Photon echo signature of vibrational superposition states created by femtosecond excitation of molecules

Holger F. Hofmann, Takao Fuji, and Takayoshi Kobayashi
Department of Physics, Faculty of Science, University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo113-0033, Japan
(March 31, 2022)

Abstract

A pair of coherent femtosecond pulse excitations applied to a molecule with strong electron-phonon coupling creates a coherent superposition of a low momentum and a high momentum wavepacket in the vibrational states of both the excited state and the ground state of the coherent transition. As the excited state is accelerated further, interference between the high momentum ground state contribution and the low momentum excited state contribution causes a photon echo. This photon echo is a direct consequence of quantum interference between separate vibrational trajectories and can therefore provide experimental evidence of the non-classical properties of molecular vibrations.
“The feature of quantum mechanics which most distinguishes it from classical mechanics is the coherent superposition of distinct physical states” [1]. In the case of molecular vibrations, the motion of a single Gaussian wavepacket usually corresponds well with the classical motion for the potential considered. However, quantum mechanics also allows coherent superpositions between two wavepackets with distinct positions and momenta. The properties of such superpositions depend on the phase between the two Gaussian wavepackets, a property that has no analog in the classical theory. The study of such superpositions should therefore provide insights into the non-classical features of quantum mechanics.

The creation and measurement of vibrational wavepackets by optical excitations has been studied both experimentally and theoretically [2–10]. In particular, the creation of a coherent superposition of two distinct Gaussian wavepackets (also referred to as a “cat state”) in a molecular vibration has been predicted if the molecule is excited by a sequence of two femtosecond pulses [4]. However, it is difficult to obtain experimental evidence indicating the successful creation of the coherent superposition. In the following, it will be shown that the nonlinear optical contributions in the formation of the superposition state automatically produce a photon echo effect that corresponds to the “which path” interference between two distinct trajectories of the molecular vibration. Thus, the vibrational photon echo may provide direct experimental evidence of quantum coherence between two vibrational wavepackets.

The Hamiltonian describing the electron-phonon interaction of an electronic two level system and a single vibrational degree of freedom may be written as

\[
\hat{H}_0 = \frac{\hat{p}^2}{2m} + V_G(\hat{x}) \otimes |G\rangle \langle G| + V_E(\hat{x}) \otimes |E\rangle \langle E|,
\]

where \(m\) is the effective mass of the vibration, and \(V_G(\hat{x})\) and \(V_E(\hat{x})\) describe the vibrational potentials associated with the electronic ground state \(|G\rangle\) and the electronic excited state \(|E\rangle\), respectively. The position operator \(\hat{x}\) and the conjugate momentum operator \(\hat{p}\) represent the dynamical variables of the vibrational mode under consideration.

Initially, the molecular system is in the electronic ground state \(|G\rangle\) and the vibrational state \(|\psi_0\rangle\) is localized near the minimum of the ground state potential \(V_G(\hat{x})\). It is therefore convenient to define this minimum as \(x = 0\) and its potential as \(V_G(0) = 0\). If the timescales considered are much shorter than the period of a molecular vibration, the vibrational wavefunction will always remain close to \(x = 0\). Moreover, the momentum is also close to zero initially, and its changes can be considered small enough to neglect the quadratic term \(\hat{p}^2/m\). The total Hamiltonian can then be linearized in \(\hat{x}\) and \(\hat{p}\). The approximate Hamiltonian reads

\[
\hat{H}_0 \approx (\hbar \omega_0 - F_E \hat{x}) \otimes |E\rangle \langle E|.
\]

with \(\hbar \omega_0 = V_E(x = 0)\)

and \(F_E = -\frac{\partial}{\partial x} V_E(x)|_{x=0}\).

This Hamiltonian describes the linear acceleration of the excited state component of the vibrational state by the force \(F_E\). In terms of the momentum eigenstate components \(\psi_G(p; t) = \langle G; p | \psi(t) \rangle\) and \(\psi_E(p; t) = \langle E; p | \psi(t) \rangle\), this acceleration can be written as
\[
\psi_G(p; t) = \psi_G(p; 0)
\]
\[
\psi_E(p; t) = \exp(-i\omega_0 t)\psi_E(p - F_E t; 0).
\] (3)

Note that this evolution of the vibrational wavefunction preserves the quantum coherence between the excited state and the ground state contributions. It is therefore not possible to assign separate “realities” to excited state and ground state molecules. Instead, any coherent overlap between the vibrational states corresponds to a coherent electronic dipole. This coherent dipole is given by the operator \(\hat{d} = |G\rangle\langle E|\). Its expectation value reads
\[
\langle \hat{d} \rangle(t) = \int dp \psi^*_G(p; t)\psi_E(p; t).
\] (4)

The electronic dipole of the molecular transition thus represents an interference between the accelerated excited state and the non-accelerated ground state. The acceleration process separates the vibrational state like a beam splitter separates the incoming fields. In a photon echo experiment, the first pulse at \(t_0 - \tau\) splits the vibrational dynamics, the second pulse at \(t_0\) “reflects” the excited state into the ground state and vice versa, and the photon echo indicates interference between two indistinguishable paths of acceleration. The ground state component of the photon echo dipole corresponds to acceleration during \(t_0 - \tau < t < t_0\) followed by a constant momentum of \(F_E\tau\) during \(t_0 < t < t_0 + \tau\), and the excited state component corresponds to zero momentum during \(t_0 - \tau < t < t_0\) followed by acceleration to a momentum of \(F_E\tau\) during \(t_0 < t < t_0 + \tau\). These trajectories are illustrated in figure [1].

In the following, we apply this description of the molecular dynamics to a pair of ultrafast excitations at times \(t_0 - \tau\) and \(t_0\). The pulses are considered to be much shorter than \(\tau\). Before the first pulse, the molecule is in its ground state, given by \(\psi_G(p) = \psi_0(p)\) and \(\psi_E(p) = 0\). Between the two pulses \((t_0 - \tau < t < t_0)\), the coherent evolution of the partially excited state is given by
\[
\psi_G(p; t) = \cos(\phi/2)\psi_0(p)
\]
\[
\psi_E(p; t) = e^{-i\omega_0(t-t_0+\tau)}\sin(\phi/2)\psi_0(p - F_E(t-t_0+\tau)),
\] (5)

where \(\phi\) is a measure of the pulse area exciting the molecule. The expectation value of the coherent dipole evolves according to
\[
\langle \hat{d} \rangle(t) = e^{-i\omega_0(t-t_0+\tau)}\frac{1}{2}\sin(\phi) \int dp \psi^*_0(p)\psi_0(p - F_E(t-t_0+\tau)),
\] (6)

which corresponds to the autocorrelation of the vibrational wave function in momentum space, \(\psi_0(p)\). The dipole dephasing time \(t_\phi\) is therefore given by
\[
t_\phi = \frac{\delta p}{F_E},
\] (7)

where \(\delta p\) is the momentum uncertainty of the initial wavepacket. If \(\delta p\) is much smaller than \(F_E\tau\), then the coherent dipole will be close to zero at \(t = t_0\).

The second pulse at \(t = t_0\) then restores dipole coherence by transferring part of the ground state component to the excited state and vice versa. The evolution of the total molecular state for \(t > t_0\) reads
\[
\psi_G(p; t) = \frac{1}{2} (1 + \cos(\phi)) \psi_0(p) - e^{-i\omega_0 \tau} \frac{1}{2} (1 - \cos(\phi)) \psi_0(p - F_E \tau)
\]
\[
\psi_E(p; t) = e^{-i\omega_0 (t-t_0)} \frac{1}{2} \sin(\phi) \psi_0(p - F_E(t-t_0))
\]
\[
+ e^{-i\omega_0 (t-t_0+\tau)} \frac{1}{2} \sin(\phi) \psi_0(p - F_E \tau - F_E(t-t_0)). \tag{8}
\]

The total vibrational state now consists of four separate contributions. Initially \((t = t_0)\), there is dipole coherence between two pairs, the one around \(p = 0\) and the one around \(p = F_E \tau\). This coherence is lost as the excited state is accelerated. The dipole dynamics of the decoherence process reads

\[
\langle \hat{d} \rangle(t) = e^{-i\omega_0 (t-t_0)} \frac{1}{2} \sin(\phi) \cos(\phi) \int d\phi \psi_0^*(p) \psi_0(p - F_E(t-t_0)). \tag{9}
\]

This corresponds to the linear response of the partially excited two level system to the second pulse. However, there is a revival of the dipole coherence in the form of a photon echo as the excited state from \(p = 0\) is accelerated to \(p = F_E \tau\) and interferes with the ground state component there. Figure 2 illustrates the coherent wavefunction at \(t = t_0 + \tau\). The dipole dynamics close to \(t = t_0 + \tau\) are given by

\[
\langle \hat{d} \rangle(t) = e^{-i\omega_0 (t-t_0-\tau)} \frac{1}{4} \sin(\phi) (1 - \cos(\phi)) \int d\phi \psi_0^*(p - F_E \tau) \psi_0(p - F_E(t-t_0)). \tag{10}
\]

This result is again equal to the autocorrelation of \(\psi_0(p)\), but it is centered around \(t = t_0 + \tau\). Figure 3 shows the sequence of pulses and the dipole response. Since the first two dipole signals are immediate responses to the exciting pulses, they suddenly appear at \(t_0 - \tau\) and at \(t_0\), followed by a gradual decay given by the autocorrelation of \(\psi_0(p)\). The echo pulse arises from the hidden coherence in the dynamics following the second pulse at \(t = t_0\). It therefore appears gradually and is symmetric around \(t = t_0\). Since dipole coherence always indicates an interference between ground state and excited state components, the echo indicates equal momentum of the accelerated excited state and the non-accelerated ground state. In terms of the average momentum of the four separate contributions, figure 2 shows the trajectories involved in the quantum interference indicated by the dipole expectation value \(\langle \hat{d} \rangle\). By comparing the dipole evolution given in figure 2 with the trajectories in figure 4, the optical signals can be related to the quantum dynamics of the vibration.

The analogy between photon echoes in inhomogeneously broadened transitions and the molecular photon echoes discussed here arises from the assumption that the position coordinate \(\hat{x}\) remains nearly constant during the experiment. The inhomogeneity is then a consequence of the randomness of the position coordinate \(\hat{x}\) given by the spatial width of the vibrational wavepacket. The main difference between the photon echo in an inhomogeneously broadened medium and the vibrational photon echo discussed here is that the coherence of the contributions from different positions corresponds to a well defined momentum. It is therefore impossible to identify each precise position \(x\) with a different molecule, since this would imply an infinite momentum uncertainty. For most practical purposes, however, the experimental setup corresponds to a conventional photon echo experiment.

In order to satisfy the assumption that \(\hat{x}\) does not change much during the experiment, the spatial shifts induced by the velocity \(p(t)/m\) during the delay time \(\tau\) must be much
smaller than the spatial width of the vibrational wavepacket. The shift in position can be determined by integrating the velocity $p(t)/m$ over time. The total shift of position thus contains a "memory" of the momentum path taken by the molecular vibration, destroying the quantum interference. At the interference point, the difference in position between the ground state component and the excited state component with $p = F_E\tau$ is

$$\Delta x = \frac{F_E\tau^2}{m}. \quad (11)$$

In momentum representation, this shift appears as a phase factor of $\exp(-ip\Delta x/\hbar)$. The maximal coherent dipole of the echo pulse is then reduced by a factor of

$$\xi = \int dp \exp \left(-i\frac{\Delta x}{\hbar}p\right)|\psi_0(p)|^2. \quad (12)$$

Since the ground state of a harmonic oscillator of frequency $\Omega$ is a Gaussian wavepacket with a momentum variance of $\delta p^2 = \hbar \Omega m/2$, the decoherence factor $\xi$ can be written as

$$\xi = \exp \left(-\frac{\delta p^2 \Delta x^2}{2\hbar^2}\right) = \exp \left(-\frac{F_E^2 \Omega}{4\hbar m \tau^4}\right). \quad (13)$$

The dependence of the decoherence factor $\xi$ on delay time $\tau$ is shown in figure 4. This fourth order exponential decay should be a typical signature of molecular photon echoes, allowing a distinction between such echoes and the echo effect caused by inhomogeneous broadening. The decoherence time $T$ is given by

$$T = \left(\frac{4\hbar m}{F_E^2 \Omega}\right)^{\frac{1}{4}}. \quad (14)$$

An estimate of the dephasing time can be obtained from typical values of $F_E \approx 10^{-8} N$, $\Omega \approx 10^{14}s^{-1}$, and $m \approx 10^{-25} kg$. For these values, the dephasing time is about $10^{-14}s$ or ten femtoseconds. In order to obtain a clear separation between the two pulses exciting the molecule, it is therefore necessary to use extremely short pulses. If the pulses do overlap, an echo can still be obtained, but since the vibrational wavepackets overlap as well the interference cannot be traced to two separate trajectories.

Equation (14) suggests that optimal results can be obtained in a molecular vibration with a high effective mass $m$, a low vibrational frequency $\Omega$ in the ground state, and a small force $F_E$ on the excited state. However, a strong force $F_E$ is necessary to ensure a short dipole dephasing time. Using $\delta p^2 = \hbar \Omega m/2$, the ratio of decoherence time $T$ and dephasing time $t_\phi$ is

$$\frac{T}{t_\phi} = 2 \left(\frac{F_E^2 \Omega}{\hbar m \Omega^3}\right)^{\frac{1}{4}}. \quad (15)$$

For the typical values given above, this ratio is about three. In order to obtain a higher ratio, it is desirable to have a lower effective mass $m$, a lower vibrational frequency $\Omega$, and a
stronger force $F_E$. The best system for observing a vibrational photon echo would thus be a system with an unusually low ground state vibrational frequency. Possibly, a very unstable bond with a shallow low curvature potential could be used. A transition to an anti-bonding state could then trigger a dissociation process with a sufficiently high initial accelerating force $F_E$ to provide rapid dephasing.

In conclusion, the results presented here highlight the possibility of using nonlinear femtosecond spectroscopy to probe the quantum nature of vibrational states. It also reveals fundamental quantum mechanical details of the interaction between the coherent dipole dynamics and the vibrational dynamics in molecular systems, thus providing some insights into the role of vibrational quantum coherence in the nonlinear optics of molecules. This method could thus provide a starting point for a more general investigation of interference effects in the dynamics of bound atoms.

**ACKNOWLEDGEMENTS**

One of us (HFH) would like to acknowledge support from the Japanese Society for the Promotion of Science, JSPS.
REFERENCES

[1] D.F. Walls and G.J. Milburn, *Quantum Optics* (Springer, Berlin 1994), p.297.
[2] A.P. Peirce, M.A. Daleh, and H. Rabitz, Phys. Rev. A 37, 4950 (1988).
[3] J.L. Krause, R.M. Whitnell, K.R. Wilson, Y.J. Yan, and S. Mukamel, J. Chem. Phys. 99, 6562 (1993).
[4] J. Janszky, A.V. Vinogradov, T. Kobayashi, and Z. Kis, Phys. Rev. A 50, 1777 (1994).
[5] B. Kohler, V. V. Yakovlev, J. Che, J. L. Krause, M. Messina, K. R. Wilson, N. Schwenter, R. M. Whitnell, and Y. Yan, Phys. Rev. Lett. 74, 3360 (1995).
[6] Z. Kis, J. Janszky, P. Adam, A.V. Vinogradov, and T. Kobayashi, Phys. Rev. A 54, 5110 (1996).
[7] A. Shnitman, I. Sofer, I. Golub, A. Yogev, M. Shapiro, Z. Chen, and P. Brumer, Phys. Rev. Lett. 76, 2886 (1996).
[8] Y. Ohtsuki, H. Kono, and Y. Fujimura, J. Chem. Phys. 109, 9318 (1999).
[9] V.G. Stavros and H.H. Fielding, J. Chem. Phys. 112, 9343 (2000).
[10] E. Hertz, O. Faucher, B. Lavorel, F. Dalla Via, and R. Chaux, Phys. Rev. A 61, 033816 (2000).
FIGURES

FIG. 1. Schematic representation of the momentum trajectories describing the acceleration of the molecular vibration in response to the femtosecond excitations at $t_0 - \tau$ and $t_0$. Filled circles mark quantum interferences between the ground and excited state trajectories. The circles at $t_0 - \tau$ and $t_0$ correspond to the dipole response caused by the short pulse excitations. The double circle at $t_0 + \tau$ does not coincide with the excitations and therefore marks the coherent dipole of the photon echo.

FIG. 2. Qualitative illustration of the vibrational wavefunction in momentum space representation at $t_0 + \tau$ for a pair of exciting pulses with a pulse area of $\phi = \pi/3$ each. The coherent dipole oscillation observed as photon echo originates from the quantum interference of the vibrational cat state components at a momentum of $F_E\tau$.

FIG. 3. Qualitative illustration of the pulse sequence $E(t)$ (top) and the dipole response $|\langle \hat{d} \rangle(t)\rangle$ (bottom) for $\phi = \pi/3$. Note that the echo pulse is symmetric around $t = t_0 + \tau$.

FIG. 4. Decoherence factor $\xi$ as a function of delay time $\tau$. $T$ is the decoherence time of the vibrational photon echo.
Figure 1

The diagram illustrates a time-axis with points $t_0$, $t_0 - \tau$, and $t_0 + \tau$. The horizontal axis is labeled $p$ and the vertical axis is labeled $t$. The point $t_0$ is marked, as well as $t_0 - \tau$ and $t_0 + \tau$. The diagram also shows the point $F_{E\tau}$ on the horizontal axis.
Figure 2

$\psi_E(p)$

$\psi_G(p)$

Echo

$p$

$p$

$0$ $F_E\tau$ $2F_E\tau$

$0$ $F_E\tau$ $2F_E\tau$
Figure 3

Pulse sequence $|E(t)|$

Dipole response $|\langle \hat{d} \rangle(t)|$

Time $t$

$t_0 - \tau$  $t_0$  $t_0 + \tau$
Figure 4

![Graph](image-url)

- $\xi$ vs. Delay time $\tau/T$