A Primer on Temperature-Controlled
Entangled-Photon Virtual-State Spectroscopy

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Abstract. Entangled two-photon absorption spectroscopy has been widely recognized as a promising tool for revealing important information about the structure and dynamics of complex molecular systems. In this contribution, we present the basics of the theory behind this technique and describe a novel experimental scheme known as temperature-controlled entangled-photon absorption spectroscopy, which constitutes the first, realistic proposal for the experimental implementation of nonlinear spectroscopy with quantum light.

1. Introduction

Nonlinear spectroscopy has become an invaluable tool across many fields of research [1, 2]. In particular, two-photon absorption (TPA) spectroscopy has proven to be extremely useful for obtaining information about a sample that would not be accessible otherwise. Even though this technique is typically implemented using pulsed laser light, recent works suggest that the use of nonclassical light, such as entangled photon pairs, may open new and exciting routes in experimental spectroscopy [3, 4, 5]. Along these lines, quantum light has enabled the observation of fascinating TPA phenomena, such as the linear scaling of the TPA rates on the photon flux [6], entanglement-induced two-photon transparency [7], the ability to select different exciton states in complex biological aggregates [8], and the control of entanglement in matter [9, 10]. Interestingly, the prediction and observation of these phenomena can be understood as a direct consequence of the relationship between the TPA signal and the properties of the quantum light that interacts with the sample [11, 12, 13].

Among different quantum-enabled techniques, entangled-photon virtual-state spectroscopy (VSS) [14, 15, 16, 17, 18, 19, 20] has proved to be a unique tool for extracting information about the intermediate “virtual” electronic transitions that contribute to the two-photon excitation of an absorbing medium. In this technique, information about virtual-state transitions are experimentally revealed by introducing a time-delay between frequency-correlated photons and averaging over experimental realizations differing in temporal correlations between them. Although VSS has been widely considered as a new promising route towards novel application in ultrasensitive detection [21, 22, 23], to date, its experimental implementation has remained rather elusive, mainly because of two major difficulties, namely the need for averaging over several TPA signals for photon pairs with different temporal correlations—which translates into the need for using hundreds of nonlinear optical sources—and the requirement of a priori knowledge of the absorbing medium’s lowest-lying intermediate energy level [14].
In this work, we describe the theory behind a novel method, based on temperature-controlled entangled-photon sources [24], which overcomes the two major difficulties of the original VSS proposal, while reducing its experimental complexity.

2. The Model

To understand the functioning of the temperature-controlled VSS technique [shown in Figure 1(a)], we first consider the interaction of an arbitrary medium with a two-photon optical field $|\Psi\rangle$, described by the Hamiltonian $\hat{H} (t) = \hat{d}(t) \hat{E}^{(+)}(t) + \text{H.c.}$, where H.c. stands for the Hermitian conjugate, $\hat{d}(t)$ is the dipole-moment operator, and $\hat{E}^{(+)}(t)$ is the positive-frequency part of the electric-field operator, which can be written as $\hat{E}^{(+)}(t) = \hat{E}_{s}^{(+)}(t) + \hat{E}_{i}^{(+)}(t)$, with “$s$” and “$i$” denoting the signal and idler fields, given by

$$E_{s,i}^{(+)}(t) = \int d\omega_{s,i} \sqrt{\frac{\hbar \omega_{s,i}}{4\pi \varepsilon_0 c A}} \hat{a}_{s,i}(\omega_{s,i}) e^{-i\omega_{s,i}t},$$

where $c$ is the speed of light, $\varepsilon_0$ is the vacuum permittivity, $A$ is the effective area of the field interacting with the sample, and $\hat{a}(\omega_{s,i})$ is the annihilation operator of a photonic mode characterized by a frequency $\omega_{s,i}$ bearing a specific polarization which, for the sake of simplicity, is assumed to be aligned with the transition dipole-moment polarization.

By assuming that the medium is initially in its ground state $|g\rangle$ (with energy $\varepsilon_g$), we can make use of second-order time-dependent perturbation theory to find that the probability that the medium is excited to a final state $|f\rangle$ (with energy $\varepsilon_f$), through a TPA process, is given by [16, 17]

$$P_{g\rightarrow f} = \left| \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{t_2} dt_1 F_d(t_1, t_2) F_E(t_1, t_2) \right|^2,$$

Figure 1. Temperature-controlled quantum nonlinear spectroscopy. (a) Schematic representation of the temperature-controlled virtual-state spectroscopy technique. (b) Degeneracy of the down-converted photons as a function of the temperature of the nonlinear crystal, considering a continuous wave pump at 405 nm. (c) Simplified model of the absorbing medium’s electronic structure.
with

\[ F_d(t_1,t_2) = \sum_{j=1}^g \bar{D}^{(j)} \ e^{-i(\varepsilon_j - \varepsilon_f)t_2} e^{-i(\varepsilon_s - \varepsilon_s)t_1}, \tag{3} \]

\[ F_s(t_1,t_2) = \langle \Psi_{js} | \hat{E}_2^+ (t_2) \hat{E}_1^+ (t_1) | \Psi \rangle + \langle \Psi_{js} | \hat{E}_3^+ (t_2) \hat{E}_2^+ (t_1) | \Psi \rangle, \tag{4} \]

where \( \bar{D}^{(j)} = (\langle j | \hat{a}^| j \rangle \langle j | \hat{a}^| g \rangle \) are the transition matrix elements of the dipole-moment operator. Note from Eq. (3) that two-photon excitation of the sample takes place via the intermediate states \( | j \rangle \) (with energy \( \varepsilon_j \)). Also, note that in Eq. (4) we have only considered the terms in which one photon from each field contributes to the TPA process, with \( | \Psi_f \rangle \) denoting the final state of the optical field, which we take it to be the vacuum state.

The theoretical model is then complete by defining the temperature-controlled entangled-photon state that interacts with the sample. For the sake of simplicity, and given that this source has been already demonstrated in Ref. [25], we assume that photon pairs are generated via type-II spontaneous parametric down-conversion (SPDC) in a periodically poled KTiOPO\(_4\) (PPKTP) crystal of length \( L \), at a temperature \( T \), and pumped by a continuous-wave laser at 405 nm. In these conditions, the generated two-photon state can be written as [25]

\[ | \Psi \rangle = \left( \frac{T_e}{\sqrt{\pi}} \right)^{1/2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \ d\omega_s d\omega_i \delta (\omega_p - \omega_s - \omega_i) \ \text{sinc} \{ T_e [\mu (T)] \} \ e^{i\omega_s \tau} \hat{a}^\dagger_s (\omega_s) \hat{a}^\dagger_i (\omega_i) | 0 \rangle, \tag{5} \]

where \( \nu = \omega_i - \omega_s \), with \( \omega_j \) \( (j = p, s, i) \) representing the frequencies of the pump, signal, and idler fields, respectively. The correlation (entanglement) time between the down-converted photons is given by \( T_e = (N_s - N_i) L/4 \), \( N_{s,i} \) being the inverse group velocities of the signal and idler photons, respectively. \( \tau \) is an external delay between the generated photons [see Figure 1(a)], and their temperature-controlled non-degeneracy is given by the function \( \mu (T) = \omega_p^0 (T) - \omega_s^0 (T) \), where \( \omega_s^0 (T) \) are the temperature-dependent central frequencies of each photon wavepacket. Figure 1(b) shows the dependence of the down-converted photon central wavelengths on the temperature of the PPKTP crystal.

Equations (1)-(5) constitute the simplest model of the interaction between quantum light and an absorbing medium. It is worth mentioning that this model could be extended by considering samples with highly populated two-exciton manifolds, where the dynamics within the single-exciton (intermediate) states plays a fundamental role. Indeed, the consideration of more complicated sample models may lead to the observation of fascinating effects, such as the manipulation of the quantum pathways of matter [8].

3. Entangled-photon virtual-state spectroscopy

With the model described in the previous section, we are now ready to show how the temperature-controlled VSS protocol works. For this, we consider the model system shown in Figure 1(c), where the energy of the two-photon excitation process \( (| g \rangle \to | f \rangle) \) corresponds to the pump wavelength \( \lambda_p = 405 \) nm. By substituting Eqs. (3)-(5) into Eq. (2), we find that the TPA signal is given by

\[ P_{g \to f} = \frac{\left| \delta \left( \frac{\Delta \lambda}{\lambda_p} \right) \right|^2}{4\pi h^2 \varepsilon_0^2 A^2} \frac{\omega_s^0 (T) \omega_p^0 (T)}{T_e} \sum_{j=1}^g D^{(j)} \left\{ \frac{1 - e^{-i[\varepsilon_j - \omega_p^0 (T)](2T_e - \tau)}}{\varepsilon_j - \omega_p^0 (T)} + \frac{1 - e^{-i[\varepsilon_j - \omega_p^0 (T)](2T_e + \tau)}}{\varepsilon_j - \omega_p^0 (T)} \right\}^2, \tag{6} \]

where \( \Delta \lambda = (\omega_p - \varepsilon_f)/2 \). For the sake of simplicity, we have artificially displaced the sample’s energy levels, so that \( \varepsilon_g = 0 \). Furthermore, we have assumed the condition \( \omega_s^0 (T) + \omega_p^0 (T) = \varepsilon_f \).
which guarantees that the two-photon field is resonant with the two-photon ($|g\rangle \rightarrow |f\rangle$) electronic transition.

To get a deeper understanding of Eq. (6), we first realize that the photon spectral non-degeneracy as a function of the crystal’s temperature [shown in Figure 1(b)] can be described by

$$\omega_s^0(T) = \omega_0 + \Delta(T),$$  
$$\omega_i^0(T) = \omega_0 - \Delta(T),$$

where $\omega_0$ is the degenerate frequency, $\omega_0 = 2\pi c/(810\text{ nm})$ for the photon source considered here, and $\Delta(T)$ is a temperature-dependent frequency shift. We can then substitute Eqs. (7)-(8) into Eq. (6) to find that the TPA signal can explicitly been written as

$$P_{g\rightarrow f} = \sum_{j,k=1} \left\{ \frac{1}{\varepsilon_j - \omega_0 - \Delta(T)} + \frac{1}{\varepsilon_j - \omega_0 + \Delta(T)} \right\} \left\{ \frac{1}{\varepsilon_k - \omega_0 - \Delta(T)} + \frac{1}{\varepsilon_k - \omega_0 + \Delta(T)} \right\}$$

$$- \left[ \frac{1}{\varepsilon_j - \omega_0 - \Delta(T)} + \frac{1}{\varepsilon_j - \omega_0 + \Delta(T)} \right] \left[ e^{-i|\varepsilon_j - \omega_0 - \Delta(T)|2T_e\tau} + e^{i|\varepsilon_j - \omega_0 + \Delta(T)|2T_e\tau} \right]$$

$$- \left[ \frac{1}{\varepsilon_j - \omega_0 - \Delta(T)} + \frac{1}{\varepsilon_j - \omega_0 + \Delta(T)} \right] \left[ e^{-i|\varepsilon_j - \omega_0 - \Delta(T)|2T_e\tau} + e^{i|\varepsilon_j - \omega_0 + \Delta(T)|2T_e\tau} \right]$$

$$+ \left[ \frac{1}{\varepsilon_j - \omega_0 - \Delta(T)} \right] \left[ e^{-i|\varepsilon_j - \omega_0 + \Delta(T)|2T_e\tau} + e^{-i|\varepsilon_j - \omega_0 - 2\Delta(T)|2T_e\tau} \right]$$

$$+ \left[ \frac{1}{\varepsilon_j - \omega_0 + \Delta(T)} \right] \left[ e^{-i|\varepsilon_j - \omega_0 - \Delta(T)|2T_e\tau} + e^{-i|\varepsilon_j - \omega_0 + 2\Delta(T)|2T_e\tau} \right].$$

$$P_{g\rightarrow f} = \sum_{j,k=1} \left\{ \frac{1}{\varepsilon_j - \omega_0 - \Delta(T)} + \frac{1}{\varepsilon_j - \omega_0 + \Delta(T)} \right\} \left\{ \frac{1}{\varepsilon_k - \omega_0 - \Delta(T)} + \frac{1}{\varepsilon_k - \omega_0 + \Delta(T)} \right\}$$

$$- \left[ \frac{1}{\varepsilon_j - \omega_0 - \Delta(T)} + \frac{1}{\varepsilon_j - \omega_0 + \Delta(T)} \right] \left[ e^{-i|\varepsilon_j - \omega_0 - \Delta(T)|2T_e\tau} + e^{i|\varepsilon_j - \omega_0 + \Delta(T)|2T_e\tau} \right]$$

$$- \left[ \frac{1}{\varepsilon_j - \omega_0 - \Delta(T)} + \frac{1}{\varepsilon_j - \omega_0 + \Delta(T)} \right] \left[ e^{-i|\varepsilon_j - \omega_0 - \Delta(T)|2T_e\tau} + e^{i|\varepsilon_j - \omega_0 + \Delta(T)|2T_e\tau} \right]$$

$$+ \left[ \frac{1}{\varepsilon_j - \omega_0 - \Delta(T)} \right] \left[ e^{-i|\varepsilon_j - \omega_0 + \Delta(T)|2T_e\tau} + e^{-i|\varepsilon_j - \omega_0 - 2\Delta(T)|2T_e\tau} \right]$$

$$+ \left[ \frac{1}{\varepsilon_j - \omega_0 + \Delta(T)} \right] \left[ e^{-i|\varepsilon_j - \omega_0 - \Delta(T)|2T_e\tau} + e^{-i|\varepsilon_j - \omega_0 + 2\Delta(T)|2T_e\tau} \right].$$

Figure 2(a) shows an example of an expected TPA signal for an arbitrary sample with four intermediate-state levels, whose energies (in terms of wavelength) are arbitrarily chosen to be
\( \lambda_j \in \{507, 534, 576, 635\} \) nm. Note the non-monotonic behavior of the TPA signal, which results from the interference between different pathways through which two-photon excitation of the medium occurs \([14, 16]\). Remarkably, it shows that the absorption properties of the medium can be tuned by modifying the time and frequency properties of the photon pairs.

The TPA signal can further be used to extract information about the electronic structure of the sample by performing a Fourier transform with respect to the delay \(\tau\). Figure 2(b) shows the normalized Fourier transform of Eq. (9). Interestingly, two characteristic patterns of X-shaped and straight lines appear. The former indicate the position (in the energy axis) of the intermediate states, \(\varepsilon_j\), whereas the latter appear at the combined frequencies \(\pm [\varepsilon_j \pm \varepsilon_k]\). The reason behind this difference between signals resides in the fact that the TPA signal of the X-shaped lines contains frequency components that are temperature dependent [second and third lines of Eq. (9)]; whereas the remaining signals are constant with the temperature [fourth and fifth lines of Eq. (9)]. Remarkably, the contrasting behavior between signals allows us to recover the electronic structure of the sample under study by simply identifying the X-shaped lines of TPA Fourier transform, without resorting to many-sample averaging or sophisticated data analysis. This is indeed a notable feature that previous proposals have failed to provide.

4. Conclusions

In this work, we have provided a basic review of the theoretical tools needed for modeling the interaction of quantum light with an arbitrary absorbing medium. In doing so, we have described a recently proposed experimental scheme for the implementation of the so-called virtual-state spectroscopy technique. This novel scheme makes use of a temperature-controlled entangled-photon source to show that the experimentally recorded two-photon absorption signal, measured as a function of the temperature of the nonlinear crystal that generates the photons, and an external delay between them, carries all relevant information regarding the electronic structure of the sample under study, which can be revealed by a simple Fourier transformation.

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