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## Temperature-Dependent NO<sub>2</sub> Sensing Mechanisms over Indium Oxide

Sergio Roso<sup>a, b</sup>, David Degler<sup>c</sup>, Eduard Llobet<sup>a</sup>, Nicolae Barsan<sup>c</sup>, Atsushi Urakawa<sup>b, \*</sup>

<sup>a</sup> Minos-Emas, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Spain

<sup>b</sup> Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 Tarragona, Spain

<sup>c</sup> Institute of Physical and Theoretical Chemistry (IPTC), University of Tuebingen, Auf der Morgenstelle 15, D-72076 Tuebingen, Germany

\* Corresponding Author: [aurakawa@iciq.es](mailto:aurakawa@iciq.es)

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### Abstract

The surface species responsible for NO<sub>2</sub> gas sensing over indium oxide was studied by *operando* DRIFTS coupled to a multivariate spectral analysis. It revealed the important roles of surface nitrites on the temperature-dependent gas sensing mechanism and the interaction of such nitrites with surface hydroxyls. A highly hydroxylated surface with high concentration of surface adsorbed H<sub>2</sub>O is beneficial to enhance the concentration of adsorbed NO<sub>2</sub>, present as nitrites, thus explaining superior sensing response at lower operating temperatures.

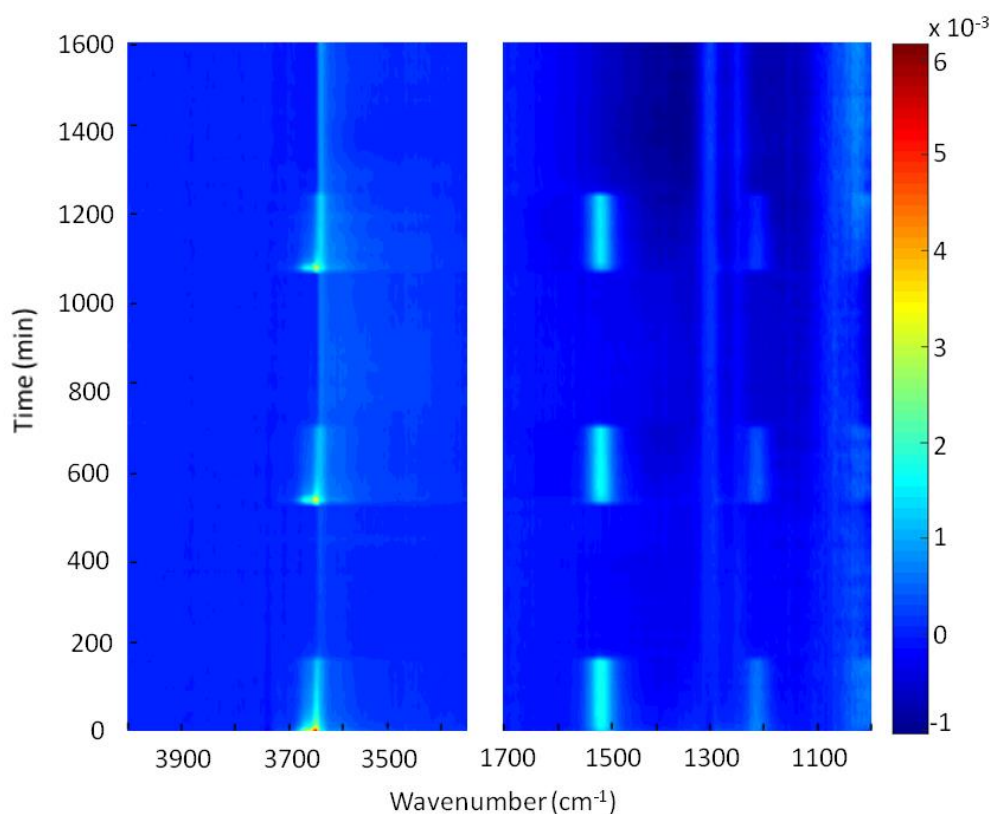
Indium oxide ( $\text{In}_2\text{O}_3$ ) has been recognized as an excellent material for the detection of oxidising gases such as  $\text{NO}_2$  and  $\text{O}_3$  through electrical resistance measurements with excellent sensitivity at the concentration in a ppb range at low temperature and even in the presence of humidity.<sup>1</sup> Some studies on  $\text{NO}_2$  sensing by  $\text{In}_2\text{O}_3$  proposed a surface vacancy based model in which oxygen vacancies act as the active adsorption sites of  $\text{NO}_2$ , further reducing it to  $\text{NO}$  and increasing adsorbed oxygen species.<sup>2</sup> As temperature increases, the amount of adsorbed oxygen species also increases as verified by XPS.<sup>3</sup> At the typical operating temperatures of 150-400 °C, the predominant species on the surface of  $\text{In}_2\text{O}_3$  gas sensors are reported to be oxygen species, either  $\text{O}_2^-$  or  $\text{O}^-$  arising from  $\text{NO}_2$ . An increase in the amount of ionosorbed oxygen species further increases the number of electrons trapped via the conduction band of the n-type indium oxide semiconductor and this translates in the observed increase in the sensor resistance. However, these results are not based on direct observation and cause controversies in the sensing mechanism. An ideal approach for the mechanistic study is a direct measurement of surface species under working, *operando*, conditions where electrical resistance is measured simultaneously to clarify the interaction of  $\text{NO}_2$  with  $\text{In}_2\text{O}_3$  surface and establish firmly the relationship between surface structure/species and gas sensing response.

This work aims at shedding light on the sensing mechanism of  $\text{In}_2\text{O}_3$  towards  $\text{NO}_2$  and its temperature dependencies by surface-sensitive diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) under *operando* conditions. The demanding and difficult spectral analyses of complexly overlapping IR bands were facilitated by multivariate analysis, specifically multivariate curve resolution (MCR),<sup>4, 5</sup> to allow spectral separation, extracting subtle spectral changes and obtaining respective concentration profiles without *a priori* knowledge and reference spectra of surface species as required in the evaluation using linear spectral combination or principal component analysis as demonstrated for the spectral analyses of IR and X-ray spectroscopy.<sup>6, 7, 8</sup>

#### *Operando DRIFTS and sensing mechanism at 350 °C*

First, we performed an *operando* DRIFTS study of the  $\text{In}_2\text{O}_3$  sensor exposed to 1 ppm of  $\text{NO}_2$  at 350 °C (Figure 1). The experiment consisted of three cycles of 3 h of  $\text{NO}_2$  exposure followed by 6 h recovery in dry air. Figure 2f shows the electrical resistance of the  $\text{In}_2\text{O}_3$  sensor under the periodic  $\text{NO}_2$  exposure. Despite the relatively low response (ca. 1.28) as gas sensor, the electrical response was excellent with an outstanding signal-to-noise ratio. The time-resolved DRIFT spectra (2D plot) of the entire experiment (Figure 1) show the presence of the bands obviously responding to the  $\text{NO}_2$  in the gas atmosphere (at ca. 1220, 1520 and 3630  $\text{cm}^{-1}$ ) and of those continuously growing (at ca. 1300 and 3630  $\text{cm}^{-1}$ ). These spectral changes clearly

indicate that there are nitrites and/or nitrates and also hydroxyl groups on/near the  $\text{In}_2\text{O}_3$  surface which are involved in the reception of  $\text{NO}_2$ . However, the common difficulty encountered in the analysis and interpretation is that the spectral features of some chemical species are overlapping, rendering them difficult or often impossible to correctly identify them by the naked eye. Therefore, we have employed a multivariate analysis, particularly MCR, to disentangle the overlapping bands and to determine their concentration profiles based on the kinetic resolution of comprising bands.<sup>9</sup>

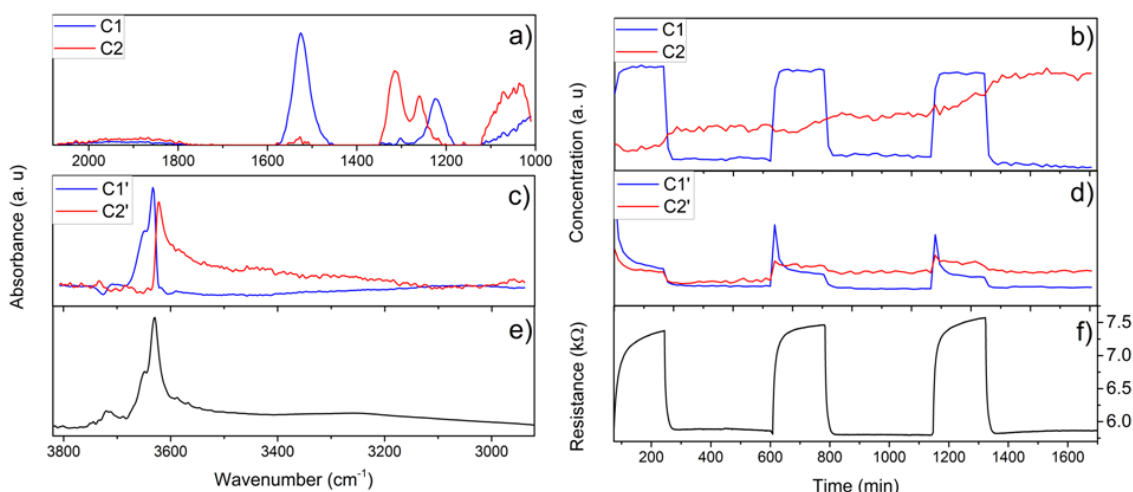


**Figure 1:** Time-resolved DRIFT spectra of the  $\text{In}_2\text{O}_3$  gas sensor under alternating exposure to 1 ppm of  $\text{NO}_2$  (3 h) and air (6 h) at 350 °C. The scale is in the unit of absorbance and the spectra are shown taking the state of the sensor in air before the  $\text{NO}_2$  exposure as the background.

The MCR analysis identified that the system comprises two surface chemical species (or two chemical states with multiple surface species) with varying distinct concentrations under the  $\text{NO}_2$  exposure and subsequent recovery phases. These chemical species are now called “components” and simply denoted as “C” with a label 1, 2, etc. (i.e. C1, C2 for 1000-2000  $\text{cm}^{-1}$  and C1’ and C2’ for 2900-3800  $\text{cm}^{-1}$ ; the numbering has no meaning and there is no intended relation between CN and CN’ (N=1,2)).

Figures 2a and 2b present the *operando* DRIFT spectra of C1 and C2 and corresponding concentration profiles which are shown on the same time-scale as that of the gas sensing response (Figure 2f). It should be noted that MCR yielded the component

spectra and concentration profiles directly from the time-resolved DRIFT spectra shown in Figure 1 and the spectra can be reconstructed by multiplying the component spectra and concentration and summing up all component contributions. Two prominent bands at 1221 and 1524  $\text{cm}^{-1}$  were detected for C1, whereas for C2 clear bands were observed at ca. 1050, 1260 and 1313  $\text{cm}^{-1}$ . Generally, asymmetric N-O stretching vibrations of nitrites and nitrates are reported to appear in the range of 1200-1500  $\text{cm}^{-1}$ . Nitrates and nitrites adsorbed over various surfaces have been extensively studied and there is profound knowledge on their vibrational modes and frequencies. However, unfortunately, the assignments and observed frequencies are diverse; one can find almost any assignment one wishes to have in the literature. It has been reported that depending on the location of the nitrate ions, i.e. surface, sub-surface or bulk, the vibrational frequencies vary<sup>10</sup> and this factor besides potential intermolecular interactions among adsorbates or with surface chemical groups (e.g. hydroxyl) may further complicate firm band assignments. For these reasons, herein we have attempted to assign the vibrational modes based mainly on the experimental observation and indications by quantum chemical calculations with minimal reference to available literature.



**Figure 2:** a) and c) Component spectra and b) and d) concentration profiles obtained after the MCR analysis of the time-resolved DRIFT spectra shown in Figure 1 for the  $\text{In}_2\text{O}_3$  gas sensor exposed at 350 °C under periodic exposure to 1 ppm  $\text{NO}_2$ . e) Hydroxyl bands identified in the  $\text{H}_2\text{O}/\text{D}_2\text{O}$  exchange experiment (alternatingly passing 10%  $\text{H}_2\text{O}/\text{D}_2\text{O}$  vapor over the sensor). The spectrum is shown taking the sensor state in  $\text{D}_2\text{O}$  as the background. f) Response of the sensor towards 1 ppm of  $\text{NO}_2$  gas at 350 °C.

The main characteristic IR-active vibrations of isolated nitrate and nitrite ions are asymmetric stretching modes (Figure S2, Supporting Information). Due to the symmetry of the ions, nitrate ion has the degenerate states for the vibrational mode at 1476  $\text{cm}^{-1}$ , while nitrite ion has one state at 1374  $\text{cm}^{-1}$  according to the quantum chemical calculation. In one literature, the frequencies of 1380 and 1260  $\text{cm}^{-1}$  are reported for free nitrate and nitrite ions, respectively.<sup>11</sup> Despite the large difference in

the numbers, it is consistent that the vibrational frequency of the stretching mode is about  $100\text{ cm}^{-1}$  higher for nitrate. Based on this, it is reasonable to conclude that the band at  $1221\text{ cm}^{-1}$  of C1 is assigned to nitrite species and the two bands observed at  $1260$  and  $1313\text{ cm}^{-1}$  of C2 are due to nitrate species with non-degenerated vibrational states because of a specific spatial orientation of the adsorbed ion on the surface. The prominent band at  $1524\text{ cm}^{-1}$  could be assigned to nitrates or nitrites according to the literature<sup>11</sup>, but here we assign that the band is due to the surface hydroxyls directly interacting with nitrite species as discussed later.

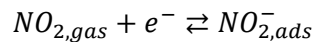
The concentration profiles of C1 and C2 clarify important insights into the surface species involved during gas sensing. The concentration of C1, assigned to surface nitrite species, responds clearly and reversibly to the gaseous  $\text{NO}_2$  concentration, matching well with the sensor response (Figure 2f). In contrast, the concentration of C2 responds irreversibly with a gradual, step-wise increase during the  $\text{NO}_2$  pulse. These observations imply that the reversibly adsorbed surface nitrite species is responsible for the change in the resistance of the sensor, whereas nitrate species is formed gradually during the  $\text{NO}_2$  pulse, likely due to slow oxidation of surface nitrites because of the low  $\text{NO}_2$  concentration at  $350\text{ }^\circ\text{C}$  to form surface, sub-surface and bulk nitrates, which cannot be decomposed in air and, therefore, irreversibly accumulate over time.

Figures 2c and 2d show MCR-processed *operando* DRIFT spectra in the OH stretching region with two distinguishable hydroxyl species with distinct chemical nature (Figure 2c) with characteristic concentration profiles (Figure 2d). Generally, a presence of isolated hydroxyl groups is indicated by the sharp bands appearing in the  $3500\text{-}3700\text{ cm}^{-1}$  while the presence of the bridging hydroxyls, via hydrogen-bonds, is clarified by the broad bands appearing in  $2900\text{-}3500\text{ cm}^{-1}$ . The component spectra and concentration profiles of C1' and C2' show that, when the  $\text{In}_2\text{O}_3$  gas sensor is exposed to  $1\text{ ppm NO}_2$ , at first there is a sharp rise in the population of C1', i.e. the terminal OH band located at higher frequency at  $3632\text{ cm}^{-1}$  with a shoulder band at  $3648\text{ cm}^{-1}$ . Subsequently the concentration of the species sharply drops and reaches a steady concentration (Figure 2d, C1'). The other hydroxyl species (C2') possesses a prominent band at  $3621\text{ cm}^{-1}$  with a broad band feature (appearing as a tail) down to  $3000\text{ cm}^{-1}$ , which was absent for C1'. This indicates that in C2' an interaction of OH group with another molecular/structural entity in various configurations like hydrogen-bonds is present. Also, the concentration profile of C2' is very different from that of C1', exhibiting increase in the concentration upon the  $\text{NO}_2$  pulse with an irreversible profile, i.e. accumulative increase over the multiple  $\text{NO}_2$  pulses. It should be noted that the hydroxyl bands presented in Figure 2c is relative (difference spectra) compared to the initial state of  $\text{In}_2\text{O}_3$  before the exposure to  $\text{NO}_2$  pulses. Hence, the positive values in the concentration spectra indicate that the hydroxyl bands were newly formed and/or that their absorbance has been enhanced due to  $\text{NO}_2$  interaction with the  $\text{In}_2\text{O}_3$  surface. Since it is not trivial to quantitatively discuss the amount of hydroxyl groups

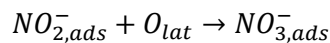
present initially, formed and interacting at the surface with the diffuse reflection sampling configuration, in this study the type of hydroxyl groups present at 350 °C in air was identified by exchanging the hydroxyl group from OH to OD. Figure 2e shows the IR spectrum of OH groups which could be exchanged to OD groups (and vice versa) by alternatingly passing 10% H<sub>2</sub>O and D<sub>2</sub>O vapor over the In<sub>2</sub>O<sub>3</sub>. The DRIFT spectrum shows that the hydroxyl groups responding to NO<sub>2</sub> pulses (C1' and C2') are already present without NO<sub>2</sub> pulses, mostly as isolated hydroxyls. This suggests that the changes are due to an increase in the absorption cross section of the hydroxyl groups, rather than to the formation of new hydroxyl groups upon NO<sub>2</sub> surface adsorption.

Assuming the constant concentration of surface hydroxyl groups during NO<sub>2</sub> sensing, we can summarize the roles of hydroxyls and surface chemical processes as follows. Firstly, when NO<sub>2</sub> adsorbs over In<sub>2</sub>O<sub>3</sub>, terminal hydroxyl (C1') promptly interacts with adsorbed NO<sub>2</sub> forming nitrite species (C1) and senses its presence (based on this the prominent band at 1524 cm<sup>-1</sup> has been assigned to nitrites interacting with hydroxyls, *vide supra*). Subsequently a transformation of surface configuration of adsorbed NO<sub>2</sub> takes place as indicated by the decrease of C1', most likely by the formation of (subsurface or bulk) nitrate species by the oxidation of adsorbed nitrites as strongly suggested by the increase of C2 (nitrates) in the middle of NO<sub>2</sub> pulses (Figure 2b, C2). The presence of hydroxyls in multi-configurations with possible hydrogen-bonds (C2') seem influenced by that of the nitrate species as indicated by irreversible, step-wise increase of the concentration of C2' over NO<sub>2</sub> pulses at the expense of lowered initial peak height of C1' concentration (Figure 2d).

We can describe the sensing mechanism at 350 °C as follows. First, the formation of the nitrite takes place:



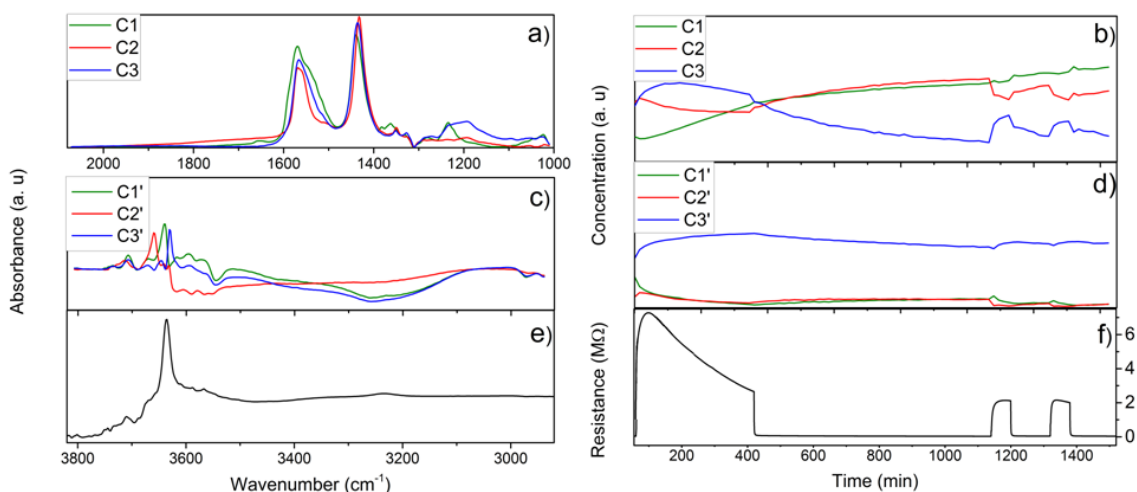
This reaction is responsible for the resistance change of the sensor. Following this reaction, oxidation of nitrite with lattice oxidation (*O<sub>lat</sub>*) can take place, irreversibly forming nitrate species.



#### *Operando DRIFTS and sensing mechanism at 130 °C*

Importantly, the response of the In<sub>2</sub>O<sub>3</sub> sensor against 1 ppm NO<sub>2</sub> is about 450 times higher at 130 °C than at 350 °C, but to date the origin of the superior sensitivity at lower temperature is unknown. Aiming at elucidating the origin of the high sensitivity, we have investigated the roles of surface species during NO<sub>2</sub> sensing at 130 °C by *operando* DRIFTS. The MCR analysis of the obtained spectra identified three components in both nitrite/nitrate and hydroxyl regions (Figures 3a-d). For this

experiment, the first cycle was a 7 h exposure to 1 ppm NO<sub>2</sub> followed by recovery in air for 12 h. The following two cycles were with 1 h NO<sub>2</sub> pulse and 2 h recovery in dry air. Similarly to Figure 2, the gas sensing response during the measurements and the DRIFT spectrum of exchangeable hydroxyl groups obtained by the H<sub>2</sub>O/D<sub>2</sub>O experiment at 130 °C are presented in Figures 3f and 3e, respectively. The broad band feature below 3500 cm<sup>-1</sup> observed in Figure 3e clearly shows the presence of a significantly higher number of hydroxyls on the sample at 130 °C than 350 °C, interacting with other surface species, likely via hydrogen-bonding.



**Figure 3:** a) and c) Component spectra and b) and d) concentration profiles obtained after the MCR analysis of the time-resolved DRIFT spectra shown in Figure S3 (Supporting Information) for the In<sub>2</sub>O<sub>3</sub> gas sensor exposed at 130 °C under periodic exposure to 1 ppm NO<sub>2</sub>. e) Hydroxyl bands identified in the H<sub>2</sub>O/D<sub>2</sub>O exchange experiment (alternatingly passing 10% H<sub>2</sub>O/D<sub>2</sub>O vapor over the sensor). The spectrum is shown taking the sensor state in D<sub>2</sub>O as the background. f) Response of the sensor towards 1 ppm of NO<sub>2</sub> gas at 130 °C.

Notably, the spectral features of the obtained components in both regions at 130 °C were very different from those observed at 350 °C. Compared to the component spectra at 350 °C (Figure 2a), there were two new prominent bands at ca. 1430 and 1560 cm<sup>-1</sup>, which were present for all three components. These bands arise from the interaction of surface hydroxyls and particularly adsorbed water with adsorbed NO<sub>2</sub> in a specific configuration as discussed further below. A careful look into the nitrite/nitrate spectral region allows categorizing the three component spectra (all nitrite species) into two families. The first family is C1 (Figure 3a) characterized by a band at 1223 cm<sup>-1</sup> as well as a shoulder band at ca. 1530 cm<sup>-1</sup>. These band positions are obviously identical to that formerly assigned to nitrites interacting with surface isolated hydroxyls (Figure 2a, C1; Figure S4, Supporting Information). The species responsible for C1 increases gradually with time, more pronouncedly during the NO<sub>2</sub> pulse. The second family includes C2 and C3 for which a very broad band at ca. 1200 cm<sup>-1</sup> was observed. A noticeable difference between C2 and C3 is the higher absorbance of the band at ca. 1200 cm<sup>-1</sup> and the broader feature of the band at ca. 1560 cm<sup>-1</sup> for C3. The profile of C3 concentration is most closely matching with the

response of the gas sensor. Interestingly, the concentration profiles of C2 and C3 are behaving oppositely and counteracting (Figure 3b), which implies that there is a transition of the chemical states between C2 and C3 during the NO<sub>2</sub> pulse and recovery phase.

The characteristic frequency region of hydroxyls provides also unique insights into the chemistry during NO<sub>2</sub> sensing process at 130 °C (Figures 3c and 3d). In this region the identified three components can also be categorized into two families; ones with the strong hydrogen-bonding features (C1' and C3') and one without (C2'). These components show distinct stretching frequencies of isolated OH in 3600-3700 cm<sup>-1</sup>. The first family (C1' and C3') shows similar, largely negative bands in 3100-3550 cm<sup>-1</sup> with a characteristic isolated hydroxyl at 3546 cm<sup>-1</sup> with a broad band centred at ca. 3250 cm<sup>-1</sup> characteristic of hydrogen-bonds. C1' and C3' mainly differs in the terminal hydroxyl stretching frequency at 3640 cm<sup>-1</sup> for C1' and 3629 cm<sup>-1</sup> for C3'. The concentration profiles of the components (Figure 3d) show that the concentration of C3' is dominating, but first the concentration of C1' then that of C3' increase. In practice, this means that the terminal hydroxyl band characteristic of C1' appears and then red-shifts to the frequency of C3' by the transformation to a different nature of hydroxyl induced by increased adsorbed NO<sub>2</sub>. By MCR this band shift is described by two components with distinct, varying concentrations.

On the other hand, the spectrum of C2' is markedly different without the feature of hydrogen-bonds but with the band of terminal hydroxyls with the high stretching frequency at 3658 cm<sup>-1</sup>. According to the concentration profile of C2' (Figure 3d), C2' increases gradually during the recovery phase in dry air. This can be reasonably understood that the terminal hydroxyls of the In<sub>2</sub>O<sub>3</sub> surface become more freely available during the recovery and they are highly isolated without strongly interacting species nearby, as implied by the high vibrational frequency (i.e. less dragging interaction of the OH stretching mode) and the absence of hydrogen-bonds. In contrast, as discussed above, the water-like spectral features with isolated and hydrogen-bonded features are present for C1' and C3' and they appear as negative bands. This is a proof that the hydroxyl groups, most likely due to surface adsorbed water, are "consumed" when NO<sub>2</sub> adsorbs on the surface (thus appear negatively with respect to the initial state before the exposure to NO<sub>2</sub>) in a way that the hydrogen-bonds are broken or rather that the IR absorption by the hydrogen-bonds is weakened. This also accompanies freeing the hydroxyls on the In<sub>2</sub>O<sub>3</sub> surface as evident from the positive bands at ca. 3600-3700 cm<sup>-1</sup>. This process takes a while to reach a stabilized state as suggested by the continuously changing sensor response for 7 h (Figure 3f). Based on these observations and interpretations, it can be concluded that C2 in the nitrite/nitrate region (Figure 3a) interacts with adsorbed NO<sub>2</sub> and reversibly forms C3, enhancing the bands at ca. 1200 and at ca. 1550 cm<sup>-1</sup> (C2 vs. C3 in Figure 3a) ascribed to nitrites interacting with surface water and hydroxyls. The broad features of the two



bands also indicate the highly flexible configuration of the surface nitrite and support the view of dissolved-in-water-like interaction of nitrites on the  $\text{In}_2\text{O}_3$  surface. The surface hydroxyls of  $\text{In}_2\text{O}_3$  seems also affected by the presence of adsorbed  $\text{NO}_2$  as indicated by the red/blue shifts of the bands (C1' vs. C3').

Regarding the irreversible change and thus the deactivation of the gas sensor,  $130\text{ }^\circ\text{C}$  is too low for the oxidation of nitrites to nitrates to take place as in the case at  $350\text{ }^\circ\text{C}$ . However, there is another cause of deactivation at such low operating temperature. The gradual increase in C1 (Figures 3a and 3b) with two prominent features at  $1223$  and  $1530\text{ cm}^{-1}$  was confirmed, indicating the formation of nitrites irreversibly increasing in concentration and interacting with surface hydroxyls of  $\text{In}_2\text{O}_3$ . Although a similar chemical process was reversibly taking place at  $350\text{ }^\circ\text{C}$  (C1, Figures 2a and 2b), the desorption process is likely too slow at  $130\text{ }^\circ\text{C}$  and the nitrite cannot be desorbed during the recovery phase. This means that this  $\text{NO}_2$  adsorption mode is mainly responsible for the changes in the electrical response at  $350\text{ }^\circ\text{C}$ , but at  $130\text{ }^\circ\text{C}$  the same mode is responsible for deactivation. This is well plausible because the magnitude of the electrical response is markedly different at the two temperatures and the factor responsible for resistance change at high temperature may cause poor response at low temperature. Further investigation at an intermediate temperature ( $250\text{ }^\circ\text{C}$ ) confirms that the behaviour of gas sensors and surface species lies between the two temperatures, supporting the temperature dependent sensing mechanisms suggested above (Figures S4 and S5, Supporting Information).

The facts that the absorbance of the bands in the nitrites/nitrates region is one order of magnitude higher at  $130\text{ }^\circ\text{C}$  (Figure S3, Supporting Information) than at  $350\text{ }^\circ\text{C}$  (Figure 1) and that the hydrogen-bonded hydroxyl groups are consumed when the sensor is exposed to  $\text{NO}_2$  at  $130\text{ }^\circ\text{C}$  suggest the important roles of hydroxyl groups and water on the surface of  $\text{In}_2\text{O}_3$  in the sensing mechanism via facilitated  $\text{NO}_2$  adsorption, thus withdrawing more electrons from the  $\text{In}_2\text{O}_3$  surface and consequently increasing the resistance. This view is also supported by the experimental observation where the presence of water vapor indeed improved the response of an  $\text{In}_2\text{O}_3$  sensor at different concentrations of  $\text{NO}_2$  at  $130\text{ }^\circ\text{C}$ .<sup>1c</sup>

## Conclusions

By means of *operando* DRIFTS, we have elucidated the surface species responsible for  $\text{NO}_2$  sensing using  $\text{In}_2\text{O}_3$  material at different temperatures where gas-sensing characteristics remarkably alter. It has been shown that the actual sensing mechanism is more complicated than previously reported and, importantly, that distinct sensing mechanisms are active depending on the temperature of sensor.

At all temperatures, the electrical response originates from NO<sub>2</sub> sorption processes, although the NO<sub>2</sub> adsorption and thus sensing mechanisms differ due to the characteristic chemical nature of the In<sub>2</sub>O<sub>3</sub> surface, especially of hydroxyls and adsorbed water, at different temperatures. At high temperature (350 °C), isolated hydroxyl groups defined by the material and synthesis method are affected by the NO<sub>2</sub> adsorption and directly interact with adsorbed NO<sub>2</sub>, inducing changes in electrical response. This NO<sub>2</sub> sorption process is reversible at 350 °C. At the same time, oxidation of surface nitrites to nitrates takes place at 350 °C and this can lead to deactivation of the surface for NO<sub>2</sub> sorption.

In contrast, at low temperature (130 °C), the gas sensing mechanism involves condition-dependent surface hydroxyls with and without hydrogen-bonds present over the In<sub>2</sub>O<sub>3</sub> surface. This “wet” surface is obviously beneficial to adsorb larger amount of NO<sub>2</sub> and thus responsible for higher sensitivity in NO<sub>2</sub> sensing at the temperature. Interestingly, at 130 °C deactivation of the sensor surface is caused by the mechanism of the active gas sensing at 350 °C, i.e. surface nitrite formation and interaction with the isolated OH group of In<sub>2</sub>O<sub>3</sub>. This surface nitrate irreversibly increases in concentration, but the electrical response due to this NO<sub>2</sub> adsorption is too low to impact on the overall response which is dominated by the “wet” NO<sub>2</sub> adsorption mechanism.

## Associated Content

## Acknowledgments

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# Supporting Information

## Temperature-Dependent NO<sub>2</sub> Sensing Mechanisms over Indium Oxide

Sergio Roso<sup>a, b</sup>, David Degler<sup>c</sup>, Eduard Llobet<sup>a</sup>, Nicolae Barsan<sup>c</sup>, Atsushi Urakawa<sup>b\*</sup>

<sup>a</sup> Minos-Emas, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Spain

<sup>b</sup> Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Technology, Av. Països Catalans 16, 43007 Tarragona, Spain

<sup>c</sup> Institute of Physical and Theoretical Chemistry (IPTC), University of Tuebingen, Auf der Morgenstelle 15, D-72076 Tuebingen, Germany

### Experimental details

The sensors were produced as follows. First, commercial In<sub>2</sub>O<sub>3</sub> (MaTeck 99.99%) powder was mixed with 1-2 propanediol and a printable ink was made. After that, the paste was printed onto an alumina substrate that contained a Pt electrode on one side and a Pt heater on the other side. The printed sensors were dried at 70 °C and annealed at 500 °C. A SEM image of the In<sub>2</sub>O<sub>3</sub> material can be observed in Figure S1 of the Supporting Information.

*Operando* measurements (DRIFTS and electrical resistance) have been recorded at the same time over the In<sub>2</sub>O<sub>3</sub> sensors. The reference spectrum was recorded in dry air before exposure to NO<sub>2</sub> gas. For the calculation of the absorbance spectra we have used:

$$absorbance = -\log_{10} \left( \frac{single\ channel\ test\ gas}{single\ channel\ reference} \right)$$

For the DRIFT spectroscopy, a Bruker Vertex80v FT-IR spectrometer (narrow-band MTC detector, internal glowbar; 1024 scans per spectrum, 4 cm<sup>-1</sup> spectral resolution) was used. The sensor was placed in a homemade *operando* cell with a KBr window, which was mounted in a diffuse reflectance spectroscopy cell (Harrick "Praying Mantis"), and it was heated using the backside heater of the substrate to the desired temperature of 130, 250 or 350 °C. Additionally, the resistance of the sensing layer was recorded by a

digital multimeter. Gases were dosed using a homemade mixing station. Finally, all the experiments were conducted using a flow of 200 ml min<sup>-1</sup>. During all the experiments, the resistance of the active layer was recorded using a digital multimeter (Keithley 2000). In order to avoid any kind of contamination, new and fresh sensors were used for every new DRIFTS measurement at different experimental conditions (i.e. different temperatures).

### SEM micrograph of In<sub>2</sub>O<sub>3</sub> gas sensor

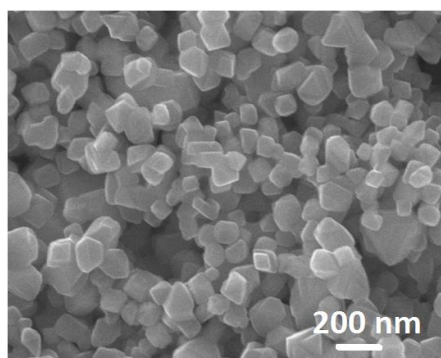


Figure S1: SEM image of the material deposited on the sensor substrate

Figure S1 shows In<sub>2</sub>O<sub>3</sub> material deposited on top of the alumina substrate. A high density of structures that range around 100 nm with no specific morphology can be observed.

### Characteristic asymmetric vibrational modes of nitrite and nitrate ions

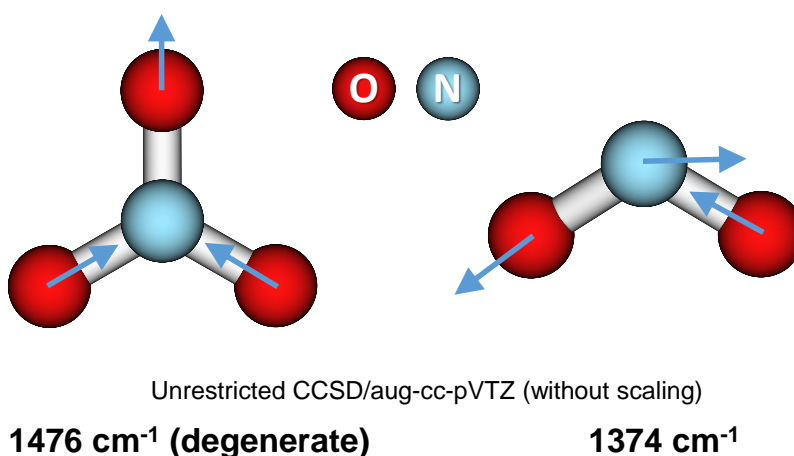


Figure S2: Asymmetric stretching modes and vibrational frequencies of nitrate (NO<sub>3</sub><sup>-</sup>) and nitrite (NO<sub>2</sub><sup>-</sup>) ions

## Time-resolved DRIFT spectra at 130 °C

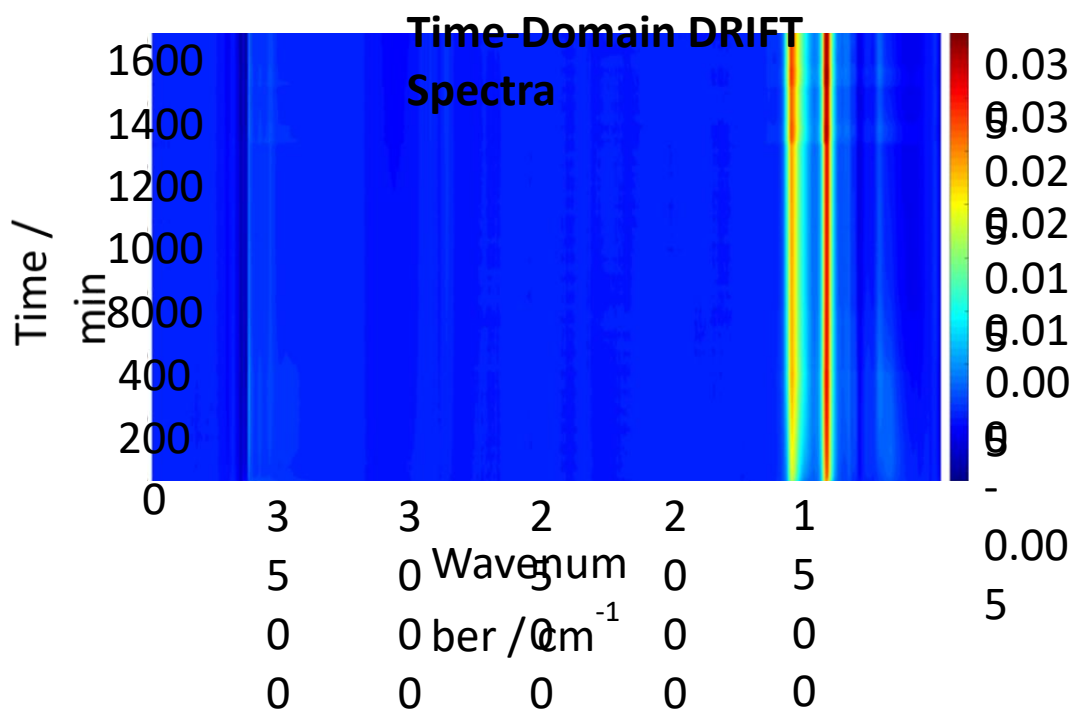


Figure S3: Time-resolved DRIFT spectra of exposure to several cycles of 1 ppm of  $\text{NO}_2$  at 130 °C (time scale identical to that of Figure 3).

## Temperature-dependency of the components DRIFT spectra and concentration profiles

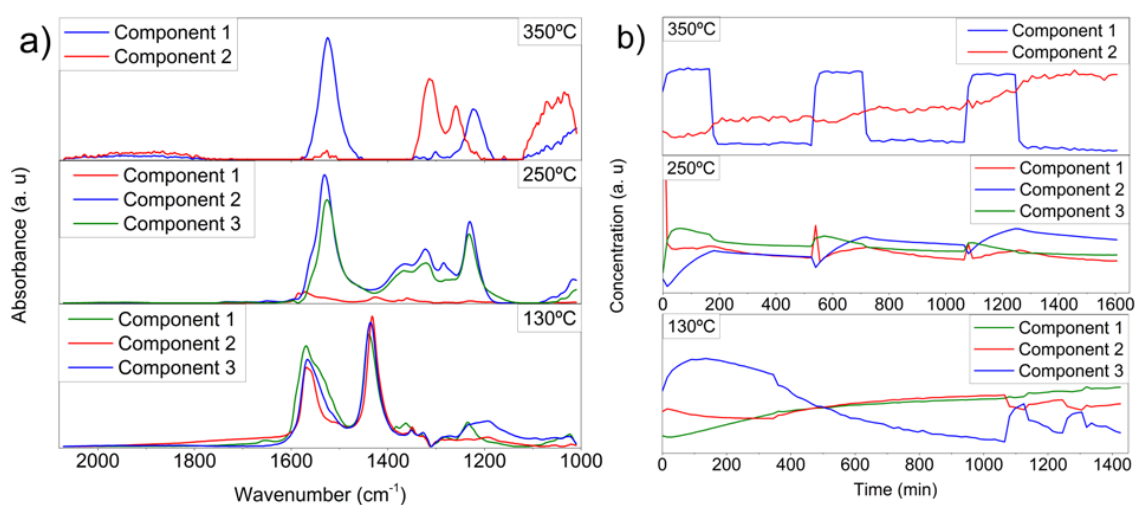


Figure S4: a) component DRIFT spectra and b) concentration profiles obtained by MCR in the nitrite/nitrate region at the three temperatures.

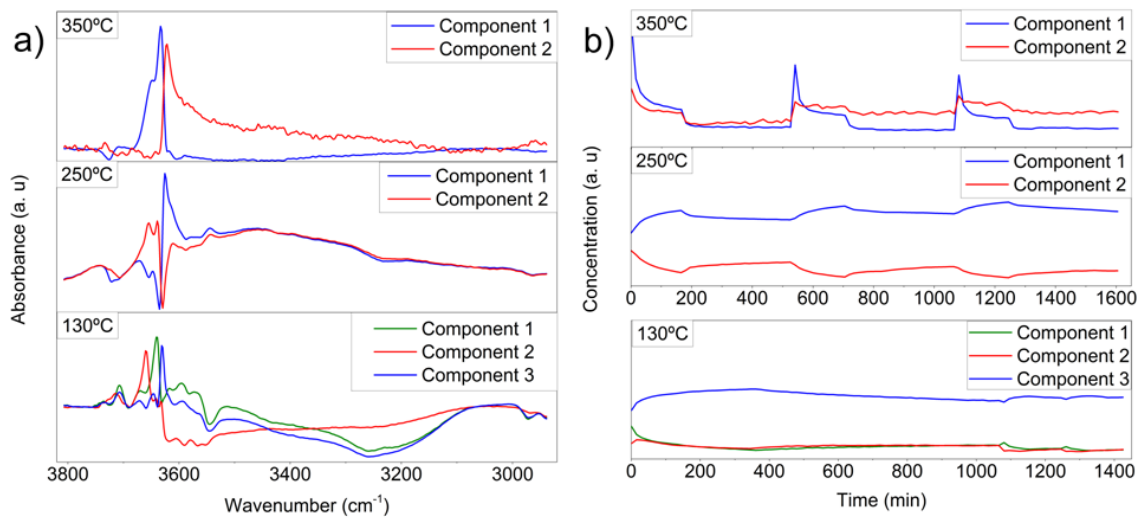


Figure S5: a) component DRIFT spectra and b) concentration profiles obtained by MCR in the hydroxyl region at the three temperatures.