Dynamics of entangled H(2p) pair generated in the photodissociation of H₂

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Abstract. We have measured the coincidence time spectra of two Lyman−α photons emitted by a pair of H(2p) atoms in the photodissociation of H₂ at the incident photon energy of 33.66 eV and at the hydrogen gas pressures of 0.40 Pa and 0.02 Pa, from which the angular distributions of two Lyman−α photons have been obtained. The experimental angular distributions indicate the generation of the entangled pair of H(2p) atoms as predicted by the theory of our group (Miyagi et al 2007 J. Phys. B 40 617) and the role of a new kind of reaction, i.e. the reaction of the entangled pair of H(2p) atoms with an H₂ molecule that efficiently changes the entanglement. It has turned out that more entangled pairs of H(2p) atoms survive at 0.02 Pa than at 0.40 Pa. The decay time constant in the coincidence time spectrum at 0.02 Pa is approximately half the lifetime of a single H(2p) atom, 1.60 ns, while the decay time constant at 0.40 Pa is in agreement with the lifetime of a single H(2p) atom. It follows that the decay faster than the lifetime of a single H(2p) atom originates from the entanglement in the pair of H(2p) atoms.

1. Introduction
A large number of studies on entanglement have been conducted since it is not only at the heart of quantum mechanics but also plays an essential role in quantum information technologies [1−4]. The advantage of massive quantum particles, in comparison with massless photons, is that they can remain stationary while the disadvantage is that their entanglement is in general fragile against interaction with environments. It is hence a subject of current interest in atomic, molecular and optical physics to figure out the dynamics of the entangled pair of atoms. In this context a fundamental question arises, i.e. ‘Is it different from the dynamics of a single atom?’ In this paper let us answer this question experimentally.

Recently Miyagi et al in our group [5] predicted that the pair of H(2p) atoms produced in the following photodissociation of H₂ is entangled,

\[
\text{H}_2 + h\nu \longrightarrow \text{H}_2(\text{the Q}_2^1\ell^1\Pi_u(1) \text{ state}) \longrightarrow \text{H}(2p) + \text{H}(2p) \longrightarrow \text{H}(1s) + \text{H}(1s) + h\nu_{Ly-\alpha} + h\nu_{Ly-\alpha},
\]

(1)

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where \( h \nu_{\alpha} \) denotes a Lyman–\( \alpha \) photon. The process (1) was found by Odagiri et al in our group with the coincidence detection of two Lyman–\( \alpha \) photons [6]. According to Miyagi et al [5], the pair of H(2p) atoms in the \( ^1\Pi_u \) state at the infinite internuclear distance \( r = +\infty \) is entangled as expressed by

\[
\left| ^1\Pi_u^+; r = \infty \right> = \frac{1}{\sqrt{2}} \left( \left| 2p_u^\uparrow(1)2p_u^\uparrow(2) \right> + \left| 2p_u^\downarrow(2)2p_u^\downarrow(1) \right> - \left| 2p_u^\downarrow(1)2p_u^\downarrow(2) \right> - \left| 2p_u^\uparrow(2)2p_u^\uparrow(1) \right> \right), \tag{2}
\]

where two protons are labelled \( a \) and \( b \) and two electrons are labelled 1 and 2. The subscripts of 0 and \( \pm 1 \) attached to 2p are the magnetic quantum numbers \( m \) with respect to the internuclear axis, i.e. the line joining the protons \( a \) and \( b \). In fact the internuclear distance is 93 \( \mu \text{m} \) when the H(2p) atoms emit the Lyman-\( \alpha \) photons, as calculated from the incident photon energy (33.66 eV as mentioned later), the dissociation limit of H(2p) + H(2p), and the lifetime of the H(2p) atom, i.e. 1.60 ns [7]. The symbol “\( \pm \)” in \( \left| ^1\Pi_u^\pm; r \right> \) in equation (2) indicates that this state gives the eigenvalue of +1 for the reflection operator at the plane determined by the internuclear axis and the unit polarization vector of the linearly polarized incident light. Another component of the \( ^1\Pi_u \) states, the \( \left| ^1\Pi_u^-; r \right> \) state, cannot be excited since the electric dipole moment for the transition \( X^1\Sigma_g^+ \rightarrow ^1\Pi_u^- \) is perpendicular to the unit polarization vector of the incident light. The entangled pair of H(2p) atoms in equation (2) emits an entangled pair of the Lyman-\( \alpha \) photons expressed as

\[
\left| \psi > \right> = \frac{1}{2} \left( \left| \gamma_a \phi_b \right> - \left| \phi_a \gamma_b \right> \right) - \left( \left| \rho_a \phi_b \right> - \left| \phi_a \rho_b \right> \right), \tag{3}
\]

where the ket-vectors \( |\gamma\rangle, |\phi\rangle, \) and \( |\rho\rangle \) are single-photon states of the Lyman-\( \alpha \) fluorescence generated through the \( 2p \rightarrow 1s \) transition in a hydrogen atom with \( \Delta m = -1, 0, \) and 1, respectively. Miyagi et al [5] found out theoretically that the angular distribution of two Lyman-\( \alpha \) photons shows a characteristic feature (blue solid line in Figure 2), which is attributed to the entanglement in the pair of the Lyman–\( \alpha \) photons (equation (3)) and thus attributed to the entanglement in the pair of H(2p) atoms (equation (2)). Measuring the angular distribution of two Lyman–\( \alpha \) photons means probing the entanglement in the pair of H(2p) atoms. We have demonstrated the generation of the entangled pair of H(2p) atoms in process (1) and revealed a remarkable effect of entanglement on the reaction and decay dynamics of a pair of H(2p) atoms by measuring the angular distribution of two Lyman–\( \alpha \) photons and analyzing the shape of the coincidence time spectra of them [8, 9]. The angular distribution of two Lyman–\( \alpha \) photons is obtained from a set of coincidence time spectra of them measured at various arrangements of photon detectors.

2. Experimental details

The outline of the experimental apparatus for the coincidence detection of two Lyman–\( \alpha \) photons is shown in Figure 1. The experiments were carried out at the BL20A of the Photon Factory, KEK. Linearly polarized synchrotron radiation was introduced into a gas cell. Each vacuum ultraviolet photon detector is composed of a microchannel plate and an MgF\(_2\) window that provides a filter range of approximately 115–150 nm. Only Lyman–\( \alpha \) fluorescence, 121.6 nm wavelength, is detected at the present incident photon energy of 33.66 eV. Two photon detectors \( c \) and \( d \) were mounted on the wall of the gas cell in such a way that they were on the line perpendicular to the incident light beam and opposite to each other. The directions of \( c \) and \( d \) are specified by angles \( \Theta_c \) and \( \Theta_d \), respectively, measured from the unit polarization vector of the linearly polarized incident light \( \hat{e} \). The positive direction of \( \Theta_c \) and \( \Theta_d \) is the counterclockwise direction when facing into the positive direction of the X axis, i.e. the propagation direction of the incident light. The coincidence time spectrum of two Lyman-\( \alpha \) photons was measured at each angle \( \Theta_c \) with keeping the relation of \( \Theta_d = \Theta_c + \pi \). The
coincidence rate normalized for the flux of the incident photons was plotted against $\Theta_c$, which gives the angular distribution, and the shape of the coincidence time spectrum was also analyzed to investigate the decay time constant. The linear dependence of the Lyman–$\alpha$ photon count rate on the hydrogen gas pressure was confirmed up to 0.80 Pa.

3. Results and discussion

3.1. Generation of the entangled pair of H(2p) atoms and its reaction dynamics

Figure 2 shows the angular distribution of two Lyman–$\alpha$ photons in the photodissociation of H$_2$ measured at the hydrogen gas pressures of 0.40 and 0.02 Pa and at 33.66 eV incident photon energy [9]. The theoretical angular distribution for the entangled photon pair (equation (3)) emitted by the entangled H(2p) pair (equation (2)) [5] is also shown (---), which is the result for H$_2$(X$^1\Sigma_g^+$) molecules randomly oriented in space. It was convoluted with the present angular resolution (+) [8]. The experimental angular distributions approach the theoretical one (+) with decreasing the pressure, which indicates the generation of the entangled H(2p) pair expressed by equation (2). There still exists a discrepancy between the experimental distribution at 0.02 Pa (▲) and the theoretical prediction (+), which may be because the pressure was still too high, the incident light was not completely linearly polarized, or both. It has turned out that more entangled pairs of H(2p) atoms expressed by equation (2) survive at 0.02 Pa than at 0.40 Pa.

Recently Jänkälä et al [10] calculated the angular distribution of two Lyman–$\alpha$ photons in process (1) in a different way from Miyagi et al [5]. Their result is shown by the dash-dotted line in Figure 2, which was the convoluted result by them with the present solid angle subtended by each photon detector, 0.64 sr. The angular distribution at 0.02 Pa is in good agreement with the result by Jänkälä et al [10]. Miyagi et al [5] calculated the two–photon correlation function in quantum optics, proportional to the coincidence detection probability of two photons, since the angular distribution of two photons is the result of the two–photon interference and thus should be calculated by means of the quantum coherence theory [11]. On the other hand, Jänkälä et al [10] calculated the differential cross section for the emission of two photons by means of the transition amplitudes including the dipole transition matrix elements and the perturbation theory using the Fermi’s golden rule. Jänkälä et al [10] took account of the molecular rotation while Miyagi et al [5] did not, which results in the difference in the procedure for obtaining the angular distribution of two Lyman–$\alpha$ photons for H$_2$ molecules randomly oriented in space. The inclusion of the molecular rotation may improve the agreement with the experimental angular distribution of two Lyman–$\alpha$ photons at 0.02 Pa. For further discussion it is
required from the experimental sides to measure both angular distributions at lower hydrogen gas pressures and degree of the polarization of the incident light. Let us stress that Jänkälä *et al* [10] also used the entangled state of two hydrogen atoms, which is the asymptotic form of the $^1\Pi_u$ state of H$_2$ as the internuclear distance becomes infinite. Thus the important conclusion mentioned above that the entangled pair of H(2p) atoms is generated and more entangled pairs of H(2p) atoms survive at 0.02 Pa than at 0.40 Pa seems correct.

Let us then discuss the origin of the pressure effect in Figure 2. As shown below, it is unlikely that the pressure effect is able to be explained by the reactions of an H(2p) or H(2s) atom with an H$_2$ molecule that may influence the angular distribution of two Lyman-$\alpha$ photons. Such reactions are listed as follows (the partner H(2p) fragment is not shown),

$$ H(2p_m) + H_2 \xrightarrow{\sigma_{pp}} H(2p_{m'}) + H_2, \quad (4) $$
$$ H(2s) + H_2 \xrightarrow{\sigma_{sp}} H(2p) + H_2, \quad (5) $$

where $\sigma_{pp}$ and $\sigma_{sp}$ are the cross sections of reactions (4) and (5), respectively. The magnetic quantum number $m$ is defined with respect to the internuclear axis of a pair of H atoms as mentioned before. We also consider reaction (6),

$$ H(2p) + H_2 \xrightarrow{\sigma_{ps}} H(2s) + H_2, \quad (6) $$

where $\sigma_{ps}$ is the cross section, because it does not influence the angular distribution but the successive reactions (6) and then (5) may influence. As mentioned in detail in [8] the mean free times of reactions...
\( \tau_{pp}, \tau_{sp}, \text{ and } \tau_{ps} \) respectively, were calculated at 0.40 Pa based on the experimental values of \( \sigma_{pp}, \sigma_{sp}, \text{ and } \sigma_{ps} \) [12, 13] as follows,

\[
\tau_{pp} = 3.5 \times 10^{-7} \text{ s}, \quad \tau_{sp} = 9 \times 10^{-7} \text{ s}, \quad \text{and} \quad \tau_{ps} = 2 \times 10^{-7} \text{ s}.
\]

Those at 0.02 Pa are twenty times. Most of the H(2p) atoms do not undergo reactions (4) and (6) since the lifetime of H(2p) atom, 1.60 ns [7], is much shorter than the mean free times of them even at 0.40 Pa. The H(2s) atoms, on the other hand, undergo reaction (5) since they are metastable. The component due to reaction (5) may have the width of \( \approx 2\tau_{sp} \) in the true coincidence peak of the coincidence time spectrum. In fact such a broad component was not observed. Thus the contribution of reaction (5) to the coincidence rate, i.e. the contribution to the angular distribution, seems small. Reactions (4) − (6) hence seem not to be able to explain the pressure effect in Figure 2. The observed linear dependence of the Lyman–α photon count rate on the hydrogen gas pressure up to 0.80 Pa mentioned above is consistent with the results in equation (7). In conclusion, it is likely that the pressure effect is attributed to the reaction of the entangled pair of H(2p) atoms expressed by equation (2) with an H\(_2\) molecule to transfer to a pair in a product state (collapse of entanglement) or another entangled pair of H(2p) atoms, e.g. a pair of H(2p) atoms in the \( | \Pi_{\alpha}^+; r = \infty \rangle \) state that degenerates with the \( | \Pi_{\alpha}^-; r = \infty \rangle \) state. We refer to this reaction as the entangled atom-pair reaction [8]. The angular distribution of two Lyman–α photons in the \( | \Gamma_{\phi a} \rangle \) state [5], i.e. the first term on the right-hand side of equation (3), is shown in Figure 2 by dashed line to see the effect of the atom-pair state. This photon pair is emitted by the atom pair in the

\[
\frac{1}{2} \left( | 2p_{1a}^1(1)2p_{0}^b(2) \rangle + | 2p_{1a}^1(2)2p_{0}^b(1) \rangle \right)
\]

state, i.e. the first two terms on the right-hand side of equation (2). The dashed line shows the result without the convolution with the angular resolution. The cross section of the entangled atom-pair reaction \( \sigma_{ap} \) was estimated to be roughly two orders of magnitude larger than \( \sigma_{pp}, \sigma_{sp}, \text{ and } \sigma_{ps} \), i.e. the value of \( \sigma_{ap} \) amounts to \( 10^{-13} - 10^{-12} \text{ cm}^2 \) [8].

3.2. Decay dynamics of the entangled pair of H(2p) atoms due to spontaneous emission

Figure 3 shows the coincidence time spectra of two Lyman–α photons measured at the same hydrogen gas pressures and incident photon energy as in Figure 2 [9]. The horizontal axis expresses the time difference \( \Delta t \), defined as

\[
\Delta t = t_d - t_c,
\]

where \( t_d \) is the time when the photon is detected by the detector \( d \) and \( t_c \) is the time when the photon is detected by the detector \( c \). The coincidence time spectra are normalized to unity at \( \Delta t = 0 \).

The incident light at the Photon Factory comprises a train of pulses with a duration of several hundred picoseconds and a pulse-to-pulse interval of 2 ns. It takes 624 ns for a bunch of charged particles to come full circle in the storage ring. The accidental coincidences have the same time structure as the incident light: a peak-to-peak interval of 2 ns and a period of 624 ns, which is in contrast with the constant accidental coincidences for the coincidence measurements with the DC incident beam. In fact, however, a time structure of the accidental coincidences was not seen and they just fluctuated randomly, mainly due to the much weaker accidental coincidences than the true one. The ratios of the true coincidence at the peak to the accidental ones were approximately 300 at 0.40 Pa and better than that at 0.02 Pa. The average of the accidental coincidences over the channels was hence subtracted. The coincidence time spectra measured at 0.40 Pa and at \( \Theta_c = 0^\circ \) and \( \pm 90^\circ \) were summed and those at 0.02 Pa and at \( \Theta_c = 0^\circ, -20^\circ, \text{ and } 90^\circ \) were also summed after the subtraction of the
accidental coincidences in order to improve the statistics and to make the statistics approximately the same at 0.40 and 0.02 Pa. In the procedure of summation the small difference in the peak channels of the true coincidence peaks was taken into account. The coincidence time spectra processed in such a way are shown in Figure 3. The cascade contribution from H(n ≥ 3) is not involved in Figure 3 since the lifetime of H(3s) is 160 ns and that of H(3d) is 15.6 ns [14]. No components with such long decay time constants are seen in the coincidence time spectra. Again there is no contribution of the reactions of an H(2p) or H(2s) atom with an H₂ molecule, as discussed in section 3.1. The coincidence time spectra in Figure 3 were obtained within the same beam time and thus the time resolution seems to have been the same. The reason for the difference between the coincidence time spectra at 0.40 Pa and 0.02 Pa is hence that more entangled pairs of H(2p) atoms survive at 0.02 Pa than at 0.40 Pa (see section 3.1).

Let us discuss the decay in the coincidence time spectra in Figure 3. Miyagi et al [5] calculated the two–photon correlation function $G^{(2)}(r_c, t_c, r_d, t_d)$, proportional to the coincidence detection probability of two Lyman–α photons at position $r_c$ and the time $t_c$ and at position $r_d$ and the time $t_d$. In their theory the point detectors $c$ and $d$ are placed at $r_c$ and $r_d$, respectively. Let us also label the point detectors $c$ and $d$ as is the same for real detectors for convenience. The coincidence time spectrum of two Lyman–α photons, \( F(\Delta t) \), is given by integrating \( G^{(2)}(r_c, t_c, r_d, t_d) \) along the straight line of \( t_d = t_c + \Delta t \) (see equation (8)) as follows [5],

\[
F(\Delta t) = K \int_{-\infty}^{+\infty} G^{(2)}(r_c, t_c, r_d, t_d + \Delta t) dt_c = \frac{K \tau_{2p} A(f_c) A(f_d)}{2} \exp(-\tau_{2p}^{-1}|\Delta t|),
\]

(9)

where \( K \) is the apparatus constant and \( \tau_{2p} \) the lifetime of a single H(2p) atom, i.e. 1.60 ns (the lifetimes of H(2p₀,±₁) atoms are 1.60 ns) [7]. The vector with hat is a unit vector of it. Equation (9) shows that
the coincidence time spectrum of two Lyman–α photons is proportional to \( \exp(-\tau_2^{-1} |\Delta t|) \) when each H(2p) atom in the entangled pair emits a Lyman–α photon independently with the lifetime of a single H(2p) atom \( \tau_{2p} \), referred to as the independent decay model. As seen in Figure 3 the decay depends on the hydrogen gas pressure and thus the experimental coincidence time spectra do not follow equation (9), which is discussed quantitatively below. Let us fit \( F'(\Delta t) \) to the experimental coincidence time spectra to obtain the decay time constant,

\[
F'(\Delta t) = A' \exp(-\tau^{-1}|\Delta t|),
\]

where \( A' \) and \( \tau \) are fitting parameters [9]. The decay time constant \( \tau \) is considered an apparent lifetime of each H(2p) atom in the pair. The best-fitted curves are shown by the solid lines in Figure 3. The time resolution of the present apparatus was not taken into account. The decay time constants obtained are [9],

\[
\begin{align*}
\tau &= (0.78 \pm 0.04) \text{ ns} \quad \text{at 0.02 Pa (▲),} \\
\tau &= (1.54 \pm 0.08) \text{ ns} \quad \text{at 0.40 Pa (●).}
\end{align*}
\]

Interestingly, the apparent lifetime of each H(2p) atom in the pair at 0.02 Pa is approximately half the lifetime of a single H(2p) atom and that at 0.40 Pa is in agreement with the lifetime of a single H(2p) atom. As mentioned in section 3.1 more entangled pairs of H(2p) atoms survive at 0.02 Pa than at 0.40 Pa. It thus follows that each H(2p) atom in the entangled pair (equation (2)) apparently decays with a lifetime shorter than that of a single H(2p) atom. The measurements of the decay time constants at lower hydrogen gas pressures with better time resolution are highly desired.

The result (11) shows that the independent decay model in the entangled pair is questioned. Sancho and Plaja [15] also indicated this point in their comment paper on [9]. In the reply to their comment [16] we pointed out the discrepancy between the coincidence time spectrum at 0.02 Pa and their theoretical prediction. The physics underlying Figure 3 still remains unravelled.

4. Conclusion
We have measured the coincidence time spectra of two Lyman–α photons emitted by a pair of H(2p) atoms in the photodissociation of H₂ at the incident photon energy of 33.66 eV and at the hydrogen gas pressures of 0.40 Pa and 0.02 Pa, from which the angular distributions of two Lyman–α photons have been obtained. In section 3.1 we have shown from the angular distributions that the entangled pair of H(2p) atoms is generated in the photodissociation of H₂ and the pressure effect on the angular distributions is attributed to the reaction of the entangled H(2p) pair with an H₂ molecule, i.e. the entangled atom–pair reaction. It has turned out that the entangled atom–pair reaction is roughly two orders of magnitude faster than the reactions of a single H(2p) or H(2s) atom with an H₂ molecule [8]. In section 3.2 we have shown from the coincidence time spectra that the decay dynamics of entangled H(2p) atoms due to the spontaneous emission is different from that of a single H(2p) atom [9].

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