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Quasielastic electron scattering from methane, methane-d4, methane-d2, ethylene, and 2-methylpropane

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Quasielastic electron scattering from gaseous species at high momentum transfer was recently reported for the first time [Cooper *et al.*, J. Electron Spectrosc. Relat. Phenom. **155**, 28 (2007)]. The first results for CH_4 and CD_4 were well explained by a classical electron Compton scattering picture in which the electron scatters independently from each atom rather than the molecule as a whole. However, an alternative possible interpretation in terms of nondipole molecular vibrational excitation is suggested by previously published quantum mechanical calculations on high momentum transfer electron scattering from diatomic molecules [Bonham and de Souza, J. Chem. Phys. **79**, 134 (1983)]. In order to determine which of these two interpretations best fits the experimental results, we have measured the quasielastic spectra of gaseous 2-methylpropane, ethylene, methane, and two isotopically substituted methanes, CH_2D_2 and CD_4, at a momentum transfer of ~20 a.u. (2.25 keV impact energy and 100° scattering angle). The experimental spectra are found to be composed of as many peaks as there are different atomic isotopes in the molecule (two for CH_4, C_2H_4, 2-methylpropane, and CD_4 and three for CH_2D_2). The peak positions are predicted accurately by the independent atom electron Compton scattering model, and the relative intensities are in reasonable agreement. The experimental results thus support classical electron Compton scattering as the origin of the signal. © *2007 American Institute of Physics*.

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I. INTRODUCTION

Electron energy loss spectra at near zero energy loss recorded at large momentum transfer (high impact energy and scattering angle) from both gaseous[1,2] and solid[3–5] samples have revealed multiple peaks with energy separations that increase with increasing momentum transfer when the molecular or solid target is composed of more than one atomic constituent. For example, Fig. 1 of Ref. 2 shows that, for gaseous methane, above a certain momentum transfer (~10 a.u.) a second electron scattering peak begins to be observed in the elastic scattering region and becomes clearly separated from the main peak at sufficiently large (~17 a.u.) momentum transfer. Conventionally,[6] for elastic scattering from gaseous species at an energy resolution of ~1 eV full width at half maximum, one would typically expect only a single peak with perhaps a small asymmetric tail on the side of increasing energy loss due to unresolved vibrational excitation. The existence of multiple peaks with q-dependent separation in the near zero energy loss region contradicts this conventional wisdom. In the present paper we will refer to these signals as quasielastic scattering.

To date, most articles dealing with this phenomenon have interpreted the observations in terms of a classical scattering model in which the incident particle is considered to scatter independently from each atom of the target system. Conservation of energy and momentum is used to predict absolute peak positions, while peak intensities are given by the Rutherford electron scattering cross section and peak widths are described in terms of a Doppler effect.[7] A second model which could explain the observations is a nondipole molecular vibrational scattering model advanced by Bonham and de Souza in 1983,[8] which predicted near-elastic signals at high momentum transfer due to complex vibrational excitation of the target molecule. Both of these interpretations are explored and compared with experimental results in the present work.

The first (classical) model is referred to in the following and elsewhere as the "electron Compton scattering" (ECS) model. It is based on some approximations that are regularly used in the field of quasielastic neutron scattering studies, also known as neutron Compton scattering (NCS).[9–12] In particular, the Born and the incoherent approximation[10] are invoked. These approximations are applicable to the high momentum transfer conditions ($r < q^{-1}$) of the current experiments. The Born approximation assumes that the electron scattering happens as a single event and is not a sum of many smaller deviations. The incoherent approximation 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.[2] The outcome is that the scattering problem is reduced to a generic binary collision involving any kinds of classical projectiles and targets independent of impact parameter or interaction. From conservation of energy and momentum, the energy transferred from the projectile to the target, $\hbar\omega$, is related to the initial momentum of the target (p_0), the mass of the target (M), and the momentum transfer (q) by

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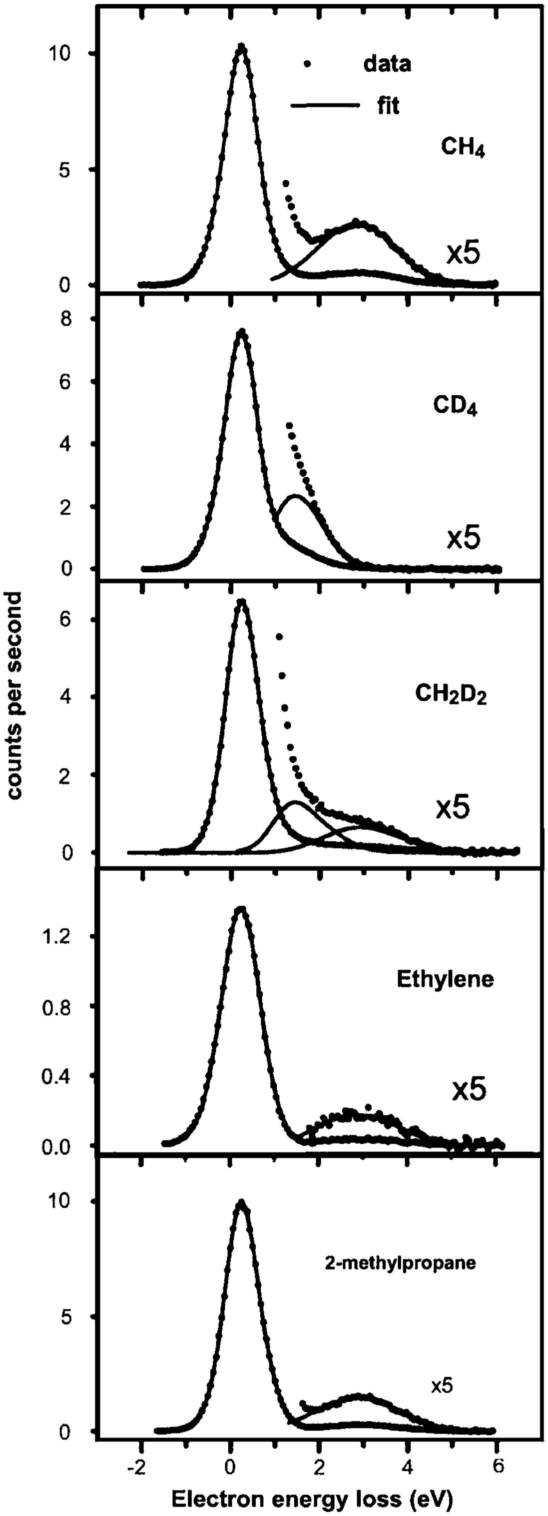

FIG. 1. Quasielastic electron scattering spectra for three isotopologues of methane (CH_4, CH_2D_2, CD_4), ethylene (C_2H_4), and 2-methylpropane (C_4H_{10}) recorded at an impact energy of 2250 eV and a scattering angle of 100°, corresponding to $q \sim 19.7$ a.u. Also shown are the sum and individual peaks from fits to the experimental data (see text for details).

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

Because the system is operating in the quasielastic regime, the electron energy loss $\hbar\omega$ in Eq. (1) is associated with the recoil energy of the target atom. It is also the peak position in the energy loss spectrum relative to the energy of electrons which are not scattered by the target. For quasielastic scattering from molecules containing atoms of different masses, Eq. (1) predicts one energy loss peak for each different atomic mass.

The ECS model predicts that quasielastic scattering intensities will follow the Rutherford cross section whereby the ratio of the intensity of quasielastic scattering from, e.g., a H relative to that from a C will be related to the relative number of each atom type in the target according to[7]

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

This leads to predicted C:H (or C:D) intensity ratios of 9 in CH_4 and CD_4, 18 in ethylene, 18 for both H:C and D:C in CH_2D_2, and 14.4 for methylpropane. Thus, among the molecules studied, the ECS model predicts that the "satellite" intensity will be the highest in methane.

The second model, referred to as molecular vibrational Compton scattering (MVCS), results in electron scattering intensity (a satellite peak) generated a few eV above the "main" translational scattering peak, which is itself at nonzero energy loss. The energy loss of the "main" peak is, however, calculated to be at a different absolute energy loss than the first energy loss peak in the ECS case while the position and intensity of the nondipole vibrational excitation satellite depend on the vibrational modes of the molecule and nondipole cross sections in a complex fashion. In a diatomic molecule the energy and intensity of the molecular vibrational Compton scattering satellite peak will depend on the reduced mass of the molecular vibration (lower masses give rise to a higher energy satellite). For more complex molecules with more vibrational modes available to be excited, the satellite intensity will also be relatively increased, and it will increase the higher the momentum transfer of the experiment. At present, the theory can predict results for diatomic molecules but cannot be applied reliably to polyatomic species. Extensions to treat polyatomics are being developed.[13] Taking the example of the diatomic molecule HCl, the calculation of the molecular vibrational Compton-like scattering[8] predicts a peak with maximum intensity near zero energy loss plus a broad (rovibrational, ~3.5 eV wide) satellite at higher energy loss. The original published calculations for HCl (Ref. 8) have been repeated using the most up-to-date code for diatomics[13] which contains a much better treatment of rotational excitation. Quantitatively, using the case of HCl at 32 a.u. momentum transfer as an example, a separation of 7.0 eV between the main peak and the satellite peak is calculated,[13] with the maximum vibrational excitation taking place at the $\nu'=6$ level (note that in the originally published paper,[8] this separation was calculated to be ~2.5 eV). Meanwhile the electron Compton scattering model predicts an energy separation of the Cl and H peaks in HCl of ~7.5 eV at 32 a.u. momentum transfer, with peak widths given by the Doppler effect.[7] These calculated main peak/satellite peak energy separations turn out to be remarkably similar to one another in this particular case

According to the MVCS model the ratios of the intensities of the satellite peaks to those of the main peaks in polyatomic hydrocarbons such as ethylene or methylpropane will be several times larger than those for methane due to the presence of many more normal modes of vibration that can be excited.[13] Therefore, comparison of quasielastic scattering spectra of complex polyatomic hydrocarbons to those for methane is one way to differentiate the electron Compton and the molecular vibrational Compton scattering models. In addition, it is clear that the ECS model predicts one peak for every atomic constituent in the target [Eq. (1)] whereas in the MVCS model a more complex relationship exists between the number of peaks in the spectrum and the number of bonds and vibrational modes in the target species.[13] The spectrum of CH_2D_2 should therefore provide evidence whether the electron Compton model is validated by the number of peaks in its quasielastic electron scattering spectrum.

The present paper presents experimental data from quasielastic electron scattering by gas phase CH_4, CH_2D_2, CD_4, ethylene, and 2-methylpropane at high momentum transfer ($q \sim 19.7$ a.u.: 2250 eV electron impact energy, 100° scattering angle). The peak positions, peak widths, and relative intensities are compared to the electron Compton and the molecular vibrational Compton scattering predictions. The quasielastic spectra of methane and CD_4 were reported earlier,[8] but new data, measured at higher electron impact energy, and thus higher q, are reported here since the C and H peaks are more clearly resolved with better statistics.

II. EXPERIMENT

Quasielastic electron energy loss spectra were recorded using the McMaster variable angle high resolution electron spectrometer (McVAHRES) which has been described in detail elsewhere.[14–16] For these experiments, an unmonochromated 2250±0.6 eV electron beam was scattered by the gaseous target which was introduced into a gas cell. Electrons scattered at high angle (100°) were decelerated and energy analyzed using a five element lens combined with an electrostatic hemispherical analyzer. The scattering angle was fixed at 100° relative to the incident electron beam. This corresponds to a momentum transfer of 19.7 a.u. Spectra were measured by varying the electron energy loss from −3 to +6 eV relative to the mean elastic signal. The instrumental resolution (~0.9 eV) for these experiments is determined from the width of the quasielastic scattering peak from the C atoms. The incident electron beam current was ~0.5 μA for 2-methylpropane, ~0.4 μA for CH_2D_2, ~1.46 μA for methane, ~1.26 μA for CD_4, and between 1.5 and 4.6 μA for ethylene. The background signal due to electronic noise and gas scattering outside the gas cell was removed by subtracting the spectrum measured at a fivefold lower chamber pressure (reduced from $\sim 5 \times 10^{-6}$ to $\sim 1 \times 10^{-6}$ torr). By leaving ~20% of the gas in the system, changes in contact potentials were minimized.

Each spectrum was measured using multiple scans over several days. Typical maximum count rates for the main peaks were 1–6 counts/s. Each molecule was measured a number of times (typical total accumulation period was 10 days). The spectra were both treated independently and averaged to investigate possible systematic errors. The gaseous samples of methylpropane (Matheson), ethylene (Liquid Carbonic Inc.), methane (Matheson), CD_4 (C/D/N isotopes), and CH_2D_2 (C/D/N isotopes, 98.9 at. % D) were obtained commercially and used directly.

III. RESULTS

The experimental background-subtracted quasielastic electron energy loss spectra determined in the present work were fitted to a linear background and a number of asymmetric Gaussian curves corresponding to the number of atomic isotopes in each molecule. The sums of the best experimental spectra, accompanied by their respective best fits, are shown in Fig. 1. The asymmetric Gaussians were constructed from either two or three symmetric Gaussians so as to best fit the data while limiting excess overlap of peaks. The particular choices of arrangements of symmetric Gaussians within the composite asymmetric Gaussian peaks were based on the "tail shape" as well as on comparisons to the peak shape fit to different spectra of the same molecule, and to peaks associated with the same atom (within the ECS model) in different molecules. For all molecules studied in the present work, three Gaussians were used to form the main (carbon) peak while two Gaussians were used in the construction of the peaks due to deuterium and hydrogen (labeled within the electron Compton scattering interpretation). The purpose of such fits is to be able to isolate the contribution from the peaks associated with each element and then extract the peak position, width, and area for each of them.

Table I shows the numerical results of the analyses performed for methane, CH_2D_2, CD_4, ethylene, and methylpropane. The uncertainties are the larger of the standard deviations of the numbers obtained from the different data sets, and the variations that arose from using different (but reasonable) starting parameters and peak shapes for the fits. The results presented in Table I are the averages of what are considered to be the best data analyses performed for each species. However, some residual uncertainties exist due to the fact that the peaks are significantly overlapped and the peak shapes are not known exactly. The fitted widths of the main (C) peaks range from 0.89(6) to 1.04(6) eV. Although these should be the same in all cases, experimental variations occur due to differences in instrumental response and/or energy scale stability as each molecule is measured. The numerical results from the fits of the CD_4 and the CH_2D_2 spectra are considered of reduced precision because of the large amount of overlap between the carbon and the deuterium peaks. This made the fitting process very difficult as many different approaches yield the same quality of overall fit but resulted in different peak positions, widths, and intensities. The uncertainties listed in Table I for these molecules take this into account as well as the above-mentioned factors.

A. Differentiating the models

The energy scales of the quasielastic electron energy loss spectra were calibrated such that the main peak (elemental C) position was set to an energy loss of 0.242 eV, as predicted by Eq. (1). With this calibration, the peaks associated

TABLE I. Peak positions, peak widths, and relative intensities in the quasielastic electron energy loss spectra of CH_4, CH_2D_2, CD_4, ethylene, and 2-methylpropane.

		Peak position (eV)		Peak widths (eV)				Peak area ratios			
Molecule	Atom	Expt.	Theor.	Expt.	Expt. deconv.	Calc. (wavefn)	Calc. (ZPE)	Expt. % of total	Rutherford	Expt. (C/X)	$R_{\mathrm{expt}}/R_{\mathrm{calc}}$
CH_2D_2	C		0.24	0.89(6)				90.6(3)			
	D	1.4(1)	1.45	1.3(2)	0.9(3)	1.19	1.07	5.3(3)	18	17(3)	1.0(2)
	H	2.9(2)	2.90	2.0(4)	1.8(5)	1.94	1.79	4.1(2)	18	22(6)	1.2(3)
CH_4	C		0.24	0.99(6)				90.2(6)			
	H	2.9(1)	2.90	2.1(2)	1.9(2)	1.94	1.79	9.8(6)	9	9.2(7)	1.02(8)
CD_4	C		0.24	0.92(6)				91.8(3)			
	D	1.44(4)	1.45	1.4(1)	1.0(2)	1.19	1.07	8.2(3)	9	11(2)	1.3(2)
Ethylene (C_2H_4)	C		0.24	1.04(6)				95.3(1)			
	H	2.91(6)	2.90	2.1(1)	1.8(2)	1.94	1.79	4.7(1)	18	20(1)	1.12(8)
Methylpropane	C		0.24	0.93(6)				93.6(3)			
(C_4H_{10})	H	2.87(8)	2.90	2.2(2)	2.0(2)	1.94	1.79	6.4(3)	14.4	15(1)	1.0(1)

with scattering by H in CH_2D_2, ethylene, methylpropane, and CH_4 are located at 2.9 ± 0.2, 2.91 ± 0.06, 2.87 ± 0.08, and 2.9 ± 0.1 eV, respectively. Each of these peak positions is in very good agreement with the energy of 2.90 eV predicted by the electron Compton scattering model. The position of the peak associated with D scattering in CH_2D_2 was 1.4 ± 0.1 eV according to our fit, while the D peak of CD_4 occurs at 1.44 ± 0.04 eV. Both values are in excellent agreement with the peak position of 1.45 eV predicted for deuterium from electron Compton scattering theory. Note also that although heavily overlapped, the signal from CH_2D_2 clearly requires three peaks for an accurate fit. Unfortunately, we do not have quantitative predictions for the main and satellite peak positions for any of these compounds within the MVCS model.[13] However, the existence of three peaks in the CH_2D_2 spectrum at predicted positions strongly supports the ECS model.

The peak shapes associated with the H (D) scattering are better visualized by subtracting the fit to the carbon peak from each of the spectra shown in Fig. 1. These sets of subtracted data are then ratioed to the area of the C peak and plotted in Fig. 2. Figure 2 also plots the signal predicted from the electron Compton scattering model using positions from Eq. (1), intensities from Eq. (2), and widths determined from the zero point energy estimates (see next section). Note that both the energy loss and amplitude scales are meaningful and thus provide a challenging test of the ECS predictions. The calculated and experimental H and D line shapes are in very reasonable agreement apart from the CD_4 data which present a non-negligible amplitude discrepancy which is possibly attributed to the difficulty in fitting the heavily overlapping peaks in this molecule. Especially noteworthy are the CH_2D_2 data, where the predicted peaks corresponding to the D and H atoms in the molecule agree closely with the (C subtracted) experimental data. This figure provides persuasive evidence that the signal arises from electron Compton scattering rather than nondipole molecular vibrational Compton scattering.

Table I compares the ratios of the C/H and C/D experimental peak areas with those calculated from Eq. (2). In general, the agreement of the calculated and experimental data is good. In fact, given that the predicted intensity ratios vary from 9 to 18, the agreement is truly remarkable. Figure 3 is a bar graph presentation of the C/H (or C/D) intensity ratios, normalized to the predictions of Eq. (2). There is larger uncertainty in the results for CH_2D_2 and CD_4 because of the difficulty in fitting the heavily overlapping peaks in these spectra. The tendency for the experimental peak area ratio to be slightly higher than the predicted peak area ratio is discussed further below. It is clear from Fig. 3 that the intensity of the satellite peaks relative to the main peak does not increase as the complexity of the molecule and the number of vibrational modes increase, contrary to the expectations of the MVCS model. In particular, the satellite peaks in 2-methylpropane and ethylene are weaker (relative to the main peak) than in the spectrum of methane. This evidence, in conjunction with the observation of two satellite peaks in the case of CH_2D_2 and widths that are consistent with the electron Compton scattering model (see below), leads us to conclude that the quasielastic scattering signal observed in the present work is best interpreted using the electron Compton scattering model. It may be that the molecular vibrational Compton scattering signal will be detected under somewhat different experimental conditions, such as higher momentum transfer or improved experimental resolution. Alternatively, further development and refinement of the MVCS theory may produce results which converge with the electron Compton scattering model.[13]

B. Peak widths

Within the electron Compton scattering model, the peak widths are to be interpreted as a combination of Doppler broadening[2] and the experimental line shape dictated by the finite instrumental resolution. The MVCS model has not yet been extended to provide quantitative widths or intensities for the satellite peak in the polyatomic species we have studied. Therefore the discussion in this section is limited to comparisons with the electron Compton scattering model.

Doppler broadening stems from the projection of the

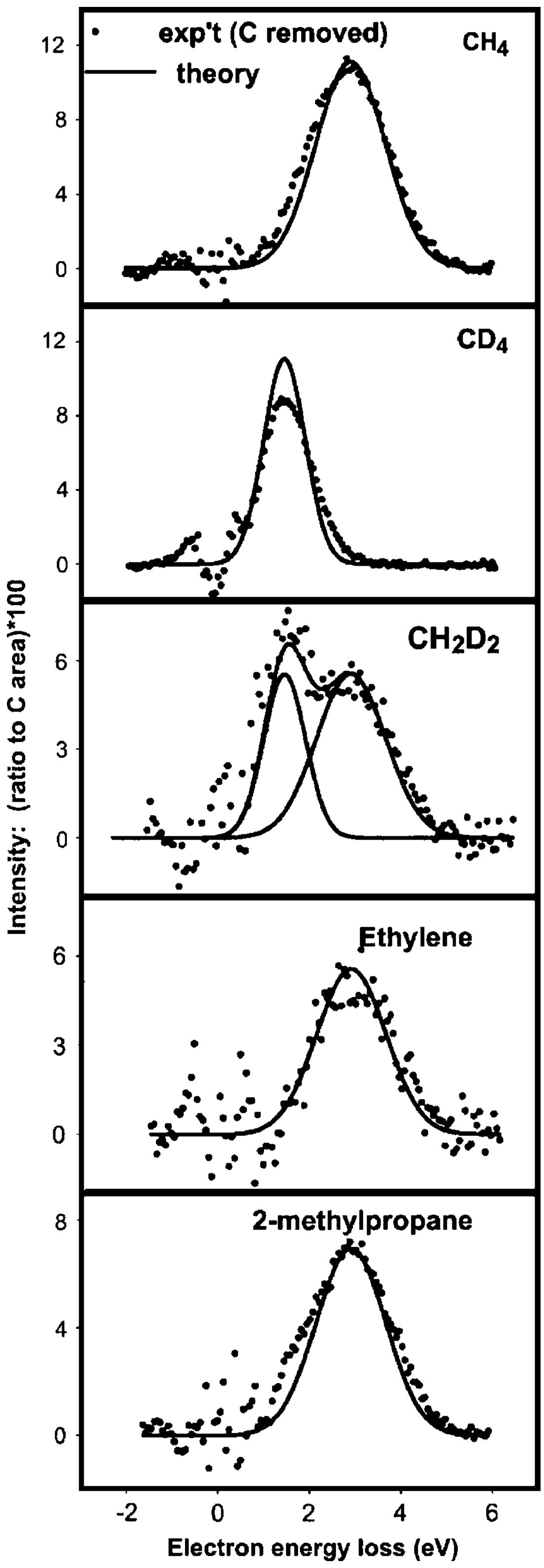

FIG. 2. The H and D components of quasielastic electron scattering for three isotopologues of methane (CH_4, CH_2D_2, CD_4), ethylene (C_2H_4), and 2-methylpropane (C_4H_{10}) isolated from the full spectra by subtracting the peak fit to the C signal. Points are experimental data. The scatter around zero energy loss reflects the inaccuracies of the C peak fit and the amplified intensity scale. The intensity scale is the ratio to the area of the C peak. The solid lines are the predictions of the electron Compton scattering treatment, i.e., Gaussians of position from Eq. (1), area from Eq. (2), and width taken from zero point energy considerations (see text).

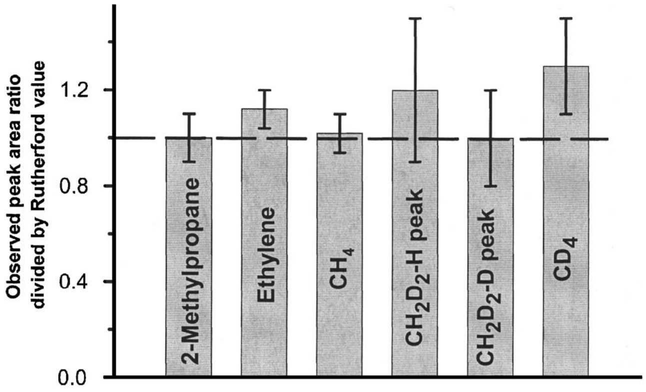

FIG. 3. Intensity ratio of the satellite ("H" and "D") peaks to the main ("C") peak normalized to the intensity ratio predicted from Eq. (2).

motion of the atoms in the molecule onto the momentum transfer. From Eq. (1) at small energy loss values, one expects approximately equal momentum transfer for carbon and hydrogen atoms ($q_C \approx q_H$). This implies a much greater velocity for the lightweight hydrogen/deuterium atoms (12 and 6 times faster than C, respectively). Therefore, the carbon peak experiences relatively little peak broadening from its motion. The predicted C peak width is <0.2 eV, much less than the instrumental resolution under these experimental conditions (~0.9 eV). Thus, we have determined the instrumental resolution of the present work from the full width at half maximum observed for the C peak. We have then determined the natural widths of the hydrogen and deuterium scattering peaks by subtracting (in quadrature) this instrumental width from their observed peak widths. These peak widths should be related to the momentum distribution of the H or D in the direction of electron momentum transfer. Since the gas molecules are randomly oriented in space, the peak width will be proportional, not to this momentum distribution itself, but to its average over the entire solid angle.[2]

The widths for the hydrogen and deuterium peaks that are associated with C–H(D) vibrational motion have been computed from C–D and C–H vibrational wave functions[2] (see Table I). The C–H and C–D stretching motions are well described by a Morse potential. At room temperature, most of the molecules are in their vibrational ground state for which there is very little anharmonicity and the quantum harmonic oscillator becomes a very good approximation. Previous calculations[2] have invoked the Heisenberg uncertainty principle to pass from the width of the calculated position space vibrational wave function to a width for the momentum space wave function and then to a mean kinetic energy $\overline{E_k}$ for the H and D atoms. The calculated values for this quantity are 0.173 and 0.132 eV for hydrogen and deuterium, respectively.[2]

Another way to derive a calculated mean kinetic energy is to use the zero point motion of the molecule. From the calculated zero point energies for methane and ethane, plus NCS results and theoretical considerations, an estimate of the kinetic energy per hydrogen in a C–H bond was calculated[2] to be ~0.15 eV.[1] This approximate value has been used in the present work. The mean kinetic energy associated with deuterium atoms was deduced from the D/H mass ratio as described in Ref. 2. This approach is justified if one considers the C–D bond as though it were an isolated "effective molecule" which is sufficient for the purposes of the current comparison.

Having calculated the mean kinetic energy $\overline{E_k}$ and the recoil energy involved in the electron-atom collision, E_r, which corresponds to the peak position in the energy loss spectrum,[2] the peak width $[2\sqrt{2\ln(2)}\sigma]$ can then be deduced from[17]

$$\sigma = \sqrt{\frac{4}{3}\overline{E_k}E_r}. \tag{3}$$

The values obtained for the peak widths derived from the calculation methods just described, compared with our experimental values derived from the curve fits, are presented in Table I. In general, the experimental widths agree reasonably with the widths derived from the zero point energy considerations, while comparison with the widths derived from the C–H (and C–D) harmonic oscillator wave function calculations are generally ~8% higher than the calculations. It should be noted, however, that the uncertainties allow the experimental values to cover the possible calculated values for both methods used. These correspondences between experimental and predicted values for peak widths suggest that Doppler broadening could entirely explain the observed widths of the quasielastic peaks.

C. Peak intensities

The measured relative H(D)/C peak area ratios in these spectra are close to but slightly below the predicted Rutherford relative cross sections[7] for H (D) atoms compared with C atoms, with one exception. Specifically, ethylene, methylpropane, CH_4, the H peak of CH_2D_2, and D peak of CD_4 show H(D)/C intensity ratios that are between ~2% and 20% below the predictions of the Rutherford model (see Table I and Fig. 3). Only the experimental D/C peak area ratio measured in CH_2D_2 is above the predicted Rutherford value. We note that the peak fitting process was especially difficult for CH_2D_2 since the C, D, and H peaks are heavily overlapped. It is therefore possible that the hydrogen peak was estimated too small and the deuterium peak concomitantly too large. The experimental data are well represented by the overall fit but this shifting of intensity from H to D is a possible systematic error. The calculated and experimental values for the area ratios in all molecules studied correspond within the estimated experimental uncertainties.

IV. SUMMARY

The quasielastic electron scattering spectra of methane and its isotopologues, plus those of ethylene and methylpropane, agree very well with the spectra calculated using the independent atom electron Compton scattering model. This provides strong support for the validity of electron Compton scattering as the mechanism of the origin of the experimentally observed signal and implies that at large momentum transfer, electrons scatter independently from the individual atoms in polyatomic molecules. The experimentally observed peak positions, intensities, and widths can all be fully explained by the electron Compton scattering model. The quantitative applicability of the electron Compton scattering model, combined with the absence of the expected increase in satellite intensity expected in more complex molecules (ethylene, methylpropane) within the MVCS model,[13] leads us to conclude that the quasielastic scattering phenomena are best interpreted as electron Compton scattering.

Note that the ECS model implies a breakdown of the Born-Oppenheimer (BO) approximation when treating light molecules, as is the case with the present experiments. The consequence is a shift toward higher energies of all the peaks in the spectrum relative to those predicted by the molecular vibrational Compton scattering model which respects the BO approximation.[13] A calibration of the absolute electron energy loss scale could therefore shed more light on the observed quasielastic electron scattering phenomena. Measurement of an elastic electron energy loss spectrum of a heavy atom such as Xe or Ar in conjunction with a light-atom containing species such as CH_4, in order to set the zero of the energy loss scale, would therefore comprise a fascinating extension to the present work. In addition, it may be possible to calibrate the intensity scales of the quasielastic spectra to absolute values by measuring elastic scattering intensities of, e.g., He or Ne. This would allow comparison of the experimental results with elastic scattering sum rules, which could determine if the BO approximation is being violated.

ACKNOWLEDGMENTS

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