

Self-assembled monolayers of supramolecular compounds for chemical sensors

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Abstract

We have studied the application of self-assembled resorcin[4]arene monolayers as chemically sensitive coatings of quartz microbalance sensors. Resorcin[4]arenes are typical supramolecular compounds with a molecular cavity formed by an aromatic ring system. The latter provides lipophilic binding sites and acts therefore as a molecular recognition structure for organic molecules. Resorcinarenes are of particular interest for the selective detection of organic molecules in the gas and liquid phase. A high level of molecular order can be achieved by using modified cage compounds: dialkylsulfide-substituted resorcin[4]arene derivatives (with 4 aromatic rings) form well-ordered monolayers at Au surfaces by a self-assembling process which occurs spontaneously in ethanol/chloroform solutions of these resorcin[4]arene derivatives. The driving force is the formation of very stable Au–S bonds and the van der Waals interaction between the alkyl chains. We present results on the structure of resorcin[4]arene monolayers and their interactions with organic molecules. These results were obtained from angle-resolved X-ray photoelectron spectroscopy (AR-XPS) and thermal desorption spectroscopy (TDS). The latter technique makes it possible to determine binding energies of the molecule/resorcin[4]arene ‘key–lock’ interaction. The binding energies are then compared with mass changes Δm which are obtained from quartz microbalance oscillators with their Au electrodes coated with resorcin[4]arene monolayers. We tested different organic molecules in the gas and liquid phase such as tetrachloroethene (C_2Cl_4), trichloroethylene ($HClC=CCl_2$), tetrachloromethane (CCl_4), chloroform ($CHCl_3$) and toluene ($H_3C-C_6H_5$). By far the most pronounced sensor response and hence highest selectivity was observed to tetrachloroethene (C_2Cl_4).

Keywords: Chemical sensors; Self-assembled monolayers; Supramolecular compounds

1. Introduction

Molecular recognition is an essential feature of many biological processes in living cells, e.g. during the specific ‘host–guest’ coupling of compounds at receptors in lipid membranes. During the last decades chemists have developed new concepts of a molecular design which are based on non-covalent interactions between individual molecules (‘supramolecular chemistry’). Typical examples are host–guest complexes where an inner guest molecule ‘fits’ into the cavity of an outer host molecule. A variety of fascinating applications arises from supramolecular chemistry [1]. Previously, host–guest interactions have been applied in chemically modified field effect transistors for the potentiometric

detection of charged species [2] and in mass-sensitive devices for the detection of neutral molecules [3].

This paper reports the molecular recognition of small neutral organic molecules by modified resorcin[4]arenes. They are synthetic receptor molecules which form a molecular cavity by four resorcinol moieties. The cavity is further rigidified by bridging the oxygen atoms of the aromatic rings with methylene groups to give a cavitand [4] which provides lipophilic binding sites for organic molecules. Similar receptor molecules were tested for the detection of organic molecules in the vapor phase [5]. A high level of molecular order of these recognition sites can be achieved by using dialkylsulfide-substituted cavitands which form well ordered monolayers at Au surfaces by a process which is called self-assembly [6] and which occurs spontaneously from ethanol/chloroform solutions of these resorcin[4]arene derivatives [7].

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The driving force is the formation of very stable Au–S bonds and van der Waals interactions between the four dialkylsulfide chains which function as pillars for the resorcin[4]arene cavitand on the gold surface.

In Fig. 1 two aspects of molecular recognition are indicated: first, a binding occurs between one tetrachloroethene molecule (C_2Cl_4) and the resorcin[4]arene cavity and, second, a selection of C_2Cl_4 occurs in the presence of other organic molecules. The recognition sites are well ordered, therefore only surface and no bulk effects must be expected.

To prove the constitution shown in Fig. 1 we performed angle resolved X-ray photoelectron spectroscopy. The use of the self-assembled monolayers as

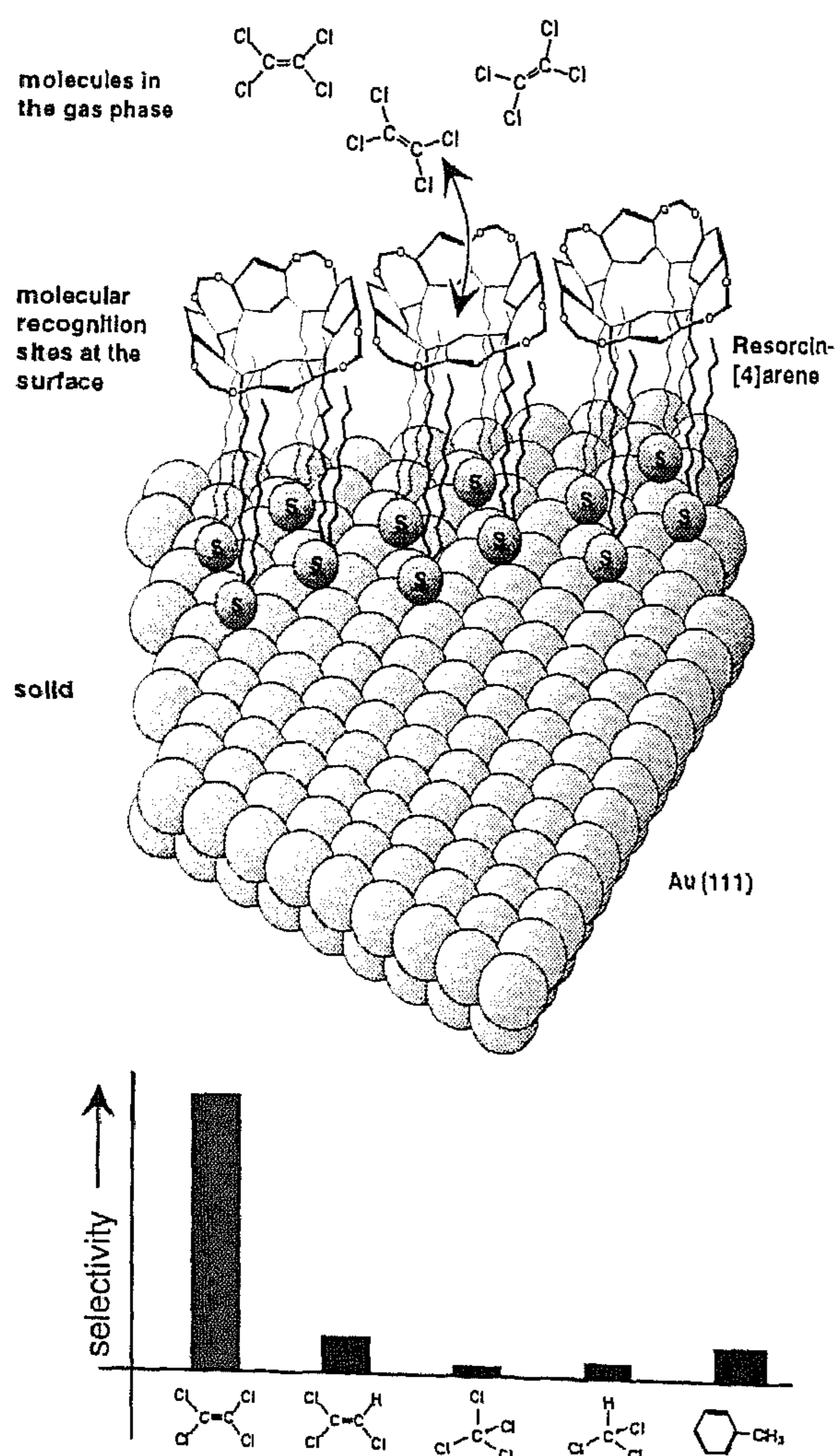


Fig. 1. Schematic representation of the molecular structure and interaction of a self-assembled monolayer of resorcin[4]arenes ('hosts') on a Au(111) surface with tetrachloroethene (C_2Cl_4) molecules ('guest') from the gas phase. This incorporation occurs with higher binding energy and hence higher selectivity for C_2Cl_4 if compared with trichloroethylene ($ClHC=CCl_2$), tetrachloromethane (CCl_4), chloroform ($CHCl_3$) and toluene ($H_3C-C_6H_5$). Selectivities correspond to mass changes which occur during exposure of the layers to partial pressures of 200 Pa at 303 K.

sensitive coatings for chemical sensors was tested with quartz microbalance oscillators in a flow-through cell where the samples were exposed to constant concentrations of different organic compounds in the ppm range in synthetic air at a constant temperature $T=303$ K. To determine the interaction energies between the resorcin[4]arene monolayer and different organic molecules we performed thermal desorption (TD) experiments.

2. Experimental

2.1. Apparatus and materials

The synthesis of the dialkylsulfide-substituted resorcin[4]arenes and the characterization of monolayers on Au(111) surfaces with contact angle and SPR thickness measurements, IR spectroscopy, and capacitance-voltage curves are described elsewhere [7].

Angle-resolved X-ray photoelectron spectroscopy was performed in a Vacuum Science Workshop spectrometer with a monochromatized Mg $K\alpha$ source, a concentric hemispherical analyzer, and a multichannel detector.

A 12 MHz, AT-cut quartz resonator was used in the quartz microbalance experiments. The coated quartz resonators were mounted in a brass gas-flow set-up and exposed to small partial pressures $10 \leq p_1 \leq 400$ Pa of tetrachloroethene (C_2Cl_4), trichloroethylene ($ClHC=CCl_2$), tetrachloromethane (CCl_4), chloroform ($CHCl_3$) and toluene ($H_3C-C_6H_5$) in synthetic air at a total pressure $p=10^5$ Pa and a constant temperature $T=303$ K. Mass changes Δm are then calculated from Δf according to Sauerbrey's equation

$$\Delta m = \frac{\Delta f \cdot A}{S_m \cdot f} \quad (1)$$

where f denotes the oscillation frequency, S_m the mass sensitivity, and A the surface area of the resorcin[4]arene monolayer.

Thermal desorption spectra were measured with a differentially pumped Balzers quadrupole mass spectrometer (QMG 420), while the temperature of the sample was increased linearly with time at a rate of 0.53 K s^{-1} .

2.2. Sample preparation

The gold electrodes of the quartz resonators were cleaned by sputtering with argon. Gold films (1500 Å) for AR-XPS and TDS were prepared by thermal evaporation subsequent to deposition of titanium onto glass substrates.

Monolayers were prepared by the immersion of these gold surfaces in 1 mM ethanol:chloroform (7:3) solutions

of the dialkylsulfide-substituted resorcin[4]arenes at 60 °C for 15 h.

3. Results and discussion

3.1. Angle resolved X-ray photoelectron spectroscopy

In AR-XPS the core electrons of certain elements are emitted upon irradiation with X-rays and their binding energies are determined with an energy analyzer [8]. This surface-sensitive technique was used to determine the elemental composition of the monolayer perpendicular to the Au surface. If the angle ϕ and hence the direction of the detected electrons in the energy analyzer is varied (see Fig. 2), atoms can be identified which are located in the outermost layer. For AR-XPS studies on resorcin[4]arene monolayers, measurements were done at low temperatures ($T=80$ K) in order to freeze molecular movements and to reduce damage which might occur during X-ray irradiation.

With the low monolayer thickness of about 2 nm, only very low intensities of the S2p_{3/2} core levels are detected at a binding energy $E_b=160.6$ eV (referenced to the Fermi energy of a gold sample). In addition, no sulfur in an oxidic form is present which would be expected if S atoms were not linked directly to the Au surface. We also found that the ratio $I_{Au4f/S2p}$ of the Au4f and S2p core level intensities does not change

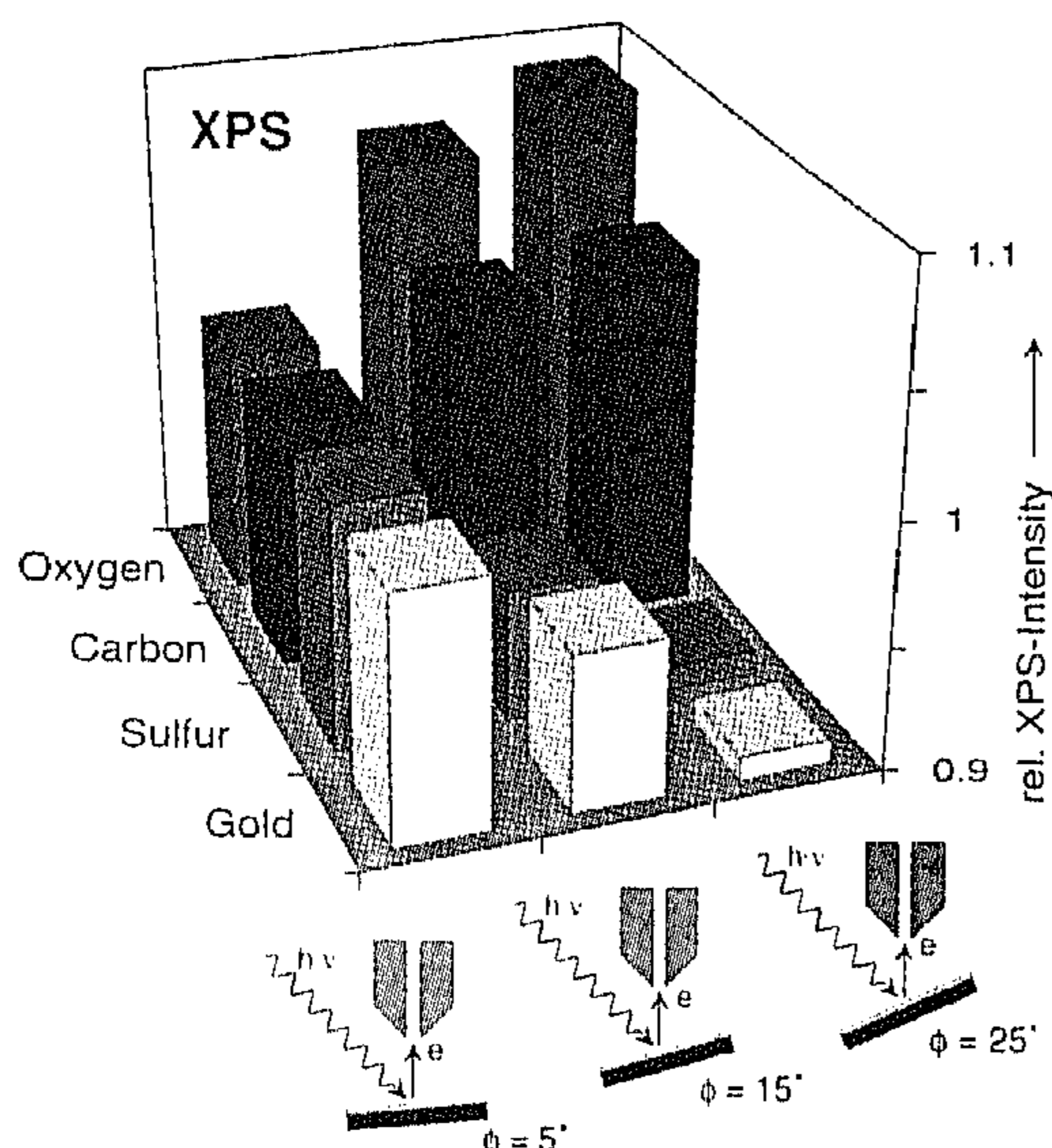


Fig. 2. Relative XPS intensities of gold (sum of Au4d and 4f core electron intensities), sulfur (S2p), carbon (C1s) and oxygen (O1s) core electron emissions at 80 K for three different 'take-up' angles ϕ between surface normal and analyzer. All intensities obtained at $\phi=5^\circ$ are normalized to the value 1 and relative XPS intensities at angles $\phi=15$ and 25° are referred to the 5° data. The geometric arrangement of the X-ray gun emitting $h\nu$, sample, emitted electrons e and the energy analyzer are shown schematically in the lower part.

upon variation of the 'up-take' angle ϕ between surface normal and analyzer. This indicates that the S atoms are located at the Au surface as indicated in Fig. 1.

The ratio $I_{Au4f/O1s}$ shows a significant dependence on the angle ϕ thus indicating that the O atoms are located at the outermost surface of the resorcin[4]arene monolayer. The C1s emission shows a perfect Gaussian-like peak at $E_b=284.0$ eV which corresponds to one uniform carbon species. These AR-XPS results confirm the model of the well-defined structure of resorcin[4]arene monolayers as shown in Fig. 1.

3.2. Quartz microbalance studies

Quartz microbalance oscillators (12 MHz, 0.36 cm² electrode area, Kristallverarbeitung Neckarbischofsheim, Germany) were used to determine the mass increase during the incorporation of C₂Cl₄ molecules into the resorcin[4]arenes. We performed these experiments in a flow-through cell where the substrate samples were exposed to constant concentrations of C₂Cl₄ in the ppm range in synthetic air (i.e. N₂/O₂ mixtures) at a constant temperature $T=303$ K. Typical results of the shift Δf in the fundamental oscillation frequency are shown in Fig. 3. Resorcin[4]arene monolayers show a fast interaction with C₂Cl₄. Steady-state values Δf are reached after short response times. Evidently, a thermodynamic equilibrium between C₂Cl₄ in the gas phase and the resorcin[4]arenes is adjusted immediately. By contrast, the interaction of C₂Cl₄ with

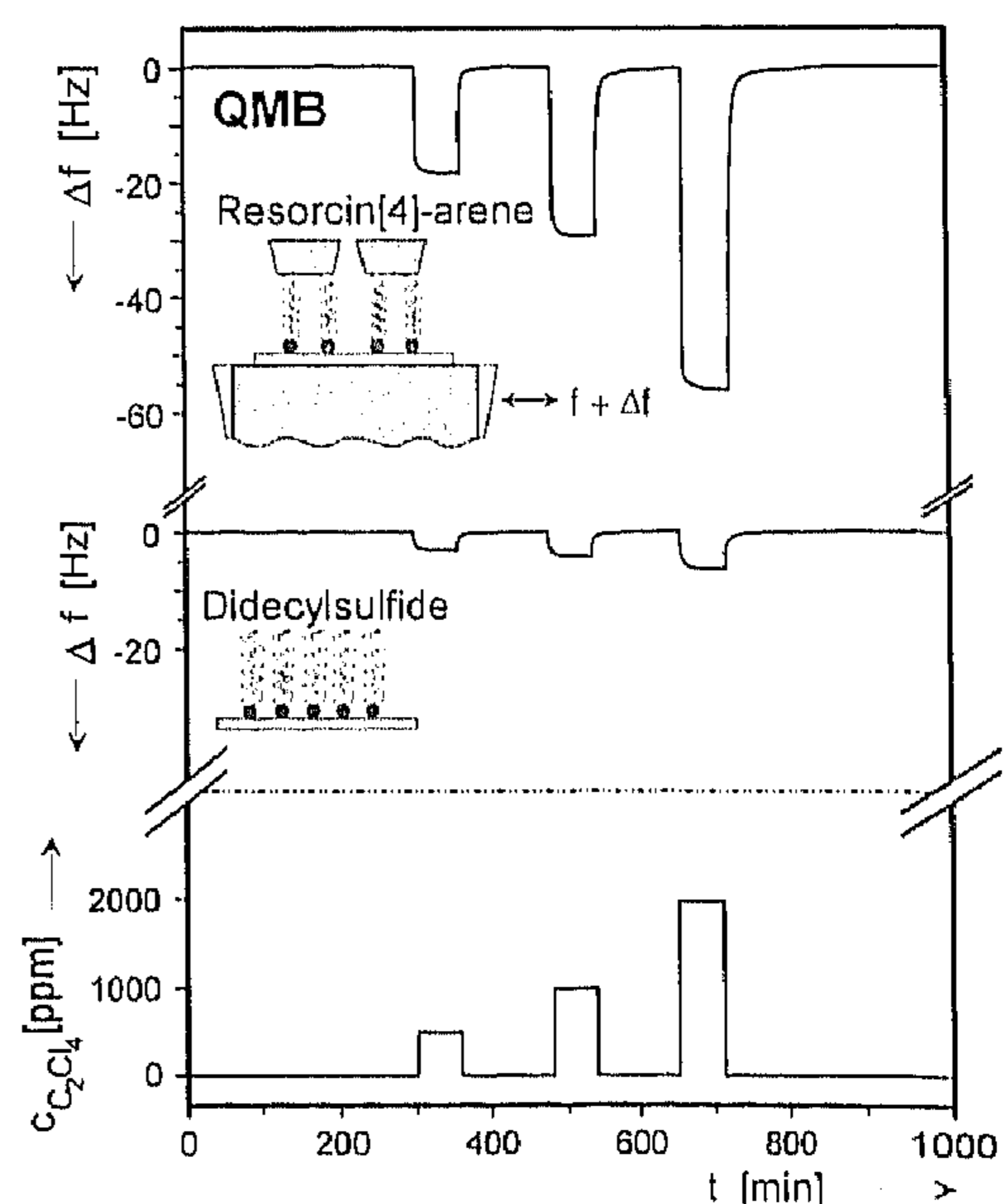


Fig. 3. Changes of frequencies Δf as a function of time t during exposure of monolayers of resorcin[4]arene and didecylsulfide to different concentrations $c_{C_2Cl_4}$ in synthetic air at $T=303$ K. For simplification, the noise of the signal of $\pm 2-3$ Hz (which mainly results from small fluctuations of the temperature which affect the oscillation frequency of the quartz) is omitted here.

didecylsulfide monolayers leads to relatively small changes Δf under the same conditions. This may be attributed to the occupation of interstitial sites of the aliphatic chains which result from their lipophilic properties. For comparison, we also determined frequency changes for other organic molecules including chloroform, trichloroethylene and toluene monitored at the same pressures and temperature (303 K). These results show that the resorcin[4]arenes have a high selectivity towards incorporation of C_2Cl_4 molecules, as indicated in Fig. 1.

3.3. Thermal desorption spectroscopy

To get information about the interaction energies between the resorcin[4]arene monolayer and different organic molecules we performed thermal desorption (TD) experiments. The selectivity in the detection of molecules is determined by the binding energy of the molecule in the cavity which may be deduced from the activation energy of desorption. Here, C_2Cl_4 is exposed to the monolayer at low temperatures in an ultra-high-vacuum chamber. Under these conditions, C_2Cl_4 molecules adsorb at the surface. If the temperature is subsequently increased at a constant rate by using a resistively heated tantalum foil, the desorption of C_2Cl_4 molecules occurs and the pressure $p_{C_2Cl_4}$ rises in the chamber at specific temperatures T . With the limited number of adsorbed molecules N_{ads} at the surface under conditions of continuous pumping in the gas phase, we observe a small $p_{C_2Cl_4}$ peak in the quadrupole mass spectrometer (Fig. 4).

The shape of the $p_{C_2Cl_4}$ curve can be described by means of common rate equations of chemical kinetics.

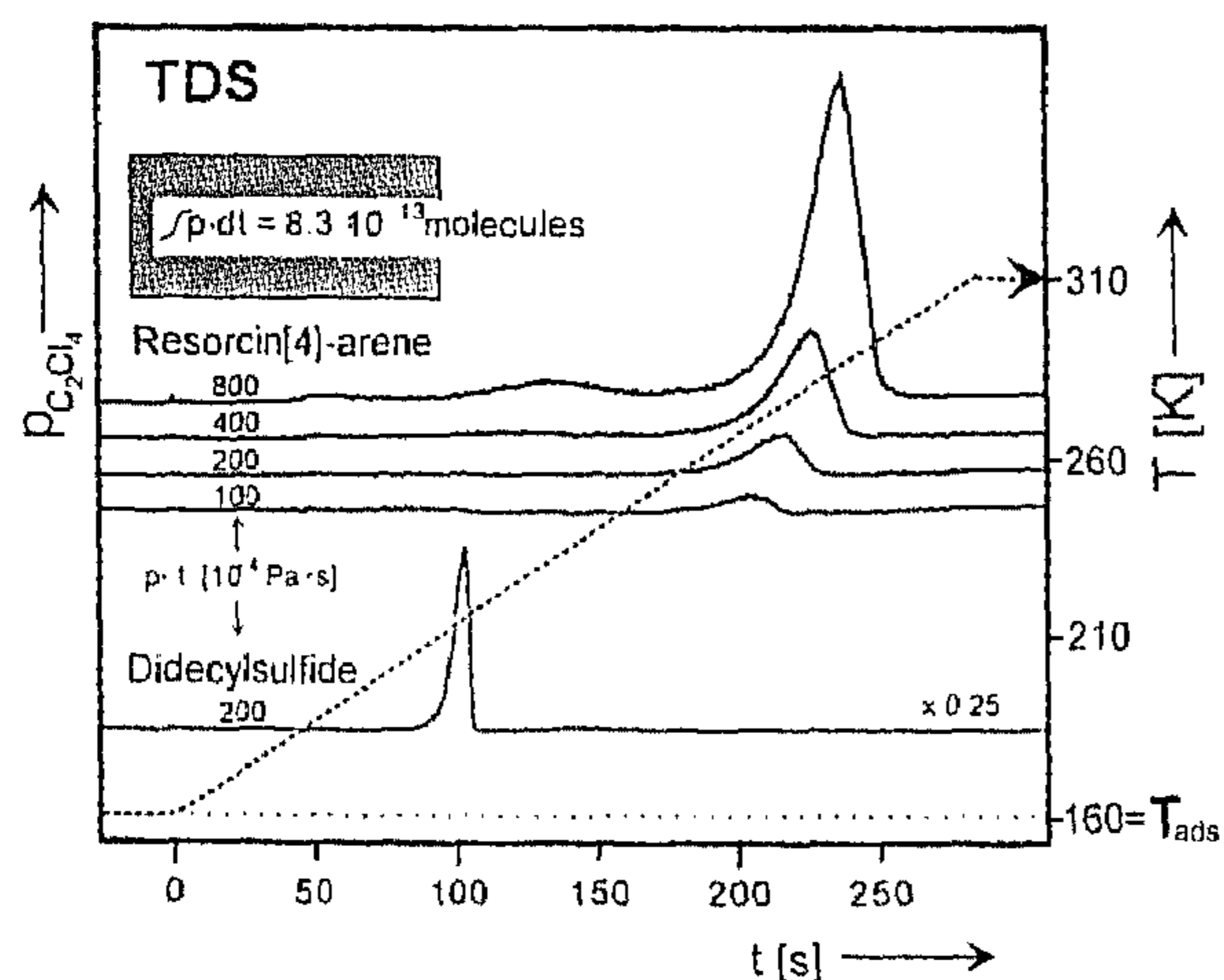


Fig. 4. Typical thermal desorption spectra (TDS) obtained after exposure of tetrachloroethene (C_2Cl_4) to a monolayer of resorcin[4]arene and of didecylsulfide, to C_2Cl_4 at $T_{ads} = 160$ K. Different TD spectra are obtained for different adsorption times 100–800 s at a pressure of 10^{-4} Pa. For comparison, the TD spectrum of didecylsulfide is also shown after an exposure of $pt = 200 \times 10^{-4}$ Pa s. The upper left area of the rectangle in the plot $p-t$ corresponds to 8.3×10^{13} molecules and is obtained by calibration.

From this we deduce activation energies and orders m of desorption, i.e. [9]

$$p_{C_2Cl_4} \sim \exp\left\{\frac{E_{act}^{des}}{k_B \cdot T}\right\} \cdot N_{ads}^m \quad (2)$$

where k_B denotes the Boltzmann constant, and N_{ads} the number of adsorbed molecules. The typical TD spectra shown in Fig. 4 indicate large differences in the position of the desorption maxima for didecylsulfide as compared with the resorcin[4]arene monolayers. For didecylsulfide only weakly bound physisorbed C_2Cl_4 molecules are found which desorb at low temperatures $T = 210$ K. For resorcin[4]arene, we observe a desorption maximum at high temperatures $T = 286$ K which clearly indicates the presence of stronger bound C_2Cl_4 molecules at the surface. The activation energy of desorption is similar to the value determined for calix[4]arene multilayers [10] and we attribute it to the desorption of C_2Cl_4 molecules from the resorcin[4]arene macrocycles (arrow in Fig. 1). By varying the exposure and hence the number of adsorbed C_2Cl_4 molecules, the order m of desorption can be determined from the shift of the desorption maximum. The evaluation of these data will not be treated here in detail. The shift of the desorption maximum to higher temperatures with increasing coverage (Fig. 4) gives evidence for an attractive interaction between the embedded C_2Cl_4 molecules at higher surface concentrations.

4. Conclusions

We have shown that resorcin[4]arenes with four dialkylsulfide pillars self-assemble to well-ordered monolayers on clean Au surfaces from ethanol/chloroform solutions. Angle-resolved photoelectron spectra give evidence that the cavitand headgroup of the resorcin[4]arenes determines the outermost surface. Fast and reversible mass increases were observed with quartz microbalance oscillators with these monolayers in interaction with organic molecules, like C_2Cl_4 . The latter results from an incorporation of C_2Cl_4 within the molecular cavities formed by the resorcin[4]arenes. Comparative thermal desorption spectra indicate binding sites with high interaction energies of C_2Cl_4 molecules at the surface of the resorcin[4]arene monolayers. These monolayers serve as a model supramolecular assembly [11] which provides well-defined surface recognition structures for organic molecules.

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