High Resolution Electron Energy Loss Spectroscopy (HREELS): a sensitive and versatile surface tool

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Abstract. We review the principles of high resolution electron energy loss spectroscopy (HREELS) and of its extensions to time, momentum and spin resolved domains. The principles of the construction design and of some results are reported and discussed. In particular, we review the different scattering mechanisms by showing paradigmatic examples of their application. Advantages and shortcomings of HREELS with respect to competing techniques are also addressed.

LIST OF ACRONYMS

ASP Acoustical Surface Plasmon
CDA Cylindrical Dflector Analyzer
ELS-LEED Energy Loss Spectroscopy Low Energy Electro Diffraction
FT-IRAS Fourier Transform Infrared Reflection Absorption Spectroscopy
FWHM Full Width at Half Maximum
HAS Helium Atom Scattering
HREELS High Resolution Electron Energy Loss Spectroscopy
IETS Inelastic Electron Tunneling Spectroscopy
IRAS Infrared Reflection Absorption Spectroscopy
LEED Low Energy Electron Diffraction
LFS LEED Fine Structures
SDA Spherical Deflector Analyzer
STM Scanning Tunneling Microscopy
STS Scanning Tunneling Spectroscopy
TR-HREELS Time Resolved High Resolution Electron Energy Loss Spectroscopy
UHV Ultra High Vacuum
LIST OF SYMBOLS

\( \psi_E \) width of the dipolar lobe
\( \xi_0 \) effective dielectric function
\( e \) electron charge
\( E_0 \) electron kinetic energy
\( h \) Planck’s constant divided by 2 \( \pi \)
\( I_{\text{loss}} \) intensity of the energy loss
\( I_{\text{el}} \) intensity of the elastically reflected beam
\( \lambda \) electron mean free path
\( k_i \) wave vector of the impinging electron
\( k_s \) wave vector of the scattered electron
\( k_B \) Boltzmann’s constant
\( m \) electron mass
\( m^* \) effective electron mass
\( M \) matrix element
\( n(\omega) \) Bose factor
\( q_{||} \) wavevector parallel to the surface
\( q_{||} \) parallel momentum
\( q_{\perp} \) normal momentum
\( \omega \) frequency
\( \omega_p \) plasmon frequency
\( \omega_{sp} \) surface plasmon frequency
\( S \) surface area
\( T \) Temperature
\( \theta \) angle of incidence of the electrons
\( u \) polarization vector
\( v_{||} \) component of velocity parallel to the surface
\( v_{\perp} \) component of velocity normal to the surface
1.1 Introduction

The investigation of surface processes is quite demanding from the point of view of the necessary sensitivity and requires probes whose interaction with the specimen is limited to the outermost atomic layers. This may be achieved with well established bulk probes, like neutrons and X-Rays, either by enhancing the surface to volume ratio of the sample, e.g. by investigating materials in form of powders, or by shooting the probe particle beam at grazing angles from the surface normal exploiting the total reflection phenomenon (occurring below a few degrees for X-Rays). The former approach suffers of very defective and poorly defined surfaces. The latter implies the use of very large and uniform samples, which may not be easily available, and/or of beams of very high brilliance present only at large scale facilities.

Alternatively, one can use probes whose interaction cross section with matter is so large to prevent sub-surface penetration. This is the case e.g. for thermal energy atoms (usually rare gases and in particular He since it is light, does not perturb the system by chemical interaction and He supersonic beams can be produced with a narrow velocity distribution) and low energy ions and electrons. The latter represent the most versatile probe particle since they are easy to produce, accelerate, focus, energy select, and detect. They have moreover a magnetic moment which makes them sensitive to surface magnetism. Finally their De Broglie wavelength becomes comparable with the atomic lattice spacing above 20 eV. The energy dependence of the electron mean free path, $\lambda$, through a material is reported in Fig.1.1. It is a universal curve, largely independent of chemical composition. It initially decreases with kinetic energy, $E_0$, reaching a minimum of half a nm around 50 eV and then slowly increases with $E_0$. In the range from 10 eV to 200 eV, the penetration depth is limited to a few atomic layers but, at grazing incidence or emission, surface sensitivity is assured up to several thousand eV. The high energy behavior corresponds to the growing cross section in the forward direction for fast projectiles. The explanation for the low energy dependence is more subtle as one has to consider that the quanta of the collective modes of the electron gas (plasmons) are in the tens eV range and that the phase space available for single particle excitations shrinks with decreasing energy. The efficacy of electron energy loss mechanisms, responsible for the removal of the electrons from the beam, decreases thus more and more when moving towards lower kinetic energies.

The favorable matching of electron wavelength and lattice spacing and the high surface sensitivity made of Low Energy Electron Diffraction (LEED) a well established tool for the investigation of surface crystallography and the principal technique for a rapid inspection of surface symmetry and of surface order. Elastic backscattering from the surface lattice involves only a minority of the impinging electrons, the rest being either inelastically scattered or ending up as sample current after penetrating into the bulk of the crystal. The intensity of the specular beam (to which the dipole scattering intensity
is proportional) is largest at low $E_0$ and at grazing incidence, conditions for which only one or just a few diffraction channels are open. The reflectivity increases, moreover, dramatically below a few eV because of quantum scattering off the attractive surface potential barrier. A high reflectivity is achieved also when the electron penetration into the bulk is hampered by energy gaps in the bulk electronic structure. The reflected beam can then come up to 30% of the incident current [1].

The relatively high cross section of the electron-atom interaction limits the environment in which electron beams can be employed to ultra high vacuum (UHV). This limitation is not too severe since vacuum is anyhow necessary to keep the investigated surfaces in a well defined state for the time needed to perform most experiments. The electron charge implies that the experimental set up must be screened from the earth magnetic field to avoid an unwanted deflection of the electron trajectories. Such screening must be the more accurate the higher the desired energy resolution. Also the work function of the electrodes of the spectrometer must be highly uniform to avoid inhomogeneous electric fields which may cause a broadening of the velocity distribution in the beam. This is achieved by coating all surfaces with a uniform graphite film. One major drawback of electrons is the necessity of avoid surface charging. Insulator surfaces can therefore be investigated only when prepared in form of ultrathin films deposited on conducting substrates [3, 4] or when the residual conductivity associated to defects is sufficiently large.

The present chapter deals with the fundamentals and with some examples of applications of High Resolution Electron Energy Loss Spectroscopy (HREELS). At the usual cathode temperature of some 2000 K, the width of the thermal energy distribution of the emitted electrons, $k_B T$, is in the
hundreds of meV. Such resolution is thus readily available without energy filtering. HREELS corresponds to the realm of a few meV full width at half maximum (FWHM) which can only be achieved by energy selecting the beam by an electrostatic device operated at pass energies in the sub-eV range. The monochromated beam is eventually accelerated to the desired energy.

When the beam strikes the surface the electrons may be either scattered elastically or inelastically or they may be resonantly captured by adsorbates thus increasing the probability to suffer an energy loss. In order to evidence inelastic events the electron beam has to be monochromatized and the scattered electrons analyzed in energy. At low kinetic energy of the impinging electrons and with the sample at, or below, room temperature loss and gain processes in the tens of meV range correspond mainly to creation and annihilation, respectively, of single vibrational quanta, such as surface phonons, and of more localized adsorbate modes. Electronic single particle transitions (i.e. interband transitions) and collective electronic excitations (plasmons and surface plasmons) occur generally in the eV range. Excitation of spin waves on magnetic samples and of Cooper pairs on superconductive materials is also possible. The inelastic scattering process may be mediated either by the long range Coulomb fields (dipole scattering) or occur at the impact with the surface atoms (impact scattering). Electron capture amplifies the latter mechanism and is often the driving force in electron induced desorption or dissociation of adsorbed species.

Dipole scattering relies on the same mechanism as the competing method of infrared absorption spectroscopy (IRAS). With respect to the latter technique HREELS has the advantages of: 1) exploring a larger portion of reciprocal space not being limited by the very small momentum of the photons;

2) allowing for small energy losses, while in IRAS photons below some 400 cm$^{-1}$ are difficult to employ being absorbed by the windows separating the IR source from the UHV chamber;

3) having a sensitivity to adsorbate coverage down to the $10^{-3}$ ML since the energy loss signal is recovered from regions with very low background, while in IRAS the absorbance corresponds to a decrease of an otherwise large reflectance. This remains true also after the improvement of IRAS sensitivity given by the introduction of the Fourier transform method (FT-IRAS).

On the other hand, IRAS is superior with respect to the achievable resolution (1 cm$^{-1}$ against 1 meV of HREELS (1 meV = 8.0651 cm$^{-1}$)) and works also at atmospheric pressure. The latter quality made IR spectroscopy more and more popular for performing experiments spanning from controlled UHV to more realistic conditions. IRAS is, moreover, much more apt for plug and play set ups, while a long training is needed to form HREELS specialists.

The impact scattering mechanism has analogy to the one operating in He atom scattering (HAS) since the energy exchange takes place during the contact of the probe particle with the surface. Given the short collision distance no limitation is present for the exchanged momentum. With respect to HAS, which presents an even higher surface sensitivity due to the inability of He
atoms to overcome the very first surface layer, electrons have the advantage to be easily removed by absorption into the walls of the vacuum vessel saving heavy and expensive pumping systems. He atom beams may, on the other hand, reach energy resolutions in the sub meV range and even neV losses could be appreciated in the recently developed spin echo spectrometers [5,6]). However, these deficiencies of HREELS are more than compensated by the higher kinetic energy which removes any limit to the energy loss value and by their other characteristics making it an economically affordable and flexible tool, definitively attractive to investigate a wide set of phenomena involving vibrational, electronic and magnetic excitations. Last but not least the success of HREELS was pushed by the production of reliable commercial spectrometers.

The present chapter is organized as follows: in the next paragraph we shall quickly revise the possible scattering mechanisms of electrons off a surface, namely dipole, impact and resonance scattering. We shall report here only the selection rules and the final formulas for the cross section under usually applicable approximations, while the reader is addressed to the original papers and reviews for a detailed mathematical treatment [7, 8]. The third paragraph is devoted to a schematic description of the design of last generation High Resolution Electron Energy Loss Spectrometers and to their developments. In particular, we shall mention Time Resolved HREELS (TR-HREELS), momentum resolved HREELS (ELS-LEED), and Spin Polarized HREELS (SPEELS). The fourth paragraph will present selected examples of HREELS experiments aimed at the study of surface chemical reactions, at measuring surface phonon dispersion or adsorbate vibrational modes (to characterize adsorption and chemical reactions), surface plasmon dispersion, surface spin waves in magnetic materials and inter-band transitions. In the fifth and last paragraph the possible future developments of HREELS will be outlined.

1.2 Inelastic Scattering Mechanisms

The scattering of electrons off surfaces is a complex phenomenon and can be treated at different levels of approximation and complexity [9]. The energy loss mechanisms are generally classified in two limits referred to as dipole and impact scattering.

1.2.1 Dipole scattering

Dipole scattering is mediated by the long range electric fields associated to the electron charge. When moving at a velocity $v$ and for a distance $d$ from the surface such fields have Fourier components extending up to a cut off frequency $\omega_c = \frac{v}{d}$ [10]. Excitation of surface and adsorbate modes through such fields can thus take place already when the electron is still far away from the surface plane. Indeed a 100 meV vibration can be excited by an electron
Fig. 1.2. A) Typical dipole scattering spectrum of an adsorbed molecule obtained with a state of the art commercial spectrometer. The energy loss intensity is enlarged by a factor of 50 with respect to the one of the specular elastic peak. The losses are due to NO adsorbed on RuO$_2$. Reprinted figure with permission from Ref. [11] Copyright (2009) by Elsevier. B) Schematic pictures of the angular dependence of the cross section for dipole scattering at low kinetic energy. Contrary to impact scattering, which is distributed over the whole solid angle, it is peaked along the specular direction. Reprinted figure with permission from Ref. [9] Copyright (1987) by Institute of Physics Publishing. C) The two most relevant dipole excitation processes: (I) the excitation of the energy loss occurs on the incoming trajectory and (II) on the outgoing trajectory. The two processes and coherent and give rise to interference. The relevant reflection coefficients $R_s(E_0)$ may thereby differ in amplitude and phase. Reprinted figure with permission from Ref. [12] Copyright (1991) by the American Physical Society. D) False loss structures mimicked by LEED Fine Structures in processes of type I of panel C. The spectrum is reported vs scattered electron kinetic energy. The corresponding dependence for the elastic reflectivity, measured for the specular beam, is shown for comparison in the lower panel. Reprinted figure with permission from Ref. [1] Copyright (1994) by the American Physical Society.

with a kinetic energy of 1 eV already at a distance of 100 Å. Given the relatively large interaction distance neighbouring oscillators will be excited nearly in phase. This scattering mechanism is therefore confined to small momentum transfers, i.e. it occurs in a narrow cone (the dipole cone) around the elastic diffraction channels as schematized in Fig. 1.2 B. A typical energy loss spectrum is reported in Fig. 1.2 A. The different peaks correspond to the excitation of single vibrational quanta and allow to infer the chemisorption state of the adsorbate.
The dipole mechanism is characterized by the following properties: a) only modes causing a change of the dipole moment will be detected. In other words, the dynamical dipole moment associated with the vibrational transition must be non-zero; b) since the Coulomb interaction is quite long range and lasts for a relatively long time (some $10^{-14}$ s) the microscopic details of the interaction potential are not needed to describe it.

Theoretical treatments were developed using either a purely classical picture (the electron is treated as a classical particle moving along a trajectory and interacting with the classical electric field of the surface excitations), or a semi-classical approach (the electron is treated classically while surface excitations are treated quantum mechanically [13]), or a complete quantum mechanical description [14–16].

In the semi-classical theory, the probability that an electron loses an energy $\hbar \omega$ to create a surface excitation at a crystal temperature $T=0$ K is given by [9]:

$$P(\omega) = \frac{4e^2}{\pi^2\hbar} \int_D d^2q ||q|| \frac{q||v^2_q}{[(\omega - q||v||)^2 + q^2||v^2_q||]^2} \times \text{Im} \frac{-1}{\xi_0(q||,\omega) + 1} \quad (1.1)$$

The first part represents the kinematic factor. It determines the angular dependence of the cross section, peaked in an intense lobe of angular width $\psi_E = \frac{\hbar \omega}{2E_0}$ around the elastic channels. Because of the factor $q||$ the intensity goes to zero for vanishing momentum.

The last factor contains the effective dielectric function of the target $\xi_0$, i.e. the surface properties. The domain of integration $D$ is determined by the angles of acceptance of monochromator and analyzer. In the semi-classical limit the surface is considered as a perfect reflector and the excitation probability equals the ratio $I_{\text{loss}}/I_{\text{el}}$, where $I_{\text{loss}}$ and $I_{\text{el}}$ are the intensity of the loss and of the elastic peak, respectively. From integration of eq. 1.1 the following relations are derived [9], where the different dependencies are caused by the different spatial confinement of the excited modes:

- $I_{\text{loss}}/I_{\text{el}} \propto \frac{1}{\cos \theta \sqrt{E_0/\omega}}$ for surface phonons and plasmons (excitations decaying exponentially into the substrate);
- $I_{\text{loss}}/I_{\text{el}} \propto \frac{1}{\cos \theta \omega}$ for adsorbate modes (confined in the adlayer).

For non metallic substrates there are no restrictions on the orientation of the observable dipoles with respect to the surface and the only requirement is the existence of a non vanishing dynamical dipole moment. For metals, on the contrary, the image dipole will enhance the intensity of perpendicular vibrations and screen out those parallel to the surface, leading to the well known metal-surface selection rule [9]: *only molecular vibrations that give dipole changes perpendicular to a metal surface can be observed in HREELS when the scattered electrons are collected close to the specular direction.*

The ultimate physical reason for this is that for metals electronic oscillations (plasma frequency) have a much higher frequency (energies of several eV).
than molecular vibrations ($\hbar \omega \leq 0.6 \text{ eV}$), so that the surface electrons can effectively screen parallel vibrations by giving rise to an image dipole in the opposite direction. This argument does not apply to semiconductors, characterized by 2-3 order of magnitude lower values of the plasma frequency and, a fortiori, to insulating samples. The metal selection rule was effectively employed to determine, e.g., the orientation of a molecular functional group with respect to a metal surface [7].

In a full quantum mechanical treatment the occurrence of different paths is included. In particular, as schematically reported in panel C of Fig. 1.2 the excitation can occur either before or after the electron impact with the surface and reflection off it. The reflection coefficient, $R_s$, may thereby depend on the electron kinetic energy, $E_0$, both in amplitude and in phase. Such different channels give rise to interference and if $R_s$ varies over the energy loss range the assumption of the proportionality of loss probability and elastic reflectivity fails. In general, such changes occur on a scale of several eV. They can, therefore, be neglected over the range of energy loss/gain of interest for vibrational spectroscopy, except for the very particular conditions corresponding to reflectivity fine structures (also called LEED fine structures, LFS). The latter are associated to reflection off the attractive image potential and can be important at low kinetic energies at the threshold conditions for the opening of the first diffraction channel besides the specular one. The assumption is, on the other hand, generally false when dealing with the larger losses associated to electronic excitations [1,17,18]). An example is given in panel D of Fig. 1.2.

As one can see the sharp losses apparent in the spectrum reported in the upper panel occur at exactly the same kinetic energies of the scattered electron as the LFS in the specular channel (lower panel). The process is thus that the incoming electrons excite the continuum of electron-hole pairs on their way to the surface and are then reflected with different $R_s(E_0)$ thus mimicking sharp losses. Such features can be easily distinguished from real ones since their apparent position in the spectrum changes with $E_0$.

For small energy losses and neglecting LFS conditions the differential cross section $\Sigma$ becomes then:

$$\frac{d^2\Sigma}{d\Omega d\hbar \omega} = \frac{2m^2e^2v_\perp^4}{\pi \hbar^5 \cos \theta_0} \frac{k_s}{k_i} \frac{|R_{II}|^2P(q_{||}, \omega)}{\left[(\omega - q_{||}v_{||})^2 + q_{||}^2 v_{\perp}^2\right]^2}$$ (1.2)

where $\Omega$ is the solid angle and $P(q_{||}, \omega)$ incorporates the information on the physics of the surface region and, under suitable assumptions [7], is given by

$$P(q_{||}, \omega) = \frac{2\hbar q_{||}}{\pi} \left[1 + n(\omega)\right] \times \text{Im} \frac{-1}{\xi(q_{||}, \omega) + 1}$$ (1.3)

Notably this form includes explicitly the temperature dependence of the intensity via the Bose factor $n(\omega)$. Its presence justifies why the energy gains
are observed only at high temperatures and for $h\omega$ values significantly lower than thermal energy $k_B T$.

### 1.2.2 Impact scattering

Impact scattering is due to the losses arising during the collision of the electrons against the ionic cores of substrate or of adsorbate atoms. Contrary to dipolar scattering, it arises therefore from a short range interaction and is therefore not limited to small momentum transfer. In a seminal paper Ho, Willis and Plummer \[19\] investigated the non-dipole electron impact excitation of the vibrational modes of H adsorbed on W(100) (see Fig. 1.3) and showed that for some of them the angle and energy dependence of the intensity deviates significantly from the one expected for dipole scattering. Impact scattering was not, however, systematically investigated until 1982 when the study of surface phonon spectra became a hot topic. The theory to compute the impact scattering cross section is more demanding than for dipole scattering, since both crystal potential and multiple scattering have to be included explicitly. The scattering probability, firstly derived by Tong, Li and Mills \[22\], has the form:

$$\frac{dP}{d\Omega} = \frac{mE_0 \cos^2 \theta_s}{2\pi^2\hbar^2 \cos \theta_0} S \left| M(k_0, k_s, q_\parallel, u) \right|^2$$  \hspace{1cm} (1.4)
Fig. 1.4. A) Typical energy loss spectrum recorded for out-of-specular conditions for Mo(110)(1x1) H. Thanks to the improved resolution (cfr Fig. 1.3, 1.5 meV against 33 meV) surface phonon losses are now well resolved. They correspond to the excitation of the Rayleigh wave (TA) and of the Longitudinal resonance (LA) at a wavevector transfer of 0.9 Å⁻¹ along the <100> crystallographic direction (Γ − H, see inset with the two dimensional surface Brillouin zone). The ratio between energy gains and energy losses is determined by the Bose factor. B) Collection of the measured electron energy losses vs momentum transfer (large symbols) and comparison with HAS (dots). The Kohn phonon anomaly is evident in the central panel and is excited both by HREELS and HAS. The deep cone corresponds, on the contrary, to the excitation of electron hole pairs which are best excited with HAS. Reprinted figures with permission from Ref. [20] Copyright (2004) by the American Physical Society and from Ref. [21] Copyright (1997) by the American Physical Society.

Where: \( \theta_0 \) and \( \theta_s \) are the impinging and scattering angles measured from the surface normal, respectively; \( E_0 \) is the primary kinetic energy; \( m \) is the electron mass; \( S \) is the surface area hit by the beam; \( M \) is the multiple scattering matrix element for an electron with initial wave vector \( k_0 \) into a state with final wave vector \( k_s \) exciting or annihilating a phonon of wave vector \( q_{||} \) (parallel to the surface) and polarization vector \( u \).

It is important to remark that, for impact scattering, there is no relation between elastic reflectivity and inelastic cross section, since both are determined independently by multiple scattering. Consequently normalization of the experimental data with respect to the specular elastic intensity makes no sense. The \( E_0 \cos^2 \theta_s \) factor in eq. 1.4 implies that the impact cross section
increases with kinetic energy and decreases with $\theta_i$ and $\theta_s$. The actual dependence of the cross section on scattering energy and geometry is, however, so strongly modulated that no forecast for the most favorable experimental conditions is possible without calculating $M$. In general, since the growing cross section is more than counterbalanced by the worsening of the HREEL spectrometer performance with $E_0$ the best conditions for observing phonons have to be searched between 20 eV and 50 eV. This is well exemplified in Fig. 1.5, which reports the oscillatory behavior of the impact scattering cross section of the $S_4$ and $S_6$ phonons of Ni(100) at $\bar{X}$, as found experimentally and predicted by theory [23]. The experimental intensities have been corrected by multiplying by $E_0$ in order to correct them with respect to the decreasing transmittivity of the spectrometer. The two modes correspond, respectively to the counterphase motion of the nearest neighbour surface atoms in the vertical direction and along the scattering plane. Without the effect of multiple scattering the HREELS cross section for $S_6$ would be roughly one order of magnitude smaller than the one for $S_4$ and its observation would have been impossible.

Since the impact scattering cross section depends on the scalar product of the phonon eigenvector and of the transferred wavevector, $\mathbf{u} \cdot (\mathbf{k}_s - \mathbf{k}_0)$, the following selection rules follow: a) shear polarized surface phonons (polarization parallel to the surface but perpendicular to the plane of incidence) cannot be excited for in-plane scattering events; b) longitudinally polarized modes have vanishing cross section in the specular direction.
1.2.3 Resonance scattering

At low kinetic energies the electrons may undergo resonant scattering. Strictly speaking it may be considered as a special kind of impact scattering with the electron remaining trapped for a while in an orbital of an adsorbate and thus increasing its energy loss probability. Resonance scattering is named after the characteristic structure of the energy dependence of the excitation cross section, which exhibits a remarkable enhancement in a limited $E_0$ range. Well known for gas phase scattering, resonance scattering was firstly reported for surfaces by Andersson and Davenport [24], who observed a non-dipolar behaviour for OH adsorbed on Ni(100). They proposed that the electron is temporarily trapped forming a charged ion (the so-called negative ion resonance). Two kinds of resonances are then possible:

a) Shape resonance, if the ground state of the so-formed ion lies above the ground state of the neutral molecule;

b) Feshbach resonance, if the ground state of the ion lies below the ground state of the neutral molecule.

A similar mechanism was later observed for both physisorbed [25–29] and chemisorbed molecules [30–34], as well as for Fuchs-Kliewer phonons of NiO(100) [64].

As an example of resonant inelastic scattering, we show in Fig. 1.6 the energy dependence of the $\nu_1$ and $\nu_{13}$ modes and of the elastic beam for benzene chemisorbed on Pd(100). The curves are neither correlated to the specular intensity (as expected for dipole scattering) nor follow the modulation expected for impact scattering. We demand the reader to the review by Palmer and Rous [36] for further details and applications of this scattering mechanism.

1.3 Experimental setups

The historical development of HREEL spectrometers is mainly correlated with significant advances in the realization of instruments combining higher monochromatic current and better resolution.

The spectrometer consists of (see Fig. 1.7): a) a cathode lens system (A lenses) to focus the beam on the entrance slit of the premonochromator; b) a double stage monochromator; c) accelerating and decelerating lenses for focusing the monochromated beam onto the sample and for focusing the reflected beam onto the entrance of the energy analyzer (B lenses); d) a single stage energy analyser; e) a channeltron and a detector lens system to focus the beam on its entrance (C lenses).

Monochromators and analyzers exploit the chromatic aberration of electrostatic deflectors operated at low pass energy. Among these, the cylindrical deflector analyzer (CDA) has proven to be superior to all other competing designs because, being a one dimensional device, one can use rectangular rather
than circular slits. The focal property depends indeed on the width of the slit (not on its height), while the space charge is distributed over all the slit area thus reducing its pernicious effects. Moreover, with respect to the spherical deflector, the CDA has the advantage that the focal position can be finely tuned to the effective position of the exit slit by the potential applied to the plates delimiting the device in the direction normal to the deflection plane. This allows to compensate the focal position for different beam divergences caused by different space charge densities (Borsch effect) thus guaranteeing the highest current throughput for all conditions. The price one has to pay is the use of rectangular rather than the better developed electrostatic cylindrical lenses and to have a ribbon (rather than cylindrical) shaped beam. The monochromatic current and the brilliance of HREELS could be dramatically optimized by computer simulations of the electron trajectories in the CDA and in the lenses. This led to a toroidal rather than cylindrical shape of monochromator and analyzer. Such calculations require the solution of 3D Laplace problems aiming at the minimization of aberrations and explicitly considering fringe fields at the collimators. In the monochromator also the effect of space charge has to be taken into account in order to optimize its
deflection angle [37]. Another important improvement was the introduction of an accelerating premonochromator for a coarse energy filtering since it reduces the effect of space charge. The reader is addressed to Ibach’s book [8] for a more detailed discussion.

We mention that spectrometers with different design have been realized for particular applications such as time resolved (TR)-EELS, ELS-LEED and spin polarised (SP-) EELS.

TR-EELS employs the principle of dispersion compensation [38]. In a conventional HREEL setup the slits at the exit of the monochromator and at the entrance of the analyzer determine the energy resolution, by cutting off electrons with different energy and thus illuminating the sample with a monochromatic beam of limited size. In dispersion compensated spectrometers these slits are removed and the sample surface is illuminated simultaneously with electrons of different energy, focused at different positions on the sample, see Fig. 1.8. This approach greatly enhances the signal level (which is proportional to the square of the energy spread) without degrading the resolution (proportional to the spatial spread) provided the aberrations of the system are small. This spectrometer allowed to record an entire 100 point spectrum in 0.1 s [38] and to monitor the evolution of a single peak (i.e. to measure
the residence time of an adsorbate on a surface) with a time resolution of 1 ms. Unfortunately, no further improvement was possible because the electron optic aberrations (large, even if the spectrometer uses a 180° spherical deflector (SDA) design which guarantees a second order focus on its exit plane) and the rigidity of the SDA with respect to focal correction for space charge make so that the high current is obtained at an unreasonable cost in energy resolution. Although remarkable, the ms time scale remains still far from the one characteristic of most surface processes, so that this approach was not further pursued.

The ELS-LEED design is schematized in Fig. 1.9 a, b and c. This spectrometer aims at improving the momentum resolution of HREELS, usually limited to some 0.02 Å⁻¹ [40] for the conventional models. In ELS-LEED the angle of incidence and of scattering are selected electronically through an octupole optic [41], as in spot profile analysis (SPA)-LEED, rather than by mechanically rotating analyzer or monochromator. The energy selection and analysis is then performed with CDA devices as in conventional HREELS. Due to the octupole deflector the electrons impinge onto the surface close to the surface normal rather than at grazing incidence. A resolution as high as 0.004 Å⁻¹ was reported [42], which was exploited, e.g., to perform quite accurate measurements of surface plasmon dispersion [43,44].

SP-EELS is employed in the investigation of magnetism at surfaces. The acronym is used to address experiments with a different degree of complexity: indeed it refers to experiments employing a polarized primary electron beam, but the polarization analysis after scattering may be either present [45] or not [46, 47]. The polarised electron beam is obtained by using a GaAs photocathode illuminated by circularly polarized light [48]. The spin polarisation of the beam is measured in a high energy Mott detector [49] or by evaluating
the anisotropy of the LEED spots intensity. Suitably designed premonochromators and monochromator with 90° and 180° deflection angle, respectively allow to perform the energy selection without mixing up the spin states [50]. A scheme of the spectrometer which was realized by Ibach et al. is reported in Fig. 1.7 [51] (see also references [52,53]).

1.4 Selected experimental results

In this paragraph we are going to demonstrate the versatility of HREELS in surface analysis, by giving an overview on some selected results covering different subfields.

1.4.1 HREELS for the study of adsorbates and surface chemistry

The surface science literature reports thousands of papers employing HREELS to characterize adsorption at surfaces and surface reactions. The analysis of
the angle and energy dependence of the vibrational losses has often been used to gain information on the adsorption site and, in particular, to discriminate between on-surface and sub-surface vibrations [54, 55]. Indeed losses whose intensity does not decrease when moving off-specular are likely to arise from impact scattering and to originate possibly from vibrations polarised parallel to the surface or involving the motion of sub-surface species. Only photoelectron diffraction, careful STM analysis or ab-initio calculations can lead to a conclusive assignment of the adsorption site, but HREELS can provide strong indications about the correctness of the starting model.

We report in the following two examples of the information provided by HREELS in the study of gas-surface interaction. Fig. 1.10 compares in-specular HREEL spectra we recently recorded after dosing CO$_2$ on a clean and on a H-covered Ni(110) surface [56]. The modes at 50, 98, 167 and 365 meV correspond, respectively, to the $\nu$(Ni–O), $\delta$(OCO), $\nu_s$(OCO) and $\nu$(CH) vibrations of formate (HCOO) and indicate the formation of this compound as an intermediate product of the CO$_2$ hydrogenation reaction catalysed by the surface. The HREEL study allowed a precise identification of the stable reaction product and, in combination with photoemission spectroscopy and ab-initio calculations, it contributed to highlight an unexpected reaction mechanism. We proved indeed that, although isolated CO$_2$ adsorbs onto the surface with the C atom down, when a HCO$_2$ complex forms, it first flips head-down binding to the surface with the two O atoms. H can thus bind to the free C end leading to HCOO formation [56].
The second example is reported in Fig. 1.11 and shows HREEL spectra recorded after dissociative $O_2$ adsorption on Ag(210) [55]. This is a stepped surface with one row wide (100) terraces and (110) step heights. Three losses are observed at 31, 40 and 56 meV (see panel A). The adsorption sites may be identified by comparison with the frequencies observed for O adsorption at pristine low Miller index surfaces. The lowest frequency corresponds to adatoms at (111) or (100) like planes and is identified by O at the (100) nanoterraces. The 40 meV mode must be related to a configuration similar to the one of the Ag-O added rows which form on Ag(110) and is assigned to O decorating the open step edges. The 56 meV mode is not present on pristine low Miller index surfaces. Its energy is too high to be due to adatom motion and too low to be due to the internal vibration of $O_2$ admolecules. Indeed it coincides with the frequency reported for AgO [57] and is therefore indicative of the formation of this type of oxide. The analysis of the different behavior of the intensities of the 40 meV and of the 56 meV peaks with respect to the electron scattering angle, reported in Fig. 1.11B confirms the different nature of their loss mechanisms. Indeed, the ratio of the 40 meV/56 meV intensities changes in favor of the higher energy mode when moving off-specular, indicating its non-dipolar nature.

As shown in Fig. 1.11 panel C the ratio of the 31 meV and of the 56 meV modes changes, moreover, as a function of the impact energies and of the angle of incidence of the $O_2$ molecules, as demonstrated by dosing with a supersonic molecular beam. The intensity of the 40 meV mode (upper panel) remains, on the other hand, approximately constant. Indeed, the former modes oscillate in counterphase, the 56 meV peak being most intense when the molecules impinge at high impact energy and close to the surface normal. An adsorption path must therefore exist for which dissociation takes place very close to the surface plane and one of the atoms resulting from the dissociation process ends up in a subsurface site (56 meV vibration) while the other sticks at the step edge (40 meV vibration). Another pathway dominates when the beam strikes the surface at more grazing incidence so that both atoms end up in super surface sites, i.e. one at the step edge (40 meV) and the other on the (100) nanoterrace (31 meV). The latter may eventually diffuse to the subsurface region when mobility is activated thermally by heating the crystal. Interestingly, such mechanism is not present for Ag(411), a surface with the same open step geometry as Ag(210) but with twice as large (100) nanoterraces [58]. This finding indicates that the relaxation of the substrate atoms at the step is crucial to open the pathway leading to surface oxide formation.

When a similar experiment is repeated for Ag(511) very different frequencies are observed. This surface is characterized by 4 atom row large (100) nanoterraces, like Ag(410), but close packet rather than open step heights. The vibrational frequencies of 33 meV and 67 meV observed after dissociative oxygen adsorption are again indicative of O chemisorption and of oxide formation. In this case, however, the oxide is not AgO but rather $Ag_2O$ [59], as unambiguously evident from the higher vibrational frequency.
1.4.2 HREELS for the measurement of dispersion curves of collective surface excitations: surface plasmons and surface phonons.

Dispersion curves are recorded by measuring the dependence of the energy of an excitation as a function of wavevector transfer, $q_\parallel$. In HREELS a monochromatic electron beam impinges onto the surface at a well defined angle with respect to the surface normal, $\theta_i$ (i.e. with a well defined impinging wave-vector $k_0$) and the scattered intensity is measured at another well defined angle, $\theta_s$, with a scattered wavevector $k_s$. Independently of the energy and momentum transfer mechanism, $q_\parallel$ can be unambiguously determined from the conservation of energy and momentum:

$$\frac{\hbar^2 k_0^2}{2m} = \frac{\hbar^2 k_s^2}{2m} + \hbar \omega$$  \hspace{1cm} (1.5)$$

$$k_0\parallel = k_s\parallel + q_\parallel$$  \hspace{1cm} (1.6)$$

where $\hbar \omega$ is the value of the energy loss and $k_0$ and $k_s$ are determined by the initial energy and by the scattering geometry. Provided that only one
quantum is involved in the process, $\hbar \omega$ and $q_{||}$ are linked by the dispersion relation of the excitation.

**Surface phonon spectra**

Besides Fuchs Kliewer modes [62–69], corresponding to the counter-phase motion of the positively and negatively charged sublattices of crystals with at least partially ionic chemical bonds (e.g. oxides or III-V and II-VI semiconductors), only optical phonons can be excited by dipole scattering (e.g. on Si surfaces). Acoustic phonons can be probed, however, by impact scattering. Since the latter increases in importance with primary electron energy, the systematic investigation of surface phonon spectra had to wait the beginning of the '80 when spectrometers capable to work with a good energy resolution also at high impact energy and with a momentum resolution of some 0.01 Å$^{-1}$ [70] were developed.

Although the very first surface phonon dispersion curve was reported by inelastic HAS, HREELS was used for the same purpose just shortly afterwards and promised immediately to be capable of overcoming the major shortcoming of HAS, i.e. the limited available energy in the incident probe particle limiting the energy loss range for helium atoms. HREELS proved thus to be superior to HAS for studying adsorption systems since one could then record simultaneously the dispersion of substrate and adsorbate modes. The resolution remains, however, worse than the one achievable with HAS (2 meV for out-of-specular investigations). The measurement of surface phonon dispersion curves involves recording a sequence of spectra at different scattering or incident angles under off-specular conditions. Given the small ratio of the energy losses associated to surface phonons and the impact energy, the transferred momentum is in first approximation constant over the relevant energy loss range and it is determined only by the scattering geometry [72].

The very first HREELS papers on surface phonon dispersion dealt with the Rayleigh mode of Ni(100) [70] and of Ni(100) c(2x2)O [71]. Most of the spectra were recorded with a primary beam energy of 180 eV to maximize the cross section and showed evidence for an adsorbate induced anomaly. Oxygen reduces thereby the interaction force between the outermost Ni planes thus reducing the Rayleigh wave frequency.

A more recent example of phonon dispersion investigation is shown in Fig. 1.4. The HREELS investigation took place at much lower impact energies [20, 21], since in the meanwhile it was recognized that optimal measurement conditions are realized by the balance of the growing inelastic cross section and the declining spectrometer performance. The investigated system, H/Mo(110), is characterized by a strong Kohn anomaly, a phonon softening at $q_{||} = 2k_F$, with $k_F$ the Fermi wavevector, caused by the nesting of the Fermi level of the adsorbate induced surface electronic state. As it is evident from the figure HREELS (● and △) and HAS (●) data coincide only for the upper branches, while the lowest one is present only in HAS. Such branch is in
fact due to the formation of electron-hole pairs rather than to the excitation of surface phonons. HREELS is indeed sensitive mainly to the displacement of the ion cores, while in HAS the interaction is mediated by the electronic surface density which can therefore be excited as well. The two techniques prove therefore to be complementary for gaining the complete insight into the physics of the studied system.

**Surface plasmons**

Surface plasmons mediate the surface response function to external electric fields and are therefore essential to describe photoemission and all other phenomena involving surface screening by electrons. Moreover, surface plasmons have been proposed to replace electrons and photons in the newly developed plasmonic devices for faster and more compact circuits.

In the long wavelength limit surface plasmons can be investigated by optical methods. Their dispersion, however, can only be measured by HREELS [40] or by ELS-LEED [41, 60]. In both techniques the surface plasmon dispersion curve is obtained by recording energy loss spectra for different scattering angles. Energy and momentum conservation allow then to calculate $q_{||}$. As an example, panel A of Fig. 1.12 reports the dispersion curves measured for the optical surface plasmon of a Ag film consisting of two dimensional (111) islands deposited on Si(111) – (7 × 7) [43]. The surface plasmon energy (i.e. the value of the energy loss) is independent of $q_{||}$ for small $q_{||}$, more precisely, until the parallel momentum equals $\frac{2\pi}{d}$ (where $d$ is the island size). For larger $q_{||}$ the surface plasmon propagates within the island and dispersion is observed. The Einstein oscillator like behaviour at small $q_{||}$ indicates therefore the occurrence of plasmon confinement inside the grains of the film. Further analysis showed that in the long wavelength limit the surface plasmon energy depends on the surface to volume ratio of the islands. Interestingly, the surface plasmons are confined also for percolated films, i.e. films showing direct current conductivity. The reason for this is that the anisotropy of the Ag surface plasmon dispersion with respect to crystal face and crystallographic direction impedes energy and wavevector matching at the boundary of the different grains of the film. The propagation of the surface plasmon across the borders of the islands is thus hindered even when they are electrically connected.

ELS-LEED was employed also to demonstrate the existence of the multipole plasmon mode for Ag surfaces [42, 73] taking advantage of the extreme reproducibility of the energy losses granted by the electrostatic deflection of the electron beam with the octupolar field.

The most important recent achievement on surface plasmon dispersion obtained by conventional HREELS concerns the observation of a novel type of collective electronic excitation, the acoustical surface plasmon. Such mode is associated to the excitation of the two-dimensional electron gas of Surface Shockley states (SSS) and exhibits a linear dispersion with vanishing energy in the zero wavelength limit [61, 74, 75], rather than the usual square-root
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Fig. 1.12. A: Dispersion of the surface plasmon as a function of $q_{||}$ for Ag films of different thickness. The experiment was performed by ELS-LEED. The thin lines mark the critical $q_{||}$ value beyond which the surface plasmon starts dispersing, which coincides with $2\pi$ times the inverse of the island diameter determined by SPA-LEED. Reprinted figure with permission from Ref. [43] Copyright (1999) by the American Physical Society. B: Dispersion of the ASP for Be(1000). The different symbols correspond to the different experimental conditions reported in the legend. The gray area denotes the realm of intraband transitions within the Surface Shockley State. Continuous and dotted lines correspond to one and two dimensional theories. Reprinted figure with permission from Ref. [61] Copyright (2007) by Nature Publishing Group.

dependence expected for a thin film. The dispersion is shown in panel B of Fig. 1.12 for Be(1000). The difficulty of performing such experiment lies in the small angle at which the scan curve cuts the ASP dispersion and in the very low cross section of this mode. More recently its existence was proved also for Cu(111) [75,76] and Au(111) [74,77]. The linear dispersion makes this mode promising for applications since it permits a distortion-less propagation of a non monochromatic signal in a future plasmonic device.

1.4.3 HREELS as a tool to evaluate the density of carriers

It is well known that the surface plasmon frequency is proportional to the square root of the density of carriers (eq. 1.7) [40]. As a consequence, given the metallic densities, the surface plasmon energy is usually of several eV. In semi-conductors and/or when metallization of an insulating material is induced (e.g. by adsorption of an electron donor) the surface plasmon energy can, on the contrary, be as low as a few meV. Under the latter condition, multiple plasmon excitation can take place, leading to an increased elastic
peak width easily detectable by HREELS. The temperature dependence of the such width can then be used to evaluate the carrier density [78, 79] and to monitor the metallization process [80].

Fig. 1.13(A) shows the temperature dependence of the specular peak width for Si(100) (filled dots) and its fit with different models including: the carrier density determined by Bose Einstein (BE) statistics (□); BE plus intrinsic carrier plasmon thermal variations (open triangles); BE plus intrinsic carrier plus depletion layer thickness thermal variations (open diamonds); BE plus intrinsic plasmon plus topmost metallic layer plasmon variations (open dots) plasmon excitation. Only the later model describes the width at the highest T proving surface metallization. The latter is determined by the removal of the dangling bond anisotropy above 900 K caused by thermal fluctuations.

In panel (B) we report a similar physics occurring for a clean and for a H-covered ZnO(1010) surface. Panels (C) and (D) report the FWHM of the elastic peak, respectively, vs. H exposure and temperature. It is evident that metallization occurs after a critical H coverage is attained, since the latter the hydrogen atoms act as electron donors. Moreover, the FWHM initially increases with temperature due to the higher probability to excite the surface plasmon mode and it reduces rapidly as soon as H desorbs.

Since in this case a broadening of the elastic peak, but no individual features were detected, the excitation responsible for it must lie below 5 meV. This result was explained by the presence of metallic (i.e. partially filled) electronic states produced by H adsorption. The carrier concentration \( n \) was then estimated by

\[
\omega_p^2 = \frac{ne^2}{\varepsilon_0 m^*} \tag{1.7}
\]

where \( \omega_{sp} = \frac{\omega_p}{\sqrt{2}} \) is the surface plasmon frequency, \( \omega_p \) the bulk plasmon frequency, \( m^* \) the effective electron mass and \( e \) its charge.

1.4.4 HREELS as a tool to investigate interband transitions

In this section we report an example of the use of HREELS to solve the apparent contradiction about the band structure of \( BC_2N \). For this semiconductor, characterized by a tunable band gap and hence of high technological interest, a gap of 2.1 eV was inferred from photoluminescence experiments, while a value of only 1.4 eV was measured by scanning tunneling spectroscopy (STS). Thanks to HREELS measurements, and applying the energy and momentum conservation laws, it was possible to determine that the difference is due to the dependence of the band gap on \( q_{||} \), as shown by the sequence of spectra reported in Fig. 1.14(a). The experimental energy gap decreases indeed with increasing parallel momentum from \( \approx 1.8 \) eV at \( q_{||} = 0.08 \text{Å}^{-1} \) to 1.4 eV at \( q_{||} = 0.32 \text{Å}^{-1} \).
Fig. 1.13. Left panel: A) Temperature induced broadening of the specular peak of Si(100) caused by the multiple excitation of a surface plasmon. The inset shows the HREEL spectra. • correspond to experimental data, other symbols and lines correspond to different theories which include from the bottom up: □ Bose-Einstein statistics, △ Bose Einstein statistics plus surface plasmon, ◊ the preceding plus depletion layer and ○ all previous ingredients plus surface metallization occurring above 900 K because of the removal of the dangling bond anisotropy. Reprinted figure with permission from Ref. [2] Copyright (1996) by the American Physical Society. Central and right panels (B): spectra recorded in-specular for the clean and H-covered ZnO(10¯10) surface; the dependence of the quasielastic peak width upon H exposure (C) and on temperature (D) is also shown. Reprinted figure with permission from Ref. [80] Copyright (2005) by the American Physical Society.

The apparent contradiction between photoluminescence and STS data can thus be explained by an indirect band gap structure. Indeed, photoluminescence estimates the values of the band gap in the long wavelength limit, while STS just samples the path with the smallest gap.

1.4.5 HREELS and superconductivity

In the previous examples HREEL spectroscopy was applied to the investigation of single crystal surfaces oriented along a well defined crystallographic direction. In case of semiconducting or insulating samples, special care is needed to avoid or to compensate for the charging of the insulating substrate, which may be achieved either by doping or by using an additional flood electron gun.

In the following we show the application of HREELS to the study of the surface of the ceramic superconductor $YBa_2Cu_3O_7$ (YBCO) [82].

Fig. 1.15 shows the evolution of the HREEL spectra vs increasing temperature. A loss feature appears at around 60 meV at the lowest T values. This energy compares well with the gap predicted by BCS theory (60 meV),
Fig. 1.14. (A) HREEL spectra recorded on a thin $BC_2N$ film at different values of $q_{||}$; (B) schematic illustration of interband transitions with zero and non zero momentum change. Reprinted figure with permission from Ref. [81] Copyright (1999) by the American Physical Society.

Fig. 1.15. HREEL spectra for YBCO recorded at a primary energy of 2.4 eV at different temperatures. Reprinted figure with permission from Ref. [82] Copyright (1990) by the American Physical Society.

but it persists also above the critical temperature of 90 K. Such dependence cannot be explained by theory and is more in line with a Bose Einstein condensation of pre-existing pairs. A similar result was reported later also for $Bi_2Sr_2CaCu_2O_8$ (BISCO) [83].
1.4.6 SP-EELS detection of spin waves

The application of HREEL spectroscopy to the study of surface magnetism came only recently thanks to the development of SP-EEL spectrometers coupling energy resolution with spin polarized beams. With such a tool it was possible to confirm the theoretical prediction on the existence of well defined spin waves at short wavelengths [84]. The first clear evidence for the experimental identification of spin waves appeared seven years later [85]: broad loss bands were observed by SP-EELS and suggested to arise from spin flip scattering of the impinging electron beam induced by a magnetic sample (ultra-thin film or magnetic surface) [45, 86]. Spin flips are produced by a Stoner excitation like mechanism implying a particle-hole excitation by the impinging electron. Electron energy losses are then possible above the energies of the exchange splitting in the ferromagnetic d band.

The spin waves are expected in the same spin flip channel, but at much lower energy loss than the one characteristic of the Stoner excitation continuum. The creation of a spin wave by the incoming electron decreases the spin angular momentum of a ferromagnet by $\hbar$. To conserve total angular momentum the beam electron spin must then flip from down (the minority spin direction) to up (majority direction). Given this definition of up and down no spin wave excitation can take place for an up-spin beam and no spin annihilation for down spin beam. Thanks to this selection rule analysing the spin distribution of the scattered beam is not necessary. Typically the loss spectrum in the spin wave region is measured both for beam polarization anti-parallel and parallel to the sample magnetization. The spin asymmetry is then defined as:

$$A = \frac{I_\downarrow - I_\uparrow}{I_\downarrow + I_\uparrow}$$

and will contain the spin wave loss feature.

The entire dispersion curve was measured for a 2 ML thick Fe film on W(110): the spin wave energies resulted to be strongly reduced with respect to the corresponding values measured for the bulk and to those predicted by theory [53]. An example of spin wave measurement is reported in Fig. 1.16 for Fe(100)p(1x1)O. [87].

1.4.7 HREELS for the investigation of liquid surfaces

Recently also liquid surfaces have attracted the attention of the surface science community [88–90]. Investigation of these systems with electron based techniques is necessarily limited to liquids with a vapour pressure low enough to allow for a reasonable mean free path of the scattered electrons. With this restriction, also HREELS can be employed. Fig. 1.17 reports an example of HREEL spectra of the 1-Ethyl-3- methylimidazolium Bis (trifluoromethylsulfonyl) amide surface (EMIM in the following), recorded at different $E_0$ and for $T=300$ K and $T=100$ K [91].
Fig. 1.16. SP-EELS spectrum recorded on Fe(001) p(1x1) O at different $q_{\parallel}$. Blue and red spectra correspond to incident electrons polarized with the spin parallel or antiparallel to the majority electrons of the sample. Several features are visible, most of which are due to surface phonons. The feature numbered 3 shows a definitive non Boltzmann factor like anisotropy between loss and gain peaks. It corresponds to the efficient creation (annihilation) of a surface magnon with electrons polarized in the same direction as minority (majority) electrons of the substrate. The upper panels report the energy loss spectra, the lower the calculated phonon spectra for (c) the O layer, (d) the outermost Fe layer. Reprinted figure with permission from Ref. [87] Copyright (2011) by the American Physical Society.

Since the penetration depth of the electrons depends on primary energy [92], the similarity of the loss features detected with different electron energies at 300 K indicates that, at this T, the structure of the surface is quite similar to the bulk structure. The picture changes at T=100 K: at low $E_0$ the well pronounced $CF_3$ and anti-symmetric O=S=O modes are almost missing while the losses around 800 cm$^{-1}$ (due to the imidazolium-H bending modes
and to the $[TF_2N]^- \text{O} = S = O$ symmetric stretch) are still present. If $E_0$ (and hence the penetration depth) is increased, the spectra recorded at 100 K become similar to those recorded at RT. These findings can be rationalized considering that, at low primary energy, only dipoles oscillating perpendicularly to the surface contribute to the spectrum recorded in-specular. The authors then concluded that a change of the molecular orientation of the outermost layer takes place at 100 K. Moreover, the elastic peak FWHM depends on $E_0$ and remarkably larger at RT than at 100 K, similarly to what observed for semiconductor surfaces with depth dependent carrier concentration [92].

1.5 The future of HREELS

We deliberately limited our overview to High Resolution Electron Energy Loss Spectroscopy, thus neglecting e.g. the stunning results obtained recently recording EELS spectra with TEM allowing to identify the elemental compositions of materials [93], to map plasmonic excitations [94] and to follow electronic structural changes with unprecedented time resolution [95]. We mention these results here because they might suggest possible future breakthroughs also for High Resolution Electron Energy Loss Spectroscopy. However, on one side, vibrational spectra of a single adsorbed molecule can now be measured with low temperature STMs by Inelastic Electron Tunneling Spectroscopy (IETS) [96]. On the other side, vibrational spectra with picosecond time sensitivity have been recorded by employing, e.g., Sum Frequency Gen-
eration. HREELS will have to compete with such alternative methods which, unlike electron spectroscopy, do not need vacuum conditions as a stringent requirement and can therefore be employed also under more realistic environments. HREELS will, however, still be useful for its unique characteristic of enabling excitations with non vanishing wave-vector, an information needed for a satisfactory description of dynamic phenomena such as surface magnons, surface plasmons and surface phonons.

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