

## Temperature-Controlled Entangled-Photon Absorption Spectroscopy

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Entangled two-photon absorption spectroscopy (TPA) has been widely recognized as a powerful tool for revealing relevant information about the structure of complex molecular systems. However, to date, the experimental implementation of this technique has remained elusive, mainly because of two major difficulties: first, the need to perform multiple experiments with two-photon states bearing different temporal correlations, which translates into the necessity to have at the experimenter's disposal tens, if not hundreds, of sources of entangled photons; second, the need to have *a priori* knowledge of the absorbing medium's lowest-lying intermediate energy level. In this work, we put forward a simple experimental scheme that successfully overcomes these two limitations. By making use of a temperature-controlled entangled-photon source, which allows the tuning of the central frequencies of the absorbed photons, we show that the TPA signal, measured as a function of the temperature of the nonlinear crystal that generates the paired photons, and a controllable delay between them, carries all information about the electronic level structure of the absorbing medium, which can be revealed by a simple Fourier transformation.

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Nonlinear spectroscopy techniques have long been used in analytical and physical chemistry for extracting information about the dynamics and structure of complex systems, from small molecules to large light-harvesting photosynthetic complexes [1–5]. Even though in the optical regime these techniques are typically implemented using laser light, recent investigations suggest that the use of nonclassical states of light, such as entangled photon pairs, may open new and exciting avenues in experimental spectroscopy [6–33]. Remarkably, quantum light has enabled the observation of fascinating two-photon absorption (TPA) phenomena, such as the linear dependence of two-photon absorption rate on photon flux [6,7], as well as the prediction of intriguing effects, such as inducing disallowed atomic transitions [8,9], two-photon-induced transparency [10,11], manipulation of quantum pathways of matter [12–17], and the control of entanglement in molecular processes [18,19].

Among different quantum-enabled techniques, entangled-photon virtual-state spectroscopy [20–33] is a promising tool for extracting information about the intermediate, energy nonconserving electronic transitions [34,35] that contribute to the two-photon excitation of a chemical or biological sample. In this technique, virtual-state transitions, a signature of the absorbing medium, are experimentally revealed by introducing a time delay between frequency-correlated photons and averaging over

many experimental realizations with differing two-photon state characteristics [20].

Regardless of some experimental concerns already raised in the original virtual-state spectroscopy (VSS) proposal, VSS has been widely considered as a new promising route towards novel applications in ultrasensitive detection because of the viability of broadband multiphoton processes at very low-intensity light levels [24,36], as well as the possibility of simultaneously probing various electronic transitions using continuous-wave single-frequency laser sources [20]. In this Letter, we propose an experimental scheme that overcomes the two major difficulties that one encounters when implementing the VSS technique, namely the need for averaging over experimental realizations differing in temporal correlations between the photons that are absorbed—which translates into the need for using hundreds of nonlinear crystals with different lengths—and the requirement of *a priori* knowledge of the absorbing medium's lowest-lying intermediate energy level.

Our scheme makes use of a temperature-controlled entangled-photon source to show that the TPA signal, to be recorded as a function of the temperature of the nonlinear crystal that produces the pair of absorbed photons, and an external signal-idler delay yield information about the electronic level structure of the absorbing medium, which can be revealed by a simple Fourier transformation. Because of its simplicity, our proposed

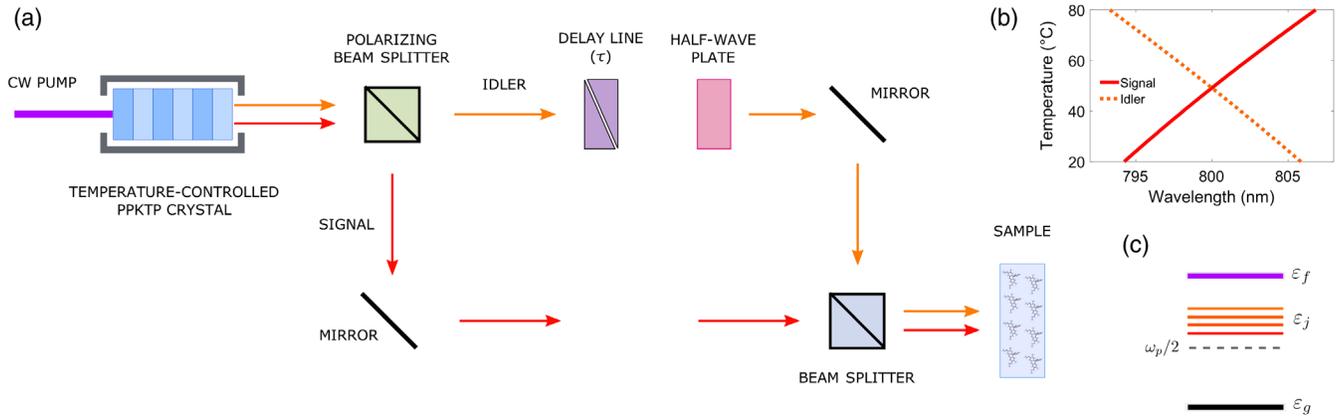


FIG. 1. Temperature-controlled quantum nonlinear spectroscopy. (a) Experimental scheme of the proposed technique. (b) Central wavelength of the down-converted photons as a function of the temperature of the PPKTP crystal, considering a continuous wave pump at 400 nm. (c) Model of the absorbing medium's electronic structure.

technique could be realized using standard and widely used temperature-controlled entangled-photon sources. In this way, our work opens up a new avenue towards the first experimental implementation of nonlinear quantum spectroscopy.

In order to describe our proposed spectroscopy technique (shown in Fig. 1), let us consider first the interaction of a two-photon optical field  $|\Psi\rangle$  with a medium, described by a simple energy-level configuration where two-photon transitions occur from an initial state  $|g\rangle$  to a doubly excited final state  $|f\rangle$  via nonresonant intermediate states denoted by  $|j\rangle$ . For simplicity, in the following, we will omit any other degree of freedom connected to vibrational modes of the sample, and assume that the lifetimes of intermediate states are much longer than the light-matter interaction time. Indeed, in this situation—which can be reached by selecting an appropriate correlation time for the photon pairs [20,23]—the effects due to dissipation in the single-excitation manifold (intermediate states) can be considered negligible.

The interaction of an electromagnetic field with a sample, in the dipole approximation, can be expressed through 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,  $\hat{E}^{(+)}(t) = \hat{E}_s^{(+)}(t) + \hat{E}_i^{(+)}(t)$ , with “s” and “i” denoting the signal and idler fields, which can be written as

$$\hat{E}_{s,i}^{(+)}(t) = \int d\omega_{s,i} \sqrt{\frac{\hbar\omega_{s,i}}{4\pi\epsilon_0 c A}} \hat{a}_{s,i}(\omega_{s,i}) e^{-i\omega_{s,i}t}, \quad (1)$$

where  $c$  is the speed of light,  $\epsilon_0$  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 spatial shape and polarization which, for the sake of simplicity, are not explicitly written.

Assuming that the medium is initially in its ground state  $|g\rangle$  (with energy  $\epsilon_g$ ), one can make use of second-order time-dependent perturbation theory to find that the probability that the medium is excited to the final state  $|f\rangle$  (with energy  $\epsilon_f$ ), through a TPA process, is given by [22,23]

$$P_{g \rightarrow f} = \left| \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{t_2} dt_1 M_{\hat{d}}(t_1, t_2) M_{\hat{E}}(t_1, t_2) \right|^2, \quad (2)$$

with

$$M_{\hat{d}}(t_1, t_2) = \sum_{j=1} D^{(j)} e^{-i(\epsilon_j - \epsilon_f)t_2} e^{-i(\epsilon_g - \epsilon_j)t_1}, \quad (3)$$

$$M_{\hat{E}}(t_1, t_2) = \langle \Psi_f | \hat{E}_s^{(+)}(t_2) \hat{E}_i^{(+)}(t_1) | \Psi \rangle + \langle \Psi_f | \hat{E}_i^{(+)}(t_2) \hat{E}_s^{(+)}(t_1) | \Psi \rangle, \quad (4)$$

where  $D^{(j)} = \langle f | \hat{d} | j \rangle \langle j | \hat{d} | g \rangle$  are the transition matrix elements of the dipole-moment operator. Note from Eq. (3) that excitation of the medium proceeds through the intermediate states  $|j\rangle$ , with energy eigenvalues  $\epsilon_j$ . Also, note that in Eq. (4), we have only written the terms in which one photon from each field contributes to the TPA process. In Eq. (4),  $|\Psi_f\rangle$  denotes the final state of the optical field, which we take to be the vacuum state.

For the sake of simplicity and so as to show the technological readiness of our proposal, we consider a source of entangled two-photon states commonly found in many laboratories [see Fig. 1(a)]. Collinear photon pairs with orthogonal polarizations are generated via type-II spontaneous parametric down-conversion (SPDC) in a periodically poled  $\text{KTiOPO}_4$  (PPKTP) crystal of length  $L$ . We assume continuous wave pumping of the crystal at 400 nm. This configuration results in frequency

anticorrelation of the down-converted photons and provides the strongest TPA signal (see Supplemental Material [37] and Refs. [23,31,32]). The wavelengths of the photons can be tuned around the degenerate wavelength (800 nm) by controlling the crystal temperature  $T$  [38]. The generated two-photon state can then be written as [39]

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

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. Experimentally, the entanglement time may be obtained by measuring the width of the Hong-Ou-Mandel dip at the degenerate frequency [39]. Note that, in writing Eq. (5), we have assumed that an external delay  $\tau$  between the signal and idler photons has been introduced. As illustrated in Fig. 1(a), this can be

experimentally implemented by introducing an optical delay line for one of the photons, once the pair has been split by means of a polarizing beam splitter (PBS). Note that the form of Eqs. (3)–(4) implies that the polarization of the fields is assumed to be equal—and parallel to the orientation of the transition dipole moments  $D^{(j)}$ —thus, a half-wave plate is included in the experimental setup so as to guarantee that both photons share the same polarization when impinging on the sample. The nondegeneracy of the photon wavelengths is given by the function  $\mu(T) = \omega_i^0(T) - \omega_s^0(T)$ , where  $\omega_{i,s}^0(T)$  stands for the temperature-dependent central frequencies of each of the photon wave packets. Figure 1(b) shows the dependence of the down-converted photon central wavelengths on the temperature of the PPKTP crystal.

The proposed quantum spectroscopy protocol works as follows. We consider the model system shown in Fig. 1(c), in which the two-photon excitation energy of the medium  $|g\rangle \rightarrow |f\rangle$  corresponds to the pump wavelength  $\lambda_p = 400$  nm. By substituting Eqs. (3)–(5) into Eq. (2), one finds that the TPA signal is expressed as

$$P_{g \rightarrow f}(\tau, T) = \frac{|\delta(\frac{\Delta_{\pm}}{2\pi})|^2}{4\pi\hbar^2 \varepsilon_0^2 c^2 A^2} \frac{\omega_i^0(T)\omega_s^0(T)}{T_e} \left| \sum_{j=1} D^{(j)} \left\{ \frac{1 - e^{-i[\varepsilon_j - \omega_i^0(T)](2T_e - \tau)}}{\varepsilon_j - \omega_i^0(T)} + \frac{1 - e^{-i[\varepsilon_j - \omega_s^0(T)](2T_e + \tau)}}{\varepsilon_j - \omega_s^0(T)} \right\} \right|^2, \quad (6)$$

where  $\Delta_{\pm} = (\omega_p - \varepsilon_f)/2$ . For the sake of simplicity, we have displaced our energy levels so that  $\varepsilon_g = 0$ . Furthermore, we have assumed the condition  $\omega_s^0(T) + \omega_i^0(T) = \varepsilon_f$ , which guarantees that the two-photon field is resonant with the transition from the ground state  $|g\rangle$  to the final state  $|f\rangle$ .

In order to show the usefulness of the technique proposed for revealing the electronic structure of a molecule, Figs. 2(a) and 2(b) show the TPA predicted spectroscopy obtained through our technique for an organic porphyrin dendrimer: tetraphenylporphyrin ( $H_2$ TPP). This dendrimer has been predicted to exhibit an intermediate state at  $9.85 \times 10^3 \text{ cm}^{-1}$ , corresponding to a wavelength of  $\sim 1015$  nm [7]. In order to further illustrate our technique we include expected results for two additional hypothetical molecular species. Figures 2(c) and 2(d) show the TPA spectroscopy for a system with two intermediate-state levels whose energies (in terms of wavelength) are arbitrarily chosen as follows:  $\lambda_j^{(2)} \in \{967, 1063\}$  nm. Figures 2(e) and 2(f) correspond to another system with four intermediate-state levels arbitrarily chosen as follows:  $\lambda_j^{(4)} \in \{914, 987, 1032, 1122\}$  nm. Figures 2(a), 2(c), and 2(e) show the normalized TPA signals as a function of the crystal's temperature and the external delay  $\tau$ . The nonmonotonic behavior of the TPA signal results from the interference between different pathways through which

two-photon excitation of the medium occurs [20,22] and, more importantly, it shows that the absorption properties of the sample can be tuned by appropriately controlling the time and frequency properties of the entangled photon pairs [24].

Figures 2(b), 2(d), and 2(f) show the normalized Fourier transform of the TPA signals with respect to the external delay. Surprisingly, two characteristic patterns of X-shaped and straight lines appear. The X-shaped lines indicate the energy of intermediate states ( $\varepsilon_j$ ), whereas the straight lines appear at the combined frequencies  $\pm[\varepsilon_j \pm \varepsilon_k]$ . The reason behind this contrasting behavior lies in the fact that the TPA signal of the former contain frequency components that are temperature dependent, while the latter are constant with temperature (see calculations in the Supplemental Material [37] for a detailed analysis on the characteristics of the TPA signal's Fourier transform).

Besides the remarkable advantage of not requiring many different sources of entangled photon pairs in the implementation of two-photon absorption spectroscopy, our scheme permits the direct and straightforward extraction of the electronic structure of an arbitrary sample by simply identifying the X-shaped lines without resorting to many-sample averaging or sophisticated data analysis. This is indeed a notable feature that previous proposals have failed to provide. Finally, it is important to remark that in order to

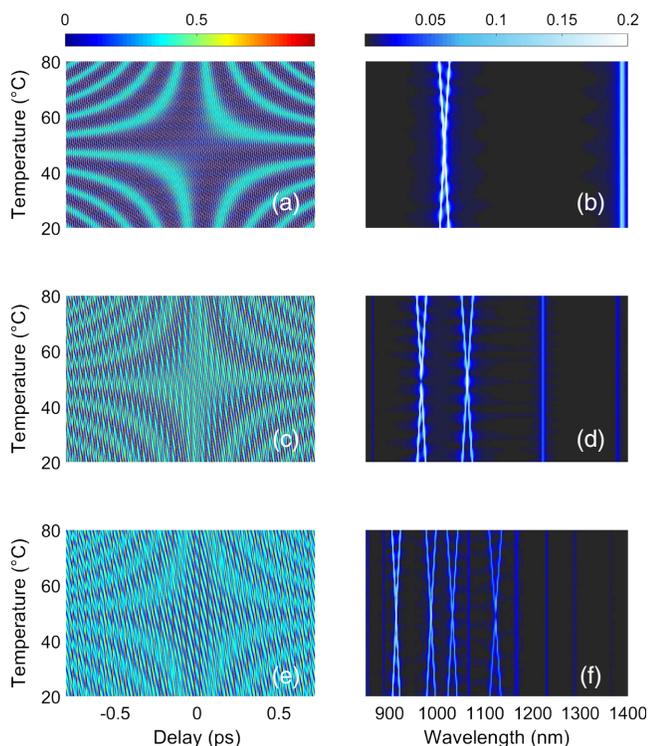


FIG. 2. Entangled-photon absorption spectroscopy for three different cases. An organic porphyrin dendrimer: tetraphenylporphyrin ( $H_2TPP$ ) [(a) and (b)], and two arbitrary systems with two-photon transitions taking place via two [(c) and (d)] and four intermediate states [(e) and (f)]. (a), (c), and (e) normalized TPA signal as a function of the crystal temperature  $T$  and the external delay  $\tau$ . (b), (d), and (f) normalized Fourier transform of the TPA signal with respect to the delay. We assume a source of entangled photon pairs with an entanglement time of  $T_e \sim 0.9$  ps. For the absorbing medium, the energies of the levels (or wavelengths) are arbitrarily chosen to be  $\lambda_j^{(2)} \in \{967, 1063\}$  nm, and  $\lambda_j^{(4)} \in \{914, 987, 1032, 1122\}$  nm, respectively. Finally, in order to obtain the precise location of the intermediate states, the frequency axis is displaced by the degenerate frequency  $\omega_0 = 2\pi c/(800 \text{ nm})$  (see Supplemental Material [37] for further details).

efficiently identify electronic levels of arbitrary samples, one needs to guarantee that the spectrum of the single photons employed is broad enough so that it overlaps with the electronic levels to be resolved. In cases where the overlap is small, one might need to consider alternative approaches, such as the use of intense entangled beam sources [31,32].

In conclusion, we have proposed an experimentally feasible, novel scheme for absorption spectroscopy based on nonclassical light. Previous proposals required the use of multiple nonlinear optics sources, which made its experimental implementation an unrealistic endeavor. Moreover, the acquisition of useful information from the measured data was not straightforward, calling for sophisticated data analysis in order to isolate information about the sought-after energy level structure of the sample under investigation.

All of this has prevented the use and further development of entangled-photon virtual-state spectroscopy.

Contrary to all previous schemes, our proposal makes use of a *single* temperature-controlled nonlinear crystal, a state-of-the-art technology widely used nowadays. Furthermore, the information about the energy level structure can be obtained directly from the experimental data. This indeed constitutes a major simplification of the technique and establishes a new route towards its first experimental demonstration, a milestone in the development of a unique tool capable of providing new and detailed information about the dynamics and chemical structure of complex molecular systems.

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