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Experimental evidence for nonclassical fourth-order interferences in the quasielastic light scattering of water

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Experimental results of quasielastic light scattering on a water-HCl mixture at $T=297$ K are reported, which demonstrate the existence of a different kind of nonclassical two-photon (fourth-order) correlation, in the absence of second-order interferences. The normalized two-photon correlation function $\lambda^{(2)}(1,2)$ shows an oscillation with an amplitude of about 25%, depending on the relative position of the two detectors and the scattering source. The equivalent measurement on CS_2 shows no such effect. The possible physical significance of the observations is briefly mentioned.

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During the last decade, several optical interference effects have been observed that are only describable in quantum-mechanical terms and violate classical theory. Prominent effects of this kind are those concerning Einstein-Podolsky-Rosen (EPR) correlations between distant, noninteracting quantum systems. Because these experiments usually involve the detection of two quantum-correlated, entangled photons by two detectors, these effects are usually referred to as "fourth-order interference" or "two-particle interference" [1]. Early experiments used a two-photon cascade as a source, cf. [2]. But most of the more recent experiments used photon pairs produced in the process of parametric down-conversion [3] because of the better time and angular correlation between the two photons of a pair. This method facilitated a large number of fundamental experiments that demonstrated the violation of Bell-type inequalities, thus proving the existence of EPR correlations and the nonlocal character of Nature.

Here we report an experimental observation of a different fourth-order interference effect in the quasielastic (or Rayleigh) light scattering of a liquid water-HCl solution at room temperature; i.e., contrary to the entangled photon pairs produced by the parametric down-conversion mechanism, the two entangled photons have here the same frequency with the exciting laser light field. Our experiment was motivated by (i) recent studies on the possible partial delocalization (short-lived) EPR correlations of adjacent protons in liquid water and other condensed systems (cf. [4,5]) and (ii) a qualitatively predicted "anomalous" component in the scattering intensity that is caused by the EPR-correlated protons [5].

A schematic of our experimental setup is shown Fig. 1. The experiment consists of a visible, plane polarized, pulsed laser beam focused in a cell containing water-HCl solution and two detectors. They face one another in such a way that a straight line—perpendicular to the laser beam and parallel to its polarization direction—connects detector 1 (D1), the focus of the laser beam, and detector 2 (D2). D1 could be moved in a plane normal to that imaginary line with a spatial resolution of about 5 μm. The absolute reproducibility (over a time period of six months) of positioning of D1 was better than ± 10 μm. The laboratory room was thermally stabilized to ± 1 °C.

The laser source is the second harmonic of an intracavity-frequency-doubled, electro-optically Q-switched, quasi-cw-pumped Nd:YAG (neodymium-doped yttrium aluminum garnet) laser. A dynamic stable resonator with a plan output mirror was chosen to keep the position and radius of the beam waist constant. The energy per pulse is 110 ± 20 μJ, the pulse width is approximately 150 ns, and the repetition rate of the laser system is set to 1000 Hz. The data accumulation rate however is reduced to about 300 Hz because of energy and pulse monitoring. An energy monitor (Analog Modules Model 811) was used to accumulate only data within an energy interval of 90–130 μJ per pulse. The laser is operated in a transversal TEM_{00} mode with a divergence of ca. 1 mrad. By observing its axial-mode beating it turned out that two longitudinal modes were oscillating simultaneously, leading to a coherence length of about 0.75 m. This beam was focused in the cell by means of a microscope objective with a focal length of 20 mm, leading to a beam diameter of 10 μm and a power density at the focus of approximately 900 MW/cm^2.

The cell is made of fused silica with all surfaces optically polished. To avoid any optical feedback and the occurrence of standing waves, all window of the cell facing each other have a wedge angle of about 2°. An azeotrope water-HCl

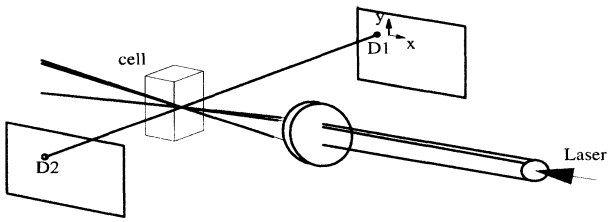

FIG. 1. Outline of the geometry of the experiment. D1 and D2: detectors.

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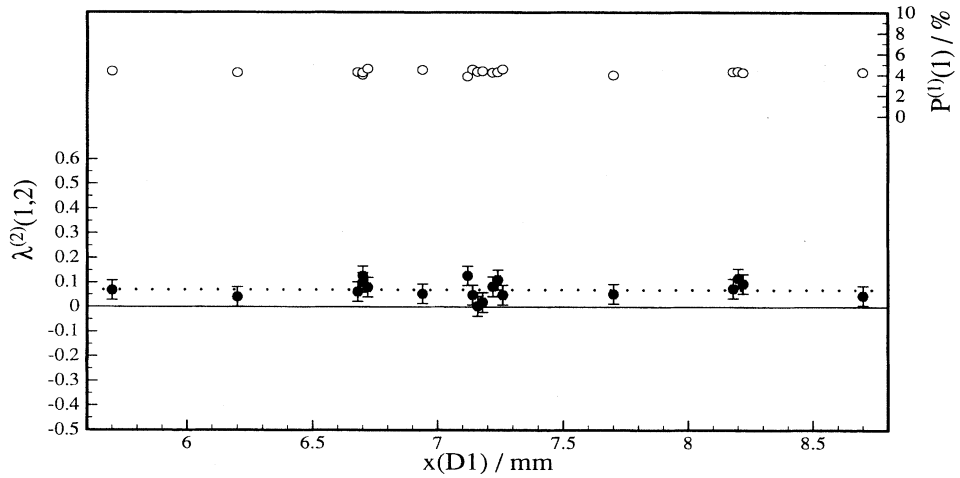

FIG. 2. Light scattering on CS_2. Abscissa: x position of detector D1. Left ordinate: measured two-photon normalized correlation function, Eq. (1). Error bars: one standard deviation. Right ordinate: measured intensities with detector D1 (for units, see text).

solution is used because it contains fewer residual dust particles after cleaning procedures (see the discussion below) than pure water.

The detectors D1 and D2, silicon avalanche photodiodes (EG&G C30902S) operated in the Geiger mode, were gated synchronously with the laser pulse for a time interval of 250 ns. This suppressed the dark count rate to a low level (less than 0.15% per pulse) making any dark count correction unnecessary. We measured the overall detection efficiency to be 49% at $\lambda = 532$ nm. Measuring the spatial dependence of the detection efficiency resulted in a 530-μm-diam full width at half maximum (FWHM) spot with a very good uniformity over the central 220 μm.

The distance between the focus in the cell and D1 and D2 was 0.865 m and 0.450 m, respectively. Neutral density filters (Schott NG9; 2 mm in front of D2; 1 mm in front of D1) were used to reduce the average counting rates of D1 and D2 to about 1% per pulse (in the series of measurements corresponding to the open symbols in Fig. 3). These filters properly regulated the intensity of the optical field and—according to quantum optical theory [6]—they did *not* alter its correlation properties; cf. also below.

The numbers of the four events feasible, namely, no photon detected, one photon detected with D1 and D2, respectively, and two photons registered by both detectors, were accumulated over typically 5×10^5 laser pulses (equivalent to about 30 min of measuring time). Let $P^{(1)}(1)$ and $P^{(1)}(2)$ to be the probabilities for detecting a photon per laser pulse with D1 and D2, respectively. Now it is possible to compare the measured probability $P^{(2)}(1,2)$ of detecting two photons with D1 and D2 simultaneously, with the number calculated on the supposition that the registrations of photons with D1 and D2 are uncorrelated. It is convenient to introduce the normalized intensity correlation function $\lambda^{(2)}(1,2)$:

$$\lambda^{(2)}(1,2)=\frac{P^{(2)}(1,2)}{P^{(1)}(1)P^{(1)}(2)}-1. \qquad (1)$$

Obviously $\lambda^{(2)}(1,2)$ should be equal to zero for uncorrelated photons detected with D1 and D2. As mentioned above, the use of the neutral density filters is not expected to alter the magnitude of $\lambda^{(2)}(1,2)$.

This detection scheme was first tested using a thermal light source leading to the expected result $\lambda^{(2)}(1,2)$ equal to zero. A second test was performed using photon pairs produced by spontaneous parametric down-conversion. The biphotonic light emerging from the crystal was focused into concentric rings in the focal plane of a lens. Both detectors were placed in this plane: one was fixed while the other scanned the plane. $\lambda^{(2)}(1,2)$ showed the expected spatial dependence first observed by Burnham and Weinberg [7], namely a strong positive peak, emerging from conservation of momentum in the process of down-conversion. It should be remarked that the detectors proved to be very efficient, making any spike filters in front of them unnecessary even in the presence of a high level of uncorrelated stray light.

An especially interesting test of the complete apparatus was performed with CS_2 instead of water in the cell. CS_2 was chosen because of its obvious lack of any hydrogen-bond network and its well known highly nonlinear susceptibility, as well as its high gain factor for nonlinear processes. In this way it could be checked once more that the described apparatus did not cause any systematic errors, and also whether an unknown nonlinear process produces correlated photons under the experimental conditions in question (e.g., conceivable spontaneous four wave mixing with the primary laser beam and its stimulated Brillouin backscattering field as the pump for such a process).

The result is shown in Fig. 2. As expected from standard theory, there is no dependence neither of the intensity [represented by $P^{(1)}(1)$] nor of the normalized two-photon correlation function $\lambda^{(2)}(1,2)$ upon the x position of detector D1 [see the geometry in Fig. 1; the nominal collinear position for detector D1 was at $x(\mathrm{D1})=7.15$ mm]. But $\lambda^{(2)}(1,2)$ is slightly positive, $\lambda^{(2)}(1,2)\approx0.07$, an effect that also occurred when measuring the $y(\mathrm{D1})$ dependence of $\lambda^{(2)}(1,2)$. Light scattering from residual dust particles in the CS_2 solution is the reason for this offset, because the intensity of the scattered light from those particles is at least an order of magnitude larger than that of the pure liquid. By averaging all laser pulses, a positive value for the normalized two-photon correlation function $\lambda^{(2)}(1,2)$ will result. For example, if $P^{(1)}(1)=0.01=P^{(1)}(2)$ in the (ideal) case of scattering of the dust-free liquid and

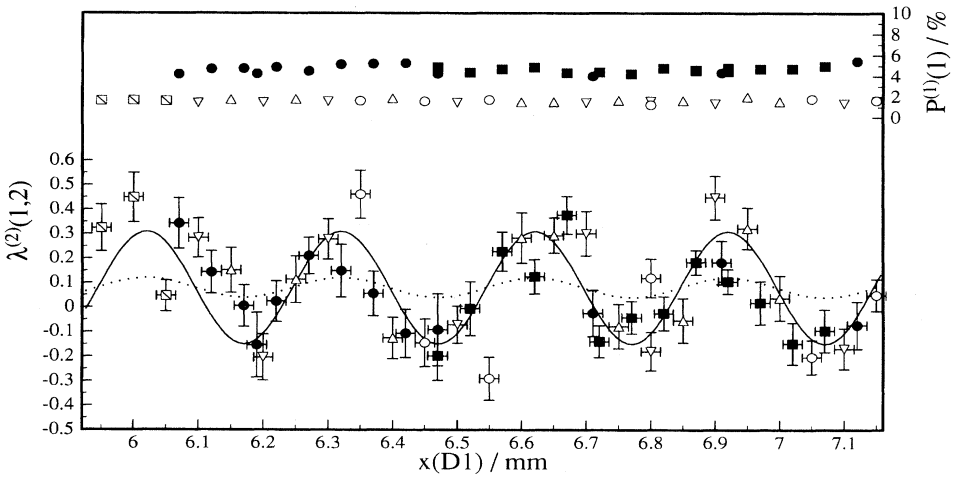

FIG. 3. Light scattering on water-HCl. Abscissa: x position of detector D1. Left ordinate: measured two-photon normalized correlation function, Eq. (1). Error bars: one standard deviation. Right ordinate: measured intensities with detector D1 (for units, see text). The different symbols representing the measured points denote individual measurements belonging to 6 different series; for details, see text.

$P^{(1)}(1)=0.10=P^{(1)}(2)$ when a dust particle emerges at the focus, a value of $\lambda^{(2)}(1,2)=0.07$ means that such a particle is present in the focus during 0.089% of all laser pulses. Note, however, that this effect can never lead to negative values for $\lambda^{(2)}(1,2)$, as was confirmed in all experiments with CS_2 in the cell.

The same proves true for fluctuations in the laser-pulse energy. By averaging the energy fluctuations, a small positive value for the offset of $\lambda^{(2)}(1,2)$ can be derived analogously. Thus, all three extensive tests mentioned above–i.e., detailed measurements using (i) thermal light, (ii) correlated photon pairs produced by parametric down-conversion, and (iii) light scattered on liquid CS_2—yielded results that were qualitatively and quantitatively consistent with standard quantum optics theory. These measurements (in addition to the standard tests of the electronic and optical components) clearly demonstrate the correct functioning of the apparatus.

On the contrary, the corresponding experiment with a water-HCl solution instead of CS_2 exhibits a completely different behavior (see Fig. 3) The results of two sets of measurements, with different ratios of the counting rates of D1 and D2 are given; see below. The counting rate $P^{(1)}(2)$ measured by the fixed detector D2 is constant; but, whereas the counting rate $P^{(1)}(1)$ exhibits no dependency upon the position of detector D1, the corresponding normalized two-photon correlation function $\lambda^{(2)}(1,2)$ shows an oscillation with an amplitude of about 25%. [There seems to occur a small modulation of $P^{(1)}(1)$ in the set of measurements marked by the closed symbols, but this proves to be accidental.]

Let us first point out the remarkable reproducibility of the effect. In Fig. 3 are shown the results of six different series of measurements performed during different days with a period of about six months. The individual points of every series are distributed over greater parts of the complex x(D1) interval.

Second, there are certain positions of D1 where $\lambda^{(2)}(1,2)$ is definitely negative. As discussed above, it is reasonable to assume a systematic positive offset for $\lambda^{(2)}(1,2)$ of about 7%, because of residual dust particles. Then the experimental data are consistent with a simple sinusoidal oscillatory behavior.

Third, the visibility or relative modulation of this interference appears *not* to depend on the ratio of the intensities $P^{(1)}(1)$ and $P^{(1)}(2)$, in contrast to all effects involving classical fields [6]. Open symbols in Fig. 3 mark measurements with a ratio $R=P^{(1)}(1)/P^{(1)}(2)$ of about $R=1$, whereas closed symbols mark the measurements with the neutral density filters changed so that the ratio R becomes $\frac{1}{10}$. As is well known (see, e.g., [8]) classical fields with randomly distributed phases do not lead to second-order interference, but nevertheless could cause an interference of fourth order. However, the visibility $V_{1,2}$ of this fourth-order interference is always less than 50% and depends on the ratio R as given by Eq. (2):

$$V_{1,2}=\frac{P^{(2)}_{\max}(1,2)-P^{(2)}_{\min}(1,2)}{P^{(2)}_{\max}(1,2)+P^{(2)}_{\min}(1,2)}=\frac{2R}{(1+R)^2}\,. \tag{2}$$

As a result the joint probability $P^{(2)}(1,2)$ can never vanish in classical optics.

On the other hand, the visibility can exceed 50% and is *independent* of the ratio R only if the photon pairs detected are quantum correlated. This has been observed experimentally in the case of photon pairs generated in the parametric down-conversion process; cf. [6,9]. In the case of our experiment, as shown in Fig. 3, the visibility of the fourth-order interference—according to classical theory—should be reduced by a factor of 3 when comparing the closed symbols with the open ones. But, if actually there is any reduction at all, this factor is definitely smaller than 0.2. Therefore we conclude that the observed modulation in the normalized two-photon correlation function cannot be attributed to an interference of classical fields, but must be due to quantum correlations of the detected photon pairs.

Fourth, in practice the detector D1 does not make observations at "points" x but each measurement represents an average over the size Δx of the detector D1. As is well known [10], this reduces the observable modulation, so that the visibility of Eq. (2) becomes

$$V_{1,2}=\frac{2R}{(1+R)^2}\,\frac{|\sin(\pi\Delta x/L)|}{(\pi\Delta x/L)}\,, \tag{3}$$

where L is the spacing of the interference fringes of fourth order. Of course it is difficult to give an exact number of the size Δx, but if we assume the fringes to extend over a considerable amount in the y direction, then it is reasonable to use a value slightly less than the measured 530-μm FWHM diameter; see above. So if we take the fringe spacing from Fig. 3 to be approximately 300 μm, then the maximal visibility will be obtained for a $\Delta x = 430$ μm. Taking this value for Δx, an actual visibility of about 100% will reduce to 22%. The full curve in Fig. 3 is a cosine corresponding to a visibility of 100% incorporating this reduction factor. This means that it represents the uppermost value of an interference of fourth order, which may be visible under the experimental conditions described. Thus, the fact that the cosine curve fits the data reasonably well indicates that the visibility of the interference may become close to 100%, if measured with sufficiently small apertures in front of the diodes [11].

Again, this indication lies beyond the limit of classical fields, thus supporting our conception of quantum-correlated photon pairs. As a comparison, the maximal visibility for fourth-order interference of classical fields for $R = \frac{1}{10}$ is shown by the dotted line (Fig. 3).

To summarize, the experimental results presented here demonstrate the existence of quantum-correlated photon pairs in the quasielastically scattered laser field on an H-bonded amorphous medium (here, liquid water-HCl). We also showed that CS_2 (whose nonlinear susceptibility is much larger than that of water) does not show the aforementioned effect. The experiment was motivated by theoretical work concerning the possible short-time partial delocalization and entanglement of adjacent protons in liquid water, see [5]. According to that work, this quantum entanglement is expected to cause variations of the cross section characterizing the scattering process under consideration. The analysis of the spatial periodicity of the two-particle interferences (Fig. 3) may be based on the corresponding theory given in Ref. [1]. In a separate paper, the observed effect and its physical interpretation will be examined in more detail.

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