Electron Paramagnetic Resonance (EPR) spectroscopy is less well known and less widely applied than NMR spectroscopy. The reason is that EPR spectroscopy requires unpaired electrons and electron pairing is usually energetically favorable. Hence, only a small fraction of pure substances exhibit EPR signals, whereas NMR spectroscopy is applicable to almost any compound one can think of. On the other hand, as electron pairing underlies the chemical bond, unpaired electrons are associated with reactivity. Accordingly, EPR spectroscopy is a very important technique for understanding radical reactions, electron transfer processes, and transition metal catalysis, which are all related to the 'reactivity of the unpaired electron'. Some species with unpaired electrons are chemically stable and can be used as spin probes to study systems where NMR spectroscopy runs into resolution limits or cannot provide sufficient information for complete characterization of structure and dynamics. These notes introduce the basics for applying EPR spectroscopy on reactive or catalytically active species as well as on spin probes.
2: Electron spin

3: Electron Zeeman Interaction
4: Hyperfine Interaction

5: Electron-Electron Interactions
6: Forbidden Electron-Nuclear Transitions

7: CW EPR Spectroscopy

8: Measurement of Small Hyperfine Couplings
• 10: Spin Probes and Spin Traps

Thumbnail: HYSCORE spectrum of a Ti(III) surface species (CC BY-NC 4.0; Junnar Jeschke in collaboration with C. Copéret, F. Allouche, V. Kalendra)