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 H₂ 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 H₂ 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 H₂, D₂, and HD (gases, T = 298 K), which are shown to be in clear contrast to conventional expectations. In short, (a) the experiments on H₂ and D₂ 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 (hq) 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, hω, is related to the initial momentum of the target (p₀) and the momentum transfer (hq) by

\[ h\omega = \frac{(hq + p_0)^2}{2M} - \frac{p_0^2}{2M} = \frac{(hq)^2}{2M} + \frac{h\cdot q \cdot p_0}{M}, \]

where M is the mass of the scattering atom. The electron energy loss hω 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...
The energy loss was scanned from $0.0255$ eV to the width of the quasielastic scattering peak of background instrumental resolution was 0.85 eV, as determined from samples of a mixture. The background was removed by subtracting the quasielastic peaks due to background air in the spectrometer. 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. 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. The 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 $b$ $(I_a/I_b)_{\text{theor}}$ will be related to $N_i$, the relative number of each atom type in the target, and their nuclear charge $Z_i$, according to

$$R_{\text{theor}} = \frac{I_a}{I_b} \text{theor} = \frac{N_aZ_a^2}{N_bZ_b^2}. \quad (2)$$

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 $4 \times 10^{-6}$ torr to $8 \times 10^{-7}$ 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.

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contradicts (by 30%) the conventionally expected result was obtained without fitting parameters. The result clearly contradicts (by 30%) the conventionally expected result

\[ R_{\text{theor}} = 1, \] as follows from Eq. (2) with \( N_H = N_D \) and \( Z_H = Z_D = 1 \). For HD we obtained the conventionally expected result

\[ \text{HD: } R_{\text{HD}} = (I_H/I_D)_{\text{exp}} = 0.96(\pm 0.05) = 1.0, \quad (4) \]

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).

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 \( \text{H}_2\text{–D}_2 \) mixture and HD, the relative intensities of the H and D peaks in these two systems differ significantly. In particular, \( R_{\text{HD}} = 1 \) in the HD quasi-elastic spectrum, as expected from Rutherford theory. However, \( R_{\text{mix}} = 0.69 \) 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 \( R_{\text{mix}} \) is equal (within experimental error) to the NCS results from the equimolar \( \text{H}_2\text{–D}_2 \) 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 \( R_{\text{HD}}(\text{NCS}) \) 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 \( \text{H}_2 \), \( \text{D}_2 \), 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 transi-

![Figure 2](image2.png)

**FIG. 2.** TOF spectrum of the \( \text{H}_2\text{–D}_2 \) mixture obtained by (e, e + ion) at an energy loss of 20 eV and 4° scattering angle.

![Figure 3](image3.png)

**FIG. 3.** Quasielectron electron energy loss spectra of the 50:50 \( \text{H}_2\text{–D}_2 \) 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 \( i = \text{H, D} \).
tions 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, \( \tau_q = M/(q\Delta p_0) \), of a two-particle 
collision [12], as first obtained in the frame of the impulse 
approximation of NCS by Sears [14]. \( \Delta p_0 \) 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 \( \tau_q(H) \approx 0.77 \times 10^{-15} \text{ s} \); i.e., the scattering happens in the 
attosecond time scale [9]. Scattering off D\(_2\) gives \( \tau_q(D) = 
2.4 \times 10^{-15} \text{ s} \).

(g) In the aforementioned NCS [9,13] and ECS [9] 
context, this effect has been theoretically ascribed to atto-
second protonic quantum entanglement and decoherence, 
also involving adjacent electrons, and to the violation of 
the BO approximation; for discussions of related theoreti-
cal models, see [19–22]. However, remarks (c) and (d) 
disagree 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 quasi-
elastic 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 atto-
second experiments.

This work was supported financially by NSERC 
(Canada) and the Canada Research Chair program. We 
thank Eric Christensen for assistance with measurements. C. A. C.-D. 
acknowledges partial support by a grant from 
the Royal Swedish Academy of Sciences.

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