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Abstract

Accurate measurements of keV electrons scattered elastically from H_2 molecules reveal a lineshape that is an intrinsic property of the target. The intrinsic width of the elastic peak is due to the non-zero momentum of a proton bound to a molecule. A more precise analysis of the lineshape shows that it deviates from Gaussian. This deviation is shown to be a consequence of the dominance of the momentum component of the protons along the molecular axis. The mean-kinetic energy of the protons in H_2 obtained based on the new peak shape agrees better with theory than the one obtained based on a Gaussian peak shape. These measurements demonstrate the possibility of a new way to study the dynamics of nuclei by electron scattering.

Keywords: elastic peak, lineshape, hydrogen

(Some figures may appear in colour only in the online journal)

1. Introduction

Scattering experiments are a central tool for enhancing our understanding of the microscopic structure of matter. In particular, electron scattering has been used to study the structure of atoms, molecules, nuclei and even nucleons. There is an important universality in these experiments. If there is structure in the target on a length scale of $1/q$, with q the momentum transfer (atomic units are used throughout), the resulting cross section shows a rich structure related to some form of 'diffraction'. If the target consists only of point-like particles on this length scale the results are readily interpreted in terms of binary collisions. These similarities are discussed, e.g., by West [1] and form a unifying framework for our understanding of experiments dealing with atomic, nuclear and elementary particle physics and the results in one field help guide the interpretation in others.

One system that has attracted no or very little attention is the collision between an electron and a nucleus that is bound to a molecule by the electrons of the system. Knowledge of this system, the topic of chemistry, is of course enormous, but the dynamics of the nucleus bound to a molecule has not been explored by electron scattering. This work will demonstrate

that the elastic peak of electrons scattered from H_2 has a peculiar (non-Gaussian) shape which can be understood as a consequence of the linear nature of this molecule.

Deflection of an energetic electron from a molecule necessarily implies the transfer of momentum from the electron to that molecule. As a consequence the kinetic energy of both the target and electron will change. For the scattering of keV electrons over large angles this transferred momentum is much larger than $1/r$ with r the inter-atomic separation and, as a consequence, the atom scatters incoherently, i.e. the transferred momentum is absorbed by a single atom and the average recoil energy $\overline{E_{rec}^i}$ is in first order just $q^2/2M$ with M the *atomic* mass [2].

Molecules are not static objects, but subject to translations, rotations and vibrations, the last affects the molecule even at $0°$ K due to the zero-point energy. This atomic motion affects the transferred energy when a keV electron collides (Doppler broadening) and results in a spread in energy after scattering which is well-resolved for light elements. The spectrum becomes then a fingerprint (Compton profile) of the atomic motion and can be used to establish the mean kinetic energy $\overline{E_{kin}^i}$ of an atom within a molecule (or a solid) [3]. The mean kinetic energy of atom i, $\overline{E_{kin}^i}$, is related to the second

moment (σ_i) of its elastic peak as:

$$\sigma_i = \sqrt{\frac{4}{3}\overline{E_{rec}^i}\,\overline{E_{kin}^i}} \ . \tag{1}$$

For scattering from heavy elements, such as Xe, σ_i is considerable smaller than our energy resolution, as $\overline{E_{rec}^i}$ is then very small. For hydrogen and deuterium σ_i is considerably larger than the energy resolution. An initial study of electron scattering from H_2 resulted in a mean kinetic energy that was unexpectedly small compared to the results obtained by semi-classical calculations of this quantity [3]. This prompted the present study.

2. Theory

In the above the fact that an atom is bound to a molecule was neglected, i.e. the scattering atom was treated as if is was free. This is not obvious as the transferred energy is often less than that required to break the bond. The underlying physics has been studied in neutron physics in general [4–6] and for H_2 in particular [7–9] where the collision of epithermal (i.e. several eV kinetic energy) neutrons with atoms imply a similar magnitude of momentum transfer as the electron collisions described here. We will hence heavily rely on the neutron literature for the interpretation of the current electron scattering measurements.

The description of the projectile–atom collision as a collision between free particles is called the plane-wave impulse approximation (PWIA). In the neutron literature it is well established that deviations from the PWIA affects the shape of the spectra in a minor, but significant, way for the momentum transfer range used here. These deviations are referred to as 'final state effects' and cause an asymmetry in the spectrum. The spectrum is then described not as a Compton profile of its momentum distribution (usually taken to be Gaussian) but as a Gaussian *plus* the third derivative of this Gaussian [4]. The contribution of this second component decreases with increasing q, as then the validity of the PWIA improves.

Within the PWIA, if the atom is stationary before the collision the energy transfer is just $q^2/2M$. If it has a momentum p before the collision than the energy transfer is given by

$$\omega = \frac{q^2}{2M} + \frac{\mathbf{q} \cdot \mathbf{p}}{M}. \tag{2}$$

This equation makes it possible to change the measured energy loss distribution into the distribution of the momentum component of p along q (p_q) using

$$p_q = \frac{M}{q}\left(\omega - \frac{q^2}{2M}\right). \tag{3}$$

In the scattering literature p_q is often called y and this procedure is then referred to as a y-scaling.

The current electron-scattering measurements are interpreted in terms of the first Born approximation (FBA). In this approach the double differential cross section $\left(\frac{d\sigma}{d\omega d\Omega}\right)$ factors out in two contributions:

$$\frac{d^2\sigma}{d\Omega d\varepsilon} = \frac{m^2}{4\pi^2}\frac{\mathbf{k}_1}{\mathbf{k}_0}W(\mathbf{q})S(\mathbf{q},\omega). \tag{4}$$

Here m is the projectile mass, and $\mathbf{k}_0$ and $\mathbf{k}_1$ its momentum before and after scattering. One contribution $W(\mathbf{q})$ is the square of the Fourier transform of the projectile-target interaction $V(\mathbf{r})$ and determines the intensity of the peak. This factor depends on the projectile. The other factor, the dynamical structure factor $S(\mathbf{q},\omega)$, determines the shape of the spectrum, and is a property of the target only. The shapes of electron and neutron spectra are thus determined by the same quantity $S(\mathbf{q},\omega)$ and can be compared directly [10]. For large q values $S(\mathbf{q},\omega)$ approaches a Compton profile.

When the data is plotted as a function of p_q the resulting distribution should be centered at 0 and symmetric, as H_2 in a gas cell has no preferred direction of motion. In reality the distribution is slightly asymmetric, and the maximum intensity is somewhat away from $q^2/2M$. This is due to the approximate nature of the PWIA.

An alternative description of these experiments was derived by Bonham *et al* [11]. They also used the FBA, but considered the respective translational, rotational and vibrational states of H_2 as the final state. In this calculation the peak shape deviates from Gaussian as well, and this should become more evident with decreasing target temperature and when the energy resolution is improved.

In a previous study [12], electron scattering from H_2 was studied at nominal room temperature in a crossed beam arrangement. The electron beam intersected with a hydrogen beam expanding through a hypodermic needle. The velocity distribution of the hydrogen beam is then far away from thermal equilibrium. The obtained mean kinetic energy was too small compared to the results of semi-classical calculations of this quantity [3].

This has prompted the current study using electrons scattered from H_2 confined in a cooled gas cell. The velocity distribution of the molecules is then much closer to thermal equilibrium and hence comparison with theory is more straightforward. The aim of this study is to increase our understanding of the shape of the hydrogen spectra, in particular its relation to the mean kinetic energy of the atoms.

3. Experiment

An electron with energy E_0 and momentum $\mathbf{k}_0$ scatters over an angle θ (nominal scattering angle 90°, *in situ* measurement showed that the gas cell, mounted on the cryostat was slightly off-centre, resulting in a scattering angle of 91.3°) and is detected with energy E_1 and momentum $\mathbf{k}_1$. The gas cell is in contact with a liquid nitrogen reservoir and a thermocouple indicated a temperature of 120° K. The gas enters the gas cell through a 50 cm long copper tube (4 mm inner diameter), also at this temperature, to ensure that it is close to thermal equilibrium.

A small amount of Xe is mixed with the hydrogen (H_2 or D_2) to establish spectrometer performance. The electron gun uses a BaO cathode, and the analyzer measures a range of
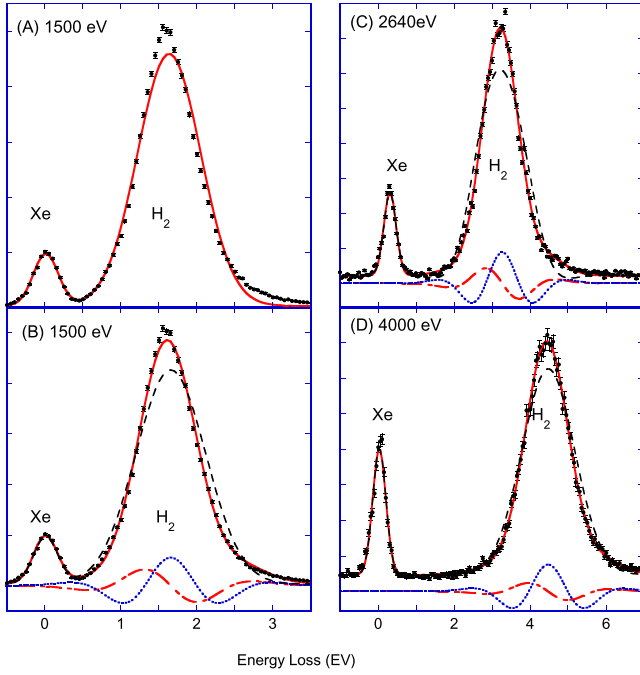
Figure 1. Spectra taken at energies as indicated for a H_2–Xe mixture. The scattering angle was 90°. In (A) the data is fitted with a single Gaussian. In (B)–(D) the fit of the spectrum (thick (red) line) consists of a Gaussian (dashed, black line) *plus* contributions proportional to the third (dash-dotted line) and fourth (dotted line) derivative of this Gaussian.
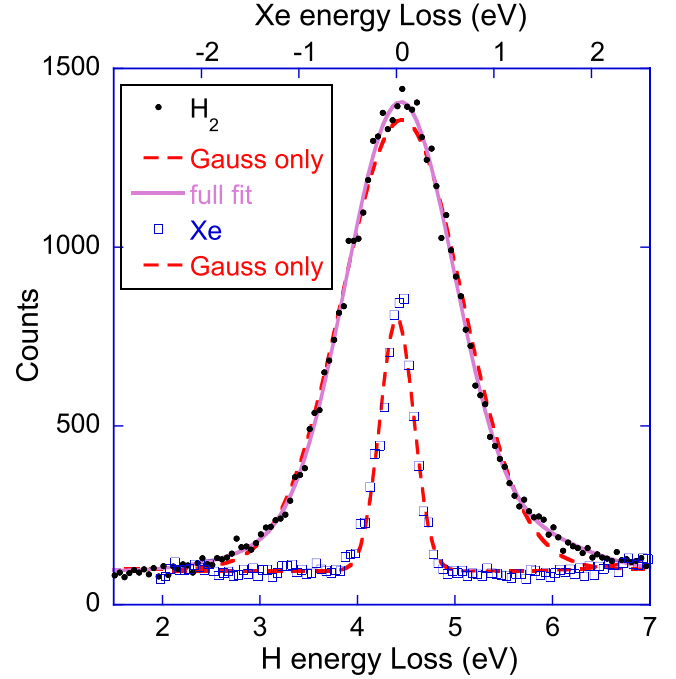

Figure 2. A comparison of the H peak with the Xe peak (shifted, see upper energy scale) obtained in the same measurement with $E_0 = 4$ keV. The sharp Xe peak can be fitted quite well with a single Gaussian. The much broader H peak shows systematic deviations from its Gaussian fit. The full fit contains two correction terms, as described in the text.

energies simultaneously [13]. The overall energy resolution, judged from the Xe peak width, is 0.35 eV. Spectra were taken at $E_0 = 1500$, 2640 and 4000 eV. The 2640 eV value was chosen to have the same momentum transfer as in [11].

4. Results

The obtained spectra (figure 1) show two peaks, a narrow one at small energy loss and a broader one at larger losses. The first one is only seen after Xe was added, and is attributed to this element. It is at a very small energy loss value due to the large mass of Xe. The zero point of the energy scale is slightly adjusted such that the Xe peak position is at $q^2/2M_{Xe}$. The width of the H peak (σ_H) is much larger than the width of the Xe peak and is thus dominated by Doppler broadening. The mean kinetic energy of Xe, a free atom, is $\frac{3}{2}kT$ and the corresponding intrinsic width can be calculated and is very small (see equation 1). The width of the Xe peak is in good approximation equal to the energy resolution.

In figure 1(A) the obtained data are described by two Gaussians positioned at the mean recoil energy loss $\overline{E_{rec}^i} = q^2/2M_i$ of H and Xe:

$$I_0(\omega) = \sum_{i=H,Xe} \frac{C_i}{\sqrt{2\pi}\,\sigma_i} e^{(-(\omega - \overline{E_{rec}^i})^2/(2\sigma_i^2))} \qquad (5)$$

This distribution is subsequently convoluted with the experimental energy resolution σ_{res} and compared to the measurement. Both peaks are thus fitted simultaneously. For Xe, σ_{Xe} is very small. In the fitting procedure its width

effectively fixes σ_{res}. With σ_{res} determined one obtains thus σ_H from the fit. The H peak is much wider than the Xe peak. The H peak deviates substantially from a Gaussian shape, whereas the sharper Xe peak does not. This is illustrated in figure 2. Thus the deviation from Gaussian of the H peak is not an instrumental artefact, as the Xe peak is not affected.

There are two causes for the peak shape of H to deviate from Gaussian:

  (a) the momentum density of the protons is not Gaussian;
  (b) the PWIA is not fully justified.

Fortunately, these two effects affect the spectrum in different ways. From the work of Sears [4] and its application in neutron scattering we know that the leading dominant correction term when the PWIA is not fully fulfilled is odd relative to $\overline{E_{rec}^i}$. In contrast, for a randomly oriented target, such as our H_2 gas, the momentum distribution should be symmetric relative to $p_q = 0$ and hence deviations from a Gaussian momentum profile should not cause any asymmetry relative to the $\overline{E_{rec}^i}$.

Any peak can be expanded in terms of Hermite polynomials, i.e. as a sum of a Gaussian plus n terms proportional to the n-fold derivative of the Gaussian [14]. If we chose the peak position of the Gaussian equal to the center of gravity of the measured loss distribution and its second moment equal to that of its width, then the first non-zero contributions in the expansion are proportional to the third and fourth derivative:

$$I(\omega) = I_0(\omega) + a\frac{d^3}{d\omega^3}I_0(\omega) + b\frac{d^4}{d\omega^4}I_0(\omega) \qquad (6)$$
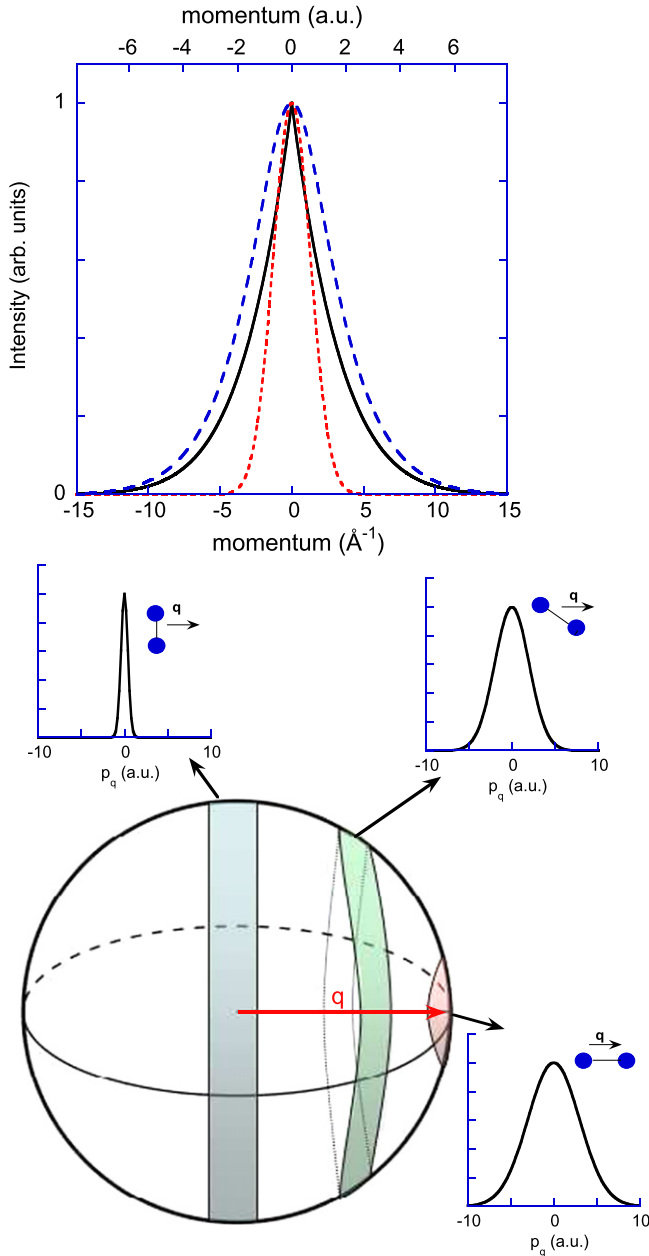
Figure 3. The lineshape for a linear molecule (a one-dimensional oscillator) obtained by averaging over all possible orientations of the molecule in space (full line). The lower half of the figure illustrates the shape of the contribution to the spectrum for different orientations of the molecular axis relative to **q**. Away from 0° K there is additional broadening due to the translational and rotational movement. Assuming the mean kinetic energy is $kT/2$ per degree of freedom this causes additional Gaussian broadening (short dash). The convolution of both curves gives the expected profile (long dashed line) for a H_2 molecule in this simple semi-classical picture.

Inclusion of these terms improves the fit considerably (see figures 1(B)–(D)). The interpretation of the origin of the two expansion terms is rather different however. The first term is odd and is a correction to the impulse approximation (final state effect). Note that this term becomes less prominent with increasing E_0 values (see figure 1). The second term is even and is due to the fact that the angular-averaged momentum

distribution of the protons is not well-represented by a Gaussian (an initial state effect). Its contribution appears independent of the E_0 values used.

An alternative approach to fitting the H peak would be assuming a Voigt intrinsic lineshape (a convolution of a Gaussian and a Lorentzian lineshape) as such a lineshape falls off less quickly than a purely Gaussian one. If such a Lorentzian tail exists, it would have to be an intrinsic property of H_2 and not an instrumental artefact, as no such tails are required to describe the Xe spectrum. A Voight lineshape is often used in the analysis of photo-emission core level spectra, and enhances the wings of the peak, compared to a purely Gaussian lineshape. In photo-emission, the Lorentzian component has a sound physical meaning as it reflects the life-time broadening of the core hole. Notice that in our case (elastic scattering) we do not create electronic excitations, and hence the concept of life-time broadening does not come into play. The second moment of a Lorentzian distribution is infinite, hence such a distribution cannot be used to extract the mean kinetic energy of an atom via equation (1).

5. Discussion

To understand why the momentum density is not Gaussian it is instructive to consider first a simple semi-classical model of the hydrogen molecule at 0° K. We follow here closely the description given by Karlsson [9]. The only quantum aspect we maintain is the vibrational motion. Before the collision H_2 is in its vibrational ground state as the excitation energy ($\hbar\omega = 0.516$ eV) is much larger than kT. The zero-point energy $\left(\frac{1}{2}\hbar\omega\right)$ is evenly divided over both atoms and over kinetic and potential energy. The mean kinetic energy of each proton due to the vibrational motion is thus 64.5 meV.

The proton is to a good approximation in a harmonic potential and moving along the molecular axis, its wave function in both real and in momentum space is described by a Gaussian. In momentum space the width (σ) of the momentum probability distribution for an oscillator with $\hbar\omega = 0.516$ eV is 2.9 a.u. In a scattering experiment for which the impulse approximation applies the spectrum of a single molecule will resemble a Gaussian (centred at $\overline{E_{rec}}$) with a width that is determined by the angle of the molecular axis and the momentum transfer vector. The width (σ, in energy) will be $2.9\frac{q}{M}$ if the molecular axis is along **q**. For a H_2 molecule for which the molecular axis is at an angle θ with **q** the width is given by $\sigma(\theta) = 2.9\frac{q}{M}\cos\theta$. The width approaches 0 if $\theta \approx 90°$. For an ensemble of randomly oriented hydrogen molecules one expects as a lineshape [9]:

$$I(\omega) = \int_0^\pi \frac{1 - \cos 2\theta}{\sqrt{2\pi}\,\sigma(\theta)} \exp^{-(\omega - \overline{E_{rec}})^2/(2\sigma(\theta)^2)} d\theta, \qquad (7)$$

where the factor $1 - \cos 2\theta$ is a consequence of averaging over all possible directions. This lineshape turns out to be rather different from a Gaussian one, with a sharp cusp-like maximum and broad wings.
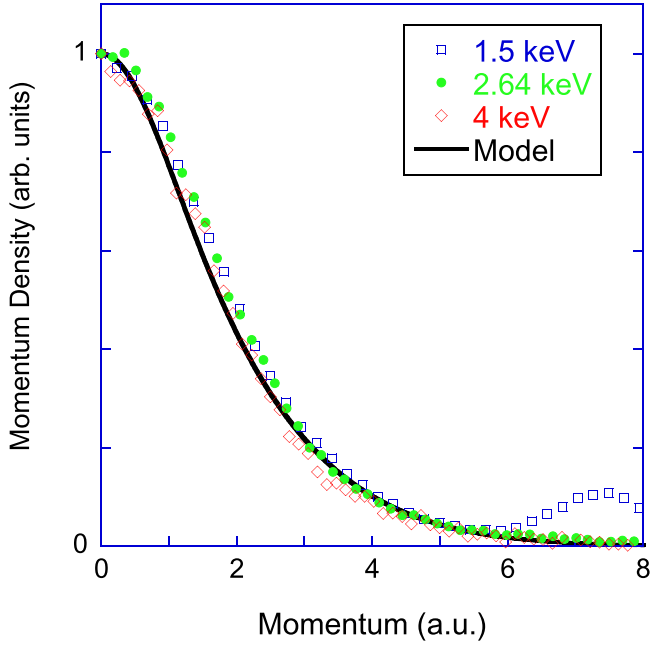
Figure 4. Momentum densities as derived for H_2 for E_0 values as indicated (symbols) compared to the momentum density of a spherically-averaged H_2 molecule (full line). The minor peak at 7 a.u. for the 1.5 keV measurement is due to Xe.

Figure 5. A comparison of the measurements for H_2 and D_2 with the results obtained with the program of [11].

At non-zero temperature there will be additional broadening due to translational and rotational motion. If we assume these can be described classically, the corresponding kinetic energy *per* atom would be $\frac{5}{4}kT$ (three translational and two rotational degrees). This broadens the sharp maximum, but the broad wings remain. This is illustrated in figure 3.

An alternative way to take the impulse correction into account is to plot the data as a function of momentum (p_q) and then add the intensity at $-p_q$ to the one at p_q. The contribution of the impulse correction is odd in p_q and will thus cancel. The shape after folding is thus the shape of the momentum distribution. This is done in figure 4 for all three energies shown in figure 1. The measurements coincide when plotted in this way, indicating the validity of the $y-$ scaling procedure. Also plotted in this figure is the result of angular averaging (equation (7)) after convolution with a Gaussian width based on Doppler broadening due to rotational and translational motion. Agreement between experiment and model calculation is good, confirming the interpretation of the experiment.

In figure 5 we compare the spectra for H_2 with those of D_2, the latter taken at twice the incoming energy. Then the $\overline{E_{rec}}$ for H and D are the same. The D peak has a similar asymmetry as the H peak, but is somewhat narrower, as expected considering the lower vibrational energy ($\hbar\omega = 0.371$ eV). The peak shapes are also compared with the result of the calculation by Bonham *et al* [11]. This alternative approach, not relying on the PWIA, results in very similar peak shapes. However, at the higher incoming energy, there is some difference in the position of the maximum.

Now consider again the mean kinetic energy of the protons and deuterons in a hydrogen molecule. The width of
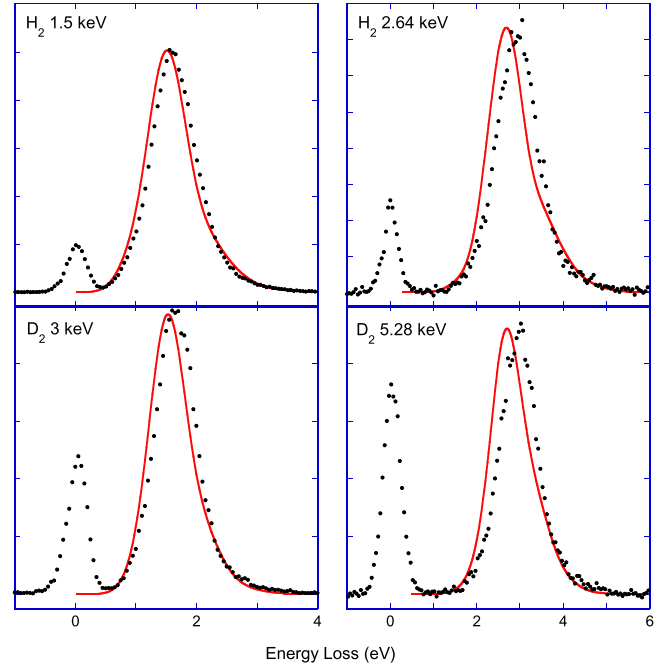
Table 1. The extracted mean kinetic energy of protons (deuteron) in H_2 (D_2) based on a single Gaussian (fit1) and a Gaussian plus two Hermite expansion terms (fit2), compared with a semi-empirical estimate of this quantity at 120° K.

molecule	E_0 eV	fit1 meV	fit2 meV	theory meV
H_2	1500	67(2)	85(3)	78.1
H_2	2640	61(2)	79(3)	78.1
H_2	4000	59(2)	76(2)	78.1
D_2	3000	46(2)	61(2)	58.6
D_2	5280	44(2)	58(2)	58.6

the Gaussian for which the best fit is obtained changes when the correction terms are included. These correction terms themselves do not contribute to the second moment of the distribution. As can be seen in the left panels of figure 1, the Gaussian component is somewhat broader when the correction terms are included. With inclusion of the correction terms in the fit we get a larger mean kinetic energy of H in H_2 compared to a simple Gaussian fit. The changes are mainly due to the non-Gaussian nature of the momentum density, and the inclusion of final state effects play only a minor role.

The experimental values for $\overline{E_{kin}^i}$ are compared to the theoretical ones in table 1. In the calculation the molecule was taken in the vibrational ground state, with $\frac{3}{2}kT$ kinetic energy due to translation motion. The rotational contribution was based on the same occupation of para and ortho levels as at room temperature, integration of the rotational specific heat curves given in [15] to 120 K plus the zero-point energy contribution of the $J = 1$ level.

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6. Conclusion

It was shown that, for keV electrons scattered over large angles, the elastic peak of hydrogen molecules has a peculiar non-Gaussian shape. The nature of this lineshape can be understood based on the dominance of the momentum component of the atoms along the molecular axis. Accommodating for this shape, one obtains a mean kinetic energy of the atoms that is closer to the theoretical estimate than that obtained when one assumes a Gaussian lineshape.

Acknowledgments

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