Comparing Electron and Neutron Compton Scattering technquies

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OUTLINE OF TALK

⇒ What is Electron Compton Scattering (ECS)?

⇒ Using ECS for measuring atomic kinetic energies

In samples of water (H_2O) and Ammonia (NH_3)

⇒ Analogy with Neutron Compton scattering (NCS)

Testing Anomalous n-H scattering intensities:

~ 30% deficiency was reported by NCS

Cooper, Hitchcock, et al, PRL100, 043204 (2008).

Chatzidimitriou-Dreismann, Vos, et al, PRL 91, 57403 (2003).

Searching for similar deficiency Using ES in H_2O and H_2+D_2

Why Use electron scattering?

Electron scat can simulate Neutron scattering Impulse Approximation

Energy conditions:At **E_n ~ 10–200 eV**, **N's** scatter from bound atoms as if atoms were free: **Neutron Compton Scat (NCS).**

De Broglie λ_n = 0.09-0.02 Å << molecular dimensions

Electron Compton Scat (ECS).

At **E_e ~ 1 – 30 keV**, **λ_e ~ 0.38Å – 0.07Å < d(H_2O)~ 3.0 Å**

Electrons scatter from bound atoms as if atoms were free:

Measuring atomic Kinetic Energies

Scatt Electr from stationary atoms **have well defined $E_e(\theta)$**

Scatt Electr from moving atoms are **Doppler broadened**

Broadening: Δ_D provides **atomic Kinetic Energy (Ke)** and also **Zero point Ke (ZPKE)**.

In exactly the same manner as in Neutron Scattering

Measuring Ke of H , O atoms in e.g. Water (H_2O)

⇒ Scattering is from free atoms in the molecule.

(Incident energy $E_e >> E_b$ (atomic binding of molecule)

Kinematics of ECS process: $m_e << M_a \sim M_p$

For $E_e \sim 4$ keV, at $\theta = 135^o$, Recoil energy:

$R_e(H) = E_e^2/2M_pc^2 \sim$ **4 eV** , $R_e(O) = R_e/16 \sim$ **0.25 eV**.

A high resolution e-spectrometer is required to measure ΔR_e

e-scattering from **stationary** atom: e-line: **E_θ is narrow**

from a **moving** atom: **E_θ is Doppler broadened**

The **broadening** provides **Ke(H) and Ke(O)** in H_2O

What is: Atomic kinetic energy & Zero-point (ZP) KE of atoms in a molecule (H_2O): Ke(H), Ke(O) ?

How to calculate Ke and ZPKe:

Consider all molecular modes of motion:

Translation, Rotation, Internal Vibrations

Calculate kinetic energy of H , O atoms in each mode, then sum up over all contributions.

Free molecule: Translation has no ZP motion

Rotation has no ZP motion

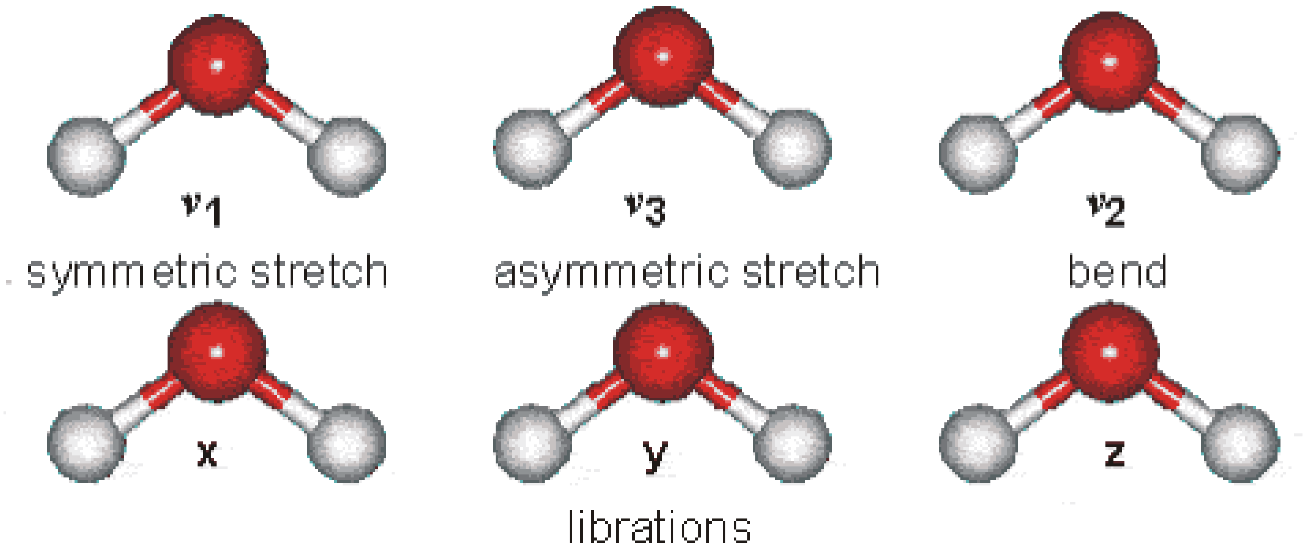
Internal Vibrations: Represented by Harm Oscillators

High ZP motion

Illustration of H-Motion in WATER (H_2O)

Vibration: Stretching ($\nu_1 + \nu_3$) + Bending ν_2

+ Kinetic + Rot-Libration



All oscillations (librations) contain Zero-point Energy

NO Zero-point Energy in Free Rotations

KE of each **H-atom** in Isolated H_2O (Vapor phase)

Exp ν_j (cm^{-1}) Vapor = 3686 3738 1596

Important: H_2O Freely rotates in Vapor

Transl ↓ **Rotation** ↓ **Vibration** ↓

$$K_e(H) = S_T \frac{3}{2}kT + S_R \frac{3}{2}kT + \sum_{j=1}^{3} S_j \frac{1}{2}\left(\frac{h\nu_j}{e^{h\nu_j/kT}-1} + \frac{h\nu_j}{2}\right)$$

S_T = **1/18** = KE fraction of each H-atom in translation (classical),

S_R = **0.475** = KE fraction of each H-atom in rotation (classical)

S_j = KE fraction of each H-atom in j^{th} internal mode of vibration

Sj calculated Using methods of IR spectroscopy

values of ν_1, ν_2, ν_3 are taken from experiment

Calculated Results of S_j and Ke
[Isolated molecules – Vapor]

ν_j (cm^{-1}) =	3686	3738	1596	Vapor
S_j =	0.467	0.477	0.464	

This method of calculation is called Semi-empirical (SE) using Exp Infra red And Frequencies

Present SE calculation - successful in vapor phase:

Super crit phase-High T (P = 65, 120, 1060 bar) # H-bonds: n ~ 1.5

Neutron scattering measurements of atomic Kinetic energies

T(K)	K_e(H) [meV] Exp*	Calc	Classical (3kT/2)
523	**169±5**	**168**	**68**
573	**172 ±3**	**172**	**74**
673	**178±4**	**179**	**87**

* C. Pantalei, et al., PRL **100**, 177801 (2008)

Conclusion: Present calculations produce Excellent agreement with **Neutron**-scattering Experiment (Vapor)

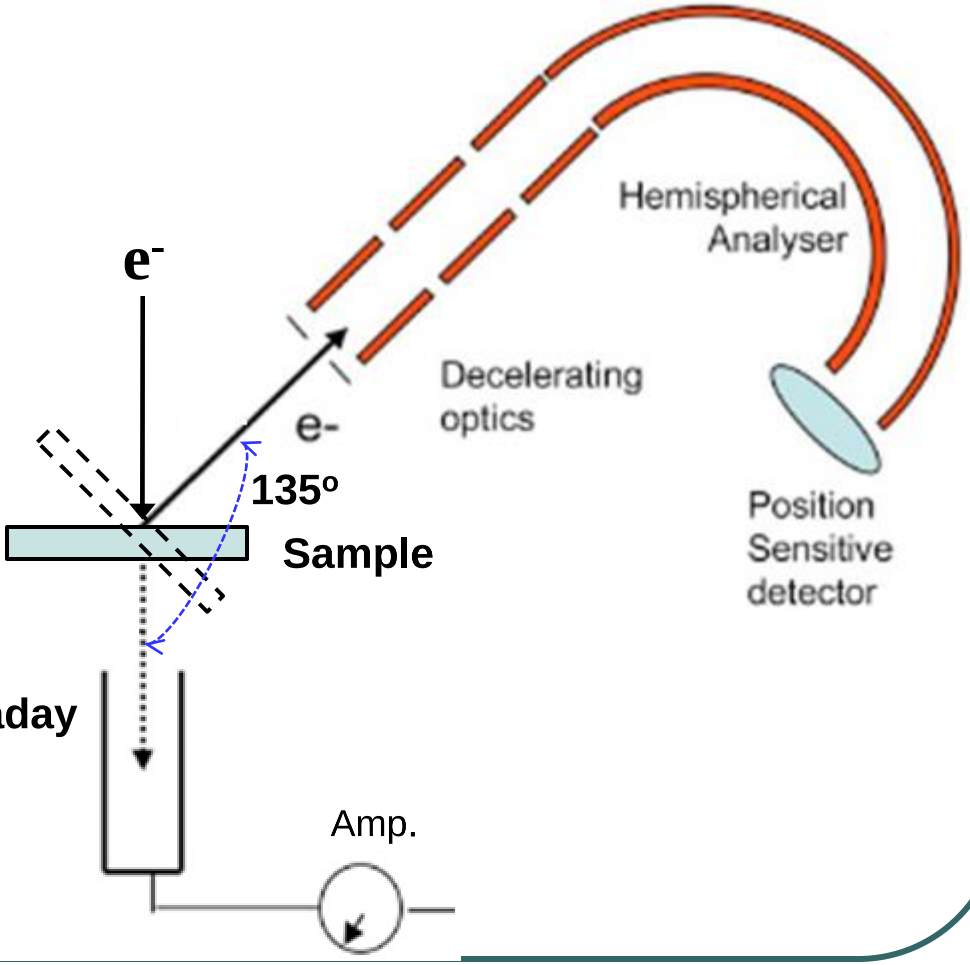
Experimental System: Energy Loss spectrometer

Vos, Went: PRB 74 (2006) 205407 **Aust Nat Univ**

- **Incident e-beam: 1-6 keV**
  Scattered elect's: 135 deg
  Sample: H_2O (ice), HD, NH_3

- **Detector**
- **High Resolution spectrometer**

$\sigma \sim 0.2$ eV



Incident e-Energy: 2 keV; H_2O vapor sample, $\theta = 135^o$,
Classical kinematics: ΔE_r(O to H)= 3.49 eV
Recoil: $E_{rH} = q^2/2M_H = 3.72$ eV, $E_{rO} = 0.233$ eV

Vos, Weigold, Moreh
JCP138 (2013) 044307

σ = Sigma ~ Peak width

E_e = kin energy

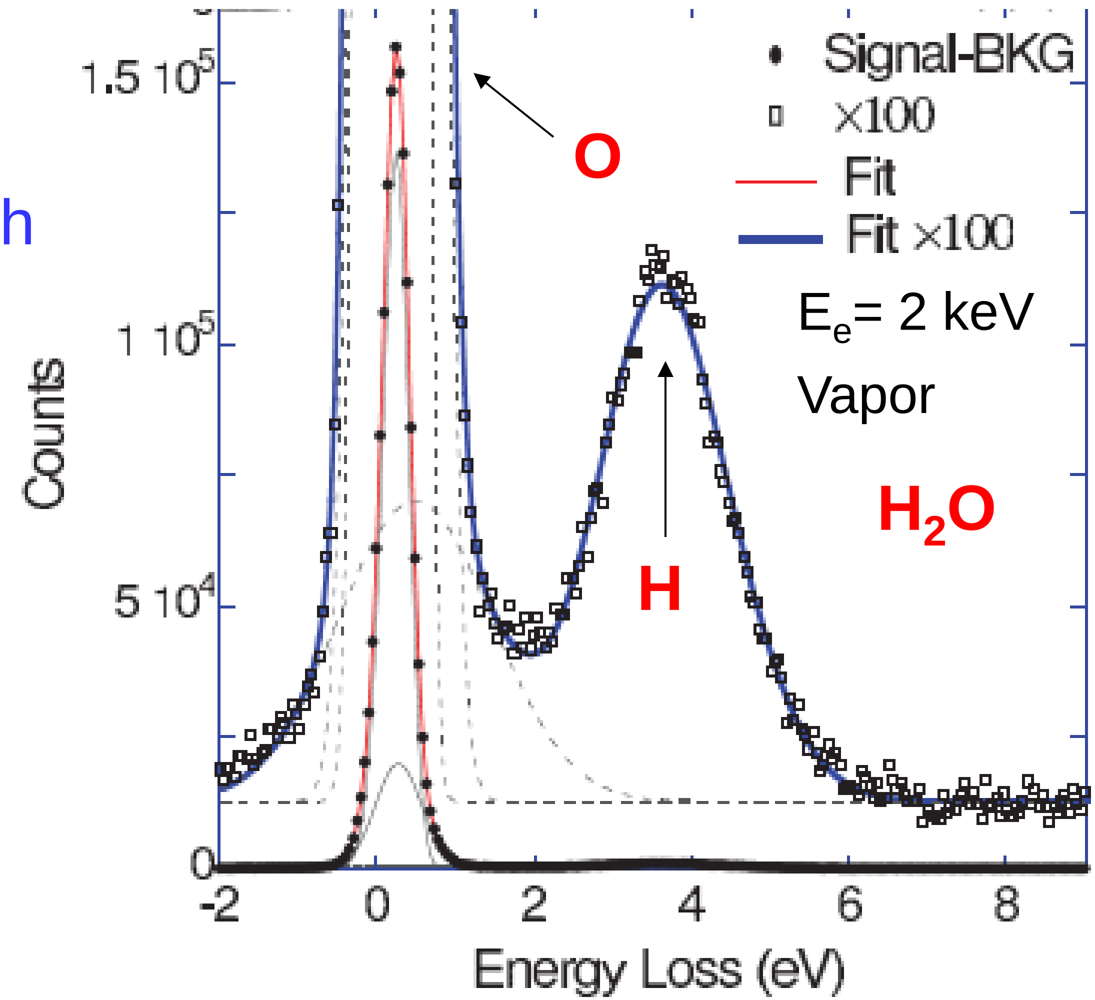
$\sigma = (4E_rE_e/3)^{0.5}$

$\sigma_H > \sigma_O$

Width caused by internal vibrations in H_2O:

Moreh, Nemirovsky:

- **JCP 130 (2009)**

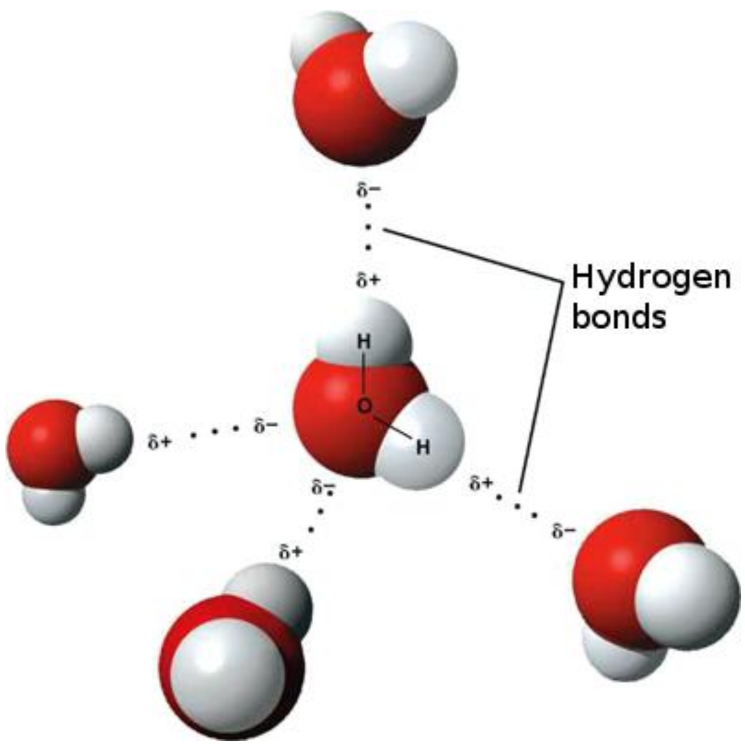


In Solid Phase (ice Ih) (T = 5 K): Differences from Vapor

Sharp (Stretch + bend freqs) ⇒ bands: **strongly weakened by H-bonds**

Free Rotation (Vapor) ZPKE = 0 ⇒ Libration (HO); ZPKE >> 0

(e-scat at 118 K) ν_{lib}=330 - 935 cm^{-1}



Vapor		**Ice Ih**
3686	⇒	3085 cm^{-1}
3738	⇒	3220 cm^{-1}
1596	⇒	1650 cm^{-1}

Ice [118K]	**Calc**	**Exp#**
	152	**149(4)meV**

#Vos, Weigold, Moreh, **JCP 138, (2013)**

(NCS) Previous Exp* : 144 (4)

*G. Reiter, PRL **97**, 247801(2006)

Model of H-bonds between molecules of water

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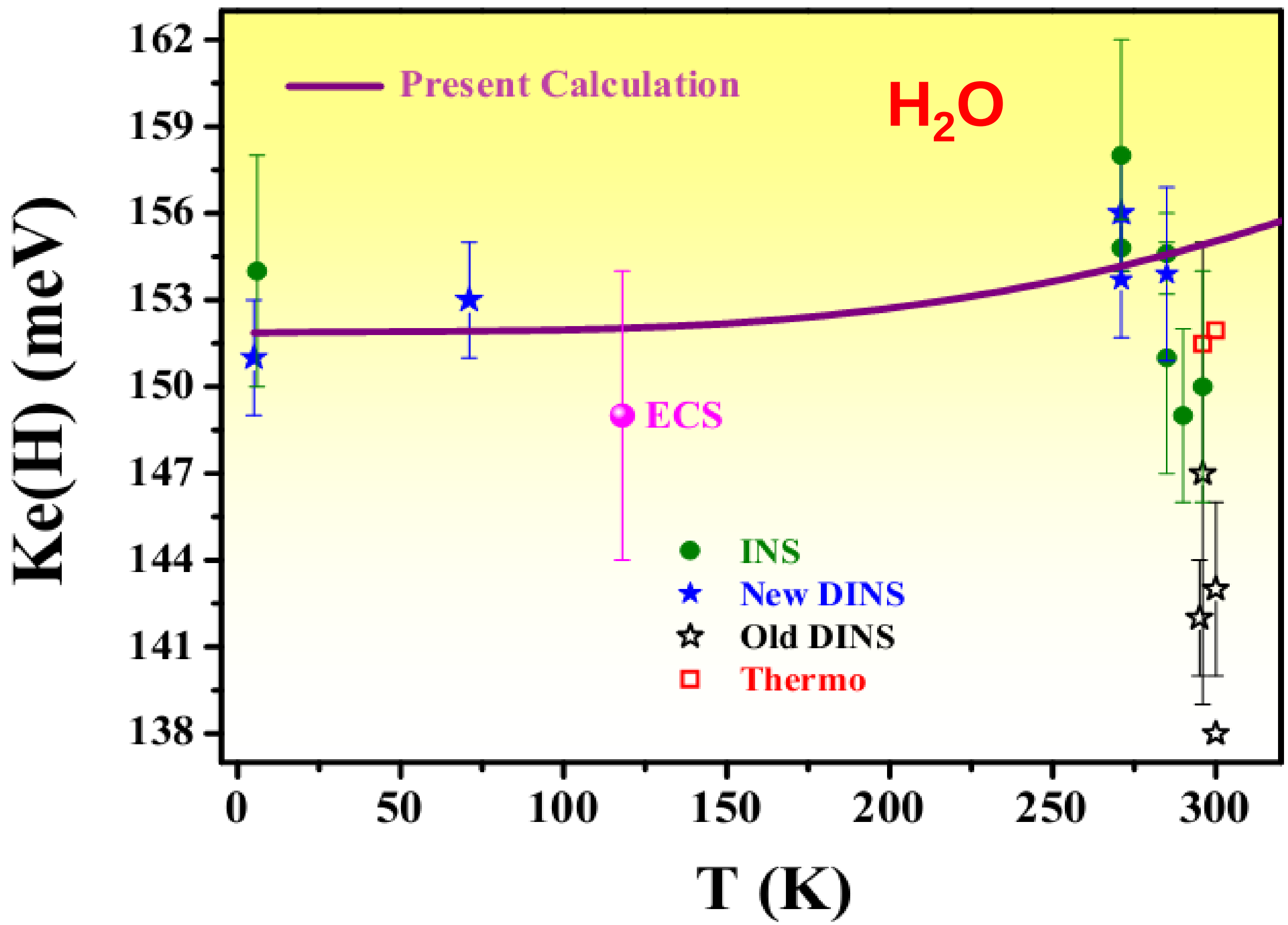
Calculated Ke(H) in H_2O (note continuity S-L-Gas)

Major part of Ke(H) is ZP motion 151 meV vs 154 meV (290K

ECS (Exp) : 149 ± 5 meV (at T=118 K)



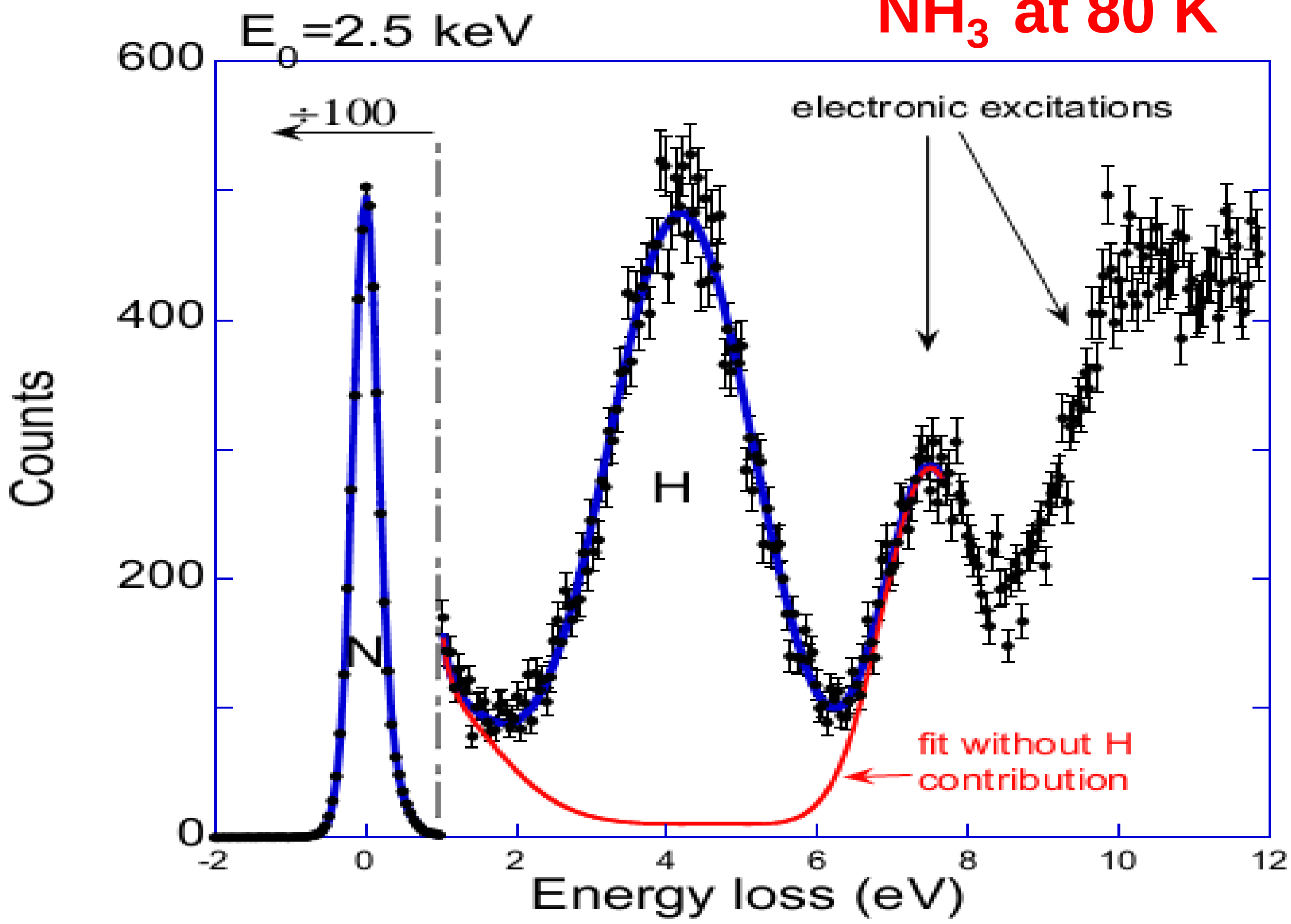
e-scattered spectrum solid NH_3 sample at 80 K.

θ = 135°. ΔE_r(N to H)= 4.17 eV vs 4.36 eV

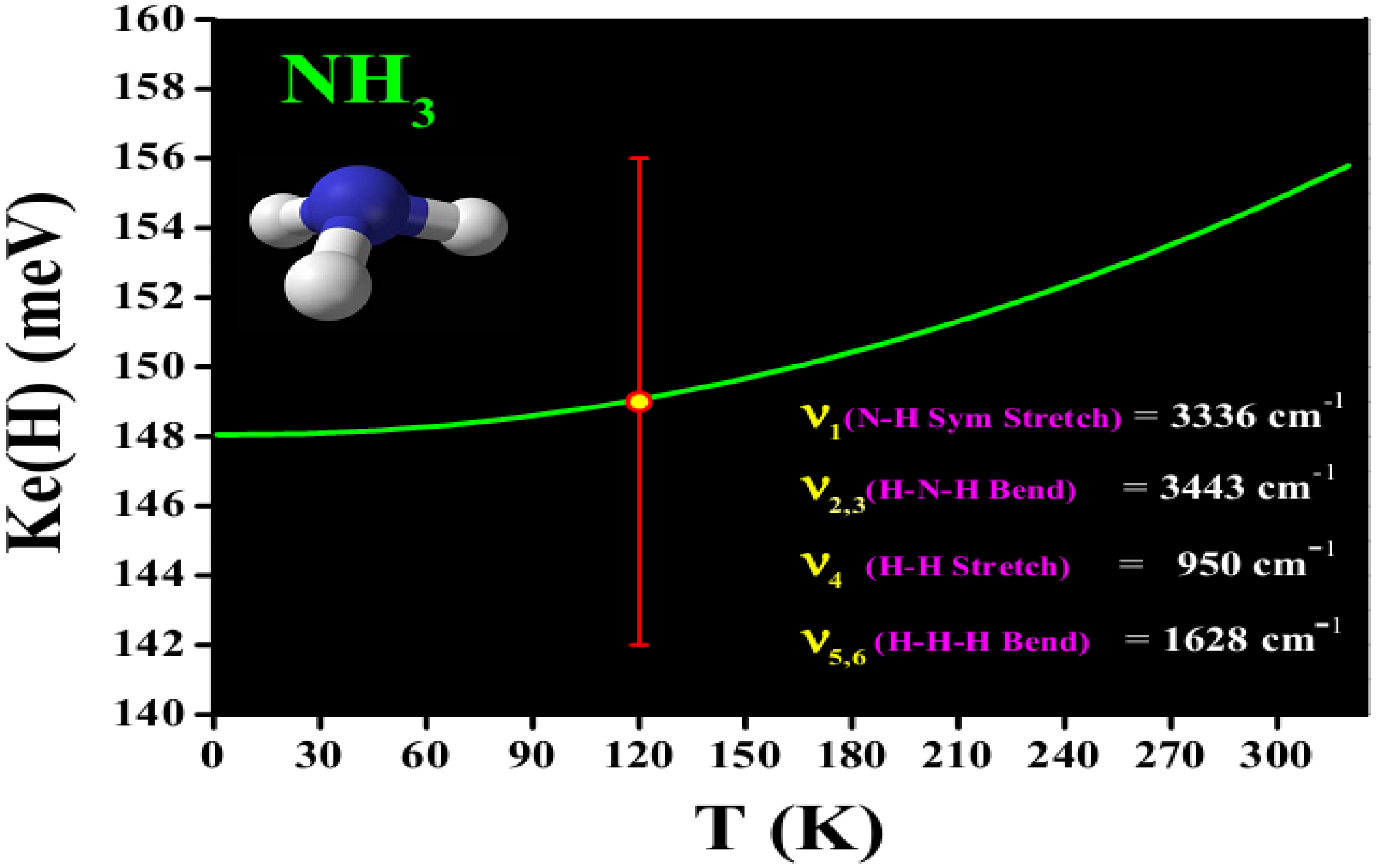
Recoil: $E_{rH} = q^2/2M_H$

Doppler Broadening of H much higher than N (Vos measurement)

NH_3 at 80 K



Calculated Ke(H) in NH_3 (note continuity S-L-Gas) Major part of Ke(H) is ZP motion 148 meV vs 150 meV (vapor) Prelim ECS (Vos Exp) : 149 ± 7 meV



Anomalous n-H scattering Intensities

Neutron experiments Reported ~ 30% Lower n-H Scattering intensity compared to n-D in H_2O/D_2O and to n-C in CH_2

Neutron Scattering xsections

σ(n-H)	σ(n-D)	σ(n-O)	σ(n-C)
82.2 b	7.64 b	4.23b	5.51b

σ(n-H)/σ(n-D) = 10.7 σ(n-H)/σ(n-O) = 19.4

Measured σ(n-H)/σ(n-D) ~ 8.5 (~ 30% less)

Test with Electron scattering: governed by Rutherford Z^2 relation. Hence, one expects: Z(H)=Z(D)=1,   Z(O) =8 ⇒

σ(e-H)/σ(e-D) = 1.0 σ(e-H)/σ(e-O) = 1/64

PRL100, 043204 (2008);   PRL 91, 57403 (2003).

Testing anomalous n-H Scattering Intensities Using e-H scattering

Initial ECS results* at ~ 30 keV using $(CH_2)_n$ sample:

Reported Similar anomalies to n-H measurements

i.e. instead of $\sigma(e\text{-}H_2)/\sigma(e\text{-}C) = 2/36 = 1/18$ of the Z^2- relation

they obtained $\sigma(e\text{-}H_2)/\sigma(e\text{-}C) = 1/23 = 0.7R$ (Rutherford)

Explanation: interaction of e^- with 2 Quantum Entangled (QE) protons in CH_2 :

Real Reason: Radiation Damage: Desorbing H & Depositing C

⇒ H/C ratio decreased ⇒ Missing H-intensity

*Chatzidimitriou-Dreismann et al: PRL **91**(2003) 057403.

Testing n-H Anomalies Using Electron Compton Scattering on H_2O

Refined ECS measurements: on H_2O / D_2O samples

At T = 118 K (ice) , E_e = 1- 6 keV we measured the ratios of scattering intensities from H , O in H_2O and D , O in D_2O

H_2O: $\sigma(e\text{-}H_2)/\sigma(e\text{-}O) = R_1$; D_2O: $\sigma(e\text{-}D_2)/\sigma(e\text{-}O) = R_2$

We found $R_1 = R_2 \Rightarrow$ No anomaly

- Vos, Weigold, Moreh, JCP **138** (2013) 044307.

Scattering Anomaly Using Electrons: Deviation from Rutherford Scattering

Large deviation of electron-proton scattering from Rutherford's formula was reported when the ratio I_H/I_D of a gas mixture H_2+D_2 and pure HD were compared

Pure gas: HD : I_H/I_D= 1= R

Gas mixture: H_2+D_2: I_H/I_D = 0.70 R ⇒ 30% deficiency

Referred to a spin effect.

*Cooper et al: PRL **100** (2008) 043204.

Explanation of e-scattering Intensity Ratio I_H/I_D in H_2+D_2 mixture

- In thermal Equilibrium: **H_2 and D_2 Velocities are Different**
- **$V_{H2} = V_{D2}\sqrt{(M_D/M_H)} = V_{D2}*\sqrt{2}$ (Vos)**

⇒ The heavier mass spends more time in interaction region with the e-beam ⇒ $\mathbf{I_D}$ stronger than $\mathbf{I_H}$

⇒ $\mathbf{I_D = \sqrt{2}*I_H}$ ⇒ $\mathbf{I_H/I_D}$ = **0.69** ⇒ **Good agreement with Measurement of Cooper et al**: PRL **100** (2008):

I_H/I_D = 0.70 ± 0.03 ⇒ **No deviation from R.**

Moreh & Nemirovsky**:** JCP **131** (2009)

CONCLUSIONS

Using ECS : Comparison to NCS

1) e-scattering important New tool for measuring Ke(H)& Zero-point kinetic energies: Major part of atomic Ke **in light molecules**

2) Similarity to Neutron Compton Scat- Measured same Ke values

   Same Doppler broadening was measured by NCS and ECS

3) In H_2O, Ke(H)=149 meV agree with ~ 152 meV at T = 0 - 300 K.

4) **SE Calculations** (assuming harmonic model+ decoupling of motions) produces Good agreement with Experiment

4) Puzzling anomalies reported using NCS were not reproduced

   using ECS. Great advantage in using ECS.

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Thank you

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