Anomalous Quasielastic Electron Scattering from Single H_2, D_2, and HD Molecules at Large Momentum Transfer: Indications of Nuclear Spin Effects

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Quasielectron electron scattering from gaseous H_2, D_2, a 50:50 mixture of H_2 and D_2, and HD is investigated with 2.25 keV impact energy and a momentum transfer $\hbar q$ of 19.7 a.u. The energy transfer is less than the dissociation energy. The spectral positions of the H and D recoil peaks agree with Rutherford scattering theory. Surprisingly, in the spectrum of the 50:50 H_2-D_2 mixture, the integrated intensity of the H peak is 31% ± 4% lower (as compared to that of D) than predicted by Rutherford scattering, despite equal screening of nuclear charges by the electrons. In contrast, the ratio of scattering intensities from H and D in HD agrees with the predictions of Rutherford scattering. Comparison is made with neutron Compton scattering results from the same systems, but at higher energy transfers causing bond breaking. Possible theoretical explanations are outlined.

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Molecular hydrogen, which provides the simplest chemical bond in nature, has always played a key role in the evaluation of new theoretical (quantum-chemical) and experimental (spectroscopic) methods. For example, the dissociation energy of H_2 has been the focus of long and well founded spectroscopic investigations by Herzberg and Monfils [1] and related extensive quantum-chemical calculations [2]. These studies revealed a serious discrepancy (by ca. 4 in 36 118 cm^{-1} [2]) between experimental and theoretical results. Finally, after 10 years of investigations, further experiments [3] confirmed the quantum-chemical predictions. This curious case was considered by many as a "triumph" of quantum chemistry. Nowadays it is often assumed that "all" spectroscopic properties of isolated H_2 molecules are theoretically understood and can be calculated with arbitrary precision.

In this Letter, we present results of a new quasielastic electron scattering experiment from H_2, D_2, and HD (gases, $T \approx 298$ K), which are shown to be in clear contrast to conventional expectations. In short, (a) the experiments on H_2 and D_2 reveal a striking anomalous shortfall of scattering from H atoms (as compared to that from D), which amounts to ca. 30%, and (b) by contrast, the corresponding results from HD show no such anomaly. These results are remarkable because the (possible) screening of the nuclear charges by the electron density is the same in all three molecules. It should be noted that the energy transfer in the quasielastic scattering is less than the dissociation energy of the molecules. Connection with related results of other experimental methods (e.g., neutron Compton scattering), and with existing theoretical models, is made below.

Electron energy loss spectra at near zero energy loss recorded at large momentum transfer (high impact energy and large scattering angle) from both gaseous [4–6] and solid [7–10] multielement samples exhibit multiple peaks with energy separations that increase with increasing momentum transfer. These types of signals are called quasielastic electron scattering. The energy separation and amplitude of these signals are explained quantitatively by Rutherford scattering [11] based on conservation of energy and momentum in *binary* collisions of the incident particle as it scatters independently from each atom of the target system. This physical picture may also be called "electron-nucleus Compton scattering" (ECS) [9] in analogy to scattering of epithermal neutrons, which is known as neutron Compton scattering (NCS) [12,13].

The Born and incoherent scattering approximations [5,6] are applicable to the high momentum transfer ($\hbar q$) conditions of the current experiments; i.e., $r^{-1} < q$ (r is interatomic distance). The Born approximation assumes the electron scattering happens as a single event and is not a sum of many smaller deviations. The incoherent approximation, which is valid for sufficiently large q, reduces the collision between the electron and the molecule to a simple binary collision between the electron and one of the individual atoms in the molecule. The outcome is that the scattering problem is reduced to a generic binary collision involving any classical projectile and target independent of impact parameter or interaction. From conservation of energy and momentum, in the framework of the impulse approximation (IA) [12–15], the energy transferred from the projectile to the target, $\hbar\omega$, is related to the initial momentum of the target ($\mathbf{p}_0$) and the momentum transfer ($\hbar\mathbf{q}$) by

$$\hbar\,\omega = \frac{(\hbar\mathbf{q} + \mathbf{p}_0)^2}{2M} - \frac{\mathbf{p}_0^2}{2M} = \frac{(\hbar\mathbf{q})^2}{2M} + \frac{\hbar\mathbf{q}\cdot\mathbf{p}_0}{M}, \qquad (1)$$

where M is the mass of the scattering atom. The electron energy loss $\hbar\omega$ is associated with the recoil energy of the target atom; cf. also [9].

For quasielastic scattering from molecules containing atoms of different masses, Eq. (1) implies one peak for each different atomic mass at the well determined spectral position $\hbar\omega = (\hbar\mathbf{q})^2/(2M)$. Each peak is Doppler broadened due to the distribution of initial momenta $\mathbf{p}_0$. Indeed the measured energy loss and Eq. (1) demonstrate that the recoiling "part" in the e-H_2 collision has an effective mass of 1 atomic mass unit (AMU), and 2 AMU in the case of D_2. At the same time, the measured separation between the H and D peaks equals that calculated; see also below. Further experiments on CH_4, CD_4, and other small molecules, using the same apparatus, have confirmed this physical picture [4–6].

This physical model predicts that quasielastic scattering intensities will follow the Rutherford cross section whereby the ratio of the intensity of quasielastic scattering from atom a relative to that from atom b $(\frac{I_a}{I_b})_{\rm theor}$ will be related to N_i, the relative number of each atom type in the target, and their nuclear charge Z_i, according to

$$R_{\rm theor} = \left(\frac{I_a}{I_b}\right)_{\rm theor} = \frac{N_a Z_a^2}{N_b Z_b^2}. \qquad (2)$$

According to this equation, the intensity depends on the charge, but not the mass, of the scatterers. Note also that the (possible) screening of nuclear charge by the electron density is the same in H_2, D_2, and HD. [It may be also noted that Eq. (2) does not presume the validity of the IA. The IA, however, plays a crucial role in investigations aiming to extract momentum distributions of target particles and associated effective Born-Oppenheimer potentials; cf. [12].]

Experimental.—Quasielastic electron energy loss spectra were recorded using an instrument described elsewhere [16–18] in which an unmonochromated 2250 eV electron beam is scattered at 100° by the target in a gas cell, corresponding to a momentum transfer of $q = 19.7$ a.u.. The energy loss was scanned from -2 to $+5$ eV, and the instrumental resolution was 0.85 eV, as determined from the width of the quasielastic scattering peak of background N_2 and O_2. The background was removed by subtracting the spectrum measured at a fivefold lower chamber pressure (reduced from 4×10^{-6} torr to 8×10^{-7} torr). Multiple scans over several days were averaged and analyzed independently to evaluate uncertainties. Typical peak count rates were 1–2 cps (counts per second). Gaseous samples of a 50:50 H_2-D_2 mixture, H_2, D_2, and HD of a stated purity of at least 98.6%, were obtained commercially and used directly. The spectra of pure H_2 and D_2 were used to accurately characterize the shapes and thus obtain an accurate fit of the spectra of the 50:50 H_2-D_2 mixture. The composition of each gas sample was measured using a time-of-flight (TOF) mass spectrometer in the same instrument [18].

Results.—The experimental background-subtracted quasielastic electron energy loss spectra for H_2, D_2, the 50:50 H_2-D_2 mixture, and HD were fit to a linear background and two asymmetric Gaussian curves to represent the H and D atomic peaks. The asymmetric Gaussians were determined by fits to the quasielastic spectra for pure H_2 and D_2. This assumes that the experimental conditions remain constant between the data collections, which was the case as far as we could determine (beam current varied by less than 10% during the 6-week study period). The results for H_2 and D_2 with their curve fits are shown in Fig. 1. The quasielastic peak shapes are not simple Gaussian, Lorentzian, or even Voigt profiles. Only by using a combination of three Gaussians and a linear background can a satisfactory curve fit be obtained. The curve fits for pure H_2 and D_2 were used to fix the parameters of the H and D-peak shapes for use in fits to the data from the H_2-D_2 mixture and HD.

The purity of HD (98.6%), H_2 (99.999%), and D_2 (99.6%) and the composition of the H_2-D_2 mixture were confirmed by mass spectrometry using an electron-ion coincidence (e, e + ion) TOF mass spectrometer in the same instrument [18]. Moreover, by varying the extraction fields of the TOF spectrometer with guidance from Simion trajectory calculations, the H_2:D_2 composition was shown to be 50:50 both on average over the whole collision chamber, and in a small region at the center where the scattering takes place. Figure 2 shows the measured TOF spectrum of the nominally equimolar H_2-D_2 mixture. The deviation of the mixture from an exact 50:50 ratio was less than 1%. Although small effects, these corrections were incorporated into the numerical analysis.

Figure 3 presents the quasielastic spectra of the equimolar H_2-D_2 mixture and HD. In both spectra, the energy separation of the H and D peaks is 1.45(4) eV, in exact agreement with the theoretical Rutherford separation [11]

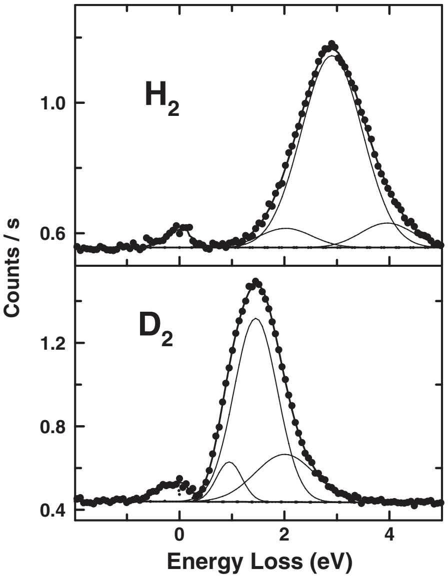

FIG. 1. Quasielastic electron energy loss spectra of H_2 and D_2, showing fits of 3 Gaussian curves to the experimental data. The small peaks on the low energy side arise from incomplete subtraction of the quasielastic peaks due to background air in the spectrometer.

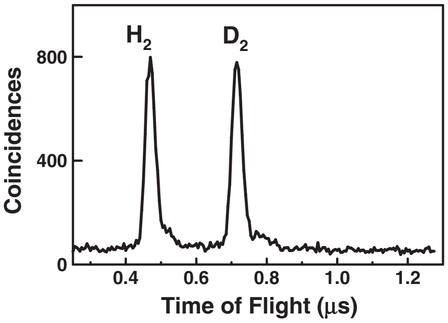

FIG. 2. TOF spectrum of the H_2-D_2 mixture obtained by (e, e + ion) at an energy loss of 20 eV and 4° scattering angle.

for this momentum transfer; cf. Eq. (1). The curve fits shown are fits of the H- and D-peak shapes determined in the H_2 and D_2 experiments to the experimental data (plus a linear background). The relative positions, widths, and areas of the three-component Gaussian curves for each peak were kept constant during these fits—only the overall positions and areas were allowed to vary. The ratio of intensities

$$(H_2, D_2)_{mix}\colon R_{mix} = (I_H/I_D)_{exp} = 0.69(\pm 0.04) \quad (3)$$

was obtained without fitting parameters. The result clearly contradicts (by 30%) the conventionally expected result $R_{theor} = 1$, as follows from Eq. (2) with $N_H = N_D$ and $Z_H = Z_D = 1$. For HD we obtained the conventionally expected result

$$HD\colon R_{HD} = (I_H/I_D)_{exp} = 0.96(\pm 0.05) \approx 1.0, \quad (4)$$

where for the fitting it was assumed that the same H- and D-peak shapes hold as in the case of the mixture. Further fits allowing for additional variation of the overall H- and D-peak widths did not provide any significant change of these intensity ratios. The stated uncertainty is the standard deviation of the values obtained from different data sets, combined with mathematical fitting uncertainties (which were very low).

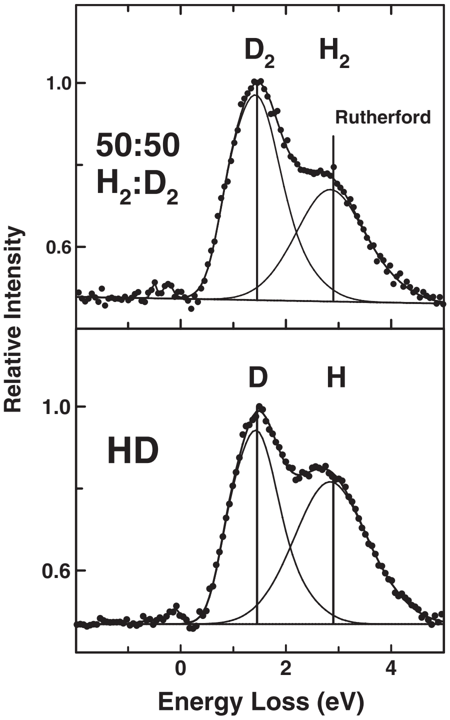

FIG. 3. Quasielectron electron energy loss spectra of the 50:50 H_2-D_2 mixture and of HD. The fits of curves representing the individual H and D scattering peaks to the experimental data are shown. The vertical lines show the calculated recoil energies $\hbar\omega_r = (\hbar q)^2/(2M_i)$ for $i = H, D$.

A theoretical analysis of the peak widths and shapes is addressed in Refs. [4–6]. These issues play no role in this Letter, which concerns integrated peak intensities only.

Additional remarks and discussion.—(a) The most surprising result of the present work is that, despite the same H/D atomic stoichiometry in the equimolar H_2-D_2 mixture and HD, the relative intensities of the H and D peaks in these two systems differ significantly. In particular, $R_{HD} \approx 1$ in the HD quasielastic spectrum, as expected from Rutherford theory. However, $R_{mix} \approx 0.69$ for the mixture; i.e., the H peak is much less intense than the D peak, thus contradicting conventional expectations of electron-nucleus Compton scattering (which do not include effects of spin).

(b) The striking anomalous decrease of R_{mix} is equal (within experimental error) to the NCS results from the equimolar H_2-D_2 mixture (liquid, $T = 20$ K), which showed an anomalous decrease of this quantity of $(30 \pm 5)\%$ [19]. An analogous similarity of neutron and electron-proton scattering results from a solid polymer was reported and discussed in Ref. [9]. However, the corresponding ratio of intensities R_{HD}(NCS) of HD measured by NCS showed the *same anomaly as the mixture*, i.e., a shortfall by ca. 30%.

(c) In view of these comparisons, a unique feature of the present experiment ought to be stressed. The electron scattering results are associated with an energy transfer *less* than the dissociation energy of the H–H (H–D and D–D) bond. In contrast, NCS [19] applied energy transfers between 5–30 eV, which may break the bonds. Thus, the present experiment concerns single, intact hydrogen molecules, whereas the NCS experiment investigated the attosecond dynamics of H–H (and H–D) bond breaking. In view of (b), these observations may have novel theoretical implications; see (g) below.

(d) It is emphasized that the (possible) screening of nuclear charge by the electron density is the same in H_2, D_2, and HD molecules within the Born-Oppenheimer (BO) approximation.

(e) The experiment shows that scattering gives rise to peaks which correspond to scattering from single H (or D) atoms; see above. While vibrational and rotational transitions are probably excited in the quasielastic scattering, the envelope of these excitations is not so extensive as to shift the peak position from the predictions of Eq. (1).

(f) In view of current theoretical work [20–22] it is important to realize the attosecond duration of an electron-atom collision, $\tau_q \approx M/(q\Delta p_0)$, of a two-particle collision [12], as first obtained in the frame of the impulse approximation of NCS by Sears [14]. Δp_0 is the width of the momentum distribution of the struck particle of mass M. Applying the harmonic oscillator model, and taking data from [23] for scattering from a proton of H_2, one gets $\tau_q(\mathrm{H}) \approx 0.77 \times 10^{-15}$ s; i.e., the scattering happens in the attosecond time scale [9]. Scattering off D_2 gives $\tau_q(\mathrm{D}) \approx 2.4 \times 10^{-15}$ s.

(g) In the aforementioned NCS [9,13] and ECS [9] context, this effect has been theoretically ascribed to attosecond protonic quantum entanglement and decoherence, also involving adjacent electrons, and to the violation of the BO approximation; for discussions of related theoretical models, see [19–22]. However, remarks (c) and (d) indicate that the BO approximation may be approximately valid here, and thus the result $R_{\mathrm{HD}} \approx 1$, Eq. (4), is in agreement with the theoretical predictions of Refs. [20,22]. But then, the intensity shortfall for H_2 relative to D_2 scattering remains unexplained. A crucial difference between the systems under consideration is that H_2 and D_2 exhibit full nuclear spin (and spatial) entanglement in their initial state, whereas HD clearly does not. Thus it appears that the spin degrees of freedom (as suggested elsewhere [21,24]) may play a significant role here. Investigation of this possibility is in progress.

In conclusion, we showed for the first time that quasielastic electron scattering from *single* H_2 and D_2 molecules at large momentum transfer, but *without breaking bonds* (and thus extending previous NCS investigations [19]), reveals an anomalous shortfall of scattering from H atoms as compared to D. Strikingly (and in contrast to the NCS results), HD exhibits no such anomaly. These findings represent a challenge to conventional (time-independent) theories of scattering and molecular spectroscopy, which may need to be supplemented by time-dependent theories (also beyond the BO approximation) to describe attosecond experiments.

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