Observing atom motion by electron-atom Compton scattering

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A very elemental method of observing the motion of the nucleus in molecules or solids is described. The observations for copper, graphite, and formvar films can be understood assuming that the electrons scatter from a moving target (vibrating atoms). The method is the complete electron analog for neutron Compton scattering. The nuclear motion causes a doppler shift in the energy of elastically scattered electrons. It is rather unusual among the methods of studying vibrations (e.g., molecular vibrations in individual molecules or phonons in solids) in that the information obtained is directly related to the momentum distribution of the probed atoms, rather than the energy difference between different vibrational states. The application of the semiclassical picture described here could fail to describe more detailed measurements. Gas-phase experiments may be more suitable for fully quantitative measurements. Indeed the experiment could be used to study the breakup of molecules after a well-defined perturbation.

I. INTRODUCTION

Collision physics is the method of choice of measuring velocity distribution of particles. The basic principles are extremely simple. One scatters elastically a particle from a target and, by analyzing the scattered particle one determines the transferred momentum $\mathbf{q}$. If the target (mass m) was moving before the collision with momentum $\mathbf{k}$, momentum and energy conservation dictates that the recoil energy E_r is given by

$$E_r = \frac{q^2}{2m} + \frac{\mathbf{k} \cdot \mathbf{q}}{m}. \tag{1}$$

This very simple mechanism has been used to study the momentum of nucleons in nuclei using high-energy electrons [1] or protons [2] as the probing particle, electron momentum distribution in atoms, molecules, and solids [3,4], using photons or electrons as the probe, as well as the (vibrational) motion of the nucleus in molecules and condensed matter using neutrons as the probing particle [5–7]. Here I intend to demonstrate that vibrational motion of atoms can also be studied using electron scattering.

Neutrons with tens of eV's of energy are traditionally used for obtaining Compton profiles of atomic vibrations. The mass of the neutron is of the order of the mass of target atoms, and hence energy is efficiently exchanged in collisions with nuclei. It is a weakly interacting probe, and thus multiple scattering effects are small. Protons have similar mass, but much stronger interaction with the target. In interactions with the target it will lose energy due to inelastic excitations of electrons, and it has a large probability of interacting with more than one nucleus. Hence protons are not a suitable probe for measuring Compton profile of nuclear

motion. Electrons at low energy have insufficient momentum. This changes however when the electron energy is increased in the keV range. At the same time the interaction of fast electrons with the target becomes weaker and weaker. The mean free path for elastic and inelastic excitations is greater than or equal to 100 Å at energies above 20 keV. Thus it appears possible, at least in principle, to measure Compton profiles using energetic electrons that have been deflected over large angles by nuclei.

The main obstacle that one has to overcome in order to use electrons for the study of lattice vibrations is the large mass difference between the electron and nuclei (even the proton mass is 1836 times larger than that of a electron). The maximum transfer of momentum (the case of 180° deflection) is twice the momentum of the incoming particle. This means that even for an electron backscattering from a proton the maximum energy transfer is 0.2%. For heavier atoms the transferred energy decreases even more, inversely proportional to the atomic mass. Thus we need a relatively monochromatic electron beam and a good quality energy analyzer in order to see the effect of energy transfer, and an even better one to resolve effect of atomic vibrations on the elastic peak.

In most electron-scattering experiments the momentum transfer to the nucleus is very small and the corresponding energy transfer can be safely neglected. Therefore electron-nucleus scattering is generally referred to as elastic scattering and we will adhere to this convention in this paper. Inelastic scattering here will refer to energy loss of the fast electrons by electronic excitations. In this paper we describe experiments using electrons between 20 and 30 keV, scattered from nuclei over 45°. These collisions have a momentum transfer between 29 and 36 a.u. [We will use atomic units (a.u.) throughout. One atomic unit of momentum corresponds to 1.89 Å^{-1}. The mass of the electron is 1 a.u. In this system the energy unit is the Hartree, corresponding to 27.21 eV]. Energy transfer for scattering from a *stationary* particle is then $q^2/2m$, i.e., between 5.8 and 8.8 eV for scattering from

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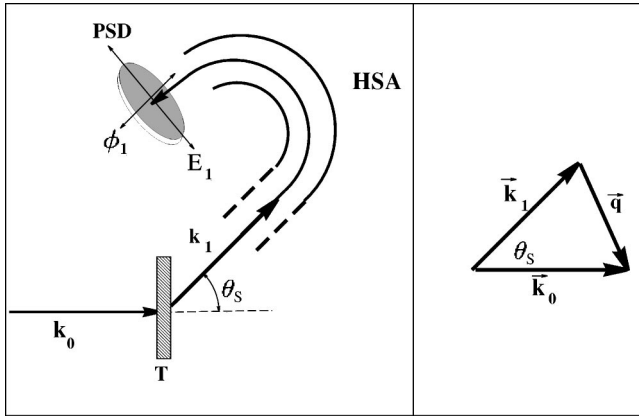
FIG. 1. Outline of the spectrometer (left). Electrons scattered over Θ_s are retarded by a lens system and analyzed for energy in a hemispherical sector analyzer (HSA) and detected using a position sensitive detector (PSD). In the right panel we show the relation between the incoming ($\mathbf{k}_0$), outgoing ($\mathbf{k}_1$), and transferred momentum ($\mathbf{q}$).

a proton. The energy resolution in the experiments described here is 0.4 eV for 25 keV electrons, i.e., 0.0016% of the electron energy. It appears thus that the effect of atomic vibrations should be observable.

II. EXPERIMENT DETAILS

These experiments were done using the ANU (e,2e) spectrometer, but operated in a mode so that we measure elastically scattered particles. This spectrometer is described in detail elsewhere [8]. Indeed the current experiment was triggered by the observation of an anomalous width of the elastic peak used in the calibration procedure of the (e,2e) analyzers. Here we briefly describe the essential parts as far as this paper is concerned. An outline is given in Fig. 1.

An electron gun (BaO cathode, energy spread 0.3 eV) produces an electron beam of 600 eV. The sample is in an enclosure that floats at voltages between 19.4 and 29.4 keV. Thus the electrons are accelerated up to 20–30 keV and impinge on a thin film (spot size 0.1 mm diameter, beam current typically 5 nA). Only electrons transmitted through this film and scattered over 44.3° are detected by the electrostatic analyzer. This angular selection is done by a 0.2-mm- or an 0.5-mm-wide slit, 130 mm away from the sample. Slit width can be chosen without breaking the vacuum, and allows for different trade-offs between count rate and energy resolution. These slits are slightly curved in such a way that we detect over a 10° sector of a 44.3° cone [8]. After passing through these slits the electrons are retarded and focused by a lens system. They enter the hemispherical analyzer with a pass energy near 400 eV. Transmitted electrons are detected by a pair of channel plates followed by a position sensitive detector (PSD, a resistive anode). The precise energy and azimuthal angle can be derived from the coordinates of the PSD. The original aim was just to calibrate the spectrometer for energy resolution. Using heavy target material we get an energy resolution near 0.4 eV.
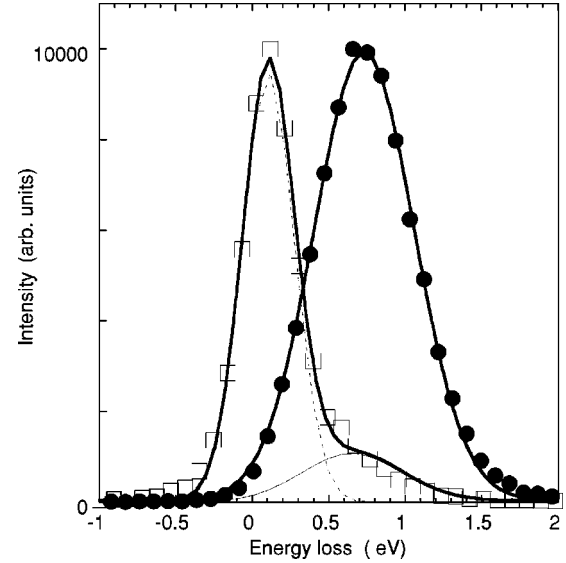

FIG. 2. Elastic peaks of a copper film evaporated on a thin carbon film (open squares) and of a carbon film itself (filled circles). The thick line represents a fit of the data with a single Gaussian (carbon film) and the sum of two Gaussians (copper/carbon film).

Besides the experimental broadening the width will be determined by the vibrational motion, i.e., the second term in Eq. (1). The motion of nuclei is an ever present phenomenon. Even at the lowest temperatures we have the zero-point motion to deal with. For atoms in a crystal, x-ray diffraction reveals that the root-mean-square displacement is between 0.1 and 0.2 a.u. This means that the corresponding momentum $\mathbf{k}$ is quite large between, 5 and 10 a.u., only between three and seven times smaller than the transferred momentum $\mathbf{q}$. Besides the zero-point motion there is a contribution due to thermal vibrations. At elevated temperatures the thermal energy approaches the classical limit of $0.5kT$ for every degree of freedom. This sets another lower limit for the momentum of the nuclei. In terms of atomic units a "room-temperature" proton with an energy of 1/40 eV has in each direction a component of momentum with average magnitude 1.8 a.u. For heavier elements, e.g., copper this value becomes 14.7 a.u.

Thus the motion-induced broadening is only somewhat smaller than the average energy shift. Both shift and broadening become progressively smaller with increasing mass. Doubling the transferred momentum will increase the energy shift fourfold, but only double the width of the peak.

III. RESULTS

As an example we show in Fig. 2 Electrons with an energy of 25 keV scattered from a thin ($\simeq 35$ Å-thick) carbon film, and from a thin carbon film covered with a similar thickness of copper. The true zero-energy loss position of the spectrometer is hard to determine on a 0.1-eV level. It depends slightly on the exact sample position, and on the long-term stability of the power supply. Therefore we shifted the peaks in Fig. 2 in such a way that the maximum corresponds to an energy-loss position as given by the $q^2/2m$ term (a shift
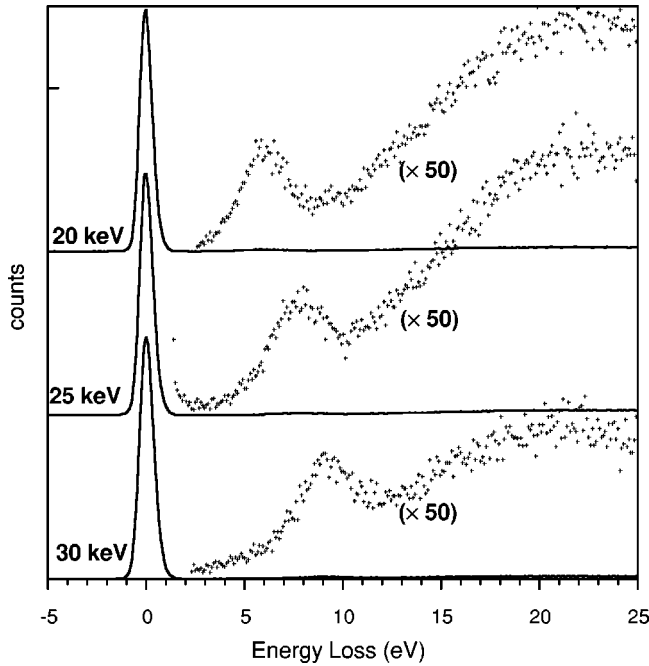
FIG. 3. Electron scattering data for a formvar film. Data were taken for 30 keV, 25 keV, and 20 keV electron energies. The hydrogen part of the spectrum is magnified 50×.

of 0.12 eV for copper, 0.65 eV for carbon). The cross section for elastic scattering is roughly proportional to Z^2. Thus for the copper/carbon sample the copper contribution dominates, but there is a shoulder visible at the right position of the carbon peak. The width of the carbon peak is clearly larger than the width of the copper peak. The energy resolution of the spectrometer will be the main origin of the width of the copper peak ($\simeq 0.40$ eV full width half maximum using the narrow, 0.2-mm slits). The carbon peak is considerable wider ($\simeq 0.76$ eV). Using 0.4 eV as the upper limit for our resolution we obtain the lower limit for the intrinsic width of the carbon peak of 0.65 eV.

For an isotropic harmonically bound solid the momentum distribution is Gaussian, and the observed width is conveniently expressed in terms of the recoil energy and the mean kinetic energy of the atoms $\bar{E}_k$. The standard deviation σ of the observed Gaussian is given by [9]:

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

Using the mean kinetic energy for graphite of 108 meV as derived from neutron Compton scattering (NCS) [10] we obtain $\sigma = 0.3$ eV, i.e., the full width at half maximum (FWHM) Γ is 0.70 eV, within the limits of error identical with our experimental estimate of 0.65 eV.

It is clear from Eq. (1) that atomic vibrations are most easily resolved for light elements. Therefore, we repeated these experiments for a formvar film. Formvar is a polymer with nominal composition $C_8O_2H_{14}$ and is conveniently prepared as thin films. These results are shown in Fig. 3. Now we used the 0.5-mm-wide slits in order to reduce the re-
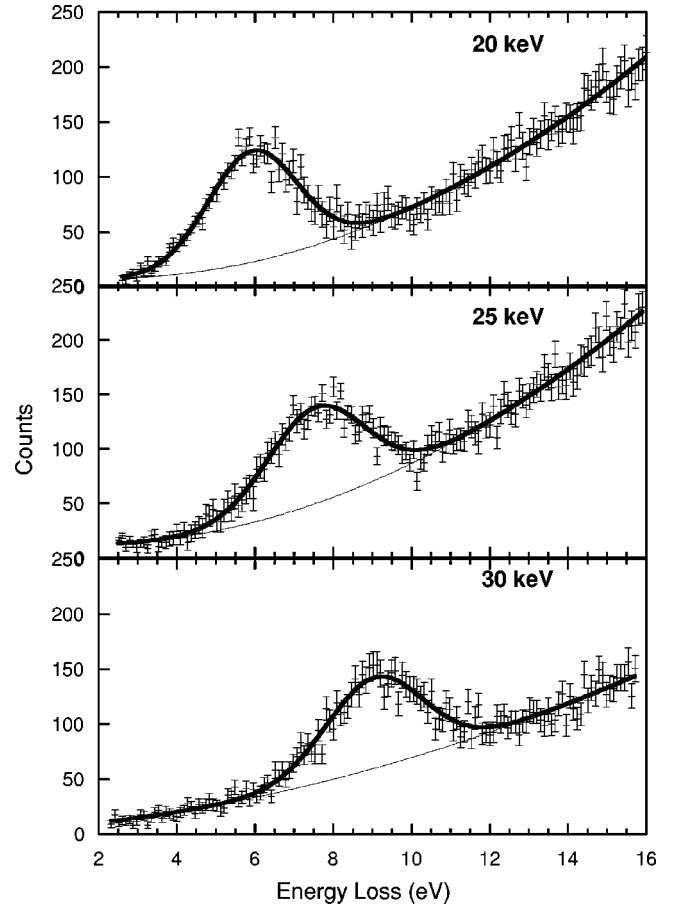

FIG. 4. Loss spectrum of a formvar film between 2 eV and 16 eV energy loss. The fits were obtained using a quadratic background and a Gaussian peak shape.

quired electron dose, as electrons are known to change the composition of organic materials [11]. Hydrogen has only a small cross section for electron scattering. Its contribution is small but well separated from the main elastic peak, but is superimposed on a background. This background is due to multiple scattering: events with electrons scattered from carbon or oxygen, but additional (inelastic) electronic excitations along the incoming and outgoing trajectories have reduced their energy. In order to make sure that the peak is not a feature of the multiple-scattering background and is to hydrogen, we repeated the experiment for different electron energies, i.e., different momentum transfers. The separation of the hydrogen peak from the main elastic peak increases proportional to the electron energy as expected. A more quantitative description was obtained from fitting these data with a polynomial and a quadratic background. These data are shown in Fig. 4 and summarized in Table I. Clearly the peak position varies with energy as expected. The width appears rather constant, whereas one expects a weak increase in peak width with increasing energy. The cross section for elastic scattering of hydrogen and carbon/oxygen is simply the Rutherford cross section, i.e., proportional to Z^2. Calculations of the cross section based on the electronic structure show that screening effects are not important under these conditions [12]. Also the ratio of the hydrogen elastic peak to

TABLE I. A summary of the measured and calculated separation of hydrogen from the main peak, full width at half maximum Γ of the hydrogen peak, and the intensity ratio of the hydrogen peak I_h and main peak I_{mn}

E_0 (keV)	q (a.u.)	ΔE_{obs} (eV)	ΔE_{calc} (eV)	Γ_{obs} (eV)	Γ_{calc} (eV)	$I_H:I_{mn}$ obs.	$I_H:I_{mn}$ calc.
20	29.2	5.9	5.8	2.6	2.6	1:41.1	1:29.7
25	32.9	7.5	7.4	2.9	2.9	1:44.8	1:29.7
30	35.9	9.0	8.8	2.9	3.2	1:51.7	1:29.7

the main (oxygen- and carbon-derived) elastic peak is underestimated. Similar discrepancies were found for NCS experiments of polystyrene and attributed to "entangled protonic states" [13,14]. However, considering the limited experience with these experiments I would not exclude more conventional systematic errors due to background choice, line-shape choice, sample purity, etc. as the cause of the discrepancy.

In order to see if the measured width of the hydrogen peak is compatible with doppler broadening we have to make an estimate of the average kinetic energy of hydrogen bonded to carbon. As a first approximation all C-H bonds will be rather similar. If we take ethane as an example, it has a calculated zero-point energy of 2 eV per molecule [15]. Half of this will be kinetic energy. Most of the kinetic energy will be in the lighter atoms, so we expect around 0.15 eV kinetic energy per proton. For hydrogen in hydrogenated amorphous carbon, Mayers *et al.* measured 146 meV using NCS [10], and they estimate on theoretical grounds energies between 156 and 183 meV for hydrogen in C-H bonds. So using 150 meV for the kinetic energy and a recoil energy of 8.0 eV we obtain $\sigma = 1.3$ eV and a full width at half maximum of 2.9 eV. This is in excellent agreement with the experimental results.

IV. DISCUSSION

It seems that both for the case of hydrogen and carbon the detected excess width is rooted in the atomic vibrations. Within experimental accuracy the electron-scattering data agree quantitatively with those observed in NCS. These experiments have a somewhat poorer resolution than the current standards in neutron Compton work ($\simeq 250$ meV FWHM), but the current experiment was not designed with electron-atom Compton scattering in mind. A dedicated spectrometer, using larger scattering angles and a monochromatized electron beam would improve the resolution easily by an order of magnitude, and would allow the study of a momentum transfer of up to 80 a.u. at 30 keV incoming energy. Under these conditions it would, for example, probably be possible to separate the oxygen and carbon contribution. Overall, the performance could be at least comparable to that of NCS at a fraction of the cost, as it does not depend on the large infrastructure required for neutron-spallation sources. I will now try to highlight some of the differences.

First and most importantly, in the electron case we have to consider energy loss due to multiple scattering of the incoming beam. This would not so much influence the study of

pure elements, as most inelastic-scattering events cause a shift of several eV's away from the elastic peak. It would only make it difficult to determine the tail at the high-energy loss-side of the spectrum. However, as is clear in the formvar case, electrons scattered from lighter elements (especially hydrogen) contribute to the spectrum at the same energy as electrons scattered from heavy nuclei in combination with additional energy loss due to inelastic scattering. This causes a background-subtraction problem, which would obscure details of the Compton profile of these light elements.

Neutrons are weakly interacting probes, hence macroscopic samples can be used. Electrons interact much more strongly with the target, hence thin samples are required. As the requirements in the momentum spread of the incoming beam are much lower in this case, compared to that realized in the present spectrometer, for $(e,2e)$ a smaller beam spot, by additional focusing, is easily obtained. This would go a long way in alleviating most of the sample-preparation problems, provided that the sample can withstand an intense electron beam.

It has not been established yet if, for electrons, these experiments can be done in a backscattering geometry using thick samples. At first sight this seems impossible, as elastic multiple scattering becomes large for thick samples. However, the competing inelastic scattering events will mean that the zero-loss peak originates within a few inelastic mean free paths of the surface. The probability that for these events two large-angle elastic deflections have occurred could be manageably small. Gas-phase studies should be possible as well (requiring electron beams of several microamperes), which would allow for measurements without multiple-scattering background, as the target density can be made arbitrarily low. For example, the ratio of the hydrogen and carbon contribution could then be established most rigorously using, for example, CH_4, as a target. Shake effects may show up at higher energy loss, as the electronic and vibrational structure are only rigorously separated within the Born-Oppenheimer approximation. As shake effects would be most likely for the case of large energy transfer, a part of the hydrogen intensity could be transferred to higher energy-loss values.

The cross section for elastic scattering of electrons increases with Z and is proportional to Z^2 for the light elements. These are the elements for which the vibrational width is most easily resolved. Unfortunately the relative hydrogen signal will be extremely small for compounds of hydrogen and high-Z materials, even if hydrogen is present in large quantities.

In conclusion, I demonstrated that high-precision analysis of the elastic peak taken at high momentum transfer reveals, to a large extent, the same information as neutron Compton scattering.

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