Quasi-elastic electron scattering from atoms and molecules

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ABSTRACT

Over the past four years we have measured quasi-elastic electron scattering spectra from molecules and atoms at large momentum transfer ($100°$ angle, 2.25 keV incident energy, $\sim$20 a.u.). The peak positions agree completely with those predicted by classical conservation of momentum and energy, assuming the electron scatters from each atom independently. However the peak intensities do not agree with expectations, particularly for light elements. According to classical electron Compton scattering, quasi-elastic peak intensities should be proportional to nuclear charge squared. However, our recent study [Phys. Rev. Lett. 100 (2008) 043204] found a significant deviation ($\sim$30%) in the intensities of the H versus D signals relative to this prediction. Here we present new quasi-elastic electron scattering data for H_2/D_2, Ar/H_2, Ar/D_2 and He/H_2 and Ar/He mixtures. The new H_2/D_2 data confirm the earlier result – quasi-elastic scattering by H is low by $\sim$31(4)% compared with D. More significantly, when compared to He the quasi-elastic scattering intensity by H is 48(6)% lower and that for D is 30(3)% lower relative to that expected from Compton scattering theory. When compared to the quasi-elastic signal from Ar, H shows a 63(6)%, D shows a 45(5)% and He shows a 35(8)% reduced intensity as compared to that expected from Compton scattering theory. When cross-compared all the results are internally consistent, confirming that quasi-elastic scattering intensities for light elements are anomalously low compared to both classical electron Compton scattering predictions and a recent quantum mechanical treatment within the first Born approximation [J. Chem. Phys. 130 (2009) 144303]. The reason for the anomalously low QEES intensities for light elements is unknown at this time.

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1. Introduction

When a fast electron scatter from a multi-element target (gas or solid) at large momentum transfer (high impact energy and large scattering angle) the spectral region around the primary beam energy exhibits multiple peaks at positions which depend on the nuclear mass of the elements involved and with energy separations that increase with increasing momentum transfer. Such signals, which have been reported recently for electron scattering from both gaseous [1–4] and solid [5–9] multi-element samples, are called quasi-elastic electron scattering (QEES). The number and energy separation of these signals are explained qualitatively by Rutherford scattering theory [10] which is based on conservation of energy and momentum in *binary* collisions of the incident particle within the assumption that the electron scatters independently from each atom of the target system – see Eq.(1):

$$\hbar\omega = \frac{(p_o + q)^2}{2M} - \frac{p_o^2}{2M} = \frac{q^2}{2M} + \frac{p_o q}{M} \tag{1}$$

The relative intensities of quasi-elastic scattering signals are less well understood. The electron Compton scattering (ECS) model [1,11–15], which is based on the first Born approximation and the impulse approximation, predicts that quasi-elastic scattering intensities will follow the Rutherford cross-section [10] whereby the ratio of the peak intensities is related to the relative number of each atom type in the target and the nuclear charges according to:

$$\frac{I_a}{I_b} = \frac{N_a Z_a^2}{N_b Z_b^2} \tag{2}$$

Early gas-phase work [1] suggested that there was a deficit in the quasi-elastic scattering intensity for H relative to that predicted by the ECS model [1,11–15], and that this intensity deficit was similar in magnitude to that reported in neutron Compton scattering intensities at equivalent q values [16–19]. A recent study of quasi-elastic electron scattering by a pre-mixed 50:50 H_2/D_2 sample found that the ratio of the cross-section for H_2 to that for D_2 was 31(4)% [4]. An effort was made to reproduce this effect theoretically using a full quantum mechanical treatment of the molecular system within the first Born theory of electron scattering [11]. That study concluded that conventional quantum mechanics and scattering theory cannot explain the observed relative quasi-elastic intensities for H_2

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and D_2. Very recently Moreh and Nemirovsky [20] have presented a theoretical discussion of the intensity anomalies in the 50:50 H_2/D_2 case which we reported earlier [4], and, as shown below, have confirmed in this study. Moreh and Nemirovsky speculate that the anomaly is caused by differences in the molecular speeds of H_2 and D_2. We will demonstrate in the present work that the experimental data does not support that conclusion.

Every possible effort was made at the time of the work reported in ref. [4] to verify the accuracy of the observation. In particular the composition of the gas mixture was analyzed by mass spectrometry analysis of the gas cell contents, sampling essentially the same volume as that which gave rise to the QEES signal. Given the unusual and potentially controversial nature of these observations we have made further measurements using different approaches to investigate the quasi-elastic electron scattering intensities of light elements. This paper reports QEES studies of H_2/D_2, Ar/H_2, Ar/D_2 and He/H_2 and Ar/He mixtures. The results of these studies verify that the QEES intensity for H relative to D is indeed ~30% below theoretical predictions. More significantly, the measurements of H and D relative to He and Ar show that QEES intensities from all three light elements are lower than theoretical predictions. The intensity relationships between all the binary mixtures are internally consistent. Here we assume Ar follows the ECS theory. Screening effects may be included as an extension of ECS [21], but this has not been done for this work, which emphasizes the experimental QEES results. If one assumes Ar follows ECS theory, then the QEES intensities for H, D and He are lower than expected by 63(6)%, 45(5)% and 35(8)% respectively.

2. Experimental

Quasi-elastic electron energy loss spectra of H_2/D_2, Ar/H_2, Ar/D_2, He/H_2 and Ar/He binary gas mixtures were recorded using an unmonochromated 2250 eV electron beam, scattered at 100° by the target in a gas cell, corresponding to a momentum transfer of $q = 19.7$ a.u. Further details of the instrumentation are described elsewhere [22,23]. The energy loss was scanned from −2 to +6 eV. The instrumental resolution was ~0.8 eV, as determined from the width of the quasi-elastic scattering peak of background N_2 and O_2. The air background was removed from the sample spectra by subtracting the spectrum measured at the spectrometer base pressure. Sample pressures were ~5×10^{-6} Torr (measured outside the collision cell) while the background pressure in the spectrometer was ~4×10^{-7} Torr. Multiple scans over several days were averaged and analyzed independently to evaluate uncertainties. Typical peak count rates were 0.5–20 counts per second (min H_2, max Ar). Gaseous samples of a 50:50 H_2–D_2 mixture, H_2, D_2, He and Ar of stated purity at least 98.6%, were obtained commercially and used directly. The QEES spectra of each pure species (H_2 and D_2, He and Ar) was also measured under the same conditions in order to obtain accurate quasi-elastic peak shapes which were then used to fit the QEES of the gaseous mixtures. This was done by least-squares fitting three Gaussian components to each pure gas spectrum (for each single pure gas peak), then using the resultant peak shapes (with the relative widths and intensities of the Gaussian components fixed) as input to a non-linear least-squares fit of the gas mixture spectra. This procedure was used for all data except the He/Ar mixture spectra, for which the pure gas He and Ar spectra were used in a manual iterative fashion to fit the spectrum of that mixture directly (without the intermediate step of the Gaussians). This was necessary due to software problems when dealing with the extensively overlapped He and Ar peaks.

The composition of each gas mixture was measured and adjusted to the specified ratio using (e, e+ion) time-of-fight (TOF) mass spectra recorded in the same instrument [23]. The (e, e+ion) experiment uses the same gas cell collision region, the same elec-
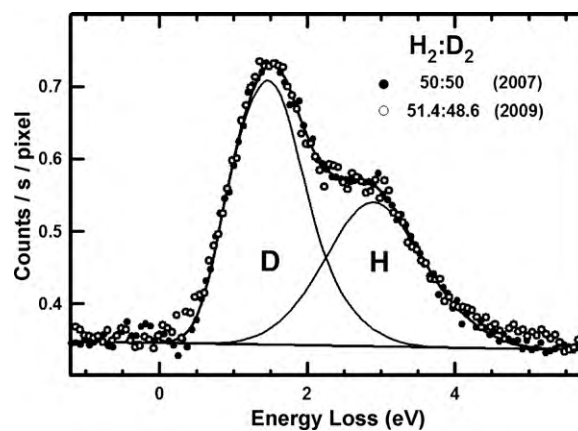

Fig. 1. Quasi-elastic electron scattering (QEES) spectrum of a 51.4:48.6 $H_2:D_2$ mixture prepared by introducing H_2 and D_2 into the spectrometer gas cell through two separate leak valves, such that the mixture occurred on the high vacuum side as the gases flowed into the cell. The QEES spectrum was recorded using 2250 eV impact energy and 100° scattering angle ($q = 19.7$ a.u.). The QEES spectrum for a commercial, pre-mixed 50:50 $H_2:D_2$ mixture reported earlier [4] is also plotted for comparison. The solid lines are fits to the data using the QEES lineshape measured from pure D_2 and pure H_2.

tron transfer and focusing lenses, and the same detection hardware as the energy loss function of the spectrometer, but the spectra were measured at small (3°) electron scattering angle. The (e, e+ion) signal is known to be closely related to photoionization mass spectra measured with a photon energy equivalent to the energy loss [24]. The m/q scales were derived from the experimental flight times using the known masses. The relative atomic and molecular populations (molar fractions) of the gas mixtures were derived from the integrated (e, e+ion) peak intensities, after correcting for the known absolute dipole photoionization cross-sections for H_2, D_2 [25,26], He [27] and Ar [28,29]. Note that since the energy losses used for the TOF spectra were chosen such that there was either very little or no molecular fragmentation (for H_2 or D_2), the dipole photoionization cross-sections for the species studied are well known from several literature sources and the electron–ion coincidences are detected for both gas constituents at the same time, there are very few error sources for the gas composition determination (the largest being the TOF peak area determinations).

Uncertainties in the final results were determined from standard deviations of the numbers over repeat experiments. Since the potential errors come from several different sources (gas composition determination, counting statistics, fitting errors), this overall error estimation method is considered more reliable than error propagation methods. The errors quoted correspond to 2σ. A visual check of the magnitudes of the quoted uncertainties are given by the error bands in the QEES spectra shown below.

3. Results

Fig. 1 presents the QEES spectrum of a ~50:50 H_2 and D_2 mixture which was prepared by introducing the H_2 and D_2 gases into the spectrometer collision cell through separate leak valves. The exact gas composition was determined to be 51.4(4) H_2 and 48.6(4) at% D_2 from (e, e+ion) measurements. The QEES data from a commercially prepared 50:50 H_2/D_2 mixture [4] is also plotted in Fig. 1 for comparison. The H/D peak intensity ratios are identical for the two measurements within statistical uncertainties. The results of a careful quantitative analysis are given in Table 1.

Fig. 2 presents the QEES spectrum of a He/H_2 mixture. The inset is the (e, e+ion) time-of-flight (TOF) mass spectrum of this mixture. There is a small amount of H_2 fragmentation visible at 30 eV energy loss (shown by the presence of the H^+ peak) – this H^+ was

Table 1
Gas compositions from (e, e+ion) mass spectrometry; predicted and observed relative intensities of quasi-elastic electron scattering signals from H_2, D_2, He and Ar.

Gas mixture	Composition (at%)	Ratio of Compton predicted intensities (1st/2nd per-atom)	Ratio of observed intensities	Observed/predicted ratio
H_2/D_2	51.4/48.6	1.06	0.72(4)	0.68(4)
H_2/He	85.1/14.9	1.43	0.74(8)	0.52(6)
H_2/Ar	98.35/1.65	0.188	0.07(1)	0.37(6)
D_2/Ar	98.71/1.29	0.236	0.13(1)	0.55(6)
He/Ar	98.45/1.55	0.781	0.51(6)	0.65(8)

included in the H_2 analyzed intensity. Previously published dipole photoionization cross-sections [25–27] were used to determine the atom% composition of the mixture. The He/H_2 peak area ratio in the QEES spectrum is summarized in Table 1. When compared to He, the signal from scattering from the H is 48(6)% lower than that predicted by the classical Compton scattering cross-section. TOF (e, e+ion) mass spectra of mixtures of H_2/Ar, D_2/Ar and He/Ar are presented in Fig. 3 from top to bottom, respectively. Analogous with the H_2/He case, there is a small amount of D_2 fragmentation visible at the 30 eV energy loss used (shown by the D^+ peak in the D_2/Ar mixture spectrum). This D^+ signal was included in the D_2 analyzed intensity. Previously published dipole photoionization cross-sections [25–27] were used to determine the atom% composition of each of these gas mixtures from the peak areas. The Ar/H_2 composition was checked using two energy losses and two dipole cross-section refs. [25,26,28] to provide a consistency check of the methodology being used.

The QEES spectra that correspond to the H_2/Ar and D_2/Ar binary mixtures are shown in Fig. 4. For the Ar/H_2 mixture the relative intensity of the H peak (summarized in Table 1), corresponds to a QEES signal for H that is anomalously low by 63(6)% compared with Ar. For the D_2/Ar mixture, curve fitting to obtain the QEES intensity for the D signal indicates a 45(6)% anomalously low intensity compared with Ar. When the Ar/H_2 and Ar/D_2 measurements are compared to the H_2/D_2 measurements, the results are internally consistent (see Table 1). This result, along with the agreement of the result from the in situ prepared H_2/D_2 mixture with the earlier result [4], significantly reinforces the reality of the anomaly published earlier [4]. More significantly, the comparison to Ar shows that QEES intensities from D are also anomalously low, although not as low as those for H. This suggests that the anomaly is related in some way to atomic mass, and thus, one might expect heavier atoms, such as He, also to show QEES intensities that are lower than expected from current theories.

Fig. 5 presents the QEES spectrum of a 1.55 at% Ar:98.45 at% He mixture. Note that the curve fit in this case is based directly on the
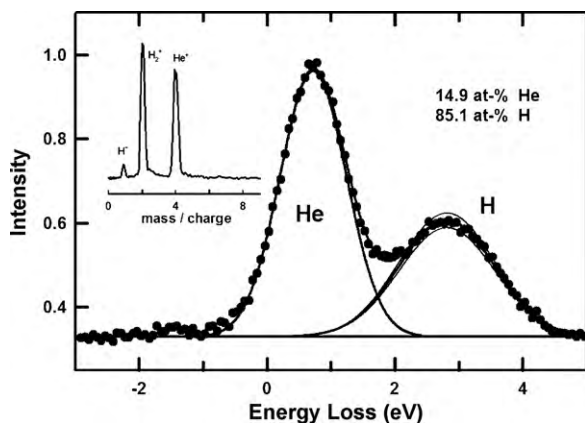
experimentally measured pure Ar and He spectra (see Section 2 for details). Due to the extensive overlap of the He and Ar signals the uncertainty in the relative intensity (indicated by the thin additional lines below and above the He fit signal) is considerably larger than in the other measurements reported in this work. Despite that, the He QEES signal is found to be 35(8)% too low relative to that for Ar compared with the relative intensities expected from ECS theory [1,11–15]. When this result is compared to those from the pairs H_2/Ar and D_2/Ar (Table 1) an internally consistent set of results are found. For example, the H/He intensity ratio is 0.52 that of its expected value based on classical Compton scattering, while the H/Ar ratio is 0.37 of its expected value. Combining these results predicts a He/Ar ratio of 0.71(6) which is reasonable compared to the experimentally measured He/Ar QEES intensity ratio of 0.65(8). Throughout this work we assume that Ar is the least likely species to deviate from the classical picture. Note that this assumption is only necessary in order to set an absolute intensity scale relative
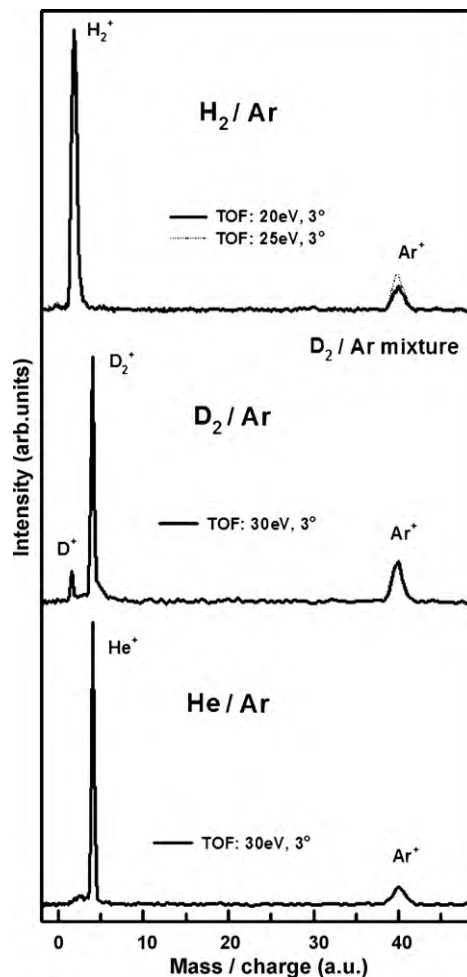

Fig. 2. QEES spectrum of a 14.9 at% He:85.1 at% H_2 mixture. The solid lines are fits to the data using the QEES lineshape measured from pure He and pure H_2. The inset plot shows an (e, e+ion) TOF mass spectrum of this mixture, recorded under conditions where electric dipole transitions dominate, used to determine the composition.

Fig. 3. (e, e+ion) time-of-flight mass spectra of H_2/Ar, D_2/Ar and He/Ar mixtures (top to bottom) recorded under conditions where electric dipole transitions dominate, used to determine the composition.
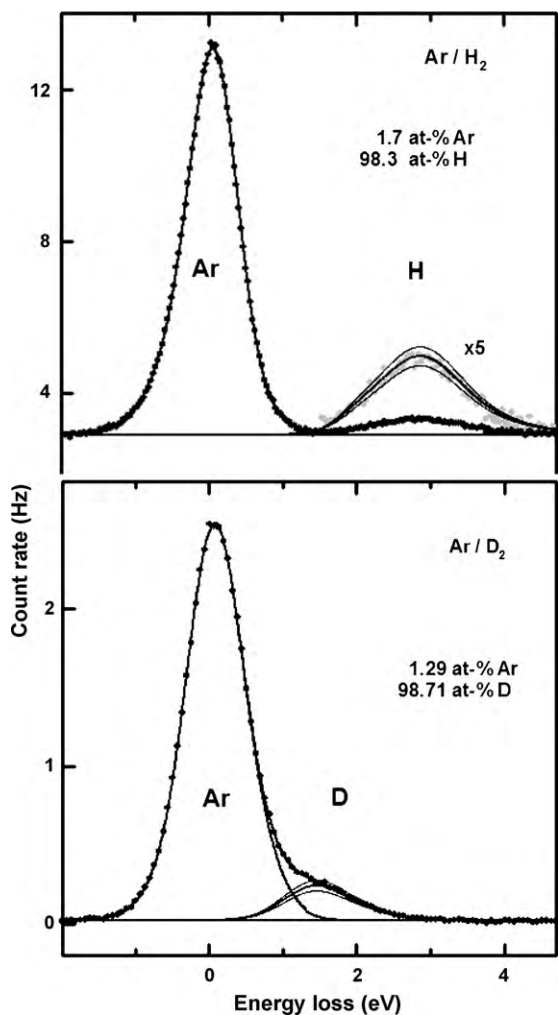
Fig. 4. QEES spectra of a 1.7 at% Ar:98.3 at% H_2 mixture (top) and a 1.29 at% Ar:98.71 at% D_2 mixture (bottom). The signal from H is expanded by a factor of 5. The solid lines are fits to the data using the QEES lineshapes derived from pure Ar, H_2 and D_2. Upper and lower bounds of possible intensity curves are indicated by the thin lines. These correspond to the uncertainties reported in Table 1 which were obtained from standard deviation of repeats.

Fig. 5. QEES spectrum of a 1.5 at% Ar:98.5 at% He mixture. The solid lines are iterative manual fits using QEES experimental spectra measured from pure Ar and pure He. The indicated upper and lower bounds of possible intensity curves for the He signal are shown by the thin lines and correspond to the uncertainties reported in Table 1.

Fig. 6. Summaries of measured quasi-elastic intensities relative to those predicted from classical electron Compton scattering theory [1,11–15], assuming the signal from Ar matches that predicted by the theory. Upper: ratio of the observed to classical ECS theory as a function of atomic mass. Lower: relative QEES intensity (ln scale) versus atomic identity.

to the ECS intensity predictions [10]. We are aware that "screening effects" would change the ECS intensity for Ar [21], but have chosen not to incorporate these. If they were included they would shift the absolute scale of all the data points, but not the relative values.

4. Discussion

Fig. 6 plots the deviation in quasi-elastic intensities relative to the predictions of the classical electron Compton scattering theory [1,11–15] for the atoms that we have measured in the present work and previously [4]. The top panel of Fig. 6 presents the measured intensity ratios relative to the classical ECS theory as a function of atomic mass, while the bottom panel plots measured and theoretical intensities on a natural log (ln) scale for each atom in this study. The ln scale was chosen in order to better display the differences between experiment and theory. H in H_2 and D in D_2 are seen to have large anomalies while He has a smaller anomaly. An effort recently made to reproduce the intensity anomalies in H_2 and D_2 theoretically [11] concluded that conventional quantum mechanics and scattering theory cannot explain the observed quasi-elastic intensities for these light elements. Given that the set of results presented in the present paper constitutes a self-consistent pic-
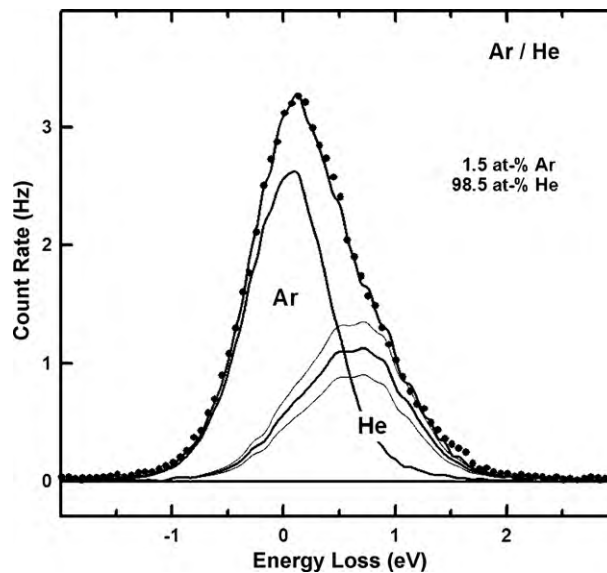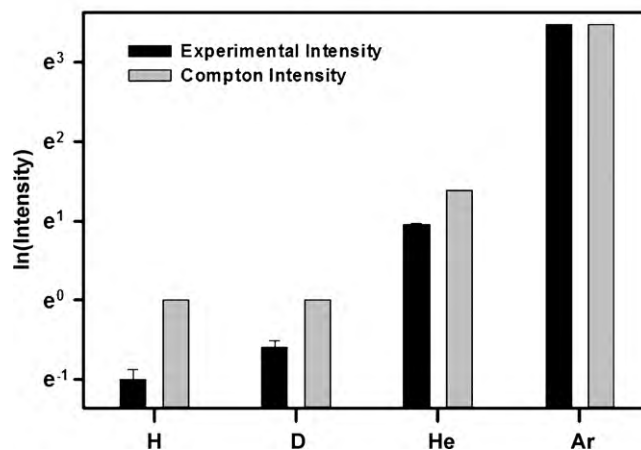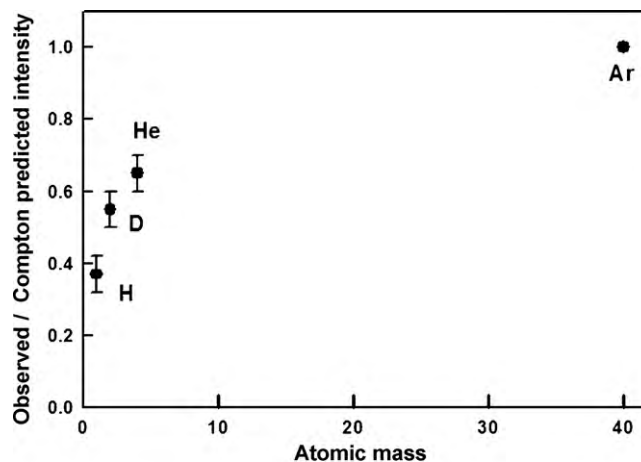
ture, it would seem that this result extends beyond just an anomaly of H relative to D. Further theoretical approaches to computing QEES intensities are required in order to reconcile experiment and theory.

Moreh and Nemirovsky recently speculated [20] that the intensity anomaly shown in Table 1 and previously published in ref. [4] is the result of H_2 having a higher speed than D_2 and hence spending less time in the interaction region, giving a lower than expected intensity by $\sim 1/3$. However, such a large effect would only be seen if the sample were an effusive gas jet which allowed free escape of the sample gas molecules. This is not the case in the present work since a gas cell was used (see Section 2). In addition, if such a molecular speed effect was the cause of the quasi-elastic anomaly, then the (e, e+ion) mass spectra would show the same anomaly since the (e, e+ion) coincidence experiment involves the same gas cell collision region, the same electron transfer and focusing lenses, and the same electron detection hardware as the energy loss function of the spectrometer. Finally, in order to experimentally check whether the arguments advanced in ref. [20] have merit, we have performed (e, e+ion) experiments on H_2/D_2 mixtures where the gas mixture was admitted either directly into the gas cell, or into the spectrometer main chamber and allowed to effuse into the gas cell. The only change to the experimental conditions was to switch the final inlet valve from one gas inlet line to another. Only small differences ($\sim 8\%$) in relative H_2/D_2 signals were found between the two experimental set-ups. The TOF (e, e+ion) experiment reported the same variation in composition, which we attribute to the differential speed effect. Since we normalize our results from the composition of the same volume determined experimentally by the TOF measurement, interaction region variations in sample concentration are fully taken into account. We conclude that the arguments advanced by Moreh and Nemirovsky in ref. [20] to explain the experimental quasi-elastic H_2/D_2 relative intensity anomaly measured in ref. [4] and in the present work, are erroneous.

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