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Heterodyne measurement of vibrational wave packets of diatomic molecules

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A method is presented for reconstructing the quantum state of vibrational wave packets in diatomic molecules by a heterodyne experiment. After the preparation of a wave packet, a femtosecond laser pulse interferes with the induced polarization and the resulting signal is frequency filtered and measured by a photodetector. The conditions are analyzed under which the resulting time- and frequency-resolved photocurrent contains the information needed to recover the quantum state of the prepared wave packet. It is shown that the vibrational wave function in the excited electronic state can be measured directly without the need of involved numerical reconstruction. Simulations of the proposed experiment are performed for sodium dimers.
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I. INTRODUCTION

During the last few years the development of methods for determining the quantum states of light and matter has been a subject of increasing interest [1]. Roughly speaking, there are two kinds of methods that have been successfully demonstrated in experiments. In quantum-state tomography the quantum state is reconstructed from the whole set of data recorded in a sequence of measurements, varying some parameters from measurement to measurement, such as the quadrature-component phase in balanced homodyning [2]. In local reconstruction the quantum state is reconstructed pointwise, i.e., for chosen parameters each set of measured data corresponds, e.g., to a point in phase space and can be used to reconstruct appropriate phase-space functions there [3]. The tomographic method was experimentally applied for the first time to the reconstruction of the quantum state of light [4], and the first experimental reconstruction of the motional quantum state of a trapped atom [5] was based on local reconstruction.

The tomographic method has also been applied to the reconstruction of the quantum state of molecular vibrations [6,7]. In the experiments, the set of data is obtained from time-resolved emission spectroscopy [8], and it is assumed that anharmonic effects of the vibrations play a minor role and can be disregarded in the reconstruction scheme. Alternatively, the desired information can also be obtained from photoelectron spectroscopy [9].

Unfortunately, the method cannot be directly transferred to anharmonic vibrations. In particular, in view of the manifold of frequencies characterizing the system it is no longer sufficient to record the dynamics only over one half of a vibrational period. It has been shown that the vibrational quantum state can be obtained through separate measurements of the time-resolved intensity and the stationary spectrum of the light emitted by the molecules [10–12]. The realization of such a method, however, requires the numerical inversion of a large set of noisy data. It has also been shown that the quantum state can be reconstructed from the time-resolved position distribution [13]. Presently, however, no experimental method is known that allows one to measure the time-resolved position distribution of a molecular vibration. Another proposal is based on the measurement of the time-resolved emission spectrum [14], where the dimension of the linear sets of equations to be inverted is substantially reduced by combining frequency separation and time resolution.

Some alternative methods that rely on other kinds of measurements have been proposed. A local reconstruction method has been proposed that allows one to determine phase-space distributions of molecular vibrations by Raman spectroscopy [15]. However, in its present version this method only applies to harmonic vibrations. A wave-packet interference technique has been proposed for measuring the quantum state of atomic Rydberg wave packets [16] and a technique of this type has also been treated for molecular systems [17].

In the present paper we study the possibility of the diagnostics of the quantum state of molecular vibrations by means of a heterodyne experiment. The detected signal can be quite large, since it scales in proportion to the reference intensity. This means that the signal-to-noise ratio of the measured data is rather better than in the case of fluorescence or photoelectron spectra measurement. We will show that this allows us to determine the vibrational quantum state in the excited electronic state, provided that the molecule is prepared in a pure state. The method then renders it possible to directly measure the quantum state without the need of involved and noise-sensitive reconstruction algorithms. Eventually, the proposed technique is not limited to harmonic vibrations.

The paper is organized as follows. To get a first insight into the proposed technique, Sec. II presents a simplified semiclassical description of the measured signal and its relation to the vibronic quantum state. In Sec. III a fully quantized theory of the complete heterodyne measurement scheme is developed. Section IV is devoted to the temporal evolution of the vibronic wave packet, and in Sec. V the kernel function connecting the prepared quantum state with the measured quantities is explicitely calculated. The possibility of direct measurement of the vibrational quantum state in the excited electronic state is studied in Sec. VI. In order to illustrate the method, in Sec. VII a numerical simulation for sodium dimers is presented. A brief summary and some conclusions are given in Sec. VIII.

II. HETERODYNE APPROACH TO STATE MEASUREMENT

A simple picture of the method is this: a pump pulse induces in the sample of molecules a polarization associated with the generation of wave packets on both the ground and excited electronic vibrational potential surfaces. This polarization radiates coherently, and thus has a well-defined time-dependent amplitude and phase that are related to the wavefunctions of the two different vibrational wave packets.

A classical reference pulse may be mixed with this signal and the resulting field is detected. This is effectively a heterodyne measurement of the radiating molecular polarization by means of the reference field, and it is well known that spectral interferometry [19] provides a way to extract phase information about an unknown time-dependent field from such a signal. One expects that the time dependence of the radiated field will yield information about the wave packets that generate it, and this is indeed the case, as can be seen from the following simple calculation.

The detected signal in the spectrally resolved heterodyne arrangement is given by [20]

$$S(\omega;\tau_{\mathrm{R}},\tau_{\mathrm{P}})=2\,\mathrm{Re}[\underline{E}^{*}(\omega;\tau_{\mathrm{R}})\underline{P}(\omega;\tau_{\mathrm{P}})],\tag{1}$$

where $\underline{P}(\omega;\tau_{\mathrm{P}})$ is the expectation value of the positive frequency component of the polarization in the molecule (the underbar notation represents quantities in the frequency domain). It arises from an entangled electronic-vibrational wave packet created at time τ_{P}. $\underline{E}^{*}(\omega;\tau_{\mathrm{R}})$ is the spectrum of the reference pulse field, with the reference arriving at the sample at time τ_{R}. The parameter ω labels the center frequency of the spectrometer passband, which is (for the simplified discussion in this section) taken to be much narrower than all other spectral features. If the quantum state of the molecule immediately after excitation at time τ_{P} is given by

$$|\psi(\tau_{\mathrm{P}})\rangle=|\phi_1(\tau_{\mathrm{P}})\rangle|1\rangle+|\phi_2(\tau_{\mathrm{P}})\rangle|2\rangle,\tag{2}$$

where

$$|\phi_1(\tau_{\mathrm{P}})\rangle=\sum_{m} c_1^{m}(\tau_{\mathrm{P}})|m\rangle,\tag{3}$$

$$|\phi_2(\tau_{\mathrm{P}})\rangle=\sum_{n} c_2^{n}(\tau_{\mathrm{P}})|n\rangle\tag{4}$$

are the quantum states of the vibrational wave packets on the ground ($|1\rangle$) and excited ($|2\rangle$) electronic surfaces, respectively. The states $|m\rangle$ and $|n\rangle$ are the eigenstates of the adiabatic vibrational Hamiltonians $\hat{H}_1$ and $\hat{H}_2$, respectively.

The time-dependent polarization for this state is proportional to the expectation value of the flip operator between the ground and excited electronic states, $\hat{A}_{12}=|1\rangle\langle 2|$,

$$P(t;\tau_{\mathrm{P}})=\langle\psi(t-\tau_{\mathrm{P}})|\hat{A}_{12}|\psi(t-\tau_{\mathrm{P}})\rangle e^{-i\omega_{21}(t-\tau_{\mathrm{P}})},\tag{5}$$

which has a spectrum for excitation in the distant past of

$$\underline{P}(\omega;\tau_{\mathrm{P}})=\int dt\, e^{i\omega t}e^{-i\omega_{21}(t-\tau_{\mathrm{P}})},$$

$$\times\langle\phi_1(\tau_{\mathrm{P}})|e^{i\hat{H}_1(t-\tau_{\mathrm{P}})/\hbar}e^{-i\hat{H}_2(t-\tau_{\mathrm{P}})/\hbar}|\phi_2(\tau_{\mathrm{P}})\rangle\tag{6}$$

$$=\sum_{m,n} c_1^{m*}(\tau_{\mathrm{P}})c_2^{n}(\tau_{\mathrm{P}})\langle m|n\rangle\delta(\omega-\omega_{21}^{nm})e^{i\omega_{21}^{nm}\tau_{\mathrm{P}}}.\tag{7}$$

The frequency ω_{21}^{nm} corresponds to the transition between the mth vibrational level in the ground electronic state and the nth vibrational level in the excited electronic state. If the reference pulse arrives at the molecule at time $\tau_{\mathrm{R}}\geqslant\tau_{\mathrm{P}}$, then the detected signal at frequency ω is proportional to the product of the reference field and that radiated by the molecule (the source field). The reference field spectrum in this case is

$$\underline{E}(\omega;\tau_{\mathrm{R}})\sim\underline{\mathcal{A}}(\omega-\omega_L)e^{i\omega\tau_{\mathrm{R}}},\tag{8}$$

where $\underline{\mathcal{A}}(\omega)$ is the spectrum of the reference pulse envelope. The detected signal can be written in terms of the complex coefficients describing the wave packets as

$$S(\omega;\tau_{\mathrm{R}},\tau_{\mathrm{P}})\sim 2\mathrm{Re}\Bigg\{\sum_{m,n} c_1^{m*}(\tau_{\mathrm{P}})c_2^{n}(\tau_{\mathrm{P}})\langle m|n\rangle\delta(\omega-\omega_{21}^{nm})$$

$$\times\exp[i(\omega_{21}^{nm}\tau_{\mathrm{P}}-\omega\tau_{\mathrm{R}})]\underline{\mathcal{A}}^{*}(\omega-\omega_{\mathrm{L}})\Bigg\}.\tag{9}$$

It is clear that the reference field in a sense ‘‘amplifies’’ the contribution of the density matrix element (given here as a product of state amplitudes) oscillating at frequency $\omega=\omega_{21}^{nm}$. Thus, by judicious choice of the spectrometer frequency and delay $\tau_{\mathrm{P}}-\tau_{\mathrm{R}}$ it is possible to extract both the amplitude and phase of this particular element.

III. MEASURED SIGNAL

In the following we give a more rigorous analysis of the scheme under realistic experimental conditions, including the passive elements involved in the experimental setup. The heterodyne measurement scheme is shown in Fig. 1. The molecules are prepared in a particular vibronic quantum state by a pump laser that drives two electronic states. This pump laser is switched on at time $t=0$ (at position $x=0$) and has a time duration t_{P}. It reaches a molecule located at the position x_0 at time x_0/c and the shutter at time x_{S}/c. At this

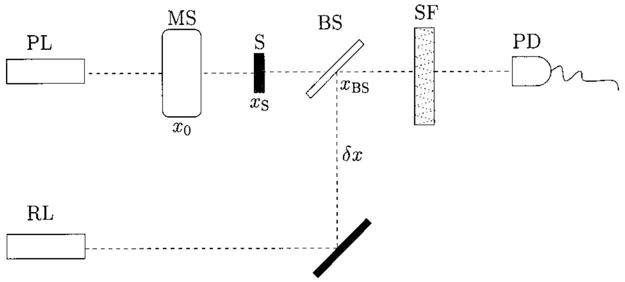

FIG. 1. Experimental scheme for the heterodyne state measurement. A pump laser (PL) at position $x=0$ is used to prepare the quantum state of a molecular sample (MS) at x_0. A shutter (S) at $x_{\rm S}$ separates the fluorescence signal of the molecular sample from the pump pulse. This signal is superimposed by a beam splitter (BS) at position $x_{\rm BS}$ with a test pulse from a reference laser (RL), δx being the path-length difference between the PL and RL. The heterodyne signal is transmitted through a spectral filter (SF) and recorded by a photodetector (PD).

time the shutter is closed, so that the pump pulse is suppressed in the measured signal. At time $t_{\rm P}+x_{\rm S}/c$ the shutter is turned on. The fluorescence field from the molecular sample is then mixed with the reference field by a beam splitter. The reference field is a short pulse of a few femtoseconds duration that is centered at time $t_{\rm R}$ (at position $-\delta x$, with δx being the difference between the path lengths of the pump and the reference fields from the laser sources to the beam splitter). The total field is spectrally filtered and detected by the photodetector at position x.

For the formalism we will closely follow an approach previously developed for analyzing a pump-probe absorption experiment [18]. The number of (time-integrated) photoelectrons, N, measured by the photodetector is given by

$$N=\xi\int dt\langle\hat{E}^{(-)}(x,t)\hat{E}^{(+)}(x,t)\rangle, \tag{10}$$

where $\hat{E}^{(-)}(x,t)$ and $\hat{E}^{(+)}(x,t)$ are the positive- and negative-frequency part, respectively, of the linearly polarized electric field arriving at the photodetector, and $\xi=\eta\epsilon_0 c$, where η is the quantum efficiency of the photodetector, ϵ_0 is the dielectric constant, and c is the speed of the light in vacuum. The positive and negative part of the fields can be decomposed into two different contributions, namely, the free-field part $\hat{E}^{(\pm)}_{\rm free}(x,t)$ (which is irradiated by the laser sources) and the source-field part $\hat{E}^{(\pm)}_{\rm s}(x,t)$ (which is irradiated by the molecules),

$$\hat{E}^{(\pm)}(x,t)=\hat{E}^{(\pm)}_{\rm free}(x,t)+\hat{E}^{(\pm)}_{\rm s}(x,t). \tag{11}$$

Inserting this expression into Eq. (10), we get

$$N=N_{\rm free}+N_{\rm s}+\xi\left[\int dt\langle\hat{E}^{(-)}_{\rm s}(x,t)\hat{E}^{(+)}_{\rm free}(x,t)\rangle+\text{c.c.}\right], \tag{12}$$

where

$$N_{\rm free}=\xi\int dt\langle\hat{E}^{(-)}_{\rm free}(x,t)\hat{E}^{(+)}_{\rm free}(x,t)\rangle \tag{13}$$

is the number of photoelectrons produced by the interaction-free field, and

$$N_{\rm s}=\xi\int dt\langle\hat{E}^{(-)}_{\rm s}(x,t)\hat{E}^{(+)}_{\rm s}(x,t)\rangle \tag{14}$$

is the small number of photoelectrons produced by molecular fluorescence, which can be disregarded. In this case, the difference signal

$$\Delta N=N_{\rm free}-N=-\xi\int dt\langle\hat{E}^{(-)}_{\rm s}(x,t)\hat{E}^{(+)}_{\rm free}(x,t)\rangle+\text{c.c.} \tag{15}$$

directly represents the interference signal we are interested in. It can be easily measured by splitting the reference pulse into two parts by using a symmetric (50:50) beam splitter. Introducing the Fourier-transformed field operators

$$\underline{\hat{E}}^{(\pm)}(x,\omega)=\int dt\, e^{\pm i\omega t}\hat{E}^{(\pm)}(x,t), \tag{16}$$

Eq. (15) can be rewritten as

$$\Delta N=-\frac{\xi}{2\pi}\int d\omega\langle\underline{\hat{E}}^{(-)}_{\rm s}(x,\omega)\underline{\hat{E}}^{(+)}_{\rm free}(x,\omega)\rangle+\text{c.c.} \tag{17}$$

The detected free field is obtained, after introducing $\hat{\mathcal{E}}^{(+)}_{\rm P}$ and $\hat{\mathcal{E}}^{(+)}_{\rm R}$ for the pump and reference fields, respectively, by the convolution

$$\hat{E}^{(+)}_{\rm free}(x,t)=\mathcal{T}\int dt'\,T(t-t'-\Delta t)\,\theta(t'-t_{\rm S})\,\hat{\mathcal{E}}^{(+)}_{\rm P}\left(t'-\frac{x}{c}\right)+\mathcal{R}\int dt'\,T(t-t'-\Delta t)\,\hat{\mathcal{E}}^{(+)}_{\rm R}\left(t'-\frac{x+\delta x}{c}\right), \tag{18}$$

where $\mathcal{T}$ and $\mathcal{R}$ are the transmission and reflection coefficients of the beam splitter (BS), and the unit-step function $\theta(t'-t_{\rm S})$ describes the effect of the shutter located at the distance $x_{\rm S}$ from the pump source. The shutter is turned on after the preparation pulse is over at the position $x_{\rm S}$, i.e., at time $t_{\rm P}+x_{\rm S}/c$. At this time the fluorescence field from the molecular sample begins to propagate behind the shutter and reaches the position x after a time $(x-x_{\rm S})/c$. Then we start to have some contributions from the fluorescence field at the position x after the time $t_{\rm S}$, given by

$$t_{\rm S}=t_{\rm P}+\frac{x}{c}. \tag{19}$$

As we see from Eq. (19) the time $t_{\rm S}$ does not depend on the position of the shutter. The spectral apparatus is described by the transmission function $T(t)$, which can be given by

$$T(t)=\theta(t)\,\gamma\exp[-(\gamma+i\omega_{\rm F})t], \tag{20}$$

with γ being the passband width and ω_{F} being the setting frequency. In Eq. (18), $\Delta t=(d-d_{\text{opt}})/c$ is the time delay due to the difference between the geometrical path d and the optical path d_{opt} through the spectrometer. Note that the chosen transmission function in Eq. (20) is, e.g., a reasonable approximation for a Fabry-Perot filter in the vicinity of one of its resonances. Because the unit-step function $\theta(t'-t_{\text{S}})$ does not overlap with the pump field $\hat{\mathcal{E}}^{(+)}_{\text{P}}(t'-x/c)$, the first integral in Eq. (18) gives no contribution to the detected field, that is, only the contribution coming from the probe pulse is detected. Defining the Fourier transformed quantities

$$\underline{\hat{\mathcal{E}}}^{(+)}_{\text{free}}(\omega)=\int dt\, e^{i\omega[t-(x+\delta x)/c]}\,\hat{\mathcal{E}}^{(+)}_{\text{R}}\left(t-\frac{x+\delta x}{c}\right) \tag{21}$$

and

$$\underline{T}(\omega)=\int dt\, e^{i\omega t}\,T(t), \tag{22}$$

Eq. (18) in Fourier space reads as

$$\underline{\hat{E}}^{(+)}_{\text{free}}(x,\omega)=\mathcal{R}\,\underline{T}(\omega)\,\underline{\hat{\mathcal{E}}}^{(+)}_{\text{free}}(\omega)\,e^{i\omega[\Delta t+(x+\delta x)/c]}. \tag{23}$$

The detected source field $\hat{E}^{(-)}_{\text{s}}(x,t)$ is given by the convolution

$$\hat{E}^{(-)}_{\text{s}}(x,t)=\mathcal{T}^*\int dt'\,T(t-t'-\Delta t)\times\theta(t'-t_{\text{S}})\hat{\mathcal{E}}^{(-)}_{\text{s}}\left(t'-\frac{x-x_0}{c}\right), \tag{24}$$

where $\hat{\mathcal{E}}^{(-)}_{\text{s}}(t)$ is the source field traveling onto the spectrometer and x_0 is the distance of the molecular source from the source of the pump pulse. Using the definition

$$\underline{\hat{\mathcal{E}}}^{(-)}_{\text{s}}(\omega)=\int dt\, e^{-i\omega[t-(x-x_0)/c]}\,\theta(t-t_{\text{S}})\hat{\mathcal{E}}^{(-)}_{\text{s}}\left(t-\frac{x-x_0}{c}\right), \tag{25}$$

together with Eq. (22), we get for Eq. (24) in Fourier space

$$\underline{\hat{E}}^{(-)}_{\text{s}}(x,\omega)=\mathcal{T}\underline{T}^*(\omega)\,\underline{\hat{\mathcal{E}}}^{(-)}_{\text{s}}(\omega)\,e^{-i\omega[(x-x_0)/c]}. \tag{26}$$

Inserting Eq. (23) and Eq. (26) into Eq. (17), we obtain

$$\Delta N=-\frac{\xi'}{2\pi}\int d\omega\,|\underline{T}(\omega)|^2\langle\underline{\hat{\mathcal{E}}}^{(-)}_{\text{s}}(\omega)\,\underline{\hat{\mathcal{E}}}^{(+)}_{\text{free}}(\omega)\rangle e^{i\omega(x_0+\delta x)/c}+\text{c.c.}, \tag{27}$$

where $\xi'=\xi\mathcal{R}\mathcal{T}^*$.

To specify the source field, let us consider a diatomic molecule with potential energies for the ground and excited electronic states as shown in Fig. 2. Solving the time-independent Schrödinger equation for each potential, the energy eigenvalues and eigenvectors for the bound vibrational states can be calculated, and the molecular density operator (for an individual molecule at the position x_0) in the energy basis can be written as

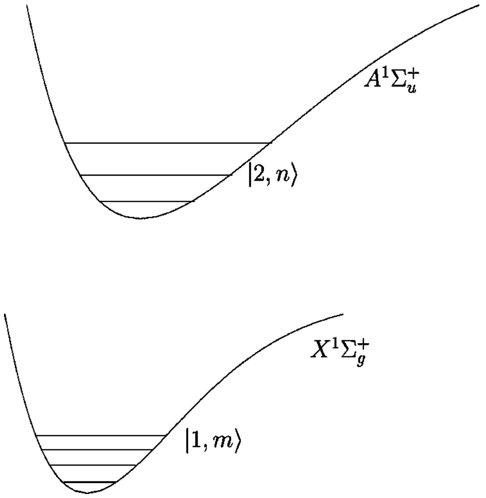

FIG. 2. Electronic potential for a sodium dimer for the electronic states $X\,^1\Sigma_g^+$ and $A\,^1\Sigma_u^+$.

$$\hat{\sigma}=\sum_{i,j=1}^{2}\sum_{n_i,m_j}\sigma_{ij}^{n_im_j}\hat{A}_{ij}^{n_im_j}, \tag{28}$$

where the indices i,j label the electronic states ($i,j=1$ for the electronic ground state and $i,j=2$ for the excited electronic state), and n_i,m_j are the corresponding vibrational quantum numbers. The vibronic flip operators

$$\hat{A}_{ij}^{n_im_j}=|i,n_i\rangle\langle j,m_j| \tag{29}$$

describe the transitions $|j,m_j\rangle\rightarrow|i,n_i\rangle$, and it is obvious that

$$\sigma_{ij}^{n_im_j}=\langle\hat{A}_{ji}^{m_jn_i}\rangle. \tag{30}$$

Following [21,22], in dipole, far-field, and rotating-wave approximations the (negative-frequency part of the) electric source field radiated by a diatomic homonuclear molecule in free space is

$$\hat{\mathcal{E}}^{(-)}_{\text{s}}(\mathbf{r},t)=\sum_{n,m}\mathbf{g}_{12}^{mn}\hat{A}_{21}^{nm}(t-|\mathbf{r}-\mathbf{r_0}|/c), \tag{31}$$

where

$$\mathbf{g}_{12}^{mn}\equiv\mathbf{g}_{12}^{mn}(\mathbf{r}-\mathbf{r_0})=\frac{(\omega_{21}^{nm})^2\langle m|n\rangle}{4\pi\epsilon_0c^2}\times\left\{\frac{\mathbf{d}_{12}}{|\mathbf{r}-\mathbf{r_0}|}-\frac{[\mathbf{d}_{12}\cdot(\mathbf{r}-\mathbf{r_0})](\mathbf{r}-\mathbf{r_0})}{|\mathbf{r}-\mathbf{r_0}|^3}\right\}. \tag{32}$$

Here, $\mathbf{r_0}$ is the position of the molecule and $\mathbf{d}_{12}$ is its electronic-transition dipole vector. For notational convenience we have omitted the electronic indices at the vibrational quantum numbers.

From Eq. (31) the source field $\underline{\hat{\mathcal{E}}}_{\mathrm{s}}^{(-)}(\omega)$ in Eq. (27) corresponds to

$$\underline{\hat{\mathcal{E}}}_{\mathrm{s}}^{(-)}(\omega)=\sum_{n,m} g_{12}^{mn}\,\underline{\hat{A}}_{21}^{nm}(\omega), \tag{33}$$

where

$$\underline{\hat{A}}_{21}^{nm}(\omega)=\int dt\;\theta(t-t_{\mathrm{S}})e^{-i\omega[t-(x-x_0)/c]}\hat{A}_{21}^{nm}\left(t-\frac{x-x_0}{c}\right), \tag{34}$$

and g_{12}^{mn} is the component of $\mathbf{g}_{12}^{mn}$ parallel to the polarization of the reference field. Inserting Eq. (33) into Eq. (27) we get the result

$$\Delta N=-\sum_{n,m}\int d\omega\,|\underline{T}(\omega)|^2\,S_{nm}(\omega)+\text{c.c.}, \tag{35}$$

with

$$S_{nm}(\omega)=\frac{\xi' g_{12}^{mn}}{2\pi}\langle\underline{\hat{A}}_{21}^{nm}(\omega)\underline{\hat{\mathcal{E}}}_{\mathrm{free}}^{(+)}(\omega)\rangle\,e^{i\omega[(x_0+\delta x)/c]}. \tag{36}$$

In the following we assume that the reference laser light is prepared in a (multimode) coherent state, so that $\underline{\hat{\mathcal{E}}}_{\mathrm{free}}^{(+)}(\omega)$ in Eq. (36) can be replaced with the corresponding c-number function $\underline{\mathcal{E}}_{\mathrm{free}}^{(+)}(\omega)$. Equation (36) then simplifies to, on recalling Eq. (30),

$$S_{nm}(\omega)=\frac{\xi' g_{12}^{mn}}{2\pi}\,\underline{\sigma}_{12}^{mn}(\omega)\,\underline{\mathcal{E}}_{\mathrm{free}}^{(+)}(\omega)\,e^{i\omega(x_0+\delta x)/c}. \tag{37}$$

Equation (35) together with Eq. (37) gives the basic relation between the measured difference heterodyne spectrum and the Fourier transforms of the vibronic density-matrix elements associated with the pump-laser-induced polarization of the molecule. The Fourier transform of the vibronic density matrix is determined by its temporal evolution after the preparation. In the following we will analyze this time evolution in some detail with the aim to clarify how the quantum information on the prepared state can be recovered from the measured quantities.

IV. TEMPORAL EVOLUTION OF THE VIBRONIC QUANTUM STATE

Let us consider the quantum-state evolution of a molecular system without taking into account retardation effects, i.e., the molecule is thought to be located at position $x=0$ and the interaction with a coherent laser pulse to be started at time $t=0$. The temporal evolution of its vibronic quantum state, described by the density-matrix operator $\hat{\varrho}$, can be obtained from the master equation

$$\frac{\partial\hat{\varrho}(t)}{\partial t}=\frac{1}{i\hbar}[\hat{H}(t),\hat{\varrho}(t)]+\hat{\mathcal{L}}\,\hat{\varrho}(t). \tag{38}$$

The Hamiltonian $\hat{H}(t)$ of the undamped system can be given by

$$\hat{H}(t)=\hat{H}_0+\hat{V}(t), \tag{39}$$

where $\hat{H}_0$ is the Hamiltonian of the free molecule,

$$\hat{H}_0=\sum_m \hbar\omega_1^m A_{11}^{mm}+\sum_n \hbar\omega_2^n A_{22}^{nn}, \tag{40}$$

and $\hat{V}(t)$ is the time-dependent interaction operator, which in dipole and the rotating-wave approximations can be written as

$$\hat{V}(t)=-\sum_{n,m}\hbar\Omega_{12}^{mn}(t)\,\hat{A}_{12}^{mn}+\text{H.c.} \tag{41}$$

Here,

$$\Omega_{12}^{mn}(t)=\frac{1}{\hbar}\langle m|n\rangle(\mathbf{d}_{12}\cdot\boldsymbol{\epsilon})\mathcal{E}^{(-)}(t) \tag{42}$$

is the Rabi frequency for the vibronic transition $|1,m\rangle\leftrightarrow|2,n\rangle$($\boldsymbol{\epsilon}$, polarization vector of the laser field). If we restrict our attention to radiative damping processes, the damping superoperator $\hat{\mathcal{L}}$ is given by

$$\begin{aligned}\hat{\mathcal{L}}\,\hat{\varrho}(t)=&-\sum_n \Gamma_n[\hat{A}_{22}^{nn}\hat{\varrho}(t)+\hat{\varrho}(t)\hat{A}_{22}^{nn}]\\&+\sum_{nm}\gamma_{21}^{nm}\hat{A}_{12}^{mn}\hat{\varrho}(t)\hat{A}_{21}^{nm},\end{aligned} \tag{43}$$

where the damping rates read

$$\gamma_{21}^{nm}=\frac{|\mathbf{d}_{12}|^2(\omega_{21}^{nm})^3|\langle m|n\rangle|^2}{6\pi\epsilon_0\hbar c^3}, \tag{44}$$

$$\Gamma_n=\tfrac{1}{2}\sum_m \gamma_{12}^{mn}. \tag{45}$$

For evaluating the quantum state of an individual molecule at position x_0, the effect of the retardation has to be taken into account. It can be easily shown that if the molecular system is in a thermal initial quantum state, its time evolution will be given as

$$\hat{\sigma}(t)=\hat{\varrho}\left(t-\frac{x_0}{c}\right), \tag{46}$$

i.e., it will only be shifted in time due to the laser-pulse retardation. Recalling Eqs. (34) and (19) the Fourier-transformed density-matrix elements $\underline{\sigma}_{12}^{mn}(\omega)$ can be calculated as

$$\underline{\sigma}_{12}^{mn}(\omega)=\int dt\,\sigma_{12}^{mn}(t)\exp[-i\omega t]\,\theta(t-t_{\mathrm{P}}-x_0/c), \tag{47}$$

where the substitution $t-(x-x_0)/c\to t$ has been performed. Taking into account Eq. (46) and changing the variable as

$$\tau=t-\frac{x_0}{c}, \tag{48}$$

we obtain

$$\begin{aligned}\sigma_{12}^{mn}(\omega)&=\int dt\,\varrho_{12}^{mn}\left(t-\frac{x_0}{c}\right)\exp[-i\omega t]\,\theta(t-t_{\mathrm{P}}-x_0/c)\\&=e^{-i\omega\frac{x_0}{c}}\int_{\tau_{\mathrm{P}}=t_{\mathrm{P}}}^{+\infty}d\tau\,\varrho_{12}^{mn}(\tau)\exp[-i\omega\tau].\end{aligned} \tag{49}$$

This result shows that the effect of the retardation is only given by a phase factor, which compensates with the one in measured signal (37). The prepared vibronic quantum state $\varrho_{12}^{mn}(t_{\mathrm{P}})$ does not dependent explicity from the position of the molecule but only on the time at which the pump pulse is turned off. It means that the field radiated by molecules located at different places adds up coherently to the signal allowing to recover the information on the prepared vibronic quantum state.

When the preparation process is over, the molecular system evolves according to master equation (38) with the interaction-free Hamiltonian $\hat{H}_0$ in place of $\hat{H}(t)$. Solving this equation we obtain

$$\varrho_{12}^{mn}(\tau)=\varrho_{12}^{mn}(\tau_{\mathrm{P}})e^{-\Gamma_n(\tau-\tau_{\mathrm{P}})}\,e^{i\omega_{21}^{nm}(\tau-\tau_{\mathrm{P}})}\qquad(\tau\geqslant\tau_{\mathrm{P}}). \tag{50}$$

We will use this equation in the next section where the relation between ΔN and the prepared quantum state $\varrho_{12}^{mn}(\tau_{\mathrm{P}})$ will be explicitely derived.

V. EVALUATION OF THE KERNEL FUNCTION

Using Eq. (47), from Eqs. (35) and (37) the measured heterodyne spectrum can be written as

$$\begin{aligned}\Delta N=&-\frac{\xi'}{2\pi}\sum_{n,m}g_{12}^{mn}\int_{\tau_{\mathrm{P}}}^{+\infty}d\tau\,\varrho_{12}^{mn}(\tau)\\&\times\int d\omega\,|T(\omega)|^2\,\mathcal{E}_{\mathrm{free}}^{(+)}(\omega)e^{-i\omega(\tau-\delta x/c)}+\mathrm{c.c.}\end{aligned} \tag{51}$$

To evaluate the second integral on the right-hand side of Eq. (51), we need explicit expressions for $|T(\omega)|^2$ and $\mathcal{E}_{\mathrm{free}}^{(+)}(\omega)$. $|T(\omega)|^2$ can be easily calculated from Eq. (22) using the transmission function in Eq. (20). In this way we derive

$$|\underline{T}(\omega)|^2=\frac{\gamma^2}{\gamma^2+(\omega-\omega_{\mathrm{F}})^2}. \tag{52}$$

The reference laser field can be written as

$$\mathcal{E}_{\mathrm{free}}^{(+)}(t)=\mathcal{A}(t)\,e^{-i\omega_{\mathrm{L}}t}, \tag{53}$$

where ω_{L} is the carrier frequency and $\mathcal{A}(t)$ is an envelope function. In particular, for a Gaussian pulse of duration τ_d the slowly varying amplitude $\mathcal{A}(t)$ reads

$$\mathcal{A}(t)=\mathcal{A}_0\exp\left[-\frac{4\,(t-t_{\mathrm{R}})^2}{\tau_d^2}\right]. \tag{54}$$

Fixing the phase of the complex constant $\mathcal{A}_0$ corresponds to fixing the reference phase of the laser. Substituting in Eq. (21) for $\mathcal{E}^{(+)}(t)$ the reference laser field given in Eq. (53) together with Eq. (54), we get

$$\underline{\mathcal{E}}_{\mathrm{free}}^{(+)}(\omega)=\underline{\mathcal{A}}(\omega-\omega_{\mathrm{L}})\,e^{i(\omega-\omega_{\mathrm{L}})\,t_{\mathrm{R}}}, \tag{55}$$

with

$$\underline{\mathcal{A}}(\omega-\omega_{\mathrm{L}})=\left(\frac{\tau_d\sqrt{\pi}}{2}\right)\mathcal{A}_0\exp\left[-\frac{\tau_d^2}{16}(\omega-\omega_{\mathrm{L}})^2\right]. \tag{56}$$

For a laser pulse of duration of some femtoseconds, the spectral envelope function $\underline{\mathcal{A}}(\omega-\omega_{\mathrm{L}})$ is very broad, typically of the order of 10^{14} Hz. If we compare this function with the spectrometer filter function given in Eq. (52), and consider as a typical value for the spectrometer resolution for our experiment $\gamma\simeq 10$ GHz, we see that the envelope function can be regarded as being constant in the interval where the spectrometer function is nonvanishing. This allows us to take the envelope function at the maximum of the spectral-filter function outside the second integral on the right-hand side in Eq. (51).

The frequency integral can now be easily evaluated and ΔN becomes

$$\begin{aligned}\Delta N=&\frac{\xi'\gamma}{2}\sum_{n,m}g_{12}^{mn}\underline{\mathcal{A}}(\omega_{\mathrm{F}}-\omega_{\mathrm{L}})\,e^{-i\omega_{\mathrm{L}}(\tau_{\mathrm{R}}-\delta x/c)}\\&\times\int_{\tau_{\mathrm{P}}}^{+\infty}d\tau\,\varrho_{12}^{mn}(\tau)\,e^{-\gamma|\tau-\tau_{\mathrm{R}}|}\,e^{-i\omega_{\mathrm{F}}(\tau-\tau_{\mathrm{R}})}+\mathrm{c.c.},\end{aligned} \tag{57}$$

where we have defined the time $\tau_{\mathrm{R}}=t_{\mathrm{R}}+\delta x/c$. Using the result in Eq. (50) we can rewrite the previous equation in the following way:

$$\begin{aligned}\Delta N=&\frac{\xi'}{2}\sum_{n,m}g_{12}^{mn}\,\underline{\mathcal{A}}(\omega_{\mathrm{F}}-\omega_{\mathrm{L}})\,\underline{H}_n(\omega_{21}^{nm}-\omega_{\mathrm{F}})\\&\times e^{-i\omega_{\mathrm{L}}(\tau_{\mathrm{P}}-\delta x/c)}\,\varrho_{12}^{mn}(\tau_{\mathrm{P}})\,e^{i(\omega_{21}^{nm}-\omega_{\mathrm{L}})\delta t}+\mathrm{c.c.},\end{aligned} \tag{58}$$

where the function

$$\begin{aligned}H_n(\omega_{21}^{nm}-\omega_{\mathrm{F}})=&\gamma\int_{\tau_{\mathrm{P}}}^{+\infty}d\tau\,e^{-\Gamma_n(\tau-\tau_{\mathrm{P}})}\\&\times e^{-\gamma|\tau-\tau_{\mathrm{R}}|}\,e^{i(\omega_{21}^{nm}-\omega_{\mathrm{F}})(\tau-\tau_{\mathrm{R}})}\end{aligned} \tag{59}$$

can be easily calculated to be

$$\begin{aligned}\underline{H}_n(\omega_{21}^{nm}-\omega_{\mathrm{F}})=&\frac{\gamma\, e^{-\Gamma_n\delta t}}{(\gamma-\Gamma_n)+i(\omega_{21}^{nm}-\omega_{\mathrm{F}})}\\ &+\frac{\gamma\, e^{-\Gamma_n\delta t}}{(\gamma+\Gamma_n)-i(\omega_{21}^{nm}-\omega_{\mathrm{F}})}\\ &-\frac{\gamma e^{-\gamma\delta t}\, e^{-i(\omega_{21}^{nm}-\omega_{\mathrm{F}})\delta t}}{(\gamma-\Gamma_n)+i(\omega_{21}^{nm}-\omega_{\mathrm{F}})}.\end{aligned}\tag{60}$$

Here $\delta t=\tau_{\mathrm{R}}-\tau_{\mathrm{P}}$. The last term in Eq. (60) contains the switch-on effect of the spectrometer.

This result can be simplified significantly if we select the values of the time delay δt and of the spectrometer resolution γ in a appropriate manner. If δt is large compared to the characteristic time of the spectrometer $1/\gamma$, the third term of Eq. (60) approaches to zero. On the other hand we must choose δt shorter than $1/\Gamma_n$ to avoid that the signal disappears due to the polarization damping. This yields for the time delay the condition

$$\frac{1}{\gamma}\ll\delta t\ll\frac{1}{\Gamma_n}.\tag{61}$$

For example, if we choose the spectrometer resolution to be 10 GHz, the delay time cannot be shorter than 100 ps, and because the decay rates Γ_n are of the order of magnitude of $10,\ldots,100$ MHz, the delay time δt cannot be longer than $10,\ldots,100$ ns. Condition (61) implies that $\exp(-\Gamma_n\,\delta t)\simeq 1$ and $\gamma\pm\Gamma_n\simeq\gamma$, and hence Eq. (60) simplifies to

$$\underline{H}_n(\omega_{21}^{nm}-\omega_{\mathrm{F}})=|\underline{T}(\omega_{21}^{nm})|^2,\tag{62}$$

i.e., to the familiar Lorentzian function.

Equation (58) is the sought relation from which the information about the vibronic quantum state prepared by the pump laser can be obtained. For this purpose we first note that the fixed difference phase between pump and reference laser can be included in the pump field, so that $\mathcal{A}(\omega_{\mathrm{F}}-\omega_{\mathrm{L}})$ can be assumed to be real. We can rewrite Eq. (58) in a more compact form,

$$\Delta N=\sum_{n,m}K_{12}^{mn}(\omega_{\mathrm{F}})|\varrho_{12}^{mn}(\tau_{\mathrm{P}})|\cos[(\omega_{21}^{nm}-\omega_{\mathrm{L}})\delta t-\phi_{12}^{mn}(\tau_{\mathrm{P}})],\tag{63}$$

with

$$K_{12}^{mn}(\omega_{\mathrm{F}})=\xi'\,g_{12}^{mn}\,\underline{\mathcal{A}}(\omega_{\mathrm{F}}-\omega_{\mathrm{L}})\,\underline{H}_n(\omega_{21}^{nm}-\omega_{\mathrm{F}}),\tag{64}$$

and $\phi_{12}^{mn}(\tau_{\mathrm{P}})$ is the phase of the matrix element $\varrho_{12}^{mn}(\tau_{\mathrm{P}})$. Measuring the difference heterodyne spectrum for different values of the experimental parameters such as ω_{F} and δt, yields a set of equations, from which the density-matrix elements $\varrho_{12}^{mn}(\tau_{\mathrm{P}})$ could be obtained numerically by using, e.g., least-squares inversion.

VI. DIRECT MEASUREMENT OF THE WAVE-PACKET QUANTUM STATE

It is worth noting that under certain conditions the vibrational quantum state in the upper electronic state can directly be measured. For this purpose let us suppose that the molecule is initially prepared in the vibronic ground state and the excitation of higher vibrational quantum states in the electronic ground state during the pump process can be disregarded. In this case only density-matrix elements $\varrho_{12}^{0n}\equiv\varrho_{12}^{0n}(\tau_{\mathrm{P}})$ are involved in Eq. (63), and the transition frequencies ω_{21}^{n0} are well separated from each other, so that the spectral apparatus well resolves the corresponding lines. Hence tuning the setting frequency ω_{F} to a chosen transition frequency ω_{21}^{n0}, the measured difference-heterodyne spectrum is only determined, in good approximation, by the corresponding density-matrix element $\varrho_{12}^{0n}(\tau_{\mathrm{P}})$,

$$\Delta N=K_{12}^{0n}(\omega_{21}^{n0})|\varrho_{12}^{0n}|\cos[(\omega_{21}^{n0}-\omega_{\mathrm{L}})\delta t-\phi_{12}^{0n}],\tag{65}$$

with

$$K_{12}^{0n}(\omega_{\mathrm{F}})=\xi'\,g_{12}^{0n}\,\underline{\mathcal{A}}(\omega_{\mathrm{F}}-\omega_{\mathrm{L}}).\tag{66}$$

In order to obtain $|\varrho_{12}^{0n}|$ and ϕ_{12}^{0n} two measurements for two delay times $\delta t^{(1)}$ and $\delta t^{(2)}$ can be performed, which give $\Delta N^{(1)}$ and $\Delta N^{(2)}$,

$$\begin{pmatrix}\Delta N^{(1)}\\ \Delta N^{(2)}\end{pmatrix}=K_{12}^{0n}(\omega_{21}^{n0})\begin{pmatrix}C_n^{(1)} & S_n^{(1)}\\ C_n^{(2)} & S_n^{(2)}\end{pmatrix}\begin{pmatrix}R_n\\ I_n\end{pmatrix},\tag{67}$$

where

$$C_n^{(i)}=\cos[(\omega_{21}^{n0}-\omega_{\mathrm{L}})\;\delta t^{(i)}],\tag{68}$$

$$S_n^{(i)}=\sin[(\omega_{21}^{n0}-\omega_{\mathrm{L}})\;\delta t^{(i)}],\tag{69}$$

and

$$R_n=|\varrho_{12}^{0n}|\,\cos\phi_{12}^{0n},\tag{70}$$

$$I_n=|\varrho_{12}^{0n}|\,\sin\phi_{12}^{0n}.\tag{71}$$

In particular, choosing the delay times $\delta t^{(1)}$ and $\delta t^{(2)}$ such that

$$(\omega_{21}^{n0}-\omega_{\mathrm{L}})\;\delta t^{(1)}=2k\pi,\tag{72}$$

$$(\omega_{21}^{n0}-\omega_{\mathrm{L}})\;\delta t^{(2)}=(2k+\tfrac{1}{2})\pi,\tag{73}$$

with k being an integer, we directly get the real and imaginary parts of the sought density-matrix elements,

$$R_n=\frac{\Delta N^{(1)}}{K_{12}^{0n}(\omega_{21}^{n0})},\tag{74}$$

$$I_n = \frac{\Delta N^{(2)}}{K_{12}^{0n}(\omega_{21}^{n0})}. \tag{75}$$

As mentioned, the molecule can be regarded as being prepared in a pure state if the pump process is short compared with the molecular damping times and the laser is prepared in a coherent state. In this case we may write

$$|\varrho_{12}^{0n}|\, e^{-i\phi_{12}^{0n}} = c_1^{0*} c_2^n, \tag{76}$$

so that from the measured density-matrix elements ϱ_{12}^{0n} the expansion coefficients c_2^n of the vibrational quantum state $|\phi_2\rangle$, Eq. (4), in the upper electronic state can be obtained according to

$$c_2^n = \frac{|\varrho_{12}^{0n}|}{c_1^{0*}} e^{-i\phi_{12}^{0n}}. \tag{77}$$

Here, the unknown coefficient c_1^0 can be chosen real and determined from the normalization condition

$$\sum_n |c_2^n|^2 = 1. \tag{78}$$

VII. NUMERICAL SIMULATION

In order to illustrate the method, we have performed computer simulations of measurements for sodium dimers. The potentials for the vibrational motion in the electronic states $X\,^1\Sigma_g^+$ and $A\,^1\Sigma_u^+$ are shown in Fig. 2. The data for these potential are taken from spectroscopic measurements [23,24]. The corresponding vibrational eigenvalue problems are solved numerically, using the method described in [25].

The absolute values of the density-matrix elements and the Wigner function of the wave-packet quantum state to be measured are shown in Figs. 3 and 4, respectively. The plots are obtained by solving the vibronic equations of motion numerically for a laser pump that consists of a sequence of three pulses of a duration of 60 fs that are separated from each other by 103 fs, one third of the wave-packet period. Experimentally, the state can be obtained for a time $t_{\mathrm{P}} = 600$ fs after starting the pump process. It is further assumed that the midfrequency of the laser pump corresponds to a wave number of 15 683.518 cm^{-1}, i.e., the laser is tuned to the vibronic transition $|1{,}0\rangle \leftrightarrow |2{,}9\rangle$, and the Rabi frequency corresponds to 50 cm^{-1}. The state exhibits a characteristic oscillation in the density matrix, where only every third element is different from zero. The interference effects between the three time-delayed excited wave packets are more evident in the phase space, where the Wigner function shows a three-peak structure with interference patterns in between (for preparation of nonclassical states in molecules, see also [26]).

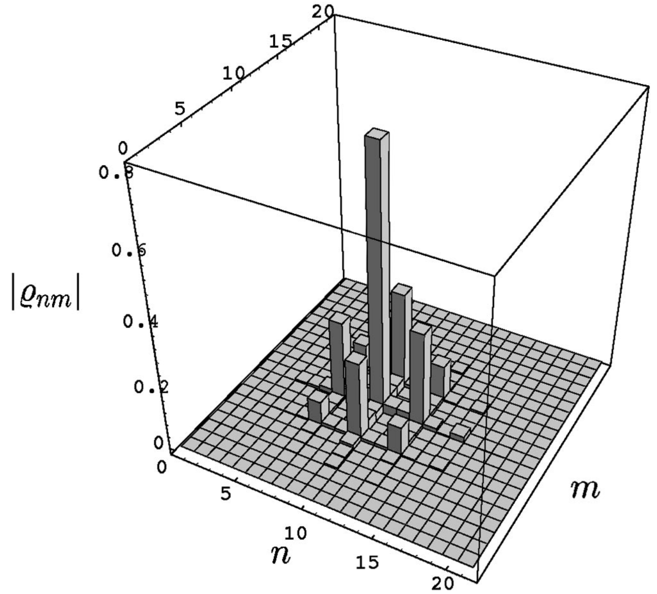

FIG. 3. Absolute values of the calculated density-matrix elements $\varrho_{nm} = c_2^{n*} c_2^m$ of the prepared vibrational wave packet in the upper electronic state in the energy basis. Experimentally, the quantum state can be obtained after pumping the molecule over 600 fs with a sequence of three pulses of a carrier frequency of 15 683.518 cm^{-1} (which corresponds to the vibronic transition $|1{,}0\rangle \leftrightarrow |2{,}9\rangle$), the time duration of the individual pulses is 60 fs, and the delay between the pulses is 103 fs, corresponding to one-third of the wave-packet period.

In Fig. 5 the measured signal is shown for an ensemble of 10^6 molecules, which is the signal coming from a single molecule according Eq. (63) multiplied by the number of molecules in the ensemble. The fluorescence field is mixed by a 50:50 symmetrical beam splitter with a reference laser pulse duration of 10 fs, midfrequency of 15 500 cm^{-1}, and power of about 10^3 W/cm^2, which corresponds to a maximal photon rate $N_{\mathrm{free}}^{\max} = 10^8$ photons s^{-1} cm^{-2} ($\eta = 1$). The delay times of about 50 ps are chosen according to Eq. (72) in Fig. 5(a), and Eq. (73) in Fig. 5(b). The passband width of the spectral apparatus is $\gamma = 30$ GHz and in a succession of

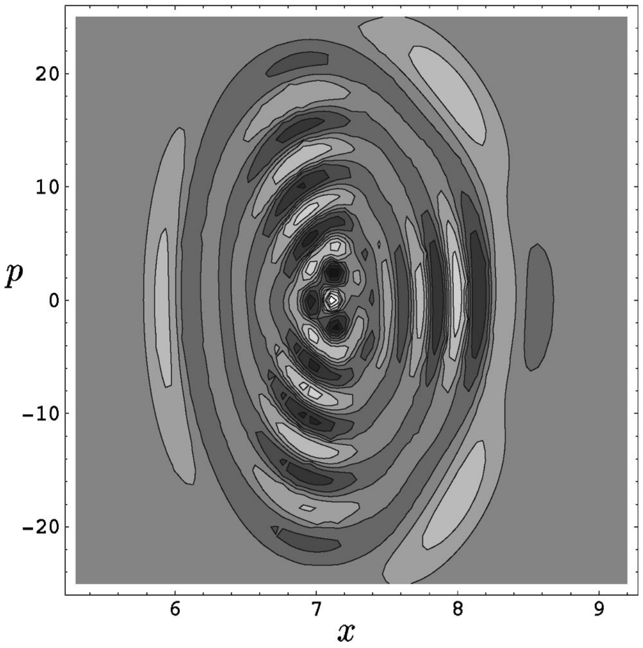

FIG. 4. Wigner function of the same vibrational wave packet as in Fig. 3, which displays the interference pattern owing to the three-pulse excitation. The position x and the momentum p are given in atomic units.

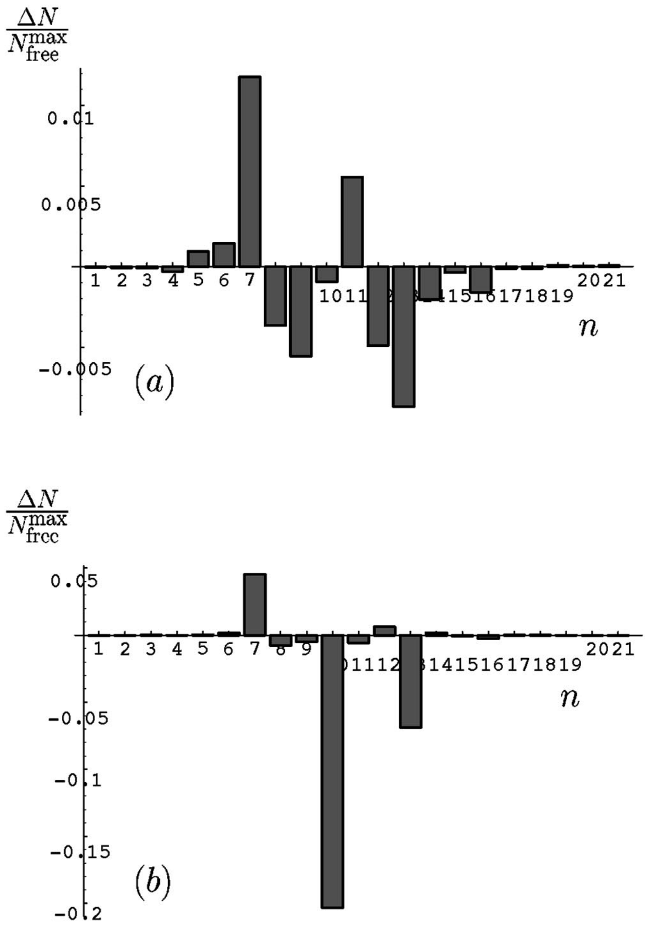

FIG. 5. Measured difference-heterodyne spectrum ΔN for the quantum state of Figs. 3 and 4. It is obtained by measuring the interference signal between the fluorescence coming from 10^6 molecules with a reference laser pulse duration of 10 fs, midfrequency of 15 500 cm^{-1}, and a peak power of about 10^3 W/cm^2 ($N_{\rm free}^{\max}=10^8$ photons s^{-1} cm^{-2} for $\eta=1$). The time delay of about 50 fs corresponds to condition (72) (a) and (73) (b), and the setting frequency of the spectral apparatus is tuned to ω_{21}^{n0}.

measurements the setting frequency is fixed such that $\omega_{\rm F}=\omega_{21}^{n0}$ for each density-matrix element ϱ_{12}^{0n} to be determined.

We show single measurements, simulated by taking into account the shot noise. To demonstrate how this noise affects the measurement procedure we have chosen a weak reference laser. In a real experiment this laser can be stronger, so that the shot-noise effect will practically disappear. From the measured difference-heterodyne lines in Fig. 5 the real and imaginary parts of the density-matrix elements ϱ_{12}^{0n} are then obtained according to Eqs. (74) and (75), respectively. Application of Eq. (77) (together with normalization) then yields the expansion coefficients of the vibrational quantum state in the upper electronic state. The result for the absolute values of the density-matrix elements is shown in Fig. 6. It is found to be in good agreement with the prepared quantum state as given in Fig. 3.

In Fig. 7 the relative error of the method,

$$\epsilon_{\rm r}=\left|\frac{|\varrho_{mn}|_{\rm R}-|\varrho_{mn}|_{\rm T}}{\max|\varrho_{mn}|_{\rm T}}\right|, \qquad (79)$$

is plotted. The subscripts R and T indicate the reconstructed

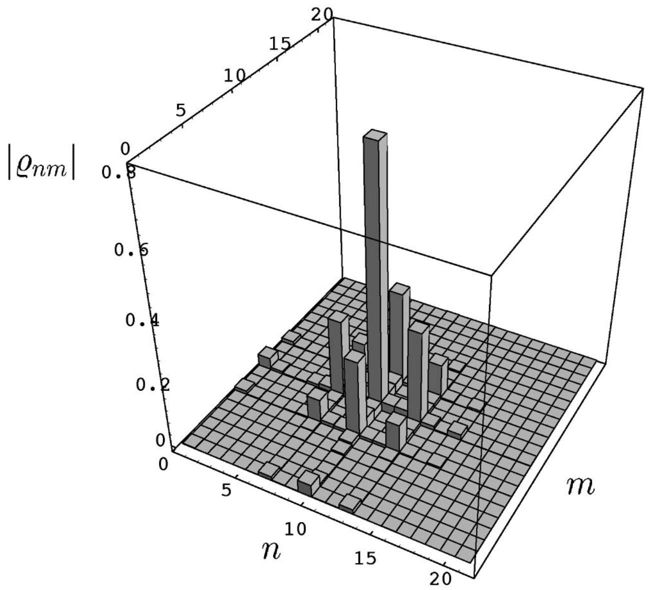

FIG. 6. Absolute values of the computer simulation of the measured density-matrix elements ϱ_{nm} of the vibrational wave packet in the upper electronic quantum state shown in Figs. 3 and 4.

and the theoretical vibrational density-matrix elements, respectively. It is seen that for the chosen parameters the reconstruction can be achieved with reasonable precision.

VIII. SUMMARY AND CONCLUSION

In the present paper we have developed the theory of a heterodyne experiment that is suited for measuring molecular quantum states. A pump-laser pulse (or a sequence of pulses) is used to prepare the vibronic molecular quantum state by coherently driving an electronic two-level transition. The fluorescence light emitted by the molecular sample in the forward direction of the pump pulse is superimposed with a

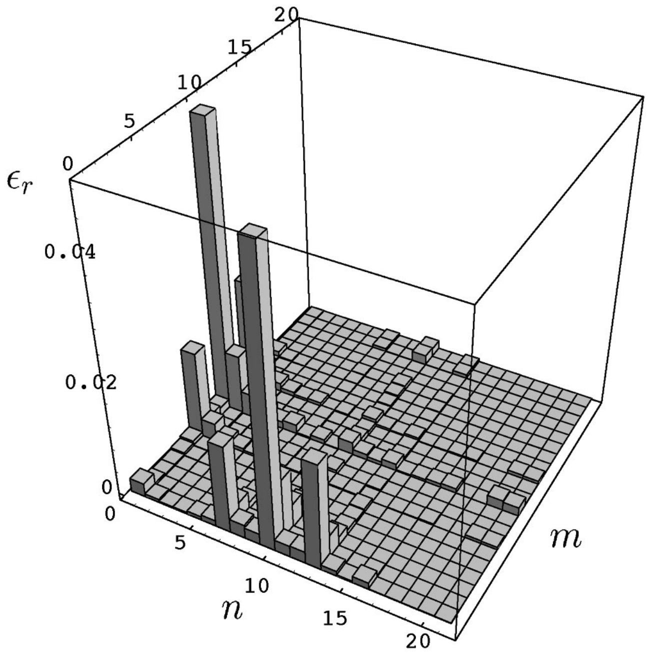

FIG. 7. Relative deviation (79) of the measured values of the vibrational density-matrix elements in Fig. 6 from the calculated values in Fig. 3.

reference laser pulse. A shutter is used to separate the signal from the pump field. The superimposed light is spectrally filtered and recorded by a photodetector. The signal of interest is the difference between the photocounts induced by the superposition of the reference light with the fluorescence and the photocounts due to the free reference field.

The measured signal depends linearly on density-matrix elements of the vibronic transition under study. It is shown that under certain conditions the method allows a direct measurement of the quantum state of a molecular vibration in the excited electronic state and the corresponding requirements are analyzed in detail. Numerical simulations show the feasibility of the method even for structured quantum states that clearly exhibit quantum interference effects in the Wigner function. The relative errors in the simulation result from a relatively weak pulse. In practice the reference pulse could be strong enough so that the sampling noise becomes meaningless, and the precision of the method is further improved.

Let us briefly discuss some other noise sources that have not been included in the calculations. We have treated dissipation by assuming radiative damping. In a molecular gas, however, additional effects like Doppler broadening and collisions may play a vital role. The values of Doppler and collision broadenings can be estimated for a gas of sodium dimers at the temperature of 300 K and a pressure of 0.1 atmospheres to be of the order of $10-100$ MHz. This is approximately of the same order of magnitude as the radiative damping included in our treatment. Since these line broadenings are not spectrally resolved under the experimental conditions of interest, the additional effects are not expected to change the measured signal significantly.

We would like to note that the experiment proposed in this paper not only allows a direct measurement of the vibrational wave packet for a particular class of pure states; it is also suited for the determination of the density-matrix elements ϱ_{12}^{mn} for general vibronic states. These elements are of some interest for their own since they contain the complete microscopic information on the polarization of the molecules.

ACKNOWLEDGMENT

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