Analytical Chemistry Cumulative Examination

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November, 2015

100 points total

1. (30 pts). Many advanced analytical instruments are very sensitive to building vibrations. These instruments include high performance transmission electron microscopes, many laser-based instruments and the scanning probe microscopes. Building vibrations are quantified in various ways, such as by giving the magnitudes of the displacement, velocity, or acceleration at a particular vibrational frequency. For example, one way to represent the vibrational noise is to plot the amplitude of the vibrations as a function of their frequency. Sharp peaks are often observed at 60 Hz due to the motors used for pumps and ventilation systems. The vibrations can be modeled as a 1-dimensional classical harmonic oscillator so that the displacement is given by

$$Z(t) = Z_0 \, sin\{2\pi\nu \, t\}$$

a) Find a relationship between the magnitude of the acceleration (A_0) and Z_0 and ν.
b) If the displacement at 60 Hz is 1 micron, give a value for the acceleration at 60 Hz in units of cm/sec^2.

2. (30 pts). The two most common scanning probe microscopes are the atomic force microscope (AFM) and the scanning tunneling microscope (STM). Explain the basic principle of operation of the AFM and STM. Include in your description a simple sketch showing the key components, the typical resolution possible with each technique, the type of samples that can be imaged, and whether or not the method is restricted to operation in air, vacuum, or liquid environments.

3. (40 pts). One of the most exciting recent developments in STM research is the ability to measure the vibrational spectrum of individual molecules on surfaces through inelastic electron tunneling spectroscopy (IETS). In a typical STM experiment, for a fixed tip position the relationship between tip current and bias voltage is simply given by Ohm's low with a constant gap resistance. Vibrational spectroscopy with IETS is based on the fact that when a threshold energy is reached for vibrational excitation, the tunneling gap resistance changes to a new value. The experiment is done by placing the tip above a single molecule at a fixed height above the surface and varying the voltage between the tip and sample.

a) (10 pts). Sketch a typical plot of I(V) versus V in an IETS experiment and indicate the point where a vibrational threshold has been reached.
b) (10 pts). In most presentations of IETS data, plots of (dI/dV), or even more commonly (d^2I/dV^2), versus V are given. Sketch typical plots of (dI/dV) versus V and of (d^2I/dV^2) versus V in an IETS experiment and indicate the point where a vibrational threshold has been reached.
c) (10 pts). Because the (d^2I/dV^2) versus V plots are typically quite noisy, it is important to establish if observed features are really due to vibrational transitions of the molecule under study. List two criteria that are commonly used to verify that features in the (d^2I/dV^2) versus V plots are really due to vibrational transitions.
d) (10 pts). The STM-IETS experiment is typically performed at liquid He temperature. Explain why.