



Electron scattering as a tool to study zero-point kinetic energies of atoms in molecules



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ABSTRACT

High resolution electron Compton scattering (ECS) is being used to study the atomic momentum distributions and hence the zero-point kinetic energies (ZPKE) of the scattering atoms. Such studies have shown that the scattering is from a single atom of the scattering sample. For an electron beam with a well defined incident energy, the scattered electron energy at any angle from each atomic species is Doppler broadened. The broadening reflects the atomic momentum distribution contributed by both the internal and external motions of the molecular system. By measuring the Doppler broadening of the scattered electron lines it was possible to determine the kinetic energy of the scattering atom including that of its zero-point motion. Thus, the atomic kinetic energies in gases such as H₂, D₂, HD, CH₄ and in H₂O, D₂O and NH₃ were measured and compared with those calculated semi-empirically using the measured optical infra red (IR) and Raman frequencies of the internal vibrations of the molecules. In general, good agreement between the measured and calculated values was found. Electron scattering was also used to study the ratio of e-scattering intensities from the H- and O-atoms in water (H₂O), where some anomalies were reported to exist.

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1. Introduction

In recent years many scattering studies were carried out using electron beams with incident energies between 1 and 40 keV. The targets were in various forms and the electrons were found to scatter independently from each atomic mass and not from the molecule as a whole. This behavior is contained in the assumption of the impulse approximation (IA) found to hold in many cases studied using the electron scattering method; it is due to the high incident electron energies compared to the vibrational energy of the atoms in the samples.

Few methods were reported in the literature in which a direct measurement of the atomic kinetic energies was carried out: (1) Nuclear resonance photon scattering (NRPS) [1], (2) neutron Compton scattering (NCS) [2,3], and (3) electron Compton scattering (ECS) [4–6]. Here we use the abbreviation ECS, to emphasize the similarities with the well-established NCS technique. When the same technique is used for determination of the composition of surfaces, it is often referred to as electron Rutherford

Backscattering (ERBS). The same spectrometer can study electronic excitations, in which case the technique is called reflection energy loss spectroscopy (RELS). The NRPS method used either gamma rays (emitted from thermal neutron capture reactions on various elements) or bremsstrahlung photons created by 4–10 MeV electrons striking a high-Z target. In the first case a nuclear reactor was employed to provide the high flux of neutrons for producing the intense photon beam; it was used extensively for several applications [1,7–9]. The other case employed an electron Linac to produce the high intensity bremsstrahlung beam [10].

The second method using NCS was found to have several properties in common with ECS in the sense that the neutron scatters from an atom in a molecule as if it was free, thus the kinematics in the two cases are quite similar. In fact, the atomic kinetic energies measured by the two methods were found in many cases to be close to each other. Moreover, as mentioned below, it was possible to check some anomalies reported by the NCS method [11–14]; the result was that those anomalies did not persist using the ECS technique [15].

The atomic kinetic energies in molecules and in solids were calculated using a semi-empirical (SE) method [1,16] in which the vibrational frequencies are taken from experiment and it is assumed that there is no coupling between the different modes

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of motion. This method was found to yield in several cases the best and the closest agreement to experiment.

Because of the small electron mass, the recoil energy transferred to the scattering atom is very small [17–19]. Thus, the scattering process operates as a mass analyzer causing the energy spectrum of the deflected electrons to split according to the masses of the scattering atoms of the molecule. In order for the energy separations between the scattering peaks to be resolved, a high resolution spectrometer had to be used [4]. The Doppler broadening $\Delta = (4K_e E_{\text{rec}})^{1/2}$ of each electron line is related to the mean kinetic energy K_e of the scattering atom and to the recoil energy E_{rec} ; it provides information on K_e in the same fashion as that of NCS [19].

The measurement of the K_e of a scattering atom in a molecule is important as it includes the part contributed by the zero-point vibrational motion and may be obtained by measuring the Doppler broadening of the scattered electron lines. In any H-containing molecule the internal kinetic energy is carried mostly by the light partner, i.e. the H-atom and can be measured with good accuracy as in NH_3 , H_2O , CH_4 (see below).

2. Experimental details

In the measurements, an electron beam with a well defined incident energy between 1 to 40 keV and low thermal spread was used. The energy analysis of the scattered electrons requires spectrometers of very high resolution to resolve the small difference in recoil energy of the atoms present as well as the total energy spread of the electrons scattered from a specific isotope. The energy resolution of our spectrometer is 0.3 eV; it includes the thermal spread of the electrons emitted from a barium oxide cathode. Besides the experimental resolution the energy of the scattered electron is affected by the Doppler broadening caused by the internal and external motions of the atoms of the sample. This is the quantity we want to measure. Fig. 1 depicts the Doppler broadened shape of electrons scattered at 135° from the H-atom (of a solid ammonia (NH_3) sample) at 80 K using a 2.5 keV incident e-beam. It shows the energy separation between the peak intensities of the electrons scattered from N- and H-atoms in NH_3 , illustrating the type of resolution required in such measurements [4]. As the N peak is much narrower than the H peak, it is immediately clear that the width of the latter is dominated by Doppler broadening. Apart from NH_3 , the samples discussed in this work are H_2 , HD, D_2 , CH_4 and H_2O . The electron incident energies employed in the studies discussed here were between 1 and 6 keV.

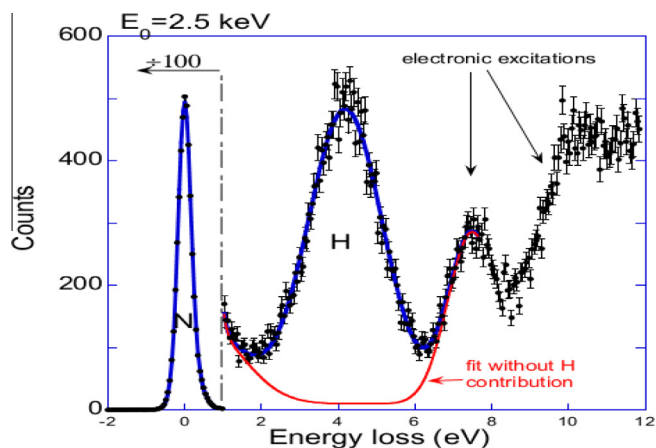


Fig. 1. Spectrum of 2.5 keV electrons scattered over 135° from a solid ammonia (NH_3) sample at 80 K. It illustrates the energy separation between the N- and H-atoms and the Doppler broadened shapes of the peaks. It also shows the fitting procedure and assumed background due to detected electrons that have also created electronic excitations in the target.

Gas phase measurements are near room temperature as the pressure differential over the nozzle is small and adiabatic cooling should thus be minor. The low temperature measurements are made from frozen samples using either a cold finger (H_2O case at 118 K) or a LN_2 cryostat (NH_3 case at ~ 80 K). From the spectra we determined the intrinsic width (Doppler broadening Δ) of the peaks (by subtracting the experimental resolution from the observed width in quadrature) and for isotropic systems the intrinsic width is related to the mean kinetic energy K_e according to [6]: $\Delta = \sqrt{\frac{4}{3} K_e E_{\text{rec}}}$. With E_{rec} the recoil energy for scattering from a stationary atom.

In the following we explain how the atomic kinetic energies were calculated.

3. Calculations and results

3.1. Diatomic gases

As an example we show how to calculate the H-kinetic energy, $K_e(\text{H})$, in a diatomic molecule such as HD in gaseous phase. Note that $K_e(\text{H})$ is contributed by three components: Translation, free rotation and internal vibration of the molecule. By assuming a decoupling of the three motions, and using the harmonic approximation, we may write [1,16]:

$$K_e(\text{H}) = S_t \frac{3}{2} kT + S_r kT + S_v \frac{h\nu_0}{2} \left(\frac{1}{e^{h\nu_0/kT} - 1} + \frac{1}{2} \right) \quad (1)$$

where S_t , S_r and S_v are the kinetic energy fractions shared by the H-atom in the translational, rotational and vibrational motions of the H-atom in the HD molecule respectively. Here, the vibrational motion of HD is represented by a harmonic quantum oscillator with frequency ν_0 (taken from experiment) [20]. Eq. (1) may be viewed as representing the kinetic energy of any isotope in H_2 , HD and D_2 . The energy fractions of Eq. (1) for those isotopic gases are listed in Table 1 from which the atomic kinetic energies of H and D were calculated (Table 1). It was assumed that the D mass is twice the H-mass and that the spring constant of the oscillator is the same for the three gases. As expected, the calculated $K_e(\text{H})$ in H_2 is smaller than that in HD but higher than $K_e(\text{D})$ in D_2 as well as in HD. This may be understood by noting that the oscillator kinetic energy in HD is divided between the H- and D-masses in a 2:1 ratio. Table 1 also lists the calculated $K_e(\text{H})$ values at 145 K and 0 K. Note that the zero-point value was calculated by accounting for the contributions from both the external-lattice and the internal motions, while in the gaseous phase where the molecule freely rotates, the major contribution to K_e is from the internal vibration. In HD at 145 K for example, the major part, 84% of $K_e(\text{H}) = 89.1$ meV, is contributed by the zero-point motion of the

Table 1

Calculated energy fractions S_t , S_r , S_v together with the kinetic energies, $K_e(\text{H})$ and $K_e(\text{D})$, at 0 K and 145 K of H_2 , HD and D_2 . Values of the experimental frequency ν_0 are also listed together with the measured K_e values using the ECS method. Indicated in the last column are the calculated total zero point energies (bold) of the H and D atoms, which include contributions from both external lattice and internal modes of motion, where the lattice modes were calculated assuming a pure Debye solid [22]. Parenthesized *italics* values are the calculated zero point energies of the internal vibrations obtained using Eq. (1).

Gas	S_t	S_r	S_v	ν_0 [cm^{-1}]	$K_e(\text{H,D})$ [meV]		
					$T = 145$ K		0 K
					Calc	Exp	Calc
H_2	1/2	1/2	1/2	4155	80.1	74	69.3 (64.5)
(H)D	1/3	2/3	2/3	3599	89.1	95	78.9 (74.5)
H(D)	2/3	1/3	1/3	3599	48.4	46	42.3 (37.3)
D_2	1/2	1/2	1/2	2939	61.3	70	50.2 (45.6)

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