th atom. The average distance, $\bar{r}$, is a good index for the breathing motion.[6)] The

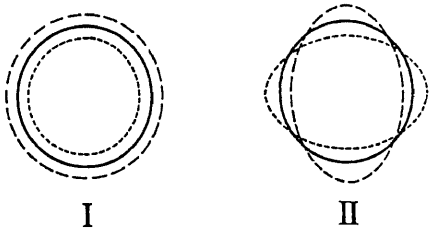

Fig. 1 Schematic drawings of the vibrational modes of a dense sphere. (I) Breathing mode. (II) Quadruple spheroidal mode.

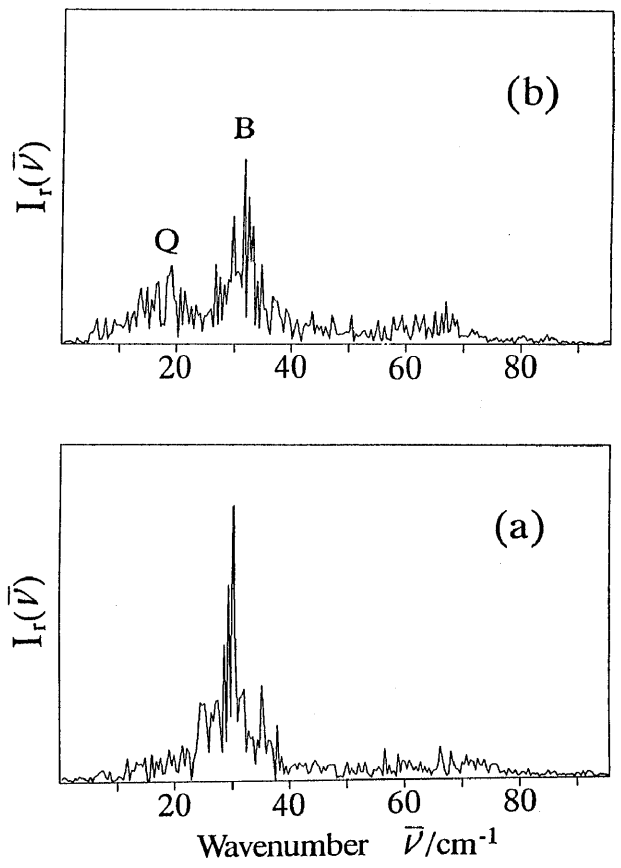

Fig. 2 Typical $I_r(\bar{\nu})$ spectra for (a) a nearly spherical Ar_{30} cluster ($I_a/I_b = 0.899, I_c/I_= 1.006$) and (b) a non-spherical Ar_{30} cluster ($I_a/I_b = 0.686, I_c/I_b = 1.737$), where I_a, I_b and I_c are the principal moments of inertia. The peaks due to the breathing (B) and quadruple spheroidal (Q) vibrations are indicated.

time-variation of $\bar{r}$ was transformed by the FFT method into the frequency spectrum, $I_r(\bar{\nu})$, in which $\bar{\nu}$ represents the wavenumber of the corresponding infrared radiation. The Lennard-Jones potential function with $\sigma = 0.34$ nm and $\epsilon = 84$ cm^{-1} was used for an Ar-Ar pair, and the potential energy of Ar_n was made by overlapping these two-body LJ potentials.

3. Results and Discussion

Typical frequency spectra are shown in Figs. 2a and 2b. Both spectra show a Gaussian-like peak at about 30 cm^{-1}, while an additional peak appears at about 20 cm^{-1} in Fig. 2b. In comparison with our previous results,[7] the peaks at 30 and 20 cm^{-1} are considered to arise from the breathing and quadruple spheroidal vibrations, respectively. Therefore, the absence of the 20 cm^{-1} peak in Fig. 2a indicates that the breathing mode is well separated from the quadruple spheroidal one in this nearly spherical isomer; the breathing vibration was selectively excited by the procedure given in the initial condition of the molecular dynamics calculation. It follows that the quadruple vibration (20 cm^{-1} peak) is excited by the mode-coupling with the breathing vibration in the non-spherical isomer.

In order to assess the strength of the mode-coupling, the following parameter, α, was adopted:

$$\alpha = \frac{\int_0^a I_r(\bar{\nu})\mathrm{d}\nu}{\int_a^b I_r(\bar{\nu})\mathrm{d}\nu}, \tag{2}$$

where $a = 30\mathrm{cm}^{-1}$ and $b = 60\mathrm{cm}^{-1}$ for Ar_{20} and $a = 25\mathrm{cm}^{-1}$ and $b = 50\mathrm{cm}^{-1}$ for Ar_{30} by taking into consideration the n-dependence of the frequencies of the breathing and quadruple spheroidal vibrations.[7] When the coupling is negligible, the α value should be nearly zero as mentioned above and is expected to increase as the coupling strength increases. Therefore, the α value thus derived is regarded as an index for the mode-separation of these vibrations. Since the breathing mode is separated perfectly from the quadruple spheroidal mode for a dense sphere, α is also thought to be an index of the sphericality of the cluster according to the mode-separation of the cluster vibrations.

First, the α values are compared with the potential energies, U_0, of the isomers in the initial structures. Since a drop is the most stable in a spherical shape, a spherical isomer is expected to have the smallest U_0 value when the cluster is considered to be a liquid drop. Figure 3 shows the α vaule of Ar_{30} as a function of U_0. As shown in the figure, the energy of the cluster has no relation with α, that is, the sphericality of the cluster. This indicates that the Ar_{30} cluster cannot be treated as a liquid drop. The same result is obtained for Ar_{20}.

Instead of using U_0, the moments of inertia were calculated and $(I_c/I_b + I_b/I_a)/2$ was adopted to assess the strength of the mode coupling; the principal inertial axes and principal moments of inertia, I_a, I_b and I_c, were derived from the calculation, where $I_c \geq I_b \geq I_a$. The α values are plotted as a function of $(I_c/I_b + I_b/I_a)/2$ in Fig. 4. It is found that the correlation of α with this value is much stronger than that with U_0. Since representation of the cluster shapes by the moments of inertia corresponds to replacement of the clusters with dense ellipsoids, the correlation indicates that the mode-separation

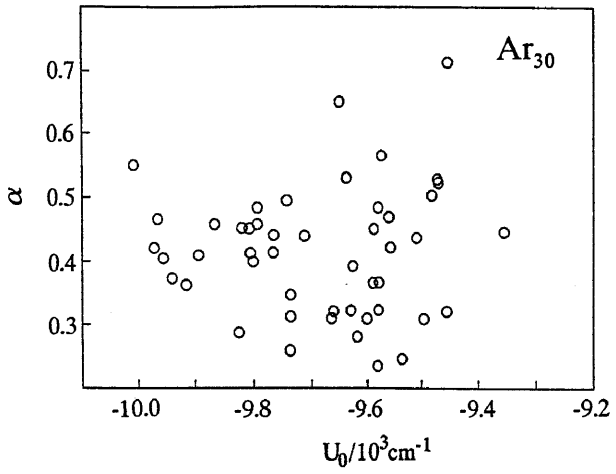

Fig. 3 α as a function of the potential energy U_0 for 48 isomers of Ar_{30}.

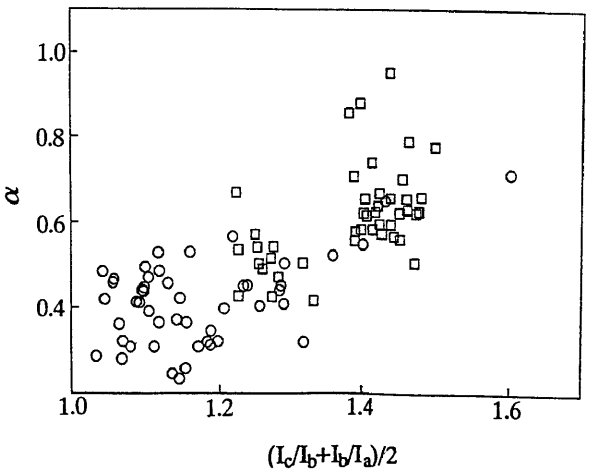

Fig. 4 α as a function of $(I_c/I_b + I_b/I_a)/2$ for Ar_{30} (open circles) and Ar_{20} (open squares).

of the vibrations in the cluster is controlled by the shape of the corresponding ellipsoid. However, there are significant scattering of the α values of the isomers which have nearly equal $(I_c/I_b + I_b/I_a)/2$. This suggests that there remains some factor originating from the fact that the clusters are really not dense ellipsoids but consist of discrete particles, Ar atoms.

The influence due to the replacement of a real cluster with a dense sphere mentioned above has been already suggested in our previous report.[7] The frequencies of the breathing vibration for nearly spherical Ar_n with $n = 13$-55 have been calculated and it has been found that they are smaller than those predicted by the dense sphere model. In the report, the dense sphere model is indicated to bocome a better approximation as n increases. Hence, the correlation shown in Fig. 4 is expected to become more definitive in larger clusters.

4. Concluding Remarks

A parameter, α, was proposed to represent the sphericality of Ar cluster on the basis of the mode-separation of the cluster vibration. Correlation between α and the shape of the dense sllipsoid used as the cluster was found. It seems that there exists a remaining factor related to the discreteness of the cluster.

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