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Entanglement of Protons in Organic Molecules: An Attosecond Neutron Scattering Study of C−H Bond Breaking

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Abstract: Interactions between adjacent particles of condensed phases can lead to quantum correlation phenomena, like quantum interference, entanglement, delocalization, and “Schrödinger’s cat” states. Such correlations are theoretically expected to be extremely short-lived because of environmental disturbances. Here, we present experimental evidence for quantum entanglement between well localized protons of C−H bonds of 2-isobutoxyethanol dissolved in D_2O. The applied experimental method is neutron Compton scattering (NCS), which has a characteristic time window in the subfemtosecond time range. Our NCS results reveal that, in the subfemtosecond time scale, the measured cross-section density, and thus, in simple terms, the effectively present concentration, of the H atoms is “anomalously” reduced by ∼20%. Affecting the microdynamics of protons of covalent C−H bonds, this novel effect may have a broad range of chemical and biological applications.

I. Introduction

Many important scientific discoveries have often been made by combining concepts from widely different areas, and fertile ideas are often formed of elements drawn from domains which are far apart (see ref 1). In this spirit, the present paper addresses a topic belonging to fundamental chemistry, that is, the breaking of a covalent C−H bond in the subfemtosecond time scale, as studied with a novel experimental method, that is, the neutron Compton scattering (NCS) technique. The primary motivation of our NCS experiments was the following question: Does the fundamental phenomenon of quantum entanglement (in short, QE) play a role in condensed molecular matter at ambient experimental conditions? The new experimental results provide strong evidence that the answer is “yes” and also reveal a hitherto unknown property of C−H dissociation dynamics.

Let us now describe the scientific background and the contents of the present paper. According to the conventional viewpoint, an elementary chemical reaction can be theoretically represented by the “motion” of nuclei (treated either as classical mass points or as quantum wave packets[2]) on Born−Oppenheimer (B−O) potential energy surfaces.[3] The latter are determined by solving the electronic time-independent Schrödinger equation, by considering the nuclei as classical mass points and keeping their positions fixed at various spatial configurations. However, nuclei are also quantum objects, and thus, they can occupy nonclassical states, which are caused by interactions between the particles themselves, as well as interactions of the particles with electronic charges in their vicinity. These states are also described as quantum entangled, quantum correlated, “Schrödinger’s cat”, Einstein−Podolsky−Rosen correlated, and so forth.[4,5]

Nowadays, multiparticle QE and its decay dynamics, called decoherence,[4,5] are the focus of several experimental and theoretical fields of physics and engineering, for instance, quantum optics, quantum computation and information, quantum cryptography, and teleportation.[5] These investigations usually deal with pairs of quantum particles (photons, atoms, ions, etc.) which are carefully isolated from their environment in order to keep QE intact for a time sufficiently long to become measurable. In condensed systems at ambient experimental conditions, however, QE is widely believed to be unimportant and/or not accessible to experiments, because of its extremely fast decoherence[4] caused by environmental disturbances.

In contrast, on the basis of previous theoretical work, we proposed to detect QE in condensed systems by means of sufficiently “fast” scattering techniques.[6] Applying the NCS method on liquid water and H_2O/D_2O mixtures at room temperature, we provided for the first time direct evidence of a considerable degree of QE between protons (or H-bonds).[7] Further NCS experiments on metallic hydrides,[8] and very recently on solid polystyrene[9] and liquid benzene (submitted), have given further evidence for the existence of this novel effect. For a nontechnical overview, see ref 10.

Starting with an outline of the experimental method and the main results in section II, we then present a simple description

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[1] Editorial. *J. Am. Chem. Soc.* **1997**, *119*, 6213.

[2] (a) Zewail, A. H. *Femtochemistry: Ultrafast Dynamics of the Chemical Bond*; World Scientific: Singapore, 1994. (b) *Femtosecond Chemistry*; Manz, J., Wöste, L. Eds.; VCH Verlagsgesellschaft: Weinheim, 1995.

[3] Bohm, A. *Quantum Mechanics: Foundations and Applications*, 3rd ed.; Springer-Verlag: New York, 1993.

[4] (a) Zurek, W. H. *Phys. Today* **1991**, *44* (10), 36−44. (b) Haroche, S. *Phys. Today* **1998**, *51* (7), 36−42. (c) Anglin, J. R.; Paz, J. P.; Zurek, W. H. *Phys. Rev. A* **1997**, *55*, 4041−4053. (d) Tegmark, M. *Phys. Rev. E* **2000**, *61*, 4194−4206.

[5] (a) Zeilinger, A. *Sci. Am.* **2000**, *282* (4), 32−41. (b) *The Physics of Quantum Information*; Bouwmeester, D., Ekert, A., Zeilinger, A., Eds.; Springer-Verlag: Berlin, 2000. (c) Nielsen, M. A.; Chuang, I. L. *Quantum Computation and Quantum Information*; Cambridge University Press: Cambridge, 2000.

[6] Chatzidimitriou-Dreismann, C. A. *Adv. Chem. Phys.* **1997**, *99*, 393−430.

[7] Chatzidimitriou-Dreismann, C. A.; Abdul-Redah, T.; Streffer, R. M. F.; Mayers, J. *Phys. Rev. Lett.* **1997**, *79*, 2839−2842.

[8] Karlsson, E. B.; Chatzidimitriou-Dreismann, C. A.; Abdul-Redah, T.; Streffer, R. M. F.; Hjörvarsson, B.; Öhrmalm, J.; Mayers, J. *Europhys. Lett.* **1999**, *46*, 617−623.

[9] Chatzidimitriou-Dreismann, C. A.; Abdul-Redah, T.; Sperling, J. *J. Chem. Phys.* **2000**, *113*, 2784−2792.

[10] Chatzidimitriou-Dreismann, C. A.; Abdul-Redah, T.; Streffer, R. M. F.; Karlsson, E. B. In *ISIS 2000 − The Rutherford Appleton Laboratory, ISIS Facility Annual Report*, Science Highlights, 2000, 58−59.

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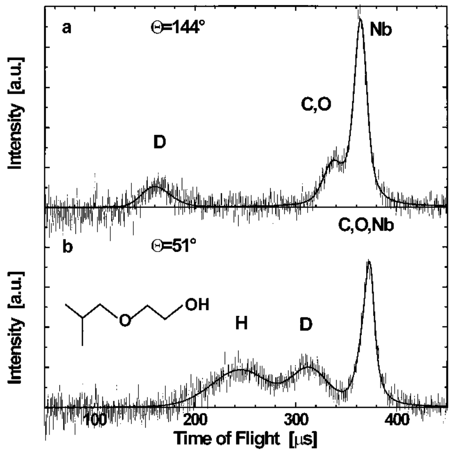

Figure 1. Time-of-flight (TOF) spectra of iso-C_4E_1 in D_2O as measured for scattering angles (a) $\theta = 144°$ and (b) $\theta = 51°$. The structure of iso-C_4E_1 is also shown. The small vertical bars represent one standard deviation error due to counting statistics. The full lines represent the fitted theoretical TOF spectra to the measured data. Note the separation of the joint C,O peak from the Nb can peak in spectrum (a), which is necessary for data analysis (see text for details).

of QE between particles in section III. In section IV, the experimental results are presented. In section V, we then offer a discussion of the physical basis, the interpretation, and some (far-reaching) consequences of the observations in rather nontechnical terms, as well as additional concluding remarks. Section VI (which represents a technical appendix) deals with relevant details of the experimental technique of NCS, the data analysis, and the sample preparation.

II. Outline of Method and Results

The experimental technique whose results are presented below is neutron Compton scattering (NCS) as applied on the eVS instrument of ISIS, Rutherford Appleton Laboratory, U.K. (for instrument description, see section VI). This instrument might be viewed as an "atom mass spectrometer": each atom should give rise to one corresponding peak in the measured time-of-flight spectrum. According to standard NCS theory, the measured integral intensity A_i of each peak must be proportional to the number density N_i of the corresponding atom i in the sample and to the corresponding total scattering cross section σ_i. Therefore, for the special case of hydrogen and any other different atom X, the equation

$$\frac{A_{\mathrm{H}}}{A_{\mathrm{X}}} = \frac{N_{\mathrm{H}}\sigma_{\mathrm{H}}}{N_{\mathrm{X}}\sigma_{\mathrm{X}}} \tag{1}$$

holds strictly within standard NCS theory (see section VI). Its validity is immediately subject to experimental test, because the particle number densities are known by sample preparation and/or by the stoichiometry of the chemical compound under investigation.

Here, we provide experimental evidence for subfemtosecond QE between well localized H atoms of C−H bonds of 2-isobutoxyethanol (iso-C_4E_1, see inset in Figure 1) dissolved in D_2O. The results presented in the following reveal a surprising effect: the neutron intensity scattered from H atoms appears to be ~20% lower than expected according to standard theory. In simple terms, one may say that 20% of the H atoms are "missing" or "invisible" to the incoming neutrons.

The following two novel features are worth mentioning already here:

(a) First, evidence for this effect concerning protons of C−H bonds was recently found in solid polystyrene.[9] Extending that finding considerably, the experimental results presented in this paper reveal the following new and crucial feature: Because the observed "anomaly" appears to be just as great in the diluted iso-C_4E_1 molecules as it was in bulk polystyrene, it must be concluded that the considered effect is mainly of *intramolecular* origin.

(b) Extending the detailed derivations of ref 9, the new theoretical considerations about QE presented in section III provide evidence that the physical origin of this effect is mainly given by electronic interactions, rather than by the well known "exchange correlations" between identical particles.

III. Quantum Entanglement and Nonseparability

Certain features of quantum physics are undeniably strange, because they contradict the intuitive, and seemingly reasonable, assumptions about how the world should behave that can be deduced from classical physics. Nonseparability and QE have emerged as the most emblematic features of quantum mechanics. Briefly stated, one can define entangled quantum states of two (or more) particles in such a way that their global state is perfectly defined, whereas the states of the separate particles remain totally undefined. Some thinking was necessary to realize how strange this is. In 1935, it led Einstein, Podolsky, and Rosen[11] to suggest that quantum mechanics is incomplete, on the basis that any theory of nature must be both "local" and "realistic".[11−13] In short, local realism, indispensable for classical mechanics, is the idea that, because the properties of one particle cannot be affected by a particle that is sufficiently far away, all properties of each particle must exist before they are measured. But nonseparability or QE contradicts this sort of local realism.[4,11−13]

Thirty years after the seminal EPR (Einstein, Podolsky, and Rosen) paper,[11] through the discovery of Bell's inequalities,[13] it became possible to test experimentally this fundamental contradiction between classical and quantum mechanics. Nowadays, it is fair to say that the overall agreement with quantum mechanics seen in all the experimental tests is already outstanding; compare, for example, ref 14. Thus, one can safely conclude that quantum mechanics is a complete theory and cannot be reconciled with classical physics.

Let us give a simple example of an entangled, nonseparable state. Let A and B be two protons of neighboring C−H bonds of one molecule (in our experiment: iso-C_4E_1, see in a later section). Furthermore, let the one-particle wave functions ψ_i (and ϕ_j) represent possible quantum states of proton A (and proton B) in the "first" (and "second") C−H bond. Because protons A and B do not exchange their positions, all ψ_i (all ϕ_j) are located around the classical position of proton A (of proton B). Quantum mechanics predicts that a possible state Ψ(A, B) of these two protons is given by

$$\Psi(\mathrm{A, B}) = c_1\psi_1(\mathrm{A})\cdot\phi_1(\mathrm{B}) + c_2\psi_2(\mathrm{A})\cdot\phi_2(\mathrm{B}) + ... \tag{2}$$

If the sum in the right-hand side (rhs) of this equation contains at least two terms, then Ψ(A, B) represents an entangled (also termed nonseparable, not factorizable, nonclassical, EPR cor-

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[11] Einstein, A.; Podolsky, B.; Rosen, N. *Phys. Rev.* **1935**, *47*, 777−780.

[12] Penrose, R. *The Emperor's New Mind*; Penguin: New York, 1991.

[13] Bell, J. S. *Physics* **1964**, *1*, 195−200.

[14] Karlsson, E. B., Brändas, B., Eds. Proceedings of the Nobel Symposium 104: Modern Studies of Basic Quantum Concepts and Phenomena. *Phys. Scr.* **1998**, T76.

related, etc.) state. This possible form of the two-proton state $\Psi(\mathrm{A, B})$ is in line with the basic superposition principle of quantum mechanics. Obviously, this $\Psi(\mathrm{A, B})$ does *not* factorize into an unentangled (also termed product) state $\Psi'(\mathrm{A})\cdot\Phi'(\mathrm{B})$, in which the wave function $\Psi'(\mathrm{A})$ depends only on coordinates (or, more generally, degrees of freedom) of proton A, and Φ' only on those of B.

Entangled states have strange properties, from the viewpoint of classical mechanics. For example, if one actually performs a local measurement on proton A and finds it in a specific state, such as $\psi_2(\mathrm{A})$, then it follows immediately and instantaneously that the "distant" proton B is in the specific state $\phi_2(\mathrm{B})$, without performing any measurement on B. (This follows from the basic reduction postulate of quantum mechanics; see refs 3 and 15, for example.) How strange this is becomes obvious by noting that the above reasoning is independent of the actual distance between A and B. Indeed, in a successful experiment demonstrating quantum cryptography using entanglement between photon pairs, this distance was about 23 km.[16]

The experiments presented here strongly suggest that spatially nonseparable, entangled states between protons in molecules do exist in the subfemtosecond time scale. Thus, in light of the preceding considerations, one may ask the following questions: Where does quantum entanglement (QE) come from? What causes the coupling between (two or more) particles leading to QE?

A. Exchange Correlations. There is a well established quantum mechanical effect leading to QE: the effect of exchange correlations arising from the identity of particles.[15] For example, such correlations lead to formation of ortho- and para-hydrogen, the wave functions of which exhibit spatial and spin entanglement. The spatial part of the total wave function of a H_2 molecule is given by

$$\Psi(\mathrm{A, B}) = \frac{1}{\sqrt{2}}[\psi(\mathrm{A})\cdot\phi(\mathrm{B}) \pm \psi(\mathrm{B})\cdot\phi(\mathrm{A})] \qquad (3)$$

where the "+" and "−" cases are combined with a singlet and a triplet spin state, respectively. Here, ψ and ϕ are single-particle states. Note that, as also in eq 2 above, this wave function does not factorize into an unentangled state, such as $\psi'(\mathrm{A})\cdot\phi'(\mathrm{B})$.

We believe that this type of QE, although possible, may be of less importance in our NCS experiments, for the following reasons:

(a) In the molecular systems under consideration, the overlapping of the spatial wave functions of two adjacent protons is negligible. It then follows from standard quantum mechanics that there is no need to antisymmetrize a two-proton state. For a clear presentation, see section 6.3 of Sakurai's textbook.[15]

(b) It should be noted that the protons under consideration do not occupy fully equivalent (and thus indistinguishable) sites, because the electronic bondings and/or (intra- and intermolecular) environments of different protons are not fully identical. This implies that the protons may become "distinguishable" by virtue of their interactions with their environments. This process is well known in many-body physics, where one often speaks about "dressing" of particles with "environmental degrees of freedom". (Such dressed particles are often called quasiparticles.)

(c) In the considered systems, protons (deuterons) of C−H (C−D) bonds do not exchange their positions. So, there is no real physical process leading to a positional exchange of two protons (such as, e.g., the free rotation of a H_2 molecule), which would correspond to the mathematical permutation of A and B in eq 3.

B. Dynamical Entanglement. There is a universal mechanism causing QE in interacting systems, which, however, is less known in the field of chemistry. Because of its relevance to the NCS experiments (see in a later section), it is described here in some detail.

For the following, it is *not* necessarily assumed that A and B are indistinguishable particles in the sense of quantum mechanics. The two particles, having Hamiltonians H_A and H_B, may interact either directly (e.g., through Coulombic forces) or indirectly (via a third subsystem, e.g., environmental electronic charges), the interaction Hamiltonian being

$$V_\mathrm{AB} \equiv V(q_\mathrm{A}, q_\mathrm{B}, q_\mathrm{env}) \qquad (4)$$

where q_x represents dynamical variables of system x and q_env refers to the additional degrees of freedom (usually called "the environment") being involved in the interaction. As usually assumed, let the state of the composite system "A and B", in short AB, at time $t = 0$ be not entangled, that is,

$$\Psi_\mathrm{AB}(0) = \Psi_\mathrm{A}\cdot\Psi_\mathrm{B}. \qquad (5)$$

In all nontrivial cases, V_AB does *not* commute with H_A or H_B, respectively,

$$[V_\mathrm{AB}, H_\mathrm{A}] \neq 0, \quad [V_\mathrm{AB}, H_\mathrm{B}] \neq 0. \qquad (6)$$

According to basic quantum mechanics, it then follows that, for $t > 0$, the complete evolution operator of the composite system AB,

$$U_\mathrm{AB}(t) = \exp\{-i(H_\mathrm{A} + H_\mathrm{B} + V_\mathrm{AB})t/\hbar\} \qquad (7)$$

does *not* factorize into a product of two "individual" evolution operators, U_A and U_B, representing the dynamics of the individual systems A and B, respectively.[3,15] Consequently, the wave function at time t, $\Psi_\mathrm{AB}(t) = U_\mathrm{AB}(t)\Psi_\mathrm{AB}(0)$, does not separate into a product of two wave functions, each of them representing the state of one of the two systems A and B;[15] that is,

$$\Psi_\mathrm{AB}(t) = U_\mathrm{AB}(t)\ \Psi_\mathrm{AB}(0) \neq \Psi'_\mathrm{A}(t)\cdot\Psi'_\mathrm{B}(t). \qquad (8)$$

As discussed above, this is tantamount to saying that $\Psi_\mathrm{AB}(t)$ represents an entangled state, and thus, (a part of) the degrees of freedom of A and B are inextricably intertwined. This wave function is then of the type given by eq 2.

Thus, QE is expected to appear quite naturally in interacting systems, like the condensed molecular systems studied in our NCS experiments. Note that the above dynamical process leading to QE is independent of the "exchange correlations mechanism" discussed above. Moreover, it should be emphasized that the QE considered here does not concern all degrees of freedom of systems A and B, but only those appearing in the interaction Hamiltonian, V_AB. This shows that *spatial* QE is of fundamental importance, because the strongest interactions of the nuclei in our molecular systems are given by the Coulombic interactions (concerning nuclei and electrons), which depend on the spatial degrees of freedom of the participating particles. Clearly, spin degrees of freedom are less important in this context.

It should be also mentioned that this type of QE creation is dominant in all investigations concerning the modern (scientific

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[15] Sakurai, J. J. *Modern Quantum Mechanics*; Addison-Wesley: Reading, 1995.

[16] Müller, A.; Zbinden, H.; Gisin, N. *Europhys. Lett.* **1996**, *33*, 335−339.

and technological) fields of quantum computation, information, communication, and cryptography. Controlling the interaction Hamiltonian(s) V_{AB} makes it possible to engineer various degrees (and types) of entanglement; compare refs 5.

IV. Results

Our NCS results presented here concern the detection of the considered QE effect in a solution of iso-C_4E_1 in D_2O, with molar composition iso-C_4E_1:D_2O = 0.0223:1 (see also section VI). As discussed below, the dilution of the amphiphile in D_2O was employed in order to increase the distance between hydrogens belonging to different molecules, thus increasing possible intramolecular contributions to the QE of protons as compared with the intermolecular ones. (This dilution also reduces the "strong" H-recoil signal, thus making the analysis of the measured time-of-flight (TOF) spectra more reliable.)

It is a crucial advantage of the NCS technique that the H- and D-peaks are well resolved. This is due to the high energies (or, equivalently, short de Broglie wavelengths) of the incoming neutrons and the related high energy and momentum transfers (see section VI). For small neutron scattering angles θ, however, the recoil peaks of C and O of the liquid mixture, and that of Nb of the metallic can, do overlap, see Figure 1b. Because of this overlapping, a considerable experimental effort has been made to determine the joint intensity of the C and O peaks, in relation to the intensity of the Nb peak. For this, 8 detectors (of 32 available ones) have been positioned in the "backward" scattering regime ($\theta > 90°$), where the momentum transfers are sufficiently larger than in the "forward" direction ($\theta < 90°$), thus causing a well visible separation of the maxima of the C and O peaks from the Nb peak; see Figure 1a (a separation of the C and O peaks is impossible with the energies of neutrons available at ISIS). Then, the ratio of the peak areas $(A_C + A_O)/A_{Nb}$ is determined. Note also that no H recoil peak exists in the "backward" direction (because neutrons and protons have the same mass and because of trivial kinematics of collision).

Having thus determined the joint intensity of the C and O recoil peaks relative to that of the Nb peak, the validity of the conventional theoretical expectation, eq 1, can be tested as follows. First, from the NCS spectra in the "forward" scattering direction, we determine the ratio $A_H/(A_C + A_O + A_{Nb})$. Second, having determined the ratio $(A_C + A_O)/A_{Nb}$ from the "backward" direction, we straightforwardly determine the ratio

$$R_{exp}(H) = A_H/(A_C + A_O), \tag{9}$$

too. R_{exp} denotes the experimentally determined ratio, to be distinguished from the conventionally expected one, R_{conv} (see below). Note that A_O in the denominator of this ratio refers to iso-C_4E_1 and D_2O as well, because both molecules contain oxygen. Moreover, it should be stressed that the calculations of all these ratios use experimentally determined quantities only; that is, they contain no additional fitting parameter. Third, we can immediately calculate the conventionally expected value of this ratio

$$R_{conv}(H) = N_H\sigma_H/(N_C\sigma_C + N_O\sigma_O), \tag{10}$$

(which is equal to 4.95 in our case), because the atom densities N_H, N_C, and N_O, are precisely known through sample preparation and chemical formulae (see section VI).

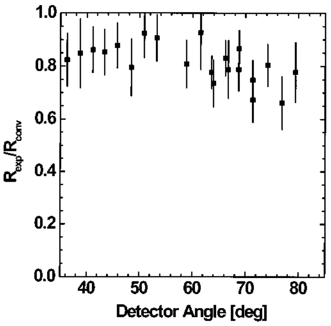

Figure 2. Ratio R_{exp}/R_{conv}, see eqs 9 and 10, associated with the neutron scattering from H, C, and O in iso-C_4E_1 and D_2O, as a function of scattering angle. The error bars (one standard deviation) are due to counting statistics only. The average of the experimentally determined values of R_{exp} is "anomalously" smaller than the conventionally expected value R_{conv} by ~20%.

The highly surprising result of our NCS experiment is that we find a strong deviation of the experimentally determined quantity $R_{exp}(H)$ from the conventionally expected $R_{conv}(H)$; that is,

$$R_{exp}(H) \approx 0.8 \cdot R_{conv}(H). \tag{11}$$

This effect is clearly visible in Figure 2. The quotient $R_{exp}(H)/R_{conv}(H)$ is presented here. The considered effect is given by the "anomalous" decrease of $R_{exp}(H)$, which is about 20%. Note that all detectors (positioned in scattering angles between 36° and 80°) have provided the same result, within experimental error, thus indicating an independence from momentum transfer or, equivalently, from the scattering time τ_{scatt} characterizing the duration of the neutron−proton collision process (see eq 14 of section VI).

V. Discussion and Conclusions

In the molecular systems containing C−H bonds considered in previous sections, the main mechanism causing spatial entanglement of protons is theoretically expected to be the Coulombic interaction between the protons and the "joint" molecular electronic charges; a general theoretical description of dynamical creation of QE is presented in section III.B (see also later in this work). Furthermore, one may expect on physical grounds that the decoherence of this QE is caused by "disturbances" associated (i) with many-body interactions in condensed phases as well as (ii) with interactions of the entangled protons with other intramolecular degrees of freedom. Recall also that the quantum dynamics describing decoherence is still not completely known and constitutes a "hot topic" of current research.[4,5,14,17]

As mentioned above, first evidence for this effect concerning protons of C−H bonds was recently found in solid polystyrene.[9] Moreover, in the work presented here, a high dilution of the amphiphile in D_2O was employed to reduce possible intermolecular contributions to the QE of protons. The results demonstrate that the magnitude of the anomalous QE effect is practically equal to that of H atoms of C−H bonds of solid (entirely protonated) polystyrene.[9] The combination of these results shows that the considered anomalous NCS effect is mainly of intramolecular origin. Furthermore, only one of the 14 H atoms of iso-C_4E_1 belongs to an O−H bond and can exchange with a D atom of D_2O, thus being "mobile" and more subject to fast decoherence. However, the magnitude of the

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(17) Giulini, D.; Joos, E.; Kiefer, C.; Kupsch, J.; Stamatescu, I.-O.; Zeh, H. D. *Decoherence and the Appearance of a Classical World in Quantum Theory*; Springer-Verlag: Berlin, 1996.

observed anomalous effect given by relation 11 is not affected by this H/D exchange, because (i) the numerical value of R_{exp}(H) is experimentally determined and (ii) the calculation of the conventionally expected value of R_{conv}(H) depends on the *total* number density of H in the sample.

According to present-day knowledge, chemical bonds are theoretically treated by solving the electronic Schrödinger equation, using the well known Born–Oppenheimer (BO) scheme[3] and obtaining the wave functions which describe the distribution of electrons in molecules. Being of fundamental importance for chemistry and biology, C–H bonds of polyatomic molecules are very well studied, for example, since the pioneering work of L. Pauling and T. Bustard; see ref 18. Furthermore, one describes a chemical reaction as the movement of nuclei considered as classical mass points or as quantum mechanical wave packets on electronic BO energy surfaces; see ref 2. Both treatments, however, have a common feature: the number of particles cannot change. More precisely, (i) in classical mechanics, particles never "disappear"; (ii) according to "standard" quantum mechanics (as presented in widely used textbooks, e.g., refs 3 and 15), in which the fundamental phenomenon of decoherence is discarded, the time evolution of the wave function of the particles is always unitary, thus conserving the normalization of the wave function and, equivalently, the number of particles.

As a consequence, these conventional theoretical approaches cannot account for the present NCS results revealing an anomalous decrease of the cross-section density of H atoms; see eq 1 and Figure 2. Here, a fundamentally different theoretical treatment is required, in which (i) the H atoms are subject to quantum entanglement and (ii) their states are subject to fast decoherence. The latter, representing a *nonunitary* time evolution process,[4,5,17] was shown to lead to the anomalous decrease of the cross-section density of protons.[9] More precisely, decoherence destroys the wave function given by eq 2, within a characteristic time τ_{dec}, and produces a nonentangled (or incoherent) mixture of states $\psi_i(A)\cdot\phi_i(B)$ with statistical weights $|c_i|^2$, where $i = 1, 2, ...$ In ref 9, we have theoretically established that the anomalous effect under consideration is caused by quantum entanglement and its subfemtosecond decoherence, if the condition (see eq 14)

$$\tau_{dec} \sim \tau_{scatt}$$

is fulfilled, that is, if the scattering time τ_{scatt}, which is known to lie in the subfemtosecond time range (see later), is roughly of the order of magnitude of the decoherence time τ_{dec}. It may be helpful to note here that, in both cases $\tau_{dec} \ll \tau_{scatt}$ and $\tau_{dec} \gg \tau_{scatt}$, the anomalous effect disappears (see the theoretical results presented under "Cases 1 and 2" in section IV of ref 9).

The short time character of the considered effect is further supported by a recent neutron interferometry (NI) experiment[19] on liquid H_2O–D_2O mixtures. It should be stressed that the NI technique measures the coherent scattering length density Nb_c of the samples. It was found that the measured Nb_c, as a function of the molar H/D compositions of the mixtures, is fully consistent with conventional theory, thus being allegedly in conflict[19] with our previous NCS results.[7] However, we demonstrated[20] that the latter is incorrect, for the simple reason that the characteristic time of NI (which is coherent and elastic) is many orders of magnitude larger than the characteristic scattering time τ_{scatt} of NCS (which, in contrast, is incoherent and highly inelastic). Therefore, no real contradiction between the results of the NI and the NCS experiments does exist.[20]

In section III.B, we considered the simplest "quantum dynamical type" of spatial QE between protons (and also electrons, see below) which we believe to be physically relevant in our NCS experimental context. As we discussed in detail, because the protons are spatially well localized in their C–H bonds and do not exchange their sites, the QE between two neighboring protons A and B should be of the type represented by eq 2, rather than of the hydrogen molecule type given by eq 3. In other terms, the well known "exchange correlations" between identical particles does not seem to play a dominant role in the present context. In this connection, a recent theoretical model[21] of our NCS effect should be mentioned, which, however, proposed the exchange correlations mechanism to be the sole source of QE.

With respect to chemistry, the following observation may be of considerable importance. The scattering time τ_{scatt} of our NCS experiments is of the order of magnitude of the characteristic time of the electronic rearrangements (τ_{electr}) accompanying the formation and/or breaking of a typical covalent bond in a molecule. In other words, within the subfemtosecond time window of this NCS process, there is no well defined separation of time scales of electronic and protonic motions, the latter being subject to the neutron–proton collision process. (It should be noted, however, that such a well defined time scale separation represents a necessary condition for the validity of the BO approximation; see ref 3.) Furthermore, in the setup of the present NCS experiment, the energy transfer from a neutron to a proton exceeds 5 eV for scattering angles larger than ~45°, which implies that the associated C–H bond is broken. Therefore, the results presented in Figure 2, taken together with their interpretation (see previously in this work and ref 9), show that the quantum phenomena of QE and decoherence play an important role in the dynamics of an elementary chemical reaction: the dissociation of a covalent C–H bond.

We attribute the observed anomalous decrease of R_{exp} (see eq 11 and Figure 2) to the light H atoms, rather than to the heavier atoms C or O. Moreover, the aforementioned subfemtosecond time scale of this effect and the fact that electrons and nuclei are strongly coupled because of the Coulombic interactions indicate that not only protonic but also electronic degrees of freedom (such as electrons "participating" in C–H bonds) may be involved in the short-lived QE under consideration.

In view of these considerations, one could speculate that protonic QE might also affect the rates of, and electron transfer in, various chemical and biochemical reactions involving H atoms. Indeed, this seems to be the case. Very recent electrochemical experiments explored the reaction rates of a water molecule splitting and/or hydrogen evolution from liquid H_2O, D_2O, and H_2O/D_2O mixtures at room temperature, measured as a function of the H/D composition. (In the frame of these investigations, a possible spin dependence of the protonic/deuteronic entanglement and its decoherence was assumed as working hypothesis.) The results revealed that these reaction rates strongly deviate from the H/D dependence predicted by standard electrochemical theory.[22]

In conclusion, the results and discussions presented above show that the subfemtosecond effect under consideration,

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(18) Levine, I. N. *Quantum Chemistry*; Prentice Hall: New Jersey, 1991.

(19) Ioffe, A.; Arif, M.; Jacobson, D. L.; Mezei, F. *Phys. Rev. Lett.* **1999**, *82*, 2322–2325.

(20) (a) Chatzidimitriou-Dreismann, C. A.; Abdul-Redah, T.; Streffer, R. M. F.; Hessmo, B. *Phys. Rev. Lett.* **2000**, *84*, 2036. (b) Ioffe, A.; Arif, M.; Jacobson, D. L.; Mezei, F. *Phys. Rev. Lett.* **2000**, *84*, 2037.

(21) Karlsson, E. B.; Lovesey, S. W. *Phys. Rev. A* **2000**, *61*, 062714-(1–7).

belonging to the field of fundamental chemistry, can be of considerable importance for a broad class of chemical and biological processes.

VI. Experimental Section

A. Sample Preparation. The molecule 2-isobutoxyethanol has been chosen, because it forms a homogeneous solution at room temperature and at the concentration used in this experiment, and because it will dissolve in water (or D_2O) over a relatively wide dilution range,[23] thus facilitating the NCS data accumulation and data analysis. Furthermore, this molecule contains only aliphatic C−H bonds (in contrast to our previous work on solid polystyrene[9] which also contains aromatic C−H bonds). The 2-isobutoxyethanol/D_2O solution was prepared by weighing 1.0235 ± 0.0001 g of iso-C_4E_1 and adding to it 7.7602 ± 0.0001 g of D_2O (99.9%; purchased from Euriso-Top), thus giving a solution with molar composition iso-C_4E_1:D_2O = 0.0223:1. After the neutron scattering measurement, the composition has been confirmed independently by density measurements with an accuracy of 0.1%. Hence, the error of the mixture composition is negligibly small compared to the error of neutron counting statistics.

The liquid sample was put in an annular Nb can which has been provided by the ISIS facility (Rutherford Appleton Laboratory). In contrast to the usually used aluminum or vanadium cans, this special can provides the feature that, because of the high mass of the niobium nuclei, a separation of the combined carbon/oxygen recoil peak (because of iso-C_4E_1 and D_2O) from the niobium recoil peak is possible. Thus, it is possible to relate the H recoil peak intensity A_H to the combined C/O recoil peak intensity ($A_C + A_O$), see section IV and Figure 1.

B. Instrument Description. The experiments have been done with the electron volt spectrometer (eVS) of the ISIS spallation source (Rutherford Appleton Laboratory, Oxfordshire, U.K.). The eVS instrument is a so-called inverted geometry spectrometer[24] which has been designed to measure directly atomic momentum distributions and single particle mean kinetic energies.[25] At the eVS instrument, the sample is exposed to a polychromatic neutron beam. It is the energy of the scattered neutrons which is analyzed. For this purpose, a nuclear resonance difference technique is used, which consists of the following. A gold foil situated between the sample and the detectors strongly absorbs neutrons over a narrow range of energies, centered at a specific Lorentzian shaped nuclear neutron absorption resonance (4908 ± 130 meV). Two measurements are taken: one with the foil between sample and detector and one with the foil removed. The difference between these two spectra gives the final time-of-flight (TOF) spectrum, examples of which are depicted in Figure 1 for (a) backward and (b) forward scattering angles. The numerical value of TOF refers to the time the neutrons need from the neutron moderator via the sample to the detector. At present, four banks of eight detectors each are available on the eVS instrument. For our experiment, three banks were put in the forward scattering direction between $35 < \theta < 80$ degrees (see Figure 2). The remaining bank was put in the backward scattering direction to extract the combined scattering signal of carbon and oxygen from that of the metallic niobium can containing the liquid sample (see Figure 1 and section IV.)

C. Incoherent and Impulse Approximations. In contrast to the work on structure determination in chemistry involving X-ray or neutron scattering in which the scattering is elastic and coherent, thus giving Bragg peaks, the scattering process in NCS is treated within the *incoherent approximation*.[26,27] The incoherent approximation, which means that interatomic interference effects are safely neglected and that each atom scatters independently from the other, is valid here because the momentum transfer q (10−120 Å^{-1}) or the wavelength of the incoming neutrons $\lambda < 0.1$ Å fulfills the requirement for incoherence that

$$q \gg \frac{2\pi}{d} \quad \text{or} \quad \lambda \ll d$$

where d is the nearest neighbor distance.

Under the prevalent experimental conditions of NCS, that is, high energy and momentum transfers, time correlations in the motion of a scatterer can be neglected,[26,27] because the characteristic time of the neutron−scatterer interaction (i.e., the "scattering time") is very short; see later in this work. Thus, the dynamic structure factor is accurately described by the *impulse approximation* (IA); that is,[26,27]

$$S(\mathbf{q},\omega) = \langle \delta(\omega - \omega_r - \mathbf{q}\cdot\mathbf{p}/M) \rangle \tag{12}$$

$$= \int n(\mathbf{p})\, \delta(\omega - \omega_r - \mathbf{q}\cdot\mathbf{p}/M)\, d\mathbf{p} \tag{13}$$

where $\langle ... \rangle = \sum p_n \langle n|...|n \rangle$ is the appropriate combined quantal and thermodynamic average (over the classical probabilities p_n) related with the condensed matter system. M and $n(\mathbf{p})$ are the mass and momentum distribution of the scattering nucleus, respectively, and $\omega_r = q^2/2M$ is the recoil energy. For convenience, one usually puts $\hbar = 1$. Equation 13 is of central importance in most NCS experiments, because it relates the scattering cross-section directly to the momentum distribution. Furthermore, $n(\mathbf{p})$ is related to the nuclear wave function by Fourier transform and, therefore, to the spatial localization of the nucleus.[25] It takes into account the fact that, if the scattering nucleus has a momentum distribution in its ground state, the δ-function centered at ω_r will be Doppler broadened.

Another crucial feature of the NCS method is the small value of the characteristic time τ_{scatt} of the neutron−nucleus interaction, the so-called "scattering time". It follows from the well established theory of NCS that each scattering angle θ corresponds to a specific momentum transfer (from the neutron to the struck nucleus, e.g., a proton) and to an associated value of τ_{scatt}. According to Sears[26] and Watson,[27] the scattering time may be defined by

$$q(\theta) v_0 \tau_{scatt} \approx 1 \tag{14}$$

where $q(\theta)$ is the momentum transfer depending on the detector angle θ and v_0 is the root-mean-square velocity of the nucleus before collision (i.e., in its initial state). For our purposes, the NCS technique is particularly suitable, because the scattering time, that is, the interaction time of the (epithermal) neutrons with the scattering nuclei, is sufficiently short, being in the subfemtosecond time scale.[7−10] This is a consequence of the large energy (3−150 eV) and momentum transfers (10−120 Å^{-1}) applied at the eVS instrument. The range of scattering times associated with the scattering angles shown in Figure 2 is τ_{scatt} = 0.05−0.6 fs for the neutrons scattered at H atoms in covalent C−H bonds.[9]

D. Data Analysis. The number of neutrons $C\Delta t$ scattered by identical nuclei (of an amorphous, nonmagnetic, homogeneous, and isotropic material) and collected in a detector during the time window Δt is proportional to the total scattering cross section σ and to the dynamic structure factor $S(q,\omega)$

$$C\Delta t \sim \frac{1}{4\pi} N\sigma \frac{k_1}{k_0} S(q,\omega) \tag{15}$$

where N is the number density of the nuclei, and k_1 and k_0 are the absolute values of the neutron wave vectors after and before the scattering process. q and ω are the momentum and energy that are transferred from the neutron to the system in the collision.

Introducing a scaling parameter[26]

$$y = \frac{M}{q}(\omega - \omega_r) \tag{16}$$

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[22] Sperling, J.; Tributsch, H.; Streffer, R. M. F.; Abdul-Redah, T.; Chatzidimitriou-Dreismann, C. A. *J. Electroanal. Chem.* **2000**, *477*, 62−70.

[23] Perron, G.; Quirion, F.; Lambert, D.; Ledoux, J.; Ghaicha, L.; Bennes, R.; Privat, M.; Desnoyers, J. E. *J. Solution Chem.* **1993**, *22*, 107.

[24] (a) Seeger, A. D.; Taylor, A. D.; Brugger, R. M. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1985**, *240*, 98−114. (b) Mayers, J.; Burke, T. M.; Newport, R. J. *J. Phys.: Condens. Matter* **1994**, *6*, 641−658.

[25] Mayers, J. *Phys. Rev. Lett.* **1993**, *71*, 1553−1556.

[26] Sears, V. F. *Phys. Rev. B* **1984**, *30*, 44−51.

[27] Watson, G. I. *J. Phys.: Condens. Matter* **1996**, *8*, 5955−5975.

and using the identity $\delta(ax) = \delta(x)/a$, the dynamic structure factor (eq 13) can be rewritten as

$$S(q,\omega) = \frac{M}{q}J(y) \tag{17}$$

For an isotropic harmonically bound nucleus the "neutron Compton profile" $J(y)$ assumes the Gaussian form

$$J(y) = \frac{1}{\sqrt{2\pi\sigma_y^2}} \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \tag{18}$$

which is centered at the recoil energy ω_r; σ_y is the standard deviation of the momentum distribution. When different atomic masses M_i are present in the sample, the scattered intensity consists of different peaks centered at different recoil energies $\omega_{r,i}$, which correspond to different TOF values in the spectrum; see Figure 1. For each nucleus of mass M the intensity of which is to be analyzed, TOF spectra are fitted with the aid of a Gaussian (eq 18) convoluted with the instrument resolution function.[24b] In our data analysis, only the amplitude is a fitting parameter. Figure 1 shows examples of measured TOF spectra (including error bars) and their fitted spectra (full lines). The area A_i under the Gaussian is determined incorporating the correction for the intrinsic angle (or momentum transfer) dependence of the scattering intensity; for more technical details, see ref 9.

The data analysis procedure also incorporates the well known transformation from the "free atom" to the "bound atom" cross section, i.e $\sigma_{\text{bound}} = \sigma_{\text{free}}\,(1 + m/M)^2$ (m: neutron mass), which is particularly relevant for light nuclei, like H, in order to facilitate the comparison between experimental NCS results and tabulated cross section values.[28]

According to conventional theory, the thus determined peak areas A_i are proportional to the product of the total scattering cross section σ_i and the number density N_i of atoms of mass M_i present in the sample, that is, $A_i \sim \sigma_i N_i$. Therefore, if the number densities of two atoms with different masses are known, then the following equation (see section II) holds strictly within conventional theory:[7]

$$\frac{A_H}{A_X} = \frac{N_H\sigma_H}{N_X\sigma_X} \tag{1}$$

where N_H/N_X is the ratio of the particle number densities of H and X, which is precisely known through sample preparation and/or chemical formulae (see section VI.A). σ_H and σ_X are the total neutron scattering cross sections of H and a different atom X. Thus, because the conventionally expected values of σ_H and σ_X are given in standard tables,[28] the validity of eq 1 is immediately subject to experimental test.

Because of the high transfers of energy and momentum applied at the eVS instrument, the recoil peaks of H, D, and the other heavier atoms (like C, O, and Nb) in the directly measured TOF spectra are well separated for a wide range of scattering angles; see Figure 1. This fact is crucial for the precision and reliability of our experiments, because it makes possible the direct determination of the ratio A_H/A_X of the areas under the recoil peaks of H and X (with X = D, C, O, Nb, etc.).

In contrast to our previous experiments on metallic niobium and palladium hydrides which showed a strong dependence of the anomalous decrease of the scattering cross section density of hydrogen on the scattering time 0.2 fs $< \tau_{\text{scatt}} < 0.6$ fs,[8,29] the strong decrease of the scattering cross section density of hydrogen in iso-C_4E_1 of this work appeared to be independent of τ_{scatt} within present experimental error. This may stem from the fact that different time windows (here 0.05 fs $< \tau_{\text{scatt}} < 0.6$ fs) are involved in the two different systems, because τ_{scatt} is also dependent on molecular properties (i.e., v_0) and not only on momentum transfer (see eq 14).

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[28] Sears, V. F. *Neutron News* **1992**, *3*, 26−37.

[29] Chatzidimitriou-Dreismann, C. A.; Abdul-Redah, T.; Sperling, J. *J. Alloys Compd.*, in press.