

## Multiphoton absorption cross section and virtual-state spectroscopy for the entangled $n$ -photon state

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Using a microscopic theory, we determine the entangled  $n$ -photon state generated both by the nonlinear process of spontaneous  $n$ -photon parametric down-conversion and in a cascade of  $n-1$  crystals with two-photon parametric down-conversions. Expressions for the entangled  $n$ -photon absorption cross sections are also obtained. The absorption cross sections exhibit a linear dependence on the photon flux density, and depend on the entanglement times characterizing photons. The effect of relative path delay in the beams is discussed. It forms the basis for extracting the quadrupole moments between states involved in the interaction from the absorption cross section measured as a function of path delay. Effects competitive with entangled three-photon absorption are discussed. [S1050-2947(98)06305-7]

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### I. INTRODUCTION

Over the years, a great deal of attention has been devoted to the problem of multiphoton absorption [1]. Different selection rules for two-photon absorption and one-photon absorption mean that the former can reveal information about transitions not accessible by one-photon processes. Simultaneous multiple-photon absorption is a standard technique used in the field of atomic and molecular physics to determine the properties of materials, such as their ionization characteristics [2]. Two- and three-photon microscopy has been developed [3], and is currently used in biophysics where it allows enhanced resolution. Nonlinear pulsed spectroscopy, based on the interaction of a sequence of ultrashort pulses with a material, developed quickly [4,5] and now provides a powerful tool for investigating the properties of materials.

In general classical light, such as that from lasers and thermal sources, has been used in these experiments. In this case, the rate of  $n$ -photon absorption is proportional to the  $n$ th power of the photon flux density, so that high photon flux densities are required for carrying out real experiments. The photon statistics of an optical field influences absorption in a remarkable way [6]. As an example, for an  $n$ -photon process, the bunching of photons associated with thermal light results in an enhancement of the multiphoton absorption rate by the factor  $n!$  [7] in comparison with that of a laser source.

Quite interesting results emerge when nonclassical light [8] is used to excite multiphoton transitions, particularly for fields comprising entangled photons. It has been shown theoretically that entangled two-photon light generated by the

process of spontaneous parametric down-conversion leads to two-photon absorption linearly (rather than quadratically) proportional to the photon flux density [9,10], and indeed can lead to a phenomenon called entangled two-photon transparency [10]. Also interesting is two-photon absorption induced by squeezed-state light, which can be generated by stimulated parametric down-conversion. In this case also, the absorption depends linearly on the photon flux density [11]. This conclusion has been confirmed experimentally [12].

Another use of entangled two-photon light is in elucidating distinctions between the predictions of classical and quantum physics [13–17]. Coincidence-count measurements with entangled two-photon states have revealed violations of Bell's inequalities [18], and have confirmed the validity of quantum mechanics at the level of statistical ensemble mean values. Moreover, theoretical investigations of similar experiments with entangled three-photon states [19] reveal the possibility that discrepancies between classical and quantum theories might be observable even with a single realization [20,21]. Entangled two-photon states are also useful for nonclassical imaging [22] and cryptography [23].

In this paper, we investigate the properties of the multiphoton absorption of entangled  $n$ -photon states generated both in the process of spontaneous  $n$ -photon parametric down-conversion and in a cascade of  $n-1$  crystals, each producing two-photon spontaneous parametric down-conversions. These schemes lead to a different form of entanglement in the generated  $n$ -photon states, which results in different dependencies of the absorption cross sections on the parameters of the entangled light. We also consider the introduction of additional path delays among the entangled photon beams, which can be useful for carrying out entangled multiphoton spectroscopy. Furthermore, a method for extracting the quadrupole moments from the measured absorption cross sections is proposed. Finally, we discuss effects that are competitive with entangled  $n$ -photon absorption; the range of photon flux densities for which nonclassical absorption is dominant is determined.

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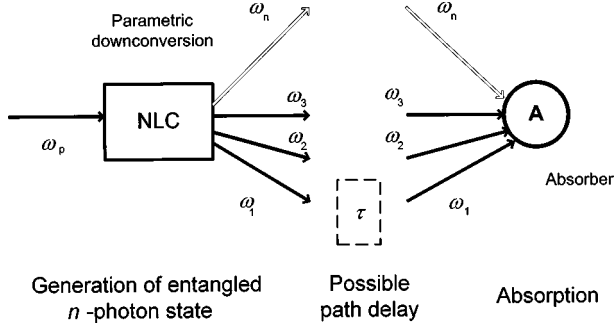


FIG. 1. Sketch of the system under investigation; nonlinear crystal (NLC) with a  $\chi^{(n)}$  nonlinearity generates  $n$  entangled photons with frequencies  $\omega_1, \dots, \omega_n$  which are combined in the absorber A;  $\tau$  denotes a possible path delay of one of the photons, which we take to be  $\omega_1$  for simplicity.

## II. ABSORPTION OF LIGHT GENERATED IN $n$ -PHOTON PARAMETRIC DOWN-CONVERSION

### A. Generation of entangled $n$ -photon states

We assume that the entangled  $n$ -photon state is generated via the nonlinear process of  $n$ -photon parametric down-conversion [24] (a sketch of the system under consideration is presented in Fig. 1). This process can be described by the following interaction Hamiltonian [8]:

$$\hat{H}_{\text{int}}(t) = \sum_{k_1} \cdots \sum_{k_n} \chi^{(n)}(\omega_p; \omega_1, \dots, \omega_n) \xi_p \frac{1}{V} \int_V d^3\mathbf{r} \times \exp(i\Delta\mathbf{k} \cdot \mathbf{r}) \exp(-i\Delta\omega t) \prod_{j=1}^n \hat{a}_{k_j}^\dagger + \text{H.c.}, \quad (1)$$

where  $\hat{a}_{k_j}^\dagger$  is the creation operator of the  $j$ th mode with frequency  $\omega_j$  and wave vector  $\mathbf{k}_j$ ,  $\xi_p$  is the coherent amplitude of the strong pump mode with frequency  $\omega_p$  and wave vector  $\mathbf{k}_p$ ,  $\chi^{(n)}$  is the  $n$ th-order susceptibility,  $V$  is the volume of the crystal, and H.c. means Hermitian conjugate. Frequency- and wave-vector mismatches are defined as  $\Delta\omega = \omega_p - \sum_{j=1}^n \omega_j$  and  $\Delta\mathbf{k} = \mathbf{k}_p - \sum_{j=1}^n \mathbf{k}_j$ , respectively. The interaction Hamiltonian in Eq. (1) contains an integration over the entire volume of the crystal, and considers the propagation of the photons generated therein within the Born approximation. This form of the Hamiltonian has been found to be suitable in the context of coincidence-count measurements [15], thereby justifying its use in our case.

Because the nonlinear process is very weak, the contributions of the vacuum state and the entangled  $n$ -photon state prevail in the wave function describing the photon field within the crystal. That means that the use of perturbation theory in second order is justified (for details, see the Appendix; see Ref. [15] for  $n=2$ ), and results in the following form for the  $n$ -photon state  $|\psi^{(n)}(\mathbf{R}, t)\rangle$ :

$$\begin{aligned} |\psi^{(n)}(\mathbf{R}, t)\rangle &= \mathcal{C} \sum_{k_1} \cdots \sum_{k_n} t_I \exp\left(-i\frac{\Delta\omega t_I}{2}\right) \\ &\times \text{sinc}\left(\frac{\Delta\omega t_I}{2}\right) \exp\left(-i\frac{(\Delta\mathbf{k})_z L_z}{2}\right) \\ &\times \text{sinc}\left(\frac{(\Delta\mathbf{k})_z L_z}{2}\right) \exp\left(i\sum_{j=1}^n \omega_j t\right) \\ &\times \exp\left(-i\sum_{j=1}^n \mathbf{k}_j^v \cdot \mathbf{R}\right) |\mathbf{k}_1, \dots, \mathbf{k}_n\rangle. \end{aligned} \quad (2)$$

The symbol  $\mathcal{C}$  denotes a normalization constant,  $t_I$  is the interaction time,  $L_z$  indicates the length of crystal,  $\mathbf{k}_j^v$  are wave vectors of the corresponding modes in vacuum, and  $\text{sinc}(x) = \sin(x)/x$ . The state  $|\mathbf{k}_1, \dots, \mathbf{k}_n\rangle$  contains one photon in each mode  $\mathbf{k}_1, \dots, \mathbf{k}_n$ .

From the point of view of the statistical properties of the photon field, the process of  $n$ -photon absorption is characterized by a matrix element of the product of  $n$  positive-frequency parts of the electric-field operators  $\hat{E}_j^{(+)}(t_j)$ , sandwiched between the entangled  $n$ -photon state and the vacuum state.

In our case, this element then has the form

$$\begin{aligned} \langle \text{vac} | \prod_{j=1}^n \hat{E}_j^{(+)}(t_j) | \psi^{(n)}(0,0) \rangle \\ = \mathcal{N} \exp\left(-i\sum_{j=1}^n \omega_j^0 t_j\right) \frac{1}{T_{21}} \text{rect}\left(\frac{t_2 - t_1}{T_{21}}\right) \\ \times \prod_{j=3}^n \delta\left((t_j - t_1) - \frac{T_{j1}}{T_{21}}(t_2 - t_1)\right), \end{aligned} \quad (3)$$

where  $\mathcal{N}$  is a normalization constant,  $\text{rect}(t)$  is the rectangular function [ $\text{rect}(t) = 1$  for  $0 \leq t \leq 1$ ,  $\text{rect}(t) = 0$  otherwise], and  $\delta(t)$  is the Dirac delta function. In deriving Eq. (3), we assumed that the central frequencies  $\omega_j^0$  and the central wave vectors  $\mathbf{k}_j^0$  fulfill the phase matching conditions  $\sum_{j=1}^n \omega_j^0 = \omega_p$  and  $\sum_{j=1}^n \mathbf{k}_j^0 = \mathbf{k}_p$ , respectively. The entanglement times  $T_{ij}$  introduced in Eq. (3) are defined by  $T_{ij} = \kappa_i - \kappa_j$ , where  $\kappa_i = L_z/v_i$ ,  $v_i$  being the group velocity of the  $j$ th photon.

The form of the matrix element in Eq. (3) reveals an important property of the entangled  $n$ -photon state. The matrix element

$$\langle \psi^{(n)}(0,0) | \prod_{j=1}^n \hat{E}_j^{(-)}(t_j) \left[ \prod_{j=1}^n \hat{E}_j^{(+)}(t_j) \right] | \psi^{(n)}(0,0) \rangle$$

describes the probability of detecting a photon of frequency  $\omega_1$  at time  $t_1$ , a photon of frequency  $\omega_2$  at time  $t_2$ , etc. Using Eq. (3), at the output plane of the crystal, we have

$$\begin{aligned}
& \langle \psi^{(n)}(0,0) \left| \prod_{j=1}^n \hat{E}_j^{(-)}(t_j) \right\rangle \left\langle \prod_{j=1}^n \hat{E}_j^{(+)}(t_j) \right| \psi^{(n)}(0,0) \rangle \\
&= |\langle \text{vac} | \prod_{j=1}^n \hat{E}_j^{(+)}(t_j) | \psi^{(n)}(0,0) \rangle|^2 \\
&\approx \text{rect} \left( \frac{t_2 - t_1}{T_{21}} \right) \prod_{j=3}^n \delta \left( (t_j - t_1) - \frac{T_{j1}}{T_{21}} (t_2 - t_1) \right). \quad (4)
\end{aligned}$$

Thus the ordering of the photons is determined by the entanglement time values. The entanglement times, in turn, are determined by the group velocities. The rect function in Eq. (3) is associated with coherently summated contributions to  $n$ -photon generation from all points within the crystal,

$$\begin{aligned}
& \langle \text{vac} | \prod_{j=1}^n \hat{E}_j^{(+)}(r_j, t_j) | \psi^{(n)}(0,0) \rangle \\
&= \mathcal{N} \exp \left( -i \sum_{j=1}^n \omega_j^0 t_j \right) \frac{1}{T_{21}} \text{rect} \left( \frac{t_2 - t_1}{T_{21}} \right) \left[ \prod_{j=3}^n \frac{1}{\sqrt{\pi} \theta_j} \exp \left\{ -\frac{1}{\theta_j^2} \left( (t_j - t_1) - \frac{T_{j1}}{T_{21}} (t_2 - t_1) \right)^2 \right\} \right] \Bigg|_{t_j \rightarrow t_j - z_j/c} \\
&\quad \times \prod_{j=2}^n \exp \left\{ -\left( \frac{x_j - x_1}{\Delta x_j} \right)^2 \right\} \exp \left\{ -\left( \frac{y_j - y_1}{\Delta y_j} \right)^2 \right\}. \quad (5)
\end{aligned}$$

The coefficients  $\Delta x_j$  and  $\Delta y_j$  for  $j=2, \dots, n$  introduced in Eq. (5) describe spatial entanglement of photons in the entangled  $n$ -photon state. When deriving Eq. (5), we assumed that the Dirac  $\delta$  functions in Eq. (3) are smoothed, and we replaced them by Gaussian functions with widths  $\theta_2, \dots, \theta_n$ . The width  $\theta_j$  is then proportional to the inverse of the spectral width of the  $j$ th photon band.

The presence of only a single  $n$ -photon entity in the optical field can be formulated by the equality

$$\begin{aligned}
& \frac{\epsilon_0^n}{\left( \prod_{j=1}^n \omega_j^0 \right)} \int d^3 r_1 \dots \int d^3 r_n \\
& \times \langle \psi^{(n)}(\mathbf{R}, t) | \left( \prod_{j=1}^n \hat{E}_j^{(-)}(r_j, t_j) \right) \\
& \times \left( \prod_{j=1}^n \hat{E}_j^{(+)}(r_j, t_j) \right) | \psi^{(n)}(\mathbf{R}, t) \rangle = 1. \quad (6)
\end{aligned}$$

The symbol  $\epsilon_0$  is the permittivity of vacuum,  $\hbar$  is the reduced Planck constant, and  $c$  is the speed of light in vacuum.

Equation (6) provides the normalization constant  $\mathcal{N}$ :

whereas the  $\delta$  functions reflect the fact that all  $n$  photons are created at the same point in the crystal. Thus, if we could know the times at which, e.g., the photons at  $\omega_1$  and  $\omega_2$  appeared at the end of the crystal, we would then approximately know the position in the crystal up to the wavelength at which all of the photons were created, and this, in turn, would determine the occurrence times of the remaining photons. However, from a quantum-mechanical point of view, the nonlinear crystal must be considered as a whole, so that we cannot consider at which position the  $n$ -photon entity was created, which leads to the indistinguishability inherent in the  $n$ -photon state.

The normalization constant  $\mathcal{N}$  in Eq. (3) must be chosen so that the field contains one  $n$ -photon entity. In order to do that it is necessary to develop a space-time formulation of the state which leads to the following matrix element:

$$\mathcal{N}^2 = \frac{\hbar^n \left( \prod_{j=1}^n \omega_j^0 \right) T_{21} \left( \prod_{j=3}^n \sqrt{2\pi} \theta_j \right)}{\epsilon_0^n c^{n-1} \mathcal{V} \left( \prod_{j=2}^n A_{e_j} \right)}. \quad (7)$$

The symbol  $A_{e_j}$  ( $A_{e_j} = \pi \Delta x_j \Delta y_j / 2$ ) denotes the entanglement area of the photon at  $\omega_j$  with respect to the photon at  $\omega_1$ , which occupies a volume  $\mathcal{V}$ .

## B. Entangled $n$ -photon absorption

The expression for the absorption cross section of light in an entangled  $n$ -photon state is derived using  $n$ th order time-dependent perturbation theory (see the Appendix). We assume the condition  $T_{21} < T_{31} < \dots < T_{n1}$ , i.e.,  $v_1 > v_2 > \dots > v_n$ . This means that the photon at  $\omega_1$  interacts with the target first, the photon at  $\omega_2$  interacts second, etc. [see Eq. (4)]. Should the inequalities among the group velocities differ from those specified above, the ordering in which the photons interact with the target will change; however, a simple relabeling of the modes will result in the formulation given here.

The resulting expression for the absorption cross section  $\sigma(T_{21}, T_{31}, \dots, T_{n1})$ , using the entangled  $n$ -photon state, becomes

$$\begin{aligned} & \sigma(T_{21}, T_{31}, \dots, T_{n1}) \\ &= 2\pi\delta\left(\varepsilon_f - \varepsilon_i - \sum_{j=1}^n \omega_j^0\right) \frac{\left(\prod_{j=1}^n \omega_j^0\right) T_{21} \left(\prod_{j=3}^n \sqrt{2\pi}\theta_j\right)}{\hbar^n \varepsilon_0^n c^n \left(\prod_{j=2}^n A_{e_j}\right)} \\ & \times \left| \sum_{j_{n-1}, \dots, j_1} d_{j_{n-1}}^n \cdots d_{j_1}^1 \frac{1 - \exp(i\Phi)}{\Phi} \right|^2, \quad (8) \end{aligned}$$

where

$$\Phi = \sum_{l=1}^n (\varepsilon_{j_l} - \varepsilon_{j_{l-1}} - \omega_l^0) \kappa_l \quad (\varepsilon_{j_0} = \varepsilon_i, \varepsilon_{j_n} = \varepsilon_f). \quad (9)$$

Here  $d_{j_1 j_2}^j$  denotes the matrix element of the dipole-moment operator between the electron states  $j_1$  and  $j_2$  for the direction given by the polarization of the  $j$ th photon, and  $\hbar\varepsilon_j$  is the energy of the  $j$ th electron eigenstate [in particular,  $\hbar\varepsilon_i$

( $\hbar\varepsilon_f$ ) represents the energy of the initial (final) state]. Equation (8) results from the coherent summation of transition amplitudes over all possible absorption times, which is inherent in the rect function of Eq. (3). The summation over  $j_n$  in Eq. (8) reflects the usual quantum interference arising from the indistinguishability of contributions from different intermediate-state transitions.

Entangled  $n$ -photon absorption is linearly dependent on the photon-flux density, which can be easily understood from the form of the square of the normalization constant  $\mathcal{N}^2$  in Eq. (7), which is linearly dependent on the factor  $c/\mathcal{V}$  which determines the photon-flux density for the ‘‘reference’’ beam. The  $n!$  enhancement [7] of the multiphoton absorption of classical thermal light does not carry over to the absorption of entangled photons because the photon-ordering is specified.

We can see from Eq. (8) that the absorption cross section is a complicated function of parameters which characterize the entanglement of photons in the optical field and those connected with the structure of the target. In order to gain insight into the expression for the absorption cross section, we explicitly write it for the case of three photons:

$$\begin{aligned} \sigma(T_{21}, T_{32}) &= 2\pi\delta(\varepsilon_f - \varepsilon_i - \omega_1^0 - \omega_2^0 - \omega_3^0) \frac{\omega_1^0 \omega_2^0 \omega_3^0 T_{21} \sqrt{2\pi}\theta_3}{\hbar^3 \varepsilon_0^3 c^3 A_{e2} A_{e3}} \\ & \times \left| \sum_{j_1, j_2} d_{f j_2}^3 d_{j_2 j_1}^2 d_{j_1 i}^1 \frac{1 - \exp\{i[T_{32}(\varepsilon_f - \varepsilon_{j_2} - \omega_3^0) - T_{21}(\varepsilon_{j_1} - \varepsilon_i - \omega_1^0)]\}}{T_{32}(\varepsilon_f - \varepsilon_{j_2} - \omega_3^0) - T_{21}(\varepsilon_{j_1} - \varepsilon_i - \omega_1^0)} \right|^2. \quad (10) \end{aligned}$$

The above expression for the absorption cross section can be further simplified assuming that the transition from the initial to a given  $j_1$  level prevails in the interaction with the photon at  $\omega_1$ , and similarly the contribution of the interaction with the photon at  $\omega_3$  is mainly from the transition from a given level  $j_2$  to the final level. In this case the absorption cross section  $\sigma(T_{21}, T_{32})$  becomes

$$\sigma(T_{21}, T_{32}) \approx \frac{\sin^2[T_{32}(\varepsilon_f - \varepsilon_{j_2} - \omega_3^0) - T_{21}(\varepsilon_{j_1} - \varepsilon_i - \omega_1^0)]}{[T_{32}(\varepsilon_f - \varepsilon_{j_2} - \omega_3^0) - T_{21}(\varepsilon_{j_1} - \varepsilon_i - \omega_1^0)]^2}, \quad (11)$$

clearly revealing the effect of the entanglement-induced transparency [10]; i.e., when  $T_{32}(\varepsilon_f - \varepsilon_{j_2} - \omega_3^0) - T_{21}(\varepsilon_{j_1} - \varepsilon_i - \omega_1^0) = l\pi$  for integer  $l$ , the absorption cross section is zero.

When we admit more intermediate levels, the absorption cross section  $\sigma(T_{21}, T_{32})$  will rarely dip to zero. However, dips of several orders of magnitude can occur in the dependence of  $\sigma(T_{21}, T_{32})$  on the entanglement times  $T_{21}$  and  $T_{32}$ . This is illustrated for the  $1s \rightarrow 4f$  transition in atomic hydrogen in Fig. 2.

The origin of the entanglement-induced transparency lies in the destructive interference among the probability amplitudes of  $n$ -photon absorption realized in different time sequences [see Eqs. (3) and (4), and the discussion following

Eq. (4)]. The interference connected with the ordering of photon absorption is not essential for achieving entanglement-induced transparency.

In the case of the entangled three-photon state, we have, in general, two entanglement times which can be adjusted to attain entanglement-induced transparency. For comparison with entanglement-induced two-photon transparency, it is useful to consider the case, e.g.,  $T_{32} \ll 1/\Delta\omega_{\text{ch}}$ , where  $\Delta\omega_{\text{ch}}$  is a characteristic detuning frequency. In this case photons at  $\omega_2$  and  $\omega_3$  have nearly the same group velocities in the crystal. The dependence of the absorption cross section  $\sigma(T_{21})$  is then the same as for the entangled two-photon state. However, in general, there are different selection rules for possible transitions from an initial to a final state for two- and three-photon processes.

For comparison with the case of nonclassical light that we have considered, we provide companion expressions for the multiphoton absorption cross section appropriate for  $n$  monochromatic classical light beams, as well as for absorption induced by a sequence of  $n$  ultrashort classical light pulses.

Consider  $n$  monochromatic waves in a multimode coherent state  $|\mathcal{E}_1, \dots, \mathcal{E}_n\rangle$  with frequencies  $\omega_1^0, \dots, \omega_n^0$  and amplitudes  $\mathcal{E}_1, \dots, \mathcal{E}_n$ . The matrix element describing the interaction with the material is then of the form

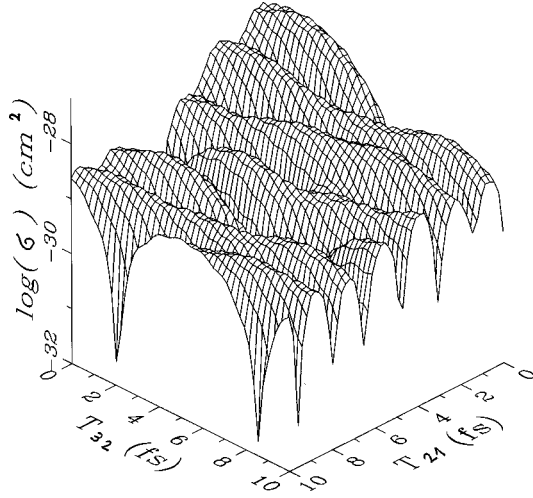


FIG. 2. Entangled three-photon absorption cross section  $\sigma(T_{21}, T_{32})$  for the transition  $1s \rightarrow 4f$  in atomic hydrogen; the state  $4f$  is assumed to be Lorentzian broadened with the lifetime  $10^{-6}$  s;  $\hbar\omega_1^0 = 4$  eV,  $\hbar\omega_2^0 = \hbar\omega_3^0 = 4.37$  eV,  $\theta_3 = 10$  fs, and  $A_{e2} = A_{e3} = 10^{-10}$  m<sup>2</sup>; log denotes a decadic logarithm.

$$\begin{aligned} & \langle \mathcal{E}_1, \dots, \mathcal{E}_n | \prod_{j=1}^n \hat{E}_j^{(+)}(t_j) | \mathcal{E}_1, \dots, \mathcal{E}_n \rangle \\ &= \prod_{j=1}^n \mathcal{E}_j \exp(-i\omega_j^0 t_j). \end{aligned} \quad (12)$$

The absorption rate  $a_{\text{mono}}$  can be written as

$$a_{\text{mono}} = \sigma_{\text{mono}} \prod_{j=1}^n I_j, \quad (13)$$

where  $I_j = |\mathcal{E}_j|^2 \epsilon_0 c / 2\hbar\omega_j^0$  is the photon flux density of the  $j$ th beam. The absorption cross section for the monochromatic waves  $\sigma_{\text{mono}}$  is readily computed to be

$$\begin{aligned} \sigma_{\text{mono}} &= \frac{\pi 2^{n+1} \left( \prod_{j=1}^n \omega_j^0 \right)}{\hbar^n \epsilon_0^n c^n} \delta \left( \varepsilon_f - \varepsilon_i - \sum_{j=1}^n \omega_j^0 \right) \\ &\times \left| \sum_P \sum_{j_1, \dots, j_{n-1}} d_{j_{n-1}}^n \cdots d_{j_1}^1 \right| \\ &\times \left( \prod_{k=1}^{n-1} \frac{1}{\varepsilon_{j_k} - \varepsilon_i - \sum_{l=1}^k \omega_l^0} \right)^2. \end{aligned} \quad (14)$$

The symbol  $\Sigma_P$  denotes the sum of terms arising by permutation over all frequencies  $\omega_1^0, \dots, \omega_n^0$  and upper indices of dipole moments.

Interaction of the target with a sequence of  $n$  ultrashort pulses with integrated amplitudes  $\tilde{\mathcal{E}}_1, \dots, \tilde{\mathcal{E}}_n$  and optical frequencies  $\omega_1^0, \dots, \omega_n^0$  comprising a multimode coherent state  $|\tilde{\mathcal{E}}_1, \dots, \tilde{\mathcal{E}}_n\rangle$  is described by the matrix element

$$\begin{aligned} & \langle \tilde{\mathcal{E}}_1, \dots, \tilde{\mathcal{E}}_n | \prod_{j=1}^n \hat{E}_j^{(+)}(t_j) | \tilde{\mathcal{E}}_1, \dots, \tilde{\mathcal{E}}_n \rangle \\ &= \prod_{j=1}^n \tilde{\mathcal{E}}_j \delta(t_j - t_j^0) \exp(-i\omega_j^0 t_j). \end{aligned} \quad (15)$$

The time  $t_j^0$  denotes the time when the  $j$ th pulse hits the target. In this case, assuming that the photon at  $\omega_k^0$  excites an electron from the level  $\varepsilon_{j_{k-1}}$  to the level  $\varepsilon_{j_k}$  for  $k = 1, \dots, n$  ( $\varepsilon_{j_0} = \varepsilon_i$ ,  $\varepsilon_{j_n} = \varepsilon_f$ ), we obtain the following expression for the absorption  $\tilde{a}_{\text{pulse}}$ :

$$\tilde{a}_{\text{pulse}}(t_1^0, \dots, t_n^0) = \tilde{\sigma}_{\text{pulse}}(t_1^0, \dots, t_n^0) \prod_{j=1}^n \tilde{I}_j, \quad (16)$$

where  $\tilde{I}_j = |\tilde{\mathcal{E}}_j|^2 \epsilon_0 c / (2\hbar\omega_j^0)$  represents the number of photons per unit area in the  $j$ th pulse. The absorption cross section for pulsed light  $\tilde{\sigma}_{\text{pulse}}$  reads

$$\begin{aligned} \tilde{\sigma}_{\text{pulse}}(t_1^0, \dots, t_n^0) &= \frac{2^n \left( \prod_{j=1}^n \omega_j^0 \right)}{\hbar^n \epsilon_0^n c^n} \\ &\times \left| \sum_{j_1, \dots, j_{n-1}} d_{j_{n-1}}^n \cdots d_{j_1}^1 \right| \\ &\times \left| \prod_{k=1}^n \exp[i(\varepsilon_{j_k} - \varepsilon_{j_{k-1}} - \omega_k^0) t_k^0] \right|^2. \end{aligned} \quad (17)$$

It is clear, therefore, that the  $n$ -photon absorption characteristics  $a_{\text{mono}}$  and  $\tilde{a}_{\text{pulse}}(t_1^0, \dots, t_n^0)$  are proportional to the product of  $n$  beam intensities, whereas the  $n$ -photon absorption of entangled light is linearly proportional to the intensity. The summation over all possible permutations of frequencies in the expression for the absorption of monochromatic light in Eq. (14) reflects the fact that the order of interaction of the photons from the various beams with the target is arbitrary. This is not the case with entangled light, for which the order of arrivals of the photons at different frequencies is determined by their group velocities in the nonlinear crystal. The absorption cross section for pulsed light  $\tilde{\sigma}_{\text{pulse}}$  depends on the differences in the arrival times of the pulses  $t_2^0 - t_1^0, \dots, t_n^0 - t_1^0$ , just as the absorption cross section  $\sigma$  for entangled light depends on the entanglement times  $T_{21}, \dots, T_{n1}$ .

### C. Effect of path delay

The absorption cross section  $\sigma(T_{21}, T_{32})$ , which is a complex function of the entanglement times, bears information about the target parameters (energies, dipole moments, etc.). This poses question about the possibility of extracting this information from the measurement of absorption cross section. Introduction of an additional delay into the path of one of the photons modifies the absorption cross section in such a way that the target parameters become more conveniently accessible from the measured absorption cross section as a function of path delay.

Introduction of a delay  $T$  into the path of the photon at  $\omega_1$  (the fastest one) results in an absorption cross section  $\sigma(T_{21}, T_{32}, T)$  of the form

$$\sigma(T_{21}, T_{32}, T) = 2\pi\delta(\varepsilon_f - \varepsilon_i - \omega_1^0 - \omega_2^0 - \omega_3^0) \frac{\omega_1^0 \omega_2^0 \omega_3^0 T_{21} \sqrt{2\pi} \theta_3}{\hbar^3 \varepsilon_0^3 c^3 A_{e2} A_{e3}} \mathcal{B}(T_{21}, T_{32}, T), \quad (18)$$

where

$$\mathcal{B}(T_{21}, T_{32}, T)$$

$$= \left| \sum_{j_1, j_2} d_{jj_2}^1 d_{j_2 j_1}^3 d_{j_1 i}^2 \frac{\exp\{i(\varepsilon_{jj_2} - \omega_1^0)T\} - \exp\{i[(\varepsilon_{j_2 j_1} - \omega_3^0)T_{32} + (\varepsilon_{jj_2} - \omega_1^0)(T - T_{21})]\}}{(\varepsilon_{j_2 j_1} - \omega_3^0)T_{32} - (\varepsilon_{jj_2} - \omega_1^0)T_{21}} \right|^2 \quad \text{for } T > T_{32} + T_{21}, \quad (19)$$

$$= \left| \sum_{j_1, j_2} d_{jj_2}^1 d_{j_2 j_1}^3 d_{j_1 i}^2 \frac{\exp\{i(\varepsilon_{jj_2} - \omega_1^0)T\} - \exp\left\{-i(\varepsilon_{j_1 i} - \omega_2^0) \frac{T_{32}}{T_{32} + T_{21}} T\right\}}{(\varepsilon_{j_2 j_1} - \omega_3^0)T_{32} - (\varepsilon_{jj_2} - \omega_1^0)T_{21}} + d_{jj_2}^3 d_{j_2 j_1}^1 d_{j_1 i}^2 \frac{\exp\{i[(\varepsilon_{j_2 j_1} - \omega_3^0)(T - T_{21}) + (\varepsilon_{jj_2} - \omega_3^0)T_{32}]\} - \exp\left\{-i(\varepsilon_{j_1 i} - \omega_2^0) \frac{T_{32}}{T_{32} + T_{21}} T\right\}}{(\varepsilon_{j_2 j_1} - \omega_1^0)T_{21} - (\varepsilon_{jj_2} - \omega_3^0)T_{32}} \right|^2 \quad \text{for } T_{32} + T_{21} > T > T_{21}, \quad (20)$$

$$= \left| \sum_{j_1, j_2} d_{jj_2}^1 d_{j_2 j_1}^3 d_{j_1 i}^2 \frac{\exp\{i(\varepsilon_{jj_2} - \omega_1^0)T\} - \exp\left\{-i(\varepsilon_{j_1 i} - \omega_2^0) \frac{T_{32}}{T_{32} + T_{21}} T\right\}}{(\varepsilon_{j_2 j_1} - \omega_3^0)T_{32} - (\varepsilon_{jj_2} - \omega_1^0)T_{21}} + d_{jj_2}^3 d_{j_2 j_1}^1 d_{j_1 i}^2 \frac{\exp\left\{i(\varepsilon_{jj_2} - \omega_3^0) \frac{T_{32}}{T_{21}} T\right\} - \exp\left\{-i(\varepsilon_{j_1 i} - \omega_2^0) \frac{T_{32}}{T_{32} + T_{21}} T\right\}}{(\varepsilon_{j_2 j_1} - \omega_1^0)T_{21} - (\varepsilon_{jj_2} - \omega_3^0)T_{32}} + d_{jj_2}^3 d_{j_2 j_1}^2 d_{j_1 i}^1 \frac{\exp\left\{i(\varepsilon_{jj_2} - \omega_3^0) \frac{T_{32}}{T_{21}} T\right\} - \exp\{i[(\varepsilon_{jj_2} - \omega_3^0)T_{32} + (\varepsilon_{j_1 i} - \omega_1^0)(T - T_{21})]\}}{(\varepsilon_{jj_2} - \omega_3^0)T_{32} - (\varepsilon_{j_1 i} - \omega_1^0)T_{21}} \right|^2 \quad \text{for } T_{21} > T > 0. \quad (21)$$

The abbreviation  $\varepsilon_{\alpha\beta} = \varepsilon_\alpha - \varepsilon_\beta$  was used in the above expressions.

In order to simplify the above formulas for  $\sigma(T_{21}, T_{32}, T)$  and to gain insight into their nature, we rewrite Eqs. (18)–(21) under the assumption  $T_{32} \ll 1/\Delta\omega_{\text{ch}}$ , whereupon

$$\sigma(T_{31}, T) = 2\pi\delta(\varepsilon_f - \varepsilon_i - \omega_1^0 - \omega_2^0 - \omega_3^0) \frac{\omega_1^0 \omega_2^0 \omega_3^0 T_{31} \sqrt{2\pi} \theta_3}{\hbar^3 \varepsilon_0^3 c^3 A_{e2} A_{e3}} \mathcal{B}(T_{31}, T) \quad (22)$$

and

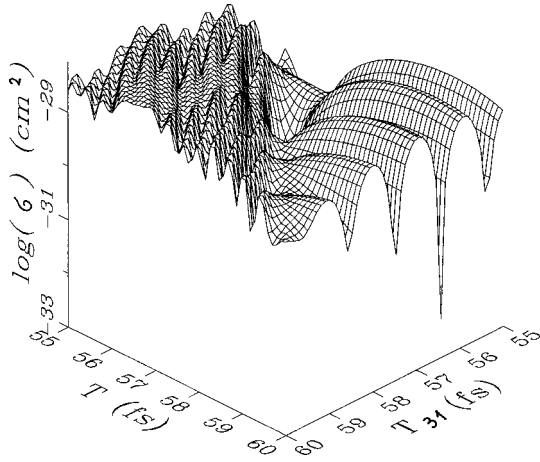


FIG. 3. Entangled three-photon absorption cross section  $\sigma(T_{31}, T)$  for the transition  $1s \rightarrow 4f$  in atomic hydrogen;  $\hbar\omega_1^0 = \hbar\omega_2^0 = \hbar\omega_3^0 = 4.25$  eV,  $T_{32} = 0$  fs; values of the other parameters are the same as those indicated in Fig. 2; log denotes a decadic logarithm.

$$\mathcal{B}(T_{31}, T) = \left| \sum_j d_{ff}^1 q_{ji}^{3,2} \frac{1 - \exp[i(\varepsilon_f - \varepsilon_j - \omega_1^0)T]}{(\varepsilon_f - \varepsilon_j - \omega_1^0)T_{31}} - \sum_j q_{ff}^{3,2} d_{ji}^1 \frac{1 - \exp[i(\varepsilon_j - \varepsilon_i - \omega_1^0)(T - T_{31})]}{(\varepsilon_j - \varepsilon_i - \omega_1^0)T_{31}} \right|^2$$

for  $0 < T < T_{31}$ ,

$$= \left| \sum_j d_{ff}^1 q_{ji}^{3,2} \exp[i(\varepsilon_f - \varepsilon_j - \omega_1^0)T] \times \frac{1 - \exp[-i(\varepsilon_f - \varepsilon_j - \omega_1^0)T_{31}]}{(\varepsilon_f - \varepsilon_j - \omega_1^0)T_{31}} \right|^2$$

for  $T > T_{31}$ .

Quadrupole moments  $q_{ji}^{3,2}$  (the notation is similar to that for dipole moments) appear as a consequence of the nearly simultaneous arrivals of photons at frequencies  $\omega_2$  and  $\omega_3$ . The nearly simultaneous arrival of two entangled photons means that the interaction of this entity with an electron is characterized only by quadrupole moments, i.e., there is no competitive channel based on the interaction via dipole moments. This feature creates a basis for the measurement of quadrupole moments associated with transitions between levels for which dipole moments are nonzero.

As indicated by the above expression for the absorption cross section  $\sigma(T_{31}, T)$ , there are two different regions of interest. In particular, for  $T < T_{31}$  three photons can arrive at the same time, which is impossible in the region in which the time delay of the photon at  $\omega_1$  exceeds the entanglement time  $T_{31}$  ( $T > T_{31}$ ). The differences in behavior are highlighted in Fig. 3 for atomic hydrogen. The behavior of  $\sigma(T_{31}, T)$  for  $T < T_{31}$  is more oscillatory as a consequence of the pairwise ‘‘interference’’ [see  $\mathcal{B}(T_{31}, T)$  in Eq. (23) for the two possible paths of excitation]. The existence of two

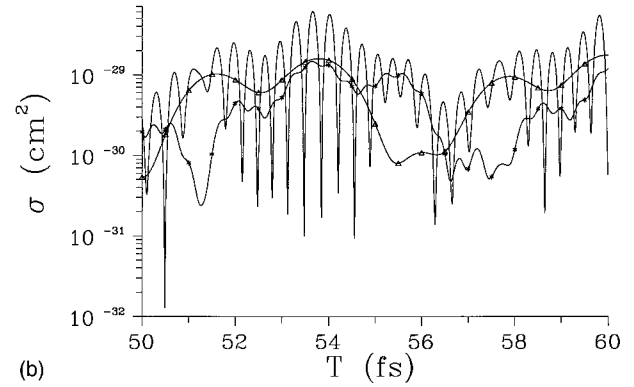
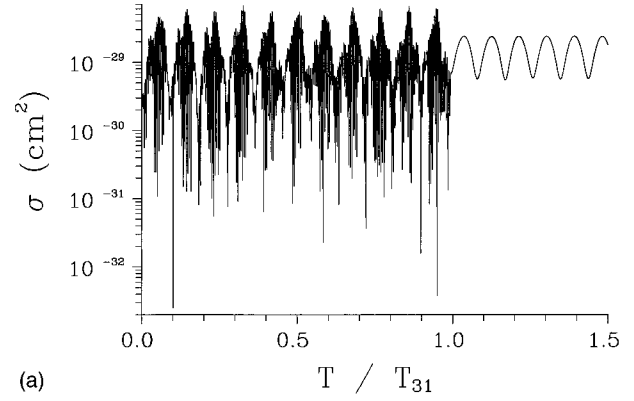


FIG. 4. Entangled three-photon absorption cross section  $\sigma(T)$  for the transition  $1s \rightarrow 4f$  in atomic hydrogen (a); entangled three-photon absorption cross section  $\sigma(T)$  (solid curve without symbols) and the contributions from the first (solid curve with triangles) and the second (solid curve with asterisks) paths (b);  $\hbar\omega_1^0 = 2$  eV,  $\hbar\omega_2^0 = \hbar\omega_3^0 = 5.37$  eV,  $T_{31} = 70$  fs, and  $T_{32} = 0$  fs; values of the other parameters are the same as those indicated in Fig. 2.

paths for the electron transition is closely related to the possibility of simultaneous arrival of all three photons.

The effect of pairwise interference produces strong oscillations in the region  $T \leq T_{31}$ , as demonstrated in Fig. 4(a). Figure 4(b) shows the absorption cross section  $\sigma(T)$  in the cases of excitation through one path, through the other path, and through both paths. In general, the stronger path deter-

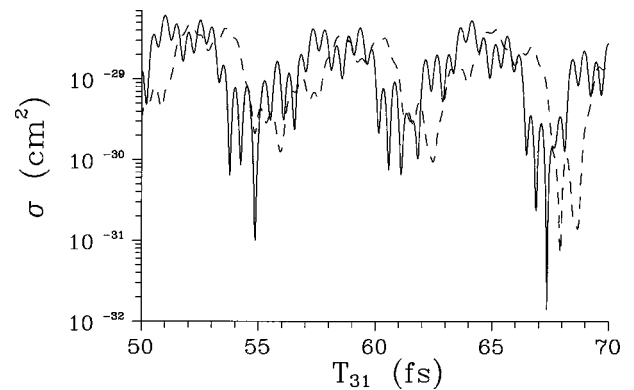


FIG. 5. Entangled three-photon absorption cross section  $\sigma(T_{31})$  for the transition  $1s \rightarrow 4f$  in atomic hydrogen for delays path delays  $T = 30$  fs (solid curve) and  $T = 31$  fs (dashed curve);  $\hbar\omega_1^0 = \hbar\omega_2^0 = \hbar\omega_3^0 = 4.25$  eV, and  $T_{32} = 0$  fs; values of the other parameters are the same as those indicated in Fig. 2.

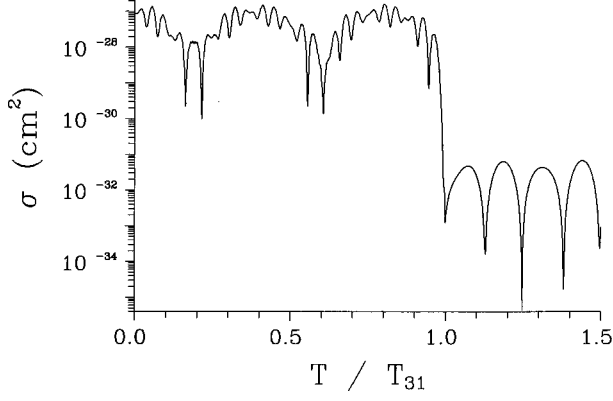


FIG. 6. Entangled three-photon absorption cross section  $\sigma(T)$  for the transition  $1s \rightarrow 4f$  in atomic hydrogen for a fixed value of the entanglement time  $T_{31} = 70$  fs;  $\hbar\omega_1^0 = 10$  eV,  $\hbar\omega_2^0 = \hbar\omega_3^0 = 1.38$  eV,  $T_{31} = 50$  fs, and  $T_{32} = 0$  fs; values of the other parameters are the same as those indicated in Fig. 2.

mines the general level of the cross section  $\sigma(T)$ , whereas the weaker path is responsible for the oscillations in  $\sigma(T)$ . If the values of the contributions from both paths are nearly the same, the effect of pairwise interference is strongest and leads to fast oscillations [see Fig. 4(b)].

In the region with  $T < T_{31}$ , there are characteristic ‘‘valleys’’ which correspond to fixed values of the quantity  $T - T_{31}$  [see Eq. (23) for  $B(T_{31}, T)$ ]. This effect can be used for a determination of entanglement time if we vary the time delay and measure the absorption of a sample.

The absorption cross section  $\sigma(T_{31})$  for  $T < T_{31}$  shows a strong dependence on the time delay  $T$ . This is illustrated by the substantial difference between the two curves for atomic hydrogen, shown in Fig. 5, which differ only by a time delay of 1 fs. The strong oscillations in  $\sigma(T_{31})$  are caused by pairwise interference [see Eq. (23) for  $B(T_{31}, T)$ ]. This clearly demonstrates a strong sensitivity of the absorption cross-section measurement on path delay.

Furthermore, the introduction of a nonzero path delay can lead to a resonant enhancement of the absorption [see the expression for  $B(T_{31}, T)$  in Eq. (23)]. This is demonstrated in Fig. 6 for atomic hydrogen, where the absorption cross section  $\sigma(T)$  is seen to be several orders of magnitude greater in the region  $T < T_{31}$  [the transition is nearly at resonance,  $\omega_1^0 = \frac{49}{50}(\varepsilon_{2p} - \varepsilon_{1s})$ ] than it is in the region  $T > T_{31}$ .

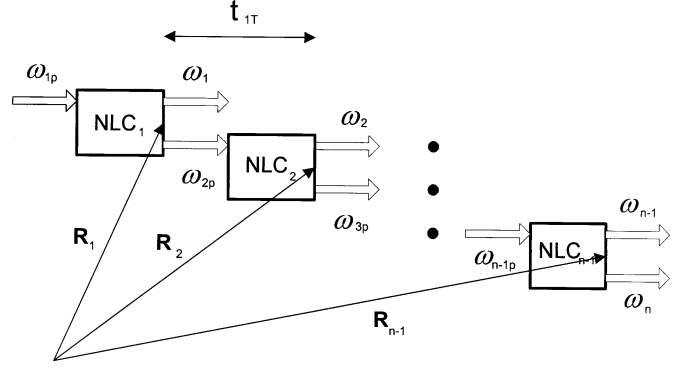


FIG. 7. Sketch of a cascade of  $n-1$  crystals,  $\text{NLC}_1, \dots, \text{NLC}_{n-1}$ , with  $\chi^{(2)}$  nonlinearities. Photons at  $\omega_1, \dots, \omega_n$  participate in the multiphoton absorption, whereas photons at  $\omega_{1p}, \dots, \omega_{n-1p}$  provide pumping.  $\mathbf{R}_j$  denotes the position vector of the output plane of the  $j$ th crystal, and  $t_{jT}$  denotes the time delay of the photon at  $\omega_{j+1p}$ .

### III. ABSORPTION OF LIGHT GENERATED IN A CASCADE OF CRYSTALS

We now proceed to investigate the absorption of entangled  $n$ -photon state light generated in a cascade of  $n-1$  crystals, each giving rise to a two-photon spontaneous parametric down-conversion process. This scheme leads to a different kind of entanglement in an optical field, resulting in different dependencies of the absorption cross section on the entanglement times involved. This scheme also provides interesting results for entangled three-photon spectroscopy.

#### A. Generation of entangled $n$ -photon states

We assume that the  $n$ -photon state is generated in a cascade of  $n-1$  crystals with two-photon parametric down-conversion processes, in which a down-converted beam from the  $(j-1)$ st crystal serves as a pump beam for the  $j$ th crystal, for  $j=2, \dots, n-1$ . The first crystal in the cascade is pumped by a strong field in a coherent state. The scheme is depicted in Fig. 7.

Interaction Hamiltonians  $\hat{H}_{\text{int}}^{(1)}, \dots, \hat{H}_{\text{int}}^{(n-1)}$  describing nonlinear three-mode interactions in the corresponding crystals have the form

$$\hat{H}_{\text{int}}^{(1)}(t) = \sum_{k_1} \sum_{k_{2p}} \chi_1^{(2)}(\omega_{1p}; \omega_1, \omega_{2p}) \frac{1}{V_1} \int_{V_1} d^3\mathbf{r} \exp(i\Delta\mathbf{k}_1 \cdot \mathbf{r}) \exp(-i\Delta\omega_1 t) \xi_{1p} \hat{a}_{k_1}^\dagger \hat{a}_{k_{2p}}^\dagger + \text{H.c.},$$

$$\hat{H}_{\text{int}}^{(j)}(t) = \sum_{k_{jp}} \sum_{k_j} \sum_{k_{j+1p}} \chi_j^{(2)}(\omega_{jp}; \omega_j, \omega_{j+1p}) \frac{1}{V_j} \int_{V_j} d^3\mathbf{r} \exp(i\Delta\mathbf{k}_j \cdot \mathbf{r}) \exp(-i\Delta\omega_j t) \hat{a}_{k_{jp}}^\dagger \hat{a}_{k_j}^\dagger \hat{a}_{k_{j+1p}}^\dagger + \text{H.c.}, \quad j=2, \dots, n-2, \quad (25)$$

$$\hat{H}_{\text{int}}^{(n-1)}(t) = \sum_{k_{n-1p}} \sum_{k_{n-1}} \sum_{k_n} \chi_{n-1}^{(2)}(\omega_{n-1p}; \omega_{n-1}, \omega_n) \frac{1}{V_{n-1}} \int_{V_{n-1}} d^3\mathbf{r} \exp(i\Delta\mathbf{k}_{n-1} \cdot \mathbf{r}) \exp(-i\Delta\omega_{n-1} t) \hat{a}_{k_{n-1p}}^\dagger \hat{a}_{k_{n-1}}^\dagger \hat{a}_{k_n}^\dagger + \text{H.c.}$$

Here  $\hat{a}_{k_\alpha}^\dagger$  ( $\hat{a}_{k_\alpha}$ ) is the creation (annihilation) operator of the  $\alpha$ th mode with frequency  $\omega_\alpha$  and wave vector in vacuum  $\mathbf{k}_\alpha^v$  for  $\alpha=1, \dots, n, 2p, \dots, n-1p$  (see the scheme in Fig. 7);  $\xi_{1p}$  is a coherent amplitude of the strong pump mode with frequency



$\omega_{1p}$  and wave vector in vacuum  $\mathbf{k}_{1p}^v$ . The symbol  $\chi_j^{(2)}$  refers to the second-order susceptibility of the  $j$ th crystal, and  $V_j$  is the volume of the  $j$ th crystal. Frequency- and wave-vector mismatches are defined as  $\Delta\omega_j = \omega_{jp} - \omega_j - \omega_{j+1p}$  ( $j = 1, \dots, n-2$ ),  $\Delta\omega_{n-1} = \omega_{n-1p} - \omega_{n-1} - \omega_n$  and  $\Delta\mathbf{k}_j = \mathbf{k}_{jp} - \mathbf{k}_j - \widetilde{\mathbf{k}}_{j+1p}$  ( $j = 1, \dots, n-2$ ),  $\Delta\mathbf{k}_{n-1} = \mathbf{k}_{n-1p} - \mathbf{k}_{n-1} - \mathbf{k}_n$ , respectively. The symbols  $\mathbf{k}_j$  and  $\mathbf{k}_{jp}$  denote wave vectors of the corresponding modes in the  $j$ th crystal;  $\widetilde{\mathbf{k}}_{jp}$  stands for a wave vector of the  $j$ th mode in the  $(j-1)$ st crystal.

As in Sec. II, we used second-order perturbation theory for the description of the three-mode interactions in all crystals, which leads to the following expression for the entangled  $n$ -photon state

$$|\psi_c^{(n)}(\mathbf{R}_1, \dots, \mathbf{R}_n, t_0)\rangle = C_c \sum_{k_1} \dots \sum_{k_n} \sum_{k_{2p}} \dots \sum_{k_{n-1p}} \left[ \prod_{j=1}^{n-1} t_{jT} \exp\left(-i \frac{\Delta\omega_j t_{jT}}{2}\right) \text{sinc}\left(\frac{\Delta\omega_j t_{jT}}{2}\right) \right] \left[ \prod_{j=1}^{n-1} \exp\left(-i \frac{(\Delta\mathbf{k}_j)_z L_{jz}}{2}\right) \right] \\ \times \text{sinc}\left(\frac{(\Delta\mathbf{k}_j)_z L_{jz}}{2}\right) \left[ \prod_{j=1}^{n-2} \exp(i\omega_{j+1p} t_{jT}) \right] \left[ \prod_{j=1}^n \exp(-i\mathbf{k}_j^v \cdot \mathbf{R}_j) \exp(i\omega_j t_0) \right] |\mathbf{k}_1, \dots, \mathbf{k}_n\rangle. \quad (26)$$

Here  $t_{jT}$  is the interaction time in the  $j$ th crystal,  $\mathbf{R}_j$  is the position vector of the output plane of the  $j$ th crystal (see Fig. 7,  $\mathbf{R}_n = \mathbf{R}_{n-1}$ ), and  $t_{jT}$  is the time needed for a photon at  $\omega_{j+1p}$  to arrive from the output plane of the  $j$ th crystal to the output plane of the  $(j+1)$ st crystal (see Fig. 7). The state  $|\mathbf{k}_1, \dots, \mathbf{k}_n\rangle$  contains one photon in each of the modes  $\mathbf{k}_1, \dots, \mathbf{k}_n$ . The symbol  $C_c$  denotes a normalization constant.

The matrix element of the product of  $n$  positive-frequency parts of the electric-field operators  $\hat{E}_j^{(+)}(r_j, t_j)$  between the state  $|\psi_c^{(n)}\rangle$  and the vacuum state  $|\text{vac}\rangle$  describing  $n$ -photon absorption can be recast into the following form (under the same conditions as in the case discussed in Sec. II):

$$\langle \text{vac} | \prod_{j=1}^n \hat{E}_j^{(+)}(\mathbf{r}_j, t_j) | \psi_c^{(n)}(\mathbf{R}_1, \dots, \mathbf{R}_n, t_0) \rangle = \mathcal{N}_c \exp\left(-i \sum_{j=1}^n \omega_j^0 \widetilde{\tau}_j\right) \left[ \prod_{j=1}^{n-2} \frac{1}{T_j \widetilde{j+1p}} \text{rect}\left(\frac{\widetilde{\tau}_j - \widetilde{\beta}_{j+1p}}{T_j \widetilde{j+1p}}\right) \right] \frac{1}{T_{n-1n}} \text{rect}\left(\frac{\widetilde{\tau}_{n-1} - \widetilde{\tau}_n}{T_{n-1n}}\right). \quad (27)$$

The symbol  $\mathcal{N}_c$  denotes a normalization constant. The times  $\widetilde{\tau}_1, \dots, \widetilde{\tau}_n$  and  $\widetilde{\beta}_{1p}, \dots, \widetilde{\beta}_{n-1p}$  are defined as

$$\begin{aligned} \widetilde{\tau}_1 &= \tau_1, \\ \widetilde{\tau}_j &= \tau_j - \sum_{l=1}^{j-1} t_{lT}, \quad j=2, \dots, n-1, \\ \widetilde{\tau}_n &= \tau_n - \sum_{l=1}^{n-2} t_{lT}, \\ \widetilde{\beta}_{jp} &= \frac{T_{j\ jp} \widetilde{\beta}_{j+1p} + T_{j\ j+1p} \widetilde{\tau}_j}{T_j \widetilde{j+1p}}, \quad j=2, \dots, n-2, \\ \widetilde{\beta}_{n-1p} &= \frac{T_{n-1\ n-1p} \widetilde{\tau}_n + T_{n-1\ n} \widetilde{\tau}_{n-1}}{T_{n-1\ n}}. \end{aligned} \quad (28)$$

In the above expression, the times  $\tau_1, \dots, \tau_n$  are introduced in accordance with the relations

$$i[\mathbf{k}_j^v \cdot (\mathbf{r}_j - \mathbf{R}_j) - \omega_j(t_j - t_0)] = -i\omega_j \tau_j, \quad j=1, \dots, n. \quad (29)$$

In the derivation of Eq. (27), we assumed that the central frequencies  $\omega_j^0$  and  $\omega_{jp}^0$  and central wave vectors  $\mathbf{k}_j^0$ ,  $\mathbf{k}_{jp}^0$ , and  $\widetilde{\mathbf{k}}_{jp}^0$  fulfill the phase matching conditions  $\omega_{jp}^0 - \omega_j^0 - \omega_{j+1p}^0 = 0$  ( $j=1, \dots, n-2$ ),  $\omega_{n-1p}^0 - \omega_{n-1}^0 - \omega_n^0 = 0$  and  $\mathbf{k}_{jp}^0 - \mathbf{k}_j^0 - \widetilde{\mathbf{k}}_{j+1p}^0 = 0$  ( $j=1, \dots, n-2$ ),  $\mathbf{k}_{n-1p}^0 - \mathbf{k}_{n-1}^0 - \mathbf{k}_n^0 = 0$ , respectively.

The entanglement times  $T_{\alpha_1 \alpha_2}$  were introduced above according to the definition  $T_{\alpha_1 \alpha_2} = \kappa_{\alpha_1} - \kappa_{\alpha_2}$  in which  $\kappa_j$

$= L_{jz}/v_j$ ,  $\kappa_n = L_{n-1z}/v_n$ ,  $\kappa_{jp} = L_{jz}/v_{jp}$ , and  $\kappa_{j\bar{p}} = L_{j-1z}/\widetilde{v}_{jp}$ . The symbols  $v_j$ ,  $v_{jp}$ , and  $\widetilde{v}_{jp}$  denote group velocities of modes in the corresponding crystals (the notation is the same as for wave vectors).

The role of times in Eq. (27) for the matrix element can be understood as follows. The difference of times  $\widetilde{\tau}_n - \widetilde{\tau}_{n-1}$  at which the photons at  $\omega_n$  and  $\omega_{n-1}$  appear at the output plane of the  $(n-1)$ st crystal lies within the entanglement time  $T_{n-1n}$  characterizing the process of two entangled photons generation in the  $(n-1)$ st crystal. If we know the times  $\widetilde{\tau}_n$  and  $\widetilde{\tau}_{n-1}$ , we can deduce up to the wavelength the position in the  $(n-1)$ st crystal, where two photons were created. This determines the time  $\widetilde{\beta}_{n-1p}$ , at which the pumping photon at  $\omega_{n-1p}$  appeared at the output plane of the  $(n-2)$ nd crystal. This time, together with the time  $\widetilde{\tau}_{n-2}$  at which the photon at  $\omega_{n-2}$  appeared at the output plane of the  $(n-2)$ nd crystal, fixes the point in the  $(n-2)$ nd crystal, in which the photons at  $\omega_{n-2}$  and  $\omega_{n-1p}$  were generated. The difference of times  $\widetilde{\beta}_{n-1p}$  and  $\widetilde{\tau}_{n-2}$  lies within the entanglement time  $T_{n-2\ n-1p}$  appropriate for the down-conversion process in the  $(n-2)$ nd crystal. The meaning of the remaining times is similar.

The case in which all  $n$  photons can arrive precisely at the same time at a target is of importance for entangled  $n$ -photon absorption. This can be achieved, e.g., by assuming, among group velocities, the relations  $v_1 > \widetilde{v}_{2p}$ ,  $v_{jp} > v_j > \widetilde{v}_{j+1p}$  ( $j=2, \dots, n-2$ ) and  $v_{n-1p} > v_{n-1} > v_n$ , and by introducing the time delay  $\sum_{l=j}^{n-2} t_{lT}$  into the path of the photon at  $\omega_j$  for  $j=1, \dots, n-2$ . In this case, the photon at  $\omega_1$  first interacts

with the target, the photon at  $\omega_2$  interacts second, and so on. The matrix element from Eq. (27) then reads

$$\begin{aligned} & \langle \text{vac} | \prod_{j=1}^n \hat{E}_j^{(+)}(t_j) | \psi_c^{(n)} \rangle \\ & = \mathcal{N}_c \exp \left( -i \sum_{j=1}^n \omega_j^0 t_j \right) \left[ \prod_{j=1}^{n-2} \frac{1}{T_{j \widetilde{j+1} p}} \text{rect} \left( \frac{t_j - \beta_{j+1 p}}{T_{j \widetilde{j+1} p}} \right) \right] \\ & \quad \times \frac{1}{T_{n-1 n}} \text{rect} \left( \frac{t_{n-1} - t_n}{T_{n-1 n}} \right). \end{aligned} \quad (30)$$

The time  $t_j$  characterizes the photon at  $\omega_j$  in the area of the target. The times  $\beta_{1p}, \dots, \beta_{n-1p}$  are defined in a similar way as are the times  $\widetilde{\beta}_{1p}, \dots, \widetilde{\beta}_{n-1p}$  in Eq. (28), i.e.,

$$\beta_{jp} = \frac{T_{j j p} \beta_{j+1 p} + T_{j p \widetilde{j+1} p} t_j}{T_{j \widetilde{j+1} p}}, \quad j=2, \dots, n-2, \quad (31)$$

### B. Entangled $n$ -photon absorption

The matrix element given in Eq. (30) appropriate for a cascade of  $n-1$  crystals determines the absorption cross section  $\sigma_c(T_{1 1 p}, T_{2 p 1 p}, \dots, T_{n-1 n-1 p}, T_{n n-1 p})$  of the entangled  $n$ -photon state

$$\begin{aligned} \sigma_c(T_{1 1 p}, T_{2 p 1 p}, \dots, T_{n-1 n-1 p}, T_{n n-1 p}) & = 2\pi \delta \left( \varepsilon_f - \varepsilon_i - \sum_{j=1}^n \omega_j^0 \right) \frac{\left( \prod_{j=1}^n \omega_j^0 \right) \left( \prod_{j=1}^{n-2} T_{j \widetilde{j+1} p j} \right) T_{n n-1}}{\hbar^n \varepsilon_0^n c^n \left( \prod_{j=1}^{n-1} A_{ej} \right)} \\ & \quad \times \left| \sum_{j_1, \dots, j_{n-1}} d_{f j_{n-1}}^n \cdots d_{j_1 i}^1 \frac{1 - \exp[i(T_{n-1 n-1 p} \alpha_{j_{n-1}} + T_{n n-1 p} \alpha_{j_n})]}{T_{n-1 n-1 p} \alpha_{j_{n-1}} + T_{n n-1 p} \alpha_{j_n}} \right. \\ & \quad \left. \times \prod_{l=1}^{n-2} \frac{1 - \exp[i(T_{l l p} \alpha_{j_l} + T_{l+1 p l p} \gamma_{j_l})]}{T_{l l p} \alpha_{j_l} + T_{l+1 p l p} \gamma_{j_l}} \right|^2. \end{aligned} \quad (33)$$

The quantities  $\alpha_{j_l}$  and  $\gamma_{j_l}$  are defined by the relations

$$\begin{aligned} \alpha_{j_1} & = \varepsilon_{j_1} - \varepsilon_i - \omega_1^0, & \alpha_{j_l} & = \varepsilon_{j_l} - \varepsilon_{j_{l-1}} - \omega_j^0, & j & = 2, \dots, n-1, \\ \alpha_{j_n} & = \varepsilon_f - \varepsilon_{j_{n-1}} - \omega_n^0, & \gamma_{j_l} & = \varepsilon_{j_l} - \varepsilon_{j_l} - \sum_{s=l+1}^n \omega_s^0, & j & = 1, \dots, n-2. \end{aligned} \quad (34)$$

The notation is the same as in Sec. II.

Again, entangled  $n$ -photon absorption is linearly proportional to the photon flux density, as can be deduced from the occurrence of the factor  $c/\mathcal{V}$  in Eq. (32) for the square of the normalization constant  $\mathcal{N}_c^2$ . The factor  $c/\mathcal{V}$  determines the photon flux density of the ‘‘reference’’ beam. The absorption cross section  $\sigma_c$  provided in Eq. (33) depends both on the entanglement times characterizing the optical field and on parameters of the target.

A cascade comprising two crystals provides a simplified expression for the absorption cross section  $\sigma_c$ :

$$\beta_{n-1 p} = \frac{T_{n-1 n-1 p} t_n + T_{n-1 p n} t_{n-1}}{T_{n-1 n}}.$$

The normalization constant  $\mathcal{N}_c$  in Eq. (30) must be chosen so that the optical field contains one  $n$ -photon entity. A space-time formulation of the description of the entangled  $n$ -photon state similar to the case discussed in Sec. II gives the result

$$\mathcal{N}_c^2 = \frac{\hbar^n \left( \prod_{j=1}^n \omega_j^0 \right) \left( \prod_{j=1}^{n-2} T_{j \widetilde{j+1} p j} \right) T_{n n-1}}{\varepsilon_0^n \mathcal{V} c^{n-1} \left( \prod_{j=1}^{n-1} A_{ej} \right)}. \quad (32)$$

The symbol  $A_{ej}$  stands for the entanglement area of the photon at  $\omega_j$  with respect to the photon at  $\omega_n$ , which occupies a volume  $\mathcal{V}$ .

$$\begin{aligned} \sigma_c(T_{2\bar{p}1}, T_{22p}, T_{32}) &= 2\pi\delta(\varepsilon_f - \varepsilon_i - \omega_1^0 - \omega_2^0 - \omega_3^0) \frac{\omega_1^0 \omega_2^0 \omega_3^0 T_{2\bar{p}1} T_{32}}{\hbar^3 \epsilon_0^3 A_{e1} A_{e2}} \\ &\times \left| \sum_{j_1, j_2} d_{jj_2}^3 d_{j_2 j_1}^2 d_{j_1 i}^1 \frac{1 - \exp\{i[-T_{22p}(\varepsilon_{j_1} - \varepsilon_i - \omega_1^0) + T_{32}(\varepsilon_f - \varepsilon_{j_2} - \omega_3^0)]\}}{-T_{22p}(\varepsilon_{j_1} - \varepsilon_i - \omega_1^0) + T_{32}(\varepsilon_f - \varepsilon_{j_2} - \omega_3^0)} \right. \\ &\times \left. \frac{1 - \exp[-iT_{2\bar{p}1}(\varepsilon_{j_1} - \varepsilon_i - \omega_1^0)]}{T_{2\bar{p}1}(\varepsilon_{j_1} - \varepsilon_i - \omega_1^0)} \right|^2. \end{aligned} \quad (35)$$

In analogy with Eq. (8) for the absorption cross section of the state generated by  $n$ -photon parametric down-conversion, entanglement-induced transparency occurs. Figure 8 demonstrates this in the three-photon case for the transition  $1s \rightarrow 4f$  in atomic hydrogen. The three entanglement times present in Eq. (35) for  $\sigma_c(T_{2\bar{p}1}, T_{22p}, T_{32})$  contrast with the expression for  $\sigma(T_{21}, T_{32})$  given in Eq. (10), for which only two entanglement times suffice. The absorption cross section  $\sigma_c(T_{2\bar{p}1}, T_{22p}, T_{32})$  in the cascade scheme is thus a more complicated function of the entanglement times. However, this complex dependence may be convenient for extracting information about target parameters.

### C. Effect of path delay

A delay introduced into the path of one photon represents a parameter which can be readily varied in an experiment, and which is useful for extracting information about energies, dipole moments, and quadrupole moments. Introducing a delay  $T$  into the path of the photon at  $\omega_1$ , under the assumption that the second crystal in the cascade is thin so that  $T_{22p} \ll 1/\Delta\omega_{\text{ch}}$  and  $T_{23} \ll 1/\Delta\omega_{\text{ch}}$ , results in an absorption cross section  $\sigma_c(T_{2\bar{p}1}, T)$  of the form

$$\sigma_c(T_{2\bar{p}1}, T) = 2\pi\delta(\varepsilon_f - \varepsilon_i - \omega_1^0 - \omega_2^0 - \omega_3^0) \frac{\omega_1^0 \omega_2^0 \omega_3^0 T_{2\bar{p}1} T_{32}}{\hbar^3 \epsilon_0^3 A_{e1} A_{e2}} \mathcal{B}_c(T_{2\bar{p}1}, T), \quad (36)$$

where

$$\mathcal{B}_c(T_{2\bar{p}1}, T) = \left| \sum_j d_{jj}^1 q_{ji}^{3,2} \frac{1 - \exp[i(\varepsilon_f - \varepsilon_j - \omega_1^0)T]}{(\varepsilon_f - \varepsilon_j - \omega_1^0)T_{2\bar{p}1}} - \sum_j q_{jj}^{3,2} d_{ji}^1 \frac{1 - \exp[i(\varepsilon_j - \varepsilon_i - \omega_1^0)(T - T_{2\bar{p}1})]}{(\varepsilon_j - \varepsilon_i - \omega_1^0)T_{2\bar{p}1}} \right|^2 \quad \text{for } 0 < T < T_{2\bar{p}1}, \quad (37)$$

$$= \left| \sum_j d_{jj}^1 q_{ji}^{3,2} \exp[i(\varepsilon_f - \varepsilon_j - \omega_1^0)T] \frac{1 - \exp[-i(\varepsilon_f - \varepsilon_j - \omega_1^0)T_{2\bar{p}1}]}{(\varepsilon_f - \varepsilon_j - \omega_1^0)T_{2\bar{p}1}} \right|^2 \quad \text{for } T > T_{2\bar{p}1}. \quad (38)$$

The absorption cross section  $\sigma_c(T_{2\bar{p}1}, T)$  in Eq. (36) is identical to that of  $\sigma(T_{31}, T)$  in Eq. (22) for three-photon down-conversion, except that the entanglement time  $T_{2\bar{p}1}$  in Eq. (36) plays the role of the entanglement time  $T_{31}$  in Eq. (22).

Although it is more complex, the cascade scheme can be more flexible. In one example, useful for spectroscopy, a compensation crystal of length  $L_{1z}$  is inserted into the photon paths  $\omega_{2p}$  and  $\omega_1$  between the down-conversion crystals. The expression for the absorption cross section  $\sigma_c(T_{2\bar{p}1}, T)$  is the same as that in Eq. (36); however, the path delay  $T$  in Eqs. (37) and (38) must be replaced by  $T + T_{2\bar{p}1}$ .

### IV. ENTANGLED THREE-PHOTON SPECTROSCOPY

The absorption cross sections for the entangled three-photon state given in Eq. (22), and for the cascade cross section given in Eq. (36), depend naturally on parameters of the material system (energies, dipole moments, and quadrupole moments), as well as on parameters characterizing the optical field (entanglement times, time delay). The latter pa-

rameters can be easily varied in an experimental setting. Measured absorption cross sections as a function of entanglement times and path delays then form a basis for determination of parameter values characterizing the material system (for details about entangled two-photon spectroscopy, see Ref. [25]).

The average of the quantity  $T_{31}\sigma(T_{31}, T)$  over the entanglement time  $T_{31}$ , which can be experimentally measured by using, e.g., a wedge-shaped nonlinear crystal, provides the following result:

$$\begin{aligned} &\langle T_{31}\sigma(T_{31}, T) \rangle_{T_{31}} \\ &= \mathcal{K} \left\{ (A - B)^2 + \sum_j A_j^2 + \sum_{j_1, j_2} B_{j_1} B_{j_2} \exp[i(\varepsilon_{j_1} - \varepsilon_{j_2})T] \right. \\ &\quad \left. + \left[ (A - B) \sum_j B_j \exp[i(\varepsilon_f - \varepsilon_j - \omega_1^0)T] + \text{c.c.} \right] \right\}, \end{aligned} \quad (39)$$

where

$$\begin{aligned}
 A_j &= \frac{q_{jj}^{3,2} d_{ji}^1}{\varepsilon_j - \varepsilon_i - \omega_1^0}, \\
 B_j &= \frac{d_{jj}^1 q_{ji}^{3,2}}{\varepsilon_f - \varepsilon_j - \omega_1^0}, \\
 A &= \sum_j A_j, \\
 B &= \sum_j B_j.
 \end{aligned} \tag{40}$$

The symbol  $\mathcal{K}$  denotes a constant. This quantity reveals the possibility of determining the coefficients  $B_j$  from the decomposition of  $\langle T_{31} \sigma(T_{31}, T) \rangle_{T_{31}}$  as a function of the path delay  $T$  into harmonics. In particular, the spectral component at the frequency  $\varepsilon_f - \varepsilon_j - \omega_1^0$  provides the value of the expression  $(A - B)B_j$ . The value of  $A - B$  can be determined from the value of one spectral component at a given frequency  $\varepsilon_{j_1} - \varepsilon_{j_2}$ . Once we know values of the parameters  $B_j$ , the energies  $\hbar \varepsilon_j$ , and the dipole moments  $d_{jj}^1$ , we can recover values of the quadrupole moments  $q_{ji}^{3,2}$  between the initial state and an arbitrary intermediate state  $j$ . In general, we can determine the entire quadrupole tensor, if we change polarizations of the modes with frequencies  $\omega_2$  and  $\omega_3$ .

The state generated by the cascade scheme using two down-conversion crystals and one compensation crystal is appropriate for determining the values of the quadrupole moments  $q_{jj}^{3,2}$  between an arbitrary intermediate state  $j$  and the final state. In this case,

$$\begin{aligned}
 &\langle T_{2\bar{p}-1}^- \sigma(T_{2\bar{p}-1}^-, T) \rangle_{T_{2\bar{p}-1}^-} \\
 &= \mathcal{K}_c \left\{ (A - B)^2 + \sum_j B_j^2 + \sum_{j_1, j_2} A_{j_1} A_{j_2} \exp[i(\varepsilon_{j_1} - \varepsilon_{j_2})T] \right. \\
 &\quad \left. - \left[ (A - B) \sum_j A_j \exp[-i(\varepsilon_j - \varepsilon_i - \omega_1^0)T] + \text{c.c.} \right] \right\}.
 \end{aligned} \tag{41}$$

The symbols  $A_j$ ,  $B_j$ ,  $A$ , and  $B$  were defined in Eq. (40), and  $\mathcal{K}_c$  is a constant. It is useful to note that the energies and dipole moments of a material can be obtained from entangled two-photon spectroscopy (for details, see Ref. [25]).

The use of pulsed light for similar considerations as above is subject to limitations because of the difficulty associated with extracting the contribution of the process described in Eq. (15) from the entire absorption. In general, there are also contributions from other multiphoton processes for such classical light, such as those in which more than one annihilated photon arises from one of the pulses while photons from one or more of the other pulse(s) do not contribute to the absorption. In the case of two-photon absorption and orthogonal dipole moments for the transitions  $i \rightarrow j$  and  $j \rightarrow f$ , orthogonally polarized pulsed beams provide a possible solution.

## V. EFFECTS COMPETITIVE WITH ENTANGLED THREE-PHOTON ABSORPTION

If the photon-flux density of entangled  $n$ -photon entities is large, there are competitive processes of nonentangled three-photon absorption (each photon from a separate entity) and of doubly entangled three-photon absorption (two photons from one entity, the third one from another entity). These processes are dependent on the third and second powers of the photon-flux density, respectively. A linear dependence of entangled  $n$ -photon absorption on the photon-flux density thus enables us to distinguish the contributions of these processes. The photon-flux density ( $I$ ) dependence of the absorption  $a$  thus takes the form

$$a(I) = \delta_1 I + \delta_2 I^2 + \delta_3 I^3, \tag{42}$$

where  $\delta_1$  is the entangled three-photon absorption cross section,  $\delta_2$  is the doubly entangled three-photon absorption cross section, and  $\delta_3$  is the nonentangled three-photon absorption cross section.

These cross sections can be determined quantum mechanically. But it is sufficient to restrict ourselves to a simple probabilistic model in order to determine at which photon-flux densities the processes proportional to the second and third powers of the photon-flux density begin to dominate.

We assume that a single photon has the absorption cross section  $\sigma_s$  and that there is a typical relaxation time  $\tau$  in the material. We further assume that  $\tau \ll T_e$  and  $\sigma_s \ll A_e$ , where  $T_e$  is a typical entanglement time of the photons, and  $A_e$  is a typical entanglement area. Strictly speaking, the assumption  $\tau \ll T_e$  is not compatible with the quantum model developed above in which relaxation in the material is not included. But in spite of this, the probabilistic model is useful for providing an estimate of the values of photon-flux densities at which entangled three-photon absorption prevails.

Simple probabilistic considerations lead to an entangled three-photon absorption cross section  $\delta_1$  of the form

$$\delta_1 = \frac{\sigma_s^3 \tau^2}{T_e^2 A_e^2}. \tag{43}$$

The absorption cross section  $\delta_2$  for the doubly entangled three-photon absorption becomes

$$\delta_2 \approx \frac{9 \sigma_s^3 \tau^2}{T_e A_e}, \tag{44}$$

whereas the nonentangled three-photon absorption is characterized by

$$\delta_3 \approx 27 \sigma_s^3 \tau^2. \tag{45}$$

If we compare the contributions from these various processes, we conclude that the process of entangled three-photon absorption prevails at lower photon-flux densities obeying the inequality

$$I < I_{th} \approx \frac{1}{9 A_e T_e}. \tag{46}$$

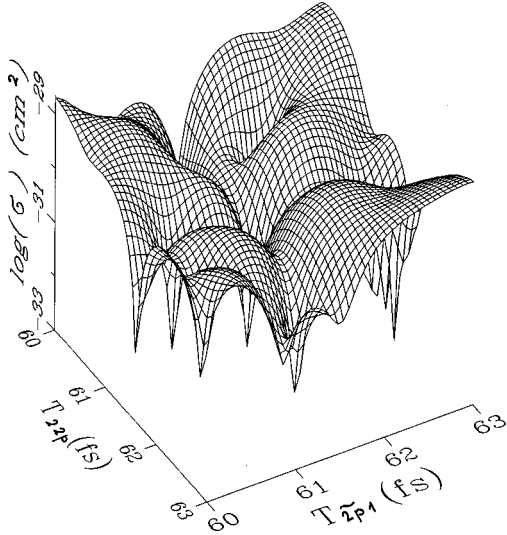


FIG. 8. Entangled three-photon absorption cross section  $\sigma(T_{2p}, T_{2p1})$  for the transition  $1s \rightarrow 4f$  in atomic hydrogen for the state generated by a cascade of two nonlinear crystals;  $\hbar\omega_1^0 = 8.92$  eV,  $\hbar\omega_2^0 = \hbar\omega_3^0 = 1.91$  eV,  $T_{32} = 50$  fs, and  $A_{e1} = A_{e2} = 10^{-10}$  m<sup>2</sup>; log denotes a decadic logarithm.

## VI. CONCLUSION

We have studied the properties of entangled  $n$ -photon states generated both by the process of  $n$ -photon parametric down-conversion and in a cascade of  $n - 1$  crystals with two-photon parametric down-conversion processes. In particular, we have found that absorption of light in such nonclassical states is proportional to the first power of the photon-flux density. We have determined the absorption cross section for light in entangled  $n$ -photon states. It depends on entanglement times of the photon field, and on parameters describing the material. Entanglement-induced transparency can arise.

Introduction of an additional delay into the path of one photon reveals the possibility of resonance enhancement of absorption. The absorption cross section as a function of entanglement time and path delay decomposes naturally into two regions according to the possibility of the simultaneous arrival of all three photons.

Dependence of the entangled three-photon absorption cross section on entanglement times and path delay enables us to determine values of material parameters. In particular, it has been shown that values of quadrupole moments between states can be extracted from the measured absorption cross sections. A probabilistic model has been used in which the effect of nonclassical entangled three-photon absorption dominates over other field-matter processes at lower intensities, enabling us to obtain an estimate for the threshold value of the photon-flux density.

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## APPENDIX A: DERIVATION OF ENTANGLED STATE AND MULTIPHOTON ABSORPTION CROSS SECTION

We consider a down-conversion crystal with  $\chi^{(n)}$  nonlinearity, pumped by a strong coherent field of amplitude  $\xi_p$ . Modes constituting the down-converted beams are taken to be in vacuum states at the onset of the nonlinear interaction (at the input plane of the crystal); thus the initial state of the field is the multimode vacuum state ( $|\psi_{\text{input}}\rangle = |\text{vac}\rangle$ ). Second-order time-dependent perturbation theory in the interaction picture provides an expression for the state  $|\psi_{\text{output}}\rangle$  of the down-converted beams at the output plane of the crystal:

$$|\psi_{\text{output}}\rangle = -\frac{i}{\hbar} \int_0^{t_I} dt' \hat{H}_{\text{int}}(t') |\psi_{\text{input}}\rangle. \quad (\text{A1})$$

The quantity  $t_I$  represents the interaction time (given by the length of the crystal), and the interaction Hamiltonian  $\hat{H}_{\text{int}}(t)$  is defined in Eq. (1).

Equation (A1), together with free-field evolution from the output plane of the crystal, leads to the expression for the entangled  $n$ -photon state provided in Eq. (2). The derivation of Eq. (2) has also assumed that the susceptibility  $\chi^{(n)}$  is frequency independent, that the phase-matching condition for the transverse components of the wave vectors is fulfilled, and that the crystal extends from  $z = -L_z$  to  $z = 0$  [15].

The matrix element  $\langle \text{vac} | \prod_{j=1}^n \hat{E}_j^{(+)}(t_j) | \psi^{(n)}(0,0) \rangle$ , appropriate for the state given in Eq. (2), reads

$$\begin{aligned} & \langle \text{vac} | \prod_{j=1}^n \hat{E}_j^{(+)}(t_j) | \psi^{(n)}(0,0) \rangle \\ &= \mathcal{C}_1 \sum_{k_1} \cdots \sum_{k_n} t_I \exp\left(-i \frac{\Delta\omega t_I}{2}\right) \text{sinc}\left(\frac{\Delta\omega t_I}{2}\right) \\ & \quad \times \exp\left(-i \frac{(\Delta\mathbf{k})_z L_z}{2}\right) \text{sinc}\left(\frac{(\Delta\mathbf{k})_z L_z}{2}\right) \\ & \quad \times \exp\left(-i \sum_{j=1}^n \omega_j t_j\right), \end{aligned} \quad (\text{A2})$$

where  $\hat{E}_j^{(+)}(t_j) \approx \sum_k \hat{a}_k \exp(-i\omega_j t_j)$ , and  $\mathcal{C}_1$  denotes a normalization constant.

We account for first-order dispersion in  $\mathbf{k}_{jz}(\omega_j)$  [i.e.,  $\mathbf{k}_{jz}(\omega_j) = \mathbf{k}_{jz}^0 + 1/v_j(\omega_j - \omega_j^0)$ , and  $1/v_j = d\mathbf{k}_{jz}/d\omega_j|_{\omega_j = \omega_j^0}$ , where  $\mathbf{k}_j^0$  is the central wave vector,  $\omega_j^0$  is the central frequency, and  $v_j$  is the group velocity of the  $j$ th mode] and phase-matching conditions for the central wave vectors ( $\sum_{j=1}^n \mathbf{k}_{jz}^0 = \mathbf{k}_{pz}^0$ ) and central frequencies ( $\sum_{j=1}^n \omega_j^0 = \omega_p$ ). Replacing the summations  $\sum_{k_1} \cdots \sum_{k_n}$  by integrations  $\int d\omega_1 \cdots \int d\omega_n$  in Eq. (A2) then provides

$$\begin{aligned}
& \langle \text{vac} | \prod_{j=1}^n \hat{E}_j^{(+)}(t_j) | \psi^{(n)}(0,0) \rangle \\
& = C_2 \exp\left(-i \sum_{j=1}^n \omega_j^0 t_j\right) \int d\nu_1 \cdots \int d\nu_n t_l \\
& \quad \times \exp\left(-i \frac{\sum_{j=1}^n \nu_j t_l}{2}\right) \text{sinc}\left(\frac{\sum_{j=1}^n \nu_j t_l}{2}\right) \\
& \quad \times \exp\left(-i \sum_{j=1}^n \frac{\nu_j L_z}{2\nu_j}\right) \text{sinc}\left(\sum_{j=1}^n \frac{\nu_j L_z}{2\nu_j}\right) \\
& \quad \times \exp\left(-i \sum_{j=1}^n \nu_j t_j\right), \tag{A3}
\end{aligned}$$

where  $C_2$  is a normalization constant and  $\nu_j = \omega_j - \omega_j^0$ . Straightforward integration, together with the relation  $t_l \text{sinc}(\omega t_l) \rightarrow 2\pi \delta(\omega)$  for  $t_l \rightarrow \infty$  (for details, see Ref. [15]), finally provides the expression given in Eq. (3).

Now we derive the expression for the entangled  $n$ -photon absorption cross section. Interaction of the field with a target is assumed to be described in the interaction representation by an interaction Hamiltonian of the form

$$\hat{H}_{\text{int}}(t) = \hat{d}(t) \hat{E}^{(+)}(t) + \text{H.c.}, \tag{A4}$$

where  $\hat{d}(t)$  is the dipole-moment operator of an electron in the target. The positive-frequency part of the electric-field operator  $\hat{E}^{(+)}(t)$  is given by

$$\hat{E}^{(+)}(t) = \sum_{j=1}^n \hat{E}_j^{(+)}(t), \tag{A5}$$

where  $\hat{E}_j^{(+)}(t)$  denote operators appropriate for the photons centered around  $\omega_j^0$ .

The probability  $p_{f \leftarrow i}$  that an electron in the target makes a transition from the initial state  $|i\rangle$  to the final state  $|f\rangle$  through  $n$ -photon absorption is provided by  $n$ th-order time-dependent perturbation theory

$$\begin{aligned}
p_{f \leftarrow i} & = \left| \frac{1}{\hbar^n} \int_{-\infty}^{\infty} dt_n \int_{-\infty}^{t_n} dt_{n-1} \cdots \int_{-\infty}^{t_2} dt_1 \right. \\
& \quad \times \langle f | \hat{d}(t_n) \cdots \hat{d}(t_1) | i \rangle \\
& \quad \left. \times \langle \phi_f | \hat{E}^{(+)}(t_n) \cdots \hat{E}^{(+)}(t_1) | \phi_i \rangle \right|^2, \tag{A6}
\end{aligned}$$

where  $|\phi_i\rangle$  ( $|\phi_f\rangle$ ) denotes the initial (final) state of the optical field.

For the entangled  $n$ -photon state [see Eq. (3)], under the condition  $T_{21} < T_{31} < \cdots < T_{n1}$  discussed in Sec. II B, the photon field described by  $\hat{E}_1^{(+)}(t)$  interacts first, and that described by  $\hat{E}_2^{(+)}(t)$  interacts second, etc. Equation (A6) then simplifies to

$$\begin{aligned}
p_{f \leftarrow i} & = \left| \frac{1}{\hbar^n} \int_{-\infty}^{\infty} dt_n \int_{-\infty}^{t_n} dt_{n-1} \cdots \int_{-\infty}^{t_2} dt_1 \right. \\
& \quad \times \langle f | \hat{d}(t_n) \cdots \hat{d}(t_1) | i \rangle \\
& \quad \left. \times \langle \text{vac} | \hat{E}_n^{(+)}(t_n) \cdots \hat{E}_1^{(+)}(t_1) | \psi^{(n)}(0,0) \rangle \right|^2. \tag{A7}
\end{aligned}$$

The expression for the absorption cross section  $\sigma(T_{21}, T_{31}, \dots, T_{n1})$  given in Eq. (8) is obtained in a straightforward manner from Eqs. (3), (7), and (A7).

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