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Polarization-sensitive coherent control of atomic collisions with nonclassical light

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In this paper we consider the mechanism of coherent control of atomic collisions by two-photon excitation of colliding atoms with nonclassical light characterized by polarization entanglement. Such modification of the well-known optical-collision method is proposed as a possible spectroscopic application of nonclassical light for study of collisional dynamics. We show that quantum correlations allow one to have a deeper control of the internal dynamics of atomic collision than do the principles of classical statistics. Our qualitative discussion is supported by numerical calculations made for ${}^1S \rightarrow {}^1P \rightarrow {}^1S$ optical transition of Mg perturbed by collisions with rare-gas atom.

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I. INTRODUCTION

Implementation of nonclassical light to the atomic and molecular spectroscopy is intriguing and is a challenging idea that is still underestimated in practice. Any proposal in this area is quite difficult to realize and, therefore, has to have clear motivation. Up to now there is only one unique experiment showing the difference between predictions of classical and quantum electrodynamics in spectroscopic problems [1]. In this experiment the population of cesium atoms in the upper state after two-photon excitation with squeezed light was measured as a function of the light intensity. The experiment revealed the linear (nonquadratic) dependence of the population in the limit of weak light intensity. Such a linear dependence just indicated the nonclassical behavior of the second-order correlation function of the squeezed light, which was responsible for the process.

From the first sight, it may seem natural to assume that it would be also interesting to follow the difference between classical and quantum predictions in study of polarization dependence of two-photon absorption by atoms. A typical example of light with nonclassical polarization properties is the radiation generated in the process of spontaneous parametric down conversion (SPDC) of type II [2–5]. In such a process the photon pairs are created in the state with entangled polarization between two orthogonal ordinary and extraordinary modes. However, if both the photons of such light were absorbed by separated atom, the observation conditions would be quite similar to the well-known scheme of correlation interferometer based on coincidence of photocounts. Indeed, atom itself is a spherically symmetric system and to observe the nonclassical correlations one needs to polarize it or put it in an external electric or magnetic field. Then atomic absorber will work similarly to polarization analyzer and the polarization dependence of two-photon transition will give us the same effects as in observing the correlations of photocounts in the polarization-sensitive correlation interferometer. The principal feature of such detection schemes is that after the measurement the hidden and unknown polarization of each of the entangled photons reduces to a certain type of polarization associated with the type of polarizer or (in the case of atomic absorber) with the direction of external field.

The situation changes dramatically if instead of one atom we consider the system of two atoms, i.e., either bound molecule or unbound quasimolecule created in collisional process. For such a system there is an internal quantization (symmetry) axis defined in the body-fixed frame. For an experiment carried on with a gas cell or in an atomic trap the orientation of the body-fixed frame stays unknown during the measurement and after absorption of both the entangled photons we will not know their polarization. For such type of polarization-sensitive two-photon excitation there is no analogy with the scheme based on coincidence of photocounts, as one has in the case of separated atomic absorber. In other words, the observation of two-photon transition in the system of two interacted atoms can be an example of a new type of polarization analyzer, which is only sensitive to the mutual internal polarization of the photon pairs. After the measurement of this type we get only the minimal and pure information about hidden polarization existing in nonclassical light.

On the other hand, significant experimental developments over the past decade have led to remarkable understanding of details of atomic collision dynamics. Studies of a broad spectrum of processes, ranging from cold and ultracold collisions [6–8], photoassociation [9,10], photodissociation [11,12], photochemical reactions [13,14], optical and fractional collisions [15,16], and collisional redistribution of light [17] have revealed novel and often surprising effects depending on variables associated with the collision alone and with properties of the light used to initiate or probe the dynamics. In many cases, dynamical correlation of internal variables of the colliding particles have played a critical role in the outcome; for light-induced processes, dependences on the cross sections due to classical characteristics of the light, viz., polarization, frequency, and intensity, have been determined. A method to obtain coherent control of the correlations in photodissociation, by using elliptically polarized light, demonstrated selectivity in the branching ratios for the process [12]. Further, general principles for coherent control of collision and reactive processes by using a single light source have recently been developed in Ref. [18] by controlling the bimolecular scattering processes. This motivated our recent proposal [19] on how the outcome of a collision may be significantly and selectively controlled by utilization of quantum-correlated light beams.

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In the present paper we further develop the idea proposed in Ref. [19]. Our discussion aims at the following two principal goals. First, we examine the two-photon optical collision as an example of special detection scheme where nontrivial polarization properties intrinsic to nonclassical light interfere with the dynamics of atomic collision. We show that it can define a new type of nonclassical polarization ratio that is different from usual polarization ratio normally used to describe the polarization dependence of the light-assisted half- or fractional-collisional processes, see Refs. [15,20]. Second, we comment on the possible use of nonclassical light in photochemistry as a tool to control the dynamics of light-assisted processes and consider the atomic collision as a simple and suitable example for preliminary discussion.

II. THE CROSS SECTION OF FRACTIONAL COLLISION FOR TWO-PHOTON EXCITATION WITH NONCLASSICAL LIGHT

A schematic diagram illustrating the principle of optical control of atomic collision is shown in Fig. 1. For the sake of simplicity consider, at first, such a fractional optical collision in assumptions of Franck-Condon approximation. Then the basic characteristics of the process, namely, location of the transition points R_1 and R_2, deflection angle ξ_{12}, and the symmetry of participating transitions, are defined relatively to internal molecular frame. In experiments carried out with a gas cell or in an atomic trap, this internal frame has random and unknown orientation in space. If the optical transitions are initiated by means of two classical light beams, the only way to control the polarization dependence of the process is to change the mutual polarizations of modes ω_1 and ω_2 in respect to any chosen laboratory frame. The situation will change if we consider such a light-assisted collisional process in a basic assumption that the photons ω_1 and ω_2 were created in the SPDC process of type II and consequently characterized by nonclassical-type correlations between their polarizations. For the polarization properties of such light there is no preferable choice of coordinate frame that makes it possible to realize polarization-sensitive control directly in the internal molecular frame.

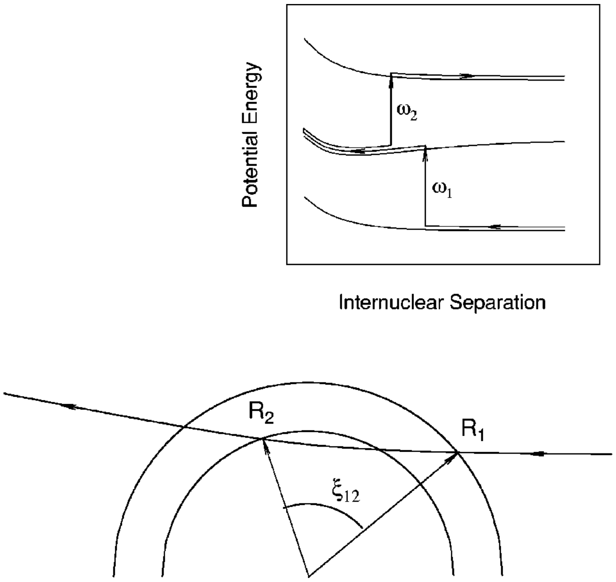

FIG. 1. Schematic diagram illustrating the principle of optical control of atomic collision.

In the most general situation, in a perturbation theory approach any two-photon process can be described in terms of the light correlation function of the second order, i.e., in terms of time (T)- and anti-time ($\widetilde{T}$)-ordered products of the Heisenberg operators of positive- and negative-frequency components of electric field amplitudes $E^{(\pm)}_{\nu}(\mathbf{r}t)$ considered as functions of space ($\mathbf{r}$) and time (t) coordinates [21]. For a weak two-mode parametric radiation with entangled orthogonally polarized components, such a correlation function can be expanded in the following sum:

$$
\begin{aligned}
D_{\nu_1\nu_2;\nu_1'\nu_2'}(t_1,t_2;t_1',t_2') &= \langle \widetilde{T}[E^{(-)}_{\nu_1'}(\mathbf{r}t_1')E^{(-)}_{\nu_2'}(\mathbf{r}t_2')]T[E^{(+)}_{\nu_1}(\mathbf{r}t_1)E^{(+)}_{\nu_2}(\mathbf{r}t_2)]\rangle \\
&= \sum_{1,2,1',2'} (\mathbf{e}_1)_{\nu_1}(\mathbf{e}_2)_{\nu_2}(\mathbf{e}^*_{1'})_{\nu_1'}(\mathbf{e}^*_{2'})_{\nu_2'}D_{121'2'}(t_1,t_2;t_1',t_2'), \qquad (1)
\end{aligned}
$$

where each of the polarization vectors $\mathbf{e}_i$, $\mathbf{e}_i'$ (with $i=1,2$) is one of the basic orthogonal output polarizations of the optical parametric oscillator (OPO). The sum over $1,2,1',2'$ is restricted by the rule $\mathbf{e}_1 \neq \mathbf{e}_2$ and $\mathbf{e}_1' \neq \mathbf{e}_2'$, so there are only four terms in the expansion (1). We will assume the steady-state and homogeneous conditions of photoexcitation and consider the correlation function only as a function of $\mathbf{r} = \mathbf{r}_1, \mathbf{r}_1', \mathbf{r}_2, \mathbf{r}_2'$, which is a spatial coordinate of the location of colliding system. The scale of the location area is assumed to be less than the radiation wavelength.

Strictly speaking, the above expansion of the full correlation function relates to the limit of weak subthreshold OPO source, generating the photon pairs, see discussion in the next section. This is the most interesting and important case for our analysis. But in a more general situation, to introduce the expansion (1), we need to cancel out the noncorrelated contribution when both the photons appear in the same polarization mode. However, even in a general situation, for methodological clarity, it can be useful to discuss the correlation function in the form (1) since it lets us compare the difference between quantum entanglement and classical understanding of mutually orthogonal but random polarizations.

Let us introduce the Fourier expansion of the time-dependent correlation function (1),

$$\tilde{D}_{12;1'2'}(\omega_1,\omega_2;\omega_1',\omega_2')=\int\int\int\int dt_1dt_2dt_1'dt_2'\exp(i\omega_1t_1+i\omega_2t_2-i\omega_1't_1'-i\omega_2't_2')D_{12;1'2'}(t_1,t_2;t_1',t_2'). \tag{2}$$

Then, as follows from general analysis presented in Ref. [22], the differential cross section of the fractional optical collision, accompanying by two-photon excitation, can be given by the following expansion:

$$\frac{d\sigma_{\mu\mu'}}{d\Omega_{\mathbf{k}}}=\sum_{1,2,1',2'}\int\int\int\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_1'}{2\pi}\frac{d\omega_2'}{2\pi}\tilde{D}_{12;1'2'}(\omega_1,\omega_2;\omega_1',\omega_2')$$
$$\times\sum_{\mu_0\mu_0'}\frac{1}{(2\pi)^2}\frac{m^2k}{\hbar^4k_0}\langle\Psi^{(-)}_{\mathbf{k}\mu}|\mathbf{d}\cdot\mathbf{e}_2G^{(+)}(\epsilon_{\mu_0}(k_0)+\hbar\omega_1)\mathbf{d}\cdot\mathbf{e}_1|\Psi^{(+)}_{\mathbf{k}_0\mu_0}\rangle\rho_{\mu_0\mu_0'}$$
$$\times\langle\Psi^{(+)}_{\mathbf{k}_0\mu_0'}|\mathbf{d}\cdot\mathbf{e}_1'^{*}G^{(-)}(\epsilon_{\mu_0'}(k_0)+\hbar\omega_1')\mathbf{d}\cdot\mathbf{e}_2'^{*}|\Psi^{(-)}_{\mathbf{k}\mu'}\rangle. \tag{3}$$

Here $\Psi^{(+)}_{\mathbf{k}_0\mu_0}$ and $\Psi^{(-)}_{\mathbf{k}\mu}$ are the so-called incoming and outgoing wave functions of the scattering problem. The former describes the state of collisional pair before photoexcitation, when the active atom is in internal quantum state μ_0 and the initial recoil momentum of atoms is $\hbar\mathbf{k}_0$. The latter describes the state of the pair after photoexcitation when the active atom comes to internal state μ and the atoms have the outgoing recoil momentum $\hbar\mathbf{k}$. The transition amplitude couples these states via the operator of transition dipole moment $\mathbf{d}$. The evolution of the system in an intermediate state is described by retarded and advanced Green operators $G^{(+)}(\epsilon)$ and $G^{(-)}(\epsilon)$, which are given by

$$G^{(\pm)}(\epsilon)=\frac{1}{\epsilon-H\pm i0}, \tag{4}$$

where H is the Hamiltonian of the diatomic system and the arguments of the Green operators in Eq. (3) are the virtual energies of the intermediate state, where $\epsilon_{\mu_0}(k_0)=\epsilon_{\mu_0}+\hbar^2k_0^2/2m$ and m is the reduced mass of atoms. The polarization state of the active atom before collision is described by its polarization density matrix $\rho_{\mu_0\mu_0'}$

In this paper we restrict our discussion to the polarization dependence of the total cross section only when the initial atomic state is unpolarized. For this particular case, after the averaging of above expansion over all the output directions of $\mathbf{k}$ the total cross section σ_0 can be written in terms of the irreducible tensor product of the light-irreducible components

$$\sigma_0=\sum_{1,2,1',2'}\sum_{X\Xi}(-)^{X+\Xi}\Phi_{X\Xi}(\mathbf{e}_1,\mathbf{e}^*_{1'})\Phi_{X-\Xi}(\mathbf{e}_2,\mathbf{e}^*_{2'})$$
$$\times Q^{(X)}_{121'2'}, \tag{5}$$

where the tensor functions

$$\Phi_{X\Xi}(\mathbf{e},\mathbf{e}'^{*})=-\sum_{\nu,\nu'}\mathrm{C}^{X\Xi}_{1\nu'\,1\nu}(\mathbf{e}'^{*})_{\nu'}e_\nu$$
$$=\sum_{\nu,\nu'}(-)^{1+\nu'}\mathrm{C}^{X\Xi}_{1\nu'\,1\nu}e'^{*}_{-\nu'}e_\nu, \tag{6}$$

considered as a function of $\mathbf{e},\mathbf{e}'=$ either $\mathbf{e}_1,\mathbf{e}_1'$ or $\mathbf{e}_2,\mathbf{e}_2'$, are the irreducible polarization components of the OPO light. Here by $\mathrm{C}^{\cdots}_{\cdots\,\cdots}$ we denote the Clebsch-Gordan coefficients in the notation of Ref. [23]. Each partial contribution of the X-rank components in the irreducible product in Eq. (5) is weighted with the collisional factor $Q^{(X)}_{121'2'}$ given by

$$Q^{(X)}_{121'2'}=\int\int\int\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_1'}{2\pi}\frac{d\omega_2'}{2\pi}$$
$$\times\tilde{D}_{121'2'}(\omega_1,\omega_2;\omega_1',\omega_2')\tilde{Q}^{(X)}(\omega_1,\omega_2;\omega_1',\omega_2'), \tag{7}$$

where the functions $\tilde{Q}^{(X)}(\omega_1,\omega_2;\omega_1',\omega_2')$ can be expressed in terms of the matrix elements of transition dipole moments defined in the basis set of radial wave functions of scattering problem. In these matrix elements the energies of the intermediate and upper states depend on the mode frequencies. The spectral behavior of collisional factors $\tilde{Q}^{(X)}(\omega_1,\omega_2;\omega_1',\omega_2')$ in quantum and semiclassical forms were discussed in Ref. [22], and we only mention here that they are internal characteristics of collision and their definition and evaluation do not depend on whether the incident light has classical or nonclassical statistics. Thus these factors can be calculated for any atomic pair similar to how it was described in Ref. [22]. The statistics of light presents only in the integrated collisional factor (7) due to the overlap with the light correlation function.

III. THE CORRELATION FUNCTION OF LIGHT WITH ENTANGLED POLARIZATION

As a practical example of the OPO generating the nonclassical light with entangled polarization, we consider the SPDC process of type II. We will assume the general nondegenerate conditions when two entangled photons can appear in either ordinary $\mathbf{e}_x$ or extraordinary $\mathbf{e}_y$ linearly polarized mode (orthogonal to z direction of the light propagation) and in different spectral modes either ω_1 or ω_2. In the ideal lossless conditions the SPDC process can be described by an unitary input-output transformation of the field operators [2]. This lets us make a straightforward analysis of any correlation function of output light. The important consequence of-this analysis is that any correlation function of arbitrary order obeys the rules of quasi-Gaussian statistics.

Let us introduce and discuss the dimensionless correlation function of the second order, normalized according to its classical limit,

$$\mathcal{D}_{121'2'}(t_1,t_2;t_1',t_2')=[TrD(\infty)]^{-1}\,D_{121'2'}(t_1,t_2;t_1',t_2'), \tag{8}$$

where the classical limit $D(\infty)$ is defined as the correlation function taken at coincidence moments $t_1'=t_1$ and $t_2'=t_2$ while approaching the limits $\tau=t_1-t_2\rightarrow\pm\infty$. Then for this correlation function there is the following Gaussian-type factorization:

$$\begin{aligned}
\mathcal{D}_{xyxy}(t_1,t_2;t_1',t_2')&=\gamma_{xx}(t_1'-t_1)\,\gamma_{yy}(t_2'-t_2)+\beta_{xy}(t_2-t_1)\,\beta_{xy}^{*}(t_2'-t_1'),\\
\mathcal{D}_{yxyx}(t_1,t_2;t_1',t_2')&=\gamma_{yy}(t_1'-t_1)\,\gamma_{xx}(t_2'-t_2)+\beta_{yx}(t_2-t_1)\,\beta_{yx}^{*}(t_2'-t_1'),\\
\mathcal{D}_{xyyx}(t_1,t_2;t_1',t_2')&=\beta_{xy}(t_2-t_1)\,\beta_{yx}^{*}(t_2'-t_1'),\\
\mathcal{D}_{yxxy}(t_1,t_2;t_1',t_2')&=\beta_{yx}(t_2-t_1)\,\beta_{xy}^{*}(t_2'-t_1').
\end{aligned} \tag{9}$$

Here each factor can be expressed by the correlation functions of annihilation $a_{i\alpha}(t)$ and creation $a_{i\alpha}^{\dagger}(t)$ Heisenberg operators in the ith spectral and αth polarization modes as follows:

$$\begin{aligned}
\gamma_{xx}(\tau)&\propto\langle a_{1x}^{\dagger}(t+\tau)a_{1x}(t)\rangle=\langle a_{2x}^{\dagger}(t+\tau)a_{2x}(t)\rangle,\\
\gamma_{yy}(\tau)&\propto\langle a_{1y}^{\dagger}(t+\tau)a_{1y}(t)\rangle=\langle a_{2y}^{\dagger}(t+\tau)a_{2y}(t)\rangle,\\
\beta_{xy}(\tau)&\propto\langle a_{2y}(t+\tau)a_{1x}(t)\rangle,\\
\beta_{yx}(\tau)&\propto\langle a_{2x}(t+\tau)a_{1y}(t)\rangle.
\end{aligned} \tag{10}$$

In pure SPDC process both the polarizations have equal output fluxes and $\gamma_{xx}(\tau)=\gamma_{yy}(\tau)=\gamma(\tau)$. This means that there is only one function $\gamma(\tau)$ characterizing the normal-type correlations in each polarization and spectral mode. But in the most general situation the anomalous correlation functions $\beta_{xy}(\tau)$ and $\beta_{yx}(\tau)$ are distinguished (basically by their complex arguments), since the different spectral modes appear here in different polarizations. Let us note here that asymmetry between spectral modes ω_1 and ω_2, existing in expansions (9), (10) and following from the spectral selection by absorber, is not an internal property of the light source and just indicates that in quasiresonant conditions the photon of the mode ω_1 should be absorbed at the first step and the photon of the mode ω_2 at the second step of excitation.

Based on the classical description of the polarization-entangled light source, only the first term in the first and in the second lines of Eqs. (9) would be acceptable. But it is the principal feature for such a light source and crucial for our following discussion that in the limit of weak subthreshold parametric generation just *the classical terms become negligible compared to the nonclassical ones*. This property is a direct consequence of the inequality $|\beta_{xy}(\tau)|,|\beta_{yx}(\tau)|\gg\gamma(\tau)$, showing that anomalous correlations are much greater than normal correlations in a weak parametric light source generating a rarefied flux of the entangled photon pairs. Below we consider such conditions for SPDC process and cancel out the classical-type correlations in Eqs. (10). Also, we simplify our discussion, by assumption that the typical correlation or coherence time in the nonclassical light is much longer than the time scale associated with atomic collision. This lets us remove the spectral-dependent collisional factor $\tilde{Q}^{(X)}(\omega_1,\omega_2;\omega_1',\omega_2')$ out of the spectral overlap integral (7) and take its arguments at the points $\omega_1=\omega_1'$ and $\omega_2=\omega_2'$ coincided with carrier mode frequencies of nonclassical light. In other words, we will treat such a collisional absorber as an example of spectral-selected but broadband photodetector near vicinities of these carrier frequencies.

According to this assumption the integral (7) is converted to a normal Fourier expansion defining the light correlation function in time representation at coincidence moments. In turn, this means that to complete the averaging procedure we only need to define the anomalous correlation functions $\beta_{xy}(\tau)$ and $\beta_{yx}(\tau)$ at the zero moment $\tau\rightarrow 0$. In the most general situation we can require

$$\begin{aligned}
|\beta_{xy}(0)|&=|\beta_{yx}(0)|=\beta,\\
\beta_{xy}(0)\,\beta_{yx}^{*}(0)&=\beta^{2}\,e^{-i\varphi},
\end{aligned} \tag{11}$$

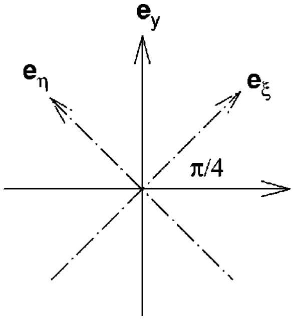

FIG. 2. Definition of basis $\{\mathbf{e}_\xi,\mathbf{e}_\eta\}$; see the text.

where the phase mismatching φ is determined by the properties of the light source. Its physical meaning will be clarified in the next section. The remaining parameter β determines the probability of two-photon excitation and in a matter of fact it is not necessary to know its magnitude if we are more interested in the polarization dependence of this process.

IV. THE NONCLASSICAL POLARIZATION RATIO

Let us substitute the correlation function in form (9) into expressions for the cross section of fractional collision (7), (5) and neglect the classical terms. Then, taking into account all the above assumptions, the final result can be written as an average over the following cooperative wave function of the photons' pair:

$$|\Psi\rangle_{12}=\frac{1}{\sqrt{2}}[|\mathbf{e}_x\rangle_1\,|\mathbf{e}_y\rangle_2+\mathbf{e}^{i\varphi}|\mathbf{e}_y\rangle_1\,|\mathbf{e}_x\rangle_2]. \tag{12}$$

For such a polarization-entangled wave function there is no particular concept of polarization in respect to each photon, but there is a strong mutual correlation between unknown polarizations of the photons.

As follows from Eq. (12) the phase φ defines the type of entanglement, since it parameterizes the possible quantum superposed states in the cooperative subspace. But one can also see that the different choices of φ can be associated with different types of mutual polarization. To show this let us introduce an alternative basis $\{\mathbf{e}_\xi,\mathbf{e}_\eta\}$ rotated to $\{\mathbf{e}_x,\mathbf{e}_y\}$-directions at $\pi/4$ angle, as shown in Fig. 2. Then, in respect to new basis, the choice $\varphi=0$ transforms the cooperative wave function to the following form:

$$|\Psi\rangle_{12}=\frac{1}{\sqrt{2}}[|\mathbf{e}_\xi\rangle_1|\mathbf{e}_\xi\rangle_2-|\mathbf{e}_\eta\rangle_1|\mathbf{e}_\eta\rangle_2], \tag{13}$$

which can be associated with parallel type of mutual polarizations. For alternative choice $\varphi=\pi$,

$$|\Psi\rangle_{12}=\frac{1}{\sqrt{2}}[|\mathbf{e}_\xi\rangle_1|\mathbf{e}_\eta\rangle_2-|\mathbf{e}_\eta\rangle_1|\mathbf{e}_\xi\rangle_2]; \tag{14}$$

the wave function preserves its form defined in the original basis. The latter choice of φ creates a state that is invariant to any rotational transformations in (x,y) plane, so it can be associated with orthogonal type of mutual polarizations.

We can define the nonclassical polarization ratio P_{EPR} as follows:

$$P_{EPR}=\frac{\sigma_0|_{\varphi=0}-\sigma_0|_{\varphi=\pi}}{\sigma_0|_{\varphi=0}+\sigma_0|_{\varphi=\pi}}=P_L+\Delta P_{int}, \tag{15}$$

where the second equality shows that this polarization ratio can be divided into the sum of usual classical polarization P_L, defined below by Eq. (16), and interference contribution ΔP_{int}.

Both the classical and nonclassical polarization ratios can be expressed in terms of spectral-dependent collisional factors $\tilde{Q}^{(X)}=\tilde{Q}^{(X)}(\omega_1,\omega_2;\omega_1,\omega_2)$. To simplify our notations we omit below the mode frequencies in their arguments. The classical polarization, showing imbalance between parallel type $(\mathbf{e}_1\|\mathbf{e}_2)$ and perpendicular type $(\mathbf{e}_1\perp\mathbf{e}_2)$ of two-photon excitation, where each of the polarization vectors are defined in respect to any laboratory frame, is given by

$$P_L=\frac{\sigma_0|_\|-\sigma_0|_\perp}{\sigma_0|_\|+\sigma_0|_\perp}=\frac{3}{2}\,\frac{\tilde{Q}^{(2)}}{\tilde{Q}^{(0)}+\frac{1}{2}\tilde{Q}^{(2)}}. \tag{16}$$

In turn, the nonclassical polarization ratio is given by

$$P_{EPR}=\frac{3}{2}\,\frac{\tilde{Q}^{(2)}-\tilde{Q}^{(1)}}{\tilde{Q}^{(0)}-\tilde{Q}^{(2)}}=P_L\frac{1-\dfrac{\tilde{Q}^{(1)}}{\tilde{Q}^{(2)}}}{1-P_L}. \tag{17}$$

As follows from these expressions, only the ratio of orientation to alignment collisional factors $\tilde{Q}^{(1)}/\tilde{Q}^{(2)}$ is an independent parameter emphasizing the difference between classical and nonclassical definitions of polarization. The first equality in Eq. (17) shows the interference nature of nonclassical polarization. Both the collisional factors, normally considered as responsible for alignment or orientation transfer, give equal contribution to the numerator of this equation. If, from the point of view of classical statistics, such an absorber had equal sensitivity to transfer the orientation and alignment and $\tilde{Q}^{(2)}=\tilde{Q}^{(1)}$, there would be no nonclassical polarization dependence. For those detunings where $\tilde{Q}^{(1)}/\tilde{Q}^{(2)}\to P_L$ there is coincidence between classical and nonclassical definitions $P_{EPR}\to P_L$ (excepting the possible uncertainty point of two-photon resonance $P_L\to 1$, see below).

Let us point out that there would be no difference if instead of the orthogonal type of entanglement in the original basis Eq. (12) we considered the parallel type. Then in rotated basis with the same choices of φ we would create only the complementary Bell's wave functions given by expressions similar to Eqs. (13) and (14) but with plus sign in them. As can be shown by a straightforward analysis, the nonclassical polarization ratio defined in the basis of complementary Bell's states can be calculated similarly to P_{EPR}. Denoting this "new" nonclassical polarization ratio as P'_{EPR} one obtains

$$P'_{EPR}=\frac{3}{2}\,\frac{\tilde{Q}^{(2)}+\tilde{Q}^{(1)}}{\tilde{Q}^{(0)}+2\tilde{Q}^{(2)}}=P_L\,\frac{1+\dfrac{\tilde{Q}^{(1)}}{\tilde{Q}^{(2)}}}{1+P_L}. \tag{18}$$

We see that P'_{EPR} is not an independent parameter, since it can be expressed via P_{EPR} and P_L. Moreover, the second equalities in Eqs. (17) and (18) show us that there is a certain symmetry in definitions of P_{EPR} and P'_{EPR} in respect to P_L and there is triple coincidence $P'_{EPR}\rightarrow P_{EPR}\rightarrow P_L$ at those points (detunings) where $\tilde{Q}^{(1)}/\tilde{Q}^{(2)}\rightarrow P_L\neq\pm 1$.

V. EXAMPLE OF $^1S\rightarrow{}^1P\rightarrow{}^1S$ FRACTIONAL COLLISION

Optical excitation of two-photon transition $^1S\rightarrow{}^1P\rightarrow{}^1S$ of active atom perturbed in collision with foreign rare-gas atom in ^1S ground state is a traditional example, which is convenient for theoretical discussion and available for experimental realization. The polarization dependence of the process can be clearly understood in quasistatic conditions in Franck-Condon-type approximation. As was recently shown in Ref. [19], the semiclassical quasistatic model of Lewis *et al.* [24], describing the single-photon optical collision, can be generalized in the case of two-photon transitions preserving all the effects of nonclassical statistics. Omitting the details, the key result of Ref. [19] is that for recoil collisions, while neglecting the rotational depolarization, the transition probability has a simple dependence on φ. Regardless of whether the excitation were via$^1\Sigma\rightarrow{}^1\Sigma\rightarrow{}^1\Sigma$ or via $^1\Sigma\rightarrow{}^1\Pi\rightarrow{}^1\Sigma$ molecular channels the nonclassical behavior of the total cross section would be given by

$$\sigma_0\propto w^{(1)}w^{(2)}(1+\cos\varphi). \tag{19}$$

Here $w^{(1)}$ and $w^{(2)}$ are the quasistatic transition probabilities at the Condon points associated with absorption of the first and the second photon, respectively. The disappearance of the cross section at $\varphi\rightarrow\pi$ just indicates the effect of polarization entanglement. Indeed, if the excitation of the colliding pair were by twin photons with cooperative wave function in form (14), the two-photon transition would be forbidden because the unknown polarization of the second photon would be always orthogonal to the unknown direction of transition dipole moment.

As we see from expression (19) in quasistatic conditions and in the limit of recoil collisions the nonclassical polarization ratio approaches unity $P_{EPR}\rightarrow 1$. At the same conditions the classical polarization ratios, depending on the transition type, approach different limits: $P_L\rightarrow 1/2$ for$^1\Sigma\rightarrow{}^1\Sigma\rightarrow{}^1\Sigma$ excitation channel or $P_L\rightarrow 7/9$ for$^1\Sigma\rightarrow{}^1\Pi\rightarrow{}^1\Sigma$ excitation channel. The difference between these three numbers and particularly inequality $P_{EPR}>P_L$ indicate that the polarization-sensitive quantum-type correlations manifest themselves more stronger than it would be allowed based on the principle of classical statistics. However, in a more general situation for the collisional trajectory of arbitrary type the last inequality can be violated and P_{EPR} can be as greater as well as less than P_L. This can be understood if we turn to the results of numerical calculations.

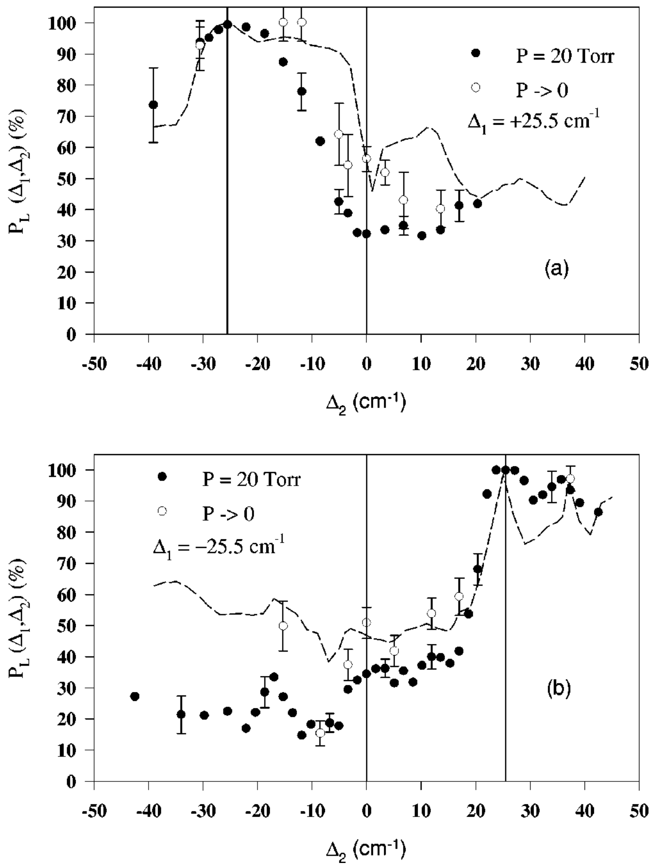

FIG. 3. Polarization spectra of Mg-Ne fractional collision $^1S\rightarrow{}^1P\rightarrow{}^1S$ interpolated to zero pressure limit of rare gas: experiment (dots) and theory (dashed curve).

Shown in Fig. 3 are both the experimental polarization spectra from Refs. [15,16] and calculated results for the optical excitation of magnesium atom by classical light in collision with neon atom at room temperature. The calculation procedure was described in detail in Ref. [22] and we just mention here that it is based on semiclassical (but not quasistatic) approach in evaluation of the collisional factors $Q^{(X)}$ with *ab initio* interaction potentials from Ref. [25]. There is a rather good agreement between experimental and theoretical spectral dependences of polarization ratio $P_L=P_L(\Delta_1,\Delta_2)$ as a function of both detunings Δ_1 and Δ_2 that reveals correct estimation of the role of rotational depolarization and of interference existing between different excitation channels. In Fig. 4 we reproduce the calculated spectra of the classical polarization ratio P_L taken from the previous graph and plot the calculated nonclassical polarization spectrum $P_{EPR}=P_{EPR}(\Delta_1,\Delta_2)$.

As follows from these spectral dependences, at the vicinities of two-photon atomic resonances $\Delta_1+\Delta_2\rightarrow 0$ the classical polarization ratio becomes greater than the nonclassical one. Indeed, in two-photon resonance the classical value approaches unity, i.e., its maximal value associated with two-photon resonance absorption on separated active atom. But the optical transition initiated by nonclassical light stay sensitive to the presence of foreign atom even in the conditions $\Delta_1+\Delta_2\rightarrow 0$. This comes from the fact that two-photon exci-

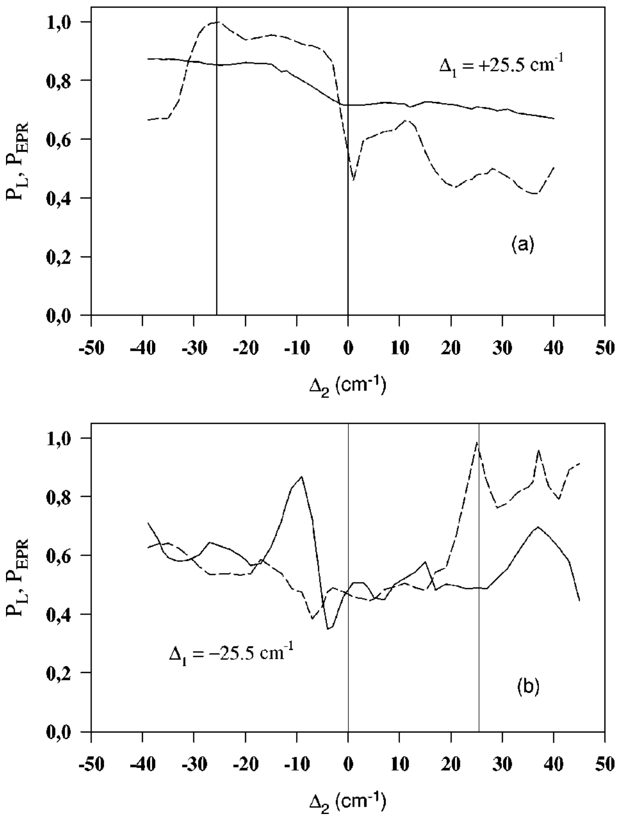

FIG. 4. Calculated polarization spectra of Mg-Ne fractional collision $^1S \rightarrow {}^1P \rightarrow {}^1S$: the classical (dashed curve) and nonclassical (solid curve) polarization ratios.

tation of free active atom at $^1S \rightarrow {}^1P \rightarrow {}^1S$ transition initiated by the photon pair described by cooperative wave function in form (12) is forbidden and only the presence of foreign particle breaks the symmetry restriction and opens the excitation channel. This circumstance can be checked if we look at the spectral dependence of total cross section. There is no singularity in the spectral dependence of the fractional collision cross section near the points of two-photon resonance $\Delta_1 + \Delta_2 \rightarrow 0$ in the case of nonclassical excitation. As a consequence in the spectral domains near two-photon resonances the nonclassical polarization P_{EPR} stays less than its classical analog P_L. Moreover, since highly excited magnesium atom in its upper $5s\ {}^1S$ state is characterized by longer acting interaction potential than in intermediate $3p\ {}^1P$ state, the direct two-photon Franck-Condon-type transition (without population of the intermediate state) can be spread on some spectral domain with $\Delta_1 + \Delta_2 > 0$.

As can be seen from the graphs shown in Fig. 4, in the far-off resonant domains, acceptable for quasistatic approach, the nonclassical polarization ratio rises and for some detunings becomes greater than the classical one. There is a tendency to approach unity for those detunings where rotational depolarization becomes negligible. That in our example, takes place for far negative detunings $\Delta_2 < 0$ and for positive detuning $\Delta_1 > 0$, see Fig. 4(a). For such detunings the excitation is mainly via separated Condon point$^1\Sigma \rightarrow {}^1\Sigma \rightarrow {}^1\Sigma$ and in recoil limit one has $P_L \rightarrow 1/2$, $P_{EPR} \rightarrow 1$. An important feature of the dependences plotted in Fig. 4(a) is that classical curve lies over the nonclassical one in a rather broad spectral domain. This is just manifestation of the dominant contribution of direct two-photon Franck-Condon transition in the classical type of photoexcitation, for which the magnitude of P_L should approach unity. With reference to Fig. 3, one can see that this circumstance agrees with experimental data. As is mentioned above, the direct two-photon excitation does not contribute to nonclassical type of photoexcitation. The nonclassical curve in Fig. 4(a) can be qualitatively understood as a result of two successive and spatially resolved single-photon Franck-Condon transitions via$^1\Sigma \rightarrow {}^1\Sigma \rightarrow {}^1\Sigma$ excitation channel. The deviation of P_{EPR} from unity is mainly caused by small but not negligible effect of rotational depolarization. The depolarization effect becomes negligible and legitimizes the recoil limit approach only for the red wing of this curve.

For negative detuning $\Delta_1 < 0$ in the red wing of Δ_2 spectrum the excitation is mainly via$^1\Sigma \rightarrow {}^1\Pi \rightarrow {}^1\Sigma$. The rotational depolarization becomes more important here and essentially reduces both the classical and nonclassical polarization ratios. In addition, the oscillated behavior of the polarization spectra indicates the presence of interference between different excitation channels in some spectral domains. In the blue wing of the classical polarization spectrum, shown in Fig. 4(b), there is a predominance of the direct two-photon Franck-Condon-type photoexcitation. In the blue wing of the nonclassical spectrum there is a combination of two pairs of successive single-photon Franck-Condon transitions that is accompanied by the interference and rotational depolarization effects. The behavior of both the classical and nonclassical dependences for negative detuning Δ_2 is more complicated to approximate it by the conditions of quasistatic approach because of the quite abrupt shape of the potential curves in this excitation domain.

VI. CONCLUSION

In this paper we have considered the mechanism of polarization-sensitive coherent control of collisional dynamics via two-photon excitation with nonclassical light characterized by polarization entanglement. We introduced an important type of polarization ratio showing the difference in excitation probability as a function of the type of entanglement. Our numerical estimations of the polarization spectra were made for semiclassical conditions of atomic collision, which are typical if the measurements were carried on with the gas cell at room temperature. Nevertheless, we can point out here that all the general expressions stay valid for the experiment with cold atoms in an atomic trap, where complete quantum descriptions of atomic collision is required.

The basic result of our discussion is that nonclassical light lets, in principle, more access to polarization-sensitive control of the elementary photochemical process, since the quantum correlations manifest themselves more strongly than classical ones do. The conditions of successive quasistatic transitions and particularly of recoil collisions, when rotational depolarization becomes negligible, seem to be the best for the polarization-sensitive control of the internal collisional dynamics. In an ideal situation of recoil collision and

Franck-Condon-type photoexcitation it may be possible to close one channel of fractional collision and to open another if they have different transition symmetry. In turn it makes possible to manipulate the dynamics of collisional process directly in the body-fixed coordinate frame, which has random and originally unknown orientation in space. However, the depolarization mechanism coming from rotation of quasimolecule during the course of collision partially reduces the effect of strong quantum correlations.

The important peculiarity of the proposed mechanism of two-photon absorption of polarization-entangled light is that the process is only sensitive to the type of entanglement and does not reduce the quantum uncertainty of photons' polarization. The polarization direction of each of the photons stays unknown after the measurement. This emphasizes the difference of the proposed type of polarization-sensitive measurement from the detection of nonclassical light by polarization-sensitive correlation interferometer, based on coincidence scheme.

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