INFRARED SPECTRA OF ACETONITRILE AND RELATED COMPOUNDS ADSORBED ON ALKALI HALIDE FILMS

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The infrared spectra of acetonitrile (CH_3CN), deuterated acetonitrile (CD_3CN), fluoromethane and deuterated fluoromethane (CH_3F and CD_3F), and chloromethane (CH_3Cl) adsorbed onto sublimated films of alkali halides were observed. In acetonitrile, the symmetric CH stretch and the CN stretch are red-shifted relative to the gas phase frequencies, while the asymmetric CH stretch is blue shifted. Surface-induced splittings have been observed in the methyl bending and rocking modes. The spectra observed for fluoromethane are in agreement with those reported by Heidberg and coworkers [a].

Temperature-dependent broadening of the asymmetric CH stretch was observed in each of the compounds. This is attributed to dephasing of this vibration by an external mode of vibration, and is noticeably diminished upon deuteration. The effect of substituent (CN, F and Cl) and surface (NaCl, NaBr, KCl and KBr) on the dephasing dynamics of the methyl rotor on these films has been characterized.

Acetonitrile exhibits an anomalously high activation energy to desorption, with a value (> 80 kJ mol^{-1}) that approaches those seen for chemisorbed systems. The vibrational shifts and splittings will be used, along with desorption kinetics, to determine the mode of adsorption for this molecule.

[a] J. Heidberg, I. Hussla, Z. Szilagyi Z. Phys. Chem. 121, 145 (1980).