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LETTERS

Interference of Optical Coherent Transients in Pentacene/*p*-Terphenyl: Femtosecond Beats Probed by Correlated Fluorescence Fluctuations

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By using two-pulse excitation with *phase-randomized* pulses in an interferometer and analyzing the *variance* of the fluctuating fluorescence intensity, femtosecond beatings have been observed in the binary crystal pentacene/p-terphenyl, P/pTP at low phonon temperatures. The THz oscillations evolve from fluctuating quantum interferences prepared by the coherent superposition of different, electronic transition dipoles in spatially different constituents (O1−O4) of the pentacene impurity. The polarization beats can be explained by a model of uncoupled two-level systems including inhomogeneous dephasing as the predominant coherence relaxational pathway.

I. Introduction

In the coherent regime of molecular excitations, optical techniques, mostly in nonlinear configurations, have revealed a series of wavelike, periodic phenomena, in the past decade, that are elegant, experimental manifestations of basic molecular quantum mechanics.[1]

The use of large frequency bandwidth ultrashort pulses has experienced spectacular advances in the study of electronic relaxation dynamics in condensed, molecular sparse-level systems. In the resonant coupling regime these pulses are broad enough to prepare several molecular (vibrational) electronic states, simultaneously, so the free evolution of coherent state excitations is a discrete superposition of individual, optical free induction decays (OFIDs) that can be resolved as an oscillatory modulation, generally referred to as a polarization or quantum interference phenomenon. Vibrational quantum beats from electronic states of organic dyes in the liquid, condensed state were observed by photon-echo experiments,[2] pump−probe measurements,[3] and the fluorescence up-conversion technique.[4]

In addition, correlation techniques had enormous impact on the research of femtosecond coherence and were used in special applications and in different energy regimes over the past decade.[5] Spontaneous fluorescence that probes the population of the excited quantum state is another (quasi-linear) optical observable that has been implemented interferometrically[6−8] and analyzed in theoretical work.[9,10] A different experimental approach to obtaining interferometric information is based on the use of *phase-randomized* pairs of pulses. In this experiment—Coherence Observation by Interference Noise (COIN)[11]—the stochasticity of the relative phases between the incoming pulses gives rise to fluctuating quantum interferences in the excited state population, which is driven by the statistical balance between enhanced absorption and amplified emission, respectively, and consequently controlled by the delay time of the pulses and the molecule's intrinsic dephasing process. Thus analyzing the fluorescence intensity fluctuations in low-dense, Doppler-free atomic two-level systems can yield direct information not only on dephasing and static level splitting[11] but also on wave packet dynamics of diatomic gases, as demonstrated, very recently, by computer experiments.[12]

In this Letter the COIN technique has been applied to a low-temperature, molecular impurity/host solid state system with the objective of demonstrating its potential in the measurement of

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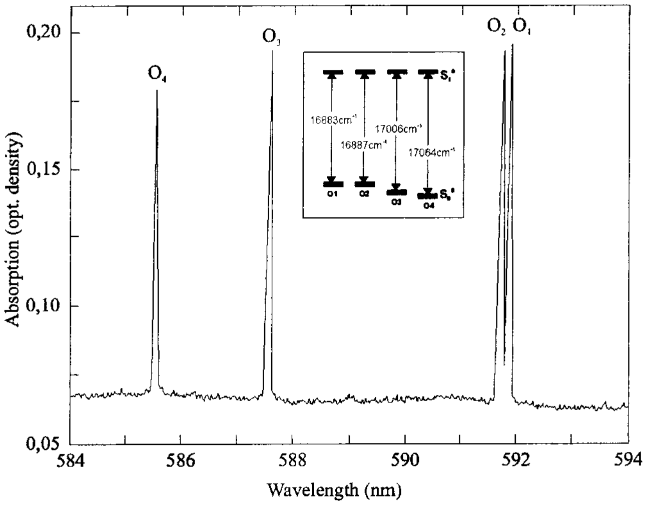

Figure 1. Absorption spectrum of P/pTP at 1.8 K. Source from ref 21. Inset shows a scheme with the transition energies of the four sites.

electronic coherence decays in a large organic molecule that, generally, shows inhomogeneous broadening (IHB) as a result of static site-energy disorder in the matrix. Since the COIN signal carrying the coherence is sensitive to intervening, quasi-continuous, multilevel systems, its decay and intensity are completely determined by the spread in resonance frequencies. Hence, coherences are, in general, expected to be very short-lived and, even on very short time scales, apparently eroded in an energy-disordered site ensemble of an organic solid. However, for some of the very few solids that, fortunately, show sparse-level structure and a width of IHB smaller than the energy level splitting, one would assume the coherence to survive on femtosecond time scales and be probed by COIN.

II. Experimental Section

To verify this concept, the organic guest/host system chosen to be a promising candidate for a discrete, multiple two-level system is a highly dilute sample of the binary crystal *p*-terphenyl (pTP) doped with pentacene (P). The spectroscopic features of this system have been studied in detail.[13] Below 190 K, the long-wavelength $S_1^{\nu=0} \leftarrow S_0^{\nu=0}$ transition ($^1L_a \leftarrow {}^1A$) of pentacene splits into very narrow and well-separated absorption lines at 16 883, 16 887, 17 006, and 17 064 cm^{-1}, which correspond to the four possible conformations of P in pTP, labeled as O1, O2, O3, and O4, respectively (Figure 1). The optical dynamics in P has been extensively studied by picosecond photon-echo experiments,[14,15] continuous wave (CW) optical nutation/OFID measurements,[16] site-selective spectroscopy,[17] and more recently, in a somewhat different context, by high-resolution, frequency-domain, single-molecule spectroscopy.[18] These experiments have revealed, directly or implicitly, the sites O1−O4 to be inhomogeneously broadened (typical widths 20−40 GHz)[16,19] by more than a factor 1000 relative to the homogeneous line width ($\Gamma \sim 8$ MHz).[16,20] Both fluorescence and pure dephasing from the thermalized $S_1^{\nu=0}$ states of the individual P sites are typically nanosecond processes at liquid He temperatures.

The P/pTP samples were grown by vacuum deposition.[21] The concentration of P in the crystal was approximately 10^{-5} mole/mole. Pulses (170 fs) from a Ti/S laser-RegA-OPA system (Coherent Inc.) have been used, which were tunable over the spectroscopic range of the $^1L_a \leftarrow {}^1A$ pentacene transitions, including the first vibrational overtone excitation ($\nu = 1$), i.e., from $\lambda = 594$ to 576 nm. The spectral fwhm of the pulses has been ~5.5 nm, which is broad enough to simultaneously excite several $S_1^{\nu=0} \leftarrow S_0^{\nu=0}$ as well as $S_1^{\nu=1} \leftarrow S_0^{\nu=0}$ transitions of the site conformers O1−O4. The pulses were sent through a Michelson interferometer with a variable delay. The relative phase between the symmetric, collinear pulses was randomized by heating the air in the stationary arm. Fluorescence was collected at a 90° geometry and detected at $\lambda_{\mathrm{emm}} = 640$ nm by means of a photomultiplier tube (R 928, Hamamatsu). Fluorescence was, in general, processed through Lock-In technique (EG&G 7260) with modulation of both arms and sum frequency detection, ensuring that only two-pulse contributions, i.e., correlated fluorescence, were measured. For each time delay, typically, 500 data values were accumulated, analyzed in terms of their variance, and plotted over the delay time. Data analysis was performed with standard fast Fourier transform (FFT) routines.

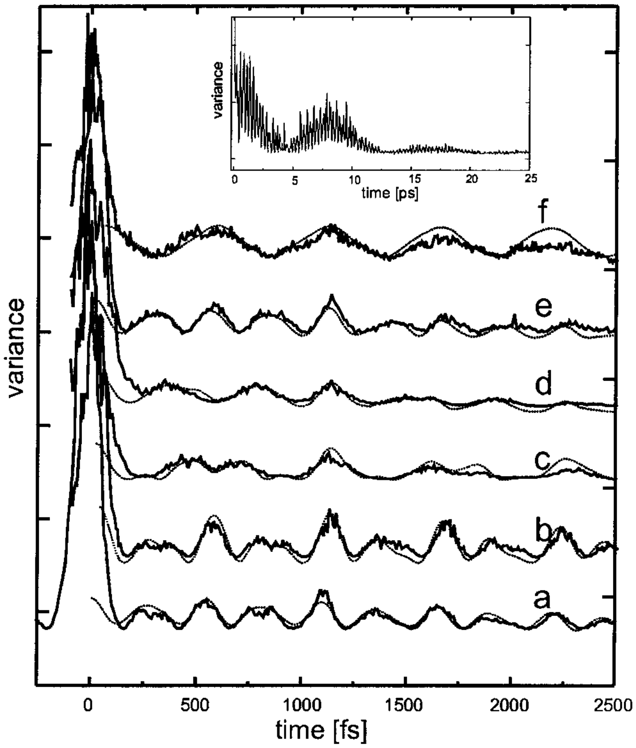

Figure 2. Modulated delay line traces of correlated fluorescence fluctuations at different excitation wavelengths (see text for details). Inset shows the scan to longer delay times.

III. Results and Discussion

Typical COIN data accumulated at $T = 3.8$ K for a series of pulse excitation center wavelengths, are shown in Figure 2, from the bottom to the top (curves in parentheses): $\lambda_{\mathrm{L}} = 590$ nm (a), 588 nm (b), 585 nm (c), 582 nm (d), 579 nm (e), and 576 nm (f), where the variance of the correlated fluorescence fluctuations (cf. formulation below) is plotted over the pulse-to-pulse delay time.

For delays $\tau > 250$ fs, i.e., the onset of nonoverlapping, delayed pulses, pronounced femtosecond oscillations are observed, which show, on time scales up to 2 ps, nearly undamped behavior. Running one of the experiments ($\lambda_{\mathrm{L}} = 589$ nm) with larger step sizes to longer time scales allows an additional, low-frequency oscillation to be resolved (inset of Figure 2). The slow oscillation regime in the inset shows significant relaxation and allows a phenomenological picosecond damping time to be evaluated: $T_2^* \approx 12$ ps, the latter value being more than a factor 1000 shorter than the pure pentacene dephasing time at comparable temperature.[19] It is therefore tempting to assume

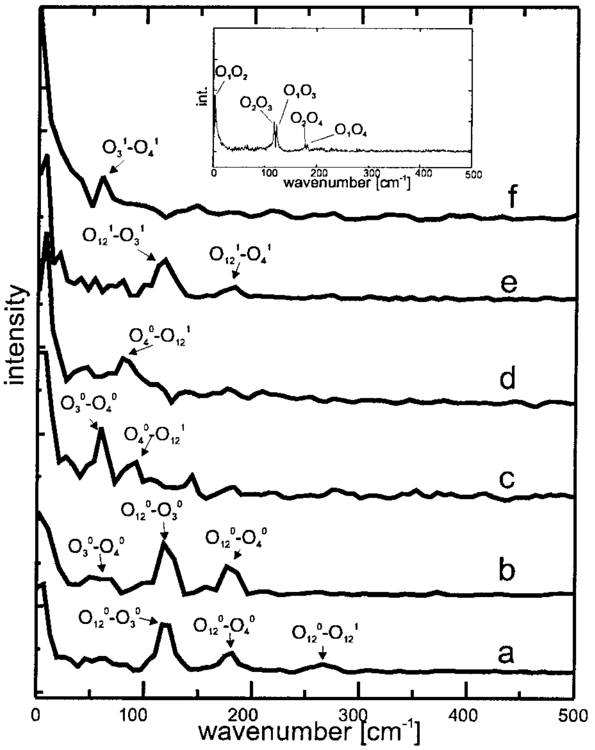

Figure 3. Results of Fourier inversion of the corresponding curves a−f from Figure 1.

that the relaxing beats, rather, map out some average value of inhomogeneous dephasing, relatable to the inhomogeneous line broadening in the spectral profiles of the individual pentacene site absorbers.

Fourier inversion of the modulated, time-domain profiles yields the set of beat-frequency patterns as displayed in Figure 3.

The spectra directly reveal the predominant differences in the transition frequencies of P sites involved in the coherent excitation process. The oscillations in curves a and b contain the interferences of the pure electronic states ($S_1^{\nu=0}$), while the curves d, e, and f are derived from superpositions where the first overtone vibrational states ($S_1^{\nu=1}$, ≈ 268 cm^{-1} above S_0[14]) are involved, with combinations $S_1^{\nu=1} + S_1^{\nu=1}$. Curve c corresponds to the intermediate regime where, in addition, superpositions of $S_1^{\nu=1} + S_1^{\nu=0}$ can be observed. The structure of the beats is strongly affected by the center frequency of the exciting laser pulses (ω_L) and its relative spectral position with regard to the molecular transition frequencies ($\omega_{0,n}$, $n = 1-4$) of the various P sites. While for the interferogram b (Figure 2) the beat frequency $\omega_{34} = 58$ cm^{-1}, corresponding to the O3 + O4 interference, is the prominent oscillation in the Fourier transform (spectrum b, Figure 2), the analysis of pattern a reconstructs beating frequencies with the main components arising from O1/O2 + O4 and O1/O2 + O3 interferences, i.e., $\omega_{14} = 181$ cm^{-1}, $\omega_{24} = 177$ cm^{-1} and $\omega_{13} = 123$ cm^{-1}, $\omega_{23} = 119$ cm^{-1}. In the asymptotic regime of the experiment (inset, Figure 2) comprising the slow oscillation as the prominent beat on a time scale of 25 ps, FFT recovers the low-energy splitting between sites O1 and O2 as $\omega_{12} = 4$ cm^{-1}, in addition to the high-frequency contributions of sites O1/O2 + O3 and O1/O2 + O4, respectively. This shows that even for longer delays the interferometric line in the COIN experiment is stable, thus allowing the entire set of OFID interferences to be extracted with high precision. To understand the quantitative relation between the measured variance, molecular electronic coherence, and modulated relaxation affected by inhomogeneous solid-state dephasing and pulse excitation detuning, a generalization of previous theoretical treatments[11,12] has to be formulated. In our experiments the minimum delay time considered is longer than the temporal width δt of the pulses, and the pulses are low intensity (several hundred picoJoule). A multiple, *uncoupled* two-level system driven by a pair of optical pulses and solved for the diagonal elements in lowest order of the field provides, therefore, a realistic approach to modeling linear fluorescence coherences on femtosecond scales. Using perturbation theory and invoking the dipole approximation in the interaction Hamiltonian, one can describe the total fluorescence intensity F of a single Lorentzian pentacene site (transition frequency ω) subject to delayed two-pulse δ excitation and moderate, homogeneous dephasing (T_2; $T_1 \rightarrow \infty$) by[11]

$$F(\tau,\omega,\phi) = 2F_0(\omega)[1 + \cos(\delta\tau + \varphi)e^{-\tau/T_2}] = 2F_0 + F_{\mathrm{int}} \tag{1}$$

where τ denotes the delay time, φ the relative phase between the pulses, and $\delta = \omega_L - \omega$ the detuning of the laser's carrier frequency ω_L with respect to the molecular transition frequency ω of a distinct pentacene site. $F_0(\omega)$ is the fluorescence after single-pulse excitation. F_{int} is the interference term formed by the correlation of the two pulses.

Since we are concerned with interpreting the early picosecond relaxation of the coherences, we neglect homogeneous dephasing as a typical *nanosecond* decay process[16] ($e^{-\tau/T_2} \rightarrow 1$) but take into consideration the effect of inhomogeneous broadening. Assuming (i) the ensemble of single O_i Lorentzians to be frequency-distributed according to a Gaussian functional form[22] $G(\omega) \propto \exp[-(\omega - \omega_i)^2/2\sigma_i^2]$ (with central frequency ω_i and standard deviation σ_i) and (ii) the excitation pulses to obey a Gaussian spectral density function, too, $I(\omega) \propto \exp[-(\omega - \omega_L)^2/2\sigma_L^2]$ (width σ_L, center frequency ω_L), one obtains the overall fluorescence intensity of site O_i by integrating over the frequency space, which, after numerous analytic procedures and algebraic rearrangements, can be solved in closed form

$$F_i(\tau,\varphi) = \int F(\tau,\omega,\varphi)\,d\omega \propto 2F_{0,i}[1 + e^{-\tau^2/2T_i^2}\cos(\Delta_i\tau + \varphi)] \tag{2}$$

with

$$F_{0,i} = \sqrt{\frac{2\pi\sigma_i\sigma_L}{\sigma_i^2 + \sigma_L^2}}\, e^{-(\omega_i-\omega_L)^2/2(\sigma_i^2+\sigma_L^2)}, \qquad T_i^2 = \frac{\sigma_i^2 + \sigma_L^2}{\sigma_i^2\sigma_L^2},$$
$$\Delta_i = \frac{\sigma_i^2\omega_L + \sigma_L^2\omega_i}{\sigma_i^2 + \sigma_L^2} - \omega_L \tag{3}$$

In our experiment, the femtosecond pulses are, naturally, much broader than the inhomogeneous width of site O_i ($\sigma_L \gg \sigma_i$), so from relations (eq 3) follows: $T_i \approx 1/\sigma_i$ and $\Delta_i \approx \omega_i - \omega_L = \delta_i$.

Finally, to formulate the total fluorescence intensity, one has to sum over the Gaussian decays of those sites that are coherently prepared in the pulse-excitation process.

$$F_{\mathrm{tot}}(\tau,\varphi) = \sum F_i(\tau,\varphi) = 2\sum F_{0,i}[1 + e^{-\tau^2/2T_i^2}\cos(\delta_i\tau + \varphi)] \tag{4}$$

One methodological approach to stabilizing the interferometer consists of setting φ to be constant (phase-locking), which allows the carrier frequency to be eliminated.[8] In the COIN experiment the stability control of the phase has been overcome by using *randomly*-phased pulses.[11] In this limit the interference term in eq 1 becomes a stochastic quantity and vanishes, when averaged over a uniform distribution of phases, yielding $1/2\pi\int_0^{2\pi} F_{\mathrm{tot}}(\tau,\varphi)\,\mathrm{d}\varphi = \langle F\rangle$. However, by averaging over the square of the measured total fluorescence, $1/2\pi\int_0^{2\pi} F_{\mathrm{tot}}{}^2(\tau,\varphi)\,\mathrm{d}\varphi = \langle F_{\mathrm{tot}}{}^2(\tau)\rangle$, and measuring the fluctuations about the average signal $\langle F\rangle$, the variance

$$\Delta F^2(\tau) = \langle F^2(\tau)\rangle - \langle F\rangle^2 \tag{5}$$

depends on the delay time and is of the same order of magnitude as the mean signal itself. Assembling the variance $\Delta F^2(\tau)$ by processing eq 4 in accord with definition eq 5, the multilevel COIN signal of pentacene reads

$$\Delta F^2(\tau) = \frac{1}{2}\sum_k\sum_l F_{0,l}F_{0,k}\mathrm{e}^{-\tau^2/2T_{kl}{}^2}\cos(\Delta_{kl}\tau) \tag{6}$$

Here $1/T_{kl}{}^2 = 1/T_l{}^2 + 1/T_k{}^2$, with $\Delta_{kl} = \Delta_k - \Delta_l = \omega_k - \omega_l$.

Well-behaved results, in accordance with the linear excitation model, are obtained when using eq 6 as a target function in preliminary fit-and-compare calculations. By using the central $S_1^{\nu=0} \leftarrow S_0$ and the vibronic $S_1^{\nu=1} \leftarrow S_0$ overtone transition frequencies ω_i of the sites O1−O4, together with a Gaussian band shape $G(\omega_i)$ as inputs and setting the width of the (Gaussian) excitation pulse to match the experimental situation (fwhm = 5.5 nm), one finds the dotted curves (superimposed to the noisy experimental data in Figure 2) as typical outputs. The computed curves are in quite satisfactory agreement with the experiments. Assuming, to a first approach, the T_{kl}'s in eq 6 to be of equal size for each of the site transition profiles, $1/T_{kl}{}^2 = 1/T_l{}^2 + 1/T_k{}^2 \simeq 2T_2{}^{*2}$, data analysis yields a best fit, *single*-Gaussian, inhomogeneous dephasing time $T_2{}^* \approx 12$ ps, corresponding to a broadened bandwidth of $2.35\sigma \approx 33$ GHz, which nicely recovers some average width of inhomogeneous broadening, as resolvable by conventional, high-resolution spectroscopy.[19]

To close, we note that for $\tau < 200$ fs the sequential pulses (δt) tend to overlap, so that higher order and convolution effects, clearly, beyond the linearity of the COIN experiment are determining the very early time scale of the interferograms. Heavily damped amplitudes of ultrafast femtosecond relaxation processes, such as the damping of electronically excited, pseudolocal phonons,[23] are, probably, concealed in the rising, leading, and trailing edge convolutions of the higher-order correlation regime. Shorter pulses, typically down to 20 fs, which allow one to record the interferogram at shorter delay times, combined with a systematic lowering of the temperature to 1.8 K are, therefore, required in forthcoming measurements. Such studies may help to deconvolve the COIN signal on time scales <100 fs and to analyze these dissipative processes still in the linear limit but, now, in terms of a more complex Hamiltonian dynamics that has to go beyond the usual parametrization in the optical Bloch equation approach. By using shorter pulses, however, higher frequency contributions will be contained in the data, because the broader bandwidth will pick up more widely spaced features in the spectrum. Ultrashort pulses in combination with the COIN interferometry are regarded to be a powerful tool to excite and probe vibrational wave packet dynamics in large polyatomics. We address this point in section IV.

IV. Discussion

In the present Letter the method of Coherence Observation by Interference Noise, COIN, has been applied as a new approach to performing coherence measurements in the solid state guest/host system pentacene/p-terphenyl. The measured quantity is the correlated fluctuations of incoherent fluorescence photons, while the information extracted from the interferograms is related to molecular coherences. THz-fluorescence oscillations can be interrogated in this solid state system, due to the delicate balance between site energy splitting and moderate inhomogeneous site broadening, on one hand, and the appropriate time-bandwidth product of the excitation laser pulses, on the other. The beat patterns originate from the coherent excitation of energetically and spatially different P sites; thus the COIN observable reflects typical polarization interferences that arise from intrinsic *heterodyne* beatings between quantum population amplitudes of, clearly, *intermolecular* superpositions.

To close, several remarks concerning the physical background of these experiments seem necessary. The interferograms of P/pTp (Figure 2) derived from correlated (but incoherent) fluorescence intensities provide the first experimental examples of an experimental Fourier transform of the P/pTp high-resolution absorption spectrum (Figure 1). Thus the experiments are interesting in that they probe interfering coherences of different P constituents brought about by static level splitting. Since the COIN signal is a convolution of the pulse-to-pulse correlation function with the optical interference response, the Fourier transform (Figure 3) produces a (shifted) absorption spectrum that, clearly, is not as good as the high-resolution spectrum. The fast beats result from the various differences of the O1−O4 transitions, and the phenomenological picosecond damping term(s) is (are) caused by the inhomogeneous line widths; so, since the absorption spectrum (Figure 1) is known in detail (line-intensities, frequencies of splittings, IHBs), the results can be reproduced, with little difficulty (cf. smooth, solid line pattern in Figure 2). In the fit procedure an average Gaussian inhomogeneous width has been used, for simplicity, but note that the vibronic transitions are not all Gaussian.[19] Thus, in a first approach, the entire set of frequencies spanning up the absorption spectrum can be recovered from the interferograms, although the reduction in the quality of information is significant. Unlike the photon-echo technique[2] and site-selective hole-burning,[17] COIN interferometry cannot eliminate inhomogeneous site broadening, it is therefore not possible to determine the natural line width of the various pentacene sites.

From the experiments reported here the critical reader may claim that nothing new is learned, other than the Fourier time-domain experiment, analogous to the absorption spectrum, can be done. This criticism is valid as long as one is concerned with discussing the pure optical response in terms of the theoretical Wiener−Khintchine theorem.[24] Accordingly, there was, indeed, no reason to think that the experiment could not be done, in the past. From the point of the experimental feasibility, however, it is not trivial to stabilize the interferometric line, in particular, on longer time scales, e.g., in the measurement of the low-frequency beat (the slow oscillation) corresponding to the O1−O2 splitting (Figure 2, inset). Running interferometric experiments either in the freely propagating mode ($\varphi = \omega_{\mathrm{L}}t$)[25] or in the limit of phase-locked pulses ($\varphi =$ const)[6] is a difficult enterprise, in general, since the probability of phase breaks increases with the length of the delay times and thus with the duration of the experiment. By using phase-randomized pulses,[11] one overcomes the problem of phase stability, so the COIN experiment is stable on longer times scales and it works, due to the fact that one measures the (correlated) *fluctuations* about the *average* signal, rather than the *average* signal itself.[11,12] Our demonstration that Fourier transform optical absorption spectroscopy on a few-level solid state system can be done is thus exclusively related to the feasibility of random-phase pulses in the interferometer and the absolute signal of the intensity fluctuations that depends, fortunately, on the delay time and is of the same order of magnitude as the central mean of the fluorescence amplitude.

The robust, high-resolution COIN technique has the potential of much broader applications. The method may become a very useful technique to measure vibrational wave packet motion whose dynamics hardly can be reconstructed from spectroscopy in the frequency domain. While conventional high-resolution absorption spectroscopy is mainly limited to the configurational space prepared by the Franck−Condon transitions, coherent wave packet propagation in interatomic potentials[26] explores new domains of nonspectroscopic, optically inactive states. We anticipate that studies in certain, diatomic molecules would allow us to probe classical recurrences, but perhaps also quantum-mechanical revivals,[12] for the detection of the latter, in particular, the stable COIN interferometry being an ideal vehicle. Furthermore, we have proposed[27] that COIN may provide a suitable tool to probe excitation transfer in coupled few-level systems and we note that the method can be applied to quantum state holography with the objective to map out Wigner-type, quantum-state representations of simple molecules.[28] Finally, we conjecture that COIN in combination with pulses of 10−20 fs temporal width will allow insight into the coherent onset of processes that determine quantum control[29] and chemical dynamics in larger molecules with deeper potentials, too. Experiments of this kind may be expected to tackle processes such as spreading, damping, and chirping[30] of vibrational wave packet motion and, presumably, establish new approaches for understanding ultrafast excited state relaxation dynamics and funneling into chemical channels.

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