

CHAPTER V

Future work

In previous chapters, we have demonstrated that TR-UPS is a powerful tool in the investigation of chemical dynamics of adsorbates on metal surfaces. This technique has great potential for revealing many of the intermediate steps of surface chemical reactions and their corresponding time scales. Thanks to this capability, future studies based on TR-UPS may provide significant insights into the mechanisms behind many catalytic processes. The results from these studies may give theorists a better theoretical understanding of catalytic processes on the atomic level. However, to date, both experimental and theoretical studies of the dynamics of surface chemical reactions are still in their infancy, and tremendous efforts will be required in this emerging field in the future. Hopefully, someday, the understanding will be mature enough to apply the knowledge obtained to engineering processes leading to cheaper and more robust catalysis. In the following chapter, several proposed improvements to the experimental setup and possible future work will be discussed. Our hope is that these ideas will be realized in our laboratories in the coming two to three years.

5.1 Time-resolved core-level spectroscopy

The photon energy of the high-harmonic generated EUV pulses used in our current TR-UPS setup is 42 eV (30 nm wavelength). The reasons for choosing this photon energy are its relatively high flux, and ease of generation, with relatively less driving laser intensity required. The 42 eV photon energy is sufficient for probing valence-band structure; however, liberating electrons from core-level orbitals will require higher photon energy. For example, the binding energies of the $1s$ (deep core-level) and $2s$ (shallow core-level) orbitals for oxygen atoms are 543 and 41.6 eV, respectively [111].

Core-level photoemission spectroscopy (or XPS) is a common technique for determining both physisorbed and chemisorbed states of adsorbates on metal surfaces. Since photoelectrons from the core levels are very sensitive to the surrounding chemical environment, XPS is widely used to study static physical phenomena on surfaces using synchrotrons. UPS is generally used to observe changes in molecular valence bands, which gives information about the dynamics of adsorbate bonding structure. XPS, on the other hand, is used to observe energy shifts of the core-level electrons, giving site-specific information about molecules in different chemical environments. Therefore, pushing the EUV photon energy to higher values will allow us to obtain more information about the system, using both UPS and XPS. Information obtained using each technique can help us to better understand the dynamics of chemical reactions.

Generally speaking, photon energy in the range of 30 to 200 eV has good surface sensitivity, since the escape depth of electrons in this energy range is under 5 Å [2]. The current record high-harmonic-generation photon energy is 460 eV (2.7 nm) using helium,

and 239 eV (5.2 nm) using neon, using a pulsed gas jet and tera-watt ultrafast pulses [3]. However, though high-harmonic generation in these high energy ranges is possible, efficient high-harmonic generation has only been demonstrated for photon energies on the order of 50 to 100 eV. To efficiently generate photons of higher energies, higher laser intensity is needed. The high laser intensity, however, leads to a higher degree of ionization of the interacting gas molecules, preventing the driving laser and the EUV light from propagating at the same speed, severely limiting the conversion efficiency. Recent results from our group have shown that by using a modulated hollow-core waveguide to periodically vary the intensity of the driving laser pulses, one can achieve efficient EUV generation even in the presence of substantial ionization. The immediate result of this work is to the shifting of the phase-matching condition to even higher photon energies. About 20 pJ generated intensity has been obtained for individual harmonics at around 100 eV photon energy using this corrugated capillary method [5]. In addition, high quality multi-layer mirrors are much easier to fabricate around 95 eV (13 nm) photon energy with mirror reflectivity better than 75% achievable, in contrast to only 25% reflectivity at around 42 eV (30 nm). Therefore, although high harmonic generation at 100 eV will have ~ 1 order of magnitude less flux than at 42 eV, higher reflectivity multi-layer mirrors can compensate for the lower generated flux, giving a comparable detected signal level.

5.2 Probing bimolecular chemical reaction on surfaces

The work presented in chapter III demonstrated that TR-UPS allows direct observation of chemical reactions on metal surfaces. We saw that when oxygen molecules rotate from the bridge site to the three-fold-hollow site on platinum, a covalent bond between the

surface and the oxygen is created, weakening the intra-molecular bond between the two oxygen atoms. This type of bond creation is generally considered to be one of the simplest chemical reactions. However, completely time-resolving bimolecular chemical reactions on surfaces has long been a major challenge for surface chemists. In particular, by identifying all the precursor states and their reacting time-scales, the reaction “bottleneck” can then be pin-pointed, perhaps improving the efficiency of the chemical reactions.

CO oxidation ($2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$) on platinum surfaces is a good candidate system for such experiments. Theoretical calculations have been performed on CO oxidation on the platinum(111) surface [103, 68]. These calculations suggest that peroxy oxygen molecules (O_2^{2-}) have a lower activation barrier for reacting with CO molecules than superoxy oxygen molecules (O_2^-). This is possibly due to the fact that peroxy oxygen has a longer O-O intra-molecular bond, and since peroxy oxygen molecules have a less corrugated potential energy surface around the hollow site, the more preferable site for chemical reactions [68]. Therefore, the catalytic channel for the platinum surface is likely to be that the platinum surface provides a dissociation pathway for the oxygen molecules, allowing oxygen molecules to move from the bridge site to the hollow site, and lowering their dissociation energy. Subsequently, the intermolecular bond cleaves, creating two excited oxygen atoms. The excited oxygen atoms can then directly react with CO molecules, finishing the oxidation process. Finally, the CO_2 molecule will leave the platinum surface, releasing the adsorption sites for another O_2 and CO molecule pair to undergo the catalytic process again.

If this picture of CO oxidation is correct, observing this process could be possible using

TR-UPS. One possible scheme for using TR-UPS to observe the spectral changes could be to look for the characteristic peak of the peroxy oxygen to appear about half a picosecond after the pump pulse arrives, indicating the movement of the oxygen molecules from the bridge site to hollow site. In the meantime, the 4σ and $1\pi/5\sigma$ features of CO molecules could be used to monitor the orientation of CO molecules. In addition, the strength of the CO peaks should diminish for longer times, due to desorption of the CO₂ molecules from the platinum surface after the oxidation process. Therefore, hopefully, CO oxidation may be time-resolved using TR-UPS (or TR-XPS).

5.3 Angle- and time-resolved photoemission spectroscopy

Currently, the TR-UPS setup cannot resolve the emission angles of photoelectrons emitted from the sample surface. In many surface science experiments, resolving the emission angle is not critical to understanding the details behind the mechanism under study. However, for some experiments, knowing angular information will significantly improve our understanding of the experimental details. For example, in the experiment observing CO oscillation periods on a platinum surface (chapter IV), photoelectrons originating from the 4σ orbital would have an emission peak along the intra-molecular axis. Therefore, if photoelectron angular information were available, a clearer picture of the CO molecular oscillation would emerge, allowing, for example, precise determination of the oscillation angle of the CO molecules.

In synchrotron-based photoemission experiments, two-dimensional hemispherical electron analyzers have recently been used to obtain precise angular distributions of emitted photoelectrons. Traditionally, hemispherical electron analyzers have not been useful in ob-

taining photoelectron angular distributions. In addition, these analyzers can only measure the photoelectron kinetic energy over a narrow energy range, and are unable to simultaneously measure a range of kinetic energies. This results in the loss of most of the photoelectrons. Therefore, these kinds of energy analyzers are only suitable for very bright light sources, such as synchrotron radiation sources. State-of-the-art two-dimensional hemispherical electron analyzers use a sophisticated electronic lens to preserve angular information, while using an MCP and a CCD camera at the detection end for two-dimensional data retrieval. The kinetic energy and emission angle of a photoelectron are mapped onto a single spot of the two-dimensional image, allowing the detector to simultaneously record a certain angular range and kinetic energy range of the photoelectrons. Thanks to such advancements, these hemispherical analyzers could be used to replace the current time-of-flight detector, providing photoelectron angular distribution information without losing the photoelectron count rate in a certain energy range. Currently, these new hemispherical electron analyzers can measure up to about $\pm 7^\circ$ photoemission angle ($\pm 15^\circ$ is under development), while simultaneously recording a 10 eV energy range with about 100 meV energy resolution [112].

Another possible design implementing angle-resolved photoemission spectroscopy borrows from the technique of “cold-target recoil-ion momentum spectroscopy” (COLTRIMS) [113, 115, 116]. COLTRIMS is used in ion-scattering experiments to simultaneously measure the kinetic energies and emission angles of ejected electrons and recoil-ions after ion collision. The key idea of COLTRIMS is the use of a strong magnetic and/or electric field inside the experimental apparatus to confine the flight paths of the ejected electrons and

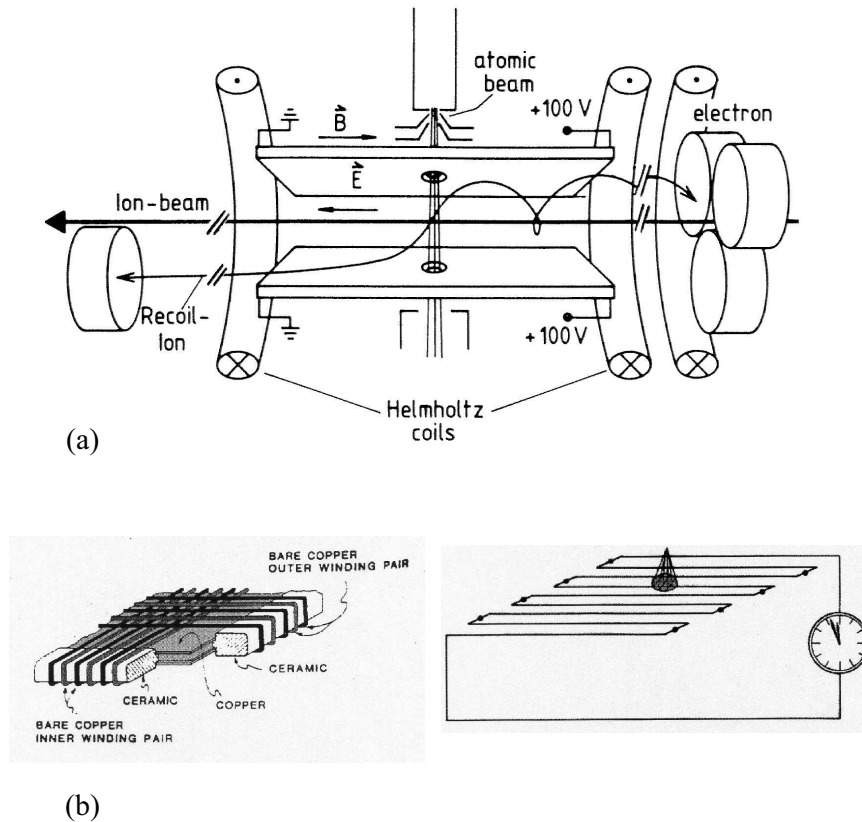


Figure 5.1: (a) Schematic drawing of “cold-target recoil-ion momentum spectroscopy” (COLTRIMS). A two-stage supersonic gas jet is installed to provide a well-defined atomic beam, which collides with an energetic ion-beam. Helmholtz coils and resistive coated parallel plates are used to generate homogeneous magnetic and electric fields to confine the recoil-ions and the ejected electrons. Position-sensitive micro-channel plates (MCP) are used to resolve the kinetic energy and emission angles of the recoil-ions and electrons. (figure reproduced from Ref. [113]) (b) The anode of the position-sensitive MCP is wrapped by a fine copper-wire (delay-line) on each dimension. When an electron strikes the anode, the position of the electrons on the detector can be extracted by measuring the time difference of the electronic signals at both ends of each delay-line. The position for each dimension can be determined independently. (figure reproduced from Ref. [114])

recoil-ions. The confined electrons and ions undergo rotational motion due to the magnetic field confinement, and their kinetic energies and emission angles can be evaluated by measuring their flight times along with their impact positions on the detector. A time- and position-sensitive detector is used to capture both the flight time and detection position simultaneously. Such kind of detectors can be realized by using a MCP scaler with its anode wrapped by a two-dimensional delay-line array. These detectors are commercially available [114]. By measuring the time difference of the electron impact signals at both ends of each delay-line, the position of the electron impact can be determined. It is possible to adapt this idea for angle-resolved photoelectron spectroscopy by putting a metal surface into the interaction region, then measuring the kinetic energies and emission angles of the photoelectrons.