Adsorption Dynamics of CVD Graphene
Investigated by a Contactless Microwave Method

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Abstract. We use a contactless microwave dielectric resonator gas sensing platform to study the adsorption dynamics of NO\textsubscript{2} gas present in air onto a graphene surface. The use of microwaves removes the need for metal contacts that would otherwise be necessary for traditional conductivity measurements, and therefore allows non-invasive determination of NO\textsubscript{2} concentrations to sub parts per million. As a result, gas–metal interactions and localised graphene doping in the vicinity of metal contacts are eliminated, with the advantage that only graphene–gas adsorbate interactions are responsible for the measured signal. We show that the sensor response for all considered concentrations can be described using a surface coverage dependent Langmuir model. We demonstrate that the possible variation of the NO\textsubscript{2} binding energy, which is frequently considered as the main parameter, plays only a secondary role compared to the rising adsorption energy barrier with increasing NO\textsubscript{2} coverage. The continuous distribution of the properties of the graphene adsorption sites used in the theoretical model is supported by our Kelvin probe and Raman surface analysis. Our results demonstrate that the non-invasive microwave method is a promising alternative platform for gas sensing. Moreover it provides valuable insights towards the understanding of the microscopic processes occurring in graphene based gas sensors, which is a key factor in the realization of reproducible and optimized device properties.

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1. Introduction

Among the many unique properties of graphene [1, 2, 3, 4, 5, 6] its applications for gas sensing has generated a wide range of interest [7, 8, 9, 10]. The charge carriers of graphene, known as Dirac fermions, have high mobilities at room temperature [11] and are highly sensitive to perturbations in the carrier density [6, 12, 13]. Upon the adsorption of p-type (n-type) dopant gas molecules onto the graphene surface, holes (electrons) are donated to the graphene surface changing the sheet conductivity [14, 15, 16, 17, 18, 19, 20, 21]. Consequently graphene molecular sensors have fast response times and high sensitivity, with the potential for single molecular detection [19, 17], and have been shown to be capable of distinguishing chemically similar gas species by analysing the response times [22, 23]. Indeed there are a number of studies that discuss improving the graphene responses by functionalising it [24, 25, 26, 27, 28, 29, 30], optimising the graphene carrier density through field effect transistor devices [31, 32, 33, 34, 35], introducing defects [24, 30, 36, 37, 38, 39], and by studying the binding affinities of graphene and graphene derived 2D materials [36, 40, 41, 42, 43, 44, 45]. Nitrogen dioxide (NO₂) sensors are particularly important for monitoring realistic city pollution levels. According to the World Health Organisations guidelines NO₂ levels should be below 100 ppb per hour [46]. However, levels as high as 0.5 ppm are typical for busy roads [47]. Moreover, higher NO₂ concentration measurements need to be reliably measured in laboratory environments due to their negative toxicological impact even for short term exposure [48]. Graphene based NO₂ gas sensors therefore have to work efficiently for concentrations ranging from ppb values to tens or hundreds of ppm.

Currently used graphene gas sensors require the deposition of metal contacts to probe the conductivity, and it is not clear to date whether the DC electrical signals reported are entirely due to gases perturbing the conductivity of graphene itself, or whether there are large contributions from the metal contacts locally doping the graphene [49, 50, 51] and/or from metal–gas adsorbate charge transfer interactions [52, 53]. To overcome this limitation we use a high Q microwave dielectric resonator perturbation technique [54, 55, 56], where the sheet resistance and conductivity of graphene can be determined without the need for invasive contacts. In our setup the graphene sheet resistance $R_s$ is inversely proportional to the frequency linewidth of a microwave resonator, $\omega$, coupled to the graphene (see supplementary information S1) [55]. Therefore, this technique provides a platform where the signal originates entirely from the graphene–gas adsorbate interaction. With this method we investigate the real time adsorption of NO₂ gas onto chemical vapour deposited (CVD) graphene on a high resistive silicon substrate, and determine how the adsorption dynamics changes as one moves from small (300 ppb) to very large NO₂ concentrations (100 ppm).

The measured time-dependent signal is determined by the rate of adsorption and desorption of NO₂ molecules on graphene. For low NO₂ concentrations the underlying
kinetics of such processes on graphene and carbon nanotubes have been previously studied using Langmuir models [57, 58], where it was shown that for low concentrations the NO$_2$ coverage is dominated by the binding energy at discrete types of adsorption sites [59, 57, 60]. For higher concentrations considered in this study we show that, in addition to the binding energy of NO$_2$ on graphene, the time dependence of the signal is largely determined by the energy barrier for adsorption, which we find to increase continuously with increasing NO$_2$ coverage rather than having a discrete set of constant values.

2. Methods

CVD Graphene was wet transferred [54] onto a high resistance silicon substrate (see supplementary information S2). The graphene sample was coupled to the evanescent field of a microwave dielectric resonator that was enclosed in copper housing. The substrate needs to be relatively insulating to optimise the quality factor of the graphene coupled resonator system - since the semi-metallic nature of graphene is the primary cause of linewidth broadening [55]. The copper housing had holes for gas to diffuse through that were too small for microwave leakage. A vector network analyser (VNA-Anritsu series 37XXXC) was used to measure the TE$_{010}$ mode at approximately 9 GHz. Temperature was controlled to 273 K $\pm$ 2 mK by means of a platinum resistance thermometer and a Conductus LTC20 temperature controller. NO$_2$ gas was diluted using synthetic air and injected into the sensor chamber. Using labview the central frequency, linewidth (full width at half maximum) and temperature were continually measured.

The sensor was exposed to concentrations of 0.3, 1, 3, 10, 50, 100 ppm NO$_2$. After each exposure, the sensor was recovered to a reproducible linewidth value, $\omega_0$, by flowing air over the sensor to promote NO$_2$ desorption. In our case the linewidth was chosen such that $\omega_0 \approx 8.7$ MHz. As a result, the graphene surface was not NO$_2$ adsorbate free, but instead had an easily reproducible partly covered state that did not require thermal treatments. In this way, the stickiest adsorption sites on the surface, which are typically defected regions of graphene [10, 30, 39], are pacified by pre-adsorbed molecules. Additionally, regions of graphene contaminated by PMMA residue from the fabrication procedure [61, 62] or airborne hydrocarbons [63] prevent NO$_2$ adsorption at the occupied site. Consequently, the measured reversible sensor response is predominantly attributed to adsorbates in regions of good quality graphene.

To evaluate the graphene surface quality, Raman spectroscopy measurements were obtained using a Renishaw InVia RM1000 Raman microscope using 514 nm laser of 0.44 mW incident power through a 100 x objective lens. Additionally, Kelvin peak force microscopy (KPFM) measurements were performed using a single pass technique [64] with Bruker’s ICON scanning probe microscope system.
Figure 1: (a) Graphene sensor response for NO\textsubscript{2} adsorption and corresponding resonant linewidth at various concentrations. NO\textsubscript{2} gas is injected into the system at time $t = 0$. Blue dashed lines correspond to the times $t=30$ seconds, 1, 5, 10 and 30 minutes after initial gas injection. Note that the $t=30$ seconds and the $t=1$ minute blue dashed lines on the far left of the graph partly overlap, so that they appear as a single thick dashed line. (b) The long time exposure sensor sensitivity limit is determined by extrapolating the maximum measured change in linewidth, $\Delta$ linewidth, to lower NO\textsubscript{2} concentrations, and comparing this with the noise floor of the measurement system (horizontal blue dashed line). (c) Sensor responses at various times (corresponding to the vertical blue dashed lines of (a)) indicate that the fastest response time occurs around 5 minutes of exposure, since for shorter exposure times there is no systematic increase in the sensor response for increasing NO\textsubscript{2} concentrations.

3. Results Section

The adsorption sensor response is defined as the change in linewidth upon gas exposure for a given time, $t$, normalised by the initial linewidth, $S(t) = (\omega(t) - \omega_0)/\omega_0$. It should be noted that $\omega_0$ needs to be consistent for all measurements as shown in the supplementary information S3. Figure 1a shows the sensor response and corresponding linewidth for NO\textsubscript{2} concentrations ranging from 0.3 to 100 ppm. In figure 1b the sensor sensitivity is determined by extrapolating the maximum change in linewidth on a natural log-log plot to the value corresponding to the minimum discernible signal (MDS). This allows an estimate of the long term sensitivity to the value of $\sim 90$ ppb. It should be noted that this value can be further improved upon by reducing the noise in the system via better graphene—resonator coupling and by optimising the cavity geometry. As a matter of notation the square brackets indicate the concentration of the species they enclose. To evaluate the fastest detection timescale capable of NO\textsubscript{2} concentration differentiation, the sensor responses at specific times (given by the dashed blue lines in figure 1a) are extracted as shown in figure 1c. Similar to figure 1b, the data can be fitted by a straight line on a natural log-log plot. After 30 s and 1 minute it is impossible to...
distinguish between the different NO$_2$ concentrations, as shown visually in figure 1c by
the horizontal lines of best fit. However after 5 minutes of exposure, the lines of best fit
have an appreciable gradient and the concentrations can be distinguished.

The sensor response curves from figure 1a can be fitted using a double exponential
expression for each NO$_2$ concentration as follows:

$$S(t) = S_e \left(1 - (1 - \alpha) \exp \left\{ -\frac{t}{\tau_1}\right\} - \alpha \exp \left\{ -\frac{t}{\tau_2}\right\}\right),$$  \hspace{1cm} (1)

where $S_e$ is the sensor response at equilibrium ($t \to \infty$), $\alpha$ determines the relative
weight of the two exponents, and $\tau_{1/2}$ are the associated time constants. Without loss
of generality we order them as $\tau_1 \leq \tau_2$, so that $\tau_1$ ($\tau_2$) corresponds to the fast (slow)
component of the sensor response. Interestingly, the fast time constant ($\tau_1$) is about
an order of magnitude smaller than the slow time constant ($\tau_2$). We note that the data
cannot be fitted with a single exponential, as we show in section S4 in the supplementary
information, while for two exponents the agreement with the experimental data is very
good (figure 1a). Figure 2 shows the values of the parameters in equation (1) fitted to
the experimentally measured NO$_2$ concentrations, $n_G$. For increasing $n_G$ the value of
$S_e$ increases, and the time constants $\tau_{1/2}$ decrease. The value of $\alpha$ is about 1 for small
$n_G$, and decreases for larger concentrations, which shows that while for small $n_G$ the
data has predominantly single-exponential behavior, for larger $n_G$ the second exponent
plays an increasingly important role. Note that while equation (1) fits the data well,
the underlying relation between this equation and the corresponding parameters with
the microscopic kinetic processes of NO$_2$ adsorption and desorption on graphene is not
clear. We will outline this relation later in this section, and also address the origin of
the emergence of two distinct time constants.

In figure 1a it can be seen that the difference in the slopes of the curves at various
concentrations decreases as time progresses. This slope corresponds to the rate of
adsorbate formation, which is approximately proportional to the time derivative of the
sensor response. We can approximate this as $dS(t)/dt = k(t) [\text{NO}_2]^{y(t)} [\text{Gr}^*]^{z(t)}$, where
Gr$^*$ represents a free graphene binding site, and where we denote $k(t)$ as the effective
time-dependent rate constant, and $y(t)$ and $z(t)$ as the partial time-dependent reaction
orders. The knowledge of the partial reaction orders in chemical kinetics is useful in
determining how reactants interact and aids in the understanding of the chemical mech-
anism. For NO$_2$ gas sensing the value of the time-dependent effective reaction order with
respect to [NO$_2$], $y(t)$, indicates how responsive the sensor is to changes in NO$_2$
concentrations, where larger values indicate better sensitivity. The value of $y(t)$ is obtained by
taking the natural logarithms of the rate equation

$$\ln \frac{dS(t)}{dt} = \ln k(t) + z(t) \ln [\text{Gr}^*] + y(t) \ln [\text{NO}_2],$$ \hspace{1cm} (2)

and extracting the time derivative of the sensor response at each time step. Note that
Figure 2: Parameters in equation (1) fitted to the experimental data in figure 1a: (a) equilibrium sensor response, $S_e$, (b) relative weight of the two exponentials, $\alpha$, and (c) time constants $\tau_1$ (black squares) and $\tau_2$ (red circles). Solid points indicate the parameters fitted to the experimental data directly, while the dashed lines correspond to fits to the theoretical model.

to obtain a smooth result we approximate the experimental data with the empirical fit with two exponentials (equation (1) and figure 1a). For every time-step $t$ we then plot the logarithm of these results as a function of $\ln[NO_2]$ (figure 3a), so that according to equation (2) the slope of the linearized curve is then equal to $y(t)$.

As can be seen from figure 3a, for each time-step the resulting logarithm of the rate increases approximately linearly as a function of $\ln[NO_2]$, indicating the validity of the above equation. The resulting time-dependent $y(t)$ is shown in figure 3b, where it can be seen that for the initial adsorption the effective reaction order is about 0.7. To put it in context, a reaction order of 1 defines a system where the rate is proportional to the concentration of NO$_2$, such that doubling the amount of NO$_2$ molecules also doubles the rate. In contrast, a partial reaction order with respect to NO$_2$ of 0 implies that the rate is independent of the NO$_2$ concentration. After approximately 35 minutes the reaction order is significantly reduced, indicating an initial rapid adsorption of NO$_2$ followed by a slower adsorption. In other words as the adsorption reaction proceeds, the probability to adsorb further NO$_2$ molecules is decreased for increasing surface coverage. As shown in figure 1, the graphene sensor is capable of reliably distinguishing the NO$_2$ concentration within 5-35 minutes, which occurs during the initial rapid adsorption phase.

The observed double exponential behavior with two time constants typically describes an adsorption process that requires an initial fast adsorption event, followed by a slow adsorption event, which can be due to the presence of two distinct types of adsorption sites on the surface [65] or due to a system limited by interparticle diffusion [66, 67].

To investigate the possibility of two discrete adsorption sites on our graphene we characterize the surface quality of the CVD graphene sensor using Raman spectroscopy.
and KPFM measurements. Figure 4a shows a typical CVD graphene Raman spectrum of the sample studied. The inset is a map of the G/2D peak intensity, where a value slightly less than 0.5 is indicative of monolayer graphene.[68] This can be seen clearly in the histograms of figure 4c and d. Figure 4b utilizes the vector analysis method described by Lee et al. [69]. Here the red line and orange line are vectors in the Pos G-Pos 2D space associated with tensile strain and doping effects respectively. The term Pos is used to indicate Raman peak position. The sample studied is shown to be slightly strained compared to pristine graphene (green marker [69]) but more interestingly the distribution aligns better with the doping vector. This is attributed to residual NO\textsubscript{2} molecules on the surface and PMMA residue from the wet transfer fabrication procedure p-doping the graphene. Fortunately, PMMA is a low loss material present at an unchanging low surface coverage (see AFM images in section S5 in the supplementary information). As such, its presence doesn’t overtly influence the microwave measurement. However, its presence does p-dope graphene in the local vicinity which will affect the graphene conductivity. Fortuitously, any enhanced NO\textsubscript{2} adsorption on graphene in the vicinity of PMMA residues is pacified by ensuring that the initial linewidth of the sensor is consistent for every measurement as described in the Methods section. Figure 4c correlates the FWHM of the 2D peak with its corresponding G/2D peak ratio. This co-localisation method shows that the majority of the monolayer graphene pixels measured correspond to graphene with a FWHM less than 40, which can be indicative of good quality graphene.[70] It should be noted that narrow lorentzian shaped 2D peaks can also be confused with few layer turbostratic graphene[71] therefore it is important to analyze FWHM of the 2D peak in the context of regions of monolayer graphene. [70]. The G/2D peak intensity histogram (figure 4d), in conjunction with the 2D histogram of figure 4c, clearly shows a continuous distribution, where the average G/2D peak intensity ratio is slightly less than 0.5. This is attributed to the sample being slightly p-doped as charge doping is known to enhance (decrease) the G (2D) peak intensity such that the G/2D peak is still indicative of monolayer graphene[72, 73]. Similarly, the
Figure 4: Surface characterisation of CVD graphene wet transferred onto a silicon substrate. (a) Representative graphene spectrum, inset 20 x 10 μm Raman intensity map of the G/2D peaks. 2D histograms of (b) the 2D vs G peak position and (c) the G/2D intensity ratio vs the 2D peak full width at half maximum. The green marker at (1581.6, 2676.9 cm\(^{-1}\)) is the value reported for suspended exfoliated graphene [69] showing only a slight increase in doping and strain of the graphene sheet which is expected for large scale wet transferred CVD graphene. 1D histograms of the (d) G/2D ratio (e) D/G ratio and (f) G peak position. (g) KPFM microscopy surface potential map and (h) corresponding histogram. D/G intensity histogram (figure 4e) also shows a continuous distribution around 0.35 indicative of low defect concentration [68]. Similarly, the G peak position histogram (figure 4f) also shows a continuous distribution; where the G peak position is sensitive to doping [68, 71]. For completeness, a full set of Raman maps of graphene are shown in the supplementary information S6.

The surface potential map of monolayer graphene and the corresponding histogram (figure 4g,h) show that despite domains of graphene of different work function, the overall distribution of states is continuous. Naturally defects/discontinuities in monolayer graphene coverage only broaden the distribution of energy states available on the graphene surface. Interestingly, due to a charge screening effect [74], multilayer regions of graphene are less doped due to interactions with the substrate. However, multilayers are not prevalent on the surface and their presence only skews the normal distribution of the surface potential histogram (as shown in figures S6 and S7 in the supplementary information S5). To summarise, the surface characterisation results show no obvious bimodal behaviour indicating two distinct adsorption sites, but rather a continuous variation of properties across the surfaces. Therefore these findings do not support the interpretation that the double exponential fit of the sensor responses (equation 1 and figure 1a) are due to two discrete types of adsorption sites.
4. Discussion

To understand the origins of the sensor response on graphene, first the effective NO$_2$ adsorption reaction on the surface is considered where

$$\text{NO}_2(g) + \text{Gr}^* \rightarrow \text{NO}_2\text{-Gr(ads)}. \quad (3)$$

This relation describes a NO$_2$ gas molecule combining with a graphene adsorption site, Gr*, to form an adsorbate species on the surface with a binding energy $E_B$. Equation (3) is an effective adsorption reaction, which can implicitly include the displacement of any pre-adsorbed species. If a different molecule, such as O$_2$ or N$_2$, is initially already bound to the Gr* binding site, this process involves a displacement reaction with the pre-adsorbed molecule by NO$_2$. Since the binding affinity of NO$_2$ is larger than that of O$_2$ and N$_2$ [75], such a replacement reaction is thermodynamically favored. In general therefore for this adsorption process to occur it is necessary to overcome an activation barrier $E_A$ [76], as illustrated schematically in figure 5a. If the surface is exposed for a given time to air with a set concentration of NO$_2$ molecules, $n_G$, then the fraction of Gr* sites occupied by NO$_2$ molecules, $n(t)$, is determined by the rate of adsorption and desorption. This process can generally be described using a modified Langmuir model [77, 78, 79]

$$\frac{dn}{dt} = n_G k_A(n) (1 - n) - k_D(n) n \quad (4)$$

where the first term on the right-hand side describes the NO$_2$ adsorption rate on an available Gr* sites, and is proportional to $n_G$ and to the probability of finding a free Gr* site, given by $1 - n$. The proportionality factor is denoted as the sticking coefficient, $k_A(n)$, and is in general a function of $n$. The second term in the equation is the rate of desorption, and is proportional to $n$, with the proportionality factor $k_D(n)$ denoted as the desorption coefficient. The Langmuir adsorption model describes the changes in the adsorbate concentration as a dynamical process determined by the adsorption and desorption of molecules. The sticking coefficient is a key parameter, which describes the probability of an impinging molecule sticking to a surface. The desorption coefficient on the other hand describes the probability that an adsorbed molecule desorbs from the surface in a given time. Most studies of graphene gas adsorption set $k_A$ equal to either a single discrete value or to a few distinct values, which vary with gas concentration. [57, 58, 59, 60] In contrast, we find that it is more realistic to model the sticking coefficient as a continuous function of adsorbate surface coverage.

The sensor response signal, $S$, mainly depends on the number of NO$_2$ adsorbates on the surface, and on the probability of these NO$_2$ molecules accepting a graphene electron.
For a given $n$ we can then write $S$ in general terms as $S(n) = c(n) \cdot n$, where $c(n)$ is the function that determines how much the linewidth changes for a given NO$_2$ surface coverage. As outlined in the introduction, $S$ is approximately equal to the relative decrease in resistance of the graphene sheet (see supplementary information section S1 and S3). This is determined by the changes in graphene carrier density due to the charge transfer from each NO$_2$ molecule, as well as by the related changes in mobility. Since these quantities are not yet directly accessible in the microwave contactless experiments, the function $c(n)$ is unknown. Therefore, the theoretical model to describe the time-dependent sensor response needs to be formulated directly in terms of $S$ rather than $n$. As shown in detail in section S7 in the supplementary information, we can reformulate equation (4) in terms of $S$ rather than $n$ as

$$
\frac{dS}{dt} = n_{c} \cdot k_{A,S}(S) \cdot (1 - S) - k_{D,S}(S) \cdot S, \tag{5}
$$

by replacing the molecular sticking and desorption coefficients with effective $S$-dependent coefficients. The relation between these effective coefficients and $k_{A}(n)$, $k_{D}(n)$ and $c(n)$ is given in equations S25 and S26 of the supplementary information, which determine how for a given $k_{A,S}(S)$, $k_{D,S}(S)$ and $c(n)$ the values of $k_{A}(n)$, $k_{D}(n)$ vary. For a given $k_{A,S}(S)$ and $k_{D,S}(S)$ we then obtain $S(t)$ by numerically solving the differential equation (5). As outlined in detail in section S7 of the supplementary information, we determine the functional form of $k_{A,S}(S)$ and $k_{D,S}(S)$ by using trial functions, and evaluating for which the resulting $S(t)$ best fits the experimental data. Note that for this fit we only use the data at 0.3 ppm and 100 ppm, which we denote as training data set. We then use the other data sets at 1, 3, 10 and 50 ppm as test data sets to verify the quality of the model. As shown in section S7 of the supplementary information, following this procedure we find that in order to describe the experimental data $k_{A,S}(S)$ needs to be an exponentially decaying function of $S$, which we expand in general terms as

$$
k_{A,S}(S) = \sum_{i=1}^{i_{\text{max}}} \tilde{k}_{A,S,i} \cdot e^{-\tilde{\alpha}_{i} \cdot S}, \tag{6}
$$

with $\tilde{k}_{A,S,i}$ and $\tilde{\alpha}_{i}$ the $i_{\text{max}}$ parameters to be fitted to the experimental training data set. For $k_{D,S}(S)$ on the other hand we find that its exact functional form is not critical for these experiments. To illustrate this we present the results for a constant $k_{D,S}(S)$, as well as for a monotonically increasing trial function $k_{D,S}(S) = k_{D,S,0} + k_{D,S,1} \cdot (1 - e^{-\beta_{1} \cdot S})$, with parameters $k_{D,S,0/1}$ and $\beta_{1}$, and show that the resulting $S(t)$ is largely identical.

Fitting this model to the experimental training data set we find good overall agreement for the time-dependent sensor response for $i_{\text{max}} = 2$, as shown in figure 5b-d (see figure S9 in the supplementary information for a detailed comparison). The quality of the
fit is similar for both the constant $k_{D,S}(S)$ as well as for the monotonically increasing function. The agreement is slightly improved in this second case, but the difference is too small to determine the exact shape of $k_{D,S}(S)$. We note that during the experimental desorption process, where NO$_2$ admixing into the air flow is stopped, it is found that the desorption of NO$_2$ is initially fast, and then proceeds at a much lower rate (see figure S4 in the supplementary information), which is indicative of $k_{D,S}(S)$ going towards 0 as $S$ goes to 0, as we find for our non-constant $k_{D,S}(S)$ (black curve in figure 5c). Overall these results show that the adsorption behavior is dominated by the exponentially decreasing $k_{A,D}(S)$, while $k_{D,S}(S)$ plays a secondary role.

For $n_G=3$, 10 and 50 ppm there are minor deviations of up to about 25% between theory and experiment, which we ascribe to the slightly varying experimental graphene sheet conditions across the different measurement runs (see figures S3 and S10 in the supplementary information). We attribute these slight deviations to varying molecular coverage of the graphene surface at $t = 0$ for each NO$_2$ concentration. For each measurement the initially present NO$_2$ molecules are expected to be bound to different random initial binding sites. Moreover, since O$_2$ is also a p-doping gas [75], the relative initial ratio of adsorbed O$_2$ and NO$_2$ molecules can vary even for the constant initial resistance that we use, and this variability in the ratio will slightly influence the measured time-dependent sensor response. Based on this comparison with the ideal model data we can therefore estimate the variations in the experimental sensor response for a specified amount of NO$_2$ to be below about 25%.

We now outline our proposed physical origin of the found exponential decrease of the effective sticking coefficient with increasing NO$_2$ coverage in the context of transition state theory (TST). Within TST chemical reactants must have sufficient energy to overcome an energy barrier to become a product. Therefore, for a NO$_2$ molecule to bind to the graphene surface, the impinging molecule must have enough thermal energy to overcome the activation energy of binding, $E_A$, so that one has $k_{A,S} \propto \exp\{-E_A/k_BT\}$ [76, 80, 81, 82], where $k_B$ is the Boltzmann constant and $T$ the temperature. In general $E_A$ can depend on $n$, and with respect to the lowest order one can assume a piece-wise linear dependence, as described by the Elovich equation [80]. Therefore, we attribute the observed exponentially large reduction in $k_{A,S}$ with increasing NO$_2$ concentrations to gradual increases in $E_A$. This increase of the average $E_A$ with increasing $n$, and equivalently $S$, has a number of origins. Since NO$_2$ molecules are negatively charged upon adsorption on graphene, they repel each other, which is expected to lead to an increase $E_A$ with increasing $n$. Furthermore, after the initial exposure to NO$_2$ the binding sites with small activation barriers are statistically more likely to be occupied first, while as time progresses more binding sites with increasingly large $E_A$ need to be occupied. figure 5a schematically illustrates potential binding pathways of an incident NO$_2$ molecule. If a binding site Gr$^*$ is free, then $E_A$ is approximately 0, while for other sites $E_A$ is the energy barrier required to displace a pre-adsorbed molecule.
Figure 5: (a) Schematic representation of the possible NO$_2$ adsorption pathways, emphasizing a graphene surface with a range of different adsorption activation energy barriers to be overcome for successful molecular adsorption. (b) Sticking and (c) desorption coefficients obtained by fitting the experimental sensor response at 0.3 and 100 ppm to equation (5). (d) Comparison of the resulting theoretical $S(t)$ (equation (5)) with the experimental results for all measured NO$_2$ concentrations. Solid black curves are for non-constant $k_{D,S}(S)$, while dashed green lines are for a constant $k_{D,S}(S)$. The light brown lines correspond to the experimental data, and are in good agreement with the theoretical results for all considered NO$_2$ concentrations.

Note that as outlined above, the function $k_{A,S}(S)$ effectively takes into account of the fact that the sticking coefficient depends both on coverage, $n$, and of the position on the graphene surface, which we can describe by an effective one dimensional variable, $x$. In the supplementary information section S7.1 we show that instead of expressing the sticking probability as a function of $S$ or $n$, it is equally possible to expand it as a position dependent quantity in terms of $x$, $k_{A,S}(x)$. Both approaches include the effects of surface inhomogeneities as well as effective interactions between adsorbed molecules in the single effective variable. We find that $k_{A,S}(x)$ is an exponentially decaying function of $x$, in analogy to what is found for $k_{A,S}(S)$, showing that both models reflect the same underlying physical phenomenon. For this position dependent model we also investigate the possibility of subdividing the surface in a set of discrete areas, corresponding to possible discrete different adsorption sites. We find that the agreement to experiment less good, and that it improves as we use an increasing number of sites, until we reach a distribution that approximately follows the continuous exponentially decaying function (see figure S9 in the supplementary information).

These results show that the adsorption process is not dominated by a small number of adsorption sites with distinct and constant properties, but rather that the properties of the adsorption sites are continuously varying over the surface and with increasing coverage. This agrees with the experimental surface characterization results showing
a continuous distribution of properties. The often found double exponential behavior in the sensor response (equation 1 and figure 2) is usually ascribed to the existence of two chemically different binding environments, which is in contrast to our results for the graphene surface. Our findings are therefore of benefit for the whole sensor field, and represent an important step in the understanding of the microscopic mechanism of graphene based gas sensing. In fact, we can apply equation (1) to fit the theoretical results for \( S(t) \) with a double exponential, and find a good agreement of the fitted \( S_e, \alpha, \) and \( \tau_{1/2} \) with the ones obtained when the fit is done directly to the experimental data (figure 2). Similarly, the effective reaction order (equation (2)) resulting from the theoretical \( S(t) \) also agrees well with experiment (figure 3c). This shows that our model leads to the experimentally observed time dependent sensor response of seemingly double-exponential form, but that the underlying physical origin is not due to the presence of two distinct adsorption sites with constant properties, but that it is mainly due to the fact that the sticking coefficient decreases exponentially with increasing coverage in a continuous way.

5. Conclusion

Since the use of microwaves to probe the adsorption of gas species on graphene does not require electrical contacts, it is possible to directly probe the adsorption of NO\(_2\) molecules on graphene without ambiguity from metal–gas interactions. We show that the NO\(_2\) adsorption occurs in two distinct regimes, a fast initial adsorption followed by a slower process, and find that the most effective operation window for gas sensing measurements is found for 5-35 minutes of exposure. The upper exposure sensing limit is limited by the adsorption kinetics, while the sensitivity and minimum sensing time are determined by the noise in the system and by the graphene–resonator coupling. We expect that future optimization of these factors will further reduce the sensitivity limit and minimum exposure time for gas sensing. We present a model that relates the sensors response to the adsorption and desorption kinetics of NO\(_2\) on graphene. A key finding is that the molecular sticking probability decreases exponentially upon increasing NO\(_2\) surface occupation, which we ascribe to an increase of the adsorption energy barrier with increased NO\(_2\) surface coverage. We find that the properties of the binding sites vary continuously on the graphene surface, rather than being clustered around discrete values, which is in good agreement with the surface characterisation results.

These results show that non-contact microwave graphene gas sensing provides an ideal platform both for a practical sensor application as well as for measuring fundamental graphene–gas interactions. There is great potential for further improvements of sensitivity and response times, and it naturally allows for incorporation of further degrees of freedom, such as applied electric fields and varying temperatures.
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