Generation of pseudo-sunlight via quantum entangled photons and the interaction with molecules

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Light incident upon molecules trigger fundamental processes in diverse systems present in nature. However, under natural conditions, such as sunlight illumination, it is impossible to assign known times for photon arrival owing to continuous pumping, and therefore, the photo-induced processes cannot be easily investigated. In this manner, time-resolved laser spectroscopy has provided detailed information and deeper insights into microscopic dynamics in a constructively interferential fashion. In this work, we theoretically demonstrate that the nature of sunlight photons can be emulated through quantum entangled photon pairs generated with the parametric down-conversion (PDC). We show that the average photon number of the sunlight in a specific frequency spectrum, e.g., the visible light, can be reconstructed by adjusting the PDC crystal length and pump frequency, and thereby molecular dynamics induced by the pseudo-sunlight can be investigated. The entanglement time, which is the hallmark of quantum entangled photons, can serve as a control knob to resolve the photon arrival times under the pseudo-sunlight irradiation, enabling investigations on real-time dynamics triggered by the pseudo-sunlight photons.

I. INTRODUCTION

Giant strides in ultrashort laser pulse technology have opened up real-time observation of dynamical processes in complex physical, chemical, and biological systems. Under natural conditions, such as sunlight illumination, known times cannot be assigned for photon arrival owing to continuous pumping, and thus, photo-induced dynamical processes cannot be easily investigated. In time-resolved optical spectroscopy, however, investigations on dynamical processes can be conducted by synchronizing the initial excitations in the entire ensemble with the use of ultrashort pulsed laser and thereby amplifying the microscopic dynamics in a constructively interferential fashion. In this manner, time-resolved laser spectroscopy has provided detailed information and deeper insights into microscopic processes in complex molecular systems. Nevertheless, the relevance of the laser spectroscopic data regarding photosynthetic proteins was challenged and whether dynamics initiated by sunlight irradiation might be different from those detected with laser spectroscopy is still being debated [1–8]. Although it is not unexpected that spectroscopic measurements do not demonstrate phenomena under sunlight illumination in the one-to-one correspondence, the debate inspired us to comprehend the occurrence of photoexcitation under natural irradiation.

Sunlight is considered as the radiation from the black-body with an effective temperature of approximately 5800 K, and thus, the coherence time is extremely short (1.3 fs) [9]. Furthermore, the photon number statistics obeys the Bose–Einstein distribution, whereas the coherent laser is characterized by the Poisson photon number statistics [10]. A variety of schemes have been proposed to generate pseudo-thermal light, e.g., the solar simulator with Xenon arc lamp and scattered laser beam from a rotating ground-glass disc [11]. However, the schemes do not provide knobs to control light on an ultrafast timescale approximate to a few femtoseconds, which is relevant for energy/charge transfer during the primary steps of photosynthesis and isomerization reaction in the first steps of vision. Therefore, a scheme to control thermal light on an ultrashort timescale to unveil how photoexcitation by natural light and the subseqent dynamics proceed should be developed.

In this work, we address quantum entangled photon pairs generated through the parametric down-conversion (PDC) in birefringent crystals [10], where a pump photon is split into two entangled photons, signal and idler photons. The two photons exhibit continuous frequency entanglement stemming from the conservation of energy and momentum. Consequently, the quantum state of the one photon in the entangled pair is a mixed state, when the other is discarded without being measured. In particular, the photon number statistics obeys the geometric distribution rather than the Poisson distribution [12–14], and therefore, the entangled photon pairs are expected to reproduce characteristics of the sunlight photons. Furthermore, it becomes possible to investigate sunlight-induced dynamical processes in molecular systems with quantitative underpinnings, because expressions of quantum states of the pseudo-sunlight photons can be theoretically obtained.

II. FREQUENCY-ENTANGLED PHOTONS

We consider the PDC process, where a pump photon with frequency ωp is split into signal and idler photons with frequencies ω1 and ω2 such that ωp = ω1 + ω2. Electric fields inside a one-dimensional nonlinear crystal are considered and the time-ordering effect during the PDC process is neglected. This approximation is relevant in describing the PDC in the low-gain regime [15], and the state vector of the generated photons is obtained as |ψPDC⟩ = exp(−iH_{PDC}/ℏ)|vac⟩ with [16]

\[ \hat{H}_{PDC} = \int d\omega_1 \int d\omega_2 f(\omega_1, \omega_2) \hat{a}^\dagger_1(\omega_1) \hat{a}^\dagger_2(\omega_2) + \text{h.c.}, \]

where \( \hat{a}^\dagger_1(\omega) \) and \( \hat{a}^\dagger_2(\omega) \) denote the creation operators of the signal and idler photons, respectively. The two-photon amplitude \( f(\omega_1, \omega_2) \) is expressed as

\[ f(\omega_1, \omega_2) = \hbar B \alpha_\rho(\omega_1 + \omega_2) \Phi(\omega_1, \omega_2), \]

where \( \alpha_\rho(\omega) \) represents the pump envelope function that is normalized as \( \int d\omega \alpha_\rho(\omega) = 1 \). In Eq. (1), \( \Phi(\omega_1, \omega_2) = \text{sinc}[\Delta k(\omega_1, \omega_2)L/2] \) is referred to as the phase-matching function: \( L \) is the crystal length and \( \Delta k(\omega_1, \omega_2) \) represents the
phase mismatch $\Delta k(\omega_1, \omega_2) = k_0(\omega_1 + \omega_2) - k_0(\omega_1) - k_0(\omega_2)$ with $k_0(\omega)$ being the wave vector with frequency $\omega$. All constants such as the second-order susceptibility of the crystal, crystal length, and pump intensity are merged into the overall factor $B$, which corresponds to the conversion efficiency of the PDC process \[16\]. Typically, $\Delta k(\omega_1, \omega_2)$ depends weakly on the frequencies $\omega_1$ and $\omega_2$; hence, $\Delta k(\omega_1, \omega_2)$ may be approximated linearly around the central frequencies of the two generated beams, $\tilde{\omega}_s$ and $\tilde{\omega}_i$ as $\Delta k(\omega_1, \omega_2)L = (\omega_1 - \tilde{\omega}_s)T_s + (\omega_2 - \tilde{\omega}_i)T_i$ with $T_s = L(v_s^{-1} - v_p^{-1})$ \[16, 17\]. In the equation, $v_r$ is the group velocity of a generated beam at frequency $\tilde{\omega}_r$, whereas $v_p$ is the group velocity of the pump laser. Without loss of generality, the relation $T_s > T_i$ can be assumed \[18\]. The difference $T_s - T_i$ is termed the entanglement time \[19, 20\], which represents the maximal time delay between the arrival of the two entangled photons.

For CW pumping, Eq. (1) is written as $f(\omega_1, \omega_2) = h\delta(\omega_1 + \omega_2 - \omega_p) r(\omega_1)$ with $r(\omega) = B \Phi(\omega, \omega_p - \omega) = B \sin[(\omega - \omega_0)T_p/2]$. Therefore, the propagator is recast into $\exp(-i \tilde{\omega}_{\text{PDC}}/h) = \exp \int \omega \, d\omega \hat{a}_s^{\dagger}(\omega) \hat{a}_i(\omega_p - \omega) - \text{h.c.}$, and the output photon state is obtained as the two-mode squeezed vacuum state \[14\],

$$|\psi_{\text{PDC}}\rangle = \prod_{\omega} \sum_{n_{\omega}=0}^{\infty} \frac{\left[\tanh r(\omega)\right]^{n_{\omega}}}{\cosh r(\omega)} |n_{\omega}\rangle_s |n_{\omega_p-\omega}\rangle_i,$$

where $|n_{\omega}\rangle_s$ is the Fock state of the photon $\sigma$ with frequency $\omega$. When the idler photon is discarded without being measured, the quantum state of the signal photon is mixed \[12–14\]. This situation is described by tracing out the idler photon’s degrees of freedom such that $\tilde{\rho}_s = Tr_l(|\psi_{\text{PDC}}\rangle \langle \psi_{\text{PDC}}|)$. Consequently, the reduced density operator of the signal photon reads $\tilde{\rho}_s = \prod_{\omega} \sum_{n_{\omega}=0}^{\infty} P_{\omega}(n_{\omega}) |n_{\omega}\rangle_s \langle n_{\omega}|$, where $P_{\omega}(n)$ represents the probability that there are $n$ photons of frequency $\omega$ in the signal photon beam, $P_{\omega}(n) = (1 - \zeta(\omega)/\zeta(\omega))^{n}$ with $\zeta(\omega) = \tanh^{2} r(\omega)$. The density operator is also expressed as $\tilde{\rho}_s = Z^{-1} \exp[- \int d\omega \ln(\zeta(\omega) \hat{a}_s^{\dagger}(\omega) \hat{a}_s(\omega))]$ with $Z$ being the partition function \[21\]. Therefore, the quantum state $\tilde{\rho}_s$ is regarded as the pseudo-thermal state in the sense that the photon-number statistics obey the geometric distribution, and the average photon number is computed as a function of $\omega$,

$$\langle \hat{n}(\omega) \rangle = \sum_{n=0}^{\infty} n P_{\omega}(n) = \frac{\zeta(\omega)}{1 - \zeta(\omega)} = \sinh^2 r(\omega).$$

Specically, when $\zeta(\omega)$ can be approximately expressed as $\zeta(\omega) \approx (1 - \omega/\omega_0) \exp(-\omega/\omega_0)$, the expression of $\langle \hat{n}(\omega) \rangle$ becomes identical to that of the thermal radiation from a black-body with temperature $T$, where $k_B$ denotes the Boltzmann constant.

Figure 1 presents the average photon number in the signal beam generated through PDC with CW pumping. The parameters employed for the calculation are given in the figure caption. These values are realizable through the use of birefringent crystals such as $\beta$-BaB$_2$O$_4$ \[18, 22\] and BiB$_3$O$_6$ \[23\]. For comparison, the thermal distribution, $\tilde{\rho}_{\text{th}}(\omega) = (e^{\omega/\omega_0} - 1)^{-1}$, at temperature $T = 5777$ K is also shown. As presented in Fig. 1, Eq. (3) is capable of reproducing the average photon number of the thermal light in a specific frequency region, such as the visible light, by adjusting the crystal length $L$ and pump frequency $\omega_p$, although the whole frequency range cannot be reconstructed. It is noteworthy that the photon number in the visible region is substantially 0 or 1, and thus, the average number is well approximated by

$$\langle \hat{n}(\omega) \rangle \approx \sum_{n=0}^{1} n P_{\omega}(n) = P_{\omega}(1) \approx \tanh^2 r(\omega).$$

This insight and the appearance of $\tanh r(\omega)$ will be critical in later discussions on the heralded signal photons.

III. INTERACTION OF PSEUDO-THERMAL LIGHT WITH MOLECULES

Theoretical expressions of quantum states of the pseudo-thermal photons enable one to investigate sunlight-induced...
molecular dynamical processes with quantitative underpinnings. Here, we discuss the electronic excitation of a molecule using pseudo-thermal light. The molecule is modeled by the electronic ground state \(|g⟩\) and electronic excited states \(|e_1⟩, |e_2⟩, \ldots\), and the Hamiltonian is given by

\[
\hat{H}_{\text{mol}} = \epsilon_g |g⟩⟨g| + \sum_{\alpha} \epsilon_\alpha |e_\alpha⟩⟨e_\alpha|.
\]

The states \(|e_\alpha⟩\) correspond to electronic excitons in the single-excitation manifold of a molecular aggregate. The optical transitions between \(|g⟩\) and \(|e_\alpha⟩\) are described by the operator \(\hat{\mu} = \sum_\alpha \mu_\alpha |e_\alpha⟩⟨g| + |g⟩⟨e_\alpha|\), where \(\mu_\alpha\) stands for the transition dipole. In general, environment-induced fluctuations in electronic energy strongly influence the excited-state dynamics in condensed phases. However, in this study we ignored the environmental degrees of freedom because the main concern here is to investigate the characteristics of pseudo-thermal light irradiation, which is qualitatively independent of the effects of the environment. For simplicity, radiative and nonradiative decays to the ground state are also neglected.

The following setup is considered: The signal and idler beams generated through PDC are split. Only signal photons interact with molecules, and idler photons propagate freely. Therefore, the total molecule-field Hamiltonian can be written as \(\hat{H}_{\text{total}} = \hat{H}_{\text{mol}} + \hat{H}_{\text{field}} + \hat{H}_{\text{int}}\). The second term in this equation, \(\hat{H}_{\text{field}}\), is the free Hamiltonian of the signal and idler photons, and the molecule-field interaction is described by \(\hat{H}_{\text{int}}\). Owing to the weak field-matter interaction, the first-order perturbative truncation in terms of \(\hat{H}_{\text{int}}\) provides a reasonable description of the electronic excitation generated under thermal light irradiation. Thus, the state vector to describe the molecular excitation together with signal and idler photons is obtained as \(|\psi_{\text{total}}(t)⟩ = (i/\hbar) \sum_\alpha \mu_\alpha \int_{-\infty}^{t} d\tau_1 e^{-i\omega_\alpha(t-\tau_1)} \hat{E}_\alpha(\tau_1)|e_\alpha⟩|\psi_{\text{PDC}}⟩\), where \(\omega_\alpha = (\epsilon_\alpha - \epsilon_\beta)/\hbar\) has been introduced. In the equation, the field operator of the signal photon \(\hat{E}_\alpha(\tau)\) can be divided into positive- and negative-frequency components, \(\hat{E}_\alpha^+(\tau) = \int d\omega \hat{a}_\omega |\hat{E}_\alpha(\omega) e^{-i\omega\tau}\) and \(\hat{E}_\alpha^-(\tau) = [\hat{E}_\alpha^+(\tau)]^\dagger\), respectively, where \(A(\omega) \propto \sqrt{\omega}\) \cite{24}. The negative-frequency component causes the rapidly oscillating term in the integrand; hence, the contribution to the electronic excitation is negligibly small. Therefore, \(\hat{E}_\alpha(\tau_1)\) can be replaced with the positive-frequency component. This rotating wave approximation is of no consequence in cases of weak field-matter interaction \cite{6, 20}, but it breaks down in the strong interaction regime \cite{25}.

When the quantum states of idler photons are not measured, the reduced density operator to describe the electronic excitation is obtained by tracing over the fields’ degrees of freedom, \(\rho_{\text{id}}(t) = \text{Tr}_{\text{id}}[|\psi_{\text{total}}(t)⟩⟨\psi_{\text{total}}(t)|]\), as such:

\[
\rho_{\text{id}}(t) = \sum_{\alpha, \beta} \mu_\alpha^\ast \mu_\beta \frac{\hbar}{\omega_\beta} e^{-i\omega_\beta t} \int_{-\infty}^{t} d\tau_2 e^{-i\omega_\beta \tau_2} \times \int_{-\infty}^{t} d\tau_1 e^{i\omega_\beta \tau_1} G_s^{(1)}(\tau_2, \tau_1) |e_\alpha⟩⟨e_\beta|,
\]

where the first-order temporal correlation function of only signal photons \(G_s^{(1)}(\tau_2, \tau_1) = \langle \hat{E}_\alpha(\tau_2)^\dagger \hat{E}_\alpha(\tau_1) \rangle\) has been introduced. In the CW pumping case, the function is expressed as \(G_s^{(1)}(\tau_2, \tau_1) = \int_{0}^{\infty} d\omega e^{i\omega(\tau_2-\tau_1)} \tilde{n}(\omega)^2\), where \(\tilde{n}(\omega)\) is the average photon number shown in Fig. 4.

By replacing \(\tilde{n}(\omega)\) with the average photon number for thermal light \(\tilde{n}_\text{th}(\omega) = (e^{\hbar\omega/kT} - 1)^{-1}\), Eq. \(5\) becomes practically identical to the expression for the density operator under the influence of the real sunlight photons [7]. Figure 2 demonstrates the time evolution of the matrix elements of the density operator under the illumination of the PDC signal photon and thermal light at 5777 K. The molecular electronic states can only interact with the light at time \(t \geq 0\). In the calculations, the average photon number shown in Fig. 1 was employed, and the electronic transition energies were set to \(\omega_{1g} = 18000 \text{ cm}^{-1}\) and \(\omega_{2g} = 18500 \text{ cm}^{-1}\) with \(\mu_{1g} = \mu_{2g}\). Because it is impossible to resolve the time at which the signal photon interacts with the molecule, it is considered that the signal photon interacts with the molecule at a uniformly random time. Consequently, the probability of observing the electronically excited molecule, \(\rho_{11}(t) = \langle e_1|\rho_{\text{total}}(t)|e_1⟩\), increases linearly with time. The same holds for the thermal light case, and therefore, the dynamics of the density matrix elements calculated for the two cases exhibit reasonably good agreement. It should be noted that the probability does not continue to mount in the long-time limit when the radiative and nonradiative decays to the ground state are considered. As demonstrated in Fig. 2, therefore, excited state dynamics induced by signal photons generated through PDC can be regarded as an emulation of the dynamics under the influence of sunlight irradiation, provided that \(\tilde{n}(\omega)\) reconstructs the spectrum of sunlight photons in a frequency range under investigation, such as the visible frequencies.

IV. DETECTION OF IDLER PHOTONS

In the previous section, we discussed pseudo-thermal light effect emulation by signal photons without detecting idler photons. However, more useful application of the PDC source can be made possible through detection of idler photons. Accordingly, spectroscopic and imaging techniques with entangled photon pairs have been proposed on the basis of coincidence counting \cite{22, 26–31}. When the quantum states of both signal and idler photons are measured, characteristic features of quantum lights, such as entanglement time, can provide novel and useful control knobs to supplement classical parameters such as frequency and time delay. In the following sections, we investigate the excited state dynamics triggered by interaction of molecules with signal photons when idler photons are detected.

The optical length between the detector for idler photons and the PDC crystal is set to be the same as the length between the crystal and the sample into which signal photons enter. The photon detection that resolves the arrival time \(t = t_i\) of the idler photons is modeled with the projection operator: \(\hat{\Pi}_i(t) = \hat{a}_i^\dagger(t_i)|\text{vac}\rangle⟨\text{vac}|\hat{a}_i(t_i)\), where \(\hat{a}_i(t) = \int d\omega \hat{a}_i(\omega)e^{-i\omega t}\) has been introduced \cite{32}. The spectral information on the idler photon is not obtained. Consequently, the quantum state of the signal photon is a mixed
state in terms of frequency, although the signal photon number is identified as unity. The frequency distribution is given by $\mathcal{D}(\omega) \propto P_\omega(1) \approx \tanh^2 r(\omega)$. In the CW pumping case, the first photon arrives at a uniformly random time [32] and the second photon certainly arrives within the entanglement time $T_e$. Thus, the probability of detecting a photon in the idler beam is time-independent: $P_i = |\langle r_{PDC}|\hat{\Pi}_i(t)|\rangle_{PDC} = Z^{-1}\int d\omega \tanh^2 r(\omega)$. When the idler photon is detected at time $t_i$, the density operator of the electronic excitation is given by $\hat{\rho}_e(t; t_i) = (1/P_i)\mathcal{T}_{r_{PDC}}[\hat{\Pi}_i(t)|\psi_{\text{total}}(t)\rangle \langle \psi_{\text{total}}(t)|]$, leading to an expression different from Eq. (5): 

$$\hat{\rho}_e(t; t_i) = \sum_{\alpha, \beta} \frac{\mu_{\alpha \beta}}{\hbar^2} e^{-i\omega_{\alpha \beta} t} \int_{-\infty}^t dt_2 e^{-i\omega_{\alpha \beta} t_2} \times \int_{-\infty}^t dt_1 e^{i\omega_{\alpha \beta} t_1} G^{(1)}(t_2, t_1; t_2, t_1) |\alpha\rangle \langle \alpha| |\beta\rangle \langle \beta|,$$

where $G^{(1)}_e(t_2, t_1; t_2, t_1) = \langle \hat{E}^{(1)}_e(t_2) \hat{E}^{(1)}_e(t_1) \rangle_{\hat{\Pi}_i(t)}$ is the first-order temporal correlation function of the heralded signal photon. The bracket represents $\langle \ldots \rangle_{\hat{\Pi}_i(t)} = T_{r_{PDC}}[\hat{\Pi}_i(t)|\psi_{\text{total}}(t)\rangle \langle \psi_{\text{total}}(t)|]$, where $\hat{\rho}_i(t)$ is the reduced density operator of the heralded signal photon given by $\hat{\rho}_i(t) = P^{-1}_{\Pi_i}T_{r_{PDC}}[\hat{\Pi}_i(t)|\psi_{\text{total}}(t)\rangle \langle \psi_{\text{total}}(t)|]$. A concrete expression of the correlation function is obtained as 

$$G^{(1)}_e(t_2, t_1; t_i) = [G^{(1)}(t_2; t_i)]^\dagger \mathcal{E}^{(1)}(t_i),$$

where the following quantity has been introduced:

$$\mathcal{E}^{(1)}(t_i) = \frac{1}{\sqrt{\tau_3}} \int_0^{\infty} d\omega e^{-i\omega(t_i-t)} A(\omega) \tanh(\omega).$$

Equation (9) could be regarded as the “electric field” that will interact with the molecule. Figure 3 presents the time evolution of the density matrix elements under the condition that the idler photon is detected at time $t = t_i$ for two values of the entanglement time, (a) $T_e = 2.5 \text{ fs}$ and (b) $T_e = 50 \text{ fs}$. The parameters chosen for Fig. 3a are the same as in Fig. 2, while the parameters employed in Fig. 3b are $\bar{\omega}_s = 18001 \text{ cm}^{-1}$ and $B = 0.11$. In contrast to the case in Fig. 2, the detection of the idler photon enables us to assign the time at which the signal photon interacts with the molecule. Thus, the probability of observing the electronically excited molecule, $\rho_{11}(t; t_i) = \langle e_1|\hat{\rho}_e(t; t_i)|e_1\rangle$, exhibits the plateau values 0 and 1. However, the rise time from 0 to 1 depends on values of the entanglement time. This can be understood through the following approximative treatment of the “electric field.” From Eq. (3), the PDC for generating pseudo-thermal light reproducing the weak intensity of sunlight corresponds to the weak down-conversion regime, $r(\omega) \ll 1$. In this limit, the approximation of $\tanh(\omega) \approx r(\omega) = B \text{sinc}[(\omega - \bar{\omega}_s)\tau_3]$, is relevant and Eq. (9) is recast as 

$$\mathcal{E}^{(1)}(t_i) \propto A(\bar{\omega}_s) \frac{2\pi}{\tau_3} \text{rect} \left( \frac{t_i - \bar{\omega}_s}{\tau_3} \right) e^{-i\bar{\omega}_s(t_i-t)},$$

where $\text{rect}(x) = 1$ for $|x| < 1/2$ and 0 otherwise. While deriving Eq. (10), the approximation of $A(\omega)r(\omega) \approx A(\bar{\omega})r(\omega)$ is employed, where $A(\omega) \propto \sqrt{\omega}$. This does not cause a fatal defect for the parameters employed in Fig. 3. Equation (10) demonstrates that the signal photon certainly arrives at the molecular sample within the entanglement time $T_e$ before or after the idler photon is detected at time $t_i$. For $t \geq t_i + \tau_3/2$, the density operator in Eq. (7) is obtained as $\hat{\rho}_e(t; t_i) \sim \sum_{\alpha, \beta} \mu_{\alpha \beta} \mu_{\beta \gamma} \text{sinc}[(\omega_{\alpha \beta} - \bar{\omega}_s)\tau_3/2] \text{sinc}[(\omega_{\beta \gamma} - \bar{\omega}_s)\tau_3/2] e^{-i\omega_{\alpha \beta}(t_i-t)}|\alpha\rangle \langle \alpha| |\beta\rangle \langle \beta|$. When the entanglement time $T_e$ is extremely short, Eq. (10) can be approximated as 

$$\mathcal{E}^{(1)}(t_i) \propto \delta(t_i - t_i).$$

In this “impulsive” limit, the time evolution of the density operator of the electronic excitation, Eq. (7), reduces to $\hat{\rho}_e(t; t_i) \sim \sum_{\alpha, \beta} \mu_{\alpha \beta} \mu_{\beta \gamma} e^{-i\omega_{\alpha \beta}(t_i-t)} |\alpha\rangle \langle \alpha| |\beta\rangle \langle \beta|$, as presented in Fig. 3a. In the case of short entanglement time, the detection time for the idler photon is considered to be the time that the signal photon arrives at the molecule. In the case of longer entanglement time, the arrival time of the signal photon becomes quantum mechanically uncertain, as is illustrated in Fig. 3b.

As aforementioned, idler photons are detected at a uniformly random time in the CW pumping case, and individual detection events are labeled with a set of detection times, $\{t_i\}$. To gain further insight into physical implications of Eq. (7), we consider the average of the density operator of the electronic
excitation, Eq. (7), for all possible realizations, \(t_i\):

\[
\langle \hat{\rho}_{el}(t; t_i) \rangle = \sum_{\alpha, \beta} \frac{\mu_{\alpha \beta} \hbar g}{\hbar^2} e^{-i\omega_{\alpha \beta} t} \int_{-\infty}^{t} d\tau_2 e^{-i\omega_{\alpha \beta} \tau_2} \\
\times \int_{-\infty}^{t} d\tau_1 e^{i\omega_{\alpha \beta} \tau_1} \langle G^{(1)}_s(\tau_2, \tau_1; t_i) \rangle \langle e_{\alpha} \rangle \langle e_{\beta} \rangle,
\]

(11)

with the averaged correlation function, \(\langle G^{(1)}_s(\tau_2, \tau_1; t_i) \rangle = \langle \hat{E}^{(1)}(\tau_2) \hat{E}^{(1)}(\tau_1) \rangle \). In the weak down-conversion regime, the approximation of \(\tanh r(\omega) \approx \bar{\eta}(\omega)\) is as in Eq. (4), and hence the “electric field” in Eq. (9) is approximately expressed as

\[
\langle \hat{E}^{(1)}(t) \rangle = \frac{1}{\sqrt{P_1 Z}} \int_{0}^{\infty} d\omega e^{-i\omega(t-t_i)} A(\omega) \sqrt{\bar{\eta}(\omega)}.
\]

(12)

Therefore, the averaged correlation function is computed as

\[
\langle G^{(1)}_s(\tau_2, t_1; t_i) \rangle \approx \int_{-\infty}^{\infty} dt_i \langle \hat{E}^{(1)}(\tau_2) \hat{E}^{(1)}(t_i) \rangle = G^{(1)}_s(\tau_2, t_1),
\]

and Eq. (11) turns out to be identical to Eq. (5). Indeed, the sample average of the density matrix elements presented in Fig. 3 in terms of \(t_i\) reproduces the curves depicted in Fig. 2. It is also interesting to note that the correlation function in Eq. (11) is practically identical to the first-order temporal correlation function for individual realizations of the transform-limited classical laser pulses investigated by Chenu and Brumer to yield the thermal light result [6] when \(\bar{\eta}(\omega)\) in Eq. (12) is replaced with \(\bar{\eta}(\omega)\). These observations indicate that the detection of the idler photon enables us to resolve the photon arrival times under the pseudosunlight irradiation. However, it should not be overlooked that this conclusion is only true for cases where Eq. (4) is an acceptable approximation, e.g., in the visible region of the sunlight. In such cases, the photon number is substantially 0 or 1, and therefore, the heralding is of no major consequence in terms of the number statistics. Rather, the statistics play a role as the frequency distribution of the heralded signal photons, as expressed in Eqs. (4) and (9).

V. SUMMARY

In this work, we theoretically demonstrated that the nature of sunlight photons can be emulated through quantum entangled photons generated with the PDC. What should be emphasized here is that one may emulate the sunlight, which is the radiation from the black-body with an effective temperature of approximately 5800 K, through controlling the system’s parameters in a mechanical fashion. Further, electronic excitations of a molecule using such pseudo-sunlight light were investigated. The key is that the entanglement time, which is a unique characteristic of the quantum entangled photons, serves as a control knob to resolve the photon arrival times under the pseudo-thermal irradiation, enabling investigations on real-time dynamics triggered by the pseudo-sunlight photons. Pinpointing the photon arrival times may pave a new path for implementing time-resolved spectroscopic experiments that directly reflects properties of natural sunlight.

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