PHYSICAL REVIEW A **81**, 043405 (2010)

# Control of dephasing in rotationally hot molecules

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(Received 19 November 2009; published 12 April 2010)

We consider a rotationally hot diatomic molecule as an example of an open quantum system, where molecular vibrational wave packets are subject to dephasing due to rovibrational coupling. We report analytical and numerical results addressing whether the dephasing rate can be controlled by adjustment of the initial wave packet phases. It appears that over long time scales, phase-only control is not possible, but for earlier time scales the possibility of phase-only control of dephasing remains. In addition, we point out that the time dependence of the dephasing process depends significantly upon the degeneracy of the rotational environment states.

DOI: 10.1103/PhysRevA.81.043405 PACS number(s): 32.80.Qk, 33.80.−b, 33.20.Vq

## I. INTRODUCTION

An open quantum system consists of a system of interest that is coupled to an environment. Nonunitary evolution of the system can then occur, including decoherence (the reduction of the purity of the system state) which destroys coherent superpositions. Since all quantum systems in nature interact with some environment, the understanding of open system dynamics is an important topic.

In this article we consider a rotationally hot diatomic molecule, defining the system as the vibrational degree of freedom and the environment as the rotational degree of freedom. This simple example of an open quantum system is relatively straightforward to examine theoretically, convenient to study experimentally, and has been actively studied [1–3]. At temperatures around 400°C (typical for production of alkali-metal dimers from an oven source), ∼100 rotational states $J$ will be populated thermally. Note that the rotational state $J$ is $(2J+1)$-fold degenerate. Since the vibrational frequency is dependent on rotational quantum number $J$ thanks to centrifugal distortion, vibrational wave packets moving on different ($J$-dependent) potential energy surfaces will dephase over time. We investigate the possibility of controlling this rotationally induced dephasing process by shaping the initial vibrational wave packet. The article by Branderhorst *et al.* [3] suggests that *phase-only* shaping of the initial wave packet can have an effect on the dephasing rate. Our work addresses the effectiveness of such phase-only shaping in this particular system.

We report analytical and numerical results. Numerical simulations show no readily apparent effect of phase-only shaping, except by interaction between the quadratic chirp of the vibrational phases and the anharmonicity. This is just an example of the well-known wave packet focusing [4] in an anharmonic potential and does not relate to the thermal dephasing dynamics. In order to understand the numerical results, analytical calculations were performed, including a calculation for zero anharmonicity (the case discussed in [3]). These calculations show that over long time scales, phase-only shaping of the initial wave packet has no effect on the dephasing. However, at intermediate time scales, the possibility of controlling the dephasing rate remains.

## II. DEPHASING OF MOLECULAR VIBRATIONAL WAVE PACKETS DUE TO ROTATIONAL TEMPERATURE

### A. Characterization and measurement of wave packet dephasing

Before discussing the details of wave packet dynamics in a rotationally hot diatomic molecule, it is important to stress the difference between rotationally induced dephasing and decoherence associated with entanglement between a system and its environment. This distinction is discussed, for example, in Chapter 2 of [5] and Chapter 3 of [6]. In [5] it is argued that a key distinction between classical noise or pure dephasing and real decoherence is that, in the latter case, the system perturbs the environment in addition to being perturbed by it.

In the standard treatment of an open system [7], we call the Hilbert space of the system $\mathcal{H}_S$ and that of the environment $\mathcal{H}_B$, so that the Hilbert space of the total system is $\mathcal{H}_S \otimes \mathcal{H}_B$. Then the total Hamiltonian is

$$H = H_S \otimes I_B + I_S \otimes H_B + H_I. \tag{1}$$

Here $H_S$ and $H_B$ are the free Hamiltonians of the system and the environment, respectively, $I_S$ and $I_B$ are the identity operators in the system and environment subspaces, and $H_I$ is the interaction Hamiltonian.

We now focus on the rovibrational motion of a diatomic molecule. Within the Born-Oppenheimer approximation, assuming the molecule is in a given electronic state $|i\rangle$, it is possible [1] to rewrite the rovibrational Hamiltonian for the total system in the following form:

$$\begin{aligned} H &= \frac{\hat{p}^2}{2\mu} + U_i(\hat{R}) + \frac{\hat{J}^2}{2\mu\hat{R}^2} \\ &= \left(\frac{\hat{p}^2}{2\mu} + U_i(\hat{R})\right) \otimes I_r + I_v \otimes \frac{1}{2\mu R_{\mathrm{eq}}^2}\hat{J}^2 \\ &\quad + \left(\frac{1}{2\mu\hat{R}^2} - \frac{1}{2\mu R_{\mathrm{eq}}^2}\right) \otimes \hat{J}^2 \end{aligned} \tag{2}$$

Here $\hat{R}$ and $\hat{p}$ are the internuclear coordinate and momentum operators, respectively, $R$ is the equilibrium internuclear distance, $\mu$ is the reduced mass, $U_i(R)$ is the molecular potential energy surface, $I_r$ and $I_v$ are the identity operators on the rotational and vibrational subspaces, respectively, and

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$\hat{J}^2$ is the angular momentum operator (in units of $\hbar^2$). In the aforementioned form, the rovibrational Hamiltonian resembles the open system Hamiltonian (1), with $H_S = \frac{\hat{p}^2}{2\mu} + U_i(\hat{R})$, $H_B = \frac{1}{2\mu R_{\text{eq}}^2}\hat{J}^2$, and $H_I = (\frac{1}{2\mu\hat{R}^2} - \frac{1}{2\mu R_{\text{eq}}^2}) \otimes \hat{J}^2$.

Note that in this case $[H_I, H_B] = 0$, so the system-environment interaction does not affect the environment states, that is, the rotational $J$ states. In this case, if the total system starts in a state $|\Psi_v(R)\rangle|J\rangle$, it evolves into $|\Psi_{v,J}(R,t)\rangle|J\rangle$, developing no entanglement. Thus, averaging over the thermal distribution in a rotational ensemble results in pure dephasing. This is to be expected, since the vibrational and rotational parts of the rovibrational wave function are always separable.

If the diatomic molecule is modeled as a Morse oscillator, the standard approximation for the energy of the state with vibrational quantum number $v$ and rotational quantum number $J$ is

$$\begin{aligned} E(v,J) = {} & \omega_e\left(v+\tfrac{1}{2}\right) - \omega_e x_e\left(v+\tfrac{1}{2}\right)^2 \\ & + \left[B_e - \alpha_e\left(v+\tfrac{1}{2}\right)\right]J(J+1) - D_e J^2(J+1)^2. \end{aligned} \tag{3}$$

Here $\omega_e$, $\omega_e x_e$, $B_e$, and $D_e$ are the usual spectroscopic constants [8]. If the rotations are confined to a plane, we instead have $J^2$ wherever $J(J+1)$ appears in (3). Since $\langle J\rangle \approx 100 \gg 1$, this difference is negligible.

Equation (3) for $E(v,J)$ can be rewritten in the following form by introducing the $J$-dependent vibrational frequency $\omega_J = \omega_e - \alpha_e J(J+1)$:

$$\begin{aligned} E(v,J) = {} & \omega_J\left(v+\tfrac{1}{2}\right) - \omega_e x_e\left(v+\tfrac{1}{2}\right)^2 + B_e J(J+1) \\ & - D_e J^2(J+1)^2. \end{aligned} \tag{4}$$

If we have, for a molecule with a given $J$, a wave packet $|\Psi_J(t)\rangle$ over the vibrational states $|vJ\rangle$ (which are $J$ dependent thanks to the centrifugal distortion), its time evolution is

$$|\Psi_J(t)\rangle = \textstyle\sum_v a_{vJ} e^{-iE(v,J)t}|vJ\rangle. \tag{5}$$

Here $a_{vJ}$ are the wave packet amplitudes. The rovibrational coupling term in $\omega_J = \omega_e - \alpha_e J^2$ will cause wave packets for different $J$ values to dephase with each other over time [9]. This dephasing process is not irreversible; there will be revivals of the phase coherence of the ensemble. In general, however, these revivals will not coincide with the revivals due to the anharmonicity $\omega_e x_e$, and from an observational standpoint the process looks like an irreversible dephasing.

Now we focus on the case of vibrational wave packets created by one-photon excitation due to a laser pulse, as in the theoretical and experimental work described in Refs. [1] and [3]. We assume that the spectral amplitudes of the pulse have their *phases* shaped at the experimenter's wish, but their *magnitudes* are unaffected by the pulse shaper. In the experiment [3] the molecules under consideration are potassium dimers at 400°C. At this temperature all molecules in the ensemble are in the electronic ground state. For simplicity, we assume that only the ground vibrational state is populated—in fact $\langle v\rangle \approx 1$ at this temperature, but the standard deviation of the thermal distribution $\Delta v_T \approx 3$—so full accuracy would require consideration of the first few vibrational levels. This assumption does not affect our conclusions since the effect of thermal occupation of different vibrational states is similar to that of rotational states. The rotational states are incoherently populated at temperature $T$; that is, the rotational density matrix is diagonal with populations $P(J) = Z^{-1}(2J+1)\exp\{\frac{-B_e J^2}{kT}\}$, where $Z$ is the partition function. Here the $2J+1$ factor appears in the 3D case and is absent in the 2D case. We perform calculations both with and without this factor.

Our goal is to see whether a phase-only shaping of the wave packet can produce substantial suppression of rovibrational dephasing. To consider control of this dephasing, it is crucial to define how the dephasing is *measured*. We follow [3] and we consider the frequency-gated fluorescence signal from the molecules. Note that this measurement is not resolved in the basis of eigenstates of the rovibrational Hamiltonian $H_i$—rather it is position resolved. We can think of the contribution to the fluorescence signal from a given wave packet $|\Psi_J(t)\rangle$ as the overlap between the wave packet and a gate function $|\Phi_G\rangle = \sum_v g_{v,J}|vJ\rangle$. The gate is a function in space (i.e., in the internuclear coordinate $R$) here given in the basis of the $|vJ\rangle$ wave functions. Since the form (in space) of the gate function should be exactly the same for all $J$, the amplitudes $g_{v,J}$ will be somewhat different for different values of $J$.

At this stage it is worth comparing the question posed here with the standard case of coherent control, for example, control of a chemical reaction. In the case where our measurement is resolved in the basis of the energy eigenstates, we can only achieve phase-only control via interference of multiple indistinguishable optical pathways [7]. Otherwise, spectral phases contribute only to phases in the various energy-eigenstate amplitudes, which have no effect when we make a measurement in this energy eigenstate-resolved basis (since only the modulus squared of the amplitudes will affect the measured yield in each eigenstate). This is the "emperor without clothes" argument in a 1989 article by Brumer and Shapiro [10]—an apparent avenue for control which cannot, in fact, work.

Since we do not consider multiple interfering optical pathways, it might appear that one-photon phase-only control could not possibly work for our system. But since our measurement of the dephasing is *not* resolved in the energy eigenbasis, the aforementioned argument does not apply, and phase-only control is *in principle* achievable.

The overlap between $|\Psi_J(t)\rangle$ and $|\Phi_G\rangle$ is

$$\begin{aligned} Q(J,t) &= \langle\Phi_G|\Psi_J(t)\rangle \\ &= \sum_v g_{vJ}^* a_{vJ} e^{-iE(v,J)t}. \end{aligned} \tag{6}$$

The function $Q(J,t)$ characterizes the electromagnetic field emitted by a molecule in a particular $J$ state, and the detected signal (the intensity of the emission) is proportional to $|Q(J,t)|^2$:

$$|Q(J,t)|^2 = \sum_v\sum_{v'} A_{vJ}A_{v'J}e^{-i\{\omega_J(v-v')-\omega_e x_e[(v+\frac{1}{2})^2-(v'+\frac{1}{2})^2]\}t}, \tag{7}$$

where $A_{vJ} = g^*_{vJ} a_{vJ}$ are complex numbers and the solely $J$ dependent terms in $E(v,J) - E(v',J)$ have canceled. We now assume the rovibrational coupling is weak and neglect the $J$ dependence of the $A_{vJ}$ factors. This is equivalent to neglecting the rotational distortion of the vibrational wave functions for the duration of the pump pulse. However, for the long-term evolution, we preserve the rovibrational distortion within the $J$-dependent *phase*, where the effect is accumulated over time. In place of $A_{vJ}$ we have the purely $v$-dependent constants $A_v = |A_v| e^{i\theta_v}$.

We assume that the intensity of the laser pulse which creates our wave packet $|\Psi_J(t)\rangle$ on an excited electronic surface is in the weak-field (perturbative) regime. This has two consequences. Firstly we may neglect the molecular alignment effect of the laser, since the aligning interaction energy will be $\ll kT$. This leaves the rotational density matrix in the form given previously. Second, in the perturbative regime each eigenstate amplitude $|A_v| e^{i\theta_v}$ in the created wave packet is proportional to the spectral amplitude of the laser field at the relevant transition frequency. For this reason, phase-only shaping of the laser pulse results *solely* in adjustment of the initial phases $\theta_v$.

Since the spontaneous emission of molecules in different $J$ states is not coherent, the total fluorescence signal from the thermal ensemble of molecules is proportional to

$$S(t) = \sum_{J=0}^{\infty} P(J) |Q(J,t)|^2 \tag{8}$$

$$= \sum_{J=0}^{\infty} \sum_{v} \sum_{v'} P(J) |A_v| |A_{v'}| \times e^{-i\{\theta_{v'} - \theta_v + \omega_J (v - v') - \omega_e x_e [(v+\frac{1}{2})^2 - (v'+\frac{1}{2})^2]\} t}. \tag{9}$$

The qualitative behavior of these functions can be summarized as follows. As the wave packet moves between the inner and outer turning points, $|Q(J,t)|^2$ will oscillate with the average vibrational period $\omega_{\bar{v}} = \frac{\partial E}{\partial v}|_{v=\bar{v}}$. For nonzero anharmonicity ($\omega_e x_e > 0$) the wave packet spreads over time. $|Q(J,t)|^2$ undergoes the well-known decay and revivals, including fractional revivals, as the $E(v,J)t$ phase factors for different $v$'s de- and rephase with one another. In principle the $J$-dependent component of the phase evolution will also display revivals [2], but these will not, in general, coincide with the revivals due to anharmonicity. Thus the combination of anharmonic and rotational dephasing will typically result in a signal $S(t)$ which oscillates at the vibrational period, decaying over time without subsequent revival.

### B. Phase-only shaping of the initial wave packet: Analytical estimates and numerical simulations

Consider the following term from Eq. (8):

$$E(v,J) - E(v',J) = \omega_J (v - v') - \omega_e x_e \times \left[ \left(v + \tfrac{1}{2}\right)^2 - \left(v' + \tfrac{1}{2}\right)^2 \right]. \tag{10}$$

Let us introduce $k = v - \bar{v}$, where $\bar{v}$ is the average $v$ in the wave packet. Then

$$\begin{aligned} E(v,J) - E(v',J) &= \tilde{\omega}_J (k - k') - \omega_e x_e (k^2 - k'^2), \\ \tilde{\omega}_J &= \omega_e - 2\omega_e x_e \left(\bar{v} + \tfrac{1}{2}\right) - \alpha_e J^2 = \omega_{\bar{v}} - \alpha_e J^2. \end{aligned} \tag{11}$$

Here $\omega_{\bar{v}}$ is the vibrational frequency at the average $v$.

To approximate the signal $S(t)$ analytically, we note that we are interested in the decay of the signal, not its oscillation with vibrational frequency. We then examine the behavior of $|Q(J,t)|^2$ at discrete time intervals $t_N = \frac{2\pi N}{\omega_{\bar{v}}}$. At times $t = t_N$ we have

$$|Q(I,t_N)|^2 = \sum_{k=-\infty}^{k=\infty} \sum_{k'=-\infty}^{k'=\infty} A_k^2 A_{k'}^2 \exp\{ i [\theta_k - \theta_{k'} + t_N \omega_e x_e (k^2 - k'^2) - t_N \Delta\Omega (k - k') I ] \}. \tag{12}$$

Here $\bar{J}$ is the mean rotational state, $I = J - \bar{J}$, and $\Delta\Omega = -2\alpha_e \bar{J}$.

We now assume a Gaussian amplitude profile $A_k = e^{-k^2/2\sigma^2}$ and replace the sums over discrete states with an integral over continuous variables $k$ and $k'$. One effect of this approximation is to remove the possibility of revivals, but this is acceptable since we are interested in the dephasing dynamics rather than the revivals. Now consider a Taylor expansion to second order of the initial phases: $\theta_k \simeq a + bk + ck^2$. The constant term has no effect since only relative phases between levels affect the signal. A linear chirp ($bk$) in the laser pulse spectrum is equivalent to a translation of the pulse in the time domain. Since we are interested in the behavior of the molecule after the pulse, we must neglect this. As a result we assume that the initial phases have only quadratic dependence in the frequency domain (i.e., linear chirp in the time domain), such that $\theta_k = ck^2$.

Completing the square in the exponent and performing the necessary Gaussian integrals yields

$$|\tilde{Q}(I,t_N)|^2 \propto e^{-\kappa(t_N) I^2} |\gamma(t_N)|^{-1}, \tag{13}$$

$$\gamma(t_N) = \sigma^{-2} + i(\omega_e x_e t_N + c), \tag{14}$$

$$\kappa(t_N) = \tfrac{1}{2} |\gamma(t_N)|^{-2} (\Delta\Omega)^2 \sigma^{-2} t_N^2. \tag{15}$$

Figure 1 shows this approximation for the case of an unchirped initial wave packet, showing its effectiveness in representing the decay in signal due to anharmonicity.

The form of $\tilde{Q}(I,t_N)$ provides insight into the dephasing mechanism, although the true behavior of the signal is not revealed until we average over the $J$ distribution. First note that the parameter $|\gamma(t_N)|^2 = \sigma^{-4} + (\omega_e x_e t_N + c)^2$ can be viewed as a measure of wave packet broadness in space. The $\sigma^{-4}$ term captures the fact that a wave packet in which few energy levels participate is broad in position space, while the $(\omega_e x_e t_N + c)^2$ term shows the anharmonic broadening and the effect of the chirp. Notice that $\gamma(0)$ is increased by either a positive or negative chirp: chirping the phases broadens the initial wave packet. We also so see that for a negative chirp, the anharmonicity will first *narrow* the wave packet before broadening it. The wave packet will be at its most narrow when $t_N = \frac{c}{\omega_e x_e}$.

In Eq. (13) we see that the broadness parameter $|\gamma(t_N)|^2$ appears both in the outer factor and within the exponential.

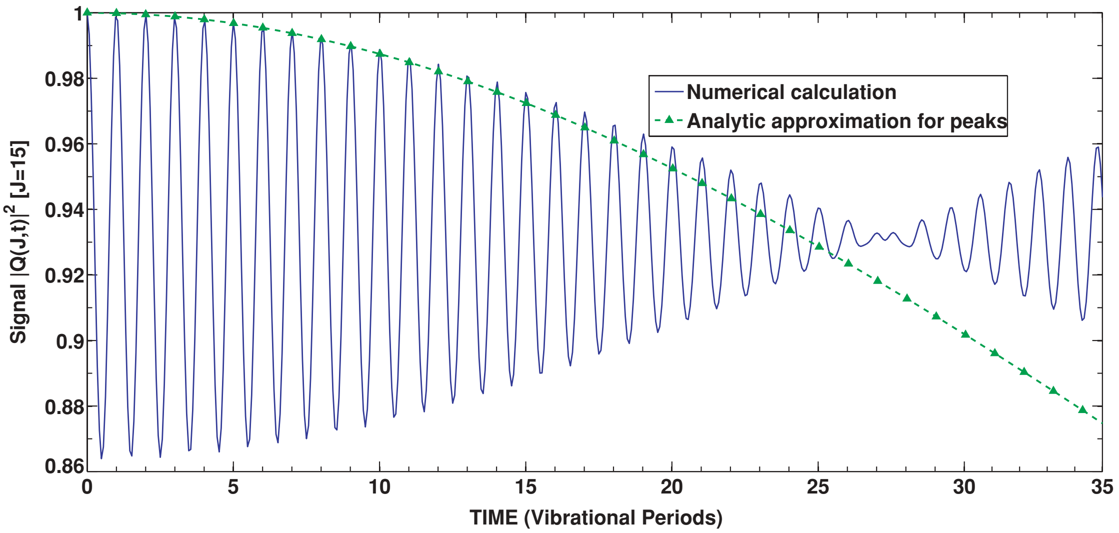

FIG. 1. (Color online) For the case of flat initial phases ($\theta_v = 0\ \forall v$), the $J = 15$ contribution to the signal $\frac{|Q(15,t)|^2}{\max[|Q(15,t)|^2]}$ (solid blue line) is compared to the analytic approximation for the peaks $\tilde{Q}(J,NT)$ (dashed green line), where $T$ is the vibrational period and $N$ is an integer. The decay and revival of the single-$J$ contribution seen here is due to the anharmonicity. The figure shows that while the approximation fails to capture the revival dynamics, it approximates the decay quite closely.

The outer factor ensures that at any given time, a broader wave packet will give a lower signal than a narrower one, since it will have a reduced overlap with the localized gate function. The role of $|\gamma(t_N)|^{-2}$ in the exponent is to decrease the instantaneous rate of decay of the signal for broader wave packets. It may appear surprising that such decay occurs in $|\tilde{Q}(I,t_N)|^2$, because for a single rotational state $I = J - \bar{J}$ there is no dephasing. Recall that the times $t_N$ are multiples of the *mean* vibrational period. For nonzero $I$, this is not the period that the wave packet will actually move with. The decay in $|\tilde{Q}(I,t_N)|^2$ is due to this disparity.

For a given value of $I$, the signal for a broader wave packet will decay more slowly over time. This can be understood by considering the extreme cases: a narrow $\delta$-function-like peak [call this wave packet $\Psi_N(R,t)$] and a broad wave packet that is completely spread out along the classical trajectory [call this $\Psi_B(R,t)$]. $\Psi_B(R,t)$ does not move along the trajectory as time increases, so its overlap with the gate function $\Psi_G(R)$ is small but constant. $\Psi_N(R,t)$ on the other hand, gives a strong signal when it is located on top of the gate function but if it is located away from the gate function then its overlap will vanish. So even a minor disparity between the wave packet's period and the mean vibrational period will cause the signal for $\Psi_N(R,t)$ to decay rapidly.

Now we turn to the averaging over the $J$ distribution. Let $\beta = B_e/kT$. Substituting into Eq. (8) and again replacing the sum with an integral, we have

$$\tilde{S}(t_N) \propto |\gamma(t_N)|^{-1} \int_0^\infty dJ\, e^{-\beta J^2 - \kappa(t_N)(J-\bar{J})^2}. \tag{16}$$

By completing the square in the exponent, we can rewrite this as follows:

$$\tilde{S}(t_N) \propto |\gamma(t_N)|^{-1} e^{-\kappa(t_N)\bar{J}(\bar{J}-J')} \int_0^\infty dJ\, e^{-[\beta+\kappa(t_N)](J-J')^2}, \tag{17}$$

$$J' = \frac{\kappa(t_N)\bar{J}}{\beta + \kappa(t_N)}. \tag{18}$$

The solution to the integral is expressed in terms of the complementary error function

$$\operatorname{erfc}(x) \propto \int_x^\infty dy e^{-y^2}$$

as

$$\tilde{S}(t_N) \propto |\gamma(t_N)|^{-1} e^{-\kappa(t_N)\bar{J}(\bar{J}-J')[\beta+\kappa(t_N)]^{-\frac{1}{2}}} \times \operatorname{erfc}\{-[\beta+\kappa(t_N)]^{\frac{1}{2}} J'\}. \tag{19}$$

Figure 2 shows this analytic approximation, compared to the full $S(t)$ calculated numerically. Figure 3 shows the result when the initial phases have a quadratic chirp $c = -0.1$.

The key result here is that in this model, contrary to the claim of Branderhorst *et al.* [3], negatively chirping the initial phases does not produce a wave packet that is inherently resistant to the rovibrational dephasing. Instead we see that this produces an initially broadened wave packet which is narrowed due to the anharmonicity, so that the signal first improves over time and subsequently decays. If there is no anharmonicity, this effect is not present.

We can study this effect qualitatively if we take the lower limit of the integral in Eq. (17) to $-\infty$. This approximation is justified since the factor $e^{-\kappa(t_N)J'^2}$ is small and goes quickly to zero as $t_N$ increases. This yields

$$\tilde{S}_{-\infty}(t_N) = [(t_N - t')A + B]^{-\frac{1}{2}}, \tag{20}$$

$$A = \beta(\omega_e x_e)^2 + \sigma^{-2}(\Delta\Omega)^2, \tag{21}$$

$$B = \beta(\sigma^{-4} + c^2) - At'^2, \tag{22}$$

$$t' = \frac{-\beta c \omega_e x_e}{A}. \tag{23}$$

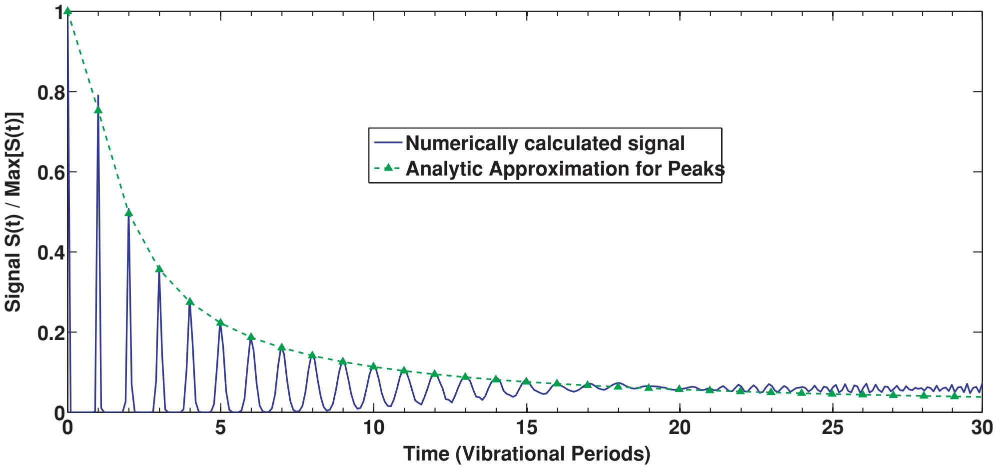

FIG. 2. (Color online) For the case of flat initial phases ($\theta_v = 0\ \forall v$), the normalized signal function $\frac{S(t)}{\max[S(t)]}$ (solid blue line) is compared to the analytic approximation for the peaks $\tilde{S}(NT)$ (dashed green line), where $T$ is the vibrational period and $N$ is an integer. The analytic approximation shows good qualitative agreement with the numerical results, demonstrating that the analytic approximation captures the decay of the signal due to rovibrational coupling.

Since $t' \propto -c$, we can see the origin of the time translation of the signal peak when a chirp is introduced. If we neglect the $\sigma^{-2}(\Delta\Omega)^2$ term in $A$, $t' = \frac{-c}{\omega_e x_e}$, which is the time at which the signal for a single value of $I$ (or equivalently $J$) has its maximum [see Eq. (13)]. While this approximation to the signal is less accurate than Eq. (17), its behavior is easier to understand. In this approximation the introduction of chirped initial phases simply time shifts the entire signal. The behavior of the numerically calculated $S(t)$ and the approximations $\tilde{S}(t_N)$ and $\tilde{S}_{-\infty}(t_N)$ are all qualitatively consistent. In this model, there is no sign of quadratically chirped phases providing any increase in inherent resistance to "decoherence," contrary to [3].

### C. Phase shaping and amplitude shaping: Squeezed coherent wave packet and two-state wave packet

Branderhorst *et al.* [3] argue that initially position-squeezed wave packets are more resistant to dephasing, since position-squeezed wave packets are approximate eigenstates of the interaction Hamiltonian [1]. Although such a wave packet is not position-squeezed at all times, it spends most of its time near the classical turning points, where it is position-squeezed. This section addresses whether this resistance to dephasing is observed in our model. In order to test this, we set the anharmonicity equal to zero and choose the initial vibrational wave packet to be a squeezed coherent wave packet displaced to the inner turning point. Creating such a wave packet would require substantial amplitude modulation and substantial phase modulation of the excitation pulse.

The complex amplitudes of each harmonic oscillator eigenstate in a squeezed coherent wave packet $|\beta_c,\xi\rangle$, with displacement parameter $\beta_c$ and squeezing parameter $\xi = |\xi|e^{i\phi_\xi}$, may be written in the form below [11], where $\mu = \cosh|\xi|$ and $\nu = e^{i\phi_\xi}\sinh|\xi|$. When the displacement $\beta_c = \pi$ and the squeezing factor $\xi$ is real, we have the desired radially squeezed wave packet at the inner turning point

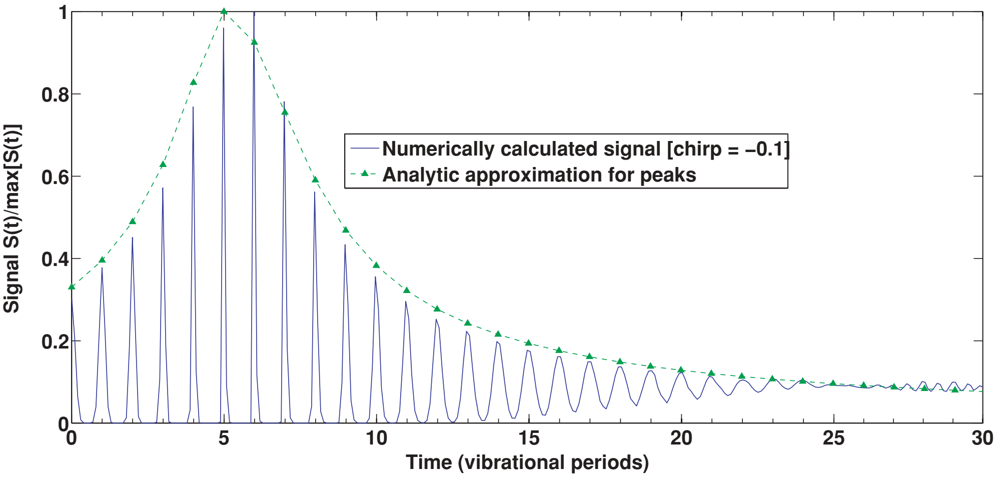

FIG. 3. (Color online) The same as Fig. 2, but with a negative quadratic chirp to the initial phases [$\theta_v = -0.1(v-\bar{v})^2$]. Again there is good qualitative agreement—the analytic model shows a similar rise and fall.

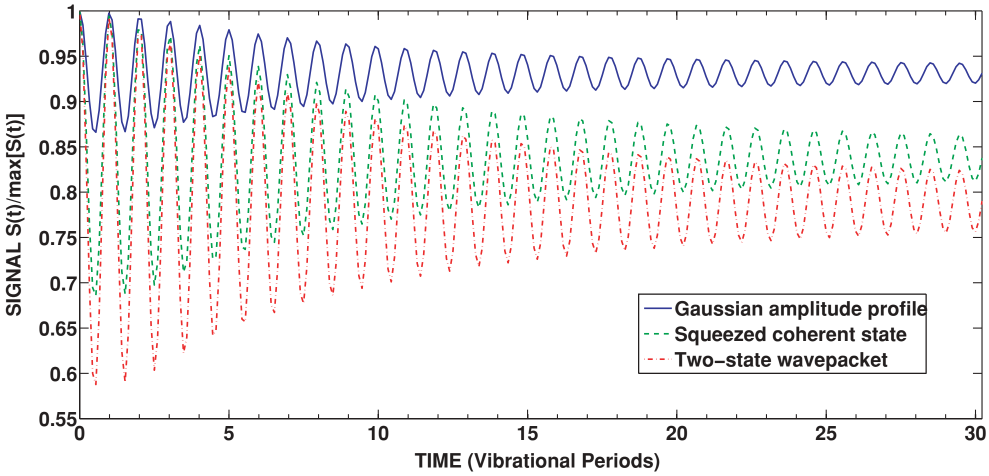

FIG. 4. (Color online) The normalized signals as a function of time for three different initial vibrational wave packets. The first has a Gaussian amplitude profile $|\Psi_g\rangle = \sum_k e^{-k^2/2\sigma^2}|k\rangle$ (solid blue line), the second is a position-squeezed coherent wave packet at the inner turning point $|\beta_c = \pi, \xi = 0.8\rangle$ (dashed green line), and the third is the wave packet consisting of two adjacent vibrational states $|\Psi_2\rangle = \frac{1}{\sqrt{2}}(|\bar{v}\rangle + |\bar{v}+1\rangle)$ (dot-dashed red line). Here anharmonicity is zero, so the decay in the signal visibility is purely due to the rovibrational coupling.

(we take $\xi = 0.8$):

$$A_n^c e^{i\theta_n^c} = \left(\frac{\nu}{2\mu}\right)^{\frac{n}{2}} \frac{1}{\sqrt{\mu n!}} \exp\left[-\frac{1}{2}\left(|\beta_c|^2 - \frac{\nu^*}{\mu}\beta_c^2\right)\right] \times H_n\left(\frac{\beta_c}{\sqrt{2\mu\nu}}\right). \tag{24}$$

Here $H_n(x)$ is the $n$th Hermite polynomial. We also consider the wave packet $|\Psi_2\rangle = \frac{1}{\sqrt{2}}(|\bar{v}\rangle + |\bar{v}+1\rangle)$ containing only two adjacent vibrational levels, which will also show beating at vibrational frequency. Figure 4 shows the signals calculated for the wave packet with Gaussian amplitude profile and the squeezed coherent wave packet. At a first glance, it appears that there is substantial difference in the surrogate measure of decoherence expressed by $S(t)$, for the three initial wave packets. However, this first impression is incorrect. In order to assess their dephasing rate, the extrema of these curves are extracted and used to calculate a visibility,

$$V = \frac{S_{\text{peak}} - S_{\text{valley}}}{S_{\text{peak}} + S_{\text{valley}}},$$

for each period. This visibility is plotted as a function of time in Fig. 5. Surprisingly, the three curves are nearly identical, showing no resistance to the dephasing process for the squeezed wave packet $|\beta_c, \xi\rangle$ or the two-state wave packet $|\Psi_2\rangle$.

The analytic work in the following sections is motivated by the need to explain why such drastic amplitude and phase adjustments of the initial wave packet seem to have no effect on the dephasing process, contrary to the conclusions of [1] and [3].

### D. Analytical investigation of the signal function $S(t)$

Since we are interested solely in the dephasing due to thermal rotational population, for the following calculation

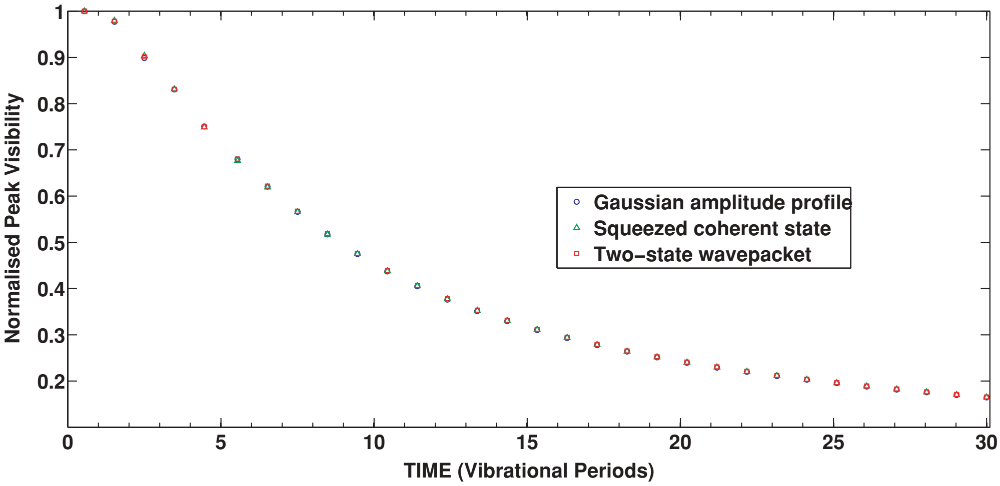

FIG. 5. (Color online) The normalized peak visibility $V/\max[V]$ as a function of time (extracted from Fig. 4) for the three initial wave packets $|\Psi_g\rangle$ (blue circles), $|\beta_c = \pi, \xi = 0.8\rangle$ (green triangles), and $|\Psi_2\rangle$ (red squares). This shows that for our model, these three different wave packets show the same dephasing behavior over time.

we will neglect the anharmonicity $\omega_e x_e$. In contrast to the previous calculation, where we have looked at $S(t)$ at specific moments, here we will look at the complete time-dependence. The main approximation is to replace the summation over $J$ with an integral. We perform the integral before the summation over $v$ and $v'$. To simplify the $J$ integral, we shall assume that the bath distribution is $P(J) \propto 2Je^{\frac{-BJ^2}{kT}}$. We will also probe the dependence of $S(t)$ on the distribution of bath states by comparing the result for $P(J) \propto 2Je^{\frac{-BJ^2}{kT}}$ with that for the 2D distribution $P_{2D}(J) \propto e^{\frac{-BJ^2}{kT}}$. The true 3D thermal distribution, then, is proportional to the sum of these two distributions.

Performing the $J$ integral yields

$$S(t) \propto \sum_v \sum_{v'} A_v A_{v'} e^{-i\omega_e(v-v')t} \frac{1+i\alpha_e J_0^2(v-v')t}{1+\alpha_e^2 J_0^4(v-v')^2 t^2}. \tag{25}$$

Here $J_0^2 = kT/B_e$. Now we define time-dependent phases $\Phi_{vv'} = \omega_e(v-v')t - (\theta_v - \theta_{v'})$ (determined by the pure vibrational dynamics) and $\phi^{\alpha}_{vv'} = \arctan\,[\alpha_e J_0^2(v-v')t]$ (determined by the dynamics due to rovibrational coupling). Then we may use the fact that $S(t)$ is real to write Eq. (25) in the following form:

$$S(t) \propto \sum_v \sum_{v'} |A_v||A_{v'}| \frac{1}{\sqrt{1+\alpha_e^2 J_0^4(v-v')^2 t^2}} \times \cos\left(\Phi_{vv'} - \phi^{\alpha}_{vv'}\right). \tag{26}$$

A first glance at Eq. (26) might suggest that the rovibrational coupling has little effect. The coherences between the levels with different $v \neq v'$ decrease as $\frac{1}{t}$ at long times and quadratically at short times. However, it is important to look closely at the effect of $\phi^{\alpha}_{v0'} = \arctan\,[\alpha_e J_0^2(v-v')t]$.

Let $\Delta v$ be the characteristic full width of the wave packet in $v$. In addition, assume $\Delta v \gg 1$. Then we can separate three main time scales.

1. Short time scales: $\Delta v \alpha_e J_0^2 t \ll 1$. In this case we have $\phi^{\alpha}_{vv'} \simeq \alpha_e J_0^2(v-v')t$. Then, $\alpha_e J_0^2$ merely acts as a correction to the vibrational frequency $\omega_e$, otherwise leaving the vibrational dynamics undisturbed:

$$S(t) \propto \sum_v \sum_{v'} |A_v||A_{v'}| \frac{1}{\sqrt{1+\alpha_e^2 J_0^4(v-v')^2 t^2}} \times \cos\,[\omega_{J_0}(v-v')t - (\theta_v - \theta_{v'})]. \tag{27}$$

Here $\omega_{J_0} = \omega_e - \alpha_e J_0^2$ is the rotationally adjusted vibrational frequency. Maxima in $S(t)$ occur at times $t_n = \frac{2\pi n}{\omega_{J_0}}$.

2. Long time scales: $\Delta v \alpha_e J_0^2 t \gg 1$. For this case, $\phi^{\alpha}_{vv'} \simeq \frac{\pi}{2}\mathrm{sign}(v-v')$ becomes independent of $v$ and the signal is given by

$$S(t) \propto S_0 + 2\sum_v \sum_{v'<v} |A_v A_{v'}| \frac{1}{\alpha_e J_0^2 |v-v'| t} \sin\Phi_{vv'}. \tag{28}$$

Here $S_0 = \sum_v |A_v|^2$. Note that $\cos\left(\Phi_{vv'} - \phi^{\alpha}_{vv'}\right)$ has been replaced with $\sin\Phi_{vv'}$, meaning that the maxima have shifted by $\frac{\pi}{2}$ compared to the very early times. The height of the maxima (thus also the contrast) is decreasing with time as $\frac{1}{t}$. Initial adjustments of $\theta_v$ can have *no* effect on the dephasing in this long time limit, since the rovibrational coupling has disappeared from the phases completely. It remains only in the slowly decreasing envelope.

3. Intermediate time scales: $\Delta v \alpha_e J_0^2 t \gtrsim 1$. $\phi^{\alpha}_{vv'}$ depends upon $v - v'$. Namely, for $v - v' = 1, 2$, we have $\phi^{\alpha}_{vv'} \lesssim 1$ and the maxima are at positions $t_n = \frac{2\pi n}{\omega_{J_0}}$. But for distant parts of the wave packet, where $v - v'$ is large, we have a different situation, and $\phi^{\alpha}_{vv'} \simeq \frac{\pi}{2}$. So for different parts of the wave packet, their contributions to $S(t)$ reach their maxima and minima at different times, and this reduces the overall contrast when we sum over $v$ and $v'$. One can in principle compensate for this spread of maxima and minima with the initial phases $\theta_v$. However, we will not be able to do so with a linear or quadratic chirp, since $\phi^{\alpha}_{vv'}$ is a nonlinear function of $v - v'$.

### E. Explanation for the numerical results of Sec. II C

At this stage we may reconsider the numerical results of Sec. II C, in particular, Fig. 5. Although these analytic results do not address the visibility directly, we can ask whether they provide any qualitative explanation for the fact that the decay of visibility is the same for the three wave packets (wave packet with Gaussian amplitude profile $|\Psi_g\rangle$, the squeezed coherent wave packet $|\beta_c,\xi\rangle$, and the wave packet containing only two adjacent states $|\Psi_2\rangle$). It is clear from examining Eq. (28) that the long-term behavior of the wave packet will be unaffected by the initial phases and dominated by the terms in the sum where $v - v'$ is small. So for both $|\Psi_g\rangle$ and $|\beta_c,\xi\rangle$ the dominant dynamics is the beating between the mean $\bar{v}$ and adjacent states; the contribution from nearest-neighbor pairs away from the mean is suppressed due to the decay of the amplitudes $A_v$ away from their maximum $A_{\bar{v}}$. At long time scales the behavior of both of these wave packets will be very similar to that of $|\Psi_2\rangle$. Note that for the parameter values used in the numerical simulation, which reflect the typical $J_0^2$ value in an experimental setup, the long time scale limit $\Delta v \alpha_e J_0^2 t \gg 1$ is achieved after only a few vibrational periods. This provides a qualitative explanation for the form of Fig. 5. Equation (28) also shows that while these three wave packets behave similarly, the dephasing is not completely unaffected by amplitude modulation of the initial wave packet. As an example we took another two-state wave packet, $|\chi_2\rangle = \frac{1}{\sqrt{2}}(|\bar{v}\rangle + |\bar{v}+2\rangle)$, and compared its dephasing to $|\Psi_2\rangle$ in Fig. 6. We see that this *amplitude* modulation has a substantial effect on the dephasing rate.

### F. Dependence on the bath distribution

One question that is worth considering when looking at a model of environment-induced dephasing is the following: how sensitively does the dephasing dynamics depend upon the exact distribution of population among the environment states? In order to address this question in our model, we repeat the calculation of Sec. II D using the 2D rotational bath distribution $P_{2D}(J) \propto e^{\frac{-BJ^2}{kT}}$. Substituting this into Eq. (8) and approximating the sum as an integral as in Eq. (25) yields the following result [cf. Eq. (26)]:

$$S(t) \propto \sum_v \sum_{v'} |A_v A_{v'}| \left(1+\alpha_e^2 J_0^4(v-v')^2 t^2\right)^{-\frac{1}{4}} \times \cos\left(\Phi_{vv'} - \tilde{\phi}_{vv'}\right), \tag{29}$$

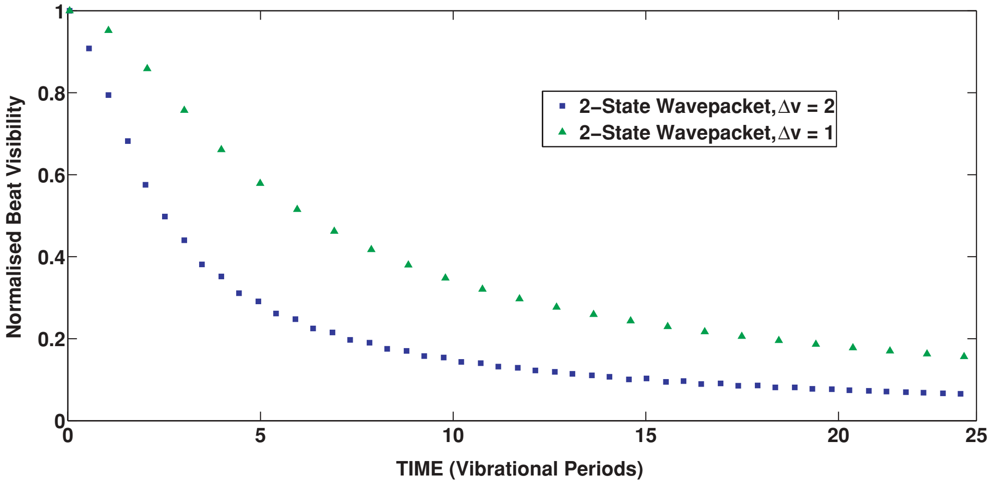

FIG. 6. (Color online) The normalized peak visibility $V/\max[V]$ as a function of time for two initial wave packets, each containing only two vibrational states separated by $\Delta v$. Naturally, the case where $\Delta v = 2$ ($|\chi_2\rangle$) (blue squares) beats with twice the frequency of $\Delta v = 1$ ($|\Psi_2\rangle$) (green triangles). We see that the dephasing behavior over time is different for the two wave packets, with the $\Delta v = 2$ wave packet dephasing more rapidly than the wave packet with $\Delta v = 1$. This demonstrates a case where *amplitude* modulation of the initial wave packet has a significant effect on the dephasing dynamics.

where $\tilde{\phi}_{vv'} = -\frac{1}{2}\phi^{\alpha}_{vv'}$ and all other quantities are defined as in Sec. II D. Therefore, changing the bath distribution alters the rovibrational dephasing angle from $\phi^{\alpha}_{vv'}$ to $\tilde{\phi}_{vv'}$ and changes the signal decay with time, so that at long times instead of decay $\propto \frac{1}{t}$ we have $\propto \frac{1}{\sqrt{t}}$. These changes—particularly the latter—are substantial. This result shows that here we have a very strong dependence of our outcome on the details of the environment states, namely, the degeneracy of each $J$ level.

## III. CONCLUSIONS

In this article we have studied rotationally induced dephasing of vibrational wave packets in hot diatomic molecules, with a view to establishing whether phase-only adjustments of the initial wave packet can affect the rate of dephasing. An analytical investigation of the fluorescence signal $S(t)$ determined that there are three relevant time scales, determined by the size of the parameter $\Delta v \alpha_e J_0^2 t$. At short time scales, dephasing has not set in and there is no need to compensate for it. At long time scales, which can be reached after as little as a few vibrational periods in typical experiments, the dephasing process can no longer be compensated at all by initial wave packet phases. Between these limits, there is an intermediate time scale where adjustments of the initial phases can, in principle, affect the dephasing rate.

The form for the signal $S(t)$ in Eq. (26) makes it clear that phase-only control of the dephasing means compensating for $\phi^{\alpha}\big((k-k'),t\big) = \arctan[\alpha_e J_0^2(k-k')t]$ by selecting the values of the initial phases $\theta_k$, where $k = v - \bar{v}$. At intermediate times we may no longer treat the arctan in $\phi^{\alpha}$ as linear. Expanding it to third order we get $\phi^{\alpha}_{kk'} \simeq \alpha_e J_0^2(k-k')t - \frac{1}{3}\alpha_e^3 J_0^6(k-k')^3 t^3$, so we would need a cubic term in the phases to compensate for this. In our numerical simulations we have tried various values of cubic chirp in the initial phases, but none have reduced the dephasing rate. To explain the difficulties with phase-only control of the dephasing, let us assume that the initial phases are $\theta_k = bk + ck^2 + dk^3$. Then the phase $\Theta(k,k',t) = \Phi_{kk'} - \phi^{\alpha}_{kk'}$ in Eq. (26) can be written as follows (letting $n = k - k'$ and $m = k + k'$):

$$\begin{aligned} \Theta(n,m,t) &= F_0(n) + F_1(n)m + F_2(n)m^2, \\ F_0(n) &= \omega_e n - bn - \phi^{\alpha}(n,t) + \tfrac{1}{4}dn^3, \\ F_1(n) &= -cn, \\ F_2(n) &= -\tfrac{3}{4}dn. \end{aligned} \tag{30}$$

Now we assume that the constants $A_k$ are Gaussian, that is, $|A_k| = e^{-\frac{k^2}{k_0^2}}$. Then equation (26) gives

$$S(t) \propto \sum_n \sum_m \frac{e^{-\frac{n^2}{2k_0^2}}}{\sqrt{1+\alpha_e^2 J_0^4 t^2 n^2}} e^{-\frac{m^2}{2k_0^2}} \times \cos[F_0(n) + F_1(n)m + F_2(n)m^2]. \tag{31}$$

The first thing to note is that the initial phases, which appear only inside the cosine, cannot affect the term $(1 + \alpha_e^2 J_0^4 t^2 n^2)^{-\frac{1}{2}}$. So there is some overall decay in the signal which cannot be avoided by adjusting the initial phases. Second, examination of $F_0$ shows that the cubic chirp $d$ can compensate for the rotational phase $\phi^{\alpha}$. However, the cubic chirp $d$ *also* appears in $F_2$; so when we perform the double sum over $n$ and $m$, this introduces a further phase scrambling in addition to the thermal dephasing. It is clear from our analysis that phase-only suppression of the dephasing process is a challenging proposition, and even when it is achieved, it can only operate over a limited time scale.

The question remains as to why our conclusions differ substantially from those of Branderhorst *et al.* [3], who reported control of the dephasing process by application of quadratically chirped excitation pulses. The key assumption in our model is neglecting the effect of rotational distortion of the vibrational wave functions during the pump pulse, that is, neglecting the $J$ dependence of the $A_{vJ}$ factors in Eq. (7). It is possible that phase-only control is more easily achieved if these distortions are taken into account.

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