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和频振动光谱研究多晶金电极/溶液界面 乙腈分子取向的 flip-flop 行为

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摘要: 应用和频振动光谱研究乙腈/金电极界面吸附, 观测到乙腈的甲基振动峰强度随电极电势而变化. 当电极电势越过零电荷电势(pzc)时, 甲基振动峰符号发生反转, 这意味着该基团取向发生反转(flip-flop). 由此而推断乙腈分子在金电极界面的吸附构型. 即在零电荷电势下, 电极界面吸附的乙腈分子构型为甲基靠近电极表面而腈基远离电极表面; 高于零电荷电势, 则变为腈基靠近电极表面而甲基远离电极表面.

关键词: 和频振动光谱; 取向反转; 金电极; 乙腈

中图分类号: O647.9

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吸附在电极表面的溶剂分子的结构及其取向随外加电势是否会发生反转(即 flip-flop 现象)一直是电极过程动力学研究的重点问题之一^[1-9]. 自 Toney 等首次从 X 射线衍射发现水分子在银电极界面上的 flip-flop 现象以来^[6], 各种谱学电化学方法, 包括表面增强拉曼光谱^[2-3], 表面红外光谱^[4], 表面增强红外光谱^[5] 和 X 射线衍射^[6-7] 等方法都已经用于该问题的研究.

和频振动光谱(SFG-VS)以其界面选择性和化学特异性以及无需对样品作特殊处理等优点日益成为表面分析及谱学电化学首选的重要研究手段. SFG-VS 是一种非线性光学检测方法, 由一束波长可调谐的红外激光与一束波长固定的可见激光同时同点入射到样品表面, 于是在反射方向上产生一束频率为以上两束入射激光频率之和的和频信号光. SFG-VS 可以给出界面分子密度、基团取向角、分子化学性质等重要信息. 目前, SFG-VS 已经广泛用于研究各种界面, 包括纳米颗粒表面、金属表面、高分子表面和离子液体表面^[8-11]. 近年来 SFG-VS 又被用来研究溶剂分子在电极界面的取向随外加电势的变化^[12-18].

乙腈是电化学研究普遍使用的非水溶剂, 了

解它在电极界面的 flip-flop 行为对于电化学领域具有普遍意义. 应用和频振动光谱研究电极界面乙腈分子的取向变化已有一些报道^[19-27]. 其中, Somorjai 等首次观测到了 Pt(111) 电极表面乙腈分子的和频信号随电极电势的变化以及该表面乙腈分子的 flip-flop 现象^[19-20].

电极/溶液界面的 flip-flop 现象是一个复杂的问题. 凡是影响电极/溶液界面双电层结构和电极过程动力学的诸多因素都会影响体系溶剂分子的取向和 flip-flop 行为. 而溶剂分子的结构、电极的种类、聚集态(单晶或多晶)、表面形态(粗糙或光滑)、晶面指数等都会产生深刻的影响. 更重要的是: flip-flop 现象是否属于电化学体系的普遍行为? 至今, 研究仍未给出一致的结论. 在电化学中, 以往为数不多的 flip-flop 研究大多集中在单晶电极表面. 事实上, 从应用的角度, 多晶电极更具有普遍的意义. 本文将重点放在研究多晶金属电极的 flip-flop 现象.

本文以多晶金电极/乙腈界面为研究对象, 运用和频振动光谱偏振分析方法, 研究了吸附在金电极表面乙腈分子的光谱性质随电极电势的变化. 发现在零电荷电势(pzc)附近, 乙腈分子的取

向随外加电势发生了 flip-flop.

1 实验

实验用的皮秒和频光谱系统(立陶宛 EKSPLA 公司)主要包括 5 个部分:皮秒激光系统,倍频系统,光学参量系统,信号发生系统和采集系统.其中,皮秒脉冲激光(波长 1064 nm,频率 10 Hz,脉冲宽度 23 ps)经过倍频和 3 个参量过程,产生用于和频光谱实验的可见光($\lambda = 532 \text{ nm}$)和可调谐的红外光(调谐范围为 $1000 \sim 4000 \text{ cm}^{-1}$),这两束光同时入射到样品界面上,产生和频信号.光谱的分辨率为 6 cm^{-1} .控制入射光和和频信号的偏振方向(如 s 方向或 p 方向,即光电场方向垂直或平行于入射面),扫描给定偏振的红外光(s 光或 p 光),获得和频振动光谱.这 3 种特定偏振方向的激光组合,简称为和频振动光谱的偏振组合.按文献惯例,偏振组合依和频、可见和红外的顺序命名.例如 ssp 表示和频信号 s 偏振方向,可见入射激光 s 偏振方向和红外入射激光 p 偏振方向.不同的偏振组合,会给出不同的光谱信息,这就是和频振动光谱中的偏振选择定则^[28].本实验采用反射式共向传播(copropagating)构型,将可见和红外激光分别以 $63^\circ \pm 1^\circ$ 和 $45^\circ \pm 1^\circ$ 的入射角入射在电解池界面,调节延时,使两束激光在空间和时间上重合,检测反射方向和频光谱信号.入射的可见激光能量在 50 mJ 附近,红外激光能量在 30 mJ 左右,实验在恒温 $22.5 \pm 0.5 \text{ }^\circ\text{C}$ 和恒湿 40% 的超净间进行.红外光的扫描步长为 2 cm^{-1} ,每个数据点用 400 个激光脉冲测量信号的累加平均得到.在输出的光谱中,和频信号强度对入射的激光能量归一化(和频信号的输出能量除以可见光和红外光的能量乘积).

本实验使用三电极体系.光谱电化学池为自行设计的薄层流动电化学池.窗口为半圆柱形的氟化钙晶体以保证各角度入射光均垂直于晶体表面.参比电极为 0.01 mol/L 银离子电极.对电极为铂丝,工作电极是多晶金电极.实验前,经机械抛光和电化学抛光成镜面,再装在光谱电化学池中.上下调节金电极表面与氟化钙窗口之间的距离为 $8 \text{ }\mu\text{m}$ 左右,以最大限度降低液体样品对红外激光的吸收.乙腈液体经过蠕动泵以一定的流速注入反应池内,保证金电极与氟化钙窗口之间的溶液保持一定的浓度.溶剂为乙腈(Aldrich, 99.9%),未做进一步处理,直接使用.支持电解质为 tetrabutylam-

monium tetrafluoroborate ($[\text{CH}_3(\text{CH}_2)_3]\text{NBF}_4$) 溶液浓度 0.165 g/L. 电极电位由恒电位仪(Princeton Applied Research, Model 263A)控制.

使用 Solartron 1255B Frequency Response Analyzer 以及 Solartron SI 1287 Electrochemical Interface System 测量电化学阻抗谱,计算体系的零电荷电势(pzc).另由循环伏安扫描确定体系的电化学窗口.

2 结果与讨论

从金电极表面吸附的乙腈分子的 SFG-VS 可以检测到两个振动峰,分别位于 2250 cm^{-1} 和 2940 cm^{-1} 处. 2250 cm^{-1} 处的峰归属于乙腈分子 CN 基团的对称伸缩振动模式,属于 $C_{\infty v}$ 对称型; 2940 cm^{-1} 处的峰指认为乙腈分子的 CH_3 基团的对称伸缩振动模式,属于 C_{3v} 对称型.对本实验构型, ppp 偏振组合的和频振动光谱峰强度很小,只有 ssp 偏振组合才能够观测到明显的谱峰形状,因此本文只给出 ssp 偏振组合的和频振动光谱.

甲基和腈基的和频振动信号强度强烈依赖于外加电势.实验测量了电化学窗口内不同电极电势下的甲基基团的和频振动光谱.在电极电势 -700 mV 下,其振动峰的强度最大,随着电极电势靠近零电荷电势点(300 mV),谱峰迅速降低.这一现象对腈基也同样存在.根据界面和频光谱理论,谱峰强度的变化有可能是由金界面吸附乙腈分子的数量变化以及分子取向变化两种因素引起.有关从光谱变化定量区分两种因素的影响,将在未来的工作中详细讨论.本文仅就观察到的甲基基团和频振动光谱作简要讨论.

图 1 示出,当电极电势从 300 mV 变至 500 mV 时,甲基的和频振动谱峰形状由原先向上的正峰转变为向下的倒峰.这是由于和频振动光谱是一种相干光谱,它是由物质的二阶极化率对光场响应产生的.实验观测到的和频振动光谱信号包含着金属界面提供的非共振二阶极化率以及甲基对称伸缩振动的红外共振二阶极化率的贡献.这两者之间会产生干涉.当金属的非共振二阶极化率和甲基的共振二阶极化率的符号相同时,形成正向干涉,也即出现正峰,而当两者反号时,则出现倒峰^[29].据图 1,当电极电势越过 pzc (300 mV) 时,该和频振动光谱峰由正峰变为倒峰,这说明了甲基的红外共振二阶极化率的符号发生变化,也即基团的取向发生了反转(flip-flop).前人研究也发

现,某些极性分子,比如水和乙腈,在单晶金属电极界面上的吸附形态会随电极电势的变化出现取向反转的现象^[6,19-20].就本文而言,当电极电势小于 300 mV 时,乙腈分子在金电极上的吸附形态为甲基靠近金属电极界面而腈基远离电极.过此,则分子取向也随之发生反转.以上表明,对电化学体系,可以利用外加电势调控吸附分子(不仅仅是溶剂分子!)在电极界面的取向.而且由图 1 给出的结果或许可以说明,乙腈分子在电极上的 flip-flop 可能当属一个普遍行为.

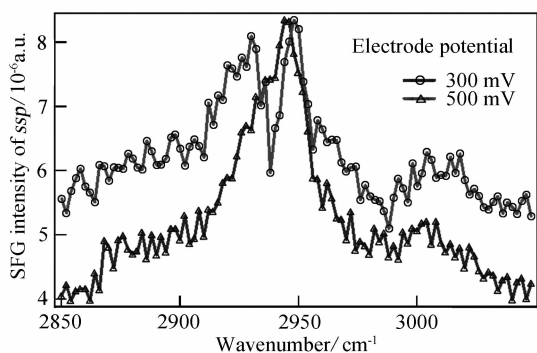


图 1 300 mV 和 500 mV 电势下金电极表面乙腈分子甲基基团 SFG 光谱(*ssp*)

Fig. 1 SFG spectra of the CH₃ groups on Au electrode at 500 mV and 300 mV

然而,以上讨论乃是根据峰强度的符号(即峰的相位)变化作出的.外加电势对吸附分子取向的调控究竟是连续的还是断续的,即在 flip-flop 之间是否还存在着某些中间态的取向,这无疑是一个极其令人关注的问题.涉及到用和频光谱如何精确测量界面吸附分子的取向角,其主要困难在于界面的局域场校正而导致的界面折射率的计算.相关研究将另文发表.

3 结 论

根据 SFG-VS 测定的乙腈/多晶金电极界面吸附取向角随电势变化的 flip-flop 现象.发现电极电势从 -700 mV 变化至 300 mV (*pzc*),乙腈分子的甲基对称伸缩振动峰强度下降;电极电势再从 300 mV 变至 500 mV 时,甲基振动峰的符号发生变化,对应于甲基基团的取向反转.据此可说明当电极电势负于零电荷电势时,乙腈分子吸附在多晶金电极表面上的构型当为甲基靠近界面而腈基远离界面的构型;但如果电极电势正于零电荷电势,则出现相反构型,即甲基远离界面而腈基靠近界面.

这是作者第 1 次用 SFG-VS 直接观测到乙腈分子在多晶金电极界面上的取向随着电极电势变化的 flip-flop 现象,同时证明了在电化学体系中,利用外加电极电势可直接调控界面吸附极性分子的取向.

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The Flip-Flop Behavior of Acetonitrile at Au Electrode Surface Investigated by Sum Frequency Generation Vibrational Spectroscopy

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Abstract: The electrochemical interface between liquid acetonitrile and polycrystal gold electrode is investigated by in situ infrared visible sum frequency generation spectroscopy (SFG-VS). The structure of acetonitrile adsorbed at polycrystal gold electrode surface is studied as a function of electrode potential. The SFG spectra of CH₃ group indicate acetonitrile orients in response to the electrode potential. The SFG signal of CH₃ group turns lower as the electrode potential changes from -700 mV to 300 mV, and vanishes around the 300 mV (pzc), then becomes a negative signal above 500 mV, which indicates that the orientation is predominately with the CH₃ group toward the metal between -700 and 300 mV and with the CN group toward the metal above 300 mV. It is the first time to observe the flip-flop behavior of acetonitrile dipole at the polycrystal gold electrode surface, which might become a common phenomenon.

Key words: sum frequency generation vibrational spectroscopy; flip-flop; gold electrode; acetonitrile