

Electron energy loss spectroscopy of liquid glycerol

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Abstract

The inelastic scattering of low energy electrons from liquid glycerol has been studied. For the first time, electron energy loss spectra of liquids are sufficiently well resolved to permit the identification of vibrations corresponding to individual bonds, namely the C–H and O–H stretching vibrations in glycerol. The angular distribution of the specular peak is very broad, indicating the absence of long-range order at the surface of the liquid. The measurement of the loss signals as a function of the primary electron energy suggests a hybrid mechanism of excitation. The excitation mechanism for the O–H vibration has a stronger impact character as compared to the C–H vibration. A negative ion resonance of glycerol is found at a primary energy of 8 eV. The signal intensities measured as a function of the specular angle of the electron beam appear to be influenced by the angular dependence of the dipole and impact scattering cross-section and a possible preferred orientation of the C–H and O–H groups at the surface of the liquid.

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1. Introduction

Electron energy loss spectroscopy (EELS) is a well-established method in the surface science of solids. Several types of inelastic losses can be investigated with the method. These include phonon [1] and plasmon [2] excitation, when investigating crystalline solid surfaces. Single electronic excitations [3] and vibrational excitations of adsorbate molecules [4] can also be observed in EEL spectra. The measurement of individual vibrational excitations by electrons is usually referred to as high-resolution electron energy loss spectroscopy (HREELS). HREELS is an excellent method for the investigation of the chemistry of surfaces, especially for the investigation of the adsorption of small molecules on solid substrates. The method permits to identify functional groups from the vibrational losses in the backscattering spectrum. For instance, the orientation of adsorbed molecules [5] and bonding site geometries [6] can be determined with HREELS. Also, chemisorption

[7] and catalytic reactions at the surface [8] have been studied extensively.

Due to the rather low inelastic mean free path of electrons and the accompanying requirement of high-vacuum conditions for the experiments, EELS has been nearly exclusively applied to solid surfaces so far. However, information such as molecular orientation and conformation is also of interest for liquid surfaces, e.g. in the study of surfactant adsorption. Investigations of liquid surfaces using EELS have been scarce until now. Ballard et al. [9] and Morgner [10] used EELS to study the electronic transition $\pi-\pi^*$ in liquid formamide. Upon continuous addition of a surfactant to the solution, the $\pi-\pi^*$ signal decreased and finally disappeared. This behavior was explained with the replacement of the formamide molecules at the surface by adsorbed surfactant molecules. Eschen et al. recorded EEL spectra in the vibrational energy range of several low-vapor pressure liquids [11]. However, vibrations of individual bonds could not be resolved.

The aim of the present work is the investigation of liquid glycerol using EELS. Using a setup that provides a sufficient experimental resolution, loss signals originating from

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vibrations of individual bonds, namely the O–H and C–H stretching vibrations in glycerol, can be expected to become resolved.

From EEL spectra also information about the scattering mechanism of the electron can be extracted. The interaction mechanism between an incoming electron and the vibrating atoms in a sample can be described assuming two limiting cases of the scattering mechanism, the long-range dipole scattering mechanism and the short-range impact scattering and resonance mechanisms. The identification of the scattering mechanism for a particular vibration can in principle be achieved from the measurement of the angular distribution of the backscattered electrons. When the molecules in the sample are arranged in a periodical order, the angular intensity distribution of a loss signal is strongly peaked in specular direction, in case the vibration is preferentially excited via dipole scattering [12]. On the other hand, the angular distribution of electrons that have undergone impact scattering is rather smooth with backscattering intensities usually varying by less than an order of magnitude with the detection angle [12]. Due to the absent long-range order at liquid surfaces, however, it is not expected that a sharp specular peak will be observed. Hence, measurements of the angular distribution of backscattered electrons cannot be used for liquid surfaces to distinguish between dipole and impact scattering.

Nevertheless, it is possible to compare the relative magnitude of dipole and impact scattering for different vibrations from EELS measurements when varying the primary electron energy E_p , since the scattering cross-sections for both mechanisms show different energy and angular dependences. According to theoretical considerations, the probability for dipole scattering varies with E_p^{-1} [13], whereas the impact scattering cross-section is predicted to vary linearly with E_p [14]. The loss intensities measured as a function of the specular angle Θ between the electron and the surface normal are predicted to be proportional to $\cos\Theta^{-1}$ for dipole scattering [13] and proportional to $\cos\Theta$ for impact scattering [14].

As is the case with many electron spectroscopic techniques, a non-uniform depth distribution of species in the sample along the surface normal may also influence the results from angular and energy-dependent measurements [15] due to the well-known exponential relationship between intensity and layer thickness [16]. As an example, a preferred orientation of the hydrocarbon backbone in the glycerol molecules in the outermost layer would result in a non-homogeneous depth distribution. The surface sensitivity of EELS can be enhanced if the angles of incidence and/or reflection between the electrons and the surface normal are increased. For glycerol, results from sum-frequency generation experiments [17] and direct recoil spectroscopy [18] indicate that the carbon chains in the glycerol molecules in the top layer of the liquid are oriented parallel to the surface normal. This orientation can be expected to give rise to a rather uniform distribution of O–H and C–H bonds along the surface normal.

In case dipole scattering is the prevalent excitation mechanism, the signal intensity from a loss signal will increase with an increasing component of the dynamic dipole moment parallel to the surface normal, which is due to the selection rule for dipole scattering [19]. Hence, the signal intensities of the O–H and C–H stretching vibration will also be influenced by possible preferred orientations of the dipoles themselves.

2. Experimental

Glycerol was chosen as liquid sample. The substance was purchased from Sigma–Aldrich with a purity of >99.5% and was degassed before usage. The low-vapor pressure of $\sim 10^{-5}$ mbar at 273 K [20] makes glycerol suited for ultra-high vacuum (UHV) spectroscopic studies. All measurements were carried out at a liquid temperature of 273 K in order to attain a low-vapor pressure. This temperature is lower than the freezing temperature of glycerol of 291 K. However, glycerol readily supercools [21] and freezing of the liquid in the vacuum chamber was not observed during the experiments. Glycerol that was contained in a flask and immersed into a cryostat at a temperature of 273 K for 3 days at ambient pressure also remained in the liquid state. In order to exclude the possibility of surface freezing, some EEL spectra were also recorded at 293 K with the same experimental parameters as for the measurements conducted at 273 K. It was found that the spectra recorded at 293 K and 273 K were identical. Hence, we can conclude that in the supercooled state no structural changes are induced at the surface that influence the spectral shape. The structure of the molecule is given in Fig. 1. Glycerol is a polar liquid ($\epsilon_{\text{rel}} = 47.2$ [22], $\mu = 2.66$ D [23]) with a high surface tension of 65.4 mN m $^{-1}$ at 273 K [24]. The surface purity was checked with X-ray photoelectron spectroscopy. XP spectra were recorded at angles of 0° and 80° between the detector and the surface normal using Al K α radiation with an energy of 1486.6 eV. The XP spectra of glycerol recorded at the two different angles showed single peaks in the regions of the carbon 1s orbital at a binding energy of 286.1 eV and the oxygen 1s orbital at 532.2 eV, which can be assigned to the carbon and oxygen atoms in glycerol, respectively, from reference measurements of other organic compounds conducted in our group [25]. Further, the intensity ratios between the oxygen and the carbon signals were found to be the same for the two different take-off angles. These results confirmed the chemical purity of the surface region of glycerol.

The EELS experiments were conducted using a UHV setup manufactured by the company SPECS according to our specifications. The electron source is a modified version

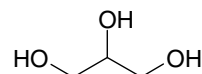


Fig. 1. Structure of glycerol.

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