Time development of surface enhanced Raman scattering from molecules absorbed on metal electrodes *

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Recently, it has been established that a 10^5–10^6 enhancement of the Raman scattering cross section of molecules chemisorbed on a metal electrode immersed in an aqueous electrolyte is possible if an oxidation/reduction cycle is performed. Using an optical multichannel analyzer consisting of a spectrograph and a low light level SIT television camera, surface enhanced Raman scattering (SERS) measurements over a wide vibrational shift range have been measured simultaneously and in real time. Correlations between the SERS peaks of Ag-cyanide and Cu-cyanide complexes with the electrochemical reaction products were made by detecting the entire Raman spectrum during the oxidation reduction cycle lasting for about 40 seconds.

Besides being sensitive to the electrochemical treatement, the SERS depends on the incident laser photon energy in relation to the energy separation between the metal Fermi level and α-level. The mechanism for SERS will be presented in terms of photon-induced electron hole pairs, formation of temporary negative moleculer of the adsorbed molecule, and reemission of the electron hole pairs.

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分子吸附在金属电极上所得的表面增强喇曼散射的时间发展

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最近已证实在进行氧化、还原循环时，浸在电介液中的金属电极上被化学吸附着的分子的喇曼散射截面有 10^5～10^6 倍的增强。采用一台包括摄谱仪及低光强SIT电视摄象机在内的光学多道分析仪，可以在宽广的振动位移范围内同时而且实时地测量表面增强喇曼散射(SERS)。氰化银和氰化铜络合物的SERS峰与电化学反应产物之间的关系可以通过历时约40秒的氧化还原循环过程中对整个喇曼谱的探测而获得。

除了对电化学处理灵敏以外，SERS还依赖于入射激光光子的能量，此能量与金属的费米能级与 α-能级之间的能量间隔有关。介绍了SERS的机理，它是用光子感生的电子空穴对，吸附分子的临时负分子的形成及电子空穴对的再发射等来描述的。