

Rotationally induced collapse and revivals of molecular vibrational wavepackets: model for environment-induced decoherence

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Abstract

We present an analytical calculation that predicts the collapse of vibrational wavepackets in molecules due to the coupling of the rotational and vibrational degrees of freedom. At longer times a new class of revivals is predicted in the vibrational degree of freedom, due to the finite size and discrete nature of the rotational reservoir. The interplay of these competing behaviours is studied in the context of current experiments, and conditions for observing the revivals are described. Furthermore, the conditions for which the molecular vibration and rotation can be regarded as a system and its reservoir-like environment are described, in which case the ro-vibrational coupling can be considered effectively as a mechanism for decoherence of the vibrational motion. Comparison of the dephasing time predicted by this model with that observed in recent experiments is made.

1. Introduction

Decoherence is a ubiquitous phenomenon. The coupling of any quantum system to its environment necessarily limits the duration of any coherent quantum dynamics within that system. As a consequence studies of decoherence are relevant to any applications that rely on coherent evolution, such as quantum-information processing.

The distinction between a system and its environment is, however, justified only from a pragmatic point of view: the system is defined by the observable corresponding to the degree

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of freedom that can be accessed in a measurement, and the auxiliary degrees of freedom (those not measured) are accounted for by the environment. Ancillary assumptions about the nature of the coupling between the observed and unobserved degrees of freedom lead to common models of a system and a reservoir.

The usual treatments of the environment as a reservoir fall into two categories: one in which the reservoir causes a randomization of a system parameter, and a second in which a course-grained average of the system–reservoir coupling is taken. The first of these is generally referred to as the Kubo formalism, the second as the Born–Markov approximation. In the latter case the environment can be thought of as a reservoir that is of infinite size and thereby inhibits the return of any type of excitation or entropy into the system.

Because of the increasing importance of decoherence in applications, an exact model of the interaction of a system with its environment without such approximations may serve as a valuable tool for studying system–environment interactions and for understanding ways to ameliorate the detrimental effects on coherent dynamics.

For certain models of system–environment coupling, there may exist so-called decoherence-free subspaces, in which the coherent excitations of the system remain despite the coupling to a reservoir. This requires certain symmetries to be present in the coupling, and allows the effects of the environment to exactly cancel for particular combinations of system states. The number of real-world systems whose Hamiltonians have the requisite symmetries is likely to be rather small.

For small molecules coherent dynamics have been studied extensively, and coherent control of the motion of both small and larger molecules is now possible, including some highly nonlinear entities. In such complex systems not much is known about the system–environment interaction, and this makes it difficult to invent methods for avoiding decoherence. Therefore it is valuable to have a simple model that can be analysed rigorously in the context of closed-loop experiments.

In this paper we show that even a simple diatomic molecule contains a large enough number of degrees of freedom and can be measured in such a way that it conforms to the standard idea of a division of the whole into a system and a reservoir. The system in this case is the vibrational degree of freedom and the reservoir is formed by the molecular rotation. Such a division may be justified because the parts satisfy two requirements: first that the interacting degrees of freedom of the reservoir are conserved quantities and second that revivals of excitations of the system happen on a timescale much longer than the relevant system dynamics. Small molecules therefore provide a good testbed for applying the concepts of learning and feedback control to effect a suppression of the effects of decoherence.

A universal feature of two coupled finite systems, such as two coupled pendula, is a revival of certain types of single-system excitations. This type of revival may be contrasted with revivals due to non-equally spaced energy levels of a single system. In general, collapse [1] and revival [2, 3] phenomena are due to a de- and re-phasing of a quantum system. The two different types of collapse and revivals can be distinguished by the underlying dynamical features that lead to their de- and re-phasing. The first type is observed when the system under consideration reveals a non-equally spaced energy spectrum, such as produced, for example, by anharmonicities in the potential of an oscillator. Examples are collapse and revivals [4–6] and fractional revivals [7–9] in the electron wavepacket of a Rydberg atom and in the atomic centre-of-mass motion in optical lattices [10, 11]. For molecules examples of such dynamics are due to the unequal spacing of rotational levels in the rotational dynamics [12, 13] and due to the anharmonicity of the molecular internuclear potential in vibrational wavepacket motion [14–16]. We show here that there is a different kind of rotationally induced collapse and revivals dynamics, unlike that due to motion in an anharmonic potential.

The second type of collapse and revivals is produced by an interaction of the observed degree of freedom with an auxiliary quantized degree of freedom. The latter need not have unequally spaced energy levels. The mere fact that it has a discrete spectrum leads to the collapse–revival phenomenon. One of the most important theoretical examples of this type of dynamics is the Jaynes–Cummings model, in which a fermionic degree of freedom is coupled to a quantized bosonic one. It has been shown that for small times a collapse occurs in the population dynamics of the fermionic degree of freedom when the bosonic one is initially in a coherent state [1]. For longer timescales it has been predicted that the collapsed dynamics will revive periodically—the so-called Jaynes–Cummings revivals [2]. For this model also the interference between temporally overlapping revivals has been studied [17] from which fractional revivals may emerge [18]. The collapse and revival dynamics has been extensively studied for initial coherent [19, 20] and thermal states [21]. Moreover, insight into the cause of revivals has been obtained by considering the dynamics of the bosonic degree of freedom in phase space [22] as well as employing the Poisson sum formula for obtaining a general method to derive approximate analytic expressions of the observable signal [23, 24]. Experimentally, the dynamics of the collapse and revivals has been observed in cavity QED in the electronic state populations of highly excited Rydberg atoms that interact with a microwave cavity field [25, 26]. The laser-induced vibronic coupling of a trapped ion in the Lamb–Dicke regime has been shown to provide a different realization of the Jaynes–Cummings model [27]. Beyond the Lamb–Dicke regime nonlinear modifications lead to substantially different revival dynamics [28] that have been experimentally observed [29].

On the other hand molecules, having electronic, vibrational and rotational degrees of freedom, provide a multitude of possibilities to study and experimentally realize collapse and revivals dynamics of different kinds. In analogy to the Jaynes–Cummings dynamics the interaction between the electronic degrees of molecules with a quantized radiation field has been numerically studied in the context of collapse and revivals in the electronic dynamics [30]. Moreover, revivals have been predicted that are caused by a laser-induced coupling of the electronic and vibrational degrees of freedom, quite analogous to the laser-induced dynamics of trapped ions [31].

However, all the above-mentioned predictions of collapse and revival in molecular dynamics neglect entirely the rotational degree of freedom. This may be justified for ultra-cold molecules, where only the lowest rotational level is populated, but for moderately cold and hot molecules we will show here that rotationally induced effects arise that may dominate the dynamics over the previously considered mechanisms. In particular, we will show that for hot molecules, as produced for example in heat pipes, a fast collapse of the vibrational wavepacket occurs that may prevent the observation of revivals due to anharmonicities or vibronic coupling and can be thought of as decoherence⁷. Furthermore, the model that we will develop in this paper, will predict a revival dynamics solely due to the ro-vibrational coupling that is of the second type described in the introduction, as opposed to purely rotational revivals that are due to non-equal rotational level spacing [12, 13]. Numerical studies of rotationally induced revivals in the vibrational motion have been performed [32] but we present here a fully analytical treatment of the ro-vibrational dynamics and the collapse and revivals.

The outline of the paper is as follows: in section 2 we first introduce and review the ro-vibrational coupling in molecules that will define the terms used throughout the paper. Section 3 then addresses the rotationally induced collapse and revival dynamics. Here the collapse and revivals are described analytically in a prescribed approximation. Emphasis is

⁷ For radiative coupling of electronic states a similar argument applies due to the electronic energy shift $\hbar B j(j+1)$ where B in general is different in the two electronic states comprising the radiatively coupled transition.

given to the case of thermally excited molecular rotations. The possibility of observing the revivals is discussed for the case of an anharmonic inter-nuclear potential in section 5. Finally the vibrational dynamics is discussed in terms of phase-space distributions in section 6 and a summary is given in section 7.

2. Molecular ro-vibrational coupling

Clearly when studying collapse and revival phenomena of molecular vibrations reference is needed to an experimental technique to actually observe the discussed effects. Time and frequency resolved measurements of the fluorescence radiation of molecules that have been initially prepared in vibrational wavepackets by ultra-short laser pulses provide such a technique [33]. Moreover, such measurements can be used to completely reconstruct the vibrational quantum state in phase space by molecular-emission tomography (MET) [34, 35].

An important feature of fluorescence measurements arises when the experimental temporal resolution allows the observation of the molecular vibration as a quantum beat signal in a spectrally filtered component of the fluorescence, as is the case for MET. Then the dynamical interplay between rotation and vibration of a molecule happens on a timescale that is resolved in the measurement whereas the rotational sub-levels are not resolved. In this section we will briefly review the ro-vibrational coupling and discuss the validity of the performed approximations.

2.1. Approximate ro-vibrational coupling

Consider a diatomic molecule of reduced mass μ being prepared in a specific electronic state. The molecular Hamiltonian in the Born–Oppenheimer approximation reads

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \hat{U}(\hat{q}) + \frac{\hat{\mathbf{J}} \cdot \hat{\mathbf{J}}}{2\mu\hat{q}^2}, \quad (1)$$

where \hat{q} and \hat{p} are the inter-nuclear position and momentum and $\hat{U}(\hat{q})$ is the adiabatic potential surface in the considered electronic state. The third term in equation (1) represents the centrifugal barrier that becomes relevant at small inter-nuclear separations, $\hat{\mathbf{J}}$ being the angular-momentum operator. In terms of the angular-momentum states $|j, m\rangle$ the Hamiltonian (1) is diagonal and independent of m , so that it can be rewritten as

$$\hat{H} = \sum_{j=0}^{\infty} \sum_{m=-j}^j |j, m\rangle\langle j, m| \otimes \hat{H}_j, \quad (2)$$

where \hat{H}_j describes the inter-nuclear vibration in the adiabatic plus centrifugal potential for the rotational level j ,

$$\hat{H}_j = \frac{\hat{p}^2}{2\mu} + \hat{U}(\hat{q}) + \frac{\hbar^2 j(j+1)}{2\mu\hat{q}^2}. \quad (3)$$

Considering for the moment amplitudes of the inter-nuclear vibration small enough that anharmonicities can be neglected, the adiabatic potential can be taken in the harmonic approximation as

$$\frac{\hat{p}^2}{2\mu} + \hat{U}(\hat{q}) \approx \hbar\omega\hat{a}^\dagger\hat{a}, \quad (4)$$

where ω is the vibrational frequency and the ground-state energy has been discarded. The bosonic annihilation and creation operators of the vibrational quanta, \hat{a} , \hat{a}^\dagger , with commutator $[\hat{a}, \hat{a}^\dagger] = 1$, are defined via

$$\hat{q} = \bar{q} + \Delta q(\hat{a}^\dagger + \hat{a}), \quad \hat{p} = i\Delta p(\hat{a}^\dagger - \hat{a}). \quad (5)$$

The equilibrium inter-nuclear separation \bar{q} is defined in the absence of rotations ($j = 0$) and the position and momentum uncertainties in the vibrational ground state are given by $\Delta q = \sqrt{\hbar/(2\mu\omega)}$ and $\Delta q\Delta p = \hbar/2$. A second-order expansion of the centrifugal energy quantum [cf (3)] around the equilibrium position \bar{q} and application of the bosonic operators results in

$$\frac{\hbar^2}{2\mu\hat{q}^2} \approx \hbar B[1 - 2\eta(\hat{a} + \hat{a}^\dagger) + 3\eta^2(\hat{a} + \hat{a}^\dagger)^2], \quad (6)$$

where $\hbar B = \hbar^2/(2\mu\bar{q}^2)$ is the rotational energy quantum for the equilibrium inter-nuclear separation \bar{q} and $\eta = \Delta q/\bar{q}$ is a measure of the localization of the vibrational wavepacket with respect to the (rotationless) equilibrium inter-nuclear separation. As can be seen from (6) this approximation is an expansion in the (typically small) localization parameter, η , that contains three rotationally induced effects: (a) a shift of the inter-nuclear separation, (b) a change of the vibrational frequency, and consequentially (c) a squeezing of the vibrational wavepacket.

This can be seen more easily by rewriting the complete j -dependent Hamiltonian (3) as

$$\hat{H}_j = \hbar[\omega_j\hat{a}^\dagger\hat{a} + \gamma_j(\hat{a}^\dagger + \hat{a}) + \xi_j(\hat{a}^{\dagger 2} + \hat{a}^2)], \quad (7)$$

where the j -dependent vibrational frequency is

$$\omega_j = \omega + \alpha_r j(j+1), \quad (8)$$

with the spectroscopic parameter $\alpha_r = 6\eta^2 B$. The squeezing described by $\xi_j = \alpha_r j(j+1)/2$ is a direct consequence of the molecule having changed its vibrational frequency. Given the rotational statistics at hand, with typically $B \ll \omega$, a time-resolved experiment with temporal resolution $\Delta t < 2\pi/\omega$ does not resolve the rotational sub-levels. The frequency shift $\alpha_r j(j+1)$ therefore appears as inhomogeneous broadening of the vibrational frequency. Note, that the inhomogeneous broadening of the electronic transition due to rotational coupling, $\hbar B j(j+1)$, has been discarded since no electronic transitions are considered here.

The displacement coefficient $\gamma_j = -2\eta B j(j+1)$, on the other hand, is related to the spectroscopic parameter D_r that would be obtained when equating the rotationally induced centrifugal force $F \propto \gamma_j$ to the force of the adiabatic potential $-\partial U(q)/\partial q$. Inserting the resulting equilibrium position into the Hamiltonian gives the well known non-rigid rotor term of strength $D_r = (2\eta B)^2/\omega$, that is, $\gamma_j = -\sqrt{D_r\omega} j(j+1)$.

2.2. Diagonalization of the ro-vibrational Hamiltonian

For each value of j the Hamiltonian (7) can be diagonalized by use of the canonical transformation

$$\hat{a}_j = \mu_j(\hat{a} + \beta_j) + \nu_j(\hat{a}^\dagger - \beta_j), \quad (9)$$

where $|\mu_j|^2 - |\nu_j|^2 = 1$ is required to ensure the bosonic commutation relation. The Hamiltonian can then be expressed in terms of the squeezed and displaced operators (9) as

$$\hat{H}_j = \hbar\omega'_j\hat{a}_j^\dagger\hat{a}_j, \quad (10)$$

with modified vibrational frequencies

$$\omega'_j = \omega_j \sqrt{1 - \left[\frac{\alpha_r j(j+1)}{\omega + \alpha_r j(j+1)} \right]^2}. \quad (11)$$

The transformation coefficients in equation (9) are determined by the modified vibrational frequencies via

$$\mu_j = \sqrt{(\omega_j + \omega'_j)/(2\omega'_j)}, \quad \beta_j = \gamma_j/\omega'_j. \quad (12)$$

To second order in the localization parameter η the modified vibrational frequency (11) is $\omega'_j \approx \omega_j$, meaning that in this approximation the squeezing effect is neglected. This can also be observed in the canonical transformation (9), that reads in the same order of approximation as

$$\hat{a}_j \approx \hat{a} + \gamma_j/\omega. \quad (13)$$

These approximations considerably simplify our further analysis and we note that we therefore treat essentially two effects: the rotationally induced shift of the vibrational frequency and the rotationally induced displacement of the inter-nuclear separation.

2.3. Rotationally induced noise functions

We now solve for the slowly varying operators, defined as

$$\hat{b}_j(t) = \hat{a}_j(t) e^{i\omega t}. \quad (14)$$

The formal solution according to the Hamiltonian (10) is given by

$$\hat{b}_j(t) = \hat{b}_j(0) e^{-i\alpha_r j(j+1)t}. \quad (15)$$

An arbitrary normally ordered correlation function in these slowly varying operators reads

$$\langle \hat{b}_j^{\dagger m}(t) \hat{b}_j^n(t) \rangle_{\text{vr}} = \langle \hat{b}_j^{\dagger m}(0) \hat{b}_j^n(0) e^{i(m-n)\alpha_r j(j+1)t} \rangle_{\text{vr}}, \quad (16)$$

where $\langle \dots \rangle_{\text{vr}}$ denotes averaging over both the vibrational and rotational degrees of freedom. From (13) we obtain $\hat{b}_j(0) = \hat{b}(0) + \gamma_j/\omega$, where the j independent operator is defined as $\hat{b}(t) = \hat{a}(t) e^{i\omega t}$. Inserting this into equation (16) we obtain

$$\langle \hat{b}_j^{\dagger m}(t) \hat{b}_j^n(t) \rangle_{\text{vr}} = \sum_{k=0}^m \sum_{l=0}^n \binom{m}{k} \binom{n}{l} F_{m-n}^{(k+l)}(t) \langle \hat{b}^{\dagger m-k}(0) \hat{b}^{n-l}(0) \rangle_{\text{v}}. \quad (17)$$

The right-hand side expectation values only involve the vibrational state. The rotationally induced effects are now separately described by the noise functions

$$F_n^{(k)}(t) = \left\langle \left(\frac{\gamma_j}{\omega} \right)^k e^{i n \alpha_r j(j+1)t} \right\rangle_r. \quad (18)$$

The k th power of γ_j/ω appearing in the noise function (18) is very small given that we have

$$\hbar B j(j+1) \ll \frac{\hbar \omega}{2\eta}. \quad (19)$$

For a thermal rotational distribution this condition reduces to $k_B T \ll \hbar \omega/\eta$, an inequality which is easily satisfied for most experiments, since both $\eta \ll 1$ and $k_B T \ll \hbar \omega$. Thus, in the case where the condition (19) holds, equation (17) can be approximated as

$$\langle \hat{b}_j^{\dagger m+n}(t) \hat{b}_j^m(t) \rangle_{\text{vr}} = F_n(t) \langle \hat{b}^{\dagger m+n}(0) \hat{b}^m(0) \rangle_{\text{v}}, \quad (20)$$

where $F_n(t) = F_n^{(0)}(t)$. Since we neglected any effects from the rotationally induced displacement γ_j by arguing that $\gamma_j/\omega \ll 1$, we may also consistently replace $\hat{b}_j(t)$ on the left-hand side of equation (20) by $\hat{b}(t)$ to finally obtain

$$\langle \hat{b}^{\dagger m+n}(t) \hat{b}^m(t) \rangle_{\text{v}} = F_n(t) \langle \hat{b}^{\dagger m+n}(0) \hat{b}^m(0) \rangle_{\text{v}}. \quad (21)$$

On both sides of equation (21) the expectation values are taken only in the vibrational states. The effects of the ro-vibrational coupling are contained in the function $F_n(t)$. This function describes the dephasing of the vibrational wavepacket due to the coupling to the non-equally spaced rotational levels. Note, that $\langle \hat{b}^{\dagger m} \hat{b}^m \rangle$ is a constant of motion and therefore no energy is transferred between rotation and vibration in this approximation.

3. Collapse and revivals

Let us assume that at time $t = 0$ the rotational and vibrational degrees of freedom of the molecule are decorrelated. The initial ro-vibrational density operator $\hat{\rho}(0)$ at time $t = 0$ is then taken in the factorized form as

$$\hat{\rho}(0) = \hat{\rho}(0) \otimes \hat{\sigma}(0), \quad (22)$$

where $\hat{\rho}(0)$ and $\hat{\sigma}(0)$ are the initial density operators describing the vibrational and rotational degrees of freedom, respectively. This assumption is justified for the case of a thermal ro-vibrational state, for example. Moreover, the preparation of a vibrational wavepacket and/or a specific rotational state by optical excitation starting from such a decorrelated state (but in the ground electronic state) will typically only introduce minor ro-vibrational correlations, so that the state can also be described by (22) in such cases to a high degree of accuracy.

Since the dynamics only depends on the rotational number j we require only the specification of the corresponding angular-momentum distribution P_j , that is obtained from $\hat{\sigma}(0)$ as

$$P_j = \sum_{m=-j}^j \langle j, m | \hat{\sigma}(0) | j, m \rangle. \quad (23)$$

Given the distribution P_j we may now proceed to evaluate the noise function,

$$F_n(t) = \sum_{j=0}^{\infty} P_j e^{in\alpha_r j(j+1)t}. \quad (24)$$

Since the order of correlation n appears as a parameter scaling the time and since $F_{-n}(t) = F_n^*(t)$, we may use from now on the scaled time $\tau = \alpha_r t / \pi$ with $n = 1$ and evaluate, instead, the function

$$F(\tau) = \sum_{j=0}^{\infty} P_j \exp[i\pi \tau j(j+1)]. \quad (25)$$

From this function we easily obtain the n -dependence by using $F_n(\tau) = F(n\tau)$.

3.1. Derivation of the collapse and revival patterns

First we note that the noise function $F(\tau)$ in (25) is strictly periodic, i.e. $F(\tau + \tau_r) = F(\tau)$ with scaled period $\tau_r = 1$. Therefore, the time τ_r denotes the revival time. Note that in contrast to other revival mechanisms, the revival time τ_r does not depend on the rotational statistics P_j . This is due to the fact that $j(j+1)$ is an even integer number. The revivals are therefore perfect copies of the initial vibrational quantum state. Moreover, we may expect fractional revivals at fractions of τ_r , as will be discussed in more detail in a subsequent section. Here we are interested in the short-time behaviour described by the collapse and the onset of the revival patterns.

By neglecting the discrete nature of the rotational levels we could replace the sum over j by an integral. Such an approximation would be valid only for the initial dephasing at small

timescales that leads to a collapse of the vibrational wavepacket. On a longer timescale a rephasing is expected that leads to revivals in the vibrational wavepacket dynamics. This only occurs with a structured reservoir.

Therefore, in order to evaluate the sum in equation (24), and determine the form of the revival patterns, we make use of the Poisson sum formula [36]. It leads to

$$F(\tau) = \frac{1}{2}P(0) + \sum_{k=-\infty}^{\infty} I_k(\tau), \quad (26)$$

where the integrals $I_k(\tau)$ in the sum are defined as

$$I_k(\tau) = \int_0^{\infty} dj P(j) e^{i\pi[\tau j(j+1) - 2kj]}. \quad (27)$$

Here $P(j)$ is the (properly normalized) continuous version of the rotational distribution P_j ⁸. The term denoted by $k = 0$ corresponds to the collapse, i.e. is given by a decaying function $I_0(\tau)$. The higher-order terms $|k| = 1, 2, \dots$, correspond to the first, second, and so on revival pattern. These patterns should not strictly be connected to well resolved revivals, for when they overlap, more complicated structures emerge, leading to fractional revivals. However, they are especially useful for studying the onset of revivals in the context of whether they may be observed in an experiment.

The integrals (27), in general, are difficult to evaluate for most distributions $P(j)$. A stationary-phase approximation may be applied to obtain analytical expressions that reveal the essential features of the collapse and revivals dynamics. The stationary phase of the exponent in (27) is

$$j_k(\tau) = \frac{k}{\tau} - \frac{1}{2}. \quad (28)$$

Since $\tau \geq 0$ only those terms with $k > 0$ have a point of stationary phase with $j_k(\tau) \geq 0$. Therefore, apart from the case $k = 0$ that will be integrated directly to obtain the collapse, we neglect those $I_k(\tau)$ without a point of the stationary phase and restrict ourselves from now on to positive k .

The integral (27) can now be approximated by evaluating the smooth rotational distribution function $P(j)$ at the point of stationary phase. After performing the remaining Gaussian integration we obtain,

$$I_k(\tau) \approx E_k(\tau) \exp[i\phi_k(\tau)], \quad (29)$$

where the phase $\phi_k(\tau)$ is given by

$$\phi_k(\tau) = \pi \left[k - \frac{k^2}{\tau} + \frac{1 - \tau}{4} \right], \quad (30)$$

and the envelope of the oscillation is

$$E_k(\tau) = \sqrt{\frac{1}{\tau}} P[j_k(\tau)]. \quad (31)$$

Equation (29) describes the revival patterns that consist of oscillations with phase (30) and envelope (31). The phase (30) is independent of the rotational distribution $P(j)$ and embodies the essential features of the ro-vibrational coupling: its time dependence produces a chirped oscillation of $I_k(\tau)$ that is due to the unequally spaced rotational spectrum.

⁸ Here we always assume that $P(0)$ is vanishingly small, so that it may be neglected. This is also justified for thermal rotational statistics. A thermal rotational distribution exhibits a pronounced peak and is small at $j = 0$ for a reasonably large temperature because of the degeneracy with respect to the orientation of the molecular rotation.

The envelope (31), however, strongly depends on the rotational distribution and is peaked at times τ_k , that are approximately determined by the mean value j_0 of the statistics,

$$\tau_k \approx \frac{k}{j_0}. \quad (32)$$

They vanish for $j_0 \rightarrow \infty$, denoting the vanishing of these revival patterns in the classical limit where the discreteness of j gradually loses its significance. The temporal width of the envelope $E_k(\tau)$ can be estimated via the mean j_0 and the variance Δj of the rotational statistics $P(j)$ as

$$\Delta \tau_k \approx k \frac{\Delta j}{j_0^2}, \quad (33)$$

showing that the spread of the revival peaks increases linearly with k . In order to resolve the k th pattern we require that $\Delta \tau_{k+1} < \tau_{k+1} - \tau_k$, from which we obtain the condition

$$j_0 > (k+1)\Delta j. \quad (34)$$

In order to resolve higher-order revival patterns an increasingly narrow rotational distribution is required.

The initial collapse, on the other hand, reads for a Gaussian rotational distribution

$$I_0(\tau) = \frac{1}{\sqrt{1 - 2\pi i \tau (\Delta j)^2}} \exp \left[\frac{i\pi \tau \{j_0(j_0 + 1) - [\pi \tau (\Delta j)^2]^2\} - 2[\pi \tau \Delta j (j_0 + \frac{1}{2})]^2}{1 + 4[\pi \tau (\Delta j)^2]^2} \right]. \quad (35)$$

The collapse time τ_c , defined by $|I_0(\tau_c)|^2 = |I_0(0)|^2/2$, can be estimated as

$$\tau_c \approx \frac{\sqrt{\ln 2}}{2\pi} \frac{1}{\Delta j (j_0 + \frac{1}{2})}. \quad (36)$$

For a Gaussian rotational distribution the envelopes of the revival patterns are

$$E_k(\tau) = \frac{1}{\sqrt{2\pi \tau \Delta j}} \exp \left[-\frac{1}{2(\Delta j)^2} \left(\frac{k}{\tau} - j_0 - \frac{1}{2} \right)^2 \right]. \quad (37)$$

Both the collapse and the first revivals, for the case where condition (34) holds and the revivals can be resolved, are shown in figure 1. One clearly observes the interferences when the revival patterns gradually overlap.

Compared to the Jaynes–Cummings dynamics as realized with an atom interacting with a cavity field, or a single trapped ion in the Lamb–Dicke regime, the rotationally induced vibrational collapse and revival dynamics in a molecule reveal some quite different features. First, in the case of Gaussian statistics of the bosonic field of mean number n_0 in the Jaynes–Cummings model the excitation dependence of the revival times is $\tau_k \propto \sqrt{n_0}$ [37] as opposed to the $1/j_0$ behaviour for the ro-vibrational coupling considered here. Furthermore, the collapse time behaves differently from the Jaynes–Cummings case, for which $\tau_c \propto \sqrt{n_0}/\Delta n$. For the rotationally induced collapse we have $\tau_c \propto 1/(j_0 \Delta j)$, cf table 1.

These differences are mainly due to the differences in the coupling in the Jaynes–Cummings model and the ro-vibrational coupling discussed here: in the Jaynes–Cummings model coupling to the number of bosonic quanta n is represented by the functional form $\sqrt{n+1} \approx \sqrt{n}$, i.e. a square-root, in the case of ro-vibrational coupling it is just the inverse function, i.e. the square $j(j+1) \approx j^2$.

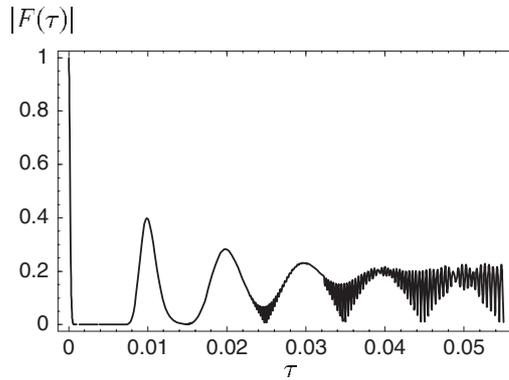


Figure 1. Collapse and revivals for a Gaussian rotational statistics with $j_0 = 100$ and $\Delta j = 10$. The modulus of the revival function $F(\tau)$ is plotted. The revivals gradually overlap and interfere for larger times, leading to complicated structures that eventually form fractional revivals.

Table 1. Comparison of the rotationally induced collapse and revivals for a Gaussian state with mean j_0 and width Δj with the corresponding case for the Jaynes–Cummings model with mean n_0 and width Δn , respectively.

	Jaynes–Cummings model	Ro-vibrational coupling
Type of coupling	$\sqrt{n + 1}$	$j(j + 1)$
Collapse time τ_c	$\propto \sqrt{n_0}/\Delta n$	$\propto 1/(j_0 \Delta j)$
Revival-pattern times τ_k	$\propto \sqrt{n_0}$	$\propto 1/j_0$

3.2. Fractional revivals

If, however, condition (34) is not fulfilled, the revival patterns substantially overlap, resulting in constructive and destructive interferences, as indicated in figure 1. Then the revival patterns (29) no longer represent individual full revivals, but their superposition gives rise to new structures that may be understood qualitatively as follows: for constructive interference of all revival patterns at a given time τ , we require the individual phases $\phi_k(\tau)$ to differ only by multiples of 2π , i.e. $\phi_{k+1}(\tau) - \phi_k(\tau) = 2\pi n_k \forall k$. Using equation (30), we obtain thereon the condition

$$\tau = \frac{2k + 1}{2n_k + 1} \quad \forall k. \tag{38}$$

For this equation to hold for all k the fraction on the right-hand side must be a constant, say $1/c$, and hence

$$n_k = c \left(k + \frac{1}{2}\right) - \frac{1}{2} \quad \forall k. \tag{39}$$

Since n_k is an integer number, c must then necessarily be an odd integer number, $c = 1, 3, 5, \dots$. Therefore the times at which the revival patterns constructively interfere are given by multiples of odd fractions of the revival time $\tau_r = 1$:

$$\tau = \frac{1}{3}, \frac{2}{3}, \frac{1}{5}, \frac{2}{5}, \frac{3}{5}, \frac{4}{5}, \dots \tag{40}$$

These are the so-called fractional revivals. It is quite interesting that these fractional revivals will only appear when the patterns (29) substantially overlap and interfere. Moreover, the fractional revival times are entirely independent of the rotational statistics. The latter only determines their strength by enabling or disabling interference between the revival patterns and

by determining the overall amplitude of the patterns. Thus, when the revival patterns do not overlap, fractional revivals are suppressed and the patterns themselves represent the revivals, with peak times given by (32). In any case, however, the onset of a revival signal is given by the peak time of the first revival pattern $\tau_1 = 1/j_0$.

4. Thermally induced collapse and revivals

In a typical vibrational-wavepacket experiment, such as those performed in [33–35], where the molecules were produced in a heat pipe, the molecular gas is initially thermalized at a temperature T . The continuous version of the angular-momentum distribution is

$$P(j) = \beta(2j + 1) \exp[-\beta j(j + 1)], \quad (41)$$

where $\beta = \hbar B/(k_B T)$, with k_B being Boltzmann's constant. The function $I_0(\tau)$ that determines the collapse can be directly integrated in equation (27) to give

$$I_0(\tau) = \frac{\tau_c}{\tau_c - i\tau}, \quad (42)$$

where the temperature-dependent collapse time τ_c is defined as the time when the modulus of the function $I_0(\tau)$ decays to $1/\sqrt{2}$:

$$\tau_c = \beta/\pi. \quad (43)$$

Furthermore, using the thermal distribution (41) we obtain from the condition (32) the times of the peaks of the revival patterns as

$$\tau_k \approx k\sqrt{\beta}. \quad (44)$$

Hence the onset of revivals is expected at the scaled time $\tau_1 \approx \sqrt{\beta}$. The explicit form of the envelope of the revival patterns for a thermal rotational distribution can be obtained as,

$$E_k(\tau) = \frac{\beta}{\sqrt{2k}} \left(\frac{2k}{\tau}\right)^{\frac{3}{2}} \exp\left\{\frac{\beta}{4}\left[1 - \left(\frac{2k}{\tau}\right)^2\right]\right\}. \quad (45)$$

The width and mean of the thermal rotational statistics are related in such a way that the condition (34) is never satisfied. Thus the envelopes of the revival patterns (45) always overlap, as can be seen from the ratio $\Delta j/j_0$ shown in figure 2. This ratio never goes below 0.5 and therefore even the first revival pattern overlaps the second pattern. The strong overlap of patterns and the appearing interference effects produce the (fractional) revivals at odd fractions of the full revival time τ_r . This can be observed in figure 3 where the dynamics up to the time of the complete revival are shown. The figure shows also that for increasing temperature (β decreasing) the fractional revivals become sharper.

The peak strength of each individual revival pattern is given by

$$\max E_k = \frac{3^{\frac{3}{4}}}{\sqrt{2k}} \beta \exp(-\frac{1}{4}\beta), \quad (46)$$

which depends on k and via β on the temperature T and the molecular rotational constant B . For the relevant range of the ratio of rotational to thermal energy, $\beta \approx 0, \dots, 0.5$, the maximum peak strength (46) is approximately linear in β . That means, that for larger temperature (smaller β) the overall strength of the revivals becomes smaller, as observed in figure 3.

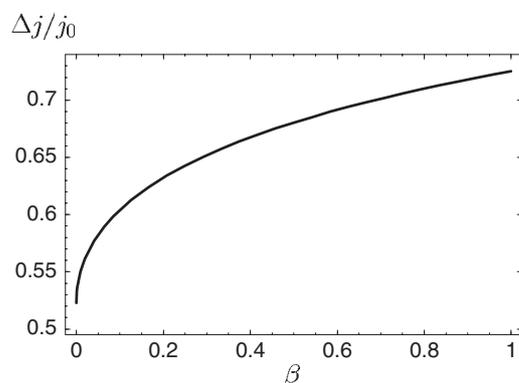


Figure 2. The dependence on β of the relative width $\Delta j/j_0$ of the thermal rotational distribution. Even for large temperatures ($\beta \rightarrow 0$) it never goes below 0.5, preventing the resolution of individual revival patterns.

5. Observability of the revivals and effective rotational reservoir

In this section we consider whether these collapse and revival phenomena may be observed experimentally. In MET the molecular vibration produces a quantum beat signal in the fluorescence of initially electronically excited molecules. In recent experiments with potassium molecules produced in a heat pipe [35], the rotational temperature was $T = 400^\circ\text{C}$, from which the time of the onset of revivals of the vibrational amplitude is calculated via (44) as $t_1 \approx 170$ ps. Given the vibrational period of $2\pi/\omega \approx 470$ fs this time corresponds to 360 vibrational periods. The radiative lifetime of the fluorescing state $A^1\Sigma_u^+$ is about 10 ns, corresponding to approximately 20 000 vibrational periods. This should be compared to 360 periods for the revival. The first full revival should therefore be observable in this system, barring other effects.

Moreover, in the heat pipe the ensemble of excited molecules that contribute to the observed signal diffuses out of the region of focus in a time t_d . Given a size of the focus region of 2 mm and a thermal speed of the potassium molecules at $T = 400^\circ\text{C}$ of $v_{\text{th}} \approx 270$ m s $^{-1}$, the maximum time the excited molecules contribute to the measured signal is $t_d \approx 7$ μs . Therefore, also the thermal diffusion should not inhibit the observation of the rotationally induced revivals.

5.1. Rotational versus anharmonic effects

As indicated in the introduction, the anharmonicity of the vibrational potential provides an auxiliary and independent mechanism for revivals in the molecular vibration. We may approximate the n -dependent vibrational frequencies $\omega(n)$ most simply by a quadratic function that describes the anharmonicity,

$$\omega(n) = \omega n + \frac{1}{2}\omega' n^2. \quad (47)$$

In such a potential the collapse of the vibrational coherence (i.e. the delocalization of the wave packet) is expected at time $\tau_c^{(\text{ah})}$ where the tails of the vibrational distribution are in phase, i.e.,

$$\frac{1}{2}[\omega'(n_0 + \Delta n/2)^2 - \omega'(n_0 - \Delta n/2)^2]\tau_c^{(\text{ah})} = 2\pi, \quad (48)$$

with n_0 and Δn being the average vibrational number and the variance, respectively. Solving equation (48) for $\tau_c^{(\text{ah})}$ we obtain

$$\tau_c^{(\text{ah})} \approx \frac{2\pi}{\omega' n_0 \Delta n}. \quad (49)$$

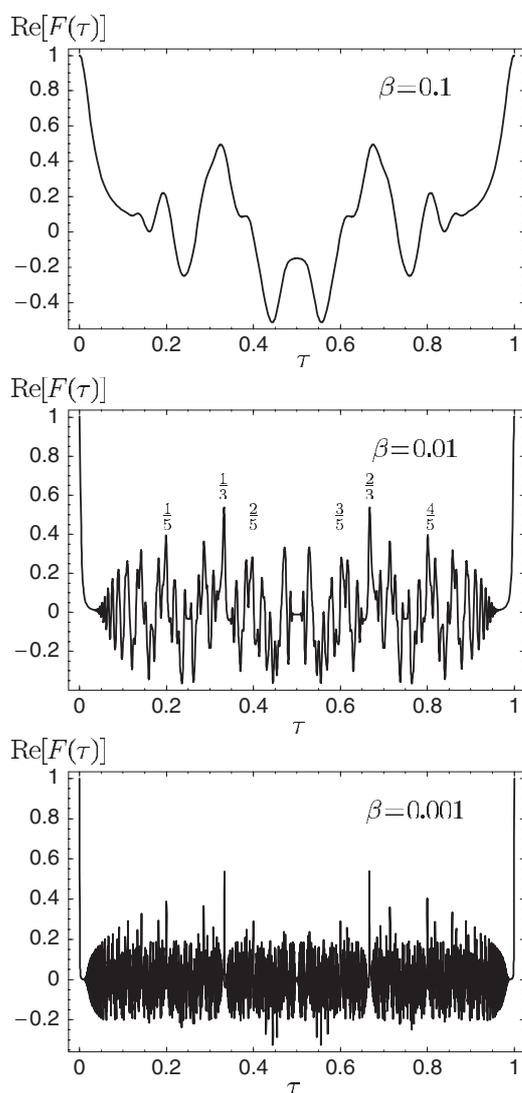


Figure 3. Fractional revivals for different thermal rotational excitations: $\beta = 0.1, 0.01, 0.001$. For $\beta = 0.01$ the first series of fractions of the full revival time have been indicated schematically by their order number.

The revivals due to the anharmonicity, on the other hand, are determined by the condition that neighbouring vibrational number states near the average excitation are in phase,

$$\frac{1}{2}[\omega'(n_0 + 1)^2 - \omega'n_0^2]\tau_r^{(\text{ah})} = 2\pi k. \quad (50)$$

From this condition the time of the k th revival is obtained as

$$\tau_r^{(\text{ah})} \approx \frac{2\pi k}{\omega'n_0}. \quad (51)$$

For potassium molecules the anharmonicity parameter of the $A^1\Sigma_u^+$ potential surface is $\omega'/(2\pi) \approx -4.5$ GHz and the typical mean vibrational excitation in the experiments is of the order of $n_0 \approx 10$. The resulting time for the first full revival is then $\tau_r^{(\text{ah})} \approx 22$ ps, i.e.

about 40 vibrational periods. However, due to the rotationally induced collapse at around seven vibrational periods the revival due to the anharmonicity is not observed in the experiment.

On the other hand, the collapse due to the anharmonicity may prevent the observation of rotationally induced revivals. In the above mentioned experiment the reconstruction of the phase-space distribution of the vibrational quantum state reveals amplitude squeezing of the vibration, $\Delta n < \sqrt{n_0}$. This may be due to the non-impulsive vibrational-wavepacket excitation via a Franck–Condon transition. In any case amplitude squeezing further prolongs the collapse time due to anharmonicity beyond the value of $\tau_c^{(ah)} \approx 7$ ps for a Poissonian distribution. Therefore, one may expect that the observed collapse is due to the rotational effect and that rotational revivals are suppressed by the anharmonic collapse.

5.2. Molecular rotation as decohering reservoir

Clearly the only possible way for rotational revivals to be observed in the presence of vibrational anharmonicities is to adjust the rotational statistics and/or the vibrational statistics in such a way that the first rotational revival coincides with one of the anharmonic revivals. A subtle adjustment of rotational reservoir and vibrational wavepacket is therefore required to enable an observation of a joint rotationally and anharmonically induced revival in the molecular vibration.

If these two revival mechanisms are not adjusted, the wavepacket collapse due to either mechanism will suppress the revivals due to the other and a decoherence mechanism emerges that operates on a timescale determined by the shortest collapse, which, in the case of [35], is the rotationally induced one. Then the molecular vibration can be considered phenomenologically, to very good approximation, as a weakly anharmonic oscillator of mean frequency ω coupled to a reservoir that provides an effective decoherence mechanism. Clearly that means that for a very long time no revival will appear, and the combined effects of ro-vibrational coupling and vibrational anharmonicity mimic an environment that acts as a reservoir of very large, in fact almost infinite, size.

6. Phase-space picture of rotationally induced collapse and revival

6.1. Dynamical evolution in phase space

An intuitive picture of the rotationally induced collapse and revival dynamics can be developed in the phase space of the molecular vibration. Since equation (21) holds for all $m, n \geq 0$, knowledge of the function $F(\tau)$ gives complete information on the vibrational quantum state at hand. We can therefore equally well generate a description of the vibrational dynamics in phase space. In order to do so, we note that the Glauber–Sudarshan phase-space distribution, $W_{s=1}(\beta, t)$, allows any normally ordered expectation value, such as in (21), to be formally expressed as a phase-space integral [38]. Performing this on both sides of (21) we obtain the relation

$$\int d^2\beta \beta^{*m} \beta^n W_1(\beta, \tau) = \int d^2\beta F[(m-n)\tau] \beta^{*m} \beta^n W_1(\beta, 0), \quad (52)$$

that relates the phase-space distribution at (scaled) time τ to its initial distribution at time $\tau = 0$, $W_1(\beta, 0)$. Since equation (52) holds for all $m, n \geq 0$, by transforming to polar coordinates, $\beta = re^{i\phi}$, and performing a discrete Fourier transform with respect to $m - n$ we obtain the P function in polar coordinates at time τ as

$$W_1(r, \vartheta, \tau) = \int_0^{2\pi} d\phi P_{cr}(\vartheta - \phi, \tau) W_1(r, \phi, 0). \quad (53)$$

Here $P_{\text{cr}}(\phi, \tau)$ describes the vibrational dephasing and rephasing due to the ro-vibrational coupling, leading to the collapse and the revivals,

$$P_{\text{cr}}(\phi, \tau) = \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} F(n\tau) e^{in\phi}. \quad (54)$$

Inserting for $F(\tau)$ the Poisson formula (26) we obtain the dephasing distribution as

$$P_{\text{cr}}(\phi, \tau) \approx \frac{1}{2} P(0) \delta(\phi) + P_c(\phi, \tau) + P_r(\phi, \tau). \quad (55)$$

Here the collapse dephasing distribution reads

$$P_c(\phi, \tau) = \frac{1}{2\pi} + \frac{1}{\pi} \text{Re} \sum_{n=1}^{\infty} I_0(n\tau) e^{in\phi}, \quad (56)$$

and the various k th revival patterns for the n -order correlations are represented by

$$P_r(\phi, \tau) = \sum_{k=1}^{\infty} \sum_{n=1}^{\infty} R_n^{(k)}(\phi, \tau), \quad (57)$$

$$R_n^{(k)}(\phi, \tau) = \frac{1}{\pi} \text{Re} [I_k(n\tau) e^{in\phi}]. \quad (58)$$

Note that (53) can be generalized to arbitrary s -parametrized quasi-probability densities, $W_s(\alpha)$, in phase space. Then the collapse and revival dynamics are described by the integral formula

$$W_s(\alpha, \tau) = \int_0^{2\pi} d\phi P_{\text{cr}}(\phi, \tau) W_s(\alpha e^{-i\phi}, 0). \quad (59)$$

6.2. Thermally induced collapse and revivals

For a thermal rotational statistics the collapse dephasing distribution (56) can be evaluated by performing the discrete Fourier transform (cf [39]). A time-dependent exponential dephasing distribution, normalized on the interval $\phi \in [0, 2\pi]$, is obtained,

$$P_c(\phi, \tau) = \frac{\tau_c/\tau \exp[-\phi\tau_c/\tau]}{1 - \exp[-2\pi\tau_c/\tau]}, \quad (60)$$

with τ_c being defined in (43). The average phase drift produced by $P_c(\phi, \tau)$ during the collapse is

$$\bar{\phi}_c(\tau) = \tau/\tau_c - \frac{2\pi}{\exp[2\pi\tau_c/\tau] - 1}, \quad (61)$$

with $\lim_{\tau \rightarrow \infty} \bar{\phi}_c(\tau) = \pi$. More importantly, the variance of the phase can be given in this case as

$$\Delta\phi_c(\tau) = \left[(\tau/\tau_c)^2 - \frac{2\pi^2}{\cosh(2\pi\tau_c/\tau) - 1} \right]^{\frac{1}{2}}, \quad (62)$$

which for small times is $\Delta\phi_c \sim \tau/\tau_c$ and for infinite time reaches the value $\lim_{\tau \rightarrow \infty} \Delta\phi_c(\tau) = \pi/\sqrt{3}$, corresponding to a constant phase distribution in the interval $[0, 2\pi]$, as shown in figure 4. The collapse of an initially coherent state of the vibrational motion in phase space is shown in figure 5, where the Husimi Q function ($s = -1$) is plotted. One clearly observes the dephasing that eventually leads to the disappearance of a coherent vibrational amplitude. This collapse has been observed recently in the context of MET [35] and our model agrees perfectly with the observed collapse time. It remains an open question whether the vibrational collapse can be controlled by close-loop learning control or optimal-control methods cf [40].

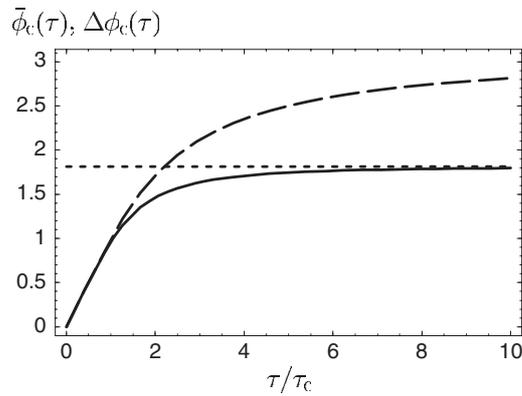


Figure 4. Time dependence of the average phase drift $\bar{\phi}_c(\tau)$ (dashed curve) and variance $\Delta\phi_c(\tau)$ (solid curve) of the collapse dephasing distribution $P_c(\phi, \tau)$.

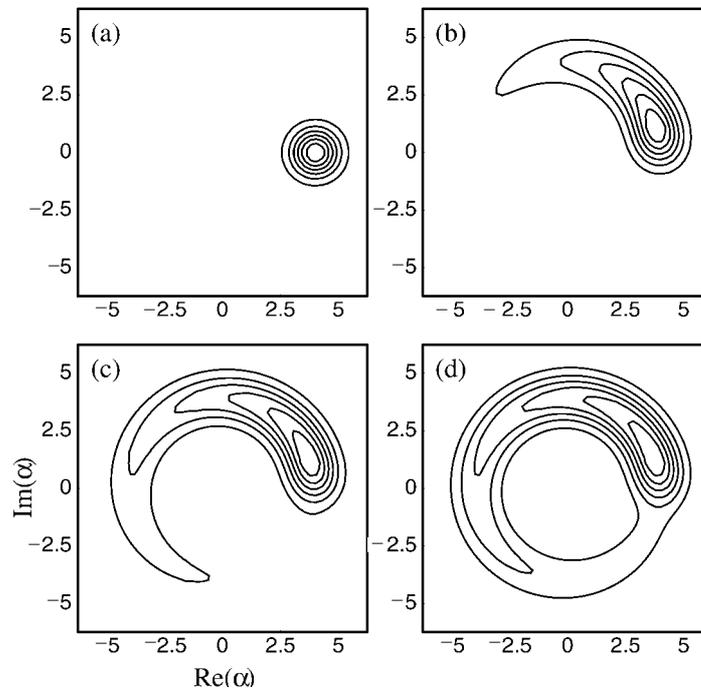


Figure 5. Collapse of an initial coherent state due to coupling to a thermal rotational distribution. The scaled and dimensionless times are $\tau/\tau_c = 1$ (a), 2 (b), 3 (c) and 4 (d).

For the phase distributions of the revival pattern $R_n^{(k)}(\phi, \tau)$ we may, in the general case, substitute for the $I_k(\tau)$ by equations (29) and (30) to obtain

$$R_n^{(k)}(\phi, \tau) = \frac{1}{\pi} E_k(\tau) \cos \left\{ n\phi + \pi \left(k + \frac{1}{4} \right) - n\pi\tau \left[\left(\frac{k}{n\tau} \right)^2 + \frac{1}{4} \right] \right\}. \quad (63)$$

These functions are $2\pi/n$ -periodic in ϕ , showing that n corresponds to the number of peaks on a circle in phase space that emerge in the revival of a n th-order correlation function. For a thermal rotational statistics, these peaks will not be resolved due to the fact that subsequent

revival patterns will strongly overlap. For a sufficiently narrow Gaussian rotational distribution, however, at least the first few revival peaks should be observable in the reconstructed phase-space distribution of the vibrational quantum state.

7. Summary and conclusions

In this paper we have shown that the ro-vibrational coupling in molecules leads to a new and interesting collapse and revival phenomena in the inter-nuclear vibration. Based on a model of the ro-vibrational coupling that takes into account terms up to second order in the localization parameter η , analytic expressions for the collapse and revival patterns of the complete quantum state have been derived for general rotational statistics.

In general the system reveals a periodicity that corresponds to a complete revival that is independent of the rotational statistics. Moreover, for a narrow rotational distribution, the calculated revival patterns appear as individual revival signals at times that are determined by the average rotational excitation. In the case of thermal rotational statistics, however, all these patterns overlap and the interference that occurs between the patterns results in constructive interference at times that are multiples of odd fractions of the complete revival time. The collapse phase of the vibrational wavepacket has been observed experimentally using MET [35]. This demonstrates the validity of the ro-vibrational coupling at high temperatures as a mechanism of decoherence. To our knowledge, the new class of rotationally induced revivals in the molecular vibrational motion has not yet been observed.

Furthermore, we have shown for typical experimental parameters and for potassium molecules that anharmonicities of the internuclear potential are less important compared to the rotationally induced effects when it comes to the collapse of the vibrational wavepacket. For an experimental observation of rotationally induced revivals of vibrational wavepackets a tailoring of vibrational and rotational statistics is required to adjust the relative significance of the revivals due to anharmonicities and to ro-vibrational coupling. In this context a non-thermal rotational distribution may prove suitable. This suggests that one should direct attention to current and future experimental developments such as cooling and quantum-state preparation, for both the vibrational and the rotational degree of freedom of molecules, which may provide the control necessary to realize the revivals.

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Glauber R J 1963 *Phys. Rev.* **131** 2766
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