

Electron Compton scattering from methane and methane-d4

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Available online 10 November 2006

Abstract

Quasi-elastic electron scattering at high-momentum transfer was measured for CH₄ and CD₄ in the gas phase. At high-momentum transfer, two scattering peaks are observed in each molecule. We interpret the splitting as due to independent Compton scattering from each nucleus, such that, at an impact energy of 2 keV and 100° scattering angle, the peaks for the C and H in CH₄ are split by 2.1 eV while those associated with the C and D in CD₄ are split by 1.1 eV. These splittings are in agreement with those predicted from Rutherford scattering of electrons from single atoms. The widths of the C, H, and D peaks are very different, and reflect the distribution of their momentum. The lineshapes of the H(D) peaks are in agreement with the momentum space vibrational wavefunction. Detailed peak area analysis reveals anomalously low intensities for the hydrogen and deuterium peaks relative to the carbon peak—the theoretical Rutherford C–H ratio is 9.0, compared with 9.8(2) (C–H) and 9.7(2) (C–D) measured in our experiments. Two possible explanations for this discrepancy, one due to deviations of the actual cross section from the Rutherford values, the other due to short lived quantum entanglement, are discussed. The Rutherford scattering interpretation is compared to that for vibrational Compton-like scattering predicted by Bonham and de Souza [R.A. Bonham, G.G.B. de Souza, J. Chem. Phys., 79 (1983) 134]. © 2006 Elsevier B.V. All rights reserved.

Keywords: Quasi-elastic electron scattering; Methane; CD₄; Rutherford scattering; Vibrational Compton-like scattering; Quantum entanglement

1. Introduction

Electron scattering depends on incident momentum and the momentum transfer, q . Scattering intensities from sources separated by $r \gg 1/q$ add incoherently; however, they add coherently if $r \leq 1/q$, leading to phenomena such as diffraction. At a scale of $1/q$, for large momentum transfer, the collision can be treated as a binary encounter of the incident electron with either a nucleus or an electron. Electron scattering at high-momentum transfer was studied initially by Boersch et al. [1] who established that the energy loss of fast electrons (20–40 keV) scattered quasi-elastically from a solid over large angles was equal to $q^2/2M$, that is it was consistent with electrons transferring momentum to single atoms (with mass M) in a Rutherford scattering fashion [2], rather than to the solid sample as a whole. At small energy losses, a broadening of the energy loss peak was also observed. It was not realized at the time but this broadening of the quasi-elastic peak can be interpreted as the Compton profile of the momentum distribution of the scattering atom in its

ground state. In atomic units, if the target atom (mass M) initially has a momentum p_0 , then the energy transfer, $\hbar\omega$, to the target, is given by:

$$\hbar\omega = \frac{(p_0 + q)^2}{2M} - \frac{p_0^2}{2M} = \frac{q^2}{2M} + \frac{p_0 \cdot q}{M} \quad (1)$$

Thus, if the mass of the scatterer is known, the measurement resolves the component of the momentum of the nucleus along the direction of momentum transfer, q . This is similar to X-ray Compton scattering in which scattering of an X-ray by a target electron resolves a component of the electron momentum. For atoms that are confined in a deep narrow potential well (strong chemical bond) the wave function of the atom is confined in coordinate space, and hence a broad distribution in momentum space. The momentum distributions of atoms in materials are related to the strength of chemical bonds. Hence, it is of fundamental interest.

Neutron scattering from solids has been used for some time to measure Compton profiles of atomic motion. The first neutron scattering experiment was reported by Rauh and Watanabe [3] in 1984, and the technique has been used for a range of studies since then [4]. In addition, several recent studies have reported anomalies in the scattering intensities of the peaks due to protons

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in the samples studied [5,6], which have been attributed to short-lived quantum entanglement affecting the proton wave function [5].

The most recent work in this field has presented both high-energy electron scattering [7] and neutron Compton scattering from thin polymer film samples of formvar [8,9] and polyethylene [9,10]. The latter conference proceedings article [10] also presented preliminary data from the gas phase work reported in this paper. The initial high-energy electron scattering data from thin films [7–10] showed quasi-elastic scattering peaks from C (and O, in the case of formvar) and H atoms, with the H peak being separated from the C peak by an energy expected of electrons scattering from single atoms, i.e., the splitting expected from Rutherford scattering considerations. It also demonstrated peak widths consistent with the momentum distributions of the nuclei. In addition, the thin film results appeared to corroborate the anomalous intensities observed in the neutron scattering work for H peaks [5,6]. However, the conclusions were somewhat ambiguous due to potential complications of electron-induced radiation damage to the samples and a significant multiple scattering background that had to be removed from the data prior to peak area analysis [8–10]. An additional electron scattering study has been performed independently by Varga et al. [11] who interpreted their results using Monte-Carlo simulations and invoked significant multiple scattering in order to explain the positions and intensities of the observed peaks.

In the present work we report high-momentum transfer quasi-elastic electron scattering from gaseous methane. In this context, it is important to stress that gas-phase targets are not affected by radiation damage since the sample is continuously refreshed, and that inter-molecular multiple scattering does not occur since the experiment is performed under high vacuum, and thus low sample density conditions (although intra-molecular multiple scattering is of course still possible). For the purpose of a well-established determination of the H-peak intensity, these two factors represent significant improvements with respect to the experimental conditions of the previous thin film electron scattering experiments [8–10]. CH₄ and CD₄ were chosen for these gas experiments since the atomic constituents are the same as in the hydrocarbons studied in the solid state [7–10] and since the simplicity of these molecules allows accurate computational modeling. To our knowledge, aside from our conference report [10], this is the first observation of signals which are unambiguously associated with electron Compton scattering from individual atoms in a gas-phase molecule.

An alternative description of high electron momentum transfer scattering from gaseous molecules was presented by Bonham and de Souza [12] in terms of a vibrational Compton-like scattering picture. Specifically they developed a quantum mechanical theory of the vibration–rotation generalized oscillator strength (VR-GOS) in terms of sum rules and used this treatment to compute results for N₂, I₂, NO, and HCl. At high-momentum transfer (above ~15 a.u.) significant vibrational excitation was predicted in the VR-GOS, which would lead experimentally to both a main peak and a secondary peak (due to vibrational excitation) a few eV higher in energy (calculated values for the shift ranged from ~0.1 to ~3.0 eV). Their results are therefore, qual-

itatively similar to the description we are proposing, but the origin of the splitting and the quantitative details are quite different. For example, for the molecule HCl, a separation of 2.5 eV between the main peak and a “satellite” peak was calculated [12], whereas Rutherford scattering (Eq. (1)) predicts an energy separation of the Cl and H peaks in HCl to be ~7.5 eV under the same scattering conditions (32 a.u. momentum transfer). Further comparisons of the atomic Compton scattering model (Eq. (1)) and the predictions of the Bonham and de Souza approach are presented below.

2. Experimental

Quasi-elastic electron scattering spectra were recorded using the McMaster Variable Angle, High Resolution Electron Spectrometer (McVAHRES). This home-built instrument has been described in detail in previous publications [13,14], including installation and performance of a position sensitive parallel electron detection system [15]. In the spectrometer configuration used for this work, an unmonochromated 2000 or 1650 eV energy electron beam was incident on the gaseous target, which was an effusive jet. The quasi-elastic scattered electrons were decelerated and energy analyzed using a five element lens/hemispherical electrostatic analyzer combination. The scattering angle was changed between 40 and 100° by rotating the analyzer/lens assembly relative to the incident electron beam. Measurements were made in constant final energy mode, such that the impact energy was scanned to produce the spectra. The impact energy is constituted from the sum of the final electron energy (2000 or 1650 eV), the measured energy loss (−4 to +6 eV), and the analyzer pass energy (13 eV). Therefore, it was varied between ~2009 and 2019 eV for the 100° spectra (Fig. 2) (~0.5% range) and 1659 and 1669 eV for the 40–100° variable angle data (~0.6% range). The energy resolution was 0.85 eV for the CH₄ experiments and 0.83 eV for the CD₄ experiments, as determined from the widths of the elastic scattering observed from the C atoms (the natural width of the C peak is expected to be ~0.15 eV, and thus the observed width is dominated by the instrumental width—see below for details). The incident beam current used was in the range of 0.5–2.0 μA and all results were normalized to constant incident current and gas pressure. The background signal due to instrumental factors and gas scattering outside the effusive jet was removed by recording spectra at 5×10^{-6} Torr and 1×10^{-6} Torr (the pressure in the spectrometer vessel, not in the jet, which is ~10 times higher) and taking the difference. Typical electron count rates were in the range of 0.3–0.6 cps/channel at 100° scattering angle (NB the full range of the parallel detector was binned into 64 channels). The gaseous samples of CH₄ and CD₄ (C/D/N isotopes), of stated purity 99 and 99.9%, respectively, were obtained commercially and were used directly.

3. Results and discussion

Fig. 1 shows electron energy loss spectra obtained using 1650 eV final electron energy at increasing scattering angle (hence, increasing momentum transfer, q) from 40 to 100°. It

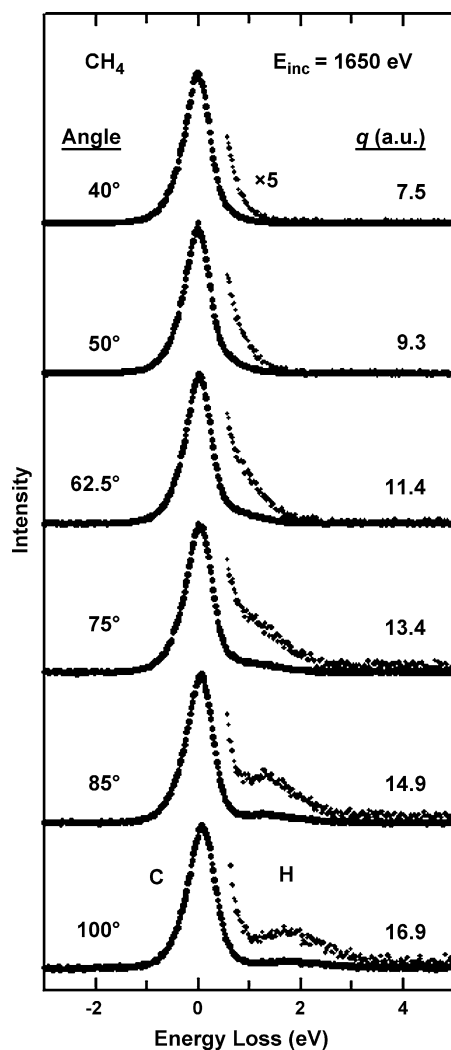


Fig. 1. Quasi-elastic electron scattering of 1650 eV incident energy electrons from methane at scattering angles of 40, 50, 62.5, 75, 85, and 100°, corresponding to the indicated momentum transfers.

is apparent that an additional peak separates from the main elastic scattering peak starting at $\sim 62.5^\circ$ scattering angle. This peak is interpreted as the quasi-elastic scattering peak due to scattering from the H atom, while the main peak derives from scattering from the C atom. These peaks are increasingly well separated at higher momentum transfer, consistent with the Rutherford picture, since the recoil energy is larger at higher momentum

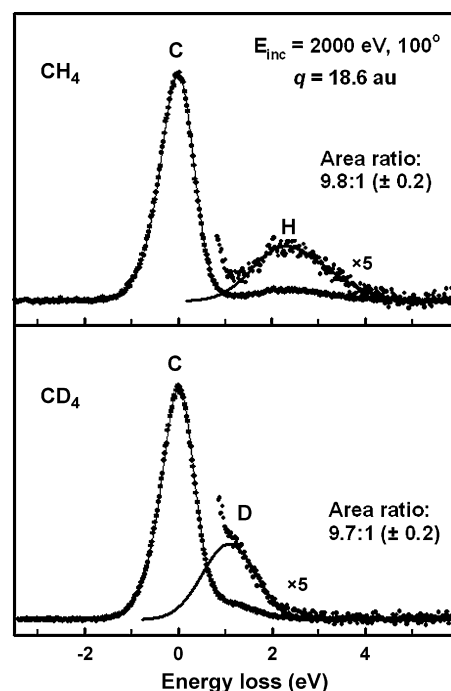


Fig. 2. Quasi-elastic electron scattering of 2000 eV incident energy electrons from CH₄ and CD₄ at 100° scattering angle (points). The lines are curve fits. See text for details.

transfer (Eq. (1)). Based on the quality of the fit to the Rutherford scattering model (see below) we interpret the splitting as the result of scattering by the individual atoms as opposed to scattering by the molecule as a whole. To the best of our knowledge, this is the first observation of this phenomenon in gas-phase molecules. The energy separation of the H peak from the C peak in these spectra is entirely consistent with simple Rutherford scattering [2], i.e., Eq. (1), which describes a two-body collision, within experimental error. This has also been found to be the case for the previously published electron scattering experiments from solid films [7–11].

The quasi-elastic scattering signal in methane was studied in more detail by collecting electron energy loss data at 2000 eV final electron energy and 100° scattering angle, for both CH₄ and CD₄, which are presented in Fig. 2. CD₄ was chosen as an additional target since the C and H(D) peak shifts are proportional to nuclear mass in the Rutherford model. These spectra are the sum of several multi-day, background-subtracted data accu-

Table 1
Peak separation (eV), widths (eV) and peak intensity ratios for quasi-elastic Compton scattering from CH₄ and CD₄ at 18.6 a.u. momentum transfer ($E_0 = 2000$ eV, $\theta = 100^\circ$)

Molecule	Peak separation (eV)		Peak widths (eV)				C/H(D) peak area ratio			
	Exp.	Calc.	C		H(D)		Exp't	Calc.	$R_{\text{calc}}/R_{\text{exp}}$	
			Exp. ^a	Calc.	Exp.	Exp-deconv ^b				Calc.
CH ₄	2.31 (5)	2.34	0.85 (1)	0.14	1.89 (4)	1.69 (4)	1.73	9.8 (2)	9.0	0.92 (2)
CD ₄	1.10 (4)	1.07	0.83 (1)	0.14	1.34 (4)	1.05 (4)	1.03	9.7 (2)	9.0	0.93 (2)

^a The observed peak width is dominated by instrumental broadening. No attempt was made to deconvolute to obtain the intrinsic (Doppler) peak width for the C peak. Instead these experimental values were used to remove the instrumental contribution from the H(D) peaks.

^b These values are following deconvolution of the instrumental resolution, as taken from the C scattering peak.

mulations. Each set of data is fit to two asymmetric Gaussian peaks plus a linear background. The asymmetric Gaussian peaks were constructed from two symmetric Gaussian profiles with fixed relative intensity and position. Table 1 gives the numerical results of this analysis for CH₄ and CD₄. The uncertainties were derived from the standard deviation of the results from curve fits to three individual data accumulations. The experimental separations of the C and the H(D) quasi-elastic peaks (Table 1) agree very well with the predictions of Rutherford scattering theory (Eq. (1)).

The widths of the H and D peaks are significantly larger than the width of the C peaks (Fig. 2), especially the H peak of CH₄. This can be interpreted as due to Doppler broadening induced by the motion of the atom. We are therefore, observing a component of the hydrogen (or deuterium) momentum distribution along the direction of the momentum transfer. As the molecules are randomly oriented in space, the width is proportional to the spherically averaged momentum distribution. We can compare our result for the width of the momentum distribution of the H atoms in CH₄ (Table 1) with results obtained from thin films of polyethylene using high-energy electron scattering [9,10] and neutron Compton scattering [16]. Earlier [10], we noted that the width of the proton momentum distribution, obtained from the observed width of the elastic peak using Eq. (1) is rather independent of momentum transfer or nature of the probing particle (electron, neutron), using experimental results from ~15 to 63 a.u. Fig. 3a compares our result for the width of the H peak (Table 1, momentum transfer of 18.6 a.u.) to the neutron and electron data for H in polyethylene (data from the left hand panel of Fig. 5 in [10]). The width of the proton momentum distribution is expressed in Å⁻¹ and is obtained from the experimental energy width by multiplying by M_H/q (see Eq. (1)).

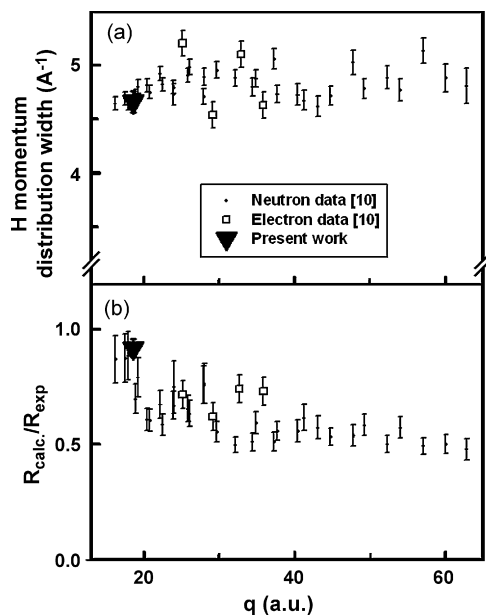


Fig. 3. (a) Width of the measured H atom momentum profile as a function of the experimental momentum transfer. (b) The expected C/H(D) peak area ratio, $R_{\text{calc.}}$, divided by the experimentally observed ratio, $R_{\text{exp.}}$, as a function of momentum transfer.

The momentum distribution of H in CH₄ is similar to that in polyethylene because the C–H bond has similar strength in both cases, which leads to similar delocalization in momentum space.

The momentum distribution for motion of a hydrogen atom in an isotropic harmonic potential is Gaussian. The width of this distribution (σ) can be calculated from the recoil energy (E_r) and the mean kinetic energy of the atoms (\bar{E}_k) according to [9,10,17]:

$$\sigma = \sqrt{\frac{4}{3} \bar{E}_k E_r} \quad (2)$$

The total intra-molecular momentum of the molecule is 0 (otherwise it would dissociate). The momentum of the C atom q_C is thus at most $4 \times q_H$ if all protons move in the same direction. More likely $q_H \approx q_C$ in which case the kinetic energy of the carbon is 12 times less than that of each proton. Using a theoretical calculation of the zero-point energy of ethane [18], plus an estimate of the proportion of this energy associated with the light H atoms guided by both neutron Compton scattering experimental results and theoretical considerations [19] it was possible [10] to approximate the amount of kinetic energy per hydrogen in a C–H bond, and hence calculate the fwhm of the H peak in CH₄ as ~ 1.6 eV (Eq. (2)). Use of a theoretical zero-point energy for methane itself [20] along with the same procedure gives an estimate that is the same within 0.02 eV. This value (1.6 eV) is reasonably close to the presently observed experimental H peak width of 1.89(4) eV (Table 1). Moreover, if the instrumental resolution of the present CH₄ experiments is taken into account (0.85 eV is quadrature subtracted), we obtain an experimental value of $\sim 1.69(4)$ eV for the natural width of the H peak, which is within $\sim 6\%$ of the theoretical estimate. The instrumental resolution was determined from the measured widths of the C peaks since the natural linedwidth of the C peaks is calculated to be ~ 0.14 eV from an estimate of 0.0125 eV kinetic energy for the C atoms [10] using the zero-point energy of ethane [18] or methane [20] and Eq. (2). This would lead to a correction of less than 0.02 eV in the experimental resolution, which we have chosen not to apply. Working backwards from the H peak width of 1.69(4) eV, the estimated mean kinetic energy of H in CH₄ is 0.17 eV. It is also possible to use the experimental peak width for D in the CD₄ spectrum (Fig. 2, Table 1) to derive the mean kinetic energy of the D atoms in CD₄. Using the same approximations described above for CH₄, we obtain a value of 0.22 eV for the mean kinetic energy of D in CD₄ by directly using the experimentally observed peak width. This becomes 0.13(2) eV after correcting for the finite instrumental resolution (0.83 eV is quadrature subtracted). The ratio of the H/D kinetic energies is 0.17 eV(H)/0.13 eV(D) ≈ 1.26 , which is within $\sim 10\%$ of the ratio of $\sqrt{2}$ expected from the H/D mass ratio of 1/2 [10].

An alternative method of calculating peak widths for comparison with the experimental values is to use C–H and C–D vibrational wavefunctions. Since the link with experiment (Eq. (2)) involves assumption of a harmonic potential, we have performed calculations using this approximation. The zero-point energy dominates for CH₄ and CD₄ at room temperature, and there is very little anharmonicity in the ground state [20].

Thus, the harmonic approximation should be valid. Trial calculations using a Morse potential for C–H gave essentially identical results to those presented here. Using parameters for the diatomic molecules CH and CD given in [21] we have calculated (zero-point) ground state wavefunctions for the H and D atoms in both position and momentum space. There are several methods that can then be used to derive an experimental peak width. First, using the uncertainty relation, $\Delta \times \Delta p \geq \hbar/2$, a mean kinetic energy of the H or D atoms can be derived from the width of the calculated position space wavefunction using the probability density. This gives 0.173 eV for CH₄ and 0.132 eV for CD₄. Transforming to momentum space wavefunctions and calculating an expectation value for the average kinetic energy of the H and D atoms gives 0.178 eV for H and 0.130 eV for D. The small differences between the two different calculation methods arise mainly from numerical errors in determining the position space probability width. Using averages of these calculated values then gives an H/D peak width ratio of 1.34, very close (within ~5%) to the classically expected $\sqrt{2}$ [10]. In addition, using the experimentally determined C–H peak separation energies (Table 1) to calculate experimental peak widths from these theoretical results gives 1.73 eV for H and 1.03 eV for D, compared with the observed widths (after subtraction of the instrumental function) of 1.69(4) and 1.05(4) eV, respectively. Thus, the widths computed from momentum space vibrational wavefunctions are identical to the observed peaks widths within experimental error.

Fig. 4 shows the 100° experimental data for CH₄ and CD₄ after subtraction of the fitted C peaks, compared with Gaussian

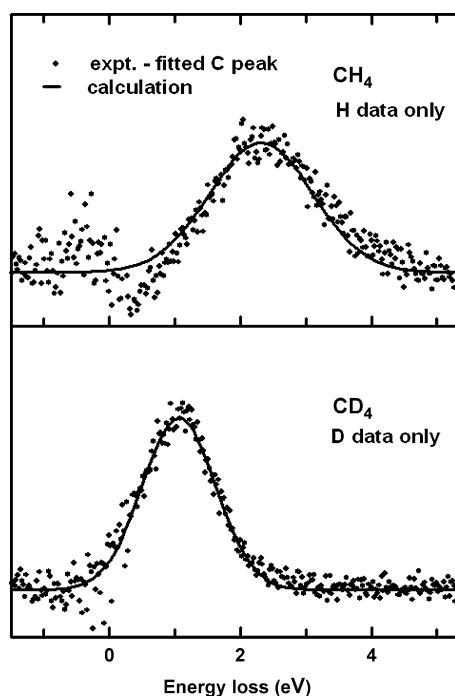


Fig. 4. The data of Fig. 2 after subtraction of the fitted C peaks, compared with the computed momentum space vibrational wavefunction. The latter are Gaussians (harmonic potential) obtained using the theoretically calculated H and D kinetic energies, along with the experimentally measured H and D peak positions, convoluted with the instrumental resolution.

curves generated from these theoretically calculated H and D average kinetic energies, combined with the experimental H and D peak positions and instrumental Gaussian functions (taken from the fits to the C peaks). Agreement between theory and experiment is very good. Note that the asymmetry in the H peak of CH₄ and the systematic errors in the fitting procedure are exaggerated in this particular plot.

Analysis of the C and H(D) peak areas by the curve fitting procedure outlined above yields the relative peak areas given in Table 1. The C to H(D) peak area ratio should be 9 if the peak intensities are given by the Rutherford cross section formula in which the cross section is proportional to Z^2 , the square of the nuclear charge. Our results indicate a significant deviation from the classical Rutherford model. Within experimental error, we find the C/H(D) intensity ratios for CH₄ and CD₄ to be the same as each other, but to be ~8% higher than that predicted by the Rutherford model. The previously published high-energy electron scattering and neutron Compton scattering results [9–11] on thin polyethylene films (along with similar results on the polymer formvar [8]) also reported “anomalously” high C/H intensity ratios. Fig. 3b (adapted from the right-hand panel of Fig. 5 in [10]) summarizes the trend in this ratio over the momentum transfer range ~15 to 63 a.u., measured by both the electron and neutron Compton scattering experiments. The data in Fig. 3b is presented in the form of $R_{\text{calc}}/R_{\text{exp}}$, which is the ratio of the “expected” C/H intensity ratio divided by the experimental C/H intensity ratio, i.e., if experiment and theory agree this value should be 1. The values of $R_{\text{calc}}/R_{\text{exp}}$ at 18.6 a.u. momentum transfer are 0.92(2) for CH₄ and 0.93(2) for CD₄ (Table 1). These are close to the values derived from the neutron Compton scattering experiments at similar momentum transfer values. The general trend in $R_{\text{calc}}/R_{\text{exp}}$ (as observed with neutron Compton scattering) is a gradual decrease in the ratio as the momentum transfer is increased (from ~0.9 below 20 a.u. momentum transfer to ~0.57 at ~60 a.u. momentum transfer). Ref. [10] reported calculations of electron scattering cross sections from C and H atoms as a function of impact energy from ~1 to 30 keV using the partial wave formalism of Salvat and Mayol [22]. Exchange and relativistic effects are included in this code but polarization effects are not. The theoretically calculated C/H intensity ratios are plotted in Fig. 4 of [10]. At higher energy the calculated ratio approaches the Rutherford cross section to within a few percent, but at energies below ~5 keV there are deviations, which depend on the scattering angle. At our experimental conditions of 2 keV impact energy and 100° scattering angle, the measured C/H(D) intensity ratio for methane is within ~3% of that predicted by these calculations. The deviation from the Rutherford C/H(D) intensity ratio, which we measure, could therefore be explained by screening of the nuclear potential by the target electron density. We note that scattering at high-momentum transfer occurs in a much smaller region around the nucleus and screening is less important than in low momentum transfer scattering.

However, the intensity deviations shown by the high-energy electron scattering results from polyethylene films [10] cannot be explained by such effects. Ref. [10] presents alternative ideas to explain the differences from Rutherford cross sections. Specifically, there is a well-established theory which has

been developed in the neutron scattering literature [4,23,24] to describe the intensity and energy loss distribution of neutrons scattered from nuclei within the first Born approximation. At high enough electron impact energy it can be expected that the results of electron scattering should be directly comparable to neutron data, since the interaction of an electron with a single atom becomes weak at high energies. At the 15–30 keV energies used in the thin film experiments [10] this condition should be completely satisfied. Indeed refs. [8,9] demonstrate good agreement between high-energy electron and neutron Compton scattering results for both polyethylene and the polymer formvar. However, the weak interaction requirement for the first Born approximation becomes somewhat questionable at the 2 keV impact energy used in the present gas-phase experiments. From the neutron scattering theory [4,24], there is a certain time, called the scattering time, after which a proton cannot interact with the scattering neutrons (electrons). Of similar order of magnitude is the so-called decoherence time, during which phase information between the struck particle (proton) and its adjacent particles (e.g. electrons) is lost [25] and the nucleus behaves like a classical particle (as in the Rutherford model [2]). It has been proposed [5,8,25] that if the momentum transfer is high enough then the scattering time will become comparable to this decoherence time and the measurement will probe the proton wavefunction (target and scatterer will become entangled, also with the adjacent electrons). The detailed theoretical analysis of this quantum dynamical process leads to a reduced scattering cross section due to this “ultra-short quantum entanglement” [25]. This effect would give rise to a lower relative H cross section, which is what is observed in both the present experiments and the previously published polymer film scattering experiments [8–11]. This also provides a potential explanation for the trend observed in the relative H intensity, which decreases with increasing momentum transfer (see Fig. 3b).

It is interesting to compare our interpretation of these experimental results in terms of independent scattering from the C and H(D) atoms, with an alternate interpretation as vibrational Compton-like scattering according to the quantum mechanical model proposed by Bonham and de Souza [12]. For electron scattering at high-momentum transfer from diatomic molecules such as HCl, the calculation of the vibrational Compton-like scattering [12] predicts a peak with maximum intensity near zero energy loss plus a broad satellite at nonzero energy loss. Quantitatively, using the case of HCl at 32 a.u. momentum transfer as an example, a separation of 2.5 eV between the main peak and a satellite was calculated [12]. Rutherford scattering (Eq. (1)) predicts an energy separation of the Cl and H peaks in HCl to be ~ 7.5 eV under the same scattering conditions. A high-momentum transfer electron scattering experiment on HCl should therefore, differentiate these two descriptions. In addition, the method described in [12] results in “satellite” peaks in polyatomic molecules such as ethane or propane which are several times more intense than for methane due to the presence of a larger number of normal modes [26]. In contrast, the Rutherford description predicts C to H intensity ratios for ethane very similar to those for CH_4 . Thus, experimental measurements of quasi-elastic scattering for a larger hydrocarbon such as ethane

or propane could be used to differentiate the Rutherford scattering interpretation from the quantum mechanical vibrational Compton-like description [12]. Finally, if quasi-elastic electron scattering could be studied at extremely high-energy resolution (5–10 meV or better), the vibrational Compton-like scattering picture would predict the existence of discrete vibrational excitations whereas the independent atom scattering picture predicts only a single peak for each atom type with a lineshape reflecting the momentum distribution of the ground state vibrational wavefunction. Of course, vibrational inelastic scattering [27] also occurs in this energy loss and momentum transfer regime. In our view this would be in addition to the Rutherford scattering effect, but could be readily differentiated by variable momentum transfer studies at high-energy resolution since the vibrational loss signal would have a fixed energy separation. Clearly both types of physical processes are possible; the question is, which one dominates? Some interesting experimental and theoretical work lies ahead to determine the relative contributions of Rutherford and vibrational Compton-like scattering. We note that further aspects of electron-molecule scattering related to these observations are presented in the contribution by Russ Bonham in the present issue [28]. Vos and Went [29], also in this issue, have proposed using solid state quasi-elastic scattering measurements as an analytical technique, within the Rutherford scattering model. They have also shown very recently that the lineshapes for high-angle electron scattering from graphite are sensitive to the anisotropy of the bonding and thus, to anisotropic internuclear motion [30].

4. Summary

We have reported the first observation of multiple peaks in quasi-elastic scattering of gases (methane) and have interpreted the signals in terms of Compton scattering of the incident electron independently from each atom in the molecule. The widths of the peaks attributed to hydrogen and deuterium are in good agreement with quantum mechanical calculations of the zero-point kinetic energy and the lineshapes are consistent with the C–H (C–D) vibrational wavefunction. Additional studies are planned or are in progress to clarify some of the issues raised in this work. These include: (1) performing similar experiments at higher electron impact energies (5 keV or higher) and at higher scattering angles; (2) measuring the quasi-elastic spectrum of HCl and C_2H_4 ; (3) measuring HD or an H_2/D_2 mixture; (4) measuring the signals with high-energy resolution.

Acknowledgements

We thank Russ Bonham for extensive discussions and advice on the vibrational Compton-like scattering theory and its predictions. This work was supported financially by NSERC (Canada) and the Canada Research Chair program.

References

- [1] H. Boersch, R. Wolter, H. Schoenbeck, *Z. Physik* 199 (1967) 124.
- [2] E. Rutherford, *Philos. Mag.* 21 (Series 6) (1911) 669.

- [3] H. Rauh, N. Watanabe, *Phys. Lett.* 100A (1984) 244.
- [4] G.I. Watson, *J. Phys.: Condens. Matter* 8 (1996) 5955.
- [5] C.A. Chatzidimitriou-Dreismann, T. Abdul-Redah, R.M.F. Streffer, J. Mayers, *Phys. Rev. Lett.* 79 (1997) 2839.
- [6] C.A. Chatzidimitriou-Dreismann, T. Abdul-Redah, R.M.F. Streffer, J. Mayers, *J. Chem. Phys.* 116 (2002) 1511.
- [7] M. Vos, *Phys. Rev. A: At. Mol. Opt. Phys.* 65 (2002), 012703.
- [8] C.A. Chatzidimitriou-Dreismann, M. Vos, C. Kleiner, T. Abdul-Redah, *Phys. Rev. Lett.* 91 (2003) 57403.
- [9] M. Vos, C.A. Chatzidimitriou-Dreismann, T. Abdul-Redah, J. Mayers, *Nucl. Instrum. Methods B* 227 (2005) 233.
- [10] M. Vos, G. Cooper, C.A. Chatzidimitriou-Dreismann, *Inst. Phys. Conf. Ser.* 183 (2005) 81.
- [11] D. Varga, K. Tokesi, Z. Berenyi, J. Toth, L. Kover, *Surf. Interface Anal.* 38 (2006) 544.
- [12] R.A. Bonham, G.G.B. de Souza, *J. Chem. Phys.* 79 (1983) 134.
- [13] I.G. Eustatiu, J.T. Francis, T. Tyliczszak, C.C. Turci, A.L.D. Kilcoyne, A.P. Hitchcock, *Chem. Phys.* 257 (2000) 235.
- [14] I.G. Eustatiu, T. Tyliczszak, A.P. Hitchcock, C.C. Turci, A.B. Rocha, C.E. Bielschowsky, *Phys. Rev. A* 61 (2000) 042505.
- [15] A.P. Hitchcock, S. Johnston, T. Tyliczszak, C.C. Turci, M. Barbatti, A.B. Rocha, C.E. Bielschowsky, *J. Electron Spectrosc. Relat. Phenom.* 123 (2002) 303.
- [16] R.M. Brugger, A.D. Taylor, C.E. Olsen, J.A. Goldstone, A.K. Soper, *Nucl. Instrum. Methods* 221 (1984) 393.
- [17] M. Paoli, R. Holt, *J. Phys. C* 21 (1988) 3633.
- [18] J. Corchado, D. Thrular, *J. Phys. Chem. A* 102 (1998) 1895.
- [19] J. Mayers, T.M. Burke, R.J. Newport, *J. Phys.: Condens. Matter* 6 (1994) 641.
- [20] J.M. Bowman, D. Wang, X. Huang, F. Huarte-Larranaga, U. Manthe, *J. Chem. Phys.* 114 (2001) 9683.
- [21] K.P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure IV, Constants of Diatomic Molecules*, Van Nostrand, New York, 1979.
- [22] F. Salvat, R. Mayol, *Comput. Phys. Commun.* 74 (1993) 358.
- [23] L.V. Hove, *Phys. Rev.* 95 (1954) 249.
- [24] V.F. Sears, *Phys. Rev. B* 30 (1984) 44.
- [25] C.A. Chatzidimitriou-Dreismann, *Laser Phys.* 15 (2005) 780.
- [26] R.A. Bonham, personal communication.
- [27] H. Hotop, M.-W. Ruf, M. Allan, I.I. Fabrikant, *Adv. At. Mol. Opt. Phys.* 49 (2003) 85.
- [28] R.A. Bonham, *J. Electron Spectrosc. Relat. Phenom.* 155 (2007) 1.
- [29] M. Vos, M.R. Went, *J. Electron Spectrosc. Relat. Phenom.* 155 (2007) 35.
- [30] M. Vos, M.R. Went, *Phys. Rev. B* 74 (2006) 205407.