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Molecular dynamics simulation of vibrational energy relaxation of highly excited molecules in fluids. I. General considerations

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Methods of implementation of classical molecular dynamics simulations of moderate size molecule vibrational energy relaxation and analysis of their results are proposed. Two different approaches are considered. The first is concerned with modeling a real nonequilibrium cooling process for the excited molecule in a solvent initially at equilibrium. In addition to the solute total, kinetic, and potential energy evolution, that define the character of the process and the rate constant or relaxation time, a great deal of important information is provided by a normal mode specific analysis of the process. Expressions for the decay of the normal mode energies, the work done by particular modes, and the vibration–rotation interaction are presented. The second approach is based on a simulation of a solute–solvent system under equilibrium conditions. In the framework of linear nonequilibrium statistical thermodynamics and normal mode representation of the solute several expressions for the rate constant are derived. In initial form, they are represented by integrals of the time correlation functions of the capacities of the solute–solvent interaction atomic or normal mode forces and include the solute heat capacity. After some approximations, which are adequate for specific cases, these expressions are transformed to combinations of those for individual oscillators with force–force time correlation functions. As an attempt to consider a strongly nonequilibrium situation we consider a two-temperature model and discuss the reason why the rate constant can be independent on the solute energy or temperature. Expressions for investigation of the energy redistribution in the solvent are derived in two forms. One of them is given in the usual form of a heat transfer equation with the source term describing the energy flux from the excited solute. The other form describes the energy redistribution in the solvent in terms of capacity time correlation functions and can be more convenient if memory effects and spatial dispersion play an important role in energy redistribution in the solvent. © *1999 American Institute of Physics.* [S0021-9606(99)51211-7]

I. INTRODUCTION

Vibrational energy relaxation (VER) of highly excited molecules is a fundamental process involved in many chemical reactions in the gas and liquid phase. Therefore, great experimental and theoretical effort has been expended over the last decades to get a quantitative understanding about the energy flux from a vibrationally excited solute to a bath gas or solvent.[1–16] If the solute is a diatomic molecule excited below the dissociation threshold VER is the main mechanism for transferring energy from an individual mode to the bath. In larger molecules intramolecular vibrational energy redistribution (IVR) to other solute modes can compete with energy transfer. For vibrationally highly excited ($>10\,000$ cm^{-1}) polyatomic molecules containing several tens of atoms, IVR is believed to be sufficiently fast[17–21] such that during collisional deactivation the energy is well equilibrated among the vibrational modes of the solute.

Nevertheless, one may expect that the contribution to the overall energy transfer of the solute varies from mode to mode as suggested by simple theoretical considerations. This is confirmed by numerous classical trajectory calculations[10,11] as well as molecular dynamics (MD) simulations,[16] which show that the efficiency of energy transfer is enhanced by the presence of low-frequency vibrational modes in the solute. So far, however, these trajectory calculations were only analyzed in terms of step size distribution functions $P(E',E)$ that define the probability that a solute with initial energy E after a collision has the energy E'. The contribution of individual modes to the energy transfer was not analyzed. One motivation behind this work is to develop a formalism that on the basis of normal mode analysis extracts mode specific information of VER from MD simulations. First results on the system azulene $(C_{10}H_8)$–CO_2 have been reported elsewhere.[21]

After Zwanzig[22] introduced force time correlation functions to describe VER in liquids, a great variety of different approaches have been developed[23,24] (see also the introduction in Ref. 25 for a short review of recent papers) and used to calculate VER rates of diatomic molecules in liquids,[25–30] in satisfactory agreement with experimental data. It has been shown[31] that for a harmonic oscillator bilinearly coupled to a harmonic bath classical and quantum mechanical approaches yield equivalent results for VER rates. Also, for more realistic models[32,33] the classical description of VER provides a reasonable representation of a quantum mechanical system,

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suggesting that VER rates for a quantum mechanical system can be obtained from classical MD simulations. Examples of quantitative agreement between classical and quantum mechanical computations of IVR in polyatomics are available,[34,35] too. However, similar classical considerations do not have to be necessarily true for VER of bigger molecules like azulene. Here, e.g., dependent on whether it is treated classically or quantum mechanically, the presence of low- and high-frequency modes leads to different energy distributions among the modes of the molecule that might alter the energy transfer mechanism. Also, zero-point energy is not known to be exactly handled by classical simulations. Nevertheless, reasonable agreement between experimental[12] and calculated[16,21] VER rates from classical MD simulations of azulene in low- and high-density CO_2 suggest that these deficiencies are of minor importance.

In principle, there are two different ways to investigate VER by means of MD simulations. One can model the non-equilibrium energy transfer process from an energetically excited solute to the solvent, or the simulation is performed with solute and solvent being in equilibrium. The latter method yields certain time correlation functions which contain information about the corresponding nonequilibrium VER process. Both techniques have been applied to a single oscillator in a bath and were shown to give nearly equivalent results if the oscillator frequency is relatively low.[27] In this paper we present methods to extract mode specific information on VER from both types of MD simulations of bigger molecules.

Furthermore, we want to address the question of energy transfer from solute to solvent by vibration–rotation interaction. For small molecules this deactivation channel can be of great importance.[17,23,36–41] Rotational energy transfer was studied in trajectory simulations[10,11] for moderate size molecules, and it is of interest to investigate the role of vibration–rotation interaction in energy transfer of such molecules in dense fluid solvents.

Finally, we investigate the behavior of the solvent in the vicinity of the solute during the energy transfer process. Instantaneous normal mode analysis[28–30] provides important information about equilibrium and dynamical properties of a solute–solvent system. However, for moderate size solutes this method encounters many technical difficulties up to now. There are a few examples[6,12] where the phenomenological heat conduction equation was used to describe the energy redistribution in the solvent. However, from experimental data[12,14] and MD simulations[16] it was shown that there is no substantial heating of the solvent around the excited solute. This observation suggests that the heat conductivity of the solvent is quite efficient, making the solvent–solute energy exchange the rate limiting step in VER. Nevertheless, a strongly nonequilibrium liquid state is maintained in the nearest vicinity of the solute during VER, which can be used to check and improve modern statistical–mechanical theories of strongly nonequilibrium processes with memory and spatial dispersion.[42–44]

The paper is organized as follows. Expressions for analyzing nonequilibrium MD simulations on VER in terms of mode specificity and vibration–rotation interaction are derived in the next section. These expressions are also used as a starting point in the third section devoted to a statistical–mechanical description of the solute–solvent system. We present a formalism to calculate relaxation times and extract mode specific information from equilibrium time correlation functions (TCF) of appropriate capacities and forces. Expressions for analyzing energy redistribution in the solvent are presented as well. The paper is finished by some concluding remarks.

II. NONEQUILIBRIUM COMPUTER SIMULATION OF VIBRATIONAL ENERGY RELAXATION

Usually experimental studies on collisional deactivation of polyatomic molecules are carried out at a very small concentration of excited molecules in a solvent. Hence, for MD simulations of these processes, a model system can be considered as containing a single solute molecule surrounded by solvent molecules. The system should be treated as a statistical mechanical ensemble, i.e., results appear as mean values of certain quantities over numerous realizations of the process, in accordance with the conditions of the ensemble chosen. For many characteristics under investigation, the type of ensemble is not important and usually an equilibrium or nonequilibrium microcanonical ensemble is used in MD simulations, whereas canonical or grand canonical ensembles are more suitable for theoretical considerations.

The interpretation of MD simulations requires specification of a set of dynamical quantities that can shed light on the process under investigation. Vibrational energy and its time derivative are the most important original characteristics of VER. Their calculation in the framework of the dynamical model described below is considered in the present section.

A. Description of the dynamical model

Let us consider the standard representation of the energy of the system under investigation as a sum of two components:

$$E = E_1 + E_2, \tag{2.1}$$

where E_1 and E_2 are the energy of the solute and solvent molecules, respectively, given by

$$E_1 = \frac{1}{2}\sum_{i=1}^{n_s} m_i \dot{\mathbf{g}}_i^2 + U_{\text{intra}}(\mathbf{g}_1,\dots,\mathbf{g}_{n_s}), \quad E_2 = \sum_{m=1}^{N} E_m, \tag{2.2}$$

$$E_m = \sum_{p=1}^{n_v} \left(\frac{1}{2} m_{mp}\dot{\mathbf{q}}_{mp}^2 + \sum_{i=1}^{n_s} \Phi_{(mp)i} + \sum_{n=1}^{N}\sum_{q=1}^{n_v} \Phi_{(mp)(nq)} \right)$$
$$+ U_{m\text{intra}}(\mathbf{q}_{m1},\dots,\mathbf{q}_{mn_v}). \tag{2.3}$$

All vectors are defined in the inertial laboratory frame. n_s and n_v are the number of atoms per solute and solvent molecule, respectively. The second and third terms on the right-hand side (rhs) of Eq. (2.3) take into account the solvent–solute $\Phi_{(mp)i}$ and solvent–solvent $\Phi_{(mp)(nq)}$ interaction by using atom–atom potentials. The last contribution represents the solvent intramolecular potential energy. Indices m,n are attributed to the solvent molecules; p and q de-

note atoms of solvent molecules, and i designates the solute atoms. $\mathbf{q}_{mp}$ is the position vector of atom p of the mth solvent molecule; $\mathbf{g}_i$ indicates the position of the ith solute atom.

The intramolecular energy can be represented in terms of stretches, bends, dihedrals, improper torsions, etc.,[45] and is not equal to a sum of pairwise interaction potentials. The energy of the solute–solvent interaction is completely assigned to the solvent part of the system energy because the main point of interest is the evolution of the solute energy.

Forces between different molecules are defined by spatial derivatives of the atom–atom potentials,

$$\mathbf{F}_{i(mp)} = -\mathbf{F}_{(mp)i} = -\frac{\partial \Phi_{i(mp)}}{\partial \mathbf{g}_i},$$

$$\mathbf{F}_{(mp)(nq)} = -\mathbf{F}_{(nq)(mp)} = -\frac{\partial \Phi_{(nq)(mp)}}{\partial \mathbf{q}_{mp}}, \quad n \neq m. \tag{2.4}$$

The force that acts on the ith solute atom from the mth solvent molecule and intermolecular solvent–solvent interaction forces are equal to the sum of the corresponding atom–atom forces,

$$\mathbf{F}_{im} = \sum_{p=1}^{n_v} \mathbf{F}_{i(mp)}, \quad \mathbf{F}_{mn} = \sum_{q=1}^{n_v} \sum_{p=1}^{n_v} \mathbf{F}_{(mp)(nq)}. \tag{2.5}$$

Due to many-body interactions intramolecular forces cannot be represented by sums of two-body interactions. In the following they are marked by superscript (i):

$$\mathbf{F}_i^{(i)} = -\frac{\partial U_{\text{intra}}}{\partial \mathbf{g}_i}, \quad \mathbf{F}_{mp}^{(i)} = -\frac{\partial U_{m\text{intra}}}{\partial \mathbf{q}_{mp}}. \tag{2.6}$$

The total external force $\mathbf{R}^{(e)}$ and the external torque $\mathbf{M}_C^{(e)}$ about the solute center of mass C are defined by external forces $\mathbf{F}_i^{(e)}$ on the solute atoms,

$$\mathbf{R}^{(e)} = \sum_{i=1}^{n_s} \mathbf{F}_i^{(e)}, \quad \mathbf{M}_C^{(e)} = \sum_{i=1}^{n_s} \mathbf{g}_{iC} \times \mathbf{F}_i^{(e)}, \quad \mathbf{F}_i^{(e)} = \sum_{m=1}^{N} \mathbf{F}_{im}. \tag{2.7}$$

B. Description of vibration–rotation interaction

Since the behavior of the vibrational degrees of freedom of the solute can be rather different from the dynamics of its translational and rotational motion,[37,40] it is necessary to separate their contribution from E_1.

According to the Eckart–Sayvetz[46–48] conditions, one should introduce a solute coordinate system defined by the equations

$$\sum_{i=1}^{n_S} m_i \mathbf{g}_{iC} = 0, \tag{2.8}$$

$$\sum_{i=1}^{n_S} m_i \mathbf{a}_i \times \Delta \mathbf{g}_{iC} = 0, \quad \Delta \mathbf{g}_{iC} = \mathbf{g}_{iC} - \mathbf{a}_i, \tag{2.9}$$

$$\mathbf{g}_{iC} = \mathbf{g}_i - \mathbf{g}_C, \quad \mathbf{g}_C = \frac{1}{M} \sum_{i=1}^{n_S} m_i \mathbf{g}_i, \quad M = \sum_{i=1}^{n_S} m_i. \tag{2.10}$$

Here $\mathbf{g}_C$ defines the position of the solute center of mass C, m_i and $\mathbf{g}_{iC}$ are the mass and the position of the nucleus i in the center of mass coordinate system, $\mathbf{a}_i$ defines the equilibrium position of the ith nucleus. The orientation of the Eckart frame necessary for calculating the equilibrium positions $\mathbf{a}_i$ of the nuclei and their displacements $\Delta \mathbf{g}_{iC}$ is defined[41,46] via instantaneous nuclei configuration $\mathbf{g}_{iC}$ according to Eq. (2.9) by introducing Eckart vectors.[46]

The second Eckart–Sayvertz condition [Eq. (2.9)] is linear in displacements of the solute nuclei $\mathbf{g}_{iC}$ from their equilibrium positions and so is most appropriate for a normal mode analysis. The time derivative of Eq. (2.9) in the Eckart frame leads to the expression

$$\sum_{i=1}^{n_S} m_i \mathbf{a}_i \times \mathbf{u}_i = 0, \tag{2.11}$$

which shows that the motion in the Eckart frame possesses nonzero angular momentum because $\mathbf{a}_i$ define equilibrium nuclei positions and $\mathbf{u}_i$ are nuclei velocities in the Eckart frame.

Decomposition of the ith nucleus velocity into translational, rotational, and vibrational contributions results in

$$\mathbf{v}_i = \dot{\mathbf{g}}_i = \mathbf{v}_C + \boldsymbol{\omega} \times \mathbf{g}_{iC} + \mathbf{u}_i, \quad \mathbf{v}_C = \dot{\mathbf{g}}_C, \tag{2.12}$$

$$\boldsymbol{\omega} = \mathbf{I}_l^{-1} \cdot \sum_{i=1}^{n_S} m_i \mathbf{a}_i \times \mathbf{v}_{iC}, \quad \mathbf{v}_{iC} = \dot{\mathbf{g}}_{iC} = \mathbf{v}_i - \mathbf{v}_C, \tag{2.13}$$

$$\mathbf{I}_l = \mathbf{I}_0 + \Delta \mathbf{I}_l, \quad \mathbf{I}_0 = \sum_{i=1}^{n_S} m_i (a_i^2 \mathbf{E} - \mathbf{a}_i \mathbf{a}_i),$$

$$\Delta \mathbf{I}_l = \sum_{i=1}^{n_S} m_i [\mathbf{a}_i \cdot \Delta \mathbf{g}_{iC} \mathbf{E} - (\tfrac{1}{2})(\mathbf{a}_i \Delta \mathbf{g}_{iC} + \Delta \mathbf{g}_{iC} \mathbf{a}_i)], \tag{2.14}$$

where $\mathbf{v}_C$, $\mathbf{u}_i$, and $\boldsymbol{\omega}$ are the center of mass and the vibrational nucleus velocities, and the angular velocity of the Eckart frame, respectively. $\mathbf{E}$ is the unit matrix; $\mathbf{I}_0$ is the moments of inertia matrix for the equilibrium solute configuration. Definitions of matrices $\mathbf{I}_l$ and $\Delta \mathbf{I}_l$ in Eq. (2.14) follow from the sum entering Eq. (2.13), in combination with Eqs. (2.12) and (2.11).

A different definition of a solute frame corresponds to the principle axes of an instantaneous configuration[41,46,49] of the molecule. The angular momentum due to vibrational velocities $\mathbf{u}_i'$ in this frame [they are defined by an equation identical to Eq. (2.12) with $\boldsymbol{\omega}'$ and $\mathbf{u}'$ instead of $\boldsymbol{\omega}$ and $\mathbf{u}$] is equal to zero,

$$\sum_{i=1}^{n_S} m_i \mathbf{g}_{iC} \times \mathbf{u}_i' = 0, \tag{2.15}$$

and the angular velocity of the principle axes frame can be calculated easily as

$$\boldsymbol{\omega}' = \mathbf{I}^{-1} \cdot \sum_{i=1}^{n_S} m_i \mathbf{g}_{iC} \times \mathbf{v}_{iC}. \tag{2.16}$$

Here the matrix of instantaneous moments of inertia,

$$\mathbf{I} = \sum_{i=1}^{n_S} m_i (\mathbf{g}_{iC} \cdot \mathbf{g}_{iC} \mathbf{E} - \mathbf{g}_{iC} \mathbf{g}_{iC}), \tag{2.17}$$

differs in second order in displacements from moments of inertia I_l in the Eckart frame.

The angular momentum of the solute about its center of mass,

$$\mathbf{L}_C = \mathbf{I} \cdot \boldsymbol{\omega}', \tag{2.18}$$

obeys the simple equation of motion,[50]

$$\dot{\mathbf{L}}_C = \mathbf{M}_C^{(e)}. \tag{2.19}$$

Such a simple expression does not exist for $\mathbf{I} \cdot \boldsymbol{\omega}$.

With account of the velocity decomposition (2.12) and Eqs. (2.9)–(2.11), the solute energy (2.2) is presented as a sum of translational, rotational, and vibrational contributions,

$$E_1 = E_{1\,\mathrm{tr}} + E_{1\,\mathrm{rot}} + E_{1\,\mathrm{vibr}}, \tag{2.20}$$

$$E_{1\,\mathrm{tr}} = \frac{1}{2} M \mathbf{v}_C^2, \quad E_{1\,\mathrm{vibr}} = \frac{1}{2} \sum_{i=1}^{n_S} m_i \mathbf{u}_i^2 + U_{\mathrm{intra}}(\mathbf{g}_1, \ldots, \mathbf{g}_{n_s}), \tag{2.21}$$

$$E_{1\,\mathrm{rot}} = \frac{1}{2} \boldsymbol{\omega}' \cdot \mathbf{I} \cdot \boldsymbol{\omega}' + \frac{\boldsymbol{\omega} + \boldsymbol{\omega}'}{2} \cdot \mathbf{I} \cdot \Delta \boldsymbol{\omega} + \boldsymbol{\omega} \cdot \mathbf{L}_{\mathrm{vibr}},$$

$$\Delta \boldsymbol{\omega} = \boldsymbol{\omega} - \boldsymbol{\omega}', \tag{2.22}$$

$$\mathbf{L}_{\mathrm{vibr}} = \sum_{i=1}^{n_S} \mathbf{g}_{iC} \times m_i \mathbf{u}_i = \sum_{i=1}^{n_S} \Delta \mathbf{g}_{iC} \times m_i \mathbf{u}_i. \tag{2.23}$$

Hear the angular momentum $\mathbf{L}_{\mathrm{vibr}}$ of the vibrational motion in the Eckart frame is introduced. For the same reason as discussed after Eq. (2.3), the last term of Eq. (2.23), which includes the vibrational velocities, is related to the rotational part of the solute energy. To facilitate further differentiation of the solute energy with respect to time, Eq. (2.22) is written in such a way that its first term is expressed in terms of $\boldsymbol{\omega}'$ rather than $\boldsymbol{\omega}$.

After the time derivative of Eq. (2.20) with account of Eqs. (2.21)–(2.23) and (2.19) is evaluated, the result can easily be specified into several contributions:

$$\dot{E}_{1\,\mathrm{tr}} = \mathbf{R}^{(e)} \cdot \mathbf{v}_C, \quad \dot{E}_{1\,\mathrm{rot}} = \mathbf{M}_C^{(e)} \cdot \boldsymbol{\omega} + N_{\mathrm{v-r}}, \tag{2.24}$$

$$\dot{E}_{1\,\mathrm{vibr}} = \sum_{i=1}^{n} \mathbf{F}_i^{(e)} \cdot \mathbf{u}_i - N_{\mathrm{v-r}}, \tag{2.25}$$

where the whole capacity of vibration–rotation coupling is given as a sum over four terms:

$$N_{\mathrm{v-r}} = N_{1\mathrm{v-r}} + N_{2\mathrm{v-r}} + N_{3\mathrm{v-r}} + N_{4\mathrm{v-r}}, \tag{2.26}$$

which represent four different channels of the vibration–rotation interaction:

$$N_{1\mathrm{v-r}} = -(\tfrac{1}{2}) \boldsymbol{\omega}' \cdot \dot{\mathbf{I}} \cdot \boldsymbol{\omega}', \tag{2.27}$$

$$N_{2\mathrm{v-r}} = \frac{d}{dt} \left(\frac{\boldsymbol{\omega} + \boldsymbol{\omega}'}{2} \cdot \mathbf{I} \cdot \Delta \boldsymbol{\omega} \right), \tag{2.28}$$

$$N_{3\mathrm{v-r}} = \frac{d}{dt} (\boldsymbol{\omega} \cdot \mathbf{L}_{\mathrm{vibr}}), \tag{2.29}$$

$$N_{4\mathrm{v-r}} = -\mathbf{M}_C^{(e)} \cdot \Delta \boldsymbol{\omega}, \tag{2.30}$$

and $\dot{\mathbf{I}}$ designates the part of the time derivative of the matrix of moments of inertia that is not connected with the principle axes rotational motion of the solute,

$$\dot{\mathbf{I}} = \sum_{i=1}^{n_S} m_i [2 \mathbf{g}_{iC} \cdot \mathbf{u}_i' \mathbf{E} - (\mathbf{g}_{iC} \mathbf{u}_i' + \mathbf{u}_i' \mathbf{g}_{iC})], \tag{2.31}$$

The first channel is connected to variations in the instantaneous moments of inertia, the second comes from the difference between the angular velocities of the Eckart and the principle axes frames, the third channel is caused straightforwardly by the vibrational velocities, and the last one is attributed to the external forces. It is hardly to be expected that the interaction terms could be estimated analytically, even for moderate size molecules. But the derived equations (2.27)–(2.30) can be used directly in MD simulations.

For the alternative definition of the solute frame, using principle axes, $\mathbf{u}$ has to be replaced by $\mathbf{u}'$ in Eq. (2.21), and only the first term in Eq. (2.22) remains. Therefore, in the time derivative of the rotational energy only a single rotation–vibration interaction term defined by Eq. (2.27) survives. Of course, this does not mean that the translation–rotation coupling is weaker in the latter treatment. Straightforward trajectory calculations[41] for isolated three-atomic molecules have shown that usually the coupling is weaker for the Eckart frame.

C. The normal mode analysis of solute vibrations

Now we proceed to analyze Eq. (2.21) for the solute vibrational energy. After introduction of mass-weighted coordinates and velocities,[48]

$$\bar{\mathbf{g}}_i = \sqrt{m_i} \Delta \mathbf{g}_i, \quad \bar{\mathbf{u}}_i = \sqrt{m_i} \mathbf{u}_i, \tag{2.32}$$

and considering the harmonic part of the solute intramolecular energy one can define the respective part of the solute energy as follows:

$$E_1^{\mathrm{harm}} = \frac{1}{2} \sum_{i=1}^{n} \bar{\mathbf{u}}_i \cdot \bar{\mathbf{u}}_i + \frac{1}{2} \sum_{i,j=1}^{n_S} \bar{\mathbf{g}}_i \cdot \mathbf{C}_{ij} \cdot \bar{\mathbf{g}}_j,$$

$$\mathbf{C}_{ij} = \frac{1}{\sqrt{m_i m_j}} \left(\frac{\partial^2 U_{\mathrm{intra}}}{\partial \mathbf{g}_i \, \partial \mathbf{g}_j} \right)_0. \tag{2.33}$$

Subscript 0 indicates that matrix $\mathbf{C}_{ij}$ is calculated at the solute equilibrium configuration.

Let $\mathbf{P}_{j\beta}$ be the orthogonal normalized eigenvector matrix that diagonalizes the mass-weighted force constant matrix $\mathbf{C}_{ij}$,

$$\sum_{i,j=1}^{n_S} \mathbf{P}_{\alpha i}^t \cdot \mathbf{C}_{ij} \cdot \mathbf{P}_{j\beta} = \omega_\alpha^2 \delta_{\alpha\beta}, \tag{2.34}$$

where ω_α is the frequency of the solute αth vibrational mode and $\delta_{\alpha\beta}$ is the Kronecker δ symbol. Then the connection between Cartesian displacements and vibrational velocities of solute nuclei and solute normal coordinates q_α and velocities $\dot{q}_\alpha$ takes the form

$$q_\alpha = \sum_{i=1}^{n_S} \mathbf{P}_{\alpha i}^t \cdot \sqrt{m_i} \Delta \mathbf{g}_i, \quad \dot{q}_\alpha = \sum_{i=1}^{n_S} \mathbf{P}_{\alpha i}^t \cdot \sqrt{m_i} \mathbf{u}_i; \tag{2.35}$$

$$\Delta \mathbf{g}_i = \frac{1}{\sqrt{m_i}} \sum_{\alpha=1}^{3n_S-6} \mathbf{P}_{i\alpha} q_\alpha, \quad \mathbf{u}_i = \frac{1}{\sqrt{m_i}} \sum_{\alpha=1}^{3n_S-6} \mathbf{P}_{i\alpha} \dot{q}_\alpha. \quad (2.36)$$

Summation in the last two expressions is carried out over all the solute vibrational degrees of freedom. Superscript t marks the transposed matrix. By introducing the normal forces,

$$Q_\alpha = \sum_{i=1}^{n_S} \mathbf{F}_i^{(e)} \cdot \frac{1}{\sqrt{m_i}} \mathbf{P}_{i\alpha} = \sum_{i=1}^{n_S} \mathbf{P}_{\alpha i}^t \cdot \frac{1}{\sqrt{m_i}} \mathbf{F}_i^{(e)}, \quad (2.37)$$

the capacity of interaction of the solute vibrational subsystem with the solvent brakes up into $3n_s-6$ (in accordance with the number of vibrational degrees of freedom) terms,

$$N_{\text{vibr}} = \sum_{i=1}^{n_S} \mathbf{F}_i^{(e)} \cdot \mathbf{u}_i = \sum_{\alpha=1}^{3n_S-6} Q_\alpha \dot{q}_\alpha. \quad (2.38)$$

Each of the terms in Eq. (2.38) describes the main part of the energy exchange between the corresponding solute normal mode and the solvent.

In general, the force on the ith solute nucleus can be divided into external $\mathbf{F}_i^{(e)}$ and internal $\mathbf{F}_i^{(i)}$ parts,

$$\mathbf{F}_i = \mathbf{F}_i^{(e)} + \mathbf{F}_i^{(i)}, \quad \mathbf{F}_i^{(i)} = -\partial U_{\text{intra}}/\partial \mathbf{g}_i. \quad (2.39)$$

The capacity of the internal forces,

$$N_{\text{intra}} = \sum_{i=1}^{n_S} \mathbf{F}_i^{(i)} \cdot \mathbf{u}_i = \sum_{\alpha=1}^{3n_S-6} Q_\alpha^{(i)} \dot{q}_\alpha, \quad (2.40)$$

determines the intramolecular energy redistribution. Each term of the sum describes the part of energy flux to a particular vibrational mode α from the other modes caused by the nonlinearity of the intramolecular potential. This is considered in some detail in the Appendix.

We note that the representation of capacities via normal velocities and normal forces is *exact*, irrespective of the accuracy of the harmonic approximation for the intramolecular motion. The orthogonal transformation of the bilinear forms of forces and velocities in Eqs. (2.35) and (2.37) by an orthogonal matrix is identical. The interpretation of the results, however, strongly depends on the validity of the underlying harmonic approximation.

III. STATISTICAL–MECHANICAL DESCRIPTION OF VIBRATIONAL ENERGY RELAXATION

Highly excited molecules possessing many vibrational degrees of freedom have a rather high kinetic temperature (determined as the average kinetic energy per vibrational degree of freedom) as compared with the ambient solvent. Hence, the state of the system is highly nonequilibrium and, in general, linear nonequilibrium statistical theory may not be used to describe the relaxation process. However, the experimental results unambiguously indicate[12,13] that in many cases the process is characterized by a single relaxation time and the rate of solute–solvent energy exchange remains proportional to the excess energy during the whole process. Thus, it seems reasonable to determine the relaxation time by considering a slightly nonequilibrium system that can be de-

scribed in the linear approximation. The results of such a linear statistical–mechanical description in terms of equilibrium time correlation functions of the corresponding quantities could be used to study different aspects of the relaxation process by MD simulations of equilibrium systems.

Subsequently, one can try to answer the question to why this linear treatment is applicable to the description of highly nonequilibrium systems and under what conditions a nonexponential decay behavior can be expected.

A. Relevant variables and their time evolution

The main quantities of interest in the study of VER are the energies of the solute vibrational degrees of freedom, its translation and rotation, and of the solvent. We make a starting assumption that the nonequilibrium mean values of these quantities describe the nonequilibrium macroscopic state of the system under consideration sufficiently well, at least with respect to VER, and they will be considered as relevant variables. This assumption is supported by fairly good agreement between our results of nonequilibrium[16,21,52] and equilibrium[53] MD simulations of the azulene–CO_2 system at low and high pressure. For a statistical–mechanical calculation of kinetic coefficients like rate constant time derivatives of the relevant variables are necessary.

In accordance with the preceding section we introduce the microscopic energy density $\hat{H}(\mathbf{r})$ as a sum of three components:

$$\hat{H}(\mathbf{r}) = \hat{H}_{1\,\text{vibr}}(\mathbf{r}) + \hat{H}_{1\,\text{rt}}(\mathbf{r}) + \hat{H}_2(\mathbf{r}), \quad (3.1)$$

where the energy density of the solute molecule is attributed to its center of mass location $\mathbf{g}$,

$$\hat{H}_{1\,\text{vibr}} = E_{1\,\text{vibr}} \delta(\mathbf{r}-\mathbf{g}), \quad (3.2)$$

$$\hat{H}_{1\,\text{rt}} = E_{1\,\text{rt}} \delta(\mathbf{r}-\mathbf{g}), \quad E_{1\,\text{rt}} = E_{1\,\text{rot}} + E_{1\,\text{tr}}, \quad (3.3)$$

and the energy density of solvent molecules is ascribed to their center of mass positions $\mathbf{q}_m$,

$$\hat{H}_2 = \sum_{m=1}^{N} E_m \delta(\mathbf{r}-\mathbf{q}_m). \quad (3.4)$$

$\delta(\mathbf{r}-\mathbf{q}_m)$ is the Dirac's δ function.

As suggested in Refs. 37 and 40 the solute rotational and translational degrees of freedom are not included in the solvent subsystem because one of the aims of our consideration is the investigation of the role these degrees of freedom play in the energy transfer from solute to solvent during vibrational energy relaxation.

When the equations of motion of the solvent and solute atoms,

$$m_i \ddot{\mathbf{g}}_i = \mathbf{F}_i^{(i)} + \sum_{m=1}^{N} \mathbf{F}_{im}, \quad (3.5)$$

$$m_{mp} \ddot{\mathbf{q}}_{mp} = \mathbf{F}_{mp}^{(i)} + \sum_{\substack{n=1 \\ n\neq m}}^{N} \mathbf{F}_{(mp)n} + \sum_{i=1}^{n_S} \mathbf{F}_{(mp)i}, \quad (3.6)$$

$$\mathbf{F}_{(mp)n} = \sum_{q=1}^{n_V} \mathbf{F}_{(mp)(nq)},$$

are taken into account, one obtains the time derivatives of the energy densities as

$$\dot{H}_k(\mathbf{r}) = I_k(\mathbf{r}) + \mathbf{\nabla_r} \cdot \mathbf{J}_k(\mathbf{r}) \equiv \hat{B}_k(\mathbf{r}), \quad k = 1\,\text{vibr}, \ 1\,\text{rt}, \ 2, \tag{3.7}$$

where $\hat{B}_k(\mathbf{r})$ are microscopic fluxes of the relevant variables.

The rhs of Eqs. (3.7) consists of source/sink terms,

$$I_{1\,\text{vibr}}(\mathbf{r}) = (N_{\text{vibr}} - N_{\text{v}-\text{r}}) \delta(\mathbf{r} - \mathbf{g}), \tag{3.8}$$

$$I_{\text{rt}}(\mathbf{r}) = (\mathbf{R}^{(e)} \cdot \mathbf{v}_C + \mathbf{M}_C^{(e)} \cdot \boldsymbol{\omega} + N_{\text{v}-\text{r}}) \delta(\mathbf{r} - \mathbf{g}), \tag{3.9}$$

$$I_2(\mathbf{r}) = -\sum_{m=1}^{N} \left(\mathbf{v}_C \cdot \sum_{i=1}^{n_S} \mathbf{F}_{im} + \boldsymbol{\omega} \cdot \sum_{i=1}^{n_S} \mathbf{g}_{iC} \times \mathbf{F}_{im} \right.$$
$$\left. + \sum_{i=1}^{n_S} \mathbf{u}_i \cdot \mathbf{F}_{im} \right) \delta(\mathbf{r} - \mathbf{q}_m) + \frac{1}{2} \sum_{n,m=1}^{N} \sum_{p,q=1}^{n_V} (\dot{\mathbf{q}}_{nq} + \dot{\mathbf{q}}_{mp})$$
$$\cdot \mathbf{F}_{(nq)(mp)} \delta(\mathbf{r} - \mathbf{q}_m), \tag{3.10}$$

which are defined by capacities of the corresponding forces, and the flow contributions,

$$\mathbf{J}_k(\mathbf{r}) = -\dot{\mathbf{g}} E_k \delta(\mathbf{r} - \mathbf{g}), \quad k = 1\,\text{vibr}, \ 1\,\text{rt}; \tag{3.11}$$

$$\mathbf{J}_2(\mathbf{r}) = -\sum_{m=1}^{N} \dot{\mathbf{q}}_m E_m \delta(\mathbf{r} - \mathbf{q}_m). \tag{3.12}$$

The decomposition (2.12) of a solute nucleus velocity is taken into account in Eq. (3.10).

The representation of the rhs of Eqs. (3.7) by two terms is not unique. For example, one usually represents[51,54] the second term of $I_2(\mathbf{r})$ as a flow term,

$$\frac{1}{2} \sum_{n,m=1}^{N} \sum_{p,q=1}^{n_V} (\dot{\mathbf{q}}_{nq} + \dot{\mathbf{q}}_{mp}) \cdot \mathbf{F}_{(nq)(mp)} \delta(\mathbf{r} - \mathbf{q}_m)$$
$$\cong \mathbf{\nabla_r} \cdot \left(\frac{1}{4} \sum_{n,m=1}^{N} \sum_{p,q=1}^{n_V} (\mathbf{q}_m - \mathbf{q}_n) \right.$$
$$\left. \times (\dot{\mathbf{q}}_{nq} + \dot{\mathbf{q}}_{mp}) \cdot \mathbf{F}_{(nq)(mp)} \delta(\mathbf{r} - \mathbf{q}_m) \right),$$

and adjoins it to $\mathbf{J}_2(\mathbf{r})$,

$$\tilde{I}_2(\mathbf{r}) = -\sum_{m=1}^{N} \left(\mathbf{v}_C \cdot \sum_{i=1}^{n_S} \mathbf{F}_{im} + \boldsymbol{\omega} \cdot \sum_{i=1}^{n_S} \mathbf{g}_{iC} \times \mathbf{F}_{im} \right.$$
$$\left. + \sum_{i=1}^{n_S} \mathbf{u}_i \cdot \mathbf{F}_{im} \right) \delta(\mathbf{r} - \mathbf{q}_m), \tag{3.13}$$

$$\tilde{\mathbf{J}}_2(\mathbf{r}) = \sum_{m=1}^{N} \left(-\dot{\mathbf{q}}_m E_m + \frac{1}{4} \sum_{n=1}^{N} \sum_{p,q=1}^{n_V} (\mathbf{q}_m - \mathbf{q}_n) \right.$$
$$\left. \times (\dot{\mathbf{q}}_{nq} + \dot{\mathbf{q}}_{mp}) \cdot \mathbf{F}_{(nq)(mp)} \right) \delta(\mathbf{r} - \mathbf{q}_m). \tag{3.14}$$

Such a definition of the solvent energy flow leads to a conventional definition of a macroscopic energy flow via heat conductivity. However, for the purposes of this work it is more convenient to represent the energy density time derivatives in the form adopted in Eqs. (3.7)–(3.12). This enables

us to trace the energy redistribution between different volume elements of the solvent during the solute relaxation process.

To construct macroscopic equations of motion the non-equilibrium ensembles method[54–57] is used. In accordance with its main condition,[54,55] the nonequilibrium and the quasiequilibrium mean values of the microscopic densities $\hat{H}_k(\mathbf{r})$ are equal. We mark such mean values by brackets $\langle \cdots \rangle_{qe}$, whereas $\langle \cdots \rangle$ is used for equilibrium mean values, and introduce the deviations of the energy densities from their equilibrium values,

$$h_k(\mathbf{r},t) = \langle \Delta \hat{H}_k \rangle_{qe}, \quad \Delta \hat{H}_k = \hat{H}_k - \langle \hat{H}_k \rangle. \tag{3.15}$$

The inverse nonequilibrium temperatures (or quasi-temperatures[57]) in energy units $\beta_k = (k_B T_k)^{-1}$ (k_B is Boltzmann's constant) are considered as the thermodynamic parameters conjugated to the corresponding energy densities. We suppose that temperatures $k_B T_k$ are equal to their kinetic values that are defined as the double mean kinetic energy per degree of freedom for the corresponding subsystem, and will not discuss different definitions[58,59] of temperature here. For the moment we take β_k to denote the deviation of the inverse temperature from its equilibrium value until we will redefine it later.

The nonequilibrium mean values of relevant variables obey[55] the evolution equations with spatial dispersion and memory,

$$\frac{\partial h_k(\mathbf{r},t)}{\partial t} + \sum_l \int \Omega_{kl}(\mathbf{r},\mathbf{r}') \beta_l(\mathbf{r}',t) d\mathbf{r}'$$
$$= \sum_l \int d\mathbf{r}' \int_{-\infty}^{t} dt' \, e^{\epsilon(t'-t)} \Xi_{kl}(\mathbf{r},t,\mathbf{r}',t') \beta_l(\mathbf{r}',t'),$$
$$k,l = 1\,\text{vibr}, \ 1\,\text{rt}, \ 2, \tag{3.16}$$

where the frequency matrix,

$$\Omega_{kl}(\mathbf{r},\mathbf{r}') = \langle \Delta \dot{\hat{H}}_k(\mathbf{r}) \Delta \hat{H}_l(\mathbf{r}') \rangle, \tag{3.17}$$

and the memory matrix,

$$\Xi_{kl}(\mathbf{r},t,\mathbf{r}',t') = \langle Q \hat{B}_k(\mathbf{r},t) \exp[iQLQ(t'-t)] Q \hat{B}_l(\mathbf{r}',t') \rangle, \tag{3.18}$$

are defined as equilibrium mean values of the corresponding microscopic fluxes (3.7). The small parameter ϵ goes to zero in the thermodynamic limit ($N \to \infty$, $V \to \infty$ at $N/V = \text{const}$, V is the volume of the system). The Liouville operator L is defined in terms of potential and kinetic energy of the system under consideration, and its action is equivalent to differentiation with respect to time $-iL\hat{A} = \dot{\hat{A}}$. $Q = (1 - P)$, where P is Mori's projection operator,[60] which acts on dynamical quantities $\hat{A}$ and projects them onto the space of the relevant variables,

$$P\hat{A} = \langle \hat{A} \rangle + \sum_{k,l} \langle \Delta \hat{H} \, \Delta \hat{H} \rangle_{kl}^{-1} \langle \hat{A} \, \Delta \hat{H}_l \rangle \Delta \hat{H}_k. \tag{3.19}$$

Cofactors of the frequency matrix have opposite time parity and hence equilibrium mean values of their products vanish. Thus, the frequency matrix is a zero matrix.

Similar time parity consideration shows that $P\hat{B}_k = 0$ and $Q\hat{B}_k = \hat{B}_k$ and the memory matrix consists of nonmodified fluxes. However, the memory matrix includes the reduced Liouville operator QLQ that modifies the time evolution of the fluxes entering the memory matrix. Under the assumption of sufficiently different time scales of evolution of the mean values of relevant variables $h_k(\mathbf{r},t)$ and the time correlation functions of fluxes $\hat{B}_k$, this modification may be neglected.[55] It means that the time correlation functions can be directly calculated by averaging products of the fluxes at two equidistant moments of time during equilibrium MD simulation runs.

Each of the nine elements of the memory matrix consists of four components. Among them there are time correlation functions of source/sink terms, flow terms, and a combination of source/sink and flow terms as well.

In the equilibrium state the system is considered as a uniform isotropic medium. In this case the correlation functions depend only on the distance $\mathbf{r}'' = \mathbf{r}' - \mathbf{r}$ between points and the time lag $t'' = t' - t$,

$$\Xi_{kl}(\mathbf{r},t,\mathbf{r}',t') = \Xi_{kl}(\mathbf{r}'',t''). \tag{3.20}$$

To close the system of evolution equations (3.16), the connection[55] between the mean values of the microscopic and thermodynamic parameters has to be written:

$$h_k(\mathbf{r},t) = -\sum_l \int C_{kl}(\mathbf{r},\mathbf{r}')\beta_k(\mathbf{r}',t), \tag{3.21}$$

where the static correlation matrix, which is composed of nonlocal heat capacities,

$$C_{kl}(\mathbf{r},\mathbf{r}') = \langle \Delta\hat{H}_k(\mathbf{r})\Delta\hat{H}_l(\mathbf{r}')\rangle = C_{kl}(\mathbf{r}''), \tag{3.22}$$

is introduced.

The system under investigation contains only one solute particle. Hence, it is necessary to prevent information loss about the statistical characteristics of this particle among the numerous solvent molecules. To this end, we consider the solvent particles in the frame of the solute particle.[61] All the mean values have to be calculated in such a way that the solute is singled out and not smeared over the system volume. Such a formulation of the problem, however, results in a violation of translational and rotational symmetry of the system. Hence, the correlation functions (3.20), (3.22) cannot be considered as functions of the distance $\mathbf{r}''$, but will depend on both vectors $\mathbf{r}'$, $\mathbf{r}$ defined in the solute particle frame. To simplify the consideration we neglect such symmetry breaking in the first approximation. This technical complication can be handled when computer simulations of a required level will be available.

B. Evolution of solute vibrational energy

In the preceding section the general equation (3.16) of evolution of different energy densities for the description of VER and its corresponding frequency and memory matrices were derived, the former being the zero matrix in our case. Now we proceed to analyze the equation describing the evolution of the solute vibrational energy that contains the main characteristics of VER. We will specify properties of the memory matrix relating to this equation and under physically reasonable assumptions derive and analyze expressions for the relaxation time, enabling us to extract mode and atom specific information on VER.

1. Vibrational energy relaxation rate

The first of the evolution equations (3.16) for the solute vibrational energy has the form

$$\frac{\partial h_{1\,\mathrm{vibr}}(\mathbf{r},t)}{\partial t} = \sum_l \int d\mathbf{r}' \int_{-\infty}^t dt'\, e^{\epsilon(t'-t)}\langle I_{1\,\mathrm{vibr}}(\mathbf{r},t)I_l(\mathbf{r}',t')\rangle\beta_l(\mathbf{r}',t') - \sum_l \nabla\cdot\int d\mathbf{r}'\int_{-\infty}^t dt'\, e^{\epsilon(t'-t)}$$

$$\times\langle I_{1\,\mathrm{vibr}}(\mathbf{r},t)\mathbf{J}_l(\mathbf{r}',t')\rangle\beta_l(\mathbf{r}',t') + \sum_l \nabla\cdot\int d\mathbf{r}'\int_{-\infty}^t dt'\, e^{\epsilon(t'-t)}\langle\mathbf{J}_{1\,\mathrm{vibr}}(\mathbf{r},t)I_l(\mathbf{r}',t')\rangle\beta_l(\mathbf{r}',t')$$

$$-\sum_l \nabla\cdot\int d\mathbf{r}'\int_{-\infty}^t dt'\, e^{\epsilon(t'-t)}\langle\mathbf{J}_{1\,\mathrm{vibr}}(\mathbf{r},t)\mathbf{J}_l(\mathbf{r}',t')\rangle\cdot\nabla\beta_l(\mathbf{r}',t'). \tag{3.23}$$

The last term of the rhs of this equation was integrated by parts. This led to the appearance of the inverse temperature gradient. The dependence of the time correlation functions on distance $\mathbf{r}''$ only was taken into account when differentiation variable $\mathbf{r}'$ was changed to $\mathbf{r}$ in the second term.

The time correlation functions in the second and third terms of Eq. (3.23) are defined as products of scalar and vector quantities and in direction are parallel to $\mathbf{r}''$. Due to the specific role of the solute, these correlation functions are not equal to zero. However, they include products of velocities of different degrees of freedom. Hence, this peculiarity

exists only at $t \neq t'$ due to dynamical correlations, and therefore the contribution of these terms is perhaps not essential. This conclusion becomes even more founded if in the time correlation functions the velocities involved belong to weakly coupled degrees of freedom, as in the case of the solute normal mode velocities on one hand and solvent velocities on the other hand.

The energy density for the solute vibrational energy can be represented as

$$h_{1\,\mathrm{vibr}}(\mathbf{r},t) = h_{1\,\mathrm{vibr}}(t)F_1(\mathbf{r},t), \tag{3.24}$$

where $F_1(\mathbf{r},t)$ is the normalized distribution function of the solute and $h_{1\,\text{vibr}}(t)$ is the mean value of the solute vibrational energy at time t. The distribution function evolution describes spatial diffusion of the solute that has no connection with energy transfer from solute to solvent. To exclude energy flux due to solute translation one has to integrate Eq. (3.23) over $\mathbf{r}$ such that the last three terms of Eq. (3.23) vanish and the evolution equation takes the form

$$\frac{dh_{1\,\text{vibr}}(t)}{dt} = \sum_l \int d\mathbf{r} \int d\mathbf{r}' \int_{-\infty}^t dt' \, e^{\epsilon(t'-t)}$$
$$\times \langle I_{1\,\text{vibr}}(\mathbf{r},t)I_l(\mathbf{r}',t')\rangle \beta_l(\mathbf{r}',t'). \quad (3.25)$$

So far only the most common approximations of non-equilibrium statistical thermodynamics were used. Equation (3.25) can be significantly simplified by adopting more particular suggestions. The rhs of this equation includes integrals over time correlation functions that are multiplied by thermodynamic parameters. As the characteristic time scale of evolution for the thermodynamics parameters (τ_{th}) and for the time correlation functions of dynamical variables (τ_{dyn}) are different (it is supposed that $\tau_{\text{th}} \gg \tau_{\text{dyn}}$) one can take the former out of the time integral. The first spatial integral over $\mathbf{r}$ can be handled due to uniformity of the solvent. In view of the fact that there is only one solute particle, it yields unity. The second integral over $\mathbf{r}'$ implies that the initial value problem should be solved because the solvent temperature field has to be defined by the solution of the full system of equations (3.16). Fortunately, there are many indications[12,14,16] that heating of the solvent in the vicinity of the solute is small in comparison to the vibrational kinetic temperature of the solvent. Hence, the rhs of Eq. (3.25) contains only inverse temperatures that are independent of spatial variables, because $\beta_{1\,\text{vibr}}$ and $\beta_{1\,\text{rt}}$ are assigned to the solute and have no spatial dependence.

Further simplifications follow from the weak contribution of the vibration–rotation interaction to vibrational energy transfer.[21,52] Hence, on the rhs of Eq. (3.25) only the term with vibrational capacity and inverse vibrational temperature survives. To eliminate the inverse temperature from this equation, the simplest approximation of Eq. (3.21),

$$h_{1\,\text{vibr}} = -(c_1 k_B T^2)\beta_{1\,\text{vibr}}, \quad (3.26)$$

can be used. Here c_1 is a heat capacity of the solute molecule.

As a result, the rate equation for the solute vibrational energy follows:

$$\frac{dh_{1\,\text{vibr}}(t)}{dt} = -k_1 h_{1\,\text{vibr}}(t), \quad k_1 = \{N_{\text{vibr}}|N_{\text{vibr}}\}/c_1 k_B T^2, \quad (3.27)$$

where the notation

$$\{a|b\} = \int_0^\infty \langle a(t)b(0)\rangle dt \quad (3.28)$$

for the time integral of a time correlation function is used.

2. Analysis of the vibrational energy relaxation rate expressions

Two different representations (normal mode and atomic) of the vibrational capacity are available according to Eq. (2.38) and they lead to different but equivalent final expressions,

$$k_1 = \sum_{\alpha,\beta=1}^{3n_S-6} k_{1\alpha\beta}, \quad k_{1\alpha\beta} = \{Q_\alpha \dot{q}_\alpha | Q_\beta \dot{q}_\beta\}/c_1 k_B T^2, \quad (3.29)$$

$$k_1 = \sum_{i,j=1}^{n_S} k_{1ij}, \quad k_{1ij} = \{\mathbf{F}_i^{(e)}\cdot\mathbf{u}_i | \mathbf{F}_j^{(e)}\cdot\mathbf{u}_j\}/c_1 k_B T^2. \quad (3.30)$$

The normal mode description permits us to interpret the solute in terms of weakly interacting quasiparticles (normal modes) in case of not too strong nonlinear interactions. However, the description of the energy flux between such a system and its environment, as a rule, cannot be realized in terms of energy exchange through individual modes. The external forces in accordance with Eq. (2.37) contribute to many normal forces simultaneously connecting the normal modes to each other, even in the case of harmonic solute. It results in a solvent assisted solute intermode energy redistribution and multimode character of solute–solvent energy exchange that displays it through nondiagonal elements of matrix $k_{1\alpha\beta}$ in Eq. (3.29) and is clearly manifested in nonequilibrium simulations.[21,52]

In the case of strong intermode coupling, none of the coefficients $k_{1\alpha\beta}$ can be given an exact physical interpretation. However, by analogy with energy transfer in a many-component system, it may be interpreted as energy transfer by the α mode due to the temperature difference between mode β and the solvent. Then, a possible interpretation of the sum,

$$k_{1\alpha} = \sum_{\beta=1}^{3n_s-6} k_{1\alpha\beta}, \quad (3.31)$$

as the rate coefficient of the solute–solvent energy transfer through mode α seems plausible. These partial rate coefficients can be interpreted as individual mode rates of energy exchange only approximately, and this interpretation is strongly dependent on values of nondiagonal elements of the matrix $k_{1\alpha\beta}$. When the coupling between different normal force capacities is weak, the nondiagonal elements can be neglected, and in this approximation the rate coefficient,

$$k_1 = \sum_{\alpha=1}^{3n_s-6} k_{1\alpha}, \quad k_{1\alpha} \cong k_{1\alpha\alpha}, \quad (3.32)$$

is represented by individual channels of energy exchange through each vibrational degree of freedom. This expression includes time correlation functions of two different sorts of variables, namely velocities and forces. Hence, it is possible to approximately uncouple the correlation functions and represent them by a product of correlation functions,

$$\langle Q_\alpha(t)\dot{q}_\alpha(t)Q_\alpha(0)\dot{q}_\alpha(0)\rangle = \langle \dot{q}_\alpha(t)\dot{q}_\alpha(0)\rangle\langle Q_\alpha(t)Q_\alpha(0)\rangle. \quad (3.33)$$

The time dependence of the normal velocities on characteristic normal force time scales is well described by har-

monic functions with frequencies of the corresponding normal vibrations. Taking into account the equipartitioning of energy, it follows that

$$\langle \dot{q}_\alpha(t)\dot{q}_\alpha(0)\rangle = \langle \dot{q}_\alpha^2(0)\rangle \cos \omega_\alpha t = k_B T \cos \omega_\alpha t, \quad (3.34)$$

$$\{Q_\alpha \dot{q}_\alpha | Q_\alpha \dot{q}_\alpha\} = (k_B T)^2 \zeta_\alpha(\omega_\alpha), \quad (3.35)$$

where the frequency-dependent normal force friction coefficient is introduced,

$$\zeta_\alpha(\omega) = (k_B T)^{-1} \int_0^\infty \langle Q_\alpha(t)Q_\alpha(0)\rangle \cos \omega t \, dt. \quad (3.36)$$

The normal forces acting on nuclei at their actual positions enter into this expression.

When the representation (3.30) is used with a similar decoupling approximation, the atomic friction coefficients,

$$\zeta_i(\omega) = (3k_B T)^{-1} \int_0^\infty \langle \mathbf{F}_i(t) \cdot \mathbf{F}_i(0)\rangle \cos \omega t \, dt, \quad (3.37)$$

due to strong interatomic interaction have to be calculated for the whole vibrational spectrum of the solute and summed with corresponding weight coefficients for each vibrational mode. Naturally, some of these weight coefficients could be very small.

Another approximation to uncouple velocities and coordinates in Eq. (3.29) can be achieved by expanding the normal forces in solute normal coordinate power series.[23,24,27,62] In the zeroth-order approximation one gets (3.35), (3.36) with normal forces $Q_\alpha^{(0)}(t)$ defined at the equilibrium positions of nuclei in Eckart's frame. In this case the expressions for the partial rate coefficients are just the same as usually derived from the Landau–Teller formula.[23-25] It is necessary to note, however, that in our case, to preserve the original dynamics of the flexible solute, the normal forces for a flexible solvent and solute as well as forces at equilibrium positions of solute nuclei have to be calculated. After additional approximations one arrives at expressions that include the normal forces under different restrictions on solute and/or solvent motion.

Of course, such approximations are questionable, especially for polyatomic solutes, and should be tested by direct molecular dynamics calculations comparing rhs's and lhs's of expressions of the type given in Eqs. (3.35)–(3.37). If all terms except zeroth order in the power series will be found to be small, both expressions for the friction coefficients at actual and equilibrium nuclei positions will result in comparable values.

It is known from investigations of small size molecules that for some systems[25,26,40] the normal force friction coefficients decrease exponentially (or even more rapidly) with frequency. In other cases[62] the frequency dependence of friction coefficients is more complicated but still their decay is fast as a function of frequency. Hence, if such a behavior of friction coefficients also prevailed for moderate size molecules, the rate coefficient for the vibrational energy transfer could be represented by a few first terms of the sum

$$k_1 = \sum_{\alpha=1}^{3n_s-6} \zeta_\alpha(\omega_\alpha)/(c_1/k_B). \quad (3.38)$$

This means that the part of the solute intramolecular energy, which is initially stored in high-frequency vibrational modes, can pass to the solvent only after intramolecular energy redistribution to low-frequency modes, which are coupled more strongly to the surrounding solvent. However, direct molecular dynamics simulations have shown[21,52,53] that this is not the case, and almost all vibrational modes participate in the energy transfer from the excited solute to the solvent.

The heat capacity of the solute vibrational subsystem in the harmonic approximation is

$$c_1/k_B = 3n_s - 6, \quad (3.39)$$

and this denominator in Eq. (3.38) indicates that the energy transfer rate is reduced if not all channels of the individual vibrational degrees of freedom are equally effective.[63]

The vibrational energy relaxation time is the reciprocal value of the rate coefficient

$$\tau = 1/k_1, \quad (3.40)$$

and can be calculated from simulated trajectories using expressions (3.29) or (3.30).

3. A two-temperature model

Strong deviations of the system from equilibrium can be considered in the framework of a two-temperature model,[54,55] when the temperatures of the solute T_1 and the solvent $T_2 \approx T$ (T is the temperature in the bulk of the solvent) are supposed to be significantly different from each other. Equation (3.25) still remains valid. However, the approximations described after this equation in the case under consideration lead to a difference of the reciprocal temperatures, which is, of course, nonlinear with respect to the temperature difference,

$$\frac{dh_{1\,vibr}(t)}{dt} = -\int_0^\infty \langle N_{vibr}(t+t')N_{vibr}(t)\rangle dt'$$
$$\times (T_1(t)-T)/T_1(t)T. \quad (3.41)$$

However, for calculating the time correlation function in this expression, one has to average over the quasiequilibrium distribution, i.e., the expression

$$\langle \dot{q}_\alpha(t+t')\dot{q}_\alpha(t)\rangle_{qe} = k_B T_1(t)\cos \omega_\alpha t' \quad (3.42)$$

is valid instead of Eq. (3.34) while the solvent temperature T should be preserved in Eq. (3.36) because the force correlation functions are mainly defined by solvent characteristics.

The variations of the vibrational energy and temperature of the solute are connected by the heat capacity,

$$dh_{1\,vibr} = c_1(T_1)dT_1. \quad (3.43)$$

The heat capacity depends on the intramolecular potential energy and thus on the solute temperature because at higher temperatures a wider area of the configurational space of the solute is covered. This dependence can be calculated during nonequilibrium simulations of VER. For not too anharmonic intramolecular potentials, a weak dependence of the heat capacity on temperature can be assumed and Eq. (3.39) gives

its accurate estimation. Thus, the denominator of the rhs in Eq. (3.41) cancels and the equation can be rewritten in the form

$$\frac{dT_1(t)}{dt} = -k_1[T_1(t) - T],\qquad(3.44)$$

which differs from Eq. (3.27) in that the rate coefficient in the latter includes the heat capacity at current solute temperature T_1 instead of the solvent temperature T in the former. The difference between the capacities will define the difference between the rate constants or the relaxation times obtained by equilibrium and nonequilibrium simulations. The variation of the characteristic heat capacity with a solute temperature will result in a nonexponential dependence of energy on time during the process of the vibrational relaxation.

Another reason for a nonexponential solute vibrational energy decay is related to the case when solute thermal quasiequilibrium state cannot be maintained during VER due to the structure of the intramolecular potential energy surface. More than one subsystem and quasitemperature have to be introduced in this case, resulting in more complex behavior of VER.

Although more exact calculations could reveal other reasons for nonexponential energy decays this crude estimation shows that the time integral of the time correlation function of the solute–solvent interaction force capacity is roughly proportional to the product of solvent and excited solute temperatures. This results in the cancellation of nonlinearity arising from the inverse temperature difference, in agreement with the experimental results.[12–15]

C. Translational and rotational motion of the solute

The equations for evolution of the translational and the rotational energies of the solute follow from Eq. (3.16). After approximations similar to those discussed in the preceding subsections we obtain the equation

$$\frac{dh_{1K}(t)}{dt} = \{N_K|N_K\}(\beta_{1K} - \beta_2), \quad K = T, R,\qquad(3.45)$$

$$N_T = \mathbf{R}^{(e)} \cdot \mathbf{v}_C, \quad N_R = \mathbf{M}_C^{(e)} \cdot \boldsymbol{\omega}.\qquad(3.46)$$

Subscripts T and R are related to translational and rotational motion, respectively. Weak coupling between rotation and translation is supposed leading to two independent equations for each type of motion. Also, we take into account results of nonequilibrium simulations,[52] which indicate negligibly small energy transfer due to the vibration–rotation interaction. Hence, only the diagonal terms are retained on the rhs of Eq. (3.45). Of course, all these suggestions can be checked by simulating appropriate time correlation functions.

The inverse temperature difference on the rhs of Eq. (3.45) is determined by the structure of source/sink terms in Eqs. (3.9) and (3.10), which contain similar contributions with opposite signs. Here this difference is indicated explicitly because the solute rotational and translational energy decays on a subpicosecond time scale[16] and the corresponding temperatures become nearly equal to the solvent temperature in the vicinity of the solute.

Treating the external force and torque that act on the solute as fluctuating δ-correlated random quantities we obtain for corresponding terms of Eq. (3.45),

$$\{N_T|N_T\} \cong \langle \mathbf{v}_C(0)\mathbf{v}_C(0)\rangle \cdot \cdot \{\mathbf{R}^{(e)}|\mathbf{R}^{(e)}\} = 3(\xi_t/M)(k_{\mathrm{B}}T)^2,\qquad(3.47)$$

$$\{N_R|N_R\} \cong \langle \boldsymbol{\omega}(0)\boldsymbol{\omega}(0)\rangle \cdot \cdot \{\mathbf{M}_C^{(e)}|\mathbf{M}_C^{(e)}\}$$
$$= \sum_{\gamma=1}^{3} (\xi_{r\gamma}/I_\gamma)(k_{\mathrm{B}}T)^2,\qquad(3.48)$$

where tensor notations are used and centered points between tensors designate their inner products, M is the total mass of the solute, ξ_t and $\xi_{r\gamma}$ are the friction constants for the solute translational and rotational motion, respectively,

$$\xi_t = (3k_{\mathrm{B}}T)^{-1} \int_0^\infty \mathbf{R}^{(e)}(t) \cdot \mathbf{R}^{(e)}(0)\,dt,$$
$$\xi_{r\gamma} = (k_{\mathrm{B}}T)^{-1} \int_0^\infty M_{C\gamma}^{(e)}(t) M_{C\gamma}^{(e)}(0)\,dt,\qquad(3.49)$$

I_γ are the principle inertia moments of the solute, $\gamma = 1,2,3$ label the coordinate axes. The coincidence of the principal axes frames for mass and friction force distributions is supposed.

Since the heat capacities of solute translational and rotational motions are each equal to $(\frac{3}{2})k_{\mathrm{B}}$, Eqs. (3.45) by analogy with Sec. III B 1 define the characteristic times of translational and rotational energy relaxation,

$$\tau_t = 2M/\xi_t, \quad \tau_r = (2/3)\sum_{\gamma=1}^{3} \xi_{r\gamma}/I_\gamma.\qquad(3.50)$$

Their values are two times higher than for momentum or angular momentum relaxation. The same value for the kinetic energy relaxation time follows when the solution of the ordinary Langevin equation for a spherical particle is used.[64,65]

D. Energy redistribution in the solvent

Equations (3.10), (3.12) or (3.13), (3.14) allow us to trace the redistribution of the solute energy transferred to the solvent by computer simulations of nonequilibrium vibrational energy relaxation processes. An analogous investigation, which is even more informative due to time correlation functions involved, is possible on the basis of equilibrium computer simulations. To this end, Eq. (3.16) has to be considered for $k=2$. The transformations described just after Eq. (3.23) should be used in this case, too.

During the solute vibrational energy relaxation its vibrational, translational, and rotational temperature should be considered as independent of the solute position due to spatial uniformity of the solvent. Hence, all the gradients of $\beta_{1\mathrm{vibr}}$ and $\beta_{1\mathrm{rt}}$ become equal to zero and the evolution equation takes the form

$$\frac{\partial h_2(\mathbf{r},t)}{\partial t} = \sum_l \int d\mathbf{r}' \int_{-\infty}^{t} dt' \, e^{\epsilon(t'-t)} \langle I_2(\mathbf{r},t) I_l(\mathbf{r}',t') \rangle \beta_l(\mathbf{r}',t') - 2 \int d\mathbf{r}' \int_{-\infty}^{t} dt' \, e^{\epsilon(t'-t)} \langle I_2(\mathbf{r},t) \mathbf{J}_2(\mathbf{r}',t') \rangle \cdot \nabla \beta_2(\mathbf{r}',t')$$

$$- \nabla \cdot \int d\mathbf{r}' \int_{-\infty}^{t} dt' \, e^{\epsilon(t'-t)} \langle \mathbf{J}_2(\mathbf{r},t) \mathbf{J}_2(\mathbf{r}',t') \rangle \cdot \nabla \beta_2(\mathbf{r}',t'). \tag{3.51}$$

The second term of the rhs of this equation contains a factor 2 as a result of a combination of two terms due to spatial symmetry properties of the respective time correlation function and it is nonzero only in the vicinity of the solute. After decomposition of velocities and spatial variables in the time correlation function of I_2 and $\mathbf{J}_2$, it can be represented as a product of the diffusion coefficient and mean force on the solute, and the term can obviously be considered as small. The last term of Eq. (3.51) in accordance with Eq. (3.12) represents the redistribution of energy due to diffusional motion of solvent particles. Thus, to a first approximation, contributions of these two terms can be neglected.

The sum in the first term of Eq. (3.51) runs over values 1 vibr, 1rt, and 2 of l. It was noted already that rotational and translational motion of solute is of minor importance for vibrational energy relaxation. Hence, corresponding terms can be dropped. I_1 and I_2 consist of capacities of solute–solvent and solvent–solvent interactions, which include velocities of different species. Again, time correlation functions involving these velocities can be neglected. Then Eq. (3.51) attains the form

$$\frac{\partial h_2(\mathbf{r},t)}{\partial t} = -p_{12}(\mathbf{r}) \beta_{1\,\text{vibr}}(t)$$

$$+ \int_V p_{22}(\mathbf{r},\mathbf{r}') [\beta_2(\mathbf{r}) - \beta_2(\mathbf{r}')] d\mathbf{r}', \tag{3.52}$$

where transfer coefficients,

$$p_{12}(\mathbf{r}) = \int_0^{\infty} \int_V d\mathbf{r}' \sum_{m,n=1}^{N} \sum_{i,j=1}^{N} \langle N_{in}(\mathbf{r},0) N_{jm}(\mathbf{r}',t') \rangle dt', \tag{3.53}$$

$$p_{22}(\mathbf{r},\mathbf{r}') = \int_0^{\infty} \sum_{m,n,m',n'}^{N} \sum_{q,p,q',p'}^{n_S} \langle N_{(nq)(mp)}(\mathbf{r},0)$$

$$\times N_{(n'q')(m'p')}(\mathbf{r}',t') \rangle dt', \tag{3.54}$$

characterize solute–solvent and solvent–solvent energy exchange rates, respectively, and are defined by corresponding microscopic capacities,

$$N_{jm}(\mathbf{r},t) = \mathbf{u}_j(t) \cdot \mathbf{F}_{jm}(t) \delta(\mathbf{r} - \mathbf{r}_m),$$

$$\tag{3.55}$$

$$N_{(nq)(mp)}(\mathbf{r},t) = \tfrac{1}{2} [\dot{\mathbf{q}}_{nq}(t) + \dot{\mathbf{q}}_{mp}(t)] \cdot \mathbf{F}_{(nq)(mp)}(t) \delta(\mathbf{r} - \mathbf{r}_m).$$

For an alternative definition of the solvent sink and flow terms (3.13), (3.14), contributions of different parts of the rhs of Eq. (3.51) should be reconsidered. With respect to solute nuclei velocities, the first term permits the same rearrangement as in the previous case. It will result in the same expression for the solute–solvent energy exchange as in Eq. (3.52). The term with $\nabla \beta_2$ can be neglected again, because it

includes time correlation functions of velocities of different species. However, the last term now gives rise to a nonlocal heat conduction term in the evolution equation. Neglecting for simplicity this nonlocality we present the final result in the form of a heat conduction equation with the source term

$$c_2 \frac{\partial T_2(\mathbf{r},t)}{\partial t} = \nabla \cdot (\kappa_2 \nabla T_2) + \frac{p_{12}(\mathbf{r})}{k_B T_2 T_{1\,\text{vibr}}}$$

$$\times [T_{1\,\text{vibr}}(t) - T_2(\mathbf{r},t)], \tag{3.56}$$

where c_2 and κ_2 are heat capacity and thermal conductivity of solvent, respectively. Apart from experimental values the former can be calculated by Eq. (3.22) and for the latter the integral of time correlation function of energy flow (3.14) might be used.[54,55]

Experimental values of the transmission coefficient p_{12} are not available, so it has to be calculated by Eq. (3.53). This expression permits us to determine the distance at which the main part of the transferred solute energy is absorbed by the solvent due to direct solute–solvent interaction. This distance is defined by a competition between the interaction force and the distribution functions that increase or decrease with separation between solute and solvent. It is evident that this distance ranges within the first coordination sphere.

Using simplifying assumptions, the temperature gradient in the vicinity of the solute may be estimated. For a typical excitation energy of 1 eV and a relaxation time of 10 ps, the energy flow through a 1 nm radius spherical surface is on the order of 10^9 W/m^2. Using a thermal conductivity of ~ 0.1 W/mK, the temperature gradient attains very high values of the order of 10^{10} K/m$=1$ K/Å. Under these conditions the nonlocality can play an important role and the description of the solvent energy redistribution in terms of Eq. (3.52) will probably be more reliable in comparison with Eq. (3.56). In the former, the nonlocality in the term that describes the intrasolvent energy redistribution is taken into account in a more direct fashion by interatomic forces, and its derivation does not include the series expansion in the inverse temperature gradients used in Eq. (3.56).

IV. CONCLUDING REMARKS

The foundations and possibilities of the nonequilibrium and equilibrium approaches for the investigation of VER by means of computer simulations have been discussed in detail. Normal mode analysis of the solute molecule vibrations was used as a basis of the procedures developed in the framework of both approaches for the interpretation of simulation results.

For nonequilibrium simulations the main characteristics of the cooling process, besides the time behavior of total, kinetic, and potential solute energy, are the capacities of normal forces and the solute–solvent energy exchange through normal modes and individual atoms. The separation of vibrational and rotational motion is carried out by the use of Eckart's as well as the solute instantaneous principle axes frame. The expression for study of vibration–rotation interaction, and its influence on VER is also formulated in terms of capacities, and in the case of Eckart's frame it consists of four terms that describe different aspects of the interaction while in the other case the only term is presented.

The use of the equilibrium simulations for the investigation of VER is not so straightforward and involves statistical–mechanical description of the process. On the basis of linear nonequilibrium statistical thermodynamics the expression for the rate constant or relaxation time in terms of normal force or atomic force capacities time correlation functions and the solute heat capacity is deduced. The same expression is derived in the framework of the two-temperature model. After additional approximations the expression is reduced to the frequency-dependent normal force friction coefficients and can be considered as a generalization of the single oscillator expression obtained from the Landau–Teller formula. Two points should be made here. At first, our result is fully classical in origin. And second, the solute heat capacity enters into the expression.

Several conditions have to be met to ensure an exponential decay of excitation. First of all, fast IVR (in comparison with VER) is needed to maintain a quasiequilibrium distribution of energy over internal vibrational degrees of freedom. The characteristic time scale of evolution of the time correlation functions of the normal force capacities or the normal forces is also required to be considerably smaller than the VER time that defines the evolution time scale for thermodynamic variables (temperatures or energy densities).

If the solute internal structure results in splitting of the internal degrees of freedom on two or more weakly connected subsystems, each of which has its own channels of energy exchange with the solvent, the state of the solute cannot be described by one thermodynamic parameter. Then, instead of one evolution equation [e.g., Eq. (3.25)], one should consider a system of equations, which, in general, leads to more complicated behavior of the solute.

The results of the two-temperature model suggest that the values of the rate constants defined by nonequilibrium and equilibrium MD simulations will not be significantly different. In this case, equilibrium simulations will also contain complementary information about nonequilibrium VER. The time and spectral behavior of different time correlation functions are of primary importance.

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APPENDIX: COUPLING BETWEEN NORMAL COORDINATES

The solute intramolecular energy can be rewritten in terms of normal coordinates:

$$E_{1\,\text{intra}} = K_1 + U_1,$$

$$K_1 = \frac{1}{2} \sum_{\alpha=1}^{3n_S-6} \dot{q}_\alpha^2, \quad U_1 = \frac{1}{2} \sum_{\alpha=1}^{3n_S-6} \omega_\alpha^2 q_\alpha^2 + U_{1\text{nl}} + U_{1\text{ext}}. \tag{A1}$$

Hear $U_{1\text{nl}}$ includes nonlinear and vibration–rotation coupling terms; $U_{1\text{ext}}$ is the energy of the solute in the solvent potential field.

The normal coordinates obey the Lagrange equations:

$$\ddot{q}_\alpha + \omega_\alpha^2 q_\alpha = Q_\alpha + Q_{\alpha\text{nl}}^{(i)} + Q_{\alpha\text{r-v}}, \tag{A2}$$

$$Q_{\alpha\text{nl}}^{(i)} = Q_\alpha^{(i)} - \omega_\alpha^2 q_\alpha, \quad \alpha = 1,2,...,3n-6; \tag{A3}$$

$Q_{\alpha\text{r-v}}$ takes into account vibration–rotation coupling.

For the harmonic part of energy of each mode one obtains the equation

$$\dot{E}_{\alpha\text{harm}} = N_{\alpha\text{vibr}} + N_{\alpha\text{nl}} + N_{\alpha\text{r-v}},$$

$$E_{\alpha\text{harm}} = (\dot{q}_\alpha^2 + \omega_\alpha^2 q_\alpha^2)/2, \quad N_{\alpha\text{vibr}} = Q_\alpha \dot{q}_\alpha, \tag{A4}$$

$$N_{\alpha\text{nl}} = Q_{\alpha\text{nl}} \dot{q}_\alpha, \quad N_{\alpha\text{r-v}} = Q_{\alpha\text{r-v}} \dot{q}_\alpha.$$

We do not develop the expression for $Q_{\alpha\text{r-v}}$ because the rotation-vibration interaction has a rather complicated structure and, moreover, it is expected to be of minor importance for energy redistribution in molecules of moderate size like azulene. The total contribution of this interaction can be estimated by Eqs. (2.26)–(2.30).

The two most important components of the rhs of Eq. (A4) are the capacities of external forces $N_{\alpha\text{vibr}}$ and the nonlinear intramolecular interactions $N_{\alpha\text{nl}}$. The latter includes energy flux from the harmonic part of mode α to its anharmonic part and to other vibrational modes. The two terms permit us to trace the energy flux within the vibrationally excited solute molecule during its relaxation to the equilibrium state.

Energy exchange between different modes is realized via nonlinear parts of the normal forces. An additional mechanism of intermode energy exchange is based on the rotation–vibration coupling. It can easily be seen that, for example, vibrational angular momentum [Eq. (2.23)] in the normal-mode representation consists of products of two different normal mode coordinates and velocities. After time differentiation, however, it will comprise components that depend on more than two normal coordinates and velocities. Also, the nonlinear normal forces $Q_{\alpha\text{nl}}$ cannot be represented by normal mode pair interactions. Hence, the intramolecular energy redistribution from a particular normal mode will not be separable into contributions involving only pairwise energy exchange between modes. The intramolecular energy flux has essentially multimode character. In addition to this, intramolecular energy redistribution is strongly dependent on solute–solvent interactions.

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A certain improvement in the description of intermode energy redistribution may be achieved by taking into account specific components of the anharmonicities.[41]

[1] M. Quack and J. Troe, in *Gas Kinetic and Energy Transfer*, edited by P. G. Ashmore and R. J. Donovan (The Chem. Soc., London, 1977), Vol. 2.

[2] I. Oref and B. S. Rabinovich, Acc. Chem. Res. **12**, 166 (1979).

[3] H. Hippler and J. Troe, in *Bimolecular Collisions*, Advances in Gas-Phase Photochemistry and Kinetics, edited by M. N. R. Ashfold and J. Baggot (Royal Soc. of Chem., London, 1989).

[4] C. B. Harris, D. E. Smith, and D. I. Russel, Chem. Rev. **90**, 481 (1990).

[5] I. Oref and D. C. Tardy, Chem. Rev. **90**, 1407 (1990).

[6] U. Sukowski, A. Seilmeier, T. Elsaesser, and S. F. Fischer, J. Chem. Phys. **93**, 4096 (1990).

[7] J. C. Owrutsky, D. Raftery, and R. M. Hochstrasser, Annu. Rev. Phys. Chem. **45**, 519 (1994).

[8] K. Lenz, M. Pfeifer, A. Lau, and T. Elsaesser, Chem. Phys. Lett. **229**, 340 (1994).

[9] G. Lendvay and G. C. Schatz, in *Advances in Chemical Kinetics and Dynamics,* edited by J. R. Barker (JAI, Greenwich, 1995), Vol. 2B

[10] R. G. Gilbert, Aust. J. Chem. **48**, 1787 (1995).

[11] T. Lenzer, K. Luther, J. Troe, R. Gilbert, and K. F. Lim, J. Chem. Phys. **103**, 626 (1995).

[12] D. Schwarzer, J. Troe, M. Votsmeier, and M. Zerezke, J. Chem. Phys. **105**, 3121 (1996).

[13] D. Schwarzer, J. Troe, and M. Zerezke, J. Chem. Phys. **107**, 8380 (1997).

[14] J. Benzler, S. Linkerdörfer, and K. Luther, J. Chem. Phys. **106**, 4992 (1997).

[15] D. Schwarzer, J. Troe, and M. Zerezke, J. Phys. Chem. A **102**, 4207 (1998).

[16] C. Heidelbach, I. Fedchenia, D. Schwarzer, and J. Schroeder, J. Chem. Phys. **108**, 10 152 (1998).

[17] A. Lauberau, S. F. Fischer, K. Spanner, and W. Kaiser, Chem. Phys. **31**, 335 (1978); R. Zygan-Maus and S. F. Fischer, *ibid.* **41**, 319 (1979).

[18] J. W. Perry, N. F. Scherer, and A. H. Zewail, Chem. Phys. Lett. **105**, 359 (1984).

[19] E. L. Silbert III, W. P. Reinhardt, and J. T. Hynes, J. Chem. Phys. **81**, 1115 (1984); M. A. Collins and H. S. Schranz, *ibid.* **100**, 2089 (1994).

[20] M. Quack, Annu. Rev. Phys. Chem. **41**, 839 (1990).

[21] C. Heidelbach, J. Schroeder, D. Schwarzer, and V. S. Vikhrenko, Chem. Phys. Lett. **291**, 333 (1998).

[22] R. Zwanzig, J. Chem. Phys. **36**, 2227 (1961).

[23] D. W. Oxtoby, Adv. Chem. Phys. **47**, 487 (1981).

[24] J. Chesnoy and G. M. Gale, Ann. Phys. (Paris) **9**, 893 (1984).

[25] S. A. Egorov and J. L. Skinner, J. Chem. Phys. **105**, 7047 (1996).

[26] S. A. Adelman, R. Mularidhar, and R. H. Stote, J. Chem. Phys. **95**, 2738 (1991).

[27] R. M. Whitnel, K. R. Wilson, and J. T. Hynes, J. Phys. Chem. **94**, 8625 (1990); J. Chem. Phys. **96**, 5354 (1992).

[28] P. Moore, A. Tokmakoff, T. Keyes, and M. D. Fayer, J. Chem. Phys. **103**, 3325 (1995).

[29] R. E. Larsen, E. F. David, G. Goodyear, and R. M. Stratt, J. Chem. Phys. **107**, 524 (1997).

[30] G. Goodyear and R. M. Stratt, J. Chem. Phys. **107**, 3098 (1997).

[31] J. S. Bader and B. J. Berne, J. Chem. Phys. **100**, 8359 (1994).

[32] S. A. Egorov and B. J. Berne, J. Chem. Phys. **107**, 6050 (1997).

[33] R. Karrlein and H. Grabert, J. Chem. Phys. **108**, 4972 (1998).

[34] E. L. Silbert III, J. T. Hynes, and W. P. Reinhardt, J. Chem. Phys. **81**, 1135 (1984).

[35] H. S. Schranz and M. A. Collins, J. Chem. Phys. **101**, 307 (1994).

[36] B. J. Berne, J. Jortner, and R. Gordon, J. Chem. Phys. **47**, 1600 (1967).

[37] S. Velsko and D. W. Oxtoby, Chem. Phys. Lett. **69**, 462 (1980).

[38] I. Ohmine, J. Chem. Phys. **85**, 3342 (1986).

[39] I. Ohmine and H. Tanaka, Chem. Rev. **93**, 2545 (1993).

[40] R. Rey and J. T. Hynes, J. Chem. Phys. **104**, 2356 (1996).

[41] Y. M. Rhee and M. S. Kim, J. Chem. Phys. **107**, 1394 (1997).

[42] B. Robertson, Phys. Rev. **144**, 151 (1967); **160**, 175 (1967).

[43] J. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).

[44] I. M. De Schepper and E. J. D. Cohen, J. Stat. Phys. **27**, 223 (1982).

[45] H. Lindner, Tetrahedron **30**, 1127 (1974).

[46] C. Eckart, Phys. Rev. **47**, 552 (1935).

[47] A. Sayvetz, J. Chem. Phys. **7**, 383 (1939).

[48] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra* (McGraw-Hill, New York, 1955).

[49] C. Eckart, Phys. Rev. **46**, 383 (1934).

[50] C. Kittel, W. D. Knight, and M. A. Ruderman, *Mechanics. Berkeley Physics Course. Vol. 1* (McGraw-Hill, New York, 1965).

[51] R. A. Pickerel, Phys. Rev. **175**, 77 (1968); J. W. Puff and N. S. Gillis, Ann. Phys. (N.Y.) **46**, 364 (1968).

[52] C. Heidelbach, V. S. Vikhrenko, D. Schwarzer, and J. Schroeder, J. Chem. Phys. **110**, 5286 (1999), following paper.

[53] C. Heidelbach, V. S. Vikhrenko, D. Schwarzer, I. I. Fedchenia, and J. Schroeder, J. Chem. Phys. (submitted).

[54] D. N. Zubarev, *Nonequilibrium Statistical Thermodynamics* (Consultants Bureau, New York, 1974).

[55] D. Zubarev, V. Morozov, and G. Repke, *Statistical Mechanics of Nonequilibrium Processes* (Akademie-Verlag, Berlin, 1996, 1997), Vols. 1, 2.

[56] R. Luzzi and A. R. Vasconcellos, Fortschr. Phys. **38**, 867 (1990); **43**, 265 (1995); J. P. Dougherty, Philos. Trans. R. Soc. London **346**, 259 (1994).

[57] R. Luzzi and A. R. Vasconcellos, J. Chem. Phys. **107**, 7383 (1997).

[58] J. Fort, D. Jou, and J. E. Llebot, Physica A **248**, 97 (1988).

[59] R. Luzzi, A. R. Vasconcellos, J Cassas-Vazquez, and D. Jou, Physica A **248**, 111 (1988).

[60] H. Grabert, *Projection Operator Techniques in Nonequilibrium Statistical Mechanics*, Springer Tracts in Modern Physics (Springer-Verlag, Berlin, 1982), Vol. 95.

[61] W. Sung and J. S. Dahler, J. Chem. Phys. **78**, 6264 (1982).

[62] R. Rey and J. T. Hynes, J. Chem. Phys. **108**, 142 (1998).

[63] An analogy with the ordinary Langevin equation $d\mathbf{p}/dt = -(\xi/m)\mathbf{p} + \mathbf{G}(t)$, where m and $\mathbf{p}$ are the particle mass and momentum and ξ and $\mathbf{G}$, the friction coefficient and the fluctuation force, respectively, can be considered. The momentum relaxation time $\tau_p = (\xi/m)$ is connected to the time correlation function of the fluctuating force by the expression $\xi = (nk_BT)^{-1}\int_0^\infty \langle \mathbf{G}(0)\cdot\mathbf{G}(t)\rangle dt$, where n is dimensionality of space (or the number of the particle degrees of freedom). In accordance with experimental results, the solute excitation energy can be described by a relaxation-type equation, $dE/dt = -(1/\tau_E)E + N(t)$, where $N(t)$ is the fluctuation capacity and the energy relaxation time, in analogy to the Langevin equation, is determined by the time correlation function of the fluctuation capacity $\tau_E^{-1} = (3n_s - 6)^{-1}(k_BT)^{-2}\int_0^\infty \langle N(0)N(t)\rangle dt$. This is just Eq. (3.27) with approximation (3.39) for the vibrational heat capacity of the solute taken into account. Of course, at first sight this analogy should not be very close because particle momentum is a vector whereas energy is a scalar quantity. However, the vibrational energy is a sum of energies of vibrational modes, and the external force capacity can be split into a sum of normal mode contributions, too. If all the modes relax independently of each other, the expression for the relaxation time of a particular mode will comprise only the respective normal mode capacity as in the case of relaxation of a particular momentum projection. This peculiarity makes the analogy between the Langevin equations for particle momentum and for vibrational energy very close and explains at an intuitive level of understanding the appearance of the number of vibrational degrees of freedom in the denominator of Eqs. (3.27), (3.29), and (3.38).

[64] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965).

[65] K. Lindenberg and B. J. West, *The Nonequilibrium Statistical Mechanics of Open and Closed Systems* (VCH, New York, 1990).