Effective numbers of modes applied to analysis of internal dynamics of weakly bound clusters

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The dependence of the volume of the chaotic component in the internal dynamics of triatomic van der Waals clusters on the angular momentum is calculated using the Monte Carlo and molecular dynamics methods. It has been found that this dependence is nonmonotonic and that its functional form varies for different values of the total energy. The effective number of rotational modes was used to clarify why a change in the volume of chaotic component of the phase space happens for certain values of the angular momentum. We conclude that a large fraction of regular trajectories in relation to all trajectories appears only when there is a possibility for the regular motion to perform a rotation different from that for a chaotic motion. When such difference is small, the regular motion disappears. The effective number of rotational modes can be used to estimate the difference in the type of rotation and is a convenient parameter which controls changes in the dynamics of the system. © *2010 American Institute of Physics*. [doi:10.1063/1.3496375]

I. INTRODUCTION

Investigations of the internal dynamics of atomic and molecular clusters are important in various areas of science, particularly, in physical chemistry, molecular biology, the theory of phase transitions in finite-size systems, and the theory of nonlinear dynamical systems. The study of the movement of particles in clusters leads to an understanding of the mechanisms of isomerization and fragmentation, thus revealing their dynamic features.

The analysis of the internal dynamics in weakly bound clusters is complicated. First, strong anharmonicity of interaction among atoms in a cluster makes the normal mode method inapplicable to describe their internal dynamics.[1] Second, rovibrational interaction cannot be considered as a small interaction. It makes ineffective a traditional approach with models such as "rigid rotator-harmonic oscillator," when intramolecular vibrations are separated from rotation, and vibration-rotation interaction is taken into account using perturbation theory.[2] Interaction of vibration and rotation in weakly bound clusters is important but so far poorly studied.[3,4] This interaction influences the redistribution of energy among internal degrees of freedom and, consequently, the rate constant of isomerization and monomolecular fragmentation. Third, the high-dimensional nature of the dynamics is often a substantial obstacle to clarifying the exact mechanisms of collective motions of particles in the clusters. In order to carry out the reduction of dimensionality effectively, it is crucial to identify a small number of collective variables that play a predominant role in the structural dynamics of clusters.[5] Finally, the phase space has areas of chaotic and regular behavior,[6–9] but the knowledge of the total energy and angular momentum is not sufficient to determine the type of motion. The set of parameters which determine regular or chaotic state of motion are currently unknown, although there are several hypotheses as described below.

There is an argument that the chaotic dynamics in rotating weakly coupled atomic and molecular clusters is a consequence of the concentration of kinetic energy in vibrational degrees of freedom;[10–13] that is, the more energy stored in vibrations, the more chaotic the dynamics becomes. At the same time, we found earlier that in triatomic argon clusters the amounts of kinetic energy in vibrational degrees of freedom are similar for regular and chaotic components.[14] This is typical for all values of angular momentum which have been studied. This fact allows us to assume that the concentration of kinetic energy in vibrational degrees of freedom is not a necessary and sufficient condition for a chaotic regime. As a result the question about parameters which control transition to chaos in such systems is left open.

In this paper we analyze the dependence of the volume of the chaotic component of phase space on the angular momentum in the internal dynamics of triatomic van der Waals clusters, calculated using the Monte Carlo and molecular dynamics methods. Earlier we explored the internal dynamics for a particular value of the total energy by the method of effective modes.[14,15] In the present paper we consider the dynamics for different values of the total energy and reveal that it varies significantly. The search for an explanation of this effect allows us to make more accurate conclusions about the origin of the chaotic regime.

The structure of the paper is as follows: Sec. II A presents a brief description of the method of effective modes. Section II B shows how nonrigid rotation can be analyzed in the framework of effective modes and effective numbers of modes. Section III presents the dynamics of weakly bound cluster on an example of triatomic Ar_3 cluster dynamics, and Sec. IV gives a summary of the work.

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II. METHODS

A. Method of effective modes

The method of effective modes allows one to simplify the analysis of the internal dynamics of nonlinear systems in multidimensional phase space and to allocate parameters that control changes in the dynamics. It is based on the expansion of collective motion of atoms in a cluster in the orthogonal components with extreme properties which we will call the effective modes.

Consider the dynamics of an N-particle cluster. Using the numerical integration of Hamilton's equations of motion, the momentum vectors $\vec{p}_i(t_j)$ can be calculated at discreet time moments $t_1, \ldots t_{N_T} \in [0,T)$; N_T is the number of integration steps. Then the trajectory of an N-particle system in the momentum subspace can be specified by an $n \times N_T$ matrix $\hat{\mathbf{p}}_{ij}$, where each n-dimensional vector $\mathbf{p}_j$ consists of the Cartesian coordinates of the momentum vectors of all particles $\vec{p}_i(t_j)$, $i=\overline{1,n}$, $j=\overline{1,N_T}$, $n=3N$, and $N_T \gg n$.

At each moment of time we represent the n-dimensional momentum of the cluster of N particles as a superposition of effective modes[15]

$$\mathbf{p}_j = \sum_{k=1}^{n} (\mathbf{p}(t_j), \mathbf{e}_k)\mathbf{e}_k, \tag{1}$$

where $(\hat{\mathbf{p}}\hat{\mathbf{p}}^*)\mathbf{e}_k = \lambda_k^2 \mathbf{e}_k$ and $\mathbf{e}_k^* \mathbf{e}_j = \delta_{kj}$. Each λ_k, $\lambda_1 \geq \lambda_2 \geq \ldots \geq \lambda_n \geq 0$ measures the amount of the time-averaged kinetic energy per mass unit captured by the respective mode

$$\lambda_k = \sqrt{2 \cdot \langle E_{\mathrm{kin}} \rangle_k}. \tag{2}$$

Here the $3N$-dimensional eigenvectors $\mathbf{e}_k$ represent the directions and relative amplitudes of the particle motions which compose the kth mode, $(\mathbf{e}_k)_i$ represents the subcomponent, corresponding to the ith particle. The product $(\mathbf{p}(t_j), \mathbf{e}_k)$ is the projection of the combined momentum of all particles $\mathbf{p}_j$ on the kth mode or the amplitude of the kth mode at the moment t_j.

Since the basis $\mathbf{e}_k$ is orthonormal (1), the kinetic energy per mass unit $(E_{\mathrm{kin}})_k$ captured by the kth mode can be calculated as follows

$$(E_{\mathrm{kin}})_k(t) = \frac{1}{2} \sum_{i=1}^{N} (\mathbf{p}(t), (\mathbf{e}_k)_i)^2. \tag{3}$$

The representation of the motion with the first m modes gives the error for the time-averaged kinetic energy per unit mass

$$\Delta_m \langle E_{\mathrm{kin}} \rangle = \frac{1}{2} \sum_{k=m+1}^{n} \lambda_k^2. \tag{4}$$

The choice of effective modes in the form (1) guarantees that any given number of the effective modes captures on the average more energy than the same number of any other modes obtained by linear expansion using an orthogonal basis.[16]

The method of effective modes is inspired by the method of bi-orthogonal decomposition, described by Lima,[17] and by the method of Karhunen–Loève decomposition described, for example, by several authors.[16,18] The method of effective modes is adapted for the analysis of nonlinear dynamics including nonrigid rotations. For many-particle systems in which interparticle interaction is described by a quadratic potential, the effective modes are equivalent to the normal modes.[19] Effective and normal modes have much in common: in both cases an orthogonal decomposition is used and the modes are independent. The difference between them is that the expansion in normal modes requires the linearization of equations of motion and the separation of vibrations from rotations.

Normal modes calculated for nonlinear systems lose the pairwise independence. Apart from our method of effective modes, there are several other modifications of the method of normal modes for the analysis of nonlinear systems. One of them is a normal mode analysis for the sequence of points along the reaction path.[20] In this method the normal modes are introduced as the oscillations which are orthogonal to the reaction coordinate. The resulting modes change along the reaction path and cannot be treated as independent, while the degree of loss of pairwise independence can be determined using the coefficients of interaction among the modes.[21] The coupling coefficients determine how one mode transforms into another during the motion along the trajectory. For a trajectory in which one mode is independent from the others, all corresponding coupling coefficients approach zero.

Another way to describe nonlinear dynamics is to introduce the instantaneous normal modes without the assumption that the system is close to the equilibrium configuration.[22] These modes result from the Taylor expansion of the potential of interaction up to quadratic terms in each point of the trajectory. The positive eigenvalues of the Hessian give vibrational modes and the negative ones are consistent with imaginary frequencies and instability of the motion with an inverted interaction potential.[23] Consequently, the presence of imaginary frequencies in the spectrum will indicate the passage over the barrier, with the proportion of such modes being interpreted as a measure of quasiliquid behavior.[24] The term "instant" is chosen to emphasize that the set of modes is different at each point of the trajectory.

All these other methods differ from the method of normal modes in that they use modes which are not pairwise independent. At the same time the linearity of transition to new coordinates is preserved. In contrast, in the method of effective modes, we choose another approach: we use the linear decomposition and allocate independent types of motion. For normal modes the predetermined basis is used, and time dependencies of amplitudes are harmonic functions. The expansion in effective modes sets the algorithm for finding a basis. This basis, in general, depends on the form of trajectory and the time dependencies of amplitudes of effective modes can be anharmonic. A more detailed description of the method of effective modes can be found in our earlier studies.[14,15]

B. Nonrigid rotation and effective modes

For the nonrigid systems, the motion in each effective mode consists of rotations and vibrations. In our previous

work[14] we have shown that it is possible to separate the energy of the overall rotation from that of the vibrational motion in each mode using the method proposed by Jellinek and Li.[25] For a system of N particles, labeled with i, at any instant moment the rotational energy per mass unit captured by the kth mode can be presented as follows

$$(E_{\mathrm{rot}})_k(t) = \frac{1}{2} \cdot (\mathbf{p}(t) \cdot \mathbf{e}_k) \cdot \left(\sum_{i=1}^{N} \vec{q}_i(t) \times (\mathbf{e}_k)_i \right) \cdot \vec{\omega}(t), \qquad (5)$$

where the vector $\vec{q}_i$ is the position of the ith particle, and the vector $\vec{\omega}(t)$ is the instantaneous angular velocity.

In the general case of free rotation of a rigid body, both the vector of angular velocity and the instantaneous axis of rotation continuously change their direction in space. Even for the inertial rotation in the absence of external torques, behavior of the instantaneous axis of rotation seems to be complicated. Within a framework of effective modes, rigid body rotation around one of its principal axes of inertia is represented by a pair of coupled modes with the same average kinetic energy and periodic sinusoidal energy exchange between them.[18] In the general case free rotation of a rigid body can be presented as a superposition of three independent rotations around stationary axes with a pair of coupled modes per each axis. Effective modes of nonrigid systems contain both rotations and vibrations, but modes in pairs still have similar values of the average rotational energy. The pairs of coupled modes can be used for conducting a comparative analysis of rigid and nonrigid rotation, as we have done earlier.[14]

As noted by Aquilanti *et al.*,[26] it is very important to be able to characterize the aggregate structure and the dynamics of a system by focusing on a few key quantities. In this paper we use the effective numbers of rotational modes as a parameter which give information about redistribution of the internal energy among different types of the collective movements of the particles. This parameter allows us to determine the number of axes of rotation and to compare the cluster's rotation with that of a rigid rotator.

We define the effective number of rotational modes $n_{\mathrm{eff}}^{\mathrm{rot}}$ as follows

$$n_{\mathrm{eff}}^{\mathrm{rot}} = 10^{-\Sigma_k \langle (E_{\mathrm{rot}}^{\mathrm{red}})_k \rangle \cdot \log \langle (E_{\mathrm{rot}}^{\mathrm{red}})_k \rangle}, \qquad (6)$$

where $\langle (E_{\mathrm{rot}}^{\mathrm{red}})_k \rangle$ is the time averaged value of rotational energy in the kth mode [Eq. (5)], divided by the time averaged value of the total rotational energy. The effective numbers of rotational modes represent the degree of equipartition of the rotational energy among the modes. The effective number of rotational modes can take values from two (when only one pair of modes is excited, and rotation is similar to the principal rotation of a rigid rotator around a fixed axis) to six (when the rotational energy is equidistributed among all modes).

Other types of effective numbers of modes, as well as their quantum-mechanical analogies, are given in our earlier work.[14]

III. DYNAMICS OF A TRIATOMIC CLUSTER

A cluster consisting of three identical rare gas atoms can be considered as a bound state of the system defined by the Hamiltonian

$$H = \sum_{i=1}^{3} \frac{p_i^2}{2m} + \sum_{i>j}^{3} U(r_{ij}). \qquad (7)$$

Here, $r_{ij} = |\vec{q}_i - \vec{q}_j|$ is the distance between the atoms, $\vec{q}_i$ and $\vec{p}_i$ are the position vector and the momentum vector of the ith atom, m is its mass, and $U(r_{ij})$ is the Lennard-Jones potential

$$U(r_{ij}) = 4U_0 \left[\left(\frac{\alpha}{r_{ij}} \right)^{12} - \left(\frac{\alpha}{r_{ij}} \right)^{6} \right], \qquad (8)$$

where U_0 is the diatomic well depth and α is its characteristic width (at the zero level). The parameters m, U_0, and α are dimensionless with $(m \cdot \alpha^2 \cdot U_0^{-1})^{1/2}$ as the unit of time. The ground state of the cluster with the total energy $E_{\mathrm{tot}} = -3$ and zero angular momentum corresponds to the structure with the atoms located at the vertices of the equilateral triangle with side $\alpha' = \sqrt[6]{2}$. If the total energy of the cluster is more than the energy of the saddle point (for the linear configuration $E_{\mathrm{lin}} = -2.03$), the reaction of isomerization between two isomers is energetically possible. The dissociation threshold for the triatomic cluster is -1.0. Motion of the system in the state with a fixed energy and the maximum (for this energy) angular momentum $M_{\max}$ can be described as rotation around the center of symmetry of the equilateral triangle situated in the plane perpendicular to the vector of the angular momentum. In this paper the angular momentum M is normalized with respect to the maximum angular momentum $M_{\max}$ for a given energy.

We used the molecular dynamics method to study the phase space structure of the rotating Ar_3 cluster as a function of two parameters, namely, the total energy E_{tot} and the total angular momentum M.[27] A microcanonical ensemble of initial conditions was formed by straightforward sampling from points distributed randomly and uniformly in the phase space in such a way that the potential energy was $U \leq E_{\mathrm{tot}}$ and the kinetic energy was $E_{\mathrm{kin}} = E_{\mathrm{tot}} - U$. We used the random number generator proposed by Matsumoto and Nishimura.[28] Further, the points were selected from the angular momentum shell of finite thickness $\Delta M = 0.001$. The Hamilton equations of motion were numerically integrated using the velocity version of the Verlet algorithm[29] with the time step $t_s = 10^{-2}$ on the time interval $\tau = 2.5 \times 10^3$ time units. Using the values of $m(^{40}\mathrm{Ar}) = 39.945$ amu, $U_0 = 99.55$ cm^{-1}, and $\alpha = 3.757/2^{1/6}$ Å, the time unit is $(m \cdot \alpha^2 \cdot U_0^{-1})^{1/2} = 1.94$ ps, the time step is $t_s = 19.4$ fs, and the time interval is $\tau = 4.85$ ns. The absolute drift in the numerical values of E_{tot} and M on the interval τ did not exceed 10^{-5} and 10^{-7}, respectively.

To determine the type of dynamics (regular or chaotic), the maximum Lyapunov exponent has been calculated using the scheme of Benettin *et al.*[30] To calculate the average volume of the chaotic component of the phase space for each value of the angular momentum, the maximum Lyapunov exponent was computed for 1000 trajectories. From 11 000 to 19 000 trajectories were evaluated for a given energy. For

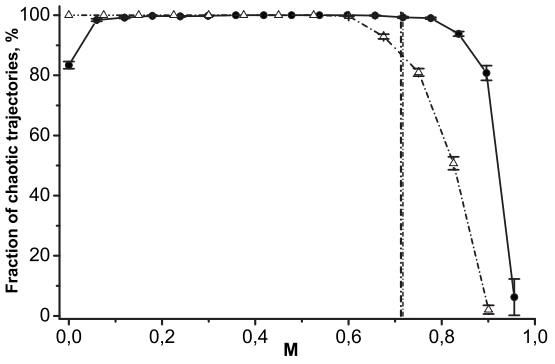

FIG. 1. Dependencies of the fraction of chaotic trajectories in relation to all trajectories on the angular momentum. The solid curve and symbols "●" correspond to the energy $E_{tot}=-1.9$ and the dotted curve and symbols "△" correspond to the energy $E_{tot}=-2.3$. Critical values of the angular momentum $M_{max}^{C_{2v}}(E_{tot}=-1.9)=0.72$ and $M_{max}^{C_{2v}}(E_{tot}=-2.3)=0.71$, related to rotation around the C_{2v} axis, are marked with the dot-dashed lines.

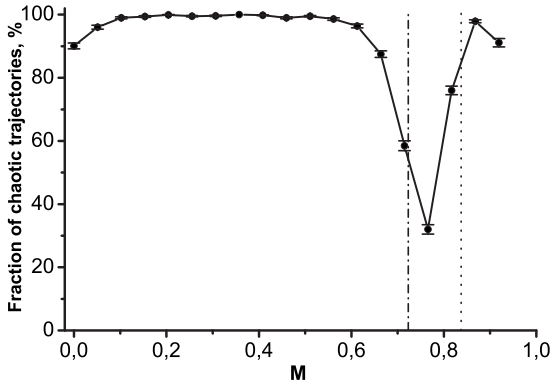

FIG. 2. Dependence of the fraction of chaotic trajectories in relation to all trajectories on the angular momentum, $E_{tot}=-1.5$. Critical values of the angular momentum $M_{max}^{C_{2v}}=0.72$ and $M_{max}^{D_{\infty h}}=0.84$ relate to rotation around the C_{2v} axis and the $D_{\infty h}$ axis correspondingly. They are marked with the dot-dashed and dotted lines.

each trajectory the effective modes were extracted (Sec. II A), the rotational energies in each mode were calculated and the effective number of rotational modes was computed (Sec. II B).

The internal dynamics of the cluster was studied for three different values of the total energy related to the two different regions of the potential energy surface. For the total energy $E_{tot}=-2.3$ only triangular configurations of the cluster can be realized. For the total energies $E_{tot}=-1.9$ and $E_{tot}=-1.5$ both triangular and linear configurations of the cluster can be reached. In Fig. 1 the dependencies of the fraction of chaotic trajectories in relation to all calculated trajectories on the angular momentum value are shown for the energies $E_{tot}=-1.9$ and $E_{tot}=-2.3$. The error σ is calculated in the usual form for the Monte-Carlo method

$$\sigma = \frac{\sqrt{f_{ch}\cdot(100-f_{ch})}}{\sqrt{N_{tot}}}, \tag{9}$$

where f_{ch} is the fraction of chaotic trajectories in relation to all calculated trajectories expressed in percentage ($f_{ch}=100\cdot N_{ch}/N_{tot}$), N_{tot} is the total number of trajectories, N_{ch} is the number of chaotic trajectories. These dependencies are nonmonotonic. When M belongs to the interval from 0.2 to 0.6 only a few regular trajectories are observed. The fraction of regular trajectories in relation to all trajectories starts to increase quickly when the total angular momentum reaches a certain value which depends on the value of the total energy. Another functional form of the dependence of the fraction of chaotic trajectories in relation to all trajectories on the angular momentum has been found for the total energy $E_{tot}=-1.5$ (Fig. 2). For this energy a noticeable increase of the volume of the chaotic component occurs when M reaches the value of 0.78 (approximately). Below we shall try to explain the results by means of effective numbers of rotational modes.

Figure 3 shows the dependence of the effective number of rotational modes on the angular momentum when the total energy $E_{tot}=-2.3$. This dependence represents redistribution of the rotational energy among the collective modes with an increase in the total angular momentum. Let us concentrate on the chaotic motion. When M is in the range from 0.2 to 0.4, the constant value of the effective number of rotational modes equals 4 (approximately). It means that two pairs of coupled rotational modes exist and the rotational energy is distributed equally between them. However, chaotic rotation in the range $M\subset(0.2;0.4)$ noticeably differs from the rotation of a rigid rotator due to the exchange of rotational energy among all effective modes.

When the angular momentum increases up to $M=0.6$ (Fig. 3) the effective number of rotational modes decreases to 2. This can be explained as follows: at each total energy there is a maximum value of normalized M above which the angular momentum vector is forced out of the molecular plane.[31] This value of M depends very slightly on the total energy, and for $E_{tot}=-2.3$ is $M_{max}^{C_{2v}}=0.71$. It can be interpreted as a reduction of tumbling with an increase of the angular momentum. Therefore it is physically reasonable that for chaotic motion the probability of rotation around the axis lying in the molecular plane decreases, and the decrease of the effective number of modes indicates a disappearance of one of two stationary axes of rotation. At the same time it should be noted that the decrease of the effective number of rotational modes occurs when $M=0.6$, instead of the value $M_{max}^{C_{2v}}=0.71$ which can be expected from the considerations above. When the angular momentum reaches the value of

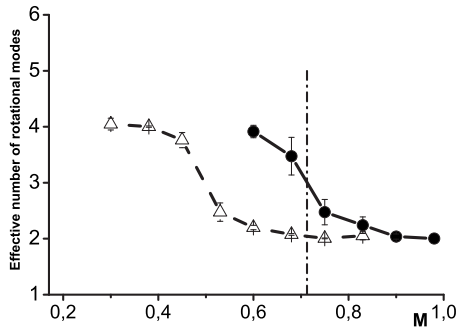

FIG. 3. Dependence of the effective number of rotational modes on the angular momentum, $E_{tot}=-2.3$. The solid curve and symbols "●" correspond to regular motion and the dotted curve and symbols "△" correspond to chaotic motion. Critical value of the angular momentum $M_{max}^{C_{2v}}=0.71$ related to rotation around the C_{2v} axis is marked with the dot-dashed line.

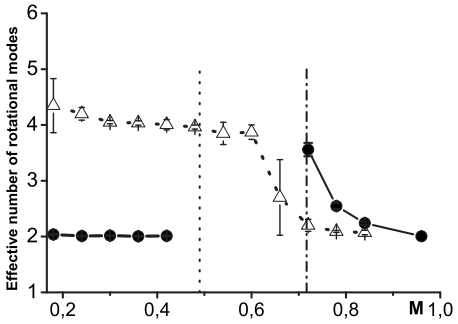

FIG. 4. Dependence of the effective number of rotational modes on the angular momentum, $E_{tot}=-1.9$. The solid curve and symbols "●" correspond to regular motion and the dotted curve and symbols "△" correspond to chaotic motion. Critical values of the angular momentum $M_{max}^{C_{2v}}=0.72$ and $M_{max}^{D_{\infty h}}=0.49$, related to rotation of the cluster in the isosceles acute triangle configuration around the C_{2v} axis and in the linear configuration around the $D_{\infty h}$ axis, respectively, are marked with the dot-dashed and dotted lines.

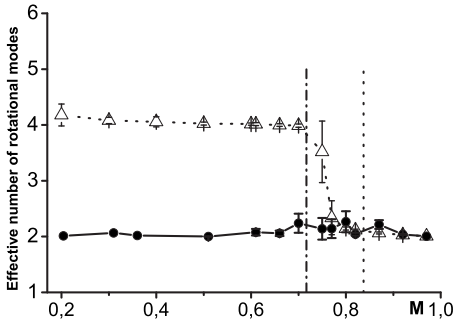

FIG. 5. Dependence of the effective number of rotational modes on the angular momentum, $E_{tot}=-1.5$. The solid curve and symbols "●" correspond to regular motion and the dotted curve and symbols "△" correspond to chaotic motion. Critical values of the angular momentum $M_{max}^{C_{2v}}=0.72$ and $M_{max}^{D_{\infty h}}=0.84$, related to rotation of the cluster in the isosceles acute triangle configuration around the C_{2v} axis and in the linear configuration around the $D_{\infty h}$ axis, respectively, are marked with the dot-dashed and dotted lines.

0.6 simultaneously with a reduction of n_{eff}^{rot} to 2 the regular component appears (in Fig. 1; $f_{ch}=99.7\%$ for $M=0.6$); but we have not found any regular trajectories for $M<0.6$. With further increase of the angular momentum up to the value of 0.8 ($M\subset(0.6;0.8)$), the effective number of rotational modes for the regular motion is larger than that for the chaotic motion (Fig. 3). When $M\subset(0.6;0.8)$ the way of rotation for the regular and chaotic components, detected by the difference in the values of effective number of rotational modes, creates a barrier that ensures a stability of regular motion and leads to the increase in the volume of the regular component. If $M<0.6$, there is always a possibility for transition to chaotic motion with the same number of axes of rotation (Figs. 3 and 1). Therefore, if the regular motion may happen, then it loses stability and becomes chaotic.

The relation between the decrease of the volume of the chaotic component and the change in the number of axes of rotation was also revealed for other values of the total energy. For example, as is shown in Fig. 4 for $E_{tot}=-1.9$ and $M<0.49$, all calculated regular trajectories are linked with the motion of atoms in the linear configuration with the only axis of rotation. Let us note that motion in the linear configuration was never found to be chaotic, thus rotation for the regular component was performed differently than that for the chaotic component. The distinction between two types of motion which we have detected through the different values of the effective number of rotational modes ($n_{eff}^{rot}=2$ for regular and $n_{eff}^{rot}=4$ for chaotic motion) creates a barrier for transition from regular to chaotic regime. When $M>M_{max}^{D_{\infty h}}=0.49$, rotation in the linear configuration becomes impossible, and the motion of atoms in the cluster occurs only in a triangular configuration. It leads to a reduction of the barrier between regular and chaotic motion and, as a consequence, to disappearance of the regular motion. With the further increase in the angular momentum a degree of chaos in the chaotic component gradually decreases, reflecting the loss of stability of one of the rotation axes of the triangular cluster. When the angular momentum reaches the value of $M=0.72$, the effective number of rotational modes for the chaotic motion decreases from four to two. At the same value of angular momentum a regular motion appears again (see Fig. 1, $f_{ch}=99.7\%$ for $M=0.72$). When $0.4<M<0.7$, no regular trajectories have been found. The effective number of rotational modes for the regular motion remains larger than for the chaotic motion until the angular momentum reaches 0.9. A similar situation was observed for $E_{tot}=-2.3$: a difference in rotation for the regular and chaotic components, detected by difference in the values of the effective numbers of rotational modes, creates a barrier that reduces the volume of chaotic component with growth of the angular momentum. Absence of such a barrier for $0.49<M<0.72$ leads to a lack of regular motion in this interval of M. We conclude that the value of the angular momentum at which a growth of the regular component volume begins depends on the total energy of the system (see Fig. 1) and can be determined accurately using the effective number of rotational modes.

The idea of a barrier helps to explain the dependence of the chaotic component volume on the angular momentum value for $E_{tot}=-1.5$, namely, a significant increase in the number of chaotic trajectories at $M>0.78$ (Fig. 2). A linear configuration is theoretically accessible while the angular moment $M<M_{max}^{D_{\infty h}}=0.84$. Regular motion in a linear configuration is more preferable than in a triangular configuration, so for $M<0.78$ all observed regular trajectories represent fluctuations of atoms around the linear configuration of the cluster. However, we have not found a movement of the atoms in a configuration close to the linear configuration of the cluster when the value of the angular momentum is larger than 0.78. Consequently, when $M>0.78$ the regular motion can occur only in a triangular configuration. At the same time for regular motion in a triangular configuration, for $M\simeq 0.78$, the effective number of rotational modes is only slightly higher than it is for the chaotic motion (see Fig. 5). The barrier dividing different types of motion is too small, leading to a substantial growth of the volume of the chaotic component.

IV. SUMMARY

The influence of rotation on the internal dynamics of small van der Waals clusters has been studied in this paper. From general considerations one can assume that for small values of angular momentum a large part of the kinetic en-

ergy is contained in the vibrations and the fraction of chaotic trajectories is large, and that this fraction should decline with an increase of the angular momentum. We calculated the dependence of the fraction of chaotic trajectories in relation to all trajectories on the angular momentum using the Monte Carlo and molecular dynamics methods and have found that it is nonmonotonic, and that its functional form varies for different values of the total energy. First, the fraction of chaotic trajectories begins to decrease starting from a certain value of the angular momentum which depends on the value of the total energy. Second, there is a substantial fraction of regular trajectories for low values of the angular momentum when the linear configuration is accessible. Third, for certain value of the total energy we observed a second increase of the fraction of chaotic trajectories for large values of the angular momentum.

We used the method of effective modes to explain these effects. The use of effective number of rotational modes has made it possible to determine the value of the angular momentum at which a considerable decrease in the volume of chaotic component occurs, and to explain all the features of the functional form of the dependence of the fraction of chaotic trajectories on the angular momentum in a unified manner. We have found that the regular motion occupies an essential part of the phase space when rotation in the regular and chaotic components is performed in different ways, namely, with different numbers of rotation axes. The latter has been evidenced by different values of the effective number of rotational modes. The difference in rotation in the regular and chaotic components creates a barrier for transition between the components, permitting the existence of a regular component. The conclusions are valid for different values of the total energy related to the different regions of the potential energy surface.

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