ABOUT EFFECTIVE MODES METHOD FOR DESCRIPTION OF INTERNAL DYNAMICS OF WEAKLY BOUND CLUSTERS

Elena Belega, Evgeny Cheremukhin[1], Dmitry Trubnikov

Abstract: New approach to describe the internal dynamics of weakly bound clusters is presented. It is based on the method of main components of nonlinear dynamical systems which was adapted to study collective modes behavior in molecular systems. The method was applied to extract the collective modes in small water clusters. It is found that the number of active collective modes depends on the initial cluster excitation and that the internal energy is partitioned nonuniformly among the modes. Calculated collective modes were used to estimate the internal temperature of small water clusters and energy intervals for their quasi-phases.

1. Introduction

Study of weakly bound clusters plays an important role in various areas of science, in particular, in physical chemistry, molecular biology, in the theory of phase transitions in finite-size systems, in the theory of nonlinear dynamic systems. Investigation of movement of particles in the clusters conducts to understanding the mechanisms of isomerization and fragmentation and to revealing their dynamic features. The study is faced with some principal difficulties: all types of particle motion are mixed. As a result the dynamics is sophisticated and can not be described by well known method of normal modes because of interaction of different types of vibrations in weakly bound clusters. This interaction influences on energy redistribution between internal degrees of freedom and, consequently, on the rate constant of isomerization and monomolecular fragmentation.

Describing the internal dynamics in the weakly bound clusters it is more reasonable to talk not about the degrees of freedom but about collective motions of the particle in the clusters. The high-dimensional nature of the dynamics is often a substantial obstacle to clarifying the exact mechanisms

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of collective motions and new approaches to identify a small number of collective variables that play a predominant role in the structural dynamics of clusters are very important. The authors of given paper suggest to use the main components method, which has been adapted to describe the internal dynamics of weakly bound atomic clusters [1] to study the collective motions in small water clusters.

2. Method of effective modes in molecular dynamics

Let us describe the internal motion of dynamical system in momentum subspace E_N^p with dimension N. Multidimensional vector of momentum $\mathbf{p}(t)$ of system with n particles and masses m_i ($i = \overline{1,n}$) can be presented as superposition of N collective modes $(N = 3n)$ at each moment of time $t \in [0, t_0)$ (where t_0 – time of observation over the system):

$$\mathbf{p}(t) = \sum_{k=1}^{N} (\mathbf{p}(t), \mathbf{e}_k) \mathbf{e}_k \ .$$

Specially ordered orthonormal basis vector set $\{\mathbf{e}_k\}_{k=\overline{1,N}} \subset E_N^p$ determines the main directions in the phase space with the maximum kinetic energies components.

Effective collective mode (i.e. main component of movement) is the projection of kinetic momentum $\hat{\mathbf{p}}_k(t) = (\mathbf{p}(t), \mathbf{e}_k) \mathbf{e}_k$ at every direction $\mathbf{e}_k$. Such basis can be constructed and ordered as a result of solution of eigen values task:

$$\mathbf{p}(t) \mathbf{p}^*(t) \mathbf{e}_k = \lambda_k^2 \mathbf{e}_k \ ,$$

$$\mathbf{p}^*(t) \mathbf{p}(t) \mathbf{g}_k = \lambda_k^2 \mathbf{g}_k \ , k = \overline{1, N} \ ,$$

where $\mathbf{g}_k$ - singular vectors conjugated to $\mathbf{e}_k$. Values $\lambda_1 \geq \lambda_2 \geq ... \geq \lambda_n \geq 0$, are sorted in the nonascending order.

The first effective mode has the maximum value of the total kinetic energy of dynamical system. First m ($m \leq N$) time-averaged effective modes have more kinetic energy than others m modes that are calculated with any another orthonormal basis set.

The value

$$\eta_k = \frac{\lambda_k^2}{\sum_{k=1}^{N} \lambda_k^2}$$

gives the contribution of the *k*-th mode to common dynamics in new coordinate system.

Contribution of k-th mode in simultaneous kinetic energy of the system can be estimated by formula:

$$E_k(t) = \lambda_k^2 \mathbf{g}_k^2(t) \sum_{i=1}^{n} \frac{(\mathbf{e}_k^i)^2}{2m_i} .$$

Time-averaged kinetic energy $\langle E_k \rangle$ in k-th mode can be calculated as:

$$\langle E_k \rangle = \frac{\lambda_k^2}{2T} \sum_{i=1}^{n} \frac{(\mathbf{e}_k^i)^2}{m_i} = \langle E \rangle \eta_k ,$$

where $\langle E \rangle$ – mean kinetic energy of system during the time of observation t_0 .

As a result K-dimensional ($K \leq N$) approximation of $\hat{\mathbf{p}}(t)$ with the mean kinetic energy $\langle \hat{E} \rangle$ can be calculated as:

$$\hat{\mathbf{p}}(t) = \sum_{k=1}^{K} (\mathbf{p}(t), \mathbf{e}_k) \mathbf{e}_k , \quad \langle \hat{E} \rangle = \sum_{k=1}^{K} \langle E_k \rangle$$

Time-averaged square error of such approximation can be predicted by formula:

$$\Delta_K \langle \hat{E} \rangle = \sum_{k=K+1}^{N} \langle E_k \rangle .$$

The values η_k give the kinetic energy distribution among collective degrees of freedom called collective modes. The effective dimension K_{eff} $\left(K_{eff} \leq N \right)$ of the momentum subspace E_N^p in which the most significant movement of dynamical system is concentrated is calculated as:

$$K_{eff} = \exp\left(-\sum_{k=1}^{N} \eta_k \ln \eta_k \right). \tag{1}$$

The effective dimension reflects the number of internal degrees of freedom filled by kinetic energy and can be used to calculate the internal temperature of the cluster. The temperature is the parameter which is borrowed from statistical physics for describing an internal state of the cluster. Standard estimation of cluster temperature calculated as:

$$T = \frac{2 \langle E \rangle}{k_B K_{df}} , \tag{2}$$

where k_B is Boltzmann constant and K_{df} is the number of internal degrees of freedom. For non-rotating cluster placed in mass center $K_{df} = 3n - Q - 6$, where Q – number of rigid bonds in the cluster. Definition (2) works well for the clusters consisting of identical atoms and is not correct for

complex multicomponent atomic and molecular systems which are clusters of water. For the last an assumption of equipartition of energy among internal degrees of freedom is not valid. Using effective phase dimension K_{eff} instead K_{df} in (2) gives the temperature T_{eff} that can estimate temperature of micro canonical ensemble of molecular systems more accurately.

2. Analyses of small water clusters dynamics

For application of the effective modes method the internal dynamics of small water clusters has been considered. Water clusters are important weakly bound complexes due to the crucial role which they play in natural processes. They belong to a class of nonrigid systems with very complicated internal dynamics. Study of the dynamics can clarify on microscopic scale a wide range of chemical problems from hydrogen bond rearrangement rules to thermodynamic properties of water. Water pentamer and tetramer ($n_{mol} = 4, 5$) were chosen for the study. Coordinates and momenta of the atoms in the cluster were calculated by classical molecular dynamics. Classical Hamiltonian of cluster can be defined as follows:

$$H(\mathbf{p}_1(t),...,\mathbf{p}_n(t), \mathbf{r}_1(t),...,\mathbf{r}_n(t)) = \sum_{i=1}^{n} \frac{\mathbf{p}_i^2(t)}{2m_i} + U(\mathbf{r}_1(t),...,\mathbf{r}_n(t)),$$

where $U(\mathbf{r}_1(t),...,\mathbf{r}_n(t))$ - potential energy of interaction between particles. Generation of different initial states of non-rotated bound cluster with initial energy $H_0 = U_0 + E_0$ was performed by Monte-Carlo method, where U_0 - is potential energy of global minima of cluster', E_0 - is initial kinetic energy. The value U_0 and initial coordinates of atoms $\mathbf{r}_i(0)$ can be found once by well known thermal annealing method for example. Setting up the initial excitation value E_0 it can possible to generate randomly initial atoms momenta $\mathbf{p}_i(0)$ that must satisfy system of equations:

$$\begin{cases} \sum_{i=1}^{n} \mathbf{p}_i(0) = 0, \\ \sum_{i=1}^{n} [\mathbf{r}_i(0), \mathbf{p}_i(0)] = 0, \\ \sum_{i=1}^{n} \frac{\mathbf{p}_i^2(0)}{2m_i} = E_0, \end{cases}$$

where $[\cdot,\cdot]$ is the vector product. For the study rigid TIP5P [2] potential was used to describe interaction between molecules in the cluster. The initial geometries of clusters obtained in this paper are placed in Fig.1.
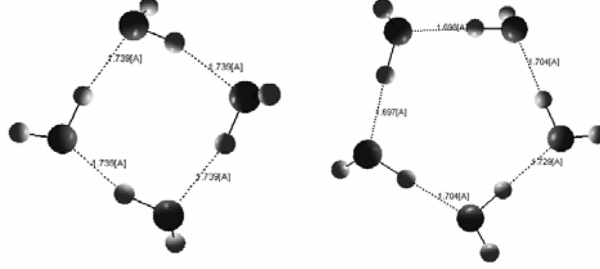
Fig.1 Water tetramer (left) and pentamer (right) initial geometry (global miminum of potential TIP5P energies: U_0=-1.233 eV for tetramer and U_0=-1.653 eV for pentamer).

For Hamilton equations numerical integration the next parameters of trajectories were chosen: the integration step h was equal to 1 fs, observed time interval $t_0 = 2-5$ ns. The Verlet algorithm provided with the accuracy of the integration in the third sing in the value of the total energy. The values of all parameters presented in this work were obtained by averaging on 10 trajectories for each initial excitation energy E_0 of the cluster.

Quasi-states of cluster of two types (A, B) of atoms usually can be determined using Lindemann parameter that calculated as:

$$\delta(AB) = \frac{2}{N_{AB}(N_{AB}-1)}\sum_{i<j}^{N_{AB}}\frac{\sqrt{\langle r_{ij}^2\rangle - \langle r_{ij}\rangle^2}}{\langle r_{ij}\rangle} , \qquad (3)$$

Where N_{AB} - number of pairs of atoms of types A and B, r_{ij} - distance between them. Solid-liquide states boundary of cluster usually determined by criteria ($\delta > 0.1$) and placed in Fig. 2 for both clusters.
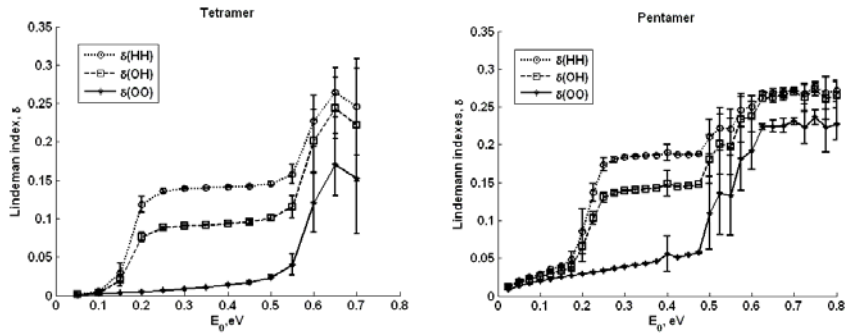

Fig.2 Lindemann' indexes for water tetramer (left) and for water pentamer (right) in dependence of excitation energy E_0.

Lindemann' parameter usually works well in systems like rare-gases clusters when isotropic types of interactions between all particles are present only. In particles with weak anisotropic bonds like water clusters that parameter doesn't fully describe liquid-solid phase transition of cluster. Analysis of parameter (3) in application for water clusters (parameters $\delta(OO), \delta(OH), \delta(HH)$ for different types of atoms) can bring typically four energy regions of cluster' states:

- Solid-like state of cluster ($\delta < 0.1$); $E_0 < 0.15$ eV for tetramer and $E_0 < 0.2$ eV for pentamer. Only small vibrations of all atoms are presented.

- 'Pre-melting' state of cluster ($\delta > 0.1$); $0.15 < E_0 < 0.5$ eV for tetramer and $0.2 < E_0 < 0.5$ eV for pentamer; There is only hydrogen atoms' activity are observed but oxygen atoms (water molecules as whole) construct stationary (with lifetime $\tau > 1$ ps) spatial structures (structural isomers).

- Liquid-like state (characterized by strong growth of δ); $0.5 < E_0 < 0.6$ eV for tetramer and $0.5 < E_0 < 0.65$ eV for pentamer; There is no stationary spatial structures and active isomerization of cluster are performed; fast breaks and creation of hydrogen bonds ($\tau \leq 1$ ps) are viewed.

- Monomolecular fragmentation (characterized by stabilization of δ); $E_0 > 0.6$ eV for tetramer and $E_0 > 0.65$ eV for pentamer.
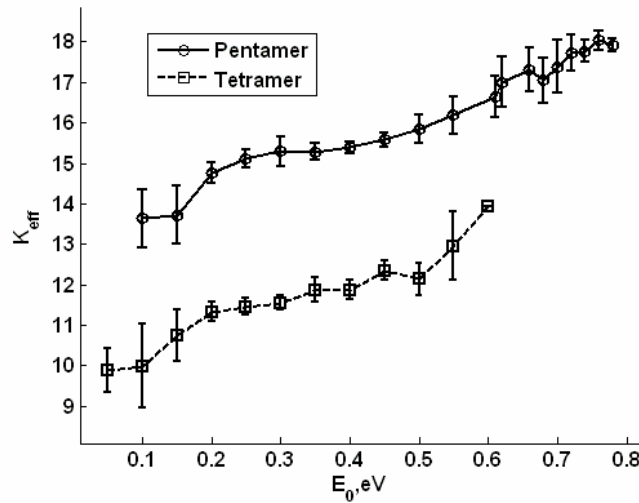

Fig.3. Effective dimensions of momentum subspace of phase spaces of water tetramer and pentamer) in dependence of excitation energy E_0.

Lindemann' parameter estimates particles activity in a general way and doesn't divide types of motions. Effective dimension of momentum phase space K_{eff} of water clusters is placed in Fig.3. Dependence K_{eff} from E_0 also can help understand dynamics activity in every quasi-phase. On the example of pentamer K_{eff} has values 13-14 in solid-like phase, stable (~15) in pre-melting state and going up to 17-18 in fragmentation region. It is interesting that in region E_0=0.3-0.4 eV value K_{eff} starts to growth due to Lindemann' index in that region have a plateau. Such behavior can be explained by faster cluster structure isomerization and motion of cluster became non-planar. For tetramer that region gives E_0=0.25-0.35eV. At energies lower that threshold there is only hydrogen atoms' activity are observed but water molecules as whole construct stationary planar structural isomers with seldom transitions ($\tau \gg 1$ ps). Collective motion of oxygen atoms performs mostly in plane. At higher energies nonplanar structures of cluster can be created sometimes so the effective dimension K_{eff} of phase space starts to growth again.

Other application of parameter K_{eff} is correction of micro canonical temperature of cluster. As it is seen in Fig.4 temperature T_{eff} calculated by formula (2) using K_{eff} as parameter has values above ~100K higher than standard one T in all ranges of energies. Someone can conclude from Fig.4 that mean kinetic energy by effective directions in the phase space (like number of freedom) has not equipartition distribution for small water clusters.
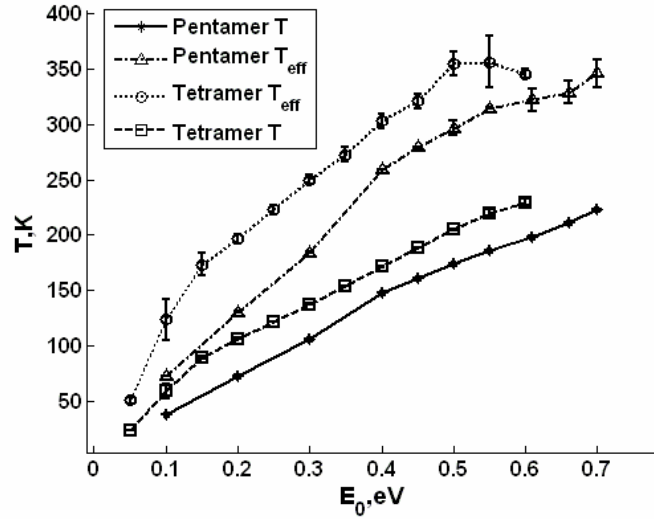

Fig.4. Temperatures of water tetramer and pentamer in dependence of excitation energy E_0 using standard approach (2) with number of freedom K_{df} (T-curves) and effective dimension of momentum phase space K_{eff} (T_{eff}-curves) as parameter.

4. Conclusions

Method of main components for collective motion analysis of weakly bonded molecular systems is presented in paper. Collective modes for water tetramer and pentamer have shown that mean kinetic energy has not equipartition distribution by different types of motion. Method of main components can help to determine number of active modes at any energy of cluster. Growing up excitation energy gradual modes activation is performed and redistribution of kinetic energy by modes is viewed. Using effective dimension of the momentum phase space together with Lindemann' parameter brings more rich information about phase quasi-states of cluster and detects isomerization and fragmentation thresholds. Method of main components can be easily adapted to other molecular systems.

References

1. Belega E. D., Rybakov A. A.,. Trubnikov D. N, Chulichkov. Effective Dimension of a Phase Trajectory in the Visualization of Dynamical Systems. // A. I. Comp. Math. and Math. Phys. V.42. 2002. P.1817-1823.
2. M.W. Mahoney, W.L. Jorgensen. A five-site model for liquid water and the reproduction of the density anomaly by rigid, nonpolarizable potential functions. // J. Chem. Phys. V.112. 2000. P.8910-8922.

Belega Elena (edbelega@gmail.com)
Eugene Cheremukhin (eacherem@gmail.com)
Dmitry Trubnikov (tdn@phys.chem.msu.ru)

Chemical Department,
M.V.Lomonosov Moscow State University,
Vorobyevy Gory, b.1,
119991, Moscow, Russia