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Anomalous neutron Compton scattering from molecular hydrogen

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Application of neutron Compton scattering, which operates in the attosecond time scale, to (a) the equimolar H_2-D_2 mixture and (b) the mixed-isotope system HD (liquids, both at 20 K), reveals a strong anomalous shortfall (about 30%) of the ratio $R=\sigma_H/\sigma_D$ of H and D cross sections. This striking effect is similar to that observed in liquid H_2O-D_2O mixtures [C. A. Chatzidimitriou-Dreismann *et al.*, Phys. Rev. Lett. **79**, 2839 (1997)]. Crucially, the shortfall of R is equal in both samples (a) and (b). This result demonstrates that quantum exchange correlations of identical nuclei play no significant role in this effect, thus refuting corresponding theoretical models claiming its interpretation. In contrast, our findings are consistent with alternative theoretical models, in which attosecond dynamics of electronic degrees of freedom (via violation of the Born-Oppenheimer approximation) is considered to participate significantly in the dynamics of an elementary neutron-proton (-deuteron) scattering process. Possible implications for attosecond chemical dynamics, e.g., the onset of bond breaking, are mentioned.

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I. INTRODUCTION

The importance of attosecond laser techniques for the investigation of "ultrafast" quantum processes in matter has been recently demonstrated.[1–4] Compton scattering may also provide information about attosecond dynamics. In his original studies, Compton investigated the energy loss of an *X* photon colliding with an electron.[5] The development of spallation neutron sources opened the way to apply the same effect to neutron scattering from condensed matter, often denoted as neutron Compton scattering (NCS).[6]

Usually NCS is utilized in order to measure the momentum distributions of "single particles," that is, of a nucleus in the ground state.[6,7] For example, the momentum distribution of the protons of liquid H_2 was measured with NCS in great detail.[7] In contrast, we proposed and applied this technique to the investigation of (theoretically predicted) short-lived and spatially restricted quantum-entangled states of protons (and deuterons) in condensed matter at ambient conditions.[8] These investigations revealed the following effect: The "anomalous" reduction of scattering intensity of *epithermal* neutrons (say, with energy about 1–200 eV) from protons, with sufficiently *large* energy and momentum transfers which is tantamount to sufficiently *short* (i.e., subfemtosecond) neutron-proton scattering time; see below.[9] In oversimplified terms, a part of the protons seems to "disappear."[10] Until now, this striking phenomenon has been observed in a considerable variety of systems.[8,11–15] Very recently, it has been confirmed with an independent experimental method, i.e., electron-proton Compton scattering (ECS) (Refs. 15–17); see also Refs. 10, 18, and 19. However, no complete theoretical explanation of the anomalous findings has been given yet.

In this paper we report NCS investigations of liquid H_2, mixtures of H_2 and D_2, and molecular HD (all at 20 K). Molecular hydrogen represents the simplest (and theoretically best investigated) chemical bond, and the intermolecular interactions in the liquid are weak. Crucial for this work is the fact that H_2 and D_2 exhibit the well-known quantum exchange correlations between identical particles,[20] which obviously are absent in HD. Based on this fact, we shall demonstrate that the presented NCS results provide a decisive experimental test of conflicting predictions made by published theoretical models,[21–26] thus leading to the refutation of one category of them.

II. EXPERIMENT

The NCS experiments were carried out with the electron-volt spectrometer VESUVIO (earlier EVS) (Refs. 27 and 28) of ISIS (Rutherford Appleton Laboratory, UK), which presently is the world's most powerful pulsed spallation neutron source. The experimental setup provides incident neutrons with kinetic energy of several tens of electron volts and a typical de Broglie wavelength $\lambda < 0.1$ Å. Since λ is much shorter than the internuclear distances, the scattering looks virtually identical to the scattering that would be observed if it were completely incoherent. Furthermore, the measured recoil peaks of H (and D) are well separated from those of heavier nuclei in the time-of-flight (TOF) spectra. This is clearly demonstrated in the inset of Fig. 1, where the TOF spectrum of HD at scattering angle $\theta=67.1°$ is shown. The peak areas A_X of atoms X were extracted from the double differential cross section $d^2\sigma/dEd\Omega$; the latter is determined from a TOF spectrum (taken at a fixed scattering angle θ) by standard procedures.[28] In the fitting procedure, the nuclear momentum distribution $n_X(p)$ of atom X is assumed to be Gaussian shaped, and the instrumental resolution function is incorporated as a convolution with the function $n_X(p)$. So-called final-state effects (FSE) are taken into account; they have been shown to cause only about ±1% deviations in the values of peak areas.[28] For a recent detailed account of the data analysis, experimental procedures, and various instrumental tests, see Ref. 28.

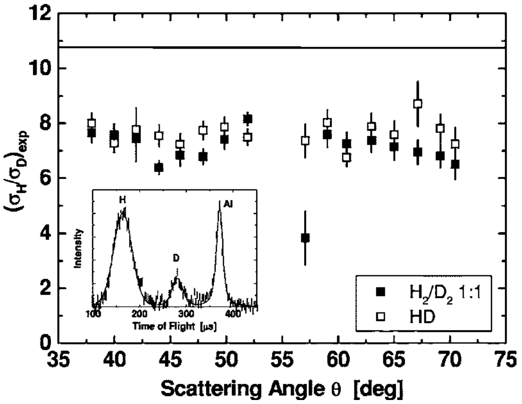

FIG. 1. The experimentally determined (with EVS) ratio $(\sigma_H/\sigma_D)_{exp}=A_H/A_D$ of H and D cross sections for (a) the H_2-D_2 mixture with atomic ratio H:D=1:1 (full squares), and (b) the mixed-isotope system HD (open squares). $T=20$ K. The data were recorded with the same experimental setup. The horizontal line at 10.7 gives the conventionally expected value; see Eq. (2). The scattering angles $\theta\approx 75°-35°$ correspond to scattering times $\tau_{scatt}\approx 200$–1000 as. Inset: TOF spectrum of HD at $\theta=67.1°$. The Al recoil peak is due to the container (flat, sample thickness 1 mm) used. One of the data points at $\theta\approx 57°$ is an outlier, which is absent in later measurements; cf. Fig. 2.

In the following, it is important to note that in NCS the duration of a neutron-proton collision (also called scattering time, τ_{sc}) amounts to about 200–1000 as; 1 as (attosecond) $=10^{-18}$ s.[11–13] For such short times one may expect that protonic entanglement is not destroyed by decoherence,[29] the latter being known to be very fast in condensed matter (see also below). The above estimate follows from the formula (derived in the frame of the so-called impulse approximation)[6,30,31]

$$\tau_{sc}|\mathbf{q}|v_0 \approx 1, \tag{1}$$

where v_0 is the root-mean-square velocity of the struck proton in the ground state before collision, and $\hbar\mathbf{q}$ is the momentum transfer from the neutron to the proton. These short scattering times are a consequence of the large energy (ΔE) and momentum transfers possible with the VESUVIO instrument (for the neutron-proton collision): $\Delta E\approx 1$–100 eV, $|\mathbf{q}|\approx 30$–200 Å^{-1}. Due to the large energy transfer—depending on the scattering angle—involved, the NCS process may cause breaking of covalent C-H (and other) bonds.[12,13,15] Therefore, it is conceivable that NCS may provide valuable information about short-time quantum dynamics of chemical reactions, i.e., the onset of bond breaking.

The liquid samples (at $T\approx 20$ K; working pressure ≈0.58 bar; densities ≈0.021–0.025 molecules/Å^3) were put in a flat Al container, providing a sample thickness of about 1 mm (wall thickness: 1 mm; sample volume: 2.6 cm^3). The mean intermolecular distance is about 3.4–3.6 Å, whereas the distance between two nuclei in a hydrogen molecule is about 0.74 Å. The high purity of the HD sample has been confirmed by analyzing its vibrational spectrum (recorded with the TOSCA spectrometer of ISIS). In contrast to the mixtures of H_2O and D_2O, no H/D exchange takes place here.

In order to test the relevance of competing theoretical models of the effect under consideration (see the discussions below), we investigated in particular:

(a) the equimolar mixture of H_2 and D_2, and

(b) the monomolecular liquid HD,

using the same experimental setup. Both systems have the same atomic composition, that is, H:D=1:1. But, system (a) contains homonuclear molecules and thus exhibits exchange correlations between indistinguishable particles,[20] whereas the heteronuclear system HD does not comprise such correlations.

Basic NCS theory[6,28] implies that the equation

$$\frac{A_H}{A_D}=\frac{N_H\sigma_H}{N_D\sigma_D}, \tag{2}$$

should be strictly valid; cf. Refs. 8, 15, and 28 for both systems. A_X represents the (measured) area under the recoil peak of nuclei X, σ_X is the tabulated total cross section of those nuclei, and N_X the particle number density.

III. RESULTS

The experimental NCS results (see Fig. 1) reveal the following features:

(i) For both samples, the basic Eq. (2) is violated; the measured ratio $(\sigma_H/\sigma_D)_{exp}=A_H/A_D$ is about 30% lower than its conventionally expected value $\sigma_H/\sigma_D=10.7$, thus disagreeing with Eq. (2). Furthermore, this anomaly is independent of the scattering angle θ and thus of momentum transfer $\hbar q$.

(ii) Within experimental error, both systems exhibit the *same* amount of anomalous scattering. This implies that quantum exchange correlations between pairs of protons (and deuterons) play no significant role in these observations (see below).

Due to the considerable theoretical implications—see Sec. IV below—of the NCS results obtained from the mixed-isotope system HD, these investigations have been extended using the "double-difference" (DD) technique, which was recently implemented at VESUVIO.[27,28] This technique provides an improved energy resolution (reduced in width by a factor of about 2; see Ref. 28), and it also completely removes the tails of the Lorentzian part of the absorption resonance of the Au analyzer.[28] NCS results obtained by application of the standard (also called "single difference," in short SD) technique are compared with those obtained using the DD technique in Fig. 2. The good agreement between the DD and SD data clearly refutes recent claims[34] that the considered effect should be an artifact caused by the overlap of H and D peaks in connection with an improper implementation of the Lorentzian resolution function. Therefore, this result gives further support to the significance of results (i) and (ii).

Further experiments have been carried out on pure H_2 and several H_2-D_2 mixtures,[33] which concerned the ratios A_H/A_{Al} of the H-peak area A_H to the Al-peak area A_{Al} (the latter being due to the cell containing the liquid). The ob-

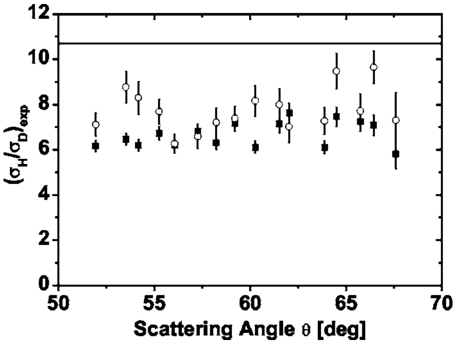

FIG. 2. The experimentally determined (with VESUVIO) ratio $(\sigma_H/\sigma_D)_{exp}$ from liquid HD at 20 K, for scattering angles $\theta > 50°$ providing spectra with good H- and D-peak separation. Full squares: Data obtained with the standard "single difference" technique. Open circles: Results obtained with the "double-difference" (DD) technique (Refs. 27 and 28).

tained results have been shown to remain unchanged under considerable variations of the instrument's scattering geometry and the sample's H:D atomic composition.[33] This further supports the good working conditions of the instrument.

IV. DISCUSSION

The θ independence of the experimentally determined cross-section ratio $(\sigma_H/\sigma_D)_{exp}$ is similar to that observed in H_2O-D_2O mixtures[8,28] and polymers.[15] On the other hand, a very strong θ-dependent ratio $(\sigma_H/\sigma_M)_{exp}$ (M: Nb, Pd) was found in the metallic hydrides Nb-H-D and Pd-H-D.[11] This difference, which was hitherto not quantitatively understood, may be caused by the specific decoherence mechanisms the struck protons are subject to due to their different electronic environments in these materials.[32]

VESUVIO is a unique instrument,[27] and consequently there has been criticism[34,35] that our effect[8] has not been confirmed on other instruments and/or with other independent methods, claiming that it may be an artifact of the experimental method and/or inappropriate data analysis.[34,35] However, these claims have been scrutinized thoroughly (by the instrument scientists of ISIS) with extensive and detailed experimental tests as well as Monte Carlo simulations, and they were refuted unequivocally.[28]

In this context, obviously, it is crucial to note that very recently this effect has been indeed confirmed by applying an independent experimental method: *electron Compton scattering* (ECS) from protons in a solid polymer, at the Australian National University, Canberra.[10,15–19] Moreover, these ECSs and their accompanying NCS results demonstrated that the considered effect is independent of the two fundamental interactions involved, i.e., the electromagnetic and strong interactions.[10,15,18]

The results of the first ECS investigations seemed to be partially affected by uncertainties concerning determination of intensities.[16] Recently, however, these and further experimental issues have been experimentally investigated and fully clarified in an extended publication by Vos *et al.*[17]

Originally, it was proposed[8] that the considered effect is caused by short-lived and spatially restricted entanglement. Since the typical neutron- and electron-proton interaction time in NCS and ECS (i.e., τ_{sc}) lies within the attosecond range, it is expected that decoherence may still not be fully effective. Recent published theoretical models attribute this effect to:

(A) Modification of scattering due to "identity of particles" in the scattering system. The influence on scattering of entanglement of the spin and spatial degrees of freedom of identical particles (i.e., quantum exchange correlations) has been stressed in Refs. 21 and 22. In particular, NCS from pairs of protons (and deuterons) has been calculated.

(B) Contribution of electronic degrees of freedom to the dynamics of a struck proton (deuteron). For example, breakdown of the Born-Oppenheimer (BO) approximation in the final state of the NCS process and (B1) additional excitations of the electronic system,[25,26] and/or (B2) decoherence accompanying short-lived spatial entanglement of a struck proton with adjacent electrons and perhaps also nuclei.[12,23,24] In the models of this category, spin entanglement and/or quantum exchange correlations between identical particles play no role.

The well-documented theoretical model (A) (Ref. 21) has been applied[22] to our original NCS results from H_2O-D_2O mixtures.[8] But, it fails to interpret the above results, because it predicts that no "anomaly" can exist in HD. Namely, not only intramolecular, but also intermolecular exchange correlations of protons cannot exist in the HD sample. To show this, note that the spin-spin coupling between two protons of two different HD molecules is dipolar and an estimate of its magnitude (for a typical distance of 3 Å, see above) amounts to $\Delta\nu \approx 28$ kHz,[36] which corresponds to about 10^{-10} eV or 10^{-6} K. This implies that spin coupling, and exchange effects, between protons belonging to different molecules are minimal. In contrast, *intra*molecular spin (and spatial) entanglement does clearly exist in H_2 and D_2. Consequently the theoretical model of Ref. 21 is in obvious conflict with the experimental result (ii), i.e., the same amount of anomalous scattering in both systems.

These considerations have an imperative implication: Any theoretical model assuming "identity" or "indistinguishability" of (two or more) scattering particles to be a necessary condition for the appearance of the considered effect is in conflict with result (ii). This implication is in line with a recently presented full calculation of the scattering function $S(q,\omega)$ by Sugimoto *et al.*,[37] who demonstrated that indistinguishability of particles cannot represent the physical origin of the observed effect.

In contrast, these experimental findings do not contradict the theoretical models of category (B), as the following illustrative estimate indicates. The characteristic time τ_{sc} of the neutron-proton collision appears to be similar to the characteristic time of "electron motion."[12] Additionally, for scattering angles $\theta > 55°$, the energy transfer from a neutron to a proton is large enough to exceed the H-H or H-D bond energy. A simple classical estimate then shows that, for $\Delta E = 50$ eV and a time $\Delta t = 500$ as, the struck proton moves about 0.5 Å away from its initial position. It thus follows that the well-known BO approximation may not be applicable in the present physical context. This has already been stressed[12,13] and constitutes the starting point of the theoretical models of Refs. 23–26. Here, however, it should be stressed that a detailed treatment of the BO failure and a quantitative estimate of its contribution to the considered NCS anomaly does not exist yet, as convincingly discussed in Ref. 38.

V. ADDITIONAL REMARKS AND CONCLUSIONS

Most recently, Senesi *et al.*[39] investigated in the most rigorous way all the criticisms raised in Ref. 34 concerning the effects of instrumental resolution and filter absorption profile, by applying directly the data analysis method of Blostein *et al.* on NCS spectra from orthorhombic ordered HCl. The obtained results demonstrated unequivocally the presence of a 34% anomalous reduction of the H cross-section density ($N_H\sigma_H$). The same anomaly was also obtained (from the same NCS spectra) applying the standard data analysis procedure of VESUVIO. Thus, it was concluded that, confirming the findings of Ref. 28, all the past NCS work on the anomalous shortfall of scattering intensity from protons appears basically sound and reliable within an accuracy level of 5–6%.[39]

Very recently, applying NCS in the 25–150 keV range, the neutron integrated scattering intensities from pure liquid H_2O relative to that of pure D_2O and also relative to H_2O-D_2O mixtures were measured by Moreh *et al.*[40] The scattering intensity ratios were claimed to agree with expected values deduced from the tabulated total cross sections within an accuracy of 2–3%. Currently, however, it was demonstrated[41] that the data reduction scheme, as performed by Moreh *et al.*, was incomplete. Consequently, the complete analysis based on standard NCS theory in the impulse approximation[28] reveals a strong anomalous ratio of scattering intensity of H_2O with that of D_2O of about 20%, thus being in surprisingly good agreement with the results of the original experiment at ISIS.[41]

Taken together, the above results and considerations indicate that the observed “anomalies” reflect a sub-femtosecond property of chemical bond dynamics, e.g., of the onset of bond breaking. Representing the simplest (and best investigated) chemical bond, molecular hydrogen appears to be particularly suitable for further theoretical investigations and/or tests of predictions of various theoretical models.

Concluding, the preceding results provide new crucial insights into the physical nature of the considered effect: They show that the equimolar H_2-D_2 mixture and the mixed-isotope system HD exhibit the same anomaly; see result (ii). This proves directly that entanglement due to identity of particles (and the associated exchange correlations) can be safely excluded as the main physical reason causing the effect. Consequently, this leads to the refutation of a significant part of published theoretical works, thus providing guidance for further theoretical investigations, and related experimental tests, towards the interpretation of the effect under consideration.

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