

Surface diffusion in the 2D-phase transition of CO₂ adsorbed on NaCl(100)

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CO₂ on NaCl(100) at coverages below one monolayer (ML) adsorbs as a 2D-lattice gas in equilibrium with an ordered 2D-condensed phase with (2x1) structure. Diffusion of isolated CO₂-molecules in the supersaturated 2D-lattice gas phase on NaCl(100) was studied by means of time-resolved, high-resolution polarization Fourier-transform infrared spectroscopy. The process was monitored by recording the time evolution of the ν_3 vibrational spectra of adsorbed CO₂ as the initially randomly distributed molecules diffuse to thermodynamically favored step and cluster sites. Performing the measurements at different substrate temperatures and applying a simple diffusion model yields the barrier for the migration process of $E_{\text{diff}} = (3.6 \pm 0.9)$ kJ/mol in good agreement to results of potential energy calculations.

The experimental as well as the theoretical results will be discussed within the context of thermodynamic data obtained at higher temperatures ($45 \leq T/K \leq 100$), especially their importance for modelling the 2D-phase transition by simulating adsorption isotherms.

1. INTRODUCTION

Substantial efforts have been devoted to the experimental as well as the theoretical investigation of surface diffusion of adsorbed molecules or atoms in the past since it plays an important role in many other surface processes under study, e.g. in adsorption/desorption, 2D-phase transitions/2D-clustering, surface reactions. A number of experimental techniques applicable to single crystal surfaces has been developed which are reviewed e.g. in [1,2]. Most of these techniques are restricted to surfaces of conducting materials since charged particles are involved. Exceptions are laser induced desorption (LID), helium atom beam scattering (HAS) and time-resolved Fourier-transform infrared spectroscopy (TR-FTIR). All three methods probe the diffusion process in real time, the first over macroscopic distances including surface steps and the other two in microscopic dimensions, yielding e.g. microscopic hopping rates. Though LID was used frequently in the past in contrast to HAS and FTIR, only the latter two can be regarded as completely nondestructive.

Since both methods can distinguish adsorbates at terrace sites from molecules at defects or islands, FTIR by a change in resonance frequency and HAS by a change in the effective scattering cross-section, they were used so far to study diffusion of lattice gas molecules from initially supersaturated low density phases to thermodynamically more favored step sites. The HAS-experiment was performed recently by Poelsema et al. with CO on Pt(111) [3], the corresponding FTIR-study by Reutt-Robey et al. [4]. In our paper we present an application of time-resolved, high-resolution polarization Fourier-transform infrared spectroscopy to study the diffusion of weakly bound physisorbed molecules on an insulator surface.

The system CO₂/NaCl(100) was chosen since it evolved to one of the best studied physisorption systems in the last years. A variety of experiments concerning structure [5-8], dynamics [8-10] and thermodynamics [11] gave insight e.g. into equilibrium geometries, structure and adsorption potentials. Nevertheless informations about the surface mobility, which is a prerequisite for complete understanding of most of the experiments mentioned above,

were not available. Especially the investigation of the 2D first order phase transition from a well ordered 2D-crystal with $p(2 \times 1)$ -structure and pg -symmetry [9] to a randomly distributed 2D-lattice gas studied in the temperature range from $45 \text{ K} < T < 100 \text{ K}$ implied a comparably high mobility in the dilute surface phase [11], whereas on the other hand applications of simple adsorption models, namely the Fowler-Guggenheim (FG) and the 2D-van der Waals (vdW) model [12] to adsorption isotherms recorded at $87 \text{ K} \leq T \leq 98 \text{ K}$ resulted in a better simulation by the model for immobile adsorbates (FG) [13]. This discrepancy can be explained with a partial mobility as will be shown in the following.

2. EXPERIMENTAL

The setup was similar to previous experiments [9,11]. In brief, it consists of a standard UHV-system (Varian, base pressure $< 2 \times 10^{-10}$ mbar) equipped with an ion gauge and a quadrupole mass spectrometer for partial pressure analysis, a homemade LHe-cryostat with additional radiation shields ($5 \text{ K} \leq T_{\text{sample}} \leq 600 \text{ K}$), a cleavage device for in situ preparation of NaCl(100)-samples and a stainless steel capillary ($\varnothing = 1.5 \text{ mm}$, distance to sample $\approx 50 \text{ mm}$) for dosing small amounts of CO_2 -gas from a separate gasinlet system (base pressure $\leq 2 \times 10^{-9}$ mbar) through a leak valve. The reproducible preparation of coverages as small as $\Theta \leq 0.01$ monolayer (ML) was possible by monitoring the pressure decrease in the gasinlet volume by means of a spinning rotor gauge (MKS, SRG-2). The temperature was controlled by NiCr/Ni and Au(Fe)/NiCr-thermocouples attached to the sample holder and a NiCr/Ni-element mounted to the sample. No temperature difference between sample and holder could be detected at $50 \text{ K} < T < 100 \text{ K}$. Thus at lower temperatures only the Au(Fe)/NiCr-element was used due to its higher sensitivity. Its long-time reproducibility and absolute accuracy was found to be $\approx \pm 1 \text{ K}$, whereas the relative accuracy at short times is better than $\pm 0.1 \text{ K}$. The sample temperature could be adjusted to $T \pm 0.2 \text{ K}$.

IR-spectra were recorded on a Bruker IFS 113v

interferometer with external detector compartment and additional optics for surface measurements [14], the optical path being evacuated to 6 and 0.2 mbar, respectively. The polarized IR-beam was filtered by an optical bandpass ($2000\text{--}2500 \text{ cm}^{-1}$) and monitored by an InSb-detector. The effective resolution was 0.16 cm^{-1} (nominal 0.1 cm^{-1}) as checked with residual gas absorption bands. A scan speed of 11 s/scan was achieved. Averaging of 32 scans within ≈ 7.3 minutes (including data processing time) yielded a peak to peak noise of $< 3 \times 10^{-4}$, which is sufficient to detect coverages of $\Theta < 10^{-4}$ ML of CO_2 on NaCl(100) [11]. All spectra presented are Blackman-Harris-apodized and two times zero-filled. Interference fringes due to the polarizer were corrected by removing the echo peaks from the interferograms before transformation.

3. RESULTS

As first we now want to summarize some details being important for a better understanding of the experiments described below. The adsorption system CO_2 -NaCl(100) is characterized by a 2D phase transition between a 2D gas phase and a 2D solid phase. Typical ν_3 -absorption spectra obtained with $^{13}\text{C}^{16}\text{O}_2$ on UHV-cleaved NaCl(100) under equilibrium conditions at 91 K are displayed in fig. 1. At low coverages a single absorption at 2278.9 cm^{-1} attributed to the 2D gas is observed (top spectra). At a transition pressure the spectra change remarkably, indicating the onset of the 2D-phase transition. Two additional absorptions at 2283.0 cm^{-1} and 2275.0 cm^{-1} appear together with the absorption of the 2D gas. These absorptions are attributed to the 2D solid phase, coexisting with the 2D gas phase. At pressures above the transition pressure we find the well-known ν_3 -doublet (top spectra) of 2D solid CO_2 on NaCl(100) for over two magnitudes in pressure. The diffusion experiments were performed as follows. After cooling down the surrounding radiation shields to 80 K the sample temperature was reduced to 77 and 17 K. At each of both temperatures a pair of p- and s-polarized spectra was taken. Spectra division showed no adsorption from the residual gas which consisted, apart from the main component H_2 ,

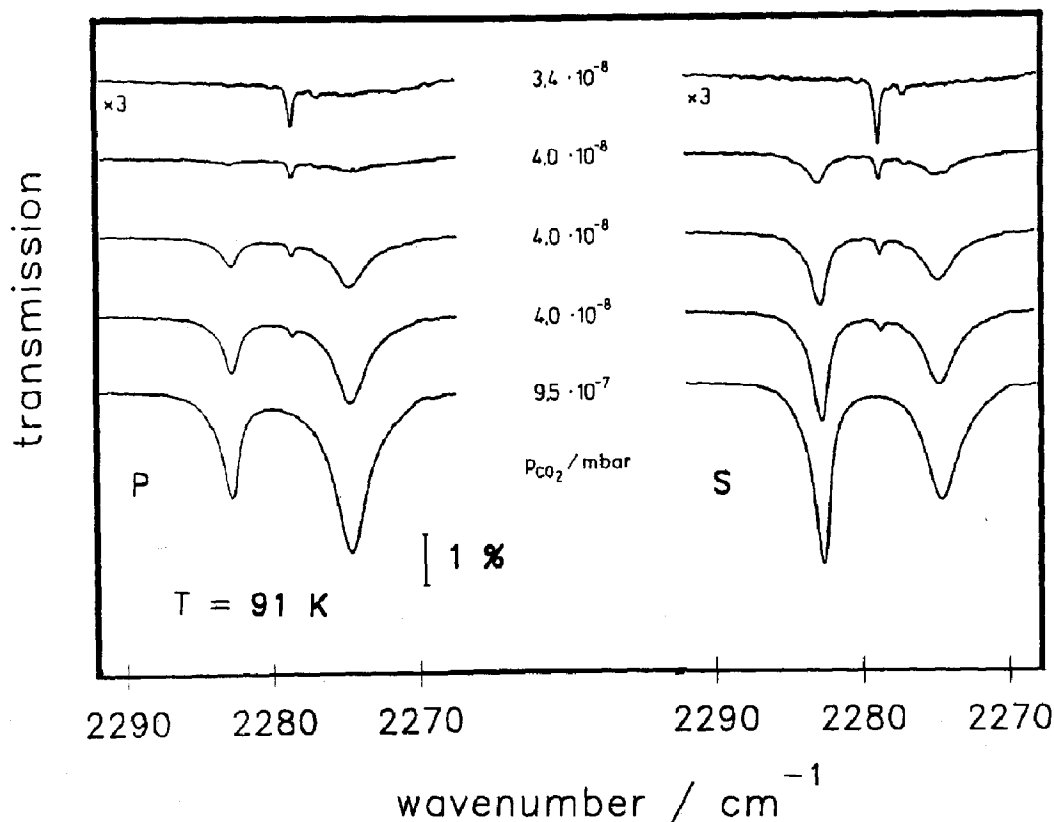


Fig. 1. p- and s-polarized FTIR-spectra of $^{13}\text{C}^{16}\text{O}_2$ on NaCl(100) at 91 K. 2D gas (top), 2D solid (bottom) and coexistence of these phases. Note the increased ordinate scaling by a factor 3 in the top spectra.

in traces of CO, CH₄ and H₂O. The adsorbate was prepared on one crystal face by dosing with the capillary. The isotope $^{13}\text{C}^{16}\text{O}_2$ was chosen to avoid overlap with baseline instabilities due to residual atmospheric CO₂ in the optical path. Isotope impurities in the probe gas caused a composition of $\approx 90.8\%$ $^{13}\text{C}^{16}\text{O}_2$, 8.6% $^{13}\text{C}^{16}\text{O}^{18}\text{O}$ and traces ($<1\%$) of $^{12}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{18}\text{O}_2$ and $^{12}\text{C}^{16}\text{O}^{18}\text{O}$. The dosed amount yielded a coverage of $\Theta \approx 0.026$ ML as revealed from the integrated area of the whole absorption (top spectra of fig. 2). The spectra show two narrow bands at $\bar{\nu} = 2278.7$ cm⁻¹ (FWHM = 0.28 cm⁻¹) and 2278.0 cm⁻¹ (FWHM = 0.26 cm⁻¹) on a broad background. Both bands contribute to the whole integrated area with $\approx 40\%$ and $\approx 14\%$ respectively. The high frequency band must be at-

tributed to the 2D-lattice gas phase of low density CO₂ adsorbed on NaCl(100), which was found at higher temperatures at 2278.8 cm⁻¹ (45 K) and 2278.9 cm⁻¹ (91 K) [11]. Uncertainties in the local adsorbate density due to the unknown spreading behaviour of the capillary might be reduced by comparison with the data obtained from equilibrium coverages at higher temperatures. At 91 K a linear relationship between coverage and linewidth (FWHM) of the lattice gas due to (dynamic or static) lateral interactions of $\Delta\text{FWHM} \approx 12$ cm⁻¹/ML was found at coverages between $0.001 \leq \Theta/\text{ML} \leq 0.01$ [15]. Assuming a similar relationship at 17 K a mean adsorbate density in the lattice gas phase of $\rho = 0.02$ -0.03 ML is implied by the measured linewidth of FWHM = 0.28 cm⁻¹, which

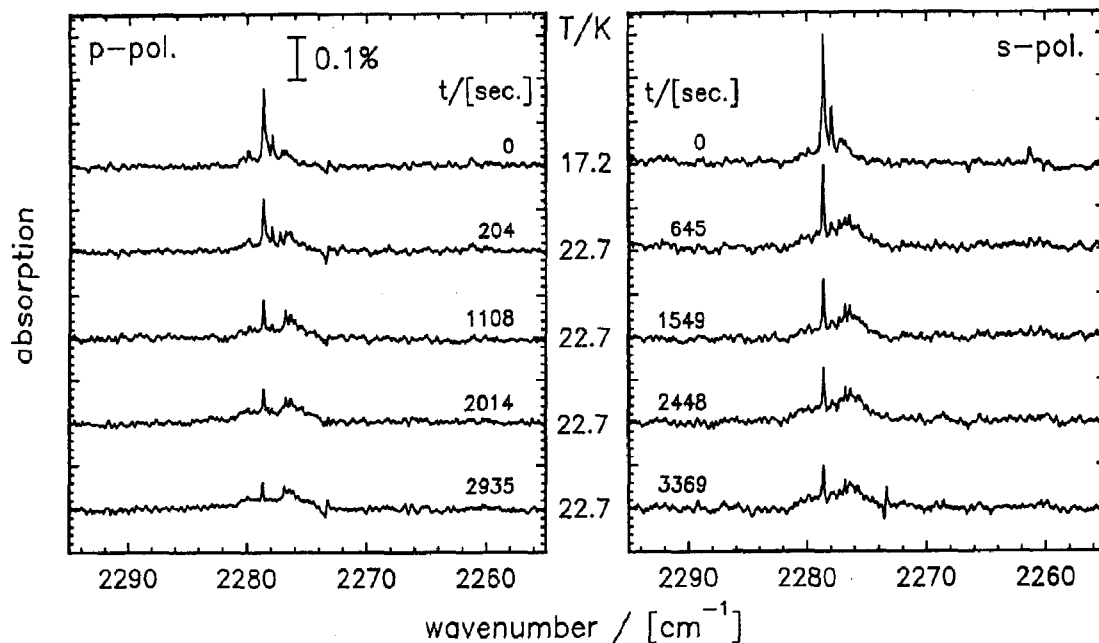


Fig. 2. p- and s-polarized absorption spectra of $^{13}\text{C}^{16}\text{O}_2$ submonolayers ($\Theta \approx 0.026$ ML) on NaCl(100) plane prepared in situ under UHV; $p < 2 \times 10^{-10}$ mbar.

means that the adsorbate must be spread homogeneously at least over the whole area probed by the IR-beam.

Fits of approximated Voigt functions to the spectra result in two additional bands at 2276.9 and 2280.0 cm^{-1} ($\text{FWHM} = 1.1\text{--}1.5$ cm^{-1}). The ratio of the integrated areas of s- and p-polarized spectra for each band within the experimental error is $A_s/A_p = 1.7$, which is predicted by theory for transition dipoles oriented parallel to the surface [14]. The spectra were constant in time ($t > 1$ h) at $T = 17.2$ K but changed remarkably following a T-jump to $T = 22.7$ K (fig. 2). The T-jump was performed within 30–45 sec., the time lag between the jump and each spectrum (mean of the sampling time) is given in the figure.

The absorption at 2278.0 cm^{-1} vanishes nearly immediately, whereas the main peak at 2278.7 cm^{-1}

decreases slowly. Correspondingly the broader background grows, resulting in a constant overall absorption. Thus no desorption was observed in concert with other experiments where desorption on the time-scale of experiment was found to become important only at $T > 77$ K [11]. This behaviour was reproduced on a second sample (not shown).

The procedure -cooling down to ≈ 17 K, dosing additional ≈ 0.022 ML, T-jump to 21–24 K- was repeated four times, yielding a final overall coverage of $\Theta \approx 0.113$ ML. The temperatures for the observation of diffusion were chosen to 21.6 K, 22.3 K, 22.7 K, 23.0 K and 23.7 K respectively. The spectra obtained directly after dosing at $T \approx 17$ K are displayed in fig. 3. The most obvious feature besides the 2D-lattice gas absorption is the growing low frequency band which shifts to 2276 cm^{-1} with increasing coverage and broadens to $\text{FWHM} \approx 6$ cm^{-1} .

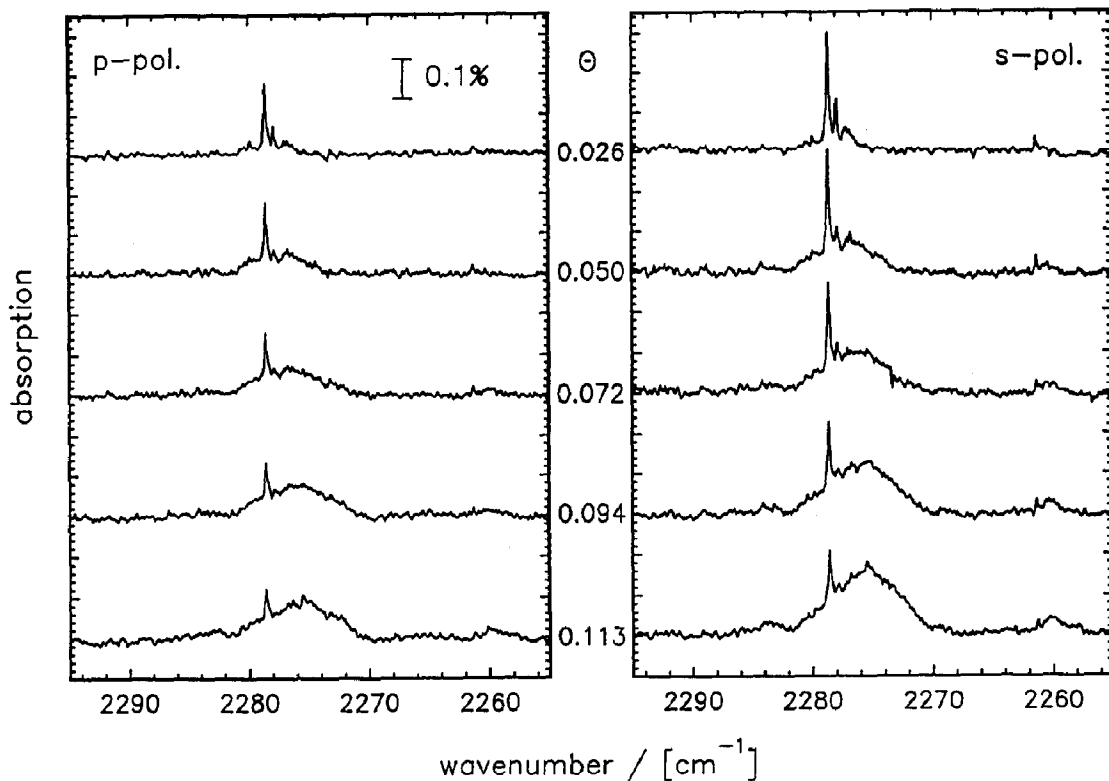


Fig. 3. p- and s-polarized absorption spectra of $^{13}\text{C}^{16}\text{O}_2$ at different coverages and $T \approx 17$ K. A T-jump to $21 \text{ K} < T < 24 \text{ K}$ followed by ~ 1 hour of diffusion at constant T was performed between each pair of spectra. The absorption of minor component $^{13}\text{C}^{16}\text{O}^{18}\text{O}$ in the adsorbate is observed around 2260 cm^{-1} .

After completing the last cycle the sample was heated in steps to 44.3 K, 56.6 K and 66.5 K (fig. 4). The initially broad singlet absorption at 2276 cm^{-1} ($T = 23.0 \text{ K}$) changes into the well known correlation field doublet of extended ordered CO_2 -islands on $\text{NaCl}(100)$ with $\bar{\nu} = 2274 \text{ cm}^{-1}$ and 2283 cm^{-1} ($T \geq 44.3 \text{ K}$). At higher temperatures ($T = 56.6 \text{ K}$ and 66.5 K) the absorption of the 2D-lattice-gas in thermodynamic equilibrium with the islands appears at 2278.8 cm^{-1} . From the temperature dependence of the density of the coexisting 2D-gas the enthalpy of 2D-sublimation was determined to $\Delta H_{\text{sub}}^{2\text{D}} = (3.0 \pm 0.1) \text{ kJ/mol}$ [11].

4. DISCUSSION

The experimental results can be summarized as follows:

a) At 17 K a 2D-lattice gas can be prepared by dosing small amounts of CO_2 -gas with a capillary. The extrapolation of thermodynamic data [16] implies an equilibrium density of $\rho_{\text{coex}}(17 \text{ K}) \approx 2 \cdot 10^{-9} \text{ ML}$ far below the detection limit. Thus this phase must be regarded as strongly supersaturated but metastable due to the low temperature.

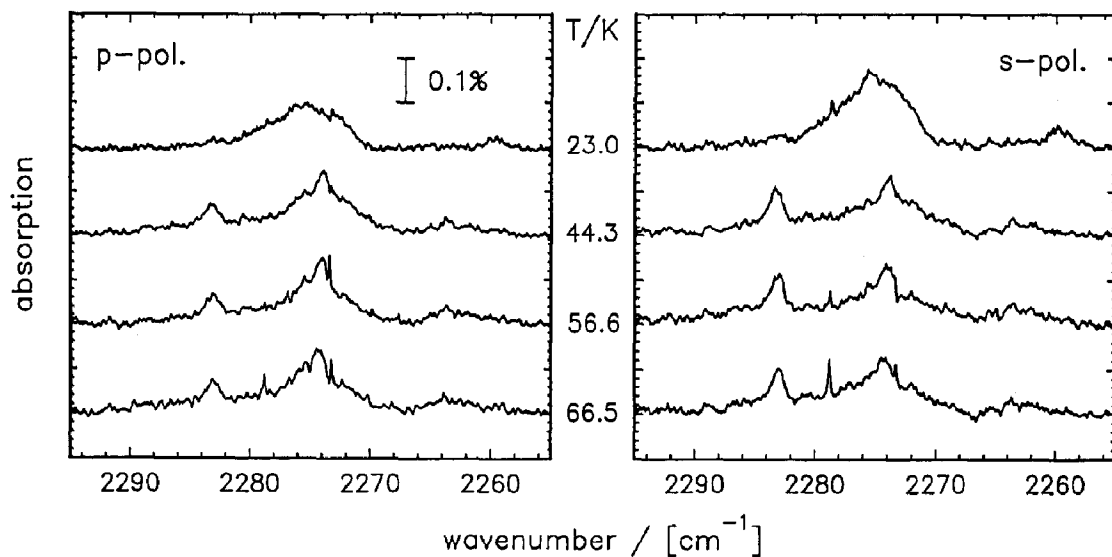


Fig. 4. Spectra of $^{13}\text{C}^{16}\text{O}_2/\text{NaCl}(100)$ at $\Theta \approx 0.113$ and different temperatures, recorded with increasing temperatures.

b) At 21 K - 24 K a decrease of the 2D-gas absorption indicates the onset of surface diffusion followed by forming of disordered clusters and/or capturing of molecules at steps. Both processes -clustering on terrace sites or at steps- are not distinguishable by FTIR-spectroscopy without further efforts. Probably both occurs, depending e.g. on the local terrace size, adsorbate density and nucleation behaviour [17].

c) At 24 K - 44 K ordering of the cluster takes place indicated by the appearance of the correlation field doublet due to islands with the monolayer structure.

4.1. Surface diffusion

Since the spectra give no information about the exact diffusion geometry -only qualitative assumptions can be made about step densities and arrangements- in a first approach one of the simplest 2D-diffusion models will be used for a quantitative evaluation of the data. Under the assumption of

circular terraces of radius r (which is as wrong as assuming a square symmetry for NaCl vacuum cleavage faces [18]) the solution of Fick's second law for the diffusion of initially randomly distributed molecules (concentration $c=c_0$ for $t=0$) to the edges ($c=0$ for $t=\infty$, i.e. all molecules leave the plane) is [19]:

$$c/c_0 = f \cdot \sum_{n=1}^{\infty} 4x_n^{-2} \cdot e^{-x_n^2 D t / r^2} \quad (1)$$

where the x_n are the positive roots of $J_0(x_n) = 0$ and J_0 is the Bessel function of the first kind of order zero. Eq. (1) is valid only in the low coverage limit since it does not conserve mass ($c_\infty = 0$) and requires a coverage independent D . The factor f was introduced to take into account a possible error in the determination of c_0 and yields (1 ± 0.05) in each fit. A least squares fit of eq. (1) to the first set of

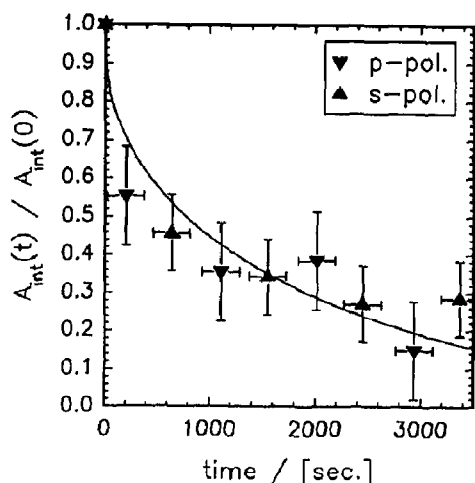


Fig. 5.

Time evolution of the integrated lattice gas absorption at $T=22.7$ K, normalized to the initial amount at $T=17.2$ K (see fig. 1). Vertical error bars are due to integration uncertainties, horizontal bars denote the sampling time (352 sec) for each data point. Its uncertainty is ± 1 sec. Solid line is a least squares fit of eq. (1) to the data.

data is shown in fig. 5, the resulting (corrected) fit parameter D/r_0^2 , including results from the other experiments, are displayed in fig. 6. The correction was made by eq. (2) by taking into account the reduced free area after each cycle due to additional adsorption of $\Delta\theta \approx 0.022$ ML.

$$r^2 = r_0^2(1 - \Delta\theta) \quad (2)$$

Application of the Arrhenius law (eq.(3))

$$\ln \frac{D}{r_0^2} = \ln \frac{D_0}{r_0^2} - \frac{E_{diff}}{RT} \quad (3)$$

yields the barrier for surface diffusion $E_{diff} =$

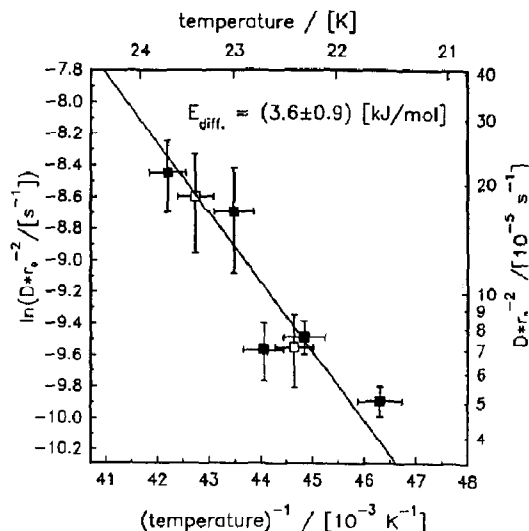


Fig. 6.

Arrhenius-plot of the corrected fit-parameter D/r_0^2 according to eq.(2). Data points marked with open squares were obtained on a second sample. They were shifted by 0.7 K (long time reproducibility and accuracy of temperature is $T \pm 1$ K) for better comparison of the slope and not taken into account for the fit. Vertical error bars denote the standard deviation from the fit of eq.(1), horizontal error bars a relative uncertainty of $T \pm 0.2$ K.

(3.6 ± 0.9) kJ/mol and the preexponential factor of $D_0/r_0^2 = 10^{4.4 \pm 2.1} \text{ s}^{-1}$.

An approximate value for r_0 can be deduced from recent HAS-experiments on UHV cleavage planes of NaCl, where the mean step distance d was found to exceed the transfer width of the instrument of 45 nm [20]. On the other hand with transmission electron microscopy (TEM) on gold decorated vacuum cleavage planes of NaCl a broad distribution of step distances ranging from the lateral experimental resolution of ≈ 4 nm to more than 1000 nm was found [18]. Since our simple model considers uniform terraces the lower limit determined by HAS of $d = 45$ nm ($\rightarrow r = 22.5$ nm) will be used in the

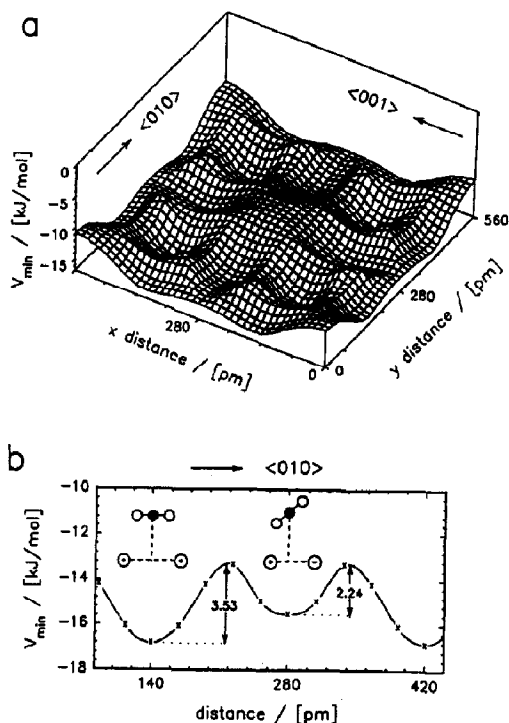


Fig. 7.

a) Potential energy surface for the CO_2 -molecule on $\text{NaCl}(100)$. The origin corresponds to the Cl^- -site whereas Na^+ is located at a distance of 280 nm in either $\langle 010 \rangle$ or $\langle 001 \rangle$ direction from the anion.

b) Projection of the calculated diffusion path onto the $\langle 010 \rangle$ direction. Solid line is a spline curve interpolation of the data. The inserts show the adsorption geometries with minimal potential energy

following to estimate the order of magnitude of D_0 and the attempt frequency ν for surface hopping (eq.(4)):

$$\nu \approx 4D_0\lambda^{-2} \quad (4)$$

with λ being the distance of a single surface hop (\equiv distance between adjacent adsorption sites). Eq. (4) can be obtained from transition state theory by

neglecting activation entropies [21]. For CO_2 on $\text{NaCl}(100)$ is $\lambda = 280$ pm (see below). Thus $D_0 \approx 10^{-6.9 \pm 2.1} \text{ cm}^2 \text{ s}^{-1}$ and $\nu \approx 10^{8.8 \pm 2.1} \text{ s}^{-1}$. D_0 is comparably low but similar values were reported in literature for other adsorption systems, e.g. $\text{Xe}/\text{W}(110)$ or $\text{H}/\text{W}(110)$ (cited in [2]). In comparison with the only TR-FTIR study of a surface diffusion process reported so far (with $\nu = 8 \cdot 10^9 \text{ s}^{-1}$ and $E_{\text{diff.}} = 18.4 \text{ kJ/mol}$ for $\text{CO}/\text{Pt}(111)$ [22]) our results seem to be reasonable since CO adsorbed on metals is stronger bonded with external vibrational modes probably at higher frequencies than CO_2 adsorbed on $\text{NaCl}(100)$ [5,8,11].

In contrast to the large uncertainties in the estimation of the preexponential factor D_0 the diffusion barrier $E_{\text{diff.}}$ is confirmed by theory. Using our model for the determination of the monolayer structure of CO_2 on $\text{NaCl}(100)$ [5] the potential energy surface for a single CO_2 molecule on $\text{NaCl}(100)$ was calculated (fig. 7a). V_{min} was obtained for several (x,y) -points above the crystal surface by optimizing the molecule-surface distance and both the azimuth and the tilt angle, similar to the method used by Lakhlifi and Girardet [23]. The absolute potential minimum with $V_{\text{min}} = -16.85 \text{ kJ/mol}$ was found above the center of the connection line between two adjacent Na^+ ions with the molecular axis parallel to the surface. The structure is displayed in the left insert in fig. 7b and confirmed by the polarization dependence of the submonolayer FTIR-spectra at higher temperatures [11] as well as at lower temperatures (figs. 1,2 and 3). The path with lowest energy between two adjacent minima is shown in fig. 7b. Thus the barrier for surface diffusion was estimated to 3.53 kJ/mol. It has to be mentioned that the used potentials are suitable to reproduce the experimental heats of adsorption of the monolayer [5,11] but not of the lattice gas. The measured value of $q_{\text{st}}^{\text{s}} = (32.4 \pm 1.1) \text{ kJ/mol}$ [11] differs roughly by a factor of two from theory. Therefore the coincidence of experimental and theoretical diffusion barrier should not be overinterpreted since the overall picture is not consistent yet. Due to oversimplifications in the diffusion model and the outlined limits of the potential calculations a larger uncertainty of $E_{\text{diff.}} \approx (3.5 \pm 2) \text{ kJ/mol}$ must be assumed.

A second minimum with $V_{\text{min}} = -15.56 \text{ kJ/mol}$ is

found above the connection line between Na^+ and Cl^- with the CO_2 molecule inclined by 41.2° towards the surface in direction of Cl^- (right insert in fig. 7b). This position is very similar to the observed arrangement in the monolayer structure [5]. The detection of molecules in the local minimum should be possible by capturing at very low temperatures but requires very rapid loss of initial energy since a few jumps during thermal equilibration would force an initial 1:1 distribution in direction of thermal equilibrium. Assuming Boltzmann distribution the population of the local minimum at 17 K is $\approx 10^{-4}$ compared with the absolute minimum. Thus the second narrow band at 2278.0 cm^{-1} in fig. 1 (top spectra) is unlikely to be caused by this adsorption site. On the other hand the amount is expected to be detectable at higher temperatures ($N_{\text{local min.}} \approx 0.15 N_{\text{lattice gas}}$). Normal coordinate analysis predicts for the ν_3 -vibration a redshift by $\approx 1.6 \text{ cm}^{-1}$ with respect to molecules in the absolute minimum. Indeed there is evidence for an additive narrow absorption at higher temperatures ($T = 91 \text{ K}$, $\bar{\nu} = 2277.2 \text{ cm}^{-1}$) [11] but considering the uncertainty of the potential as well as the insufficient noise level in the spectra a more detailed investigation requires theoretical and experimental improvements.

4.2. 2D-cluster growth and ordering

Cluster growth (without distinction between nucleation at ideal terrace sites and step sites) was observed even at 17 K (top spectra in fig. 1). Broad features were detected in the first spectra contributing with 40-50% to the integrated area of the whole absorption. Since the effective defect density on typical crystals found by decoration with CO_2 never exceeded 11% (usually $\approx 8\%$ [11]) this absorption can not be explained by capturing of molecules impinging directly from the gas phase during adsorption. Excluding greater inhomogeneities in the gas flow this initial clustering must have been occurred directly after adsorption, probably during the equilibration time where the heat of adsorption ($q_{\text{a}}^{\text{s}} = (32.4 \pm 1.1) \text{ kJ/mol}$ [11]) dissipates. This allows the molecules to perform a number of surface jumps before being frozen and immobilized in thermal equilibrium with the surface at 17 K. The high

defect density of $\Theta_{\text{def.}} \approx 8\%$ found by decoration with CO_2 yields a 10 nm distance square lattice of steps under the assumption that one NaCl step ion pair causes one defect site ($d \approx 2a_0/\Theta_{\text{def.}}$, $a_0 = 0.4 \text{ nm}$). This is in agreement with the HAS data assuming inhomogeneous step distributions. Highly disturbed areas do not contribute to the diffracted intensity but to the background and therefore line-width analysis of diffraction peaks only give weighted averages of terrace sizes in contrast to the direct decoration method.

Initial clustering at 17 K could explain the reduction of the yielded 2D-lattice gas by $\approx 50\%$ between the first and the last adsorption cycle compared with the overall reduction of the free area of only $\approx 11.3\%$, while equal amounts were dosed in each case.

Between 24.0 and 44.3 K ordering of the clusters takes place. Long range ordering is indicated by the onset of the correlation field, whereas a change in the local adsorbate geometry is indicated by the different polarization dependencies of the spectra. At $T \leq 24 \text{ K}$ a molecular orientation parallel to the surface is observed in contrast to the equilibrium structure at higher temperatures where the molecules are inclined by 34° towards the surface.

The temperature range corresponds to the transition temperature at $\approx 35 \text{ K}$ where crystallisation of amorphous CO_2 was observed [24]. Additionally in previous adsorption experiments with coverages $1 \text{ ML} < \Theta < 1.2 \text{ ML}$ of CO_2 on $\text{NaCl}(100)$ [9,25] a dramatic change in the IR-absorption of the first layer was found reproducible below 40 K. Both give strong evidence for the immobilisation of CO_2 -molecules on top of a CO_2 -layer at $T < 40 \text{ K}$. Thus ordering of the clusters between 24 and 44 K (fig. 4) is favored by first an increased mobility of CO_2 molecules bonded to other CO_2 molecules and second an increased equilibrium density of the 2D-lattice gas phase (e.g. $\rho_{\text{coex.}} \approx 3 \cdot 10^{-5} \text{ ML}$ at $T = 35 \text{ K}$).

Mobility of CO_2 on $\text{NaCl}(100)$ terraces is high at this temperature and does not limit the achievement of surface equilibrium at $T > 35 \text{ K}$, consistent with thermodynamic studies at $45 \text{ K} < T < 100 \text{ K}$ [11]. In contrast referring to adsorption models, the adsorbate has to be regarded as mostly immobile since

the mobile portion of the lattice gas $x_{\text{mob.}} \approx \exp(-E_{\text{diff.}}/RT)$ [12] is $x_{\text{mob.}} < 1.5\%$ at $T < 100$ K. This means that even at the highest temperatures studied the majority of the adsorbed molecules has not enough thermal energy to overcome the diffusion barrier.

Using this results the system $\text{CO}_2/\text{NaCl}(100)$ is expected to fulfill the conditions for immobile adsorbates rather than for mobile adsorption.

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