

Analyte-Analyte Interactions Influencing the PDMS-Yield

W. Tuszynski, F. Kieseling, E.R. Hilt

*Fachbereich Physik, Carl von Ossietzky-Universität
PO Box 2503, W-2900 Oldenburg, Germany*

Introduction:

The isolation of analyte molecules in a matrix or on a substrate makes PDMS-spectra more reproducible and often enhances the detection sensitivity, especially if the formation of stable analyte ions is supported by chemical or other process-induced interactions between analyte and matrix/substrate. These interactions have a strong influence on the PDMS-yield. The PDMS-yield is also strongly dependent on analyte-analyte interactions if the analyte concentration is high. For example, high local concentrations which are produced by self-aggregation or cluster formation have a considerable effect on the PDMS-yield. Precise informations about the amount and the formation of molecules on the sample are required for studying these correlations. We applied optical spectroscopy methods for characterizing our samples. The absorption of light from the near IR to UV (via diffuse reflectance) and the fluorescence (steady state and time-resolved) were determined. Many informations about sample composition and structure can be obtained by evaluating the optical spectra. The determination of low analyte concentrations is one of the very useful advantages of this application. For example, a coverage of 6×10^{12} adsorbates per cm^2 can be determined precisely enough by the diffuse reflectance method.

Experimental:

The count rates of samples with different dye molecules applied to nitrocellulose (NC) have been determined. The dyes were malachite green (MG), rhodamine 6G (R6G), and chlorophyll-a (Chl-a). The amount of analytes adsorbed on the substrate has been varied in the range from 6×10^{12} to 8×10^{15} per cm^2 as determined by optical measurements. PDMS-spectra were recorded by our spectrometer OLDA 1 which we built in cooperation with K. Wien, TH Darmstadt. This linear TOF-instrument is equipped with an 80 cm flight tube, two double stage multichannel plates for start or stop signals, and a time digital converter CTM/M2 connected with a DMI-card, both from Y. LeBeyec, IPN Orsay. Mass resolution is about 700. The operating voltage was usually + 10 kV, the run time 30 min. The samples were prepared by applying 5 μl solution to a 1 cm^2 NC film which was made by electrospraying 40 μl of a 2 mg/ml acetone solution on an aluminized polyester foil.

Results:

The count rate of the molecular ion peak increases linearly with the amount of dye molecules at a coverage of less than 8×10^{14} analytes per cm^2 . This result has been obtained with Chl-a as well as with MG and R6G which are known to be preionized. The count rate of the Chl-a fragment ion peaks shows also a linear dependence at this range of coverage. The count rates turn into saturation between 8×10^{14} and 8×10^{15} analytes per cm^2 . The relative fluorescence yield of R6G samples increases linearly with the amount of R6G on NC at a coverage of less than 5×10^{14} per cm^2 . The fluorescence first saturates and then decreases with higher values.

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Discussion:

The linear dependence of the count rates on the amount of analytes observed at low coverage is attributed to the linearly increasing probability that isolated adsorbates are "hit" by a passing fission fragment. The nonlinear behaviour observed at larger coverage is obviously due to increasing interactions between the analytes. The resulting effect is a competition between adjacent analytes leading to a considerable modification of the count rates and probably of the relative ion yields. The linearly increasing R6G fluorescence at low coverage demonstrates clearly the existence of isolated R6G molecules on the NC. The fluorescence saturates and decreases at higher coverage due to the growing probability of energy transfer processes at smaller distances between neighbouring dye molecules. These processes are produced by dipole-dipole interaction and finally give rise to decreasing fluorescence quantum yields. In consideration of the fluorescence data, the mean distance between adjacent R6G molecules is estimated to be about 6 nm at 8×10^{14} per cm^2 , i.e. it slowly approaches the molecular size. Quantitative evaluations of the experimental PDMS data are under way, which start from randomly distributed molecules on the surface, to determine the intermolecular force and the geometry of the desorption area.