



Photon statistics as an experimental test discriminating between theories of spin-selective radical–ion-pair reactions

A.T. Dellis, I.K. Kominis*

Department of Physics, University of Crete, Heraklion 71103, Greece

ARTICLE INFO

Article history:

Received 14 May 2011

In final form 12 June 2012

Available online 18 June 2012

ABSTRACT

Radical–ion-pair reactions were recently shown to represent a rich biophysical laboratory for the application of quantum measurement theory methods and concepts. We here propose a concrete experimental test that can clearly discriminate among the fundamental master equations currently attempting to describe the quantum dynamics of these reactions. The proposed measurement based on photon statistics of fluorescing radical pairs is shown to be molecular-model-independent and capable of elucidating the singlet–triplet decoherence inherent in the radical–ion-pair recombination process.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Spin-selective radical–ion-pair reactions represent a rich biophysical/biochemical system in which spin degrees of freedom can dramatically influence the fate of biologically significant chemical reactions. The study of radical–ion-pair reactions is at the core of spin chemistry [1], by now a mature research field directly related to photochemistry [2] and photosynthesis [3]. Radical–ion-pair reactions determine the late-stage dynamics in photosynthetic reaction centers [4,5], and furthermore there is increasing evidence that radical–ion-pair reactions underlie the avian compass mechanism, i.e. the biochemical compass used by migratory birds to navigate through the geomagnetic field [6–12]. Hence the fundamental understanding of these reactions is of high scientific interest.

Radical–ion pairs are molecular ions created by a charge transfer from a photo-excited D⁺A donor–acceptor molecular dyad DA, schematically described by the reaction $DA \rightarrow D^+A \rightarrow D^{\cdot+}A^{\cdot-}$, where the two dots represent the two unpaired electrons. The magnetic nuclei of the donor and acceptor molecules couple to the two electrons via the hyperfine interaction, leading to singlet–triplet mixing, i.e. a coherent oscillation of the spin state of the electrons. The reaction is terminated by the reverse charge transfer, resulting to the charge recombination of the radical–ion-pair and the formation of the neutral reaction products. It is angular momentum conservation at this step that empowers the molecule's spin degrees of freedom to determine the reaction's fate: only singlet state radical–ion pairs can recombine to reform the neutral DA molecules, whereas triplet radical–ion pairs recombine to a different metastable triplet neutral product.

The fundamental quantum dynamics of radical–ion-pair (RP) reactions rest on a master equation satisfied by ρ , the density matrix describing the spin state of the molecule's two electrons and magnetic nuclei. This master equation has to describe (i) the unitary evolution of ρ due to the magnetic interactions within the radical–ion pairs, which is straightforward, (ii) the loss of radical–ion pairs due to the recombination reaction leading to the creation of neutral products and (iii) the state change of unrecombined radical–ion pairs. The perplexity of the combined presence of all those phenomena is partly the reason behind the ongoing debate on the particular form of this master equation. The current standing of this debate is the following. Kominis derived [13] a master equation for the term (iii) and put forward a master equation [14] for the reaction term (ii). Another master equation was introduced by Jones and Hore [15], while several authors [16–18] argued in favor of the traditional master equation of spin chemistry. So the same physical system is currently described by three theories. This situation is clearly unsatisfactory, and although theoretical arguments could in principle point to the fundamentally correct theory [19–21], the need for an experiment with discriminatory power is obvious. We will here propose exactly such an experiment.

2. Photon statistics

We will first describe the proposed measurement and explain the physics behind it in the next section. We consider radical pairs with equal singlet and triplet recombination rates, $k_S = k_T = k$. We note that different situations with e.g. just a single recombination channel (for example $k_T = 0$) or asymmetric recombination rates (for example $k_T \gg k_S$) yield qualitatively identical results. We also consider each singlet recombination event to be accompanied by a photon emission. Let \mathcal{N}_t and \mathcal{N}_{t+dt} represent the photon counts in the time intervals $(t, t + dt)$ and $(t + dt, t + 2dt)$. We assume that

* Corresponding author.

E-mail address: ikominis@physics.uoc.gr (I.K. Kominis).

the photon emission takes place at a rate r much faster than k_S . Again, relaxing this assumption does not alter the results, unless $r \ll k_S$ (see Section 4). Thus, the stochastic variables \mathcal{N}_t and \mathcal{N}_{t+dt} have expectation values $N_t = k_S dt \text{Tr}\{Q_S \rho_t\}$ and $N_{t+dt} = k_S dt \text{Tr}\{Q_S \rho_{t+dt}\}$, respectively, given by the singlet recombination products during the respective time intervals. The probability to actually observe n_t (n_{t+dt}) photons is given by the Poisson distribution with expectation value N_t (N_{t+dt}).

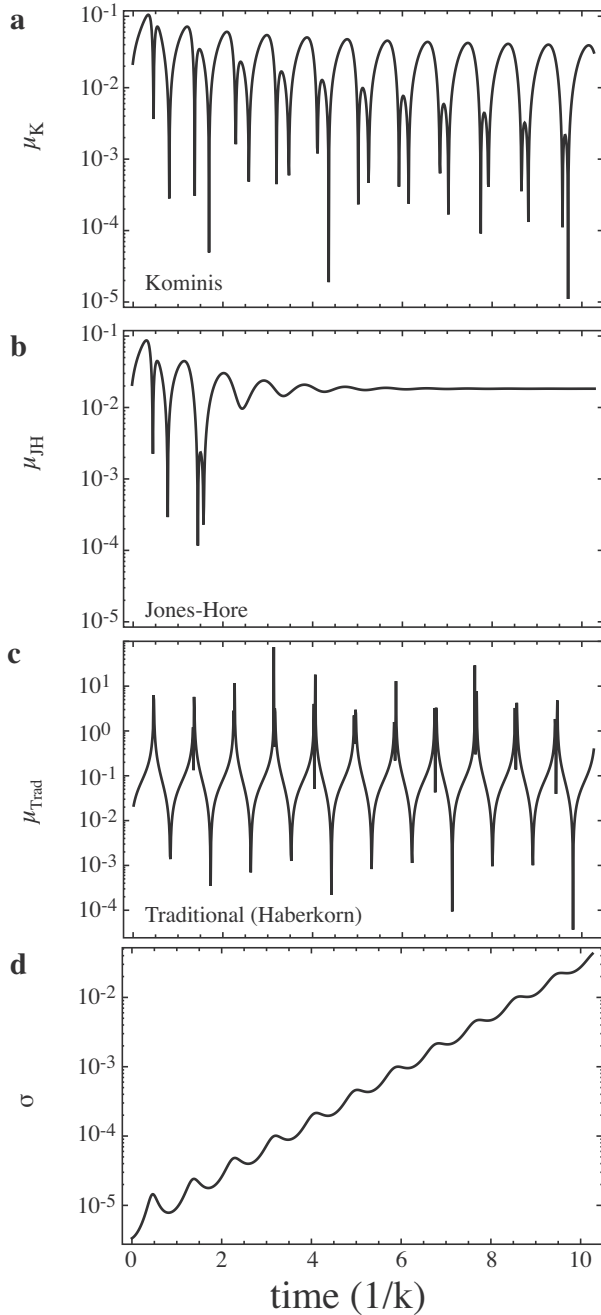


Figure 1. We numerically integrate the three master equations for a magnetic Hamiltonian of the form $\mathcal{H} = \omega_1 s_{1z} + \omega_2 s_{2z}$. The two Larmor frequencies are proportional to the respective g -factors, and we took $\Delta g = 2 \times 10^{-3}$, and $\omega_1/k \approx \omega_2/k = 4 \times 10^3$, whereas $\omega_2 - \omega_1 = 4k$. We plot μ , the expectation value of $\delta\mathcal{N}$, for the (a) Kominis, (b) the Jones–Hore and (c) the traditional (Haberkorn) theory. For σ , the statistical error plotted in (d), to be small enough to allow a statistically meaningful comparison between data and theoretical expectation, we chose an initial number of RPs 10^{13} and we calculate the expected photon counts in a time interval Δt from $N_t = \int_t^{t+\Delta t} k(Q_S) dt$, where $\Delta t = 0.006/k$.

We now define the stochastic variable $\delta\mathcal{N} \equiv (\mathcal{N}_{t+dt} - \mathcal{N}_t)/N_t$. The difference of two Poisson stochastic variables follows the Skellam distribution, according to which the probability that $n_t - n_{t+dt} = k$ is given by $f(k; N_t, N_{t+dt}) = e^{-(N_t + N_{t+dt})} (N_t/N_{t+dt})^{k/2} I_{|k|}(2\sqrt{N_t N_{t+dt}})$, where $I_k(x)$ is the modified Bessel function of the first kind. The mean and variance of the Skellam distribution are $N_t - N_{t+dt}$ and $N_t + N_{t+dt}$, respectively. Therefore the mean and variance of $\delta\mathcal{N}$ are $\mu = (N_{t+dt} - N_t)/N_t$ and $\sigma^2 = (N_t + N_{t+dt})/N_t^2$, respectively. Since $N_t \approx N_{t+dt}$, the standard deviation can be simplified to $\sigma = \sqrt{2/N_t}$. We consider an RP with arbitrary hyperfine interactions. At high enough magnetic fields, we ignore all hyperfine interactions and keep just the Δg contribution to S–T mixing. Thus the comparison between the various theories is completely robust and independent of the details of the molecule’s hyperfine interactions. In Figure 1a–c we plot the expectation value μ according to the three aforementioned theories. We also calculate (Figure 1d) the standard deviation σ (roughly the same for all theories). It is clear that the oscillations in μ_K decay rather slowly compared to the oscillations in μ_{JH} , which disappear at a rate on the order of k . Furthermore, the statistical error σ remains small enough for the oscillations in μ_K to be detectable for a long time well beyond $1/k$. In the following we also elaborate on the predictions of the traditional theory.

3. Physical explanation

What is the physical meaning of $\mu = \langle \delta\mathcal{N} \rangle$ and its decay? The expectation value of $\delta\mathcal{N}$ is a measure of singlet–triplet (S–T) coherence. Indeed, it is easily seen that $\mu = d\langle Q_S \rangle_t / \langle Q_S \rangle_t$, where $d\langle Q_S \rangle_t = \langle Q_S \rangle_{t+dt} - \langle Q_S \rangle_t$. Obviously, μ is maximum when the slope $d\langle Q_S \rangle_t / dt$ is maximum. The maxima of the slope $d\langle Q_S \rangle_t / dt$ occur in between the peaks and troughs of $\langle Q_S \rangle_t$, which are points of minimum singlet–triplet (S–T) coherence. In other words, the maxima (minima) of μ occur at instants in time when there is maximum (minimum) S–T coherence. Hence it is in the treatment of S–T coherence where the theories fundamentally differ. We will now quantify the above considerations.

3.1. Loss of singlet–triplet coherence due to S–T dephasing

The traditional master equation of spin chemistry reads

$$d\rho/dt = -i[\mathcal{H}, \rho] - \frac{k_S}{2}(Q_S\rho + \rho Q_S) - \frac{k_T}{2}(Q_T\rho + \rho Q_T) \quad (1)$$

The master equation derived by Kominis reads [14]

$$d\rho/dt = -i[\mathcal{H}, \rho] - k(Q_S\rho + \rho Q_S - 2Q_S\rho Q_S) - (1 - p_{\text{coh}})k(Q_S\rho Q_S + Q_T\rho Q_T) - p_{\text{coh}}\left(\frac{dn_S}{dt} + \frac{dn_T}{dt}\right)\frac{\rho}{\text{Tr}\{\rho\}} \quad (2)$$

where $dn_S = kdt\langle Q_S \rangle_t$, $dn_T = kdt\langle Q_T \rangle_t$ and p_{coh} is the measure of S–T coherence introduced in [14]. The second, trace-preserving Lindblad term of (2) takes into account the fundamental S–T decoherence brought about by the continuous measurement of the RP’s spin state induced by the intra-molecule reservoirs [13,14]. The last two terms are the reaction terms that affect in ρ the change resulting from the recombination of RPs. The master equation derived by Jones and Hore [15] reads

$$d\rho/dt = -i[\mathcal{H}, \rho] - 2k(Q_S\rho + \rho Q_S - 2Q_S\rho Q_S) - k(Q_S\rho Q_S + Q_T\rho Q_T) \quad (3)$$

This master equation follows from (2) by doubling the S–T dephasing rate and setting $p_{\text{coh}} = 0$ for all times. The fact that the quantity $Q_S\rho + \rho Q_S - 2Q_S\rho Q_S$ represents S–T coherence can be easily shown rather generally. Multiplying ρ from left and right by $1 = Q_S + Q_T$, it follows that ρ can be written as $\rho = \bar{\rho} + \tilde{\rho}$, where

$\bar{\rho} = Q_S \rho Q_S + Q_T \rho Q_T$ is the incoherent and $\tilde{\rho} = Q_S \rho Q_T + Q_T \rho Q_S$ the coherent part of ρ . It is easily seen that $Q_S \rho + \rho Q_S - 2Q_S \rho Q_S = \tilde{\rho}$, proving the above claim. The magnetic Hamiltonian is the generator of S–T coherence. The steady state S–T coherence is determined by its generation rate through \mathcal{H} and its dissipation rate through the second term in the master Eqs. (2) and (3). Because S–T coherence decays at double the rate in the Jones–Hore theory than in Kominis' theory, it is seen that the steady state of S–T coherence (oscillation amplitude of μ) quickly approaches zero in the former, and a non-zero value in the latter.

The predictions of the traditional (Haberkorn) theory are shown in Figure 1c. It is seen that μ exceeds unity. This is due to the fact that the traditional theory does not capture the physics of S–T dephasing that the other two theories do, hence the surviving RPs oscillate through the same minimum of $\langle Q_S \rangle$, which in this example is zero. Thus (a) there are points in time where μ has a small denominator, and (b) the oscillations in μ are undiminished. To summarize, the traditional theory predicts unceasing maximum S–T coherence, the theory of Kominis predicts a steady-state non-zero S–T coherence, whereas the Jones–Hore theory predicts an S–T coherence quickly (in a time on the order of the reaction time) decaying to zero.

4. Experimental implementation

The proposed experiment can be realized in RPs at which quantum beats arising from the coherent oscillation between the singlet and triplet states can be observed, as for example in transient-EPR experiments [22]. Interestingly, RPs which also recombine with a concomitant photon emission or even absorption have been extensively studied e.g. by Molin [23], although these studies have the additional complication of RP diffusion, absent from the simple model of a fixed dyad considered here. An additional complication is the decay rate of the fluorescing exciplex mentioned earlier. If RPs accumulate in a slowly decaying exciplex (i.e. $r \ll k_S$) then quantum beats will be hardly observable.

Moreover, there are solid state systems which could be used for the purpose of the proposed experiment. For example, in the P^+I^- RP found in photosynthetic reaction centers [24,25], the triplet recombination results in the formation of 3P molecules which can absorb 870 nm photons. The absorption (and thus at latter times the emission) statistics of these photons carry information similar to what is considered here.

A final point has to do with spin relaxation. The difference between the predictions of the various theories will fade away if other spin-relaxation mechanisms are dominant beyond the fundamental S–T decoherence process inherent in the recombination process of RPs. The physical origin of this decoherence process has been exhaustively explained in [13,14,21]. Additional relaxation mechanisms can in principle be suppressed, e.g. by performing the measurement at low enough temperatures. There exist several experiments where such relaxation channels appear to be slower than the recombination rates, as for example the ones reported in [26–28].

5. Conclusions

We stress that the particular measurement we propose is model-independent, in the following sense. Clearly the time evolution of observables like $\langle Q_S \rangle$ or the magnetic-field effect (MFE) are predicted to be different by the three theories. However, in practice it would be difficult for the measurement to discern absolute differences in $\langle Q_S \rangle$ or the MFE signal, since it would be possible to attribute those to an imperfect understanding of e.g. the RP's magnetic interactions. In contrast, in the measurement we propose, normalizing the photon count difference by N_t and measuring at high enough magnetic fields where the S–T mixing is dominated by Δg largely alleviates this problem, and the three theories predict clearly distinguishable trends, no matter what the details of the molecular interactions are.

Acknowledgements

We would like to acknowledge the John S. Latsis Public Benefit Foundation for financial support under the 2011 scientific program project “Quantum-Limited Biochemical Magnetometers”, as well as the European Union (European Social Fund ESF) and Greek Operational Program “Education and Lifelong Learning” of the National Strategic Reference Framework (NSRF) – Research Funding Program “Heracleitus II. Investing in knowledge society through the European Social Fund”.

References

- [1] U. Steiner, T. Ulrich, Chem. Rev. 89 (1989) 51.
- [2] N.J. Turro, J.C. Scaiano, V. Ramamurthy, Principles of Molecular Photochemistry: An Introduction, University Science Press, 2008.
- [3] R.E. Blankenship, Molecular Mechanisms of Photosynthesis, John Wiley & Sons, 2002.
- [4] S.G. Boxer, Biochim. Biophys. Acta 726 (1983) 265.
- [5] S.G. Boxer, C.E.D. Chidsey, M.G. Roelofs, Ann. Rev. Phys. Chem. 34 (1983) 389.
- [6] K. Schulten, Adv. Solid State Phys. 22 (1982) 61.
- [7] W. Wiltchko, R. Wiltchko, J. Exp. Biol. 199 (1996) 29.
- [8] T. Ritz, S. Adem, K. Schulten, Biophys. J. 78 (2000) 707.
- [9] W. Wiltchko, R. Wiltchko, Comp. Physiol. A 191 (2005) 675.
- [10] I.A. Solov'yov, D.E. Chandler, K. Schulten, Biophys. J. 92 (2007) 2711.
- [11] K. Maeda et al., Nature (London) 453 (2008) 387.
- [12] C.T. Rodgers, P.J. Hore, Proc. Natl. Acad. Sci. USA 106 (2009) 353.
- [13] I.K. Kominis, Phys. Rev. E 80 (2009) 056115.
- [14] I.K. Kominis, Phys. Rev. E 83 (2011) 056118.
- [15] J.A. Jones, P.J. Hore, Chem. Phys. Lett. 488 (2010) 90.
- [16] A.I. Shushin, J. Chem. Phys. 133 (2010) 044505.
- [17] P.A. Purtov, Chem. Phys. Lett. 496 (2010) 335.
- [18] K.L. Ivanov, M.V. Petrova, N.N. Lukzen, K. Maeda, J. Phys. Chem. A 114 (2010) 9447.
- [19] I.K. Kominis, Chem. Phys. Lett. 508 (2011) 182.
- [20] J.A. Jones, K. Maeda, U.E. Steiner, P.J. Hore, Chem. Phys. Lett. 508 (2011) 184.
- [21] I.K. Kominis, Chem. Phys. Lett., <http://dx.doi.org/10.1016/j.cplett.2012.06.014>.
- [22] G. Kothe et al., Chem. Phys. Lett. 186 (1991) 474.
- [23] Y.N. Molin, Bull. Korean Chem. Soc. 20 (1999) 7.
- [24] S.G. Boxer, C.E.D. Chidsey, M.G. Roelofs, Annu. Rev. Phys. Chem. 34 (1983) 389.
- [25] R.A. Goldstein, S.G. Boxer, Biochim. Biophys. Acta 997 (1989) 70.
- [26] B. van Dijk, J.K.H. Carpenter, A.J. Hoff, P.J. Hore, J. Phys. Chem. B 102 (1998) 464.
- [27] Y. Kubori, S. Yamauchi, K. Akiyama, S. Tero-Kubota, H. Imahori, S. Fukuzumi, J.R. Norris, Proc. Natl. Acad. Sci. USA 102 (2005) 10017.
- [28] K. Maeda et al., Chem. Commun. 47 (2011) 6563.