Vibrational energy transport in acetylbenzonitrile described by an ab initio-based quantum tier model

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Performing comprehensive quantum-chemical calculations, a vibrational Hamiltonian of acetylbenzonitrile is constructed, on the basis of which a quantum-mechanical “tier model” is developed that describes the vibrational dynamics following excitation of the CN stretch mode. Taking into account 36 vibrational modes and cubic and quartic anharmonic couplings between up to three different modes, the tier model calculations are shown to qualitatively reproduce the main findings of the experiments of Rubtsov and coworkers (J. Phys. Chem. B 115 (2011) 11063), including the energy relaxation of the initially excited CN mode and the structure-dependent vibrational transport. Moreover, the calculations suggest that the experimentally measured cross-peak among the CN and CO modes does not correspond to direct excitation of the CO normal mode but rather reflects excited low-frequency vibrations that anharmonically couple to the CO mode. Complementary quasiclassical trajectory calculations are found to be in good overall agreement with the quantum calculations.

I. INTRODUCTION

Recent multidimensional spectroscopy experiments allow us to monitor the pathways and mechanisms of redistribution and transport of vibrational energy in condensed phase molecular systems [1-9]. For example, Dlott and coworkers observed ballistic energy transport along polymer chains [2], Rubtsov and coworkers measured structure-dependent energy transport in acetylbenzonitrile in solution [4], Hamm and coworkers reported on diffusive energy transfer along a peptide helix [3], and Mizutani et al. demonstrated anisotropic energy flow in proteins [8]. To model the vibrational dynamics observed in these experiments, so far mostly perturbative Golden Rule-type formulations or classical trajectory calculations have been employed [10-19]. In an effort to extend these works towards a quantum-dynamical treatment beyond the lowest order of perturbation theory, in this work we adopt the so-called tier model originally proposed by Sibert, Reinhardt, and Hynes [20], and compare the outcome of these calculations to classical nonequilibrium trajectory simulations.

To briefly introduce the main idea, we consider the Hamiltonian $H = H_0 + V$, where the harmonic part

$$H_0 = \sum_{k=1}^{M} \left( \frac{p_k^2}{2} + \frac{1}{2} \omega_k^2 q_k^2 \right)$$

(1)

is characterized by harmonic frequencies $\omega_k$, mass-weighted normal mode coordinates $q_k$ and corresponding momenta $p_k$. Vibrational energy redistribution is caused by anharmonic interactions which are described by

$$V = \frac{1}{3!} \sum_{ijk} C_{ijk}^{(3)} q_i q_j q_k + \frac{1}{4!} \sum_{ijkl} C_{ijkl}^{(4)} q_i q_j q_k q_l + \cdots$$

(2)

where $C_{ijk}^{(3)}$ and $C_{ijkl}^{(4)}$ denote third- and forth-order coupling coefficients, respectively. Adopting a time-dependent formulation, we expand the wave function as $|\Psi(t)\rangle = \sum_{\alpha} C_{\alpha}(t)|\alpha\rangle$, where basis states $|\alpha\rangle = |n_1, n_2, \ldots, n_M\rangle$ are build from harmonic oscillator eigenfunctions $|n\rangle$. The resulting time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt} C_{\alpha} = \sum_{\beta} H_{\alpha\beta} C_{\beta}$$

(3)

with Hamiltonian matrix elements $H_{\alpha\beta} \equiv \langle \alpha | H | \beta \rangle$ describe the time evolution of the system with respect to some initial condition $|\Psi(0)\rangle$. For example, in a typical laser experiment a high-frequency mode is excited at time $t = 0$ (e.g., $|\Psi(0)\rangle = |0_1, 0_2, \ldots, 1_M\rangle$) and the subsequent vibrational energy redistribution is measured by monitoring the time-dependent energy content

$$E_k(t) = \frac{1}{2} \langle \Psi(t) | \left( p_k^2 + \omega_k^2 q_k^2 \right) |\Psi(t)\rangle$$

(4)
of the normal modes of the system. Alternatively, it may be instructive to consider some local modes of the molecule, which directly reflect the spatial energy distribution of the system. For example, one may calculate the kinetic energy of, say a local CO vibration, which can approximately be obtained from (see Appendix)

$$E_{\text{CO}}(t) = \frac{1}{2} \sum_{i,k} U_{ik} \hbar \omega_k n_k(t),$$  \tag{5}$$

where index $i$ runs over the $x$, $y$ and $z$ components of the Cartesian coordinates of the C and O atoms, index $k$ labels the normal modes with eigenvector matrix $U$, $n_k(t)$ represents the occupation number of these modes, and the zero-point energy was subtracted.

While the above outlined approach in principle is straightforward, in practice it suffers from the exponential scaling of the dimension of the state space \{\ket{\alpha}\} with the number $M$ of vibrational degrees of freedom considered. To overcome this problem, a large number of methods have been proposed, ranging from numerically exact treatments such as the multi-configurational time-dependent Hartree (MCTDH) approach [21–23] to simple classical trajectory calculations [24]. The maybe most popular approach used to calculate transition rates $k_{\beta\alpha}$ in condensed-phase systems is the Golden Rule expression [25]

$$k_{\beta\alpha} \propto |\langle \beta | V | \alpha \rangle|^2 \delta(E_\beta - E_\alpha),$$  \tag{6}$$

which is based on first-order time-dependent perturbation theory. Starting from some (e.g., experimentally defined) initial state $|\alpha\rangle$, the Golden Rule only requires states $|\beta\rangle$ that can be reached by a first-order transition. In practice, one estimates the strength of the transition by the Fermi resonance parameter [16, 26]

$$f_{\beta\alpha} = \frac{|\langle \beta | V | \alpha \rangle|}{E_\beta - E_\alpha},$$  \tag{7}$$

and includes only transition with

$$E_\beta - E_\alpha \leq E_{\text{th}} \quad \text{and} \quad f_{\beta\alpha} \geq f_{\text{min}},$$  \tag{8}$$

where $E_{\text{th}}$ and $f_{\text{min}}$ are suitably chosen cut-off parameters. In this way, the Golden Rule approach only considers the few states of interest for first-order transitions (instead of the total, typically huge dimension of the underlying state space).

The so-called tier model represents a generalization of this idea to higher orders of time-dependent perturbation theory [20, 26–31]. Starting from an initial state $|\alpha\rangle = |\alpha^{(0)}\rangle$ (zeroth order), all first-order transitions with sufficient strength $f_{\alpha\beta} \geq f_{\text{min}}$ yield first-order states $|\beta^{(1)}\rangle$ (first tier, corresponding to a Golden Rule description), which subsequently give rise to second-order states $|\gamma^{(2)}\rangle$ (second tier), and so on. The procedure generates a network in state space shown in Fig. 1, which only includes states that are of importance up to a given order and therefore avoids to directly deal with the exponential size of the underlying state space. In this way, a problem-adapted basis set is constructed, for which we solve the time-dependent Schrödinger equation (3). The efficiency of the method obviously depends on how many tiers with how many states need to be used in order to model a given system to some desired accuracy.

In this work, we wish to apply the tier model ansatz to describe the vibrational dynamics of acetylbenzonitrile (AcPhCN) in chloroform. Upon excitation of the CN stretch mode and by probing a localized CO mode, Rubtsov and coworkers [4] showed that the vibrational energy relaxation and energy transport varies for the ortho, meta and para isomers of AcPhCN (Fig. 2). In particular, they found a clear correlation between the number of bonds connecting the CN mode and the CO mode and the occurrence time of the corresponding cross peak in the two-dimensional infrared spectrum. By performing comprehensive quantum-chemical calculations to parameterize the vibrational Hamiltonian [Eqs. (1) and (2)], we construct a tier model that accounts for the vibrational dynamics of AcPhCN following excitation of the CN stretching mode. The quantum dynamics study is complemented by quasiclassical trajectory simulations using the same model Hamiltonian, which allows us to identify quantum-mechanical effects (as described by the tier calculations) and nonperturbative effects (as described by the trajectory calculations) of the vibrational dynamics.

II. THEORY AND METHODS

A. Quantum-chemical calculations

All quantum-chemical calculations were performed at the B3LYP/6-31+G(d) theoretical level using Gaussian09 [32]. The effect of the chloroform solvent was implicitly treated through the polarizable continuum model (PCM) [33]. After minimizing the structures of the three
different isomers of AcPhCN, standard normal mode analysis was performed, which yields the mass-weighted Hessian matrix $\mathbf{K}$, the corresponding eigenvector matrix $\mathbf{U}$ and the diagonal eigenvalue matrix $\Lambda = \{\omega_i^2\}$, i.e., $\mathbf{KU}^\dagger = \Lambda \mathbf{U}$. Based on the resulting normal modes $\{\mathbf{q}_i\}$, we introduced corresponding harmonic basis states $|\alpha \rangle = |n_1, n_2, \ldots, n_M \rangle$.

To calculate the anharmonic potential $V$ in Eq. (2), we employed the $n$-mode coupling representation ($n$MR) [34–38]. Writing $V = V^{1MR} + V^{2MR} + V^{3MR} + \ldots$, we obtain

$$V^{1MR} = \sum_i \frac{1}{6} C_i^{(3)} q_i^4 + \frac{1}{24} C_i^{(4)} q_i^4,$$

$$V^{2MR} = \sum_{i \neq j} \frac{1}{2} C^{(3)}_{ij} q_i q_j^2 + \frac{1}{6} C^{(4)}_{ij} q_i q_j^3 + \sum_{i < j} \frac{1}{4} C^{(4)}_{ij} q_i^2 q_j^2,$$

$$V^{3MR} = \sum_{i < j < k} C^{(3)}_{ijk} q_i q_j q_k + \sum_{i \neq j < k} \frac{1}{2} C^{(4)}_{ijk} q_i^2 q_j q_k,$$  \hfill (9)

that is, the term $V^{nMR}$ accounts for the interactions between $n$ different modes. In the present case of AcPhCN, we included terms containing up to $n = 3$ modes. A calculation of the resulting anharmonic frequencies of AcPhCN using second-order vibrational quasi-degenerate perturbation theory [36] yields in general good agreement with the experimental frequencies. An exception is the CN mode, where (e.g., for the meta isomer) the calculated harmonic (2329 cm$^{-1}$) and anharmonic (2296 cm$^{-1}$) frequencies are well above the experimental frequency (2236 cm$^{-1}$). To better account for the experimental situation, we therefore red-shifted the CN mode of all isomers by 60 cm$^{-1}$.

The 3rd and 4th order coupling coefficients are calculated by numerical differentiation of the Hessian matrix [37]

$$K_{ab}(\mathbf{x}) = \frac{1}{\sqrt{m_a m_b}} \frac{\partial^2 V}{\partial x_a \partial x_b},$$  \hfill (10)

where $x_a$ is the $a$-th component of the Cartesian coordinate $\mathbf{x}$ and $m_a$ is the associated mass. Configurations slightly shifted from the equilibrium geometry $\mathbf{x}_0$ are generated via

$$(\mathbf{x}^\pm_a)_a = (\mathbf{x}_0)_a \pm \delta_1 U_{ai} \sqrt{m_a},$$  \hfill (11)

where $\delta_1$ denotes the step-size of the numerical differentiation, which is taken as $\delta_1 = \sqrt{h/\omega_0} \delta_0$ with $\delta_0 = 0.5$ [38]. The 3rd and 4th order coupling coefficients are then calculated as

$$C^{(3)}_{ijk} = \sum_{ab} \frac{K_{ab}(\mathbf{x}^+_i) - K_{ab}(\mathbf{x}^-_i)}{2\delta_1} U_{aj} U_{bk},$$  \hfill (12)$$C^{(4)}_{ijk} = \sum_{ab} \frac{K_{ab}(\mathbf{x}^+_i) + K_{ab}(\mathbf{x}^-_i) - 2K_{ab}(\mathbf{x}_0)}{\delta_1^2} U_{aj} U_{bk}.$$

B. Tier model

As explained in the Introduction, the applicability and efficiency of the tier model crucially depends on how many tiers with how many states are required to model the vibrational energy redistribution of AcPhCN to some desired accuracy. In a first step, we therefore determined the normal modes to be included in the model. Since initially the CN stretching mode ($\omega \approx 2330$ cm$^{-1}$) is excited, we can safely neglect all modes of higher frequency (such as CH stretches). Moreover, we did not include the five lowest normal modes ($\omega \lesssim 230$ cm$^{-1}$, reflecting, e.g., methyl group rotations), since standard expansions such as in Eq. (9) are known to lead to artifacts due to the large anharmonicity of these modes. In this way, $M = 36$ normal modes are taken into account.

Next, we need to select the contributing states of the various tiers. Including interaction terms with $q_k^2$ up to $n = 3$ with $|l| q_k^l m \propto \delta_{l,m,\pm3}$, maximal three quanta are exchanged in a single transition. Starting from initial state $|\alpha^{(0)}\rangle = |n_1^{(0)}, n_2^{(0)}, \ldots, n_M^{(0)}\rangle$ (zeroth order), we consider all possible states of the first tier $|\beta^{(1)}\rangle = |n_1^{(1)}, n_2^{(1)}, \ldots, n_M^{(1)}\rangle$ with $n_i^{(1)} = n_i^{(0)} \pm p$ ($p = 0, 1, 2, 3$). By calculating the Fermi parameter $f_{\alpha \beta}$ [Eq. (7)] for these states, we use condition (8) to further restrict the state space. In this way, all first-tier states are determined. For each first-tier state, we then repeat the procedure to select the second-tier states $|\gamma^{(2)}\rangle$ (from which the third-tier states are determined). States identical to states already found for a previous tier are discarded as...
well as states with \( n_i > n_{\text{max}} = 10 \). Using thresholds \( E_{\text{th}} = 200 \text{ cm}^{-1} \) as well as \( f_{\text{min}} = 0.006, 0.06 \) and \( 0.2 \) for the 1st, 2nd, and 3rd tier, respectively, the resulting dimensions of the relevant Hilbert space for the three isomers of AcPhCN (given as sum of the number of states of the three tiers) are \( 54+825+3229 = 4108 \) (ortho), \( 51+806+3146 = 4003 \) (meta), and \( 47+670+2176 = 2893 \) (para). Employing the resulting Hamiltonian matrix \( \mathcal{H}_{\alpha\beta} = \langle \alpha | H | \beta \rangle \), the time-dependent Schrödinger equation (3) is solved using a leap-frog algorithm [39] with a time step \( \Delta t = 0.1 \text{ fs} \).

C. Classical trajectory calculations

Using the anharmonic model Hamiltonian described above, we also performed nonequilibrium classical trajectory simulations of the vibrational dynamics. To solve Newton’s equation, we employed Yoshida’s 6th-order symmetric integrator [40] with a time step of 0.05 fs. Using classical action-angle variables as in [11, 14], we initially assigned a thermal energy of \( k_B T \) to all normal modes, except for the CN mode which was excited by one quantum \( h \omega \). We decided against including zero-point energy into the CN mode (see, e.g., the discussion in Refs. 11, 41), as test calculations yielded somewhat better results in this case. In this way we prepared 300 initial states, ran classical trajectories and calculated ensemble averaged normal mode energies [Eq. (4)]. Trajectories that escaped from the energy basin (a few %) due to the approximate description of the anharmonic Hamiltonian were excluded in the analysis. For easy comparison to the quantum results, all classical vibrational energies were shifted such that \( E_k(t=0) = 0 \).

III. RESULTS AND DISCUSSION

A. Convergence of tier model

We first want to study the convergence of the tier-model with respect to the number of tiers and the number of states per tier. To address the latter point, we consider the time evolution of the normal mode energy of the initially excited CN mode for different cut-off values of \( f_{\text{min}} \) and \( E_{\text{th}} \) [see Eq. (8)]. As a representative example, Fig. 3a shows the CN mode energy for the ortho isomer of AcPhCN, which is seen to decay on a picosecond time scale. Compared are three-tier calculations using our standard thresholds given above and by 50 % reduced thresholds, for which the dimension of the state space doubles. Up to about 4 ps, the agreement between the results for the two thresholds is excellent, for longer times we find deviations up to \( \approx 10 \% \). For our purposes, it seems sufficient to use the smaller basis set in all remaining calculations. Moreover, we consider the effects of the number of tiers on the relaxation dynamics of the CN mode energy. Figure 3b reveals that the Golden Rule result (corresponding to tier 1) is only sufficient for a few hundreds of femtoseconds. Including two tiers appears appropriate for a few picoseconds, where the results are qualitatively similar to our 3-tiers calculations. At longer times, we may also expect contributions from higher tiers which, however, is beyond the scope of this paper.

B. Vibrational energy redistribution

We now wish to employ the above developed tier model to discuss the photoinduced vibrational dynamics of AcPhCN. Focusing first on the ortho isomer, Fig. 4(a) shows the time evolution of the normal mode energy of the initially excited CN mode. To facilitate the comparison to experiment, here and in all following figures the vibrational energies [Eqs. (4) and (5)] are multiplied with a phenomenological damping factor \( \exp(-t/\tau) \) with \( \tau = 14 \text{ ps} \), which accounts for the dissipation of the molecule’s vibrational energy into chloroform solvent [4, 42]. An exponential fit to the resulting CN energy \( E_{CN}(t) \) gives 5.6 ps, which is in qualitative agreement with the experimental result of 3.4 ps [4].

The energy of the initially excited CN mode is redistributed into a number of weakly excited vibrations, most prominently deformation modes of the phenyl ring. As a representative example, Fig. 4(b) shows the time evolution of a ring deformation mode at 1088 cm\(^{-1}\), which picks up \( \approx 150 \text{ cm}^{-1} \) of vibrational energy within a few picoseconds. To provide an overview of the vibrational energy redistribution following CN excitation, Fig. 5 presents the integrated energy change \( \Delta E_k = 1/(12 \text{ ps}) \int_0^{12 \text{ ps}} E_k(t) dt - E_k(0) \) of the included normal modes of AcPhCN. Apart from the ring deformation vibrations at 1088 cm\(^{-1}\) (mode #21) and 1211 cm\(^{-1}\) (mode #24), the out-of-plane modes at 393 cm\(^{-1}\) (mode #3), 617 cm\(^{-1}\) (mode #10) and 786 cm\(^{-1}\) (mode #13) are found to receive significant energy. An analysis of the dominant Fermi resonance parameters [Eq. (7)] of the tier model reveals that the ring deformation modes are excited by tier-1 transitions, while the out-of-plane modes
require higher tier transitions to gain energy. The situation is similar for the meta and para isomers of AcPhCN in the sense that again some ring deformation modes and out-of-plane modes are excited. The specific modes and relaxation pathways, however, differ for the three isomers (data not shown).

C. Local motion of CO group

When we consider the energy redistribution of AcPhCN shown in Fig. 4, we find virtually no excitation of the CO normal mode. The result is consistent with an analysis of our tier model which reveals the absence of an energy transfer path to the CO mode. This finding is interesting, since the measured cross peak of the initially excited CN mode to the distant CO mode was assigned to vibrational energy redistribution between these two modes [4]. Nonetheless the finding is in line with the interpretation of the two-dimensional infrared spectrum of Rubtsov and coworkers, where the cross peak may be caused by excited low-frequency vibrations that are spatially close to the probed mode and anharmonically coupled to the CO mode [15, 43, 44].

To describe the local excitation of AcPhCN in the vicinity of the CO atoms, we suggest to consider the kinetic energy of the local CO motion, \( E_{\text{kin}}^{\text{CO}}(t) \) defined in Eq. (5). In a classical picture, \( E_{\text{kin}}^{\text{CO}}(t) \) can be imagined to report on the “local temperature” around the CO atoms (notwithstanding the problems to properly define such a temperature) [15]. To discuss the difference between normal and local vibrations (as well as kinetic and total energy), we first reconsider the CN mode shown in Fig. 4(a). We find that the kinetic energy of the local mode \( E_{\text{kin}}^{\text{CN}}(t) \) is about half the normal mode energy \( E_{\text{CN}}(t) \) of this mode. This reflects the equipartition theorem, \( \langle E_{\text{kin}} \rangle = \langle E_{\text{pot}} \rangle = \frac{1}{2} \langle E \rangle \), which is expected to hold for high-frequency modes that are fairly harmonic. Moreover

\[ \text{FIG. 4: Quantum-mechanical (top) and classical (bottom) time evolution of the energy of selected vibrations of the ortho isomer of AcPhCN, showing (a) the initially photoexcited CN mode, (b) a deformation mode of the phenyl ring, and (c) the distant CO vibration of the system. Compared are the normal mode energy [Eq. (4), blue], (twice) the kinetic energy of the corresponding local mode [Eq. (5), purple]. In all cases, the zero point energy was subtracted.} \]

\[ \text{FIG. 5: (a) Quantum (red) and classical (green) results for the energy change } \Delta E_k \text{ of the normal modes of AcPhCN. The arrows indicate the ring deformation mode at 1088 cm}^{-1} \text{ (#21) and the CO normal mode (#35). (b) Contributions of normal modes to the local motion of the CO group as described by } E_{\text{kin}}^{\text{CO}}. \text{ The inset shows an illustration of the structural change along normal mode #9 (604 cm}^{-1}).\]
it suggests that the kinetic energies of normal and local vibrations are roughly the same for a localized excited vibrational mode.

While we get similar results for the weakly excited ring deformation mode (Fig. 4(b)), the situation is quite different for the distant CO vibration. Although the corresponding normal mode is not excited, the C and O atoms nonetheless reveal significant local motion, which is reflected in a nonzero kinetic energy of the corresponding local mode $E_{\text{CO}}^{\text{kin}}$. This finding is readily explained by Eq. (5) which expands the kinetic energy of the CO local mode in terms of the normal modes of the system. Showing the resulting (time-integrated) normal mode contributions, Fig. 5b reveals that particularly normal modes with low frequency contribute to $E_{\text{CO}}^{\text{kin}}$. As an example, the inset of the figure shows an illustration of the structural change along normal mode #9. The vibration reveals a global motion of the COCH$_3$ group with respect to the phenyl ring, which obviously results in motion of the CO and thus contributes to $E_{\text{CO}}^{\text{kin}}$.

D. Structure dependent energy flow

We are now in a position to investigate the structural dependence of the vibrational energy redistribution observed for AcPhCN. Comparing results obtained for the ortho, meta and para isomers, Fig. 6 depicts the time evolution of (twice) the quantum-mechanical kinetic energy of (a) the initially excited CN mode and (b) the distant CO vibration of the system. For the CN mode, we find relaxation times of 5.6, 7.8 and 6.7 ps for ortho, meta and para isomer, respectively. The calculations compare favorably to the experimental results of 3.4, 7.1 and 7.2 ps for ortho, meta and para isomer, respectively [4]. Notably, they reproduce the experimentally observed trend that the CN mode of the ortho isomer decays somewhat faster. Considering the CO vibration, Fig. 6(b) reveals that the CO energy of the ortho and meta isomers both rise on a timescale of 1.5 ps, while the para isomer receives about half of the energy on a 1 ps timescale. The experiments revealed similar numbers (0.2, 2.2 and 2.8 ps for the deconvoluted signals [4]), except that the CO response of the ortho isomer is significantly faster than in the other cases, which is presumably caused by some relaxation pathway not considered in our model. This may be due to the neglect of low-frequency modes of AcPhCN (cf. Sec. II.B) and strongly coupling modes of the solvent molecules.

E. Comparison to classical trajectory calculations

Let us finally compare the above quantum results to the outcome of classical trajectory calculations (see Methods). As shown in the lower panels of Fig. 4, the classical results for the vibrational energies of the CN mode, the ring deformation and the CO mode match the corresponding quantum results quite well. A notable exception represents the normal mode energy of the CO vibration, which is classically excited although no quantum excitation can occur. Presenting the energy changes of the normal modes, Fig. 5 provides a more detailed picture of the quantum and classical vibrational energy redistribution in AcPhCN. While the overall features are nicely reproduced, we generally find that the quantum calculations are more mode selective, while the classical results appear more averaged. In particular, the tier model calculations predict that several modes do not get any energy at all. These findings may be caused by the absence of quantization conditions in classical mechanics, but in part may also be due to our restriction to only three tiers.

Despite well-known ambiguities concerning the quantum-classical initial conditions of the trajectory calculations and the associated discussion of quantum correction factors, this finding again shows that classical nonequilibrium calculations often describe well the energy transport in biomolecules [11, 14, 41]. This is promising, since classical trajectory calculations are readily performed for much larger systems using standard molecular mechanics force fields.

IV. CONCLUDING REMARKS

Performing comprehensive quantum-chemical calculations, we have parameterized a vibrational Hamiltonian of acetylbenzonitrile (AcPhCN) and constructed a tier model to describe the vibrational dynamics of AcPhCN following excitation of the CN stretch mode. In a first step, the convergence of the tier-model with respect to the number of tiers and the number of states per tier was tested. We have shown that the common Golden Rule result (corresponding to tier 1) is only sufficient for a few hundreds of femtoseconds, while the tier model is expected to provide at least qualitative correct results for the first few picoseconds. Moreover, we have performed complementary quasiclassical trajectory cal-
calculations, which in general were found to reproduce the energy redistribution of the quantum calculations quite well.

To study the structure dependent energy transport, we have considered the kinetic energy of the vibrational modes of AcPhCN in chloroform. The tier model calculations have been shown to qualitatively reproduce the main findings of the experiments of Rubtsov and coworkers [4], including the energy relaxation of the initially excited CN mode and isomer-dependent vibrational redistribution. The general performance of the model seems remarkable, in particular in the light of the fact that the cooling of photoexcited AcPhCN in the chloroform solvent was simply modeled by an overall phenomenological relaxation term. We have shown that the cross-peak among the CN and CO modes measured in the two-dimensional infrared spectrum does not necessarily correspond to direct excitation of the CN normal mode but may rather reflect excited low-frequency vibrations that are spatially close to the probed mode and anharmonically couple to the CO mode [15, 43]. To account for this transient feature of infrared spectra, we have proposed to consider the kinetic energy of the local CO mode, which can be imagined to report on the "local temperature" around the CO atoms.

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**V. APPENDIX: DERIVATION OF EQ. (5)**

Given mass-weighted Cartesian coordinates \( Q_i \) and momenta \( P_i \) \((i = 1, \ldots, 3N)\), the corresponding normal mode coordinates \( q_k \) and momenta \( p_k \) \((k = 1, \ldots, 3N - 6)\) are related via

\[
P_i = \sum_k U_{ik} p_k, \quad Q_i - Q_i^{\text{ini}} = \sum_k U_{ik} q_k,
\]

where \( U_{ik} \) represents the eigenvector matrix of the transformation. The kinetic energy associated with a component \((x, y \text{ or } z)\) of an atom is given by

\[
E_i^{\text{kin}} = \frac{P_i^2}{2} = \frac{1}{2} \sum_{k,l} U_{ik} U_{il} \langle p_k p_l \rangle, \quad \langle p_k p_l \rangle = \sum_{\alpha, \beta} C_{ik}^\alpha(t) C_{il}^\beta(t) \langle \alpha | p_k^\beta | \beta \rangle.
\]

The somewhat cumbersome calculations simplify considerably if we assume that \( \langle p_k p_k \rangle \ll \langle p_k p_l \rangle \) (which, though, may not be well fulfilled by low-frequency modes). Assuming furthermore that \(|\langle \alpha | p_k^\beta | \beta \rangle| \ll \langle \alpha | p_k^\beta | \alpha \rangle|\) (which is typically well fulfilled), we obtain

\[
E_i^{\text{kin}} = \frac{1}{2} \sum_k U_{ik}^2 \sum_{\alpha} (C_{ik}^\alpha(t))^2 \langle \alpha | p_k^\alpha | \alpha \rangle
= \frac{1}{2} \sum_k U_{ik}^2 \hbar \omega_k (n_k(t)+1/2),
\]

where \( n_k(t) \) is the occupation probability of normal mode \( k \). The kinetic energy \( E_{\text{CO}}^{\text{kin}}(t) \) of the diatomic CO vibrations in Eq. (5) is obtained by sumation of the \( i = x, y \) and \( z \) components of the Cartesian coordinates of the two atoms. In the case of the ring deformation mode, we included the kinetic energy of all six C atoms of the phenyl ring, and subsequently scaled the energy by a factor 0.5 in order to roughly account for the fact that only half of the ring atoms contribute to the corresponding normal mode. We note that the kinetic energy \( E_{\text{CO}}^{\text{kin}}(t) \) includes the relative motion of the two atoms to each other (the local mode) as well as the relative motion of the two atoms with respect to the rest of the molecule. Owing to its approximate nature, Eq. (16) allows us to express the atomic kinetic energy in terms of a simple sum over its normal mode contributions.


