Reconstructing vibrational states in warm molecules using four-wave mixing with femtosecond laser pulses

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We propose a method to reconstruct the vibrational quantum state of molecules excited by a general excitation laser pulse. Unlike existing methods, we do not require the molecules before excitation to be in a pure state, allowing us to treat the important case of initially thermally excited molecules. Even if only a single initial level is appreciably populated, initial levels with small populations can still give major contributions to the unknown vibrational state, making it essential to take them into account. In addition to the excitation pulse, the method uses two incident, short laser pulses in a non-co-linear geometry to create four-wave mixing in the molecules. The measurements used in the reconstruction are spectra of the outgoing four-wave mixing pulse at different time delays of the excitation laser pulse. An important point is that the method does not require detailed knowledge of molecular transition moments between excited states nor of any of the incoming laser pulses, but circumvents this requirement by using one or more calibration laser pulses in a separate experiment either before or after the main data are recorded. The only requirements for the calibration laser pulses are that the constant parts of their spectrums should together cover the spectral range of the excitation laser pulse, and the constant part of each should have sufficient spectral overlap with one other calibration pulse to populate two of the same levels. Finally, we discuss the extension of the reconstruction method in this paper to more general situations, hereby presenting the new idea of quantum state reconstruction through perturbations with calibration.

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I. INTRODUCTION

Everything worth knowing about a molecule at any given time is its physical state. Hence, whether one's interest lies in interaction of radiation with the molecule, chemical reactivity or intra-molecular processes, the state contains this information. Evidently, it is of great interest to be able to determine the state of a molecule. In this theoretical paper, we show how one can determine a molecular state in a four-wave mixing experiment. The method presented is particularly useful for determining the molecular states prepared by a single, optically tailored femtosecond laser pulse. Production of this type of laser pulses has been demonstrated [1]-[3] and they have been used to produce specific vibrational states in molecules [4], [5].

Finding the state within a quantum mechanical description is complicated, as there is no single observable giving the quantum state. This is well-known for pure states, i.e. states that can be characterized by a single wave function, where there is no observable directly revealing this complex wave function. The same absence is true for the more general case of mixed states, which are states that can be characterized by a density matrix, but not necessarily by a single wave function. In this paper, we shall be treating such mixed states, paying special attention to thermal states; a type of mixed state that describes a quantum system at a finite temperature. In particular, we will concentrate on finding the vibrational state of an initially thermal molecule, which has been excited to an unknown vibrational state by a short laser pulse.

Although the state is not directly observable, one can determine the state from measurements. This is the field of study known as quantum state reconstruction. On each member of an ensemble, one or more commuting measurements are performed, whereafter this member is discarded. This ensemble must be large enough that the measured values are close to their true expectation values, which obviously requires numerous measurements of each quantity. Fortunately, in the method presented below there will be a vast number of molecules in each experimental run, ensuring excellent statistics.

In the broader picture, there has recently been growing interest in reconstructing quantum states for various systems, for a review see [6]. The general problem of quantum state reconstruction is experimentally and theoretically challenging, and methods tend to apply to only a very particular setting. The most well-known is the tomographic reconstruction of harmonic oscillator states from measurements of spatial distributions [7], [8]. Other systems include particles in traps (neutral atoms [2] and
ions [10], general one-dimensional systems [11], dissociating diatomic molecules [12] and the angular state of a dynamically aligned molecule [13].

Earlier works directly related to this paper have proposed reconstructing vibrational states for diatomic molecules using heterodyne detection of fluorescence [14], for general molecules using time- and frequency- resolved fluorescence [15], [16], and using time- and frequency-integrated fluorescence and a known reference state for quantum state holography [17]. Common for these proposals is the requirement that the initial state be a pure state. Realistically, fulfilling this requirement in turn demands a sufficiently low temperature of the molecules before the creation of the vibrational excitation. This initial temperature must be so low that only the lowest vibrational level is populated. For many molecules this is unpractical, e.g. gaseous iodine, where practical temperatures populates more than one vibrational state, lest the iodine is deposited [4], [19]. It is important to note that even though the initial thermal state’s ground vibrational state population is usually much larger than that of all other vibrational states, it does not guarantee that this gives the dominating contribution to the unknown excited state. For instance, in the experiment on molecular iodine described in [19], the ground and first excited vibrational level in the initial thermal state give approximately equal contributions to the unknown excited state, even though the ratio of populations is about 2.5 : 1. This is mainly due to the different Franck-Condon factors involved in the formation of the unknown excited state by the first laser pulse. Hence, taking several initially thermally populated levels into account can be essential to understanding the excited state formed.

The paper is arranged as follows: In section II we identify the type of quantum state being reconstructed and give a brief description of what is required of the measurements. In section III we outline an experimental implementation of the required measurements and give an overview of the energy- and time-regimes involved. In section IV we show by calculation how to reconstruct the unknown vibrational quantum state. In section V we discuss the generality of the reconstruction procedure and conclude the paper.

II. STATES AND MEASUREMENTS

Having established the importance of the physical state and its reconstruction, we will now specify what we mean by the physical state and what the measurements for reconstruction must fulfill.

It is essential to distinguish between the state of a system and its dynamics. The state contains the answer to all questions we may ask the system at a certain point in time, i.e. the result of all thinkable one-time measurements at this time. In sharp contrast to this state is the concept of dynamics, which is prescriptions for finding the state at a later time, from knowing it at an earlier time.

In the subject of state reconstruction, and in this paper in particular, the goal is to determine the state of a system. The type of state we will find in this paper is an unknown vibrational state of a sample of molecules, coherently excited from an initial thermal state. Specifically, we will restrict the reconstruction of the unknown vibrational state to the electronic state(s) it populates, denoted by the electronic index $a$, and thus not find correlations with the initial thermal population. This is exactly what is usually meant by the concept of an excited vibrational state. For transparency, we restrict ourselves to the most important case where the initial thermal state is limited to the electronic ground state, with possibly several vibrational levels populated. The excitation that forms the unknown vibrational state need not be perturbative in the sense that it may transfer a large fraction of the initial thermally populated level to the electronic state $a$. Nevertheless, it must leave a non-vanishing population in the initial state and not transfer population back to other of the initially populated levels.

Since the initial state is a mixed state, we cannot describe it by a single wave function, and because coherent excitations preserve the mixed character, neither can we describe the excited vibrational state this way [20]. A sufficing description is the density matrix, for which the initial thermal state would be diagonal in the energy basis, but we shall take a more transparent course.

As the states originating in different energy levels in the initial thermal state are incoherent with respect to each other, and the vibrational state we seek is coherently excited from these, we can describe the system as an incoherent sum of vector states (corresponding to wave functions). By an incoherent sum, we mean forming a sum of the states, each with a phase factor $\exp(i\theta_k)$ labeled after the original energy level $k$ in the initial thermal state from which the coherent excitation took place. These phase factors will be averaged over when taking inner products, making incoherent cross-terms vanish. In this paper, each incoherent term will be labeled by a left subscript, such as $k\beta$. To illustrate this, consider the example of a thermal state of a molecule with the only energy levels populated being the vibrational levels $k = 0$ and $k = 1$ in the electronic ground state. We then imagine exciting a vibrational state in another electronic level $a$, the vibrational eigenstates $|\phi_{a,l}\rangle$ herein being labeled by index $l$. The excited state will then be:

$$|\psi_a\rangle = \sum_k |k\psi_a\rangle = |k=0\psi_a\rangle e^{i\theta_0} + |k=1\psi_a\rangle e^{i\theta_1} = e^{i\theta_0} \sum_l \alpha_l |\phi_{a,l}\rangle + e^{i\theta_1} \sum_l \beta_l |\phi_{a,l}\rangle,$$

where the $k\beta_l$ are expansion coefficients. What we mean by “finding the unknown vibrational state” is thus determining all the complex expansion coefficients $k\beta_l$. With the incoherent averaging, inner products between states
originating from different levels in the initial thermal state vanish, e.g.
\[
\langle k=0|\psi_a|\hat{A}|k=1|\psi_a \rangle \propto \int_0^{2\pi} d\theta_0 e^{-i\theta_0} \int_0^{2\pi} d\theta_1 e^{i\theta_1} = 0,
\]
where \(\hat{A}\) can be any operator. Thus, we will not see any cross-terms between states originating in different energy levels of the initial thermal state, whence we will conveniently treat these states for different \(k\) separately. However, one should notice that it is still possible to see interference in an intensity signal between the light formed from different incoherent levels. This can be easily seen by considering the two electric fields formed from the transitions from level \(a\) to the electronic ground state 0:
\[
\begin{align*}
    k=0 & \quad E(t) \propto d^2/dt^2 \langle k=0|\psi_0|\hat{d}|k=0|\psi_a \rangle \\
    k=1 & \quad E(t) \propto d^2/dt^2 \langle k=1|\psi_0|\hat{d}|k=1|\psi_a \rangle,
\end{align*}
\]
where \(\hat{d}\) is the scalar product of the dipole moment operator with the electric field’s polarization vector. Since the incoherent \(\theta_i\)-factors cancel in each electric field, we will observe interference in the intensity signal \(I \propto |k=0E(t) + k=1E(t)|^2\).

Having accounted for what we mean by the state, we now turn our attention to measurements. To accomplish the state reconstruction, we will require knowledge of the results of enough measurements to uniquely determine the state [21]. Such a set of measurements is known as a quorum.

Finding a quorum can be straightforward or tedious, depending on both the system and the level of description. In a classical system of particles, one quorum is given by measurements of the coordinates and momenta of all particles at a fixed point of time. In contrast, the quantum mechanical description used in this paper makes finding a practically realizable quorum much more challenging. We will use the prevalent approach which is to perform the same type of measurement at different points of time, thereby letting the dynamics reveal the state, see e.g., [3], [11]. Using this approach, one is almost always forced to assume full knowledge of the dynamical laws of the physical system. However, we shall largely circumvent such assumptions by instead performing a calibration of the measurement apparatus. Specifically, we will show that spectra of a four-wave mixing laser pulse, created at different times after the formation of an excited vibrational state, encompass a quorum for determining the set \(\{k,\beta_t\}\).

III. EXPERIMENTAL IMPLEMENTATION OUTLINE

In this section we outline a pump-probe experiment where one can record the data necessary for the vibrational state reconstruction. This is a four-wave mixing experiment where one sends in three laser pulses 1-3 from different directions on a molecular sample, and records the spectrum of the outgoing four-wave mixing (FW) pulse [22], [18]. Laser pulse 1 reaches the molecular sample first and can be regarded as a pump pulse, since it has the effect of creating the unknown vibrational quantum state in the molecules. Pulses 2 and 3 arrive at the molecules long after pulse 1 is over, and can thus be regarded as probe pulses. The time \(\tau\) when pulse 1 creates the unknown state is varied from one experimental run to the next, retaining the timing of pulses 2 and 3. One then measures the spectrum of the resulting FW pulse. The time sequence of the four laser pulses is outlined in Fig. 1. One should notice that even though the pulses 1 – 3 should individually be the same from one run to the next, there is no requirement of relative phase stabilization.

![Figure 1: Time sequence of the laser pulses. First, pulse 1 excites a vibrational state in a sample of thermal molecules at time \(\tau\). When pulse 1 is over, the molecules are probed using the pulses 2 and 3. While the pulses 1-3 are always the same, the time \(\tau\) is varied from one experimental run to the next. The interaction of the three pulses 1-3 with the molecules gives rise to a four-wave mixing (FW) pulse. The spectrum of this FW pulse is measured together with the current value of \(\tau\). Of further notice is that the emission of the coherent FW pulse can continue long after the incident pulses 1 – 3 have died out, since the emission is due to an excitation in the molecules. For transparency, we will in section V assume that pulse 2 and 3 have no temporal overlap, as shown. However, this is not a requirement of our method, and we will relax this assumption in section V allowing for overlapping probe pulses as used in [11]. To keep the theoretical treatment transparent, we will now introduce several simplifying assumptions. We emphasize that these are not formal requirements, and are only included for clarity. Indeed, we will do away with them in section V. The laser pulses involved will all cause transitions in the molecules, dominated by dipole transitions. In Fig. 2 we show an overview of such a series of transitions, each being accompanied by a change of the electronic state. We have sketched the four electronic states 0 and \(a-c\), and within each of these several vibrational states. Furthermore, the figure shows that the transitions due to pulse 2 always occurs before transitions due to pulse 3. Realistically, this could be the case if pulse 2 precedes pulse 3 so that they have no temporal overlap, as shown in Fig. 1. We also require that only a single photon from pulses 2 and 3 are involved in each transition. Finally, we neglect...
the rotational degrees of freedom. This constitutes the most transparent situation, and we shall initially calculate the spectrum of the FW pulse in section IV using these assumptions. In section V we will then discuss how to relax these non-essential assumptions.

One can experimentally justify the implicit assumption made in Fig. 2 that only a single photon from each of the incoming laser pulses is involved in each transition. Using the non-co-linear, so-called folded BOX-configuration shown in Fig. 3 one sends in pulses 1-3 from three different directions. Each angle between the pulse propagation direction is small, typically a few degrees. One can select out the FW signal caused by pretransfer population back to other of the thermally populated levels (i.e. other $k$-indices). We can then expand the unknown state $|k\psi_{a}(\tau)\rangle$ on the vibrational eigenstates $|\phi_{\alpha,l}\rangle$ with energy $\hbar\omega_{\phi}^{l}$, belonging to the electronic level $\alpha$:

$$|k\psi_{a}(\tau)\rangle_{t} = e^{i\theta_{k}} \sum_{\nu} k\beta_{\nu l} |\phi_{\alpha,l}\rangle e^{i\omega_{\nu}^{l} k\tau / \hbar} e^{-i\omega_{\nu}^{l} t_{2}} , \quad (2)$$

where the $k\beta_{\nu}$ are expansion coefficients and the transition frequencies $\omega_{\nu}^{\alpha l}$ between the vibrational states $\nu$ and $\nu'$ in their respective electronic states $\alpha$ and $\alpha'$ are given by:

$$\omega_{\nu,\nu'}^{\alpha l} = \omega_{\phi}^{l} - \omega_{\phi}^{l'} .$$

Unlike pulse 1, the probing pulses 2 and 3 must be perturbative. Using the electric field $E_{2}(t)$ of pulse 2, we find:

$$|k\psi_{b}(\tau)\rangle_{t} = -\frac{i q}{\hbar} \int_{-\infty}^{t_{2}} dt_{2} e^{-i\hat{H}_{E}(t_{2}-t_{2}) / \hbar} E_{2}(t_{2}) \times \hat{d} \left[ |k\psi_{a}(\tau)\rangle_{t} \right]_{t_{2}} . \quad (3)$$

where $\hat{H}_{E}$ is the vibrational Hamiltonian in the electronic state $\alpha$, $q = -e$ is the electron’s charge, and $\hat{d}$ is the dipole moment operator. The corresponding expression for $|k\psi_{c}(\tau)\rangle_{t}$ can be found similarly:

$$|k\psi_{c}(\tau)\rangle_{t} = \frac{q^{2}}{\hbar^{2}} \int_{-\infty}^{t} dt_{3} \int_{-\infty}^{t_{3}} dt_{2} e^{-i\hat{H}_{E}(t_{3}-t_{3}) / \hbar} E_{2}(t_{3}) \times \hat{d} e^{-i\hat{H}_{E}(t_{2}-t_{2}) / \hbar} E_{2}(t_{2}) \times \hat{d} \left[ |k\psi_{a}(\tau)\rangle_{t} \right]_{t_{2}} . \quad (4)$$

We introduce the Fourier transforms of the electric fields:

$$E_{r}(t_{r}) = \int_{-\infty}^{\infty} d\omega_{r} E_{r}(\omega_{r}) e^{-i\omega_{r} t_{r}} , \quad r = 2, 3 . \quad (5)$$

Furthermore, we use identities resolved on the vibrational states $\nu$ of the electronic state $\alpha$, including both bound and continuum states:

$$\hat{I}_{\alpha} = \sum_{\nu} \langle \phi_{\alpha,\nu} | \langle \phi_{\alpha,\nu} | \rangle . \quad (6)$$

Finally, we abbreviate $q / \hbar$ times the dipole transition moments between the vibrational levels $\nu$ and $\nu'$ in their respective electronic states $\alpha$ and $\alpha'$:

$$\mathcal{D}_{\nu,\nu'}^{\alpha l} = \frac{q}{\hbar} \langle \phi_{\alpha,\nu} | \hat{d} | \phi_{\alpha',\nu'} \rangle . \quad (7)$$

IV. THEORY

In this section, we shall theoretically treat the situation outlined in the previous section, aiming at reconstructing the quantum state formed by pulse 1. We will accomplish this through calculating the spectrum of the FW pulse.

We recall from section II that we initially have a thermal state, where each energy level $k$ may be treated independently on the quantum level. Concentrating on a fixed $k$, the total state formed by the three laser pulses can be written as:

$$|k\psi(\tau)\rangle_{t} = |k\psi_{0}(\tau)\rangle_{t} + |k\psi_{a}(\tau)\rangle_{t} + |k\psi_{b}(\tau)\rangle_{t} + |k\psi_{c}(\tau)\rangle_{t} , \quad (1)$$

where the superscript denotes which pulse has formed the state from the previous, the right subscript denotes the electronic state, and $t$ is the time. In each of the perturbation orders, we shall for clarity retain only terms leading to coherent FW emission. The parameter $\tau$ signifies the time shown in Fig. 3 the time when the unknown excited state is formed. This state $|k\psi_{a}(\tau)\rangle$ does not need to be formed perturbatively, as long as it leaves a non-vanishing population in the $|k\psi_{0}(\tau)\rangle$-state, and it does not transfer population back to other of the thermally populated levels (i.e. other $k$-indices).
Laser pulse 1 creates a vibrational state in the electronic state dominating contribution to the through electronic states. Next, the state created with pulse 1 is probed through a four-wave mixing process using pulses 2 and 3 to transfer the system negative frequency components of pulse 2 is to stimulate emission as shown in Fig. 2, the $k$ yields for the contribution caused by the $k$th initially populated level:

$$\frac{d^2}{dt^2}[kd(t,\tau)] = \frac{d^2}{dt^2}\langle \psi^{(3)}_k(\tau)|\hat{d}|\psi^{(0)}_0\rangle_t.$$ (8)
The measurements at our disposal are spectral intensities for each delay \( \tau \), i.e., a two-dimensional spectrogram. Even though we measure intensities and not electric fields, the signal is found from squaring the electric field \( S(\omega, \tau) \propto |E_{FW}(\omega, \tau)|^2 \). Therefore, dividing the signal by \( \omega^4 \), we can find the following quantities:

\[
\frac{S(\omega, \tau)}{\omega^4} = N \left| \tilde{d}(\omega, \tau) \right|^2 = N \sum_{i,l',k,k'} C_i(\omega) \tilde{C}_{l'}^{*}(\omega) \beta_{l'i} \beta_{k,k'}^* \times e^{i \left( \omega_{i,l'} - \omega_{k,k'} \right) \tau}, \tag{11}
\]

where the overall positive factor \( N \) is introduced for two reasons: First, we do not know the absolute populations created by the pulses, and second, we wish to avoid the difficulties connected with measuring absolute signal strengths. To extract the \( \beta_i \)'s, a first step is to isolate single terms \( k C_i(\omega) \beta_{l'} \beta_{k,k'} \) from the sum in Eq. (11). We can use Fourier transformation with respect to \( \tau \) to extract a single or a few terms of this type. The number of terms found from such a procedure equals the number of recurrences in the transition frequencies at the chosen frequency \( \Omega \):

\[
F(\Omega, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} S(\omega, \tau) e^{-i\Omega \tau} d\tau = N \frac{1}{2\pi} \int_{-\infty}^{\infty} \left| \tilde{d}(\omega, \tau) \right|^2 e^{-i\Omega \tau} d\tau = N \sum_{k} C_i(\omega) \beta_{l'i} \beta_{k,k'} \beta_{k,k'}^*, \tag{12}
\]

with the primed sum running over indices \((k, k', l, l')\) so that \( \Omega = \omega_{i,l'} - \omega_{k,k'} \). Even though the \( \tau \)-integral in Eq. (12) runs over all values of \( \tau \), one cannot achieve this in real experiments. Both the inevitable truncation of the \( \tau \)-interval and decay processes will cause a broadening of the peaks in \( F(\Omega, \omega) \) as a function of \( \Omega \), in turn leading to an increased number of frequency recurrences. Although a concern in principle, it will be seen that it is possible in typical experiments to use (a discrete version of) Eq. (12) to find sums with just a single or a few terms. We will aim to extract single terms from these sums. Obviously, choosing \( \Omega = 0 \) gives many terms, among them the ones with \( l = l' \), making it difficult to extract any single one. Fortunately, it will turn out that we will not need these, so we shall henceforth look for terms with \( l \neq l' \).

To select out a single or a few terms from the function \( F(\Omega, \omega) \) in Eq. (12), we must make appropriate choices of the variables \( \Omega \) and \( \omega \). In the following subsection IV.A, we shall present a method to do this for the \( k \) that can be selected by proper choice of \( \omega \): case (I). This is usually the case for the lowest populated (ground) state \( k = 0 \) (see e.g., 19) and for any \( k \) that are energetically separated from their neighboring vibrational levels by more than the combined width of the laser pulses. Further below, in subsection IV.C, we will present how to deal with the remaining \( k \) through making a weak assumption on the spectrum - case (II). Finally, in subsection IV.D, we will discuss how to do the reconstruction if the two above methods fail.

### A. Emission due to single \( k \)'s: Case (I)

We turn our focus to the group of \( k \) states that belong to case (I). Choosing the frequency \( \Omega = \omega_{i,l'} \), we see that the sum Eq. (12) contains terms with all \( k \neq k' \). Even though this is a complication, we can circumvent it in this case by using the freedom in choosing \( \omega \) to select \( k \) by making all \( k C_i(\omega) \) vanish, except for a single \( k \). This situation is illustrated in Fig. 4.

In the usual experimental situation where the signal \( S(\omega, \tau) \) is simultaneously recorded for all frequencies \( \omega \) in a wide range, we also know \( F(\Omega, \omega) \) for this range of \( \omega \). To find out if only one \( k \) contributes at a fixed \( \omega \), one simply checks whether \( F(\omega_{i,l'} - \omega_{k,k'}, \omega) = 0 \) for all \( k' \neq k \).

To avoid testing too many values of \( \omega \) by the above procedure, one can readily determine the approximate \( \omega \)-range of interest. From the easy measurements of the
central frequency and widths of pulses 1-3, one can locate a limited $\omega$-interval where one expects the $FW$ signal from each $k$. In such considerations, one can also benefit from knowing approximate potential surfaces to get an idea of which transitions have appreciable transition matrix elements.

Thus, by wisely selecting certain values of $\omega$, we can limit the primed sum Eq. (12) to run only over $l$ and $l'$. If there are degeneracies in the frequencies $\omega_{l,l'}$, it can still be possible to find the elements indirectly. Since the details depend on the problem at hand, we illustrate this with an example.

$$\sum_{l,l'}$$

Say, $\omega_{l,l'}^{a,a} = \omega_{l,l'}^{b,b}$, and we have Fourier transformed to find the following sum, suppressing the $k$-index and $\omega$-variable for clarity:

$$\begin{align*}
F(\Omega) &= NC_l \beta_l C^0_{l,l} \beta^0_{l'} + NC_{l'} \beta_{l'} C^0_{l',l} \beta^0_{l}.
\end{align*}$$

(13)

Provided that we can find each of the following coefficients and that none of them are zero, we can form the quotient:

$$\frac{NC_l \beta_l C^0_{l,l} \beta^0_{l'} \times NC_{l'} \beta_{l'} C^0_{l',l} \beta^0_{l}}{NC_{l'} \beta_{l'} C^0_{l',l} \beta^0_{l}} = NC_l \beta_l C^0_{l,l} \beta^0_{l'},$$

allowing us to extract each of the terms in Eq. (13). Thus, we can use intermediate levels to obtain each term in sums, otherwise hidden because of the degeneracy in the transition energies.

In principle, we could similarly find all such products $NC_l \beta_l C^0_{l',l'} \beta^0_{l'}$, including $l = l'$. Though having all these products permits a nice statistical treatment through singular value decomposition of the outer product matrix, it can be difficult to measure $NC_l \beta_l C^0_{l,l'} \beta^0_{l'}$, with the integers $l$ and $l'$ differing by more than a few. This is because terms with $l$ and $l'$ significantly different correspond to quantum beats between distant levels in the unknown excited state. Fortunately, these are not necessary because of our freedom of choosing normalization and phase of each $|k \psi^{(1)}_a\rangle$, as will be clear below.

We have now reached the limit of what we can extract from the $(\omega, \tau)$-spectrograms. To find the unknown quantum state through the $\beta_l$’s, we need to know the $C_l(\omega)$’s. These are in turn both difficult to calculate, one reason being the regularization of the apparent divergencies in Eq. (10), and more importantly require detailed knowledge of the electric fields of the pulses 2 and 3, of the dipole matrix elements $D_{\alpha,\beta'}^{a,a'}$ and of the transition frequencies $\omega_{\nu,\nu'}$. One may rightly argue that with the knowledge of the dipole transition moments, it would have been easier to measure the field of the single pulse 1 and simply calculate the unknown quantum state by propagation using the dynamical laws. Therefore, we shall take a completely different approach which circumvents both regularizations, detailed knowledge of electric fields, and knowledge of transition matrix elements and transition energies between excited states.

### B. Calibration pulse

In this subsection, we introduce one or more calibration pulses aimed at creating excited quantum states in the electronic level $a$ with known calibration expansion coefficients $k \beta^{cal}_{l}$. This is a different approach than heterodyne detection or other reference pulse techniques, since the calibration experiment is a separate experiment from the one where the reconstruction data are recorded. Hence, by performing exactly the same experiments as above, except with the calibration pulse substituted for pulse 1, we will find products of the form $NC \ k C_l(\omega) \ k' C^0_{l'}(\omega)$. These will in turn be used in the reconstruction experiment with pulse 1 to find the coefficients $k \beta_l$. Let us consider this in detail.

Contrary to pulse 1, we will require that the calibration pulse be perturbative, because this gives simple expressions for the state created in the calibration. We find this state similarly to Eq. (3), letting the upper limit in the integration tend to infinity since the electric field $E_{cal}(t' + \tau)$ vanishes for times long before the pulses 2 and 3 are turned on:

$$|k \psi^{cal}_a(\tau)\rangle_{t_2} = -\frac{id}{\hbar} \int_{-\infty}^{\infty} dt' \ e^{-iH_a(t_2-t')/\hbar} E_{cal}(t' - \tau) \times \hat{d} e^{-iH_0(t'-0)/\hbar} |k \psi^{(0)}_0\rangle_0$$

$$= -i \ e^{i\theta_k} \sum_l D_{l,k}^{a,0} \ E(\omega_{l,k}^{a,0}) |\phi_{a,l}\rangle \times e^{i\omega_{l,k}^{a,0} t_2}.$$

(14)
Comparing Eq. (11) to Eq. (2), we see that the expansion coefficients of the calibration state are

\[ k\beta_i = -iD_{l,k}^{a,0} C_{l}^{a,0}(a) \].

(15)

Thus, by knowing the dipole transition elements \( D_{l,k}^{a,0} \) and the frequency-components of the electric field of a calibration pulse, we can calculate the expansion coefficients of the vibrational calibration state created in the electronic state \( a \). For convenience, one can merely use a calibration pulse that has a constant spectrum over the relevant frequencies \( \omega_{k}, \) giving calibration expansion coefficients of the levels according to the values of the dipole transition matrix elements. It is therefore not necessary to have detailed information about the calibration pulses, but we must know the transition dipole matrix elements between the electronic states 0 and \( a \). Fortunately, these are typically readily measured, e.g. by fluorescence spectroscopy, or calculated. In contrast, it is more difficult to find similar elements between two excited states - elements we fortunately do not need to know.

In the remaining part of this subsection we will be considering a single \( k \), and we shall suppress this index for clarity.

For the calibration to be useful, the calibration data recorded must enable us to determine the \( \beta_i \)'s up to a common non-zero complex factor. We will accomplish this by determining products \( \beta_i \beta_i^* \) up to an overall complex factor, common for all products. The measurements with pulse 1 gives quantities \( N_1 C_i(\omega) \beta_i C_i^*(\omega) \beta_i^* \), precisely allowing us to determine \( N_1 \beta_i \beta_i^* \) if we know \( C_i(\omega)C_i^*(\omega) \). These mapping coefficient products can in turn be found, up to a common factor \( N_C \), from the calibration data \( N_C C_i(\omega) \beta_i \beta_i^* C_i^*(\omega) \beta_i^* \), where the \( \beta_i \) are known. By division, we can hence find products of the form \( N_i \beta_i \beta_i^* \). To determine the \( \beta_i \)'s individually, we simply set one of these equal to one, use the products to determine the rest, and finally normalize. Therefore, there is no benefit in knowing one of these products where neither \( l \) or \( l' \) enter in another product. Consequently, we must know the range of \( l's \) that are populated by pulse 1 (from its spectral center and width) and be able to find products \( N_i \beta_i \beta_i^* \) where all populated \( l \)'s enter, and no product has both an \( l \) and an \( l' \) that do not enter in another. Furthermore, one is free to use data from more than one value of \( \omega \), as long as each data set can be related to data at all other values of \( \omega \). This is sufficiently fulfilled if one can determine a product \( N_C C_i(\omega)C_i^*(\omega) \) at one value of \( \omega \) that contains an \( l \) also contained at in a product at another value of \( \omega \).

In case it is not convenient to populate all these levels with a single calibration pulse, more can be used in subsequent calibrations. Since we can allow for only a single undetermined overall complex factor, it is necessary to relate the data from one calibration pulse to the others. For instance, it is sufficient to determine a single \( N_{C1} C_i(\omega)C_i^*(\omega) \) from one calibration \( C1 \) which can also be determined in another calibration \( C2 \) to find the ratio \( N_{C1}/N_{C2} \).

All this having been said, we illustrate the procedure with a brief example. Let us say that we are interested in reconstructing the vibrational state originating in a certain \( k \) (which we suppress for clarity), and we desire the expansion coefficients \( \beta_i \) with \( l \in \{1, 2, 3, 4, 5\} \). We employ two calibration pulses \( C1 \) and \( C2 \). \( C1 \) has a constant spectrum in a range sufficient to populate levels 1-4 and \( C2 \) similarly populates levels 3-5. Measuring at the two frequencies \( \omega_a \) and \( \omega_b \) where other \( k' \neq k \) give only negligible contributions, it is found that there is good signal strength for the following terms:

\[
\begin{align*}
N_{C1} C_1(\omega_a)C_1^*(\omega_a) & \text{ pulse } C1 \\
N_{C1} C_2(\omega_a)C_2^*(\omega_a) & \text{ pulse } C1 \\
N_{C1} C_3(\omega_b)C_3^*(\omega_b) & \text{ pulse } C2 \\
N_{C2} C_3(\omega_b)C_5^*(\omega_b) & \text{ pulse } C2
\end{align*}
\]

where we have already divided out the known calibration expansion coefficients \( \beta_{\text{cal}} \beta_{\text{cal}}^* \), up to a factor absorbed in the \( N_C \)'s. The element \( C_3(\omega_b)C_5^*(\omega_b) \) recurring in both pulses serves the special purpose of relating the two pulses by showing us the ratio of the numbers \( N_{C1} \) and \( N_{C2} \). Hereafter, the actual experiment is performed with pulse 1. In the table below, we show how one obtains the products \( N_i \beta_i \beta_i^* \) from measurements and calibration data.

| Measurement: | Used calibration: | We find: |
|---------------|-------------------|----------|
| \( N_{C1} C_1(\omega_a)C_1^*(\omega_a) \) | \( N_{C1} C_1(\omega_a)C_1^*(\omega_a) \) | \( N_{C1} C_1(\omega_a)C_1^*(\omega_a) \) |
| \( N_{C1} C_2(\omega_a)C_2^*(\omega_a) \) | \( N_{C1} C_2(\omega_a)C_2^*(\omega_a) \) | \( N_{C1} C_2(\omega_a)C_2^*(\omega_a) \) |
| \( N_{C1} C_3(\omega_b)C_3^*(\omega_b) \) | \( N_{C1} C_3(\omega_b)C_3^*(\omega_b) \) | \( N_{C1} C_3(\omega_b)C_3^*(\omega_b) \) |
| \( N_{C2} C_3(\omega_b)C_5^*(\omega_b) \) | \( N_{C2} C_3(\omega_b)C_5^*(\omega_b) \) | \( N_{C2} C_3(\omega_b)C_5^*(\omega_b) \) |

Since we have the freedom of choosing the normalization constant \( N' \), we can arbitrarily set \( \beta_1 = 1 \), from which we can use the following lines in the table to find (in order) \( N' \beta_2, N' \beta_4, N' \beta_3 \), and from the last line \( N' \beta_5 \). Finally, the state can be normalized by appropriately choosing \( N' \). We have thus found the set of complex numbers \( \{\beta_i\} \), both their magnitude and phase, and we have thereby performed the reconstruction of the state formed by pulse 1.

Having been concerned with how to use small sets of measurements, it should be said that in a typical experimental situation, one will have much more data than is minimally required. This abundance of data can be used to further improve the statistics of the reconstructed values.

Finally, it may be of note that we can easily find the individual mapping coefficients \( C_i(\omega) \) from the calibration data, up to a common factor (rather than just products of two coefficients). This is done in the exact same way as finding the \( \{\beta_i\} \), i.e. by setting one of the \( C_i(\omega) = 1 \), and using the products to find the rest. Thereby dynamical information about the molecule can be obtained.
C. Interference between different \( k \): Case (II)

We turn our attention to case (II) where not all \( k \) can be isolated from Eq. (12) by proper choice of \( \omega \). This situation, encountered in [19], is illustrated in Fig. 5 for two initially populated \( k \)-levels. Here the wave-packet originating in \( k = 1 \) cannot be found by the above procedure.

\[ \omega = \omega_0, \quad k = 0 \]

\[ \omega = \omega_1, \quad k = 1 \]

\[ \omega = \omega_0 \]

\[ \omega = \omega_1 \]

\[ k = 0 \]

\[ k = 0 \text{ dominates} \]

\[ k = 0 \text{ and } k = 1 \]

\[ \text{Interference} \]

\[ \text{No pure } k = 1 \text{ region} \]

\[ \tau \]

Figure 5: Schematic illustration of a spectrogram Eq. (11) in case (II). The vertical lines signify maxima in the signal \( S(\omega, \tau)/\omega^2 \), with contributions from different initial levels explicitly shown. In contrast to Fig. 4, we cannot find values of \( \omega \) for which only \( k = 1 \) contributes. Still, one can first find the \( 0, \beta_i \)'s through the procedure described in section [VIII]. These coefficients can afterwards be used to extract the \( 1, \beta_i \) by using the frequencies in \( F(\Omega, \omega) \) that arise from optical interferences between the \( k = 0 \) and \( k' = 1 \) signals. If there are more overlapping \( k' \) signals than the two shown, the \( \nu, \beta_i \) from these can be extracted by similar means.

However, if just a single \( k \) can be isolated by choosing \( \omega = \omega_1 \), we can by the above method find the \( 0, \beta_i \)'s for this \( k = 0 \) (usually the ground state) up to a common phase factor. In this subsection we describe how the \( k \neq 0, \beta_i \) can be found if the spectrum fulfills certain conditions. For transparency, we initially focus on the situation in Fig. 5 where we seek the coefficients \( 1, \beta_i \). For our method to work, we demand that some of the frequencies \( \Omega_{i,l}^{0,1} = \omega_{i,l}^{a,a} - \omega_{k=0,k'=1}^{0,0} \), arising from optical interferences between \( k = 0 \) and \( k = 1 \), must be spectrally resolved from the pure \( k = 0 \) and \( k = 1 \) signals having \( \Omega_{i,l}^{k,k} = \omega_{i,l}^{a,a} \). Having this requirement fulfilled, we can extract the quantities \( F(\Omega_{i,l}^{0,1}, \omega_1) = 0C_l(\omega_1)_{0, \beta_i}C_l^*(\omega_1)_{1, \beta_i} \). In the calibration experiment, we can hence determine the mapping coefficient product \( 0C_l(\omega_1)_{1, \beta_i}C_l^*(\omega_1)_{1, \beta_i} \) up to a common multiplicative factor and, by using the \( 0, \beta_i \) found in the experiment (using \( \omega = \omega_0 \)), we can find \( 1, \beta_i \) (using \( \omega = \omega_1 \)).

Similarly to case (I), we do not require spectral resolution of all frequencies \( \Omega_{i,l}^{0,1} \) and \( \Omega_{i,l}^{k,k} \). Indeed, to determine all \( 1, \beta_i \), we just need one resolvable \( \Omega_{i,l}^{0,1} \) for each \( l \) at some \( \omega_1 \), and that the corresponding \( 0, \beta_i \) is non-zero.

If more than two values of \( k \) overlap, these can be found through similar means; either by their interference with \( k = 0 \) or recursively, i.e. \( k + 1 \) is found from \( k \). In conclusion, we can completely reconstruct the state in case (II).

D. Case (III)

The treatments of cases (I) and (II) above were based on the assumption that at least a single \( k \) can be isolated from \( F(\Omega, \omega) \) by appropriately choosing \( \omega \). If such an \( \omega \) cannot be found, the situation is radically different. Still maintaining that we wish to avoid making assumptions about the mapping coefficients \( lC_l(\omega) \), one solution is to perform several experimental runs at different temperatures of the initial state. There are two main effects that change the spectrograms as the temperature is varied: Temperature dependent decoherence processes and thermal population of the initial state. The most important decoherence process will usually be collisional decoherence (pressure broadening), with a smaller contribution from Doppler broadening. In any case, these two effects broaden the spectral lines, scaling as \( \sqrt{T} \) for fixed particle density. For moderate temperature ranges, this is only a small effect; indeed we can ignore it altogether as long as the required spectral resolution is not washed out. In contrast, the initial state populations scale exponentially with \( 1/T \), greatly changing the spectrogram. It is exactly this change we can use to our advantage. Thus, the terms in Eq. (12) having \( k = k' \) will scale differently with temperature for each \( k \), and differently from terms with \( k \neq k' \). Demanding here that pulse 1 be perturbative, these variations with temperature simply follows the Boltzmann distribution corresponding to the energy of the \( k' \)th level in the initial thermal state. By forming linear combinations of \( F(\Omega, \omega) \) recorded at different temperatures with weights calculable from the corresponding Boltzmann distributions, one can find each of the individual terms with \( k = k' \) and with \( k \neq k' \). For example, if \( k_1 \) and \( k_2 \) both enter in Eq. (12), one can find all the terms individually; i.e. terms containing \((k_1, k_1),(k_2, k_2)\) and \((k_1, k_2)\). Consequently, it is possible to modify the above reconstruction method so it can be used, even if all \( k \) cannot be selected individually by choosing special values of \( \omega \).

V. DISCUSSION

Having presented above a specific implementation of the reconstruction method, we will now discuss how to do away with the clarifying, but non-essential, assumptions we made in section [VIII]. We discuss first the effects of rotation in subsection [VIII] whereafter we will move on to discuss the possible generalizations of the method in subsection [VIII].
A. Rotations

In the above, we completely neglected rotations, the qualitative correctness of which we will now justify. Though of general validity, we will for concreteness discuss diatomic molecules with rotational energy $E_{rot} = J(J+1)$, where $J$ is the angular momentum quantum number. If rotational states up to a certain $J_{max}$ are appreciably populated, the number of rotational states involved is circa $(J_{max} + 1)^2$. In an experiment where the temperature is high enough to populate several vibrational $k$ states, the number of entering rotational states will be large - of the order $N_{rot} \approx 10^4$ for the lowest vibrational state in the experiment [10]. All these rotational states are initially incoherent, and we can label each of them after their initial quantum number $J$ and its projection $M$: The initial state is therefore incoherent in all of the indices $k, J$ and $M$. Thus, by analogy with Eq. (8), the dipole moment leading to coherent $FW$ emission only contains contributions of the form $k,J,Md(t,\tau) = \langle \psi^{(3)}(t)|\psi^{(0)}(0)\rangle \tau$. For linearly polarized pulses, each of the one-photon transitions shown in Fig. 2 changes $J$ by 0 or $\pm 1$ while $M$ is conserved. Whether $\Delta J = 0$ is allowed depends on the symmetry of the electronic states $0 - c$. In the diatomic case, $\Delta J = 0$ requires one of the involved states in a one-photon transition to have non-zero electronic angular momentum. As a consequence, all the transition energies between vibrational levels $l$ and $l'$ entering in Eq. (11) (for clarity, with $k = k'$) will be split into many $\omega_{\alpha,\alpha'} \approx \hbar^2/2BJ$ with $J_1$ and $J_2$ differing by at most two. As known from field free alignment, some of these terms will interfere destructively after a time $T_{di} = \pi\hbar/2BJ$ and have a full revival after $T_{rot} = \pi\hbar/B$ where $J$ is the mean value of $J$ [23]. To elucidate which terms interfere destructively, one can write down the frequency dependent dipole moment for $\psi^{(0)}$ using the mapping coefficients and unknown coefficients dependent on the temperature through their rotational states. Since $\Delta J = 0$ is measured whereby the transition frequencies depend only on $J$, we find $N_{rot}(\Delta J = 0) \approx N_{rot}^2$ terms of the form $|d_{J,M,\Delta J}|^2$ with identical $\tau$-dependence; the majority $(N_{rot}^2)$ coming from $|d_{J,M,\Delta J}|^2$. These terms will all stay in phase and give rise to a signal at all delay times $\tau$, scaling as $N_{rot}^2$. The remaining $8N_{rot}^2 - 2N_{rot} \approx 8N_{rot}^2$ terms will have different $\tau$-dependent phases, and will be out of phase a time $T_{di}$ after formation by pulse 1. This makes their contribution to the signal scale as $N_{rot}$, except at the fractional and full revivals. Summarizing, for delays greater than $T_{di}$, but smaller than major rotational revivals, the terms with $\Delta J = 0$ will completely dominate the signal due to the scaling $N_{rot}^2 \gg N_{rot}$. Because all these terms have the same $\tau$-dependence, one can completely ignore the rotational degrees of freedom. A similar argument can be applied to pulse 2 and 3 showing that to avoid diminishing the signal further due to rotational interference (i.e. loose about 8/9 of the signal), it is beneficial to send in pulse 2 and 3 so close in time that approximately no rotational evolution takes place during their separation time. Having accounted for the scalings of the different contributions to the signal, we must also account for the possible delay times in an experiment. Due to collisional decoherence, it is typically only possible to measure the spectrogram for values of $\tau$ much smaller than the rotational revival time. Conversely, the vibrational periods are short enough to go through many cycles before the signal is washed away by decoherence. In conclusion, it is qualitatively correct to ignore the rotational degrees of freedom as long as (i) $N_{rot} \gg 1$, (ii) $\Delta J = 0$ transitions are allowed, (iii) we limit the $\tau$-interval for the Fourier transform in Eq. (12) so that pulse 1 ends more than $T_{di}$ before pulse 2 and 3, and (iv) we avoid values of $\tau$ so that pulse 2 arrives at a major fractional rotational revival.

The rotations also introduces ro-vibrational coupling, which effectively contributes an additional line-broadening. Though usually negligible, this effect scales with the absolute temperature as $T$ - more rapidly than pressure and doppler broadening. What limits the usable temperature is that the required spectral resolution may not be washed out by these line broadenings.

Lastly, it was suggested in section [V D] to perform experiments at different temperatures, altering both the vibrational and rotational populations. Being unable to resolve the individual rotational states within a vibrational level, we have taken all these rotational sub-levels to be included in their common vibrational level. In this way, all mapping coefficients contain sums over rotational levels and it is necessary to consider how these mapping coefficients change with temperature due to the changed rotational content. There could be two causes of such a change. Firstly, the transition frequencies $\omega_{\alpha,\alpha',J',\nu'}$ in Eq. (10) depend on $J$. Since $\Delta J = 0, \pm 1$ in each transition, these differences in transition frequencies are rather small and may be negligible. If not, one can merely separate pulses 2 and 3 by more than $T_{di}$, ensuring that only $\Delta J = 0$ is measured whereby the transition frequencies are independent of $J$. Secondly, it must be clarified how the mapping coefficients change with temperature due to the changed rotational content. An easy situation arises, however, for linear molecules where many rotational states are populated. Here, the electronic angular momentum in all states $0 - c$ is of the order 1 and the main contribution to the signal comes from $J \gg 1$. Then, the transitions depend only slowly on $J$, and the change in difference in rotational distributions with temperature may be ignored altogether.
### B. Generalizations of the method

Having dealt with rotations, we turn to relaxing the other assumptions made in section [III] and the possible generalizations of the method. All of these generalizations are centered around the use of calibration and around the linearity in expansion coefficients arising because of the perturbative character of the pulses 2 and 3, see e.g. Eq. (9).

First, is easy to see that this structure will be the same regardless of whether we are restricted to dipole transitions or also include higher multi-pole transitions. While this may not be of much relevance in four-wave mixing experiments, it shows the general principle: While the mapping coefficients \( kC_k(\omega) \) become more complicated, these are still fully accounted for because of the use of calibration pulses.

Second, the implicit assumption made in Fig. 2 and in section [IV] that the photon from pulse 2 enters the interaction before the photon from pulse 3 can also be relaxed. Similarly to the incorporation of multi-pole transitions above, one can sum over the different paths through the energy landscape traced out by the different sequences of absorption of photons from the pulses 2 and 3. For instance, if there is temporal overlap of the probe pulses 2 and 3, a major contribution to the electric field can be caused by an inner product of the form \( \langle k\psi_a^{(1)}(\tau)|d_\tau|k\psi_b^{(2)} \rangle \). Here, \( |k\psi_b^{(2)} \rangle \) is independent of \( \tau \), and is formed from the initial state by absorption of a photon from pulse 2 followed by stimulated emission of a photon to pulse 3. Like other energetic paths, this preserves the linearity in the \( k\beta \)'s and the signal’s dependence on \( \tau \). Indeed, one could even incorporate multi-photon transitions and still retain the structure of Eq. (11) and the reconstruction procedure from section [IVB] provided that the truncated perturbation series is an accurate description at each level of perturbation. If the molecular electronic levels are conveniently spaced, one can even use another number of pulses for the above procedure, down to a minimum of two (one for excitation and one for probing). The special importance of the FW situation is that it uses the smallest number of pulses in the widespread situation where only two electronic levels \( 0 = b \) and \( a = c \) are used. Though our method allows for both different numbers of incoming pulses and for multi-photon transitions, the non-co-linear geometry still plays an important role. Its advantage lies not in selecting certain electronic states, but rather in avoiding the strong background from pulses 1-3. Additionally, it gives a reasonably simple way of finding the \( \omega \)-interval that allows us to select a certain \( k' = k \) in Eq. (12).

Third, it is unnecessary that the electronic indices 0 and \( a-c \) denote single electronic states. These could as well be groups of states, where the vibrational indices \( k-n \) simply denotes all states in these groups. With this generalization it also becomes apparent that we do not need to make the Born-Oppenheimer approximation to maintain Eq. (9). Without this approximation, we cannot speak of vibrational and electronic states, but we make instead the more general statement that we find the quantum state in the group of energy levels labeled by \( a \).

Fourth, the unknown state does not need to be formed by a single laser pulse. What made it convenient to use the single laser pulse 1 above, was that the BOX-configuration made it possible to distinguish the signal from the states having interacted with pulse 1 by the direction of the FW-pulse. Nevertheless, any coherent process forming an unknown state in the group of levels \( a \) will work, provided that there remains population in the original group 0 levels (i.e. the states labeled by \( k \)), and no population is transferred back to these levels by the excitation process.

Fifth, the method above is easily extended to the case of correlated initial states, rather than just thermal ones. The difference from the above treatment is that there can now be quantum correlations between the different \( k \)-levels. To treat this situation, one simply writes down the density operator corresponding to the vector Eq. (11), retaining the \( (k,k') \)-correlations. Similarly to the treatment above, one looks for the coherent FW-terms in the emitted radiation with the appropriate direction. If one can again find \( \omega \)-values where the mapping coefficients are non-zero for a single \( k \) only, one can use the method above to find the same density matrix elements that we found previously. These are the elements arising due to the diagonal terms in the energy basis of the initial state. The difference, compared to the thermal case, is that there is additional information about the state found in an \( \omega \)-region approximately \( \omega_{0}^{0,0} \) from the \( (k,k) \)-region. This being said, it may well be easier to find the \( (k,k') \)-correlations in the initial state, instead of trying to extract them from the unknown excited state.

Sixth and finally, there is no requirement that the different \( k \) refers to the same molecule. If one wanted to examine a weak emission from a molecule \( A \), it could be possible to perform the above experiment on a mixture of \( A \) with another, more strongly emitting molecule \( B \). In the spectrogram region where the signals from \( A \) and \( B \) overlap, the strong electric field from \( B \) amplify the signal from \( A \) rather like the idea of mixing a weak signal with that of a strong local oscillator in heterodyne detection. The basic principle behind this was demonstrated by Engel et al. [20].

By discussing these generalizations, we hope to have given the reader the impression that doing quantum state reconstruction by perturbative processes with calibration is a very general approach with wide applicability.

In conclusion, we have presented a method to reconstruct an unknown vibrational quantum state, coherently excited from an initial thermal state. By using one or more calibration pulses, we have shown how to circumvent knowledge of the perturbative probing process, and we have suggested that this idea may be of much greater applicability in quantum state reconstruction.
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