



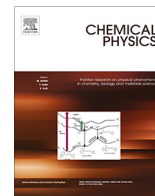
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Entangled photons from single atoms and molecules

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ABSTRACT

The first two-photon entanglement experiment performed 50 years ago by Kocher and Commins (KC) provided isolated pairs of entangled photons from an atomic three-state fluorescence cascade. In view of questioning of Bell's theorem, data from these experiments are re-analyzed and shown sufficiently precise to confirm quantum mechanical and dismiss semi-classical theory without need for Bell's inequalities. Polarization photon correlation anisotropy (A) is useful: A is near unity as predicted quantum mechanically and well above the semi-classic range, $0 \leq A \leq 1/2$. Although yet to be found, one may envisage a three-state molecule emitting entangled photon pairs, in analogy with the KC atomic system. Antibunching in fluorescence from single molecules in matrix and entangled photons from quantum dots promise it be possible. Molecules can have advantages to parametric down-conversion as the latter photon distribution is Poissonian and unsuitable for producing isolated pairs of entangled photons. Analytical molecular applications of entangled light are also envisaged.

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1. Introduction¹

Statistical characterization of quantum correlations has been guided for half a century by Bell's inequalities [10,11]. In 1935, in a provocative paper, Einstein, Podolsky and Rosen suggested a hypothetical experiment capable of testing some apparently paradoxical predictions of quantum theory, the EPR paradox [12]. Einstein believed quantum mechanical descriptions of physical systems to be correct only if supplemented with statistical distributions involving certain hidden variables but von Neumann [13] presented a mathematical proof that any hidden-variable theory must be in conflict with quantum mechanics. Bell argued that the proofs, although mathematically correct, rested upon physically unrealistic assumptions and showed that regardless of choice of hidden-parameter framework expectation values will obey certain inequalities [10,11].

The EPR paradox is philosophically interesting and has led also to a paradigmatic concept: "entanglement" (Schrödinger: "Verschränkung") [14] with roots in the wave-particle duality, today finding spreading applicability as briefly reviewed here. In 1950 Wu and Shaknow [15], based on a suggestion by Wheeler

[16], demonstrated that the angular correlation of annihilation radiation from positron-electron pairs quantitatively fulfills the asymmetry predicted by quantum pair theory. I will along similar lines consider the asymmetry of the first polarized photon correlation experiments with visible light and show that these are sufficiently precise to rule out local hidden-variable theories with reasonable statistical accuracy, and useful in general (e.g., molecular) contexts.

Today's quantum photon theory and technology follows in my view from mainly two strands of seminal experiments:

1. The discovery by Hanbury Brown and Twiss [17,18] that photons from a thermal source have a tendency to arrive in bunches – an effect characteristic of thermal bosons which can be explained in terms of classical fields.
2. Photon bunching studies by Mandel and coworkers [19,20] with the discovery of photon *antibunching* by Kimble, Dagenais and Mandel [21], predicted by Fano [22], Glauber [23] and Stoler [24] as a purely quantum field phenomenon.

A seminal experiment by Kocher and Commins [1] demonstrated the generation of isolated pairs of entangled photons by an atomic fluorescence cascade and is the focus of this communication. In its wake followed several studies using this technique combined with a suggestion by Clauser, Horne, Shimony and Holt how to test Bell's inequality by measuring at four combinations of orientations of the polarizers [25–27]. Also two-photon correlation experiments using laser parametric down-conversion

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¹ This study was inspired by the first two-photon entanglement experiment by Kocher and Commins [1] which is reanalyzed in view of recent questions regarding applicability of Bell's theorem [2–7]. Antibunching effects in fluorescence from single molecules [8] and entangled photons emerging from quantum dots [9] further suggest that molecules may be interesting alternatives to atoms for producing isolated pairs of entangled photons.

technique were reported strongly violating the Bell inequality, however, also substantially the classical probability [28].

Therefore, and also in view of recent discussions regarding applicability of Bell's theorem [2–7], we here reanalyze data from the first polarized photon correlation experiments and show that these are sufficiently precise to rule out local hidden-variable theories with reasonable statistical accuracy, without the need for Bell inequality as discriminator. Polarization photon correlation anisotropy (A) is suggested as an alternative discriminator. For the polarized photon correlation data, A is found close to unity, as expected quantum mechanically, and thus well above the interval $0 \leq A \leq 1/2$ of hidden-variable and local-realism theories.

Among molecular applications of wave-particle dualism and entanglement one may note the anti-bunching of fluorescence of photons from trapped single molecules [8] as well as evaluating entanglement in chemical situations such as between electronic and vibrational degrees of freedom in ground or excited states of a molecule [29]. Also, potential future molecular sources for entangled photon pairs related to selective two-photon absorption [30,31] or emission from quantum dots [9] will be discussed. It should be noted that besides entanglement of photons, which is the focus of this paper, recent research has demonstrated a wide variety of novel applications of entangled states of atoms, spins, super-conducting qubits, nanoparticles etc. and how they may be generated in various quantum systems [32–36].

Finally, among more speculative applications of entanglement we note long-range communication [37] as well as cosmological impact of another 1935 paper by Einstein, together with Rosen on general relativity [38], on the basis of which quantum entanglement has been suggested recently as a geometric time-space “glue” [39–41].

2. Results

This report has focus on the entangled-photon-pair experiment by Kocher and Commins [1], described in Figs. 1 and 2, the consequences of which seem to have been largely overlooked in the literature, presumably because they were overshadowed by the many attempts at the time to find experiments suitable to Bell tests. In 1964 Bell [11] had shown that earlier mathematical proofs of inconsistency of hidden-variable theories, which were all considered physically unrealistic, could be replaced by a theorem based on a physically reasonable variant of EPR suggested in a Gedanken-experiment by Bohm [42,43]. One observes the decay of a spin-zero system into a pair of spin-1/2 particles, which are highly correlated because of the various conservation laws so that the total wave function for the pair will remain intact:

$$\Psi(r_1, r_2) = 2^{-1/2}(\phi_1(\alpha)\phi_2(\beta) - \phi_1(\beta)\phi_2(\alpha)) \quad (1)$$

with ϕ_1 and ϕ_2 the wave functions for the isolated particles and α and β denoting their opposite spins. The counter-intuitive (paradoxical) thing is that Ψ in Eq. (1) is not factorable like $\phi_1(\alpha)\phi_2(\beta)$, meaning that the particles 1 and 2 are coupled (“entangled”) so it is first when the spin of one particle is probed – which leads to a collapse of Ψ – that the spin of the other particle is finally settled – irrespective of what distance and time may have elapsed since the separation of the two particles. Alternatively, pairs of photons may be envisaged in an analogous non-factorizing state: but while Eq. (1) refers to fermions (antisymmetric with respect to exchange of particles), since photons are bosons the minus sign should be changed to a plus sign (for derivations see SI). The spin is replaced by photon polarization that may be probed using polarizers.

Bell's theorem became important in that it points to a number of possible decisive experimental tests of hidden-variable theories. One such experiment was proposed by Clauser, Horne, Shimony

and Holt, together with their generalization of Bell's theorem (denoted the CHSH inequality) [25]. It was based on the polarized photon correlation experiment by Kocher and Commins [1] and used the same apparatus. A reason why the latter was discarded at the time as inconclusive was that it “unfortunately” [26] only measured at parallel and perpendicular polarizer settings.

It is true that the difference between the theoretical quantum result and the Bell limit is maximum close to $\pi/8$ and $3\pi/8$ (red arrows in Fig. 3). However, the maximum difference between the quantum mechanical and any semi-classical description is instead to be found at 0 and $\pi/2$ polarizer settings (green arrows in Fig. 3 where the dashed curve shows the maximum normalized correlation for the classical case), i.e., just where Kocher and Commins made their measurements. Indeed, based on their experimental results we here demonstrate, without need for Bell's theorem, that the classical descriptions cannot reproduce the experimental results while the quantum mechanical model can.

As light source for their experiment, Kocher and Commins used the cascade of the electric-dipole allowed fluorescence transitions $6^1S_0 \rightarrow 4^1P_1 \rightarrow 4^1S_0$ of calcium atoms excited by a hydrogen arc as shown in Fig. 1. The two transitions give rise to light of 551 nm (green) and 423 nm (violet) wavelength which is detected by two photomultipliers preceded by Polaroid type polarizers set at either parallel or perpendicular mutual polarizations. Time analysis permits a direct display of the coincidence rate as function of delay time: pulses from the two photomultipliers are fed into the start and stop inputs of a time-to-height converter. The photons are also sorted by wavelength filters as indicated in Fig. 1, green to the left and violet to the right.

An asymmetry is expected in the time correlation because the 4^1P intermediate state decays exponentially (life time 4.5 ns) so the $6^1S_0 \rightarrow 4^1P_1$ photon should generally come first, followed by a $4^1P_1 \rightarrow 4^1S_0$ photon in the classic view. However, while a slight asymmetry is noticed in the coincidence statistics for parallel polarizer setting (Fig. 2A) we find it remarkably small compared to the conspicuous asymmetric correlation seen in absence of polarizers with a slow decay for positive times consistent with the several ns long average lifetime of the intermediate state (Fig. 2B).

One trivial explanation of absence of asymmetry could be that the correlated photons are not emitted from identical atoms but arise from an unspecific Hanbury-Brown-Twiss effect of a thermal source. Another explanation could be that the entangled pair of photons arises from accidental events when the $6^1S_0 \rightarrow 4^1P_1$ and $4^1P_1 \rightarrow 4^1S_0$ emissions occur almost at the same time (as suggested within 0.1 fs [44]). This is an interesting point, albeit outside the main scope of this paper which focuses on measured factual correlations rather than their possible particulate origin. As we can show below, however, both of these trivial explanations can be dismissed as impossible. In a later paper Kocher shows [45], based on quantum arguments for time correlations in the detection of successively emitted photons, that an exponential feature is expected for positive times with an asymmetric shape indeed reflecting the average lifetime of the intermediate state (see SI).

The most amazing result, however, is the large difference in coincidence counts between the polarizer settings (Fig. 2A): the parallel setting showing a conspicuous coincidence peak, while the perpendicular one is showing essentially shot noise. This noise coincides with the background at parallel polarizer setting outside the coincidence region. A statistical analysis of the counting amplitudes for the parallel and perpendicular polarizations is collected in Table 1 also including data at 0° and 90° obtained by Freedman and Clauser using Kocher's apparatus [26]. The data are represented as R_θ/R_0 where R_θ refers to correlation with angle θ between the polarizer settings and R_0 removed polarizers (note that R_0 is not

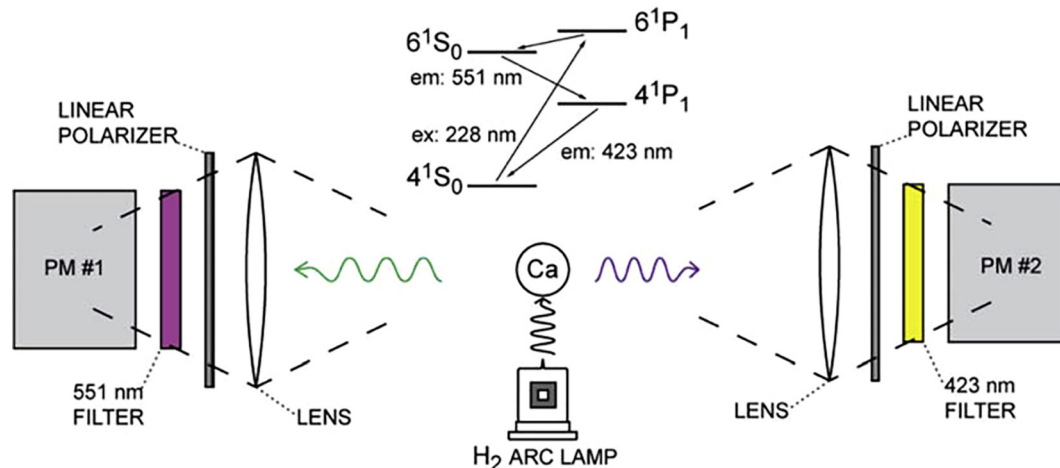


Fig. 1. Schematic diagram of apparatus of Kocher and Commins [1] together with electronic energy diagram of Ca atom cascade showing excitation and fluorescence paths. The 6^1S_0 state emits 551 nm radiation by a transition to the long-lived (4.5 ns) 4^1P_1 state, in turn radiating at 423 nm by transition to the ground state. Coordinate axes: z-axis = line between photomultipliers PM #1 and PM #2, x-axis = propagation direction of exciting beam, y-axis = normal to paper plane.

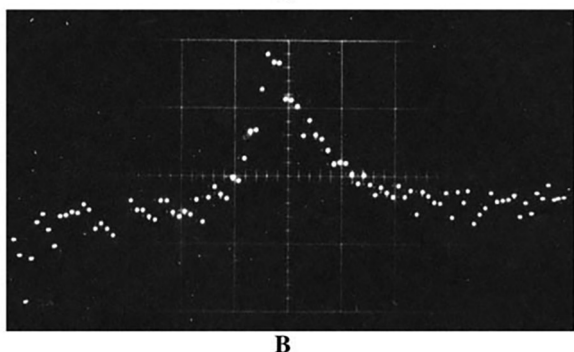
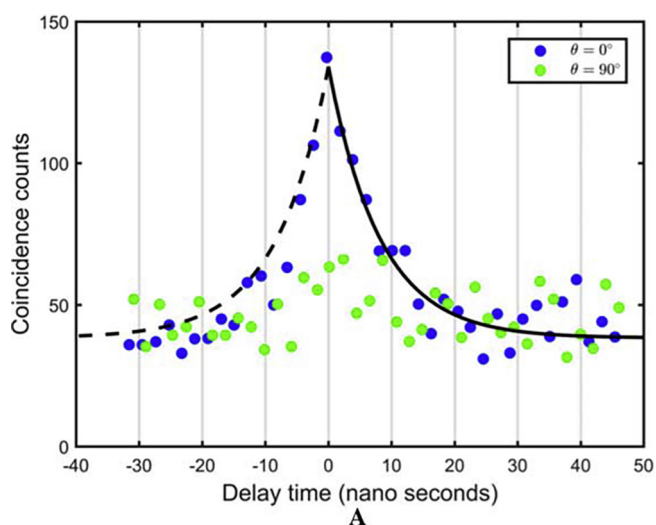


Fig. 2. A: Coincidence photon counts as a function of relative time delay for parallel ($\theta = 0^\circ$, blue) and perpendicular ($\theta = 90^\circ$, green) polarizer settings (data from Kocher and Commins [1]). The curve fitting (exponential, see SI) for $\theta = 0^\circ$ was made to the data points to the right (positive time) in order to visualize any asymmetry of the correlation function (the right-hand curve mirrored as dashed curve to the left to guide the eye). B: Coincidence photon counts as a function of relative time delay with polarizers removed (data from Kocher's PhD thesis). The trailing on the right hand side (positive time) – giving an asymmetric shape to the peak – reflects the single-photon counting effect of the decaying 4^1P_1 state (average life time ~ 4.5 ns). Published with kind permission from Dr. Kocher.

needed if instead anisotropy A is evaluated, *vide infra*). Table 1 and Fig. 3 also display the theoretical boundaries predicted quantum mechanically and semi-classically.

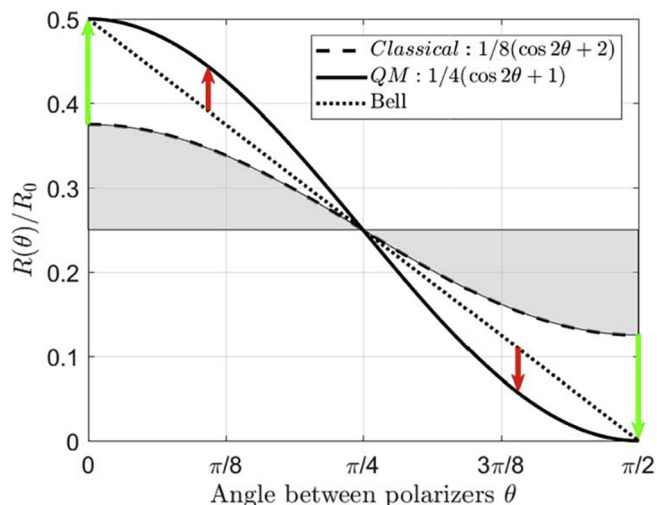


Fig. 3. Photon correlations as a function of angle θ between polarizer settings, predicted by quantum mechanical theory (solid curve), according to Eq. (3), and by classical theories (shaded area). The dashed curve shows maximum values of correlation in case the photons have identical polarization—Eq. (2). The horizontal line at $R_0/R_0 = 1/4$ represents the completely uncorrelated classical case. For comparison Bell's inequality is also shown (dotted straight line $R_0/R_0 = 1/2 - \theta/\pi$). Red arrows show the maximum difference between the QM prediction and the Bell boundary (near $\pi/8$ and $3\pi/8$). Green arrows show the maximum difference between the classical and the QM descriptions.

Kocher and Commins also report having made runs with different orientations of the fixed polarizers (data not shown) and note in each case correlations that only depend on the relative angle between the polarizer axes – they note a correlation consistent with the square of the scalar product of unit vectors in the directions of the electric dipole transition moments. Such an interpretation may look incorrect if the emitting fields of the Ca atoms are statistically isotropic, however, the result is indeed in accord with the quantum mechanical analysis, which only depends on the angle between the polarizer directions (for derivation, see SI).

The theoretical relations between the counting rate R_θ for a polarizer setting with the angle θ between the polarization directions, normalized with respect to counting rate R_0 in absence of polarizers, are as follows (see Fig. 3 and derivations in SI) for the semi-classical and quantum mechanical models, described by Eq. (2) and Eq. (3), respectively:

Table 1

Experimental coincidence statistics R_θ/R_0 , and anisotropy A (see Eq. (6)), together with theoretical boundaries according to semi-classic Eq. (2), Eq. (4) and quantum mechanical Eq. (3), Eq. (5) theories.

		Experiment		Theory	
		K ^a	F ^b	QM	SC
R_θ/R_0	$\theta = 0^\circ$	0.5 ± 0.1	0.49 ± 0.02	0.50	0.25–0.37
	$\theta = 90^\circ$	0.07 ± 0.05	0.007 ± 0.01	0	0.12–0.25
A		0.8 ± 0.2	0.97 ± 0.04	1.00	0–0.5

^a K: Kocher PhD Thesis; Kocher and Commins [1].

^b F: Freedman PhD Thesis; Freedman and Clauser [26].

$$R_\theta/R_0 = (1/8)(\cos 2\theta + 2) \quad (2)$$

$$R_\theta/R_0 = (1/4)(\cos 2\theta + 1) \quad (3)$$

Eq. (2) is derived at the assumption that the two photons have the same polarization. For the fully uncorrelated case, also included below, $R_\theta/R_0 = 1/4$ for all θ . Obviously, the biggest difference between these functions is at $\theta = 0^\circ$ and 90° . The boundaries of the semi-classical and quantum mechanical descriptions are given below by Eq. (4) and Eq. (5), respectively:

$$\frac{1}{4} \leq \frac{R(0^\circ)}{R_0} \leq \frac{3}{8} \text{ and } \frac{1}{8} \leq \frac{R(90^\circ)}{R_0} \leq \frac{1}{4} \quad (4)$$

$$\frac{R(0^\circ)}{R_0} = \frac{1}{2} \text{ and } \frac{R(90^\circ)}{R_0} = 0 \quad (5)$$

In the classical case the lower boundary of Eq. (4) can be described in a simple way: the average probability that the “first” photon passes a polarizer is 50% compared to the situation without a polarizer. If the second photon is uncorrelated as to polarization it has 50% probability of passing its polarizer too, the total probability for coincidence is thus 1/4. However, it is possible, and in some experimental settings even likely, that the two photons have practically identical polarizations that is under which assumption Eq. (2) has been derived, in order to determine the upper classical boundary. An argument for the same polarization could be the parallel transition moments for the electric dipole allowed $S \rightarrow P_X$ and $P_X \rightarrow S$ atomic emissions. The QM relations Eq. (3) and Eq. (5) can be derived using the quantized-field description of photonic states developed by Glauber (see also SI) [23].

In order to further reduce the uncertainty by eliminating R_0 we define the polarization photon correlation anisotropy, A :

$$A = \frac{R(\theta = 0^\circ) - R(\theta = 90^\circ)}{R(\theta = 0^\circ) + R(\theta = 90^\circ)} \quad (6)$$

Obviously, $A = 1$ for the quantum mechanical description while it could be found in the interval $0 \leq A \leq 1/2$ for semi-classical descriptions (shaded area in Fig. 3). One may define A also in terms of general correlations (using Bell's notations):

$$A(\mathbf{a}, \mathbf{u}) = \frac{P(\mathbf{a}, \mathbf{b}) - P(\mathbf{u}, \mathbf{b})}{P(\mathbf{a}, \mathbf{b}) + P(\mathbf{u}, \mathbf{b})} \quad (7)$$

with

$$P(\mathbf{a}, \mathbf{b}) = \int \rho(\lambda) A_\lambda(\mathbf{a}) B_\lambda(\mathbf{b}) d\lambda \quad (8)$$

where ρ is a classical probability density and λ represents extra (hidden) parameters. The fact that A is internally normalized should make it less prone to systematic errors of the experiment and also generally better suited for absolute discrimination than the Bell inequality (cf. red and green arrows in Fig. 3). As for the criticism raised regarding applicability of Bell's theorem we do not take any stand in that discussion but here only point in the direction of alternative, clear ways of disproving the local hidden-variable

and local-realism descriptions. Of course, should the questioning of validity of Bell's theorem be found justified our line of disproof could become particularly interesting. Also, the suggested function A could be a useful alternative for the characterization of various quantized states in the context of quantum optics and computing.

It has not escaped my notice that the temporal resolution of the coincidence in Fig. 2A, with effectively absence of the asymmetry one would expect if, as in the classical description, the green photon were to trigger the count and the violet photon stop it, leaves an amazing weird wave-particle duality picture of the entangled pair of photons and how their quantized fields make their way in synchrony through both polarizers when parallel.

3. Discussion

The revisit of the Kocher and Commins study is, despite the many years that have elapsed since it was made, interesting not only from a historic point of view but also from several fundamental aspects. This is one of the very first examples of a single-photon correlation experiment and it stands out by addressing some of the important scientific and philosophical problems associated with the Einstein, Podolsky and Rosen paradox. Note that in contrast to today's efficient laser parametric down-conversion and interference techniques, but unfortunately very noisy high photon fluxes, we here deal with measurements made on sparsely separated definite pairs of entangled photons the correlation of which we will now discuss.

But first let us emphasize the most important conclusion from Table 1, as following from Eq. (2) and Eq. (3), and Fig. 3, viz. the closeness of A to 1, being clearly above 1/2, demonstrating that the quantum mechanical description holds but *not* any of those based on classical local fields. This is a beautiful illustration and retort to the paradox presented by Einstein, Podolsky and Rosen in 1935, showing that quantum mechanics is complete enough to describe the two-photon experiment.

In the Kocher and Commins experiment the two-photon beams, the green and the violet, are assumed to be statistically unpolarized. Photosselection by the exciting radiation from the hydrogen arc (unpolarized but yet, of course, displaying its electric fields perpendicular to its propagation direction, x , see SI) can be anticipated to provide some anisotropy promoting transition moments in the yz -plane. If the excitation to the 6^1P_1 state is treated as a separate process it would transiently perturb and lower the spherical symmetry of the Ca atom (to $C_{\infty v}$) and make the electric dipole transition moments of the emitting transitions $6^1S_0 \rightarrow 4^1P_1 \rightarrow 4^1S_0$ have some preference for the unique C_∞ axis macroscopically preferentially oriented in the yz -plane and, as a consequence, y -polarization for photons emitted in the z direction. However, the photo-selection effect should randomize fast ($< fs$) and no polarization remains on a temporal or spatial scale of relevance, as could be verified also experimentally from independence of count rates on polarizer setting in case one polarizer is removed. Consequently,

the transmission probability is 1/2 for either of the linear polarizers, irrespective of its orientation (see SI).

According to the Einstein, Podolsky and Rosen way of reasoning, the green and violet photons, and their respective detector systems, constitute two separable systems since at the time of measurement they do no longer interact. With this local realism picture the expected value of the anisotropy A should be 0, or if the photo-selection somehow were to produce identical polarizations of the two photons, at most $A = 1/2$ as shown by Eq. (2), Table 1, i.e., $0 \leq A \leq 1/2$ for any local realism theory. Thus, the observation of $A \approx 1$ disproves the local realism theory and shows that the quantum mechanical theory is complete enough to accurately describe the experiment. This can be considered a relatively solid disproof of the local realism theory (by 25 standard deviations if the beams are assumed unpolarised as controls indicate they are).

It is relevant also to ask whether the measured coincidences are entirely due to true entanglement between two subsequent cascade photons from one single Ca atom or if a Hanbury Brown Twiss (HBT) effect might contribute, i.e., spontaneously coherent photons due to accidental coincidence of emissions from two different Ca atoms in the finite excited gas volume element. In the Kocher-Commins experiment the coincidence rate of photon pairs is typically 1 per 30 s (compared to 1 count/s in absence of polarizers) and the Ca beam density approximately 10^{10} atoms per cm^3 , roughly the measurement volume. Given these conditions and the rather large effective solid angle of the collecting lenses (0.3 rad), we consider contributions from HBT possible to exclude on statistical grounds.

Can we then generally dismiss any hidden-variable theory based on the observed experimental excellent agreement with quantum mechanics and total disagreement with the semi-classical descriptions? The answer is unfortunately not a straight 'yes'. Just as for the Wu and Shakhov experiment [15] we can here only say that the quantum mechanical interpretation gives the right answer as judged by agreement with experiment, in contrast to the local realism models which do not. This means we can exclude the local realism as provided by the classical physics models considering the two photons and their respective detectors as separable or classically superimposable entities. Still some may claim that certain hidden parameter models might provide 'loop-holes', should one apply a more stringent philosophical approach as Clauser et al. did for the 'objective' [46] and 'realistic' [47] local theories, loopholes that are dismissed by Aspect [48] and others in various sophisticated experiments. However, it is outside the scope of this paper to comment on those hidden-parameter models, loopholes and conspiracy theories that have been put forward and challenged over the years in Don Quijote-like fights to invalidate practical aspects of quantum entanglement such as time and space reversibility effects etc. My only ambition here is to present a way by which the quantum and local realism theories may be judicially distinguished using a simplistic polarization correlation experiment.

As for molecules as potential sources of entangled photons, such systems could be interesting from several aspects and be advantageous to parametric down-conversion, the most widely used source of entangled light, in that the latter photon distribution is Poissonian and therefore less selective. By way of contrast, an atomic or molecular three-level system would produce clean pairs of entangled photons, unfortunately at a very low flux. Recently entangled photons from artificial "atom-like" [49] semiconductor systems (GaAs quantum dots) [9] as well as antibunching emission from single molecules immobilized in matrix [8] have been reported but, as far as the author knows, never isolated photon pairs from discrete molecules. An interesting aspect of the semiconductor artificial atoms is that their emitted light is not Poissonian, an advantage they share with atoms and presumably natural molecules too.

A problem with most spin-conserved molecular sets of electronic states is that they do not offer a simple three-level cascade system where not one of the transitions is forbidden by parity. To take simple heterocyclic five-membered molecules as a typical example (e.g., thiophene, furan or pyrrol which are all interesting in molecular electron semi-conductor contexts), the first two π -electronic excitations, which are allowed with mutually orthogonal electric dipole transition moments [50], lead to excited states that lie energetically close but may communicate only through a magnetic-dipole allowed transition. Vibronic internal energy transfer might be a way to create a three-level cascade, but unfortunately then with too low yield and, in addition, band broadening that even at low temperatures will blur the three-state matrix element for two-photon emission and thus obstruct entanglement.

Applying a "retro-synthetic" view, one should look for molecules with three-level excitation schemes exhibiting effective two-photon absorption properties. One such system was found with amyloid protein aggregates where tyrosine dimers were a source of symmetric excitons [30], here the alternating parity may instead be of help to exclude single-photon transitions, like in thiophene, but favour two-photon transitions [51]. Strong two-photon absorption has been reported likewise for conjugated porphyrin dimers, possibly as a result of double-resonance enhancement in a three-level electron structure [31]. An interesting recent observation is the extremely high quantum efficiency of entangled photons to produce emission in a fluorescent molecule [52], which may suggest a novel high-sensitivity analytical-chemical application of entangled light.

4. Conclusions

This paper highlights some observations that may be interesting to pursue in future applications of entangled photons from single atoms and molecules. Against questions raised regarding applicability of Bell's inequalities, and of two-photon correlation results in parametric down-conversion experiments, data from the first visible-light entangled photon experiment from single atoms were reanalyzed. The polarization photon correlation anisotropy (A) is proposed as a discrimination tool: A is found close to 1, as predicted quantum mechanically, and well above the interval $0 \leq A \leq 1/2$ of local realism models based on classical fields. The maximum difference between correlations based on physical field models for quantum and semi-classical theories is expected to be found at parallel and perpendicular polarizer orientations, in contrast to what is usually assumed optimal in Bell tests. Whereas parametric down-conversion-produced light is Poissonian, pairs of entangled photons emerging from single atoms are isolated, with non-Poissonian distribution. Similarly, artificial atom quantum dots, and most likely molecules too, have the advantage of producing non-Poissonian entangled photons. A shape difference is noticed in the time-resolved correlation spectrum suggesting that entangled photons may exhibit a more symmetric coincidence spectrum compared to the clearly asymmetric photon distribution in absence of polarizers as a result of delayed fluorescence of the intermediate state. Finally, entangled photon-interactions with molecules are suggested a potentially interesting new research field, with applications to both absorption and emission of entangled photon pairs, for analytical purposes and as sources of entangled light, respectively.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.chemphys.2018.04.001>.

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