Atomic-Scale Optical and Vibrational Spectroscopy with Low Loss EELS

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Infrared and optical spectroscopies are effective characterization techniques, but they are diffraction limited to thousands of Ångstroms. Although aberration correctors and monochromators continue to improve, and it is possible to perform subatomic resolution electron energy loss spectroscopy (EELS) at unprecedented energy resolution, it is argued that low loss features can be severely delocalized (up to hundreds of Ångstroms for optical excitations and millions of Ångstroms for vibrational states) which would suggest poor prospects for atomic resolution imaging [1]. Here, we go beyond the traditional multipole expansions, develop an exact treatment of the near-field inelastic scattering that predicts atomic-scale resolution for optical and vibrational excitations, and present selection rules in this new regime.

While the dipole approximation succeeds for high loss, large probe experiments, very-low loss experiments enter a regime where multipole expansions converge poorly and no longer hold [2,3]. By removing the multipole approximation and implementing the exact transition potential, we show that it is possible to image surprisingly low loss transitions at the Ångstrom scale. Interestingly the monopole term is scale invariant and therefore contributes a high-resolution component even in the low loss limit. By treating the incident electron beam as a point source as opposed to a plane wave, we can solve the perturbation analytically to obtain a Green's function, which can then be convolved with a known probe shape to approximate the full spatially resolved inelastic scattering probability. The work we present investigates transitions of a solvable hydrogenic atom and harmonic vibrational mode, but the selection rules and qualitative behavior remain the same for any system.

We predict a spatial resolution of 1.5 Å for a 1 eV hydrogenic optical transition induced by a 100 keV beam (Fig. 1,2). For a 100 meV phonon in the harmonic approximation with bond length fluctuation of 0.1Å, we calculate a resolution of 0.5 Å (five times the wavefunction size) (Fig. 3,4). Furthermore, in this near field regime, we have a new set of selection rules. Angular momentum conservation prohibits on-atom transitions between states with $\Delta m \neq 0$. Furthermore, donut shaped profiles are seen for $\Delta m = \pm 1$. These results predict that the new generation of corrected, monochromated microscopes are able to resolve low loss (optical/infrared) transitions and may eventually be able to probe vibrational spectra at the atomic scale. Such characterization would allow for better understanding of behavior at the molecular scale [5].

References

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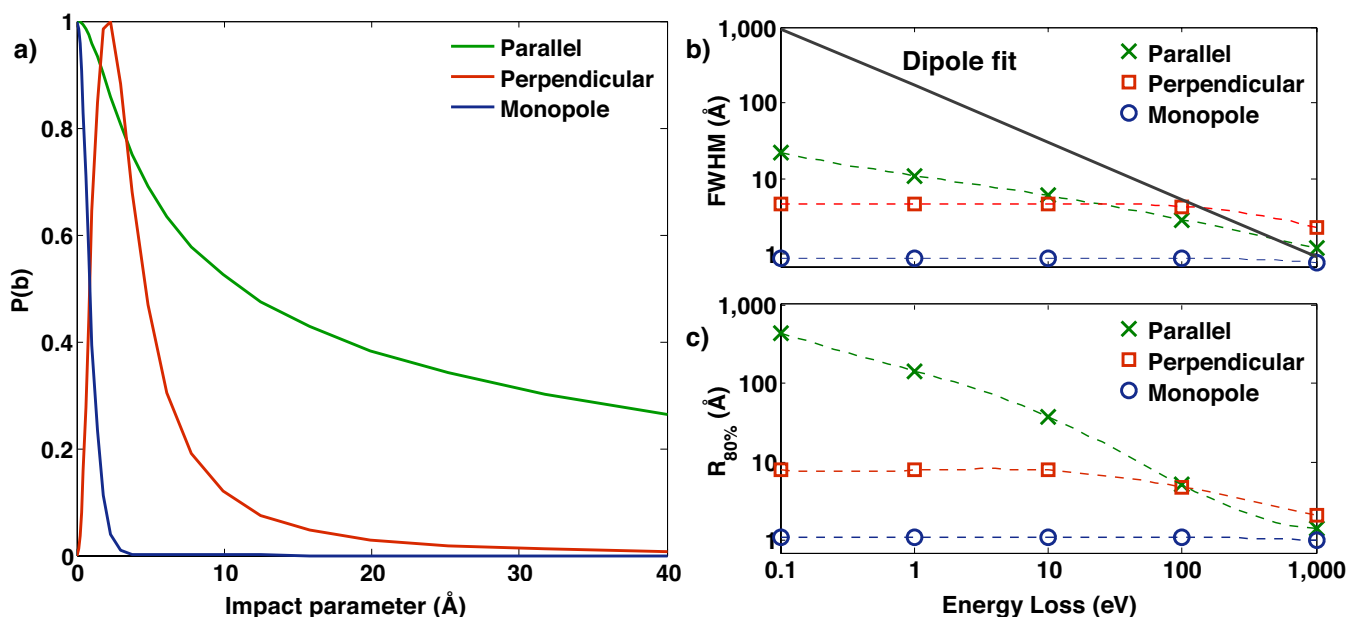
Figure 1. (a) Normalized transition probabilities for the monopole and two dipole terms of a 1eV hydrogenic transition, as functions of distance from beam to atom. The dipole transitions are delocalized while the monopole remains tightly bound. (b) Full width half max and (c) $R_{80\%}$ of hydrogenic transition for varying values in energy loss. The monopole transition remains near the size of the wave function, while the dipole transitions can be orders of magnitude larger. The dipole theory predicts a dependency of FWHM$\sim$E$^{-3/4}$ [4].
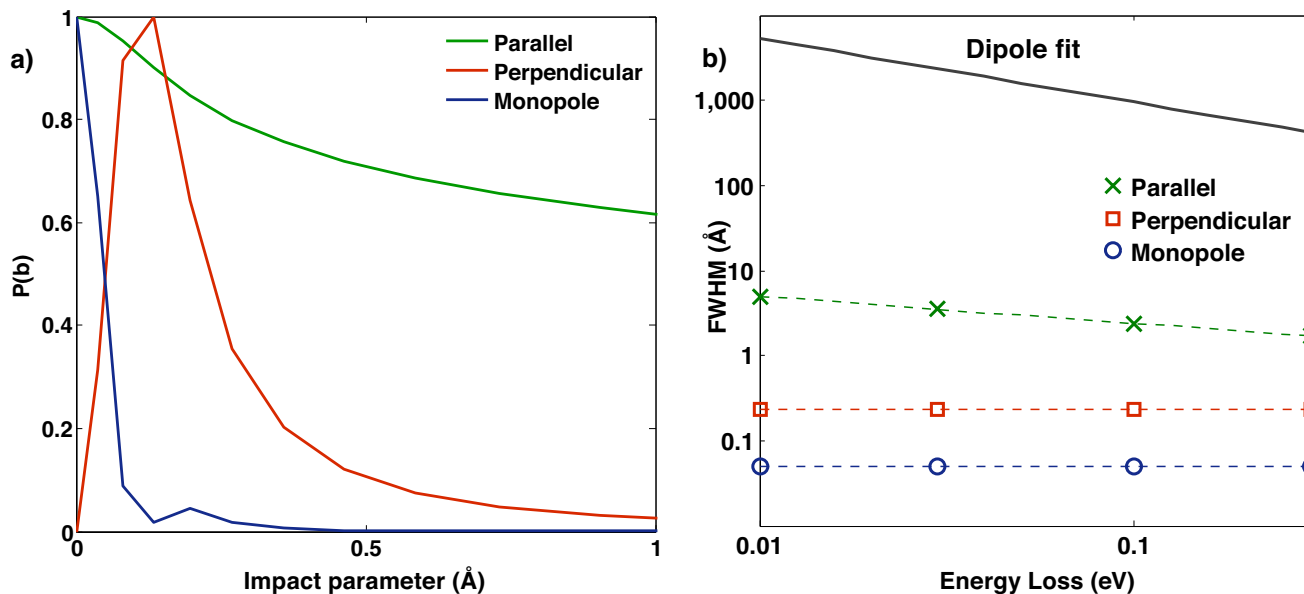
Figure 2. (a) Normalized transition probabilities for the monopole and two dipole terms of a 100meV harmonic vibration transition. These correspond to theoretical scattering profiles of a vibrational mode. (b) Full width half max harmonic vibration transition for varying values in energy loss.