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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, ~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 (~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 ~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.

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):

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

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:

$$\frac{I_a}{I_b} = \frac{N_a Z_a^2}{N_b Z_b^2} \quad (2)$$

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 $\sim 5 \times 10^{-6}$ Torr (measured outside the collision cell) while the background pressure in the spectrometer was $\sim 4 \times 10^{-7}$ 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 electron 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).

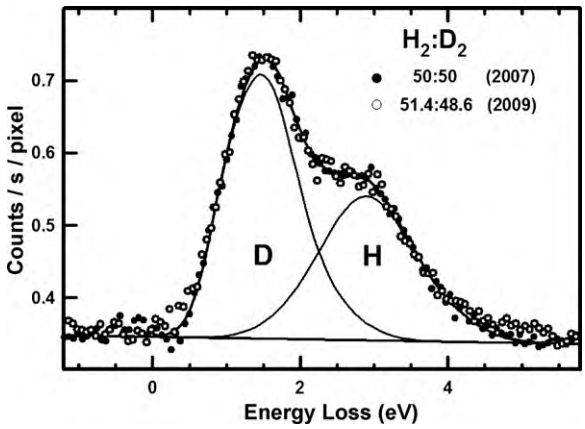

Fig. 1. Quasi-elastic electron scattering (QEES) spectrum of a 51.4:48.6 H_2:D_2 mixture prepared by introducing H_2 and D_2 into the spectrometer gas cell through two separate leak valves, such that the mixture occurred on the high vacuum side as the gases flowed into the cell. The QEES spectrum was 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.

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