

和频振动光谱同位素效应

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当分子振动基团的原子被其同位素取代后, 振动频率发生位移的同时光谱强度也会改变。Crawford推导了光谱强度加和规则 (Intensity Sum Rule), 定量解释了同位素分子的红外光谱强度关系以及拉曼光谱强度关系。和频振动光谱 (SFVS) 是一种具有界面选择性的光谱方法, 可识别界面基团和表征界面结构。SFVS

测量界面分子基团的二阶极化率 χ_{mn}^k , χ_{mn}^k 与红外偶极和拉曼极化率张量的关系为: $\chi_{mn}^k \propto \frac{\partial \alpha_{mn}}{\partial Q_k} \cdot \frac{\partial \mu_l}{\partial Q_k}$ 。

受红外和拉曼光谱的强度加和规则启发, 我们推导了和频振动光谱的加和规则。与红外和Raman光谱的强度加和规则不同, 和频振动光谱是振幅加和规则 (Amplitude Sum Rule), 体现了和频振动光谱的相干性。通过定量测量和比较水和重水界面的和频振动光谱强度, 发现自由OH峰强度约是自由OD峰强度的1.5倍, 而形成氢键的OH峰强度约为形成氢键的OD峰强度的0.9倍。自由OH (OD) 和形成氢键的OH (OD) 在和频振动光谱强度上表现出不同的同位素取代效应, 前者符合和频振动光谱振幅加和规则, 而后者不符合。这表最上层的水分子分子内的振动是去耦合的, 并且分子间相互作用对表面水的氢键光谱有很大贡献。

关键词: 和频振动光谱; 同位素效应; 振幅加和规则; 水界面; 分子相互作用

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Investigation of the isotope effect on the Sum frequency vibrational spectra intensity

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The Amplitude Sum Rule in SFVS is deduced in order to explain the spectral intensity difference between the air/water and air/heavy water interfaces. Different from the Intensity Sum Rule in IR and Raman spectra, the sum in SFVS is over the amplitudes, which reveals the coherence instinct of SFVS. The SFVS spectra of water and heavy water are investigated and based on the principle and hypothesis of the Amplitude Sum Rule, it is found that the free OH (or OD) vibrations at the topmost layer is decoupled from both inter-and intra- molecular coupling while the hydrogen-bonded water molecules suffers intermolecular interactions. And more, the intermolecular interactions are stronger for hydrogen-bonded heavy water molecules than for hydrogen-bonded water molecules.