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# Description of nonrigid rotation in small atomic clusters

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**Abstract.** The dependence of the internal dynamics of triatomic van der Waals clusters on the rate of nonrigid rotation has been studied. The method of decomposition of the system's motion into orthogonal modes of the motion has been proposed. Additionally, a new method of separation of the kinetic energy, captured by the modes, into rotational and vibrational components has been developed. It has been found that the most significant factor for the chaotic behavior of the cluster is the partitioning of the vibrational and rotational energies among the modes.

**PACS.** 36.40.-c Atomic and molecular clusters – 05.45.-a Nonlinear dynamics and chaos

## 1 Introduction

Atomic and molecular clusters, being intermediates between separate atoms and molecules on the one hand and the condensed phase on the other hand, often demonstrate properties which are distinctly different from those of either gases or solids, or liquids. Investigation of these properties is of a great importance for establishing the relation between the microworld of atoms and molecules and the macroworld of condensed phase and for unravelling the mechanisms governing the transitions between these two worlds.

The difference between the internal dynamics of van der Waals (vdW) clusters and that of molecules arises from the different nature and strength of interaction between atoms in molecules and atoms in vdW clusters. Atoms in molecules are trapped in their potential energy wells due to strong chemical interactions within the molecules. High energy barriers exist between such wells. Dynamics of the atomic motion in molecules can be treated as weakly coupled small-amplitude vibrations around the minima. To consider vibrations in molecules one can usually use the normal-mode approximation. For vdW clusters, the strength of interactions among the atoms is weaker. There are numerous potential energy wells, which have low depths and small barriers separating them. Dynamics in such wells can not be represented as the set of uncoupled oscillations, and normal-mode approximation cannot be applied. Besides, the rotation in vdW clusters is essentially non-rigid, and the interaction between the rotational and vibrational motions is significant. Consequently, the commonly used framework of near rigid or "semirigid" systems, in which the rotational motion is executed in conjunction with oscillations, often of small amplitude, is not valid. In spite of the objective difficulties, the classical dynamics studies of the atomic clusters, which have been undertaken during the last decades, revealed an extremely important and intricate role of the total angular momentum [1].

It has also been shown, that due to the nonlinearity of interaction among the particles, the dynamics of vdW clusters exhibits significant degree of chaos [2]. The extent of chaos in the clusters is not uniquely defined by its total energy and angular momentum, but instead strongly depends on the initial state of the cluster [1]. There are several hypotheses about parameters, which control the extent of chaos in clusters [3,4], but in general the problem is not resolved yet. The aim of this paper is to investigate the influence of rotation on the internal dynamics of vdW clusters.

We will try to overcome the difficulties, mentioned above, by using the method developed earlier by us, which we call "method of effective modes of the motion". These method is similar to the method of bi-orthogonal decomposition, described in [5], and the method of Karhunen-Loève decomposition, described, for example, in [6,7].

The structure of this paper is as follows: Section 2.1 presents a basic description of the method of effective modes of motion. In Sections 2.2 and 2.3 the method is supplemented with the method of separation of the kinetic energy, captured by the modes, into rotational and vibrational components. In Section 3 the dynamics of triatomic $Ar_3$ clusters is described, and Section 4 gives the summary of the work.

## 2 Methods

### 2.1 Method of effective modes of motion

The main idea of this method is to decompose the motion in $n$-dimensional phase space into $m$, $(m = 1, 2...n)$,

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orthogonal components (modes of motion) with the extremal properties. Among all $m$-dimensional components of the phase trajectory, the superposition of $m$ modes approximates the dynamical properties in the most accurate manner [8]. We observe the evolution of the system at the discreet time moments $t_1, ...t_{N_T} \in [0, T)$, using the numerical integration of Hamilton equations of motion ($N_T$ is the number of steps of integration). At any moment $t_j$ we get a vector of the phase coordinates $\boldsymbol{q}(t_j) = [\boldsymbol{x}(t_j), \boldsymbol{p}(t_j)]$, where $\boldsymbol{x}(t_j)$ is the position vector and $\boldsymbol{p}(t_j)$ is the momentum vector. Let us focus on the momentum subspace, in which the trajectory is specified by the $n \times N_T$ matrix, that can be written in the form

$$\hat{\mathbf{p}} = \hat{\mathbf{p}}_{ij} = p_i(t_j), \quad i = \overline{1, n}, \quad j = \overline{1, N_T}, \tag{1}$$

where $n$ is the number of degrees of freedom, $N_T \gg n$. Using singular value decomposition of the matrix (1), the latter can be represented in the form

$$\mathbf{p}_j = \sum_{k=1}^{n} \lambda_k \, \mathbf{g}_k^j \, \mathbf{e}_k, \tag{2}$$

where $\lambda_k$, $\lambda_1 \geq \lambda_2 \geq ... \geq \lambda_n \geq 0$ are called singular values, and the vector sets $\mathbf{e}_k$ and $\mathbf{g}_k$ are called singular bases. The vectors $\mathbf{e}_k$ gives the directions of the $k$th mode of the motion, or, in more detail, directions and relative amplitudes of the motion of the particles. The product $\lambda_k \, \mathbf{g}_k^j$ gives the projection of the momentum subspace $\hat{\mathbf{p}}$ on the $k$th mode, or the amplitude of the $k$th mode at any moment $t$:

$$\lambda_k \, \mathbf{g}_k^j = (\mathbf{p}(t), \mathbf{e}_k). \tag{3}$$

The value $\eta(k)$, defined as

$$\eta(k) = \frac{\lambda_k^2}{\sum\limits_{k=1}^{n} \lambda_k^2}, \tag{4}$$

gives the weight of the $k$th mode in the new system of coordinates. For the momentum subspace, the sum $\sum_{k=1}^{n} \lambda_k^2$ represents twice the value of kinetic energy of the system, and $\eta(k)$ represents the time-averaged kinetic energy, contained in the $k$th mode. The error of the approximation of the motion with $m$ modes (the error in the kinetic energy) is given by $\gamma$, which is calculated from:

$$\gamma(m) = \sum_{k=m+1}^{n} \lambda_k^2. \tag{5}$$

It has been shown that for the many-particle systems, whose inter-particle interaction obey to quadratic potential, the effective modes could be reduced to the normal modes [9]. In contrast to the normal modes, the time dependence of amplitudes of the effective modes can be inharmonic. Besides, it can be showed that the rotation of the rigid body around one of the principal axis of inertia could be represented by the two coupling modes with equivalent energy and periodic sinusoidal energy transfer between them [7]. In the general case rotation of the rigid body can be represented with three pairs of coupling modes with the properties described above. The value of the kinetic energy, captured by each pair of modes, remains constant during the simulation.

### 2.2 Method of separation of the kinetic energy captured by the modes into rotational and vibrational component

For nonrigid systems, the motion in each effective mode consists of rotational and vibrational components. It is possible to separate the energy of the overall rotation from that of the vibrational motion, using the procedure suggested in [10]. The advantage of this scheme is that it is admissible for any $N$-body system irrespective of the degree of nonrigidity. As it can be seen below, we have adopted this framework for the separation of the kinetic energy, stored in every single mode.

Let us consider the system of $N$ particles, indexed with $i$. At first, we need to know the value of the kinetic energy captured by each mode at any instant moment $t$. Multidimensional vector $\mathbf{p}$ is defined as $3N$-vector, consisting of $3N$ projections of momentums of all particles, or as $N$ vectors of momentum of each particle:

$$\mathbf{p} = \begin{pmatrix} \mathbf{p}_1 \\ ... \\ \mathbf{p}_N \end{pmatrix}. \tag{6}$$

Using the method of effective modes of motion, for each particle, the vector $p$ is given as

$$\mathbf{p}_i = \sum_{k=1}^{3N} (\mathbf{p}(t), \mathbf{e}_k)_i \cdot (\mathbf{e}_k)_i, \tag{7}$$

where $(\mathbf{e}_k)$ is defined as follows:

$$(\mathbf{e}_k) = \begin{pmatrix} (\mathbf{e}_k)_1 \\ ... \\ (\mathbf{e}_k)_N \end{pmatrix}. \tag{8}$$

Since the basis $(\mathbf{e}_k)$ is the orthonormal basis, at any $t$ the kinetic energy $(E_{kin})_k$, captured by the $k$th mode, can be written as

$$(E_{kin})_k = \sum_{i=1}^{N} \frac{{(\mathbf{p}(t), \mathbf{e}_k)_i}^2}{2m_i}. \tag{9}$$

The instantaneous energy of the overall rotation can be defined as follows (see [10]):

$$E_{rot}(t) = \frac{1}{2}(\mathbf{M} \cdot \boldsymbol{\omega}(t)), \tag{10}$$

where $\mathbf{M}$ is the total angular momentum of the system, and the instantaneous angular velocity $\boldsymbol{\omega}(t)$ is:

$$\boldsymbol{\omega}(t) = \mathbf{I}^{-1}(t) \cdot \mathbf{M}, \tag{11}$$

where $\mathbf{I}(t)$ is the instantaneous tensor of inertia. If the system consists of $N$ particles with masses $m_i$, than this tensor can be expressed through the coordinates $\mathbf{r}_i = \{x_i, y_i, z_i\}$ of the particles as $3 \times 3$ matrix with elements

$$\mathbf{I}_{\alpha\alpha}(t) = \sum_{i=1}(m_i(r_i^2(t) - \alpha_i^2(t))), \tag{12}$$

$$\mathbf{I}_{\alpha\beta}(t) = -\sum_{i=1}(m_i(\alpha_i(t)\beta_i(t)); \ \alpha, \beta(\neq \alpha) = x, y, z. \tag{13}$$

Using equation (7), for the total angular momentum we have an expression

$$\mathbf{M} = \sum_{i=1}^{N} \mathbf{r}_i \times \mathbf{p}_i = \sum_{i=1}^{N} \mathbf{r}_i \times \left( \sum_{k=1}^{N} (\mathbf{p}(t), \mathbf{e}_k) \cdot (\mathbf{e}_k)_i \right). \tag{14}$$

Changing the sequence of summing in the formula (14), we get an expression

$$\mathbf{M} = \sum_{k=1}^{N} (\mathbf{p}(t), \mathbf{e}_k) \cdot \left( \sum_{i=1}^{N} \mathbf{r}_i \times (\mathbf{e}_k)_i \right). \tag{15}$$

Consequently, at any instant moment for the energy of the overall rotation we have:

$$E_{rot} = \frac{1}{2} \sum_{k=1}^{N} \left[ \left( (\mathbf{p}(t), \mathbf{e}_k) \sum_{i=1}^{3} \mathbf{r}_i(t) \times (\mathbf{e}_k)_i \right) \cdot \boldsymbol{\omega}(t) \right], \tag{16}$$

and for the rotational energy captured by the $k$th mode we have

$$(E_{rot})_k = \frac{1}{2} (\mathbf{p}(t), \mathbf{e}_k) \left( \sum_{i=1}^{3} \mathbf{r}_i(t) \times (\mathbf{e}_k)_i \right) \cdot \boldsymbol{\omega}(t). \tag{17}$$

Besides, we can calculate the vibrational energy captured by the $k$th mode as the rest part of the kinetic energy captured by the $k$th mode:

$$(E_{vib})_k = (E_{kin})_k - (E_{rot})_k. \tag{18}$$

### 2.3 Effective numbers of modes

Let us define the effective number of modes $n_{\mathit{eff}}$ as

$$n_{\mathit{eff}} = 10^{-\sum\limits_{k} a_k \log a_k}, \tag{19}$$

where $a_k$ is the relative part of the time-averaged kinetic (or rotational, or vibrational) energy, captured by the $k$th mode. The effective numbers of modes represent the degree of equipartition of the energies among the modes. Each effective number can takes on a value from one (when whole energy is in the one mode only) to six (when the energy is equidistributed between all the modes).

Similar concept is used in the quantum-mechanical approach. Then the wave function of a system is expanded using the wave functions of it's stationary states, the degree of equipartition among different basis functions is used as the characteristic of the set of decomposition coefficients $\{a\}$. For the quantitative expression of the degree of equipartition one can use such parameters as the relationship of participation $P_n = \sum_m |a_{nm}|^4$, the entropy $S_n = -\sum |a_{nm}|^2 \ln |a_m|^2$ and the effective number of states $n^* = P_n^{-1}$ or $n^* = \exp S_n$ [11,12]. As it was found in the most of theoretical studies [11], the more chaotic is the system, the higher is the degree of equipartition.

Also we can use the effective numbers of modes to derive the temperature ($\theta$) of the clusters. If the equidistribution of the kinetic energy between degrees of freedom exists, then the internal temperature of cluster could be defined as follows:

$$\theta = 2\langle E_{vib} \rangle / \, k_B n_{df}, \tag{20}$$

where $E_{vib}$ is the time or ensemble average of the vibrational energy, $n_{df}$ is the number of the degrees of freedom and $k_B$ is Boltzmann constant. In other cases we suggest to use the effective number of modes instead of the number of degrees of freedom in equation (20), as more reliable.

## 3 Dynamics of a triatomic cluster

The cluster consisting of three identical rare gas atoms can be considered as a bound or long-lived, quasibound state of the system defined by the Hamiltonian

$$H = \sum_{i=1}^{3} \frac{\mathbf{p}_i}{2m} + \sum_{i=1}^{3} U(r_{ij}). \tag{21}$$

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

$$U(r_{ij}) = 4U_0 \left[ \left( \frac{\alpha}{r_{ij}} \right)^{12} - \left( \frac{\alpha}{r_{ij}} \right)^{6} \right], \tag{22}$$

where $U_0$ is the diatomic well depth and $\alpha$ is its characteristic width (at the zero level). Parameters $m$, $U_0$ and $\alpha$ are taken as dimensionless, with $(m\alpha U_0)^{\frac{1}{2}}$ as the unit of time. The ground state of the cluster with the total energy $E = -3$ and zero angular momentum corresponds to the structure with the atoms located at the vertices of an equilateral triangle with side $\alpha' = \alpha \sqrt[6]{2}$. When the total energy exceeds the value of $E_{lin} = -2.03$, then the passage though the linear saddle point is allowed. The dissociation threshold for the triatomic cluster is $-1.0$. The motion of the system in the state with a fixed energy and the maximal (for this energy) angular momentum $M_{\mathtt{max}}$ can be described as the rotation around the center of symmetry of the equilateral triangle situated in the plane perpendicular to the angular momentum. In this paper the angular momentum is normalized on the maximum angular momentum $M_{\mathtt{max}}$ for a given energy.

We used molecular dynamics to study the phase space structure of rotating $\mathrm{Ar}_3$ cluster as a function of two parameters, namely the total energy $E_{tot}$ and the total angular momentum [13]. A microcanonical ensemble of initial conditions was formed by straightforward sampling

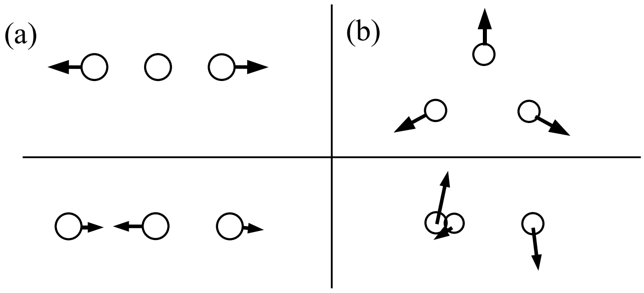

**Fig. 1.** Motion of the particles in the first two modes for the regular motion of nonrotating Ar$_3$ cluster, $E = -1.5$; (a) linear configuration, (b) triangular configuration.

from points distributed randomly and uniformly in coordinate space such that the potential energy $U \leq E_{tot}$ and in momentum space such that the kinetic energy $E_{kin} = E_{tot} - U$. 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 [14] with a time step $t_s = 10^{-2}$ on the time interval $\tau = 2.5 \times 10^3$ time units. Using values of $m(^{40}\mathrm{Ar}) = 39.945$ amu, $U_0 = 99.55$ cm$^{-1}$, and $\alpha = 3.757/2^{\frac{1}{6}}$ Å, the time unit is $(m\alpha U_0)^{\frac{1}{2}} = 1.94$ ps, the time step is $t_s = 19.4$ fs, and the time interval is $\tau = 4.85$ ns. The absolute drift in numerical values of $E_{tot}$ and $M$ on the interval $\tau$ did not exceed $10^{-5}$ and $10^{-7}$, respectively.

For a given value of $E_{tot}$ and $M = |\mathbf{M}|$ a set of 100 trajectories was used. For the determination of the type of the motion the maximum Lyapunov exponent $\sigma$ has been calculated using the scheme of Benettin et al. [16]. For each trajectory the effective modes were extracted (Sect. 2.1), rotational and vibrational kinetic energies in every mode (Sect. 2.2) were calculated, and the numbers of rotational and vibrational modes were computed (Sect. 2.3).

One can see (Fig. 1) that for the regular motion of nonrotating cluster the effective modes are similar to the normal modes. Arrows show directions of the momentum of each atom in the cluster. The length of each arrow is proportional to the time-averaged magnitude of the atom's momentum in the corresponding mode. Atoms are pictured as circles at the points, which corresponds to the time-averaged positions of the atoms over the time interval from 0 to $T$. For the regular motion in linear configuration (Fig. 1a), two first obtained modes coincided with the normal modes of motion for the linear triatomic molecule with the harmonic potential of interactions. And for the motion in the triangular structure (Fig. 1b), only the first mode is similar to the normal mode for the described earlier triatomic molecule.

The dependence of the number of rotational modes on the normalized angular momentum is shown in Figure 2. When $M$ belongs to the range from 0.2 to 0.7, one can see the constant value (approximately 4) of the number of rotational modes for the chaotic motion. It means that for the chaotic motion two rotations about orthogonal axes exist. As for the regular motion, one can see the constant value (approximately 2) of the number of rotational modes. It means that for the whole regular component rotation about one axis is much more probable.

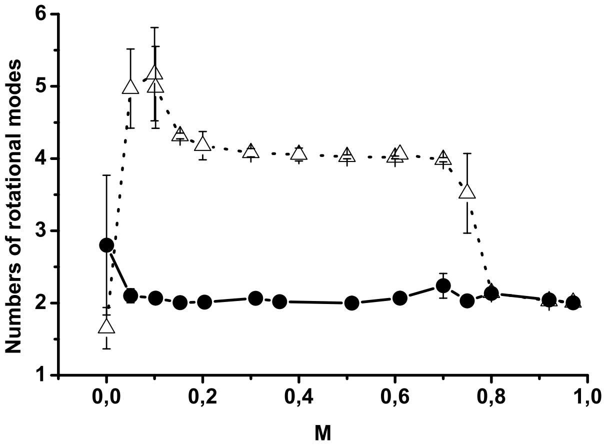

**Fig. 2.** Dependence of the numbers of rotational modes on the total angular momentum, $E = -1.5$. The solid line and symbols (●) correspond to the regular motion and the dotted line and symbols (△) correspond to the chaotic motion.

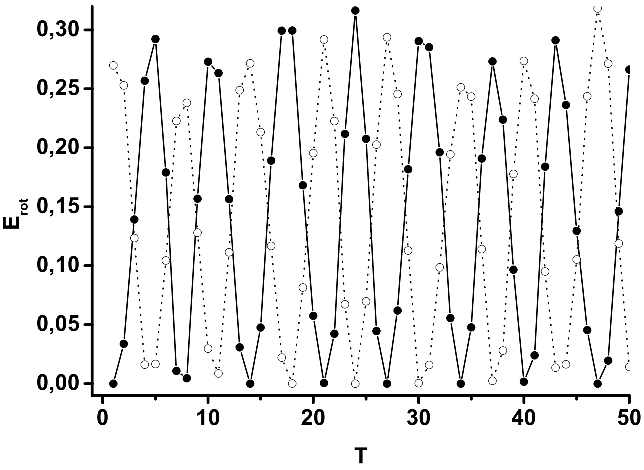

**Fig. 3.** Time dependence of the rotational energy, captured by the first two modes, for the regular motion, $E = -1.5$, $M = 0.61$. The solid line and symbols (●) correspond to the first mode and the dotted line and symbols (○) correspond to the second mode.

Now let us look at the time dependence of the rotational energy in the first two modes (Fig. 3). One can see that the amounts of the rotational energy captured by the modes are synchronized in time for the regular component (also one can see the sinusoidal nature of these plots), in just the same way as in the case of the solid-body rotation. For the chaotic component the rotational energy is distributed chaotically between the modes, the same as in the case of non-rigid rotation.

When $M$ becomes higher than 0.7, the number of rotational modes decreases. It has been shown earlier [15], that

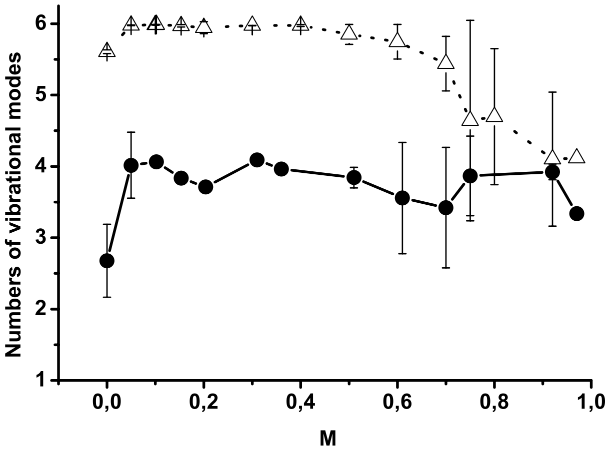

**Fig. 4.** Dependence of the numbers of vibrational modes on the total angular momentum, $E = -1.5$. The solid line and symbols (●) correspond to the regular motion and the dotted line and symbols (△) correspond to the chaotic motion.

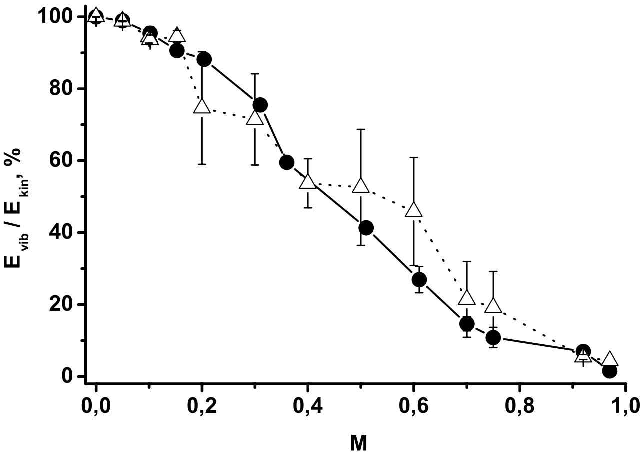

**Fig. 5.** Dependence of the normalized vibrational energy on the angular momentum for regular and chaotic components, $E = -1.5$. The solid line and symbols (●) correspond to regular motion, the dotted line and symbols (△) correspond to the chaotic motion.

at a fixed total energy there is a maximum value of the normalized $M$, above which the angular momentum vector is forced out of the molecular plane. For the total energy $E = -1.5$ this happens when the angular momentum becomes greater than $M = 0.723$. This can be interpreted as reduction of the tumbling (the motion of the angle between the angular momentum vector and the normal to the molecular plane), when the angular momentum is being increased. Therefore it is physically reasonable, that for the chaotic motion rotation around the axis lying in the molecular plane becomes much smaller, and for $M > 0.8$ we have the number of rotational modes near the value of 2.

In Figure 4 the dependence of the numbers of vibrational modes on the normalized angular momentum is shown. One can see that when we turn the rotation on, the number of vibrational modes increases. We call it the effect of mode activation, and this effect makes questionable widespread belief that introduction of the rotational motion regularizes the dynamics [4,15]. When the angular momentum is still growing, the numbers of vibrational modes are kept constant for every type of motion (regular and chaotic), until the value of angular momentum reaches almost 0.7. Then many factors, such as the reduction in tumbling, the reduction of the value of vibrational energy and the increase in rigidity, make the numbers of vibrational modes lower and the measure of inaccuracy higher. As one can see in Figure 5, there is no significant difference in the amount of the total kinetic energy, stored in vibrations, for the regular and chaotic motion. This fact is in a conflict with the widespread point of view that the major contribution to the chaotic motion comes from the energy stored in the vibrational modes, and that the amount of the energy in those modes defines the dynamics [3,4]. But, according to our results (Fig. 4), for a broad band of values of the angular momentum there is a significant difference in the distribution of the vibrational energy among the modes. Actually, we obtained the value in the neighbourhood of 4 for the numbers of vibrational modes for the regular motion, and the value in the neighbourhood of 6 with relatively small error for the chaotic motion, that means almost full equidistribution of vibrational energy among modes. Summarizing the results, we can say, that the distribution of the vibrational energy among the modes defines the type of dynamics of the cluster.

## 4 Summary

We have shown that the method of the effective modes of motion helps to analyze the internal dynamics of small vdW clusters. By using this method a detailed description of the influence of the rotation on the internal dynamics was achieved. Suggested method of the separation of the energy, captured by the modes, into rotational and vibrational components makes possible to describe the channels of the energy transfer in vdW clusters. Using the numbers of rotational and vibrational modes, we have found the peculiarity of regular component, consisted in a restriction on the number of axes for allowed rotation. Besides, we have demonstrated that the type of dynamics in the cluster depends mainly on the distribution of the vibrational energy among the modes, but not on the amount of energy stored in the vibrational motion.

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