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Corresponding Author:	Konstantin Hadjiivanov Bulgarian Academy of Sciences Sofia, Sofia BULGARIA
Corresponding Author's Institution:	Bulgarian Academy of Sciences
Corresponding Author E-Mail:	kih@svr.igic.bas.bg
Order of Authors:	Nikola L Drenchev
	Kristina K Chakarova
	Oleg V Lagunov
	Mihail Y Mihaylov
	Elena Z. Ivanova
	Ina Strauss
	Konstantin Hadjiivanov
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1 **TITLE:**
2 *In situ* FTIR Spectroscopy as a Tool for Investigation of Gas/Solid Interaction: Water-Enhanced
3 CO_2 Adsorption in UiO-66 Metal-Organic Framework
4
5 **AUTHORS AND AFFILIATIONS:**
6 Nikola L. Drenchev[1], Kristina K. Chakarova[1], Oleg V. Lagunov[1], Mihail Y. Mihaylov[1], Elena Z.
7 Ivanova[1], Ina Strauss[2], Konstantin I. Hadjiivanov[1,3]
8 [1] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria
9 [2] Institute of Physical Chemistry and Electrochemistry, Leibniz Universität Hannover, Hannover,
10 Germany
11 [3] Bulgarian Academy of Sciences, Sofia, Bulgaria
12
13 **Corresponding Author:**
14 Konstantin I Hadjiivanov   (kih@svr.igic.bas.bg)
15 Tel: +359 896754385
16
17 **Email Addresses of Co-authors:**
18 Nikola Drenchev   (ndrenchev@svr.igic.bas.bg)
19 Kristina Chakarova   (kristina@svr.igic.bas.bg)
20 Oleg Lagunov   (oleg@svr.igic.bas.bg)
21 Mihail Mihaylov   (misho@svr.igic.bas.bg)
22 Elena Ivanova   (eivanova@svr.igic.bas.bg)
23 Ina Strauss   (ina.strauss@pci.uni-hannover.de)
24
25 **KEYWORDS:**
26 Adsorption, Brønsted acidity, CO_2 capture, FTIR spectroscopy, Lewis acidity, Metal-organic
27 frameworks, Probe molecules, Surface characterization, UiO-66.
28
29 **SUMMARY:**
30 The use of FTIR spectroscopy for investigation of the surface properties of polycrystalline solids
31 is described. Preparation of sample pellets, activation procedures, characterization with probe
32 molecules and model studies of CO_2 adsorption are discussed.
33
34 **ABSTRACT:**
35 In situ infrared spectroscopy is an inexpensive, highly sensitive, and selective valuable tool to
36 investigate the interaction of polycrystalline solids with adsorbates. Vibrational spectra provide
37 information on the chemical nature of adsorbed species and their structure. Thus, they are very
38 useful for obtaining molecular level understanding of surface species. The IR spectrum of the
39 sample itself gives some direct information about the material. General conclusions can be drawn
40 concerning hydroxyl groups, some stable surface species and impurities. However, the spectrum
41 of the sample is "blind" with respect to the presence of coordinatively unsaturated ions and gives
42 rather poor information about the acidity of surface hydroxyls, species decisive for the
43 adsorption and catalytic properties of the materials. Furthermore, no discrimination between
44 bulk and surface species can be made. These problems are solved by the use of probe molecules,

45 substances that interact specifically with the surface; the alteration of some spectral features of
46 these molecules as a result of adsorption provides valuable information about the nature,
47 properties, location, concentration, etc., of the surface sites.

48

49 The experimental protocol for in-situ IR studies of gas/sample interaction includes preparation
50 of a sample pellet, activation of the material, initial spectral characterization through the analysis
51 of the background spectra, characterization by probe molecules, and study of the interaction
52 with a particular set of gas mixtures. In this paper we investigate a zirconium terephthalate metal
53 organic framework, $Zr_6O_4(OH)_4(BDC)_6$ (BDC = benzene-1,4-dicarboxylate), namely UiO-66 (UiO
54 refers to University of Oslo). The acid sites of the UiO-66 sample are determined by using CO and
55 CD_3CN as molecular probes. Furthermore, we have demonstrated that CO_2 is adsorbed on basic
56 sites exposed on dehydroxylated UiO-66. Introduction of water to the system produces hydroxyl
57 groups acting as additional CO_2 adsorption sites. As a result, CO_2 adsorption capacity of the
58 sample is strongly enhanced.

59

60 **INTRODUCTION:**
61 Adsorption and heterogeneous catalysis are processes that are important for a wide range of
62 industrial applications[1,2]. These processes occur on solid surfaces and therefore detailed
63 characterization of these surface is decisive for understanding the processes and for rational
64 design of new effective materials. To ensure high efficiency, the adsorbents and catalysts
65 normally possess high specific surface area and are usually applied in the form of pelletized
66 powders. Characterization of these materials is a primary research goal that can be achieved with
67 the utilization of various analytical techniques.

68

69 Without any doubt, in situ infrared spectroscopy is one of the most commonly used methods for
70 studying surface compounds[2-11]. The infrared spectral region corresponds to vibrations between
71 atoms, which depend on the symmetry of the molecules, the strength of the bonds, the mass of
72 the atoms, and other molecular constants. Therefore, infrared spectra contain rich information
73 on the structure and symmetry of the adsorbed molecules and on the adsorbent-adsorbate and
74 adsorbate-adsorbate interactions. By studying the adsorption of suitably selected compounds
75 (so-called probe molecules), it is possible to obtain rich information on the structure and
76 chemical composition of the surface, the nature, the acidity or basicity of the active sites, the
77 oxidation and coordination state of the surface-situated cations, the acidity of hydroxyl groups,
78 etc.[3-11]. Via infrared spectroscopy, the pathways for chemical transformation of molecules on the
79 surface and the variety of reaction intermediates can be identified, which is a prerequisite for
80 clarifying the mechanisms of catalytic reactions. The transmission mode of IR is mostly used, but
81 in situ diffuse-reflectance IR spectroscopy is also utilized and, although based on different
82 experimental protocol, gives very similar information[12-16]. Usually IR spectroscopy is combined
83 with other complementary techniques that allow obtaining more profound information.

84

85 In general, there are two reasons for studying surface compounds. First, the adsorption of
86 molecular probes is used to characterize the surface of a given material. Secondly, information is
87 sought about a particular process involving adsorption. The mechanisms of catalytic reactions
88 are most often studied in this way. It should be noted that the two cases are not strictly

89   distinguishable, and in the study of a particular adsorption process, information can be obtained
90   both on the surface of the adsorbent and on the mechanism of a catalytic reaction.
91
92   The spectral detection of surface species requires that they have a sufficiently high concentration
93   in the infrared beam path. An optimal concentration of adsorbed compounds can be achieved by
94   using a self-supporting pellet of the sample containing about 2–10 mg cm^{-2} of the substance.
95   Thicker pellets are practically opaque for the infrared beam, whereas making and using thinner
96   tablets has technical difficulties.
97
98   The pellets for IR studies are prepared by compressing sample powder between optically smooth
99   dies of a pre-ground sample. Typically, they are characterized by high transparency in the IR
100 region and have good mechanical properties.
101
102 In some cases, it is not possible to prepare a pellet which is thin (transparent) enough; then, a
103 carrier is used: a metal grid, silicon or a KBr wafer. When using KBr, care must be taken because
104 it can easily be oxidized either by the sample (if it possesses oxidizing properties) or by some
105 adsorbates (e.g. NO_2)[10].
106
107 Normally, organic impurities, adsorbed water, carbonates, etc. are present on the surface of the
108 as-prepared adsorbents and catalysts. Therefore, the surface must be cleaned before
109 measurements. This is achieved by activation, which usually consists of two stages: (i) a thermo-
110 oxidation treatment (aimed at the oxidation of organic pollutants) and (ii) thermo-vacuum
111 treatment (mainly directed to the removal of adsorbed water and impurities such as
112 bicarbonates, carbonates, nitrates, etc.). Typically, activation temperatures vary between
113 573 and 773 K. In some particular cases, the activation can be performed even at room
114 temperature. For some specific materials (supported metals, metal-organic frameworks), the
115 thermo-oxidation treatment is omitted because it can affect the sample.
116
117 As a rule, the sample activation is performed in situ in purpose made vacuum cells. Various
118 laboratories use cells of different designs and made by different materials (metal, glass, quartz),
119 but with a number of common features. An example of a simple glass IR cell is shown on **Figure
120 1**. The sample pellet is placed in a mobile holder that has two basic positions. In the first position
121 the holder secures the pellet perpendicular to the infrared beam. In this part, the cell is equipped
122 with windows from material that is transparent to infrared radiation (typically KBr or CaF_2). In the
123 second position, the holder secures the sample in a heating zone. In this zone, the cell includes
124 an external furnace. Movement of the pellet from one place to another is accomplished by means
125 of a magnet or a metal chain (for vertical constructions). The cells also provide the possibility of
126 fixing the pellet in an intermediate position both outside the furnace and the infrared beam area,
127 allowing easy registration of the background spectrum while cooling the sample down to room
128 temperature. In our laboratory we use horizontal cells. This design prevents accidental release of
129 the sample holder, which may cause the sample and even the cell to break.
130
131 In many cases, it is necessary to perform adsorption at low temperature. For this purpose, low-
132 temperature cells are used in which the volume around the sample, when in the path of the

infrared beam, is cooled with liquid nitrogen (**Figure 2**). In order to protect the cell windows from condensation of water from the air, a thermal buffer (e.g. from constantly circulating water) is applied between them and the cool zone. In some other cases, adsorption should be carried out at high temperatures, using purpose-made IR cells. The IR cells are always directly connected to vacuum/gas manifold system, allowing the adsorption experiments to be conducted in situ.

One of the main shortcomings of transmission infrared spectroscopy in the study of surface species is the existence of spectral regions in which, due to their own absorbance, the samples are opaque. When vibrational modes of adsorbed compounds fall into these regions, they cannot be registered.

The IR spectrum of the sample itself gives some direct information about the material. In the most favorable cases, general conclusions can be drawn concerning the surface hydroxyl groups and some stable surface species, such as sulfates, oxo-groups, foreign phases, etc. However, the IR spectrum of the sample is "blind" with respect to the presence of coordinatively unsaturated ions and gives scarce information about the acidity of surface hydroxyl groups, both species having decisive role for the adsorption and catalytic properties of the materials. Furthermore, no discrimination between bulk and surface species can be made. These problems are solved by the use of probe molecules. These are substances that interact specifically with the surface; the alteration of their spectral features as a result of adsorption provides indirect information about the nature, properties, location, concentration, etc. of the surface sites. Probe molecules are categorized into several groups, e.g., for determination of surface acidity or basicity, establishing the oxidation state of coordinatively unsaturated cations and the number of their coordination vacancies, obtaining information on the accessibility and location of surface sites, etc. There are several basic requirements for the probe molecules[7,8]: (i) the functional group or atom with which the molecule binds to the surface should be well known, (ii) the molecule should have a pronounced acidic or basic character, (iii) the molecule should bind to the same type of adsorption sites and the formed surface species should have the same structure; (iv) the adsorption complexes should be sufficiently stable, (v) the molecule should possess spectral parameters (frequency, spectral split, spectral shift) sufficiently sensitive to the surface property to be determined; (vi) in case the molecules are adsorbed on more than one type of sites, it is necessary that the different adsorption complexes can be reliably distinguished on the basis of their spectral characteristics; (vii) the informative spectral parameters should fall within the area where the sample is transparent; (viii) the absorption bands of the surface complexes should be characterized by sufficiently high intensity, and (ix) the molecule should not chemically modify the surface. There is virtually no compound that can satisfy all of the above requirements. Therefore, prior to the study, careful selection of a suitable probe molecule is necessary.

Another application of IR spectroscopy is to study the interaction between the substrate and one or more adsorbates of practical interest. In these cases, a variety of tricks are applied, such as co-adsorption with probe molecules (for establishing the nature of the adsorption sites), full or partial isotopic substitutions (for determination of the structure of the surface species), interaction with different reagents (to establish the reactivity of the species), variable-temperature experiments (for calculation of the entropy and enthalpy of adsorption), etc.

178 Finally, IR spectroscopy is used for mechanistic studies. In this way *operando* spectroscopy
179 (spectroscopy in real reaction conditions) is applied[12,17-18]. However, a solid knowledge base must
180 be obtained beforehand through in situ experiments.

182 In this article we describe the protocol we use for IR characterization of different materials and
183 illustrate the power of the technique by demonstrating the water-enhanced CO_2 adsorption on
184 a metal-organic framework (UiO-66) material. For the experiments we used a Nicolet 6700 FTIR
185 spectrometer. The spectra were registered accumulating 64 scans at a spectral resolution of 2
186 cm^{-1}.

188 **PROTOCOL:**
189 **1. Synthesis of UiO-66**

191 NOTE: The UiO-66 sample was synthesized via a hydrothermal synthesis following a modified
192 recipe reported elsewhere[19].

194 1.1. Dissolve 0.28 g of zirconium chloride in 4.5 mL of dimethylformamide. Then, prepare
195 another solution consisting of 0.42 g of terephthalic acid and 4.4 g of benzoic acid in 10 mL of
196 dimethylformamide. Heat the solutions to 423 K, combine them in a polytetrafluoroethylene
197 lined autoclave and place in a conventional oven at 453 K for 24 h.

199 1.2. After the reaction, wash the resultant crystals 3x with CH_3OH and then dry them at 313 K.

201 **2. Making pellets**

203 2.1. Making self-supporting pellets

205 2.1.1. Spread uniformly, using a grid, about 20 mg of the sample powder on the polished surface
206 of a pressing die. If the powder sticks to the metal surface, use mica or clear packing tape glued
207 to the die. Place another die on top with the polished side facing the powder. Ensure even
208 distribution of the specimen with several gentle rotating movements.

210 2.1.2. Then put the two cylinders in a hydraulic press and apply 0.2 tons of pressure. After about
211 two minutes, reduce slowly the pressure and remove the cylinders from the press. If the pellet is
212 not formed, repeat the procedure, applying a higher pressure.

214 2.1.3. Using a scalpel or a blade, cut out a piece of the pellet with dimensions of about 10 mm x
215 10 mm. Measure the geometric surface and the weight of the pellet.

217 NOTE: Some powders resist tableting. If the pellet is in pieces, a tungsten grid can be used as a
218 carrier[20]. In other cases, the concentration of the adsorption sites is very high and the IR bands
219 of the adsorbed species are too intense to be measured accurately. The solution is to prepare a
220 pellet containing smaller amount of the substance. To achieve this, the substance is dispersed on

221 preliminary prepared wafer that is transparent in the required IR regions. The wafer material
222 could be silicon[21] or KBr[22]. Below is a description of this technique for making a pellet with a
223 sample spread on a KBr wafer.

2.2. Making KBr-supported pellets

2.2.1. Prepare a KBr pellet by the conventional technique. After pressing, pull up the piston from die set and spread the desired amount of sample powder uniformly on the KBr pellet, then put the piston back. Press the pellet with a hydraulic press.

NOTE. Initial control of the suitability of the pellet for IR studies is made by analyzing its IR spectrum.

3. Pretreatment of the sample

3.1. Positioning of the pellet

3.1.1. Place the pellet into the sample holder. Put the sample holder into the IR cell and move the sample to the middle of the oven zone.

3.2. Connecting to the vacuum/adsorption apparatus

3.2.1. Connect the cell to the vacuum/adsorption apparatus, placing between them a reservoir with known volume, in this case about 0.5 mL. Evacuate the system.

3.3. Activation of the sample at 573 K

3.3.1. Adjust the activation temperature to 573 K, (recommended heating rate of 2–5 K min^{-1}). Then, evacuate the sample at this temperature for 1 h.

NOTE: The sample is heated by an external furnace. The heating temperature has to be calibrated for each IR cell.

3.4. Activation of the sample at RT.

3.4.1. To obtain sample activated at RT, just evacuate it for 1 h without heating.

NOTE: The activation aims for obtaining a clean surface. Control of the surface state is made through analysis of the IR spectra. If the procedure has not ensured a clean surface, it is necessary to repeat the activation, possibly at higher temperature or for a longer time.

4. Registering sample spectrum

4.1. Registering a background spectrum

265

266 4.1.1. Using a magnet, move the pellet outside the oven and wait for 10 min in order to reach
267 room (or ambient) temperature. During that time register a background spectrum.

268

269 4.2. Registering a sample spectrum

270

271 4.2.1. Move the pellet to the IR beam path and register the sample spectrum (**Figure 3**).

272

273 NOTE: The sample spectrum is used for background when performing the adsorption studies.
274 Therefore, obtaining good quality sample spectrum is very important for the whole experiments.
275 If the spectrum is of bad quality and noisy, prepare a new, thinner pellet.

276

277 **5. Adsorption of CD$_3$CN at room temperature.**

278

279 5.1. Successive adsorption of small doses

280

281 5.1.1. Ensure the sample is situated on the IR beam path. Introduce a small dose, namely 0.5
282 μmol, of the adsorbate to the cell, in this case deuterated acetonitrile. Record an IR spectrum.
283 Then, introduce a second (next) dose of the adsorbate and repeat the procedure. Do this until no
284 more changes in the spectrum occur.

285

286 5.2. Stability of adsorbed species

287

288 5.2.1. Evacuate the sample recording spectra until no more changes occur. Then, move the
289 sample to the oven with a preset temperature of 323 K.

290

291 5.2.2. After 15 min evacuation at this temperature, place the pellet outside the oven and wait for
292 10 min in order to reach ambient temperature. During that time register a fresh background
293 spectrum. Move the pellet to the IR beam path and register the sample spectrum.

294

295 5.2.3. Repeat the procedure increasing the oven temperature with steps of 50 K until obtaining
296 a spectrum coinciding with the initial sample spectrum.

297

298 **6. Adsorption of CO at 100 K**

299

300 6.1. Cooling the sample

301

302 6.1.1. To prevent deep cooling of the cell windows during the low-temperature experiments, first
303 turn on the water circulation system. Then ensure the sample is situated on the IR beam path.
304 Fill in the cell reservoir with liquid nitrogen and keep it full during the whole experiment.

305

306 6.2. Recording low-temperature spectra

307

308 6.2.1. After cooling the sample, record a spectrum. Then introduce adsorbate, in this particular

309 case CO, on successive small doses, 0.5 μmol each. Record a spectrum after each dose. Finish this
310 set of experiments with CO equilibrium pressure of 2 mbar.

312 6.2.2. Then start to decrease the equilibrium pressure, first by dilution and then by evacuation at
313 low temperature, again recording spectra. Mark the pressure in each spectrum.

315 6.3. Recording spectra at increasing temperature

317 6.3.1. When no more changes occur, stop filling the reservoir with liquid nitrogen and record
318 spectra under dynamic vacuum and at increasing temperature.

320 NOTE: The spectrum of the sample recorded at low temperature slightly differs from that
321 registered at room temperature. This causes problems with the sample spectrum (used for
322 subtraction) at intermediate temperatures. Usually the temperature variation slightly changes
323 the slope of the spectrum, but if the changes are serious, one should record spectra without
324 adsorbate at different temperatures and use them as appropriate backgrounds. To ensure
325 constant temperature during all low-temperature experiments, add ca. 1 mbar pressure of He
326 into the cell before introduction of the probe molecule.

328 **7. Treatment of the spectra**

330 7.1. Loading source spectra

332 7.1.1. Load a spectrum with adsorbed substance (a), the sample spectrum before adsorption (b)
333 and a spectrum of the gas phase adsorbate (c) registered at the same pressure/temperature as
334 spectrum (a).

336 7.2. Treatment

338 7.2.1. Subtract spectrum (b) from spectrum (a). From the resulting spectrum subtract spectrum
339 (c) using interactive subtraction. The resulting spectrum is a superimposition of the spectrum of
340 the adsorbed substance and the changes in the sample background, as also shown in **Figure 4**.
341 For instance, the stretching modes of adsorbed CO are observed in the region between 2200 and
342 2100 cm^{-1} while the CO-induced shift of the ν(OH) modes can be monitored in the hydroxyl
343 stretching regions.

345 7.3. Quantifying

347 7.3.1. To quantify the adsorbed amount (see **Figure 5**) calculate the integral absorbance of a
348 chosen band due to adsorbed species. Plot the absorbance vs. the introduced amount of
349 adsorbate or vs. its equilibrium pressure.

351 **REPRESENTATIVE RESULTS:**
352 Here we report results on the water-induced enhancement of the CO$_2$ adsorption capacity of the

UiO-66 metal organic framework. Thorough sample characterization, including confirmation of the structure, is reported elsewhere[23].

The activation of UiO-66 was performed by evacuation at desired temperature in order to avoid affecting the organic linkers of the MOF by oxidative treatment. The IR spectrum of UiO-66 registered after evacuation at ambient temperature (**Figure 3**) contains bands due to the linker, residual dimethylformamide (1667 and 1096 cm^{-1}), terephthalic acid and esters (1732 and 1704 cm^{-1}), and isolated (3673 cm^{-1}) and H-bonded (3500-3000 cm^{-1}) structural OH groups. Evacuation at 573 K leads to almost full disappearance of the residuals and of the structural hydroxyls, i.e., after this pretreatment the sample is practically clean and dehydroxylated.

Samples evacuated at room temperature and at 573 K were characterized by probe molecules (CD_3CN and CO). Adsorption of CD_3CN - a probe molecule for assessing acidity - on the just evacuated sample reveals existence of Brønsted acid sites (hydroxyl groups) through C-N stretching bands at 2276 and 2270 cm^{-1}. At the same time, the OH band is red shifted by 170 and 250 $cm^{-1,}$ indicating a weak Brønsted acidity. With sample activated at 573 K, the bands indicating Brønsted acidity are practically absent, which is consistent with the observed sample dehydroxylation. However, a band at 2299 cm^{-1}, due to CD_3CN on Zr^{4+} Lewis acid sites, is present (**Figure 6**). More details are reported elsewhere[23].

Low temperature CO adsorption on a sample evacuated at ambient temperature (**Figure 4**) revealed CO polarized by OH groups through a band at 2153 cm^{-1} (the unstable bands at 2136 and 2132 cm^{-1} are associated with physically adsorbed CO). Simultaneously, the original OH band is red shifted from 3676 to 3599 cm^{-1}, i.e. by 77 cm^{-1}, confirming the weak acidity of the hydroxyls. With a sample evacuated at 573 K, a very weak band due to CO polarized by hydroxyl groups was detected at 2154 cm^{-1}, confirming again the low hydroxyl concentration in the sample. Importantly, no CO coordinated to Zr^{4+} sites was detected. This observation shows that the Lewis acid sites can be monitored only by relatively strong bases, as CD_3CN, probably via structural re-arrangement in the Zr^{4+} environment.

Carbon dioxide (50 mbar) was put in contact with a sample evacuated at 573 K. The adsorbed CO_2 is monitored by the antisymmetric stretching modes at 2336 cm^{-1} (**Figure 7**). Another weak satellite at 2325 cm^{-1} was also registered and associated with the so-called "hot" CO_2 combination band[22]. Then water (ca. 1 mbar partial pressure) was introduced into the system, which led to gradual development of a high-frequency shoulder at 2340 cm^{-1} which finally dominated the spectrum in the region. In concert, bands due to isolated (3673 cm^{-1}) and H-bonded structural hydroxyls (μ_3-OH⋯OCO adducts at 3647 cm^{-1} and μ_3-OH⋯OH_2 complexes at 3300 cm^{-1}) developed. Note that no erosion of the initial band at 2336 cm^{-1} was detected, which indicates that, similarly to CO, CO_2 is not able to form complexes with Zr^{4+} sites on the 573 K-activated sample.

In conclusions, the results show that water vapor hydroxylates the sample, creating structural hydroxyl groups that act as CO_2 adsorption sites. This observation is important because it (i) evidences that CO_2 adsorption could be enhanced in humid atmosphere and (ii) reveals the

397   mechanism of this phenomenon.
398
399   **FIGURE AND TABLE LEGENDS:**
400   **Figure 1. Simple horizontal glass IR cell for adsorption studies.** (**A**) Photograph of the cell. (**B**)
401   Scheme of the cell. The sample pellet is put into the holder which can be moved along the cell
402   with a ferrite block magnet (60 mm x 30 mm x 10 mm, magnetization Y35). Position (1) is in the
403   sample oven and allows thermal treatment. Position (2) is intermediate and allows tempering
404   the sample and registering background immediately before registering the sample spectrum. In
405   position (3), the sample is fixed perpendicularly to the IR beam for taking spectrum. To ensure
406   transmission of the IR beam, the cell is equipped with IR transparent windows. The cell can be
407   connected to a vacuum/adsorption device.
408
409   **Figure 2. Scheme of low-temperature IR cell**. When the sample is fixed in a position on the path
410   of the IR beam, it is surrounded by a Dewar which can be filled with liquid nitrogen. Between the
411   Dewar and the cell windows there is a water circulating system aimed at keeping the temperature
412   of the window enough high (to prevent condensation of water vapors).
413
414   **Figure 3. FTIR spectra of UiO-66**. Sample evacuated at room temperature (a) and at 573 K (b).
415   The bands at 1732, 1704 and 1667 cm^{-1} are due to organic residues and are removed by
416   evacuation at 573 K. The band at 3350 cm^{-1} characterizes OH groups H-bonded to the organic
417   residues. The band at 3673 cm^{-1} arises from the structural μ_3-OH groups and practically
418   disappears after evacuation at 573 K, indicating sample dehydroxylation.
419
420   **Figure 4. Typical difference spectrum.** This spectrum (a) is obtained after low-temperature CO
421   adsorption on UiO-66 activated at room temperature, followed by evacuation. The spectrum
422   consists of bands due to adsorbed CO (marked with *), as well as positive (marked with +) and
423   negative (marked with -) bands due to alteration of the sample own spectrum. In particular, the
424   negative bands at 3676 and 3669 cm^{-1} and the positive band at 3599 cm^{-1} show the CO-induced
425   shift of $\nu(OH)$ of the μ_3-hydroxyls, and the shift value is a measure for the acidity of the OH
426   groups. The top inset compares spectrum (a) in the carbonyl stretching region with a spectrum
427   (b) registered at analogous conditions with a sample pre-evacuated at 573 K for 1 h. The bottom
428   inset compares spectrum (a) in the carbonyl stretching region with a spectrum (c), registered in
429   the presence of 1 mbar equilibrium pressure of CO.
430
431   **Figure 5. Typical plot showing the dependence of the absorbance of a particular band *vs.* the**
432   **amount of introduced adsorbate.** Extrapolation (see dotted lines) shows the adsorbate uptake.
433   The plots can be used for calculation of the extinction coefficient of the IR band.
434
435   **Figure 6. Difference spectra of CD₃CN adsorbed on UiO-66.** Sample activated at room
436   temperature (a) and at 573 K (b). The band at 2299 cm^{-1} is due to Zr^{4+}-NCCD$_3$ complexes, those
437   at 2276 and 2270 cm^{-1} to OH-NCCD$_3$ species, and at 2260 cm^{-1} to physically adsorbed CD$_3$CN. The
438   formation of OH-NCCD$_3$ species is visible also by the shift of the μ_3-OH band from 3673 to 3423
439   cm^{-1}.
440

441 **Figure 7. Water enhanced CO₂ adsorption on UiO-66.** FTIR spectra of CO_2 (50 mbar equilibrium
442 pressure) adsorbed on UiO-66 activated at 573 K (a) and time development of the spectra after
443 introduction of water vapor (1 mbar equilibrium pressure) into the system (b–e). The new band
444 developed at 2340 cm^{-1} is due to OH···OCO adducts and is consistent with sample hydroxylation.
445

446 **DISCUSSION:**
447 The initial step, preparation of the sample pellet, is critical for the whole experiments. If the pellet
448 is thick, the spectra are noisy, which hinders their analysis. Attention should be paid when using
449 a pellet that is not self-supporting. In this case, special care should be taken in order to ensure
450 that no interaction occurs between the supporting wafer and the sample or the adsorbates.
451 Another critical step of the procedure is appropriate sample activation. The activation conditions
452 depend on the sample nature and on the aims of the experiments. For instance, oxidative
453 pretreatment could destroy some samples, as metal-organic and covalent-organic frameworks
454 can oxidize supported metals. High activation temperature could lead to sample sintering or
455 structure collapse. In this point of view, removal of foreign species by chemical treatment before
456 making pellet is applied in some cases.
457

458 Deuterated acetonitrile (CD_3CN) and CO are probe molecules widely used for measuring surface
459 acidity[8,9]. CD_3CN is bound to acid sites (both Lewis and Brønsted) via its nitrogen atom[8]. Upon
460 coordination to metal cation, the C–N modes (2263 cm^{-1} in gas phase) shift to higher frequencies
461 (up to 2335 cm^{-1}) and the shift increases with the acidity of the Lewis sites. CD_3CN is bonded to
462 the hydroxyl groups through an H-bond and the C-N modes are typically observed in the region
463 of 2300–2270 cm^{-1}: the higher the frequency, the stronger the H-bond. In this case the ν(OH)
464 modes are red shifted and the value of the shift is a quantitative measure of the acidity of the
465 hydroxyls. Carbon monoxide is coordinated to surface metal or cationic sites and the ν(CO)
466 frequency is highly sensitive to the oxidation and coordination state of the center[9]. With d^0 metal
467 cations, the ν(CO) frequency is blue shifted with respect to the gas-phase frequency (2143 cm^{-1})
468 and the shift value is proportional to the cation acidity. When bound to hydroxyl groups *via* a H-
469 bond, CO causes a red shift of the ν(OH) modes and the $\Delta\nu$(OH) value is used as a measure of the
470 acidity of the hydroxyl.
471

472 A very important issue is the proper functionalization of the vacuum/gas manifold system.
473 Entering of air to the system could lead to accumulation of water on the sample and partial or
474 even full blocking of the adsorption sites. With reduced samples, re-oxidation could occur. The
475 purity of the adsorbates is also very important. Sometimes, traces of impurities could affect the
476 results. For instance, hydrogen adsorption is normally weak and high H_2 equilibrium pressures
477 are applied even at low temperature. Even ppm levels of N_2 impurities could strongly affect the
478 spectra because normally N_2 is more strongly bound to the same sites where hydrogen is
479 adsorbed. When performing low temperature experiments, some water could condense on the
480 outer surface of the optical windows. This could hinder or distort the analysis in the OH stretching
481 region, giving information on the acidity of the hydroxyl groups. If, for some reason, the technical
482 problem could be not resolved, one could continue with the experiment using deuterated
483 samples based on the fact that the OD region lies far away from the OH region. Deuteration can
484 also be applied in cases where the sample is opaque in the OH region. In order to obtain the

485 energetic characteristics of the adsorption (entropy, enthalpy), one should perform variable-
486 temperature experiments where the exact measurement of the sample temperature is
487 essential[24].

489 The amount of gas adsorbate introduced by one dose can be adjusted by its pressure and by
490 knowing the volume of the reservoir. To calculate the adsorbate density, one needs to know the
491 mass of the pellet and the specific surface area of the material. Successive adsorption of
492 adsorbate known doses allows the quantification of adsorption. A typical plot of the absorption
493 vs. adsorbed amount is shown in **Figure 4**. It allows calculation of the extinction coefficient and
494 the number of adsorption sites with knowledge of the sample weight. However, performing
495 dosed adsorption is often accompanied by the so-called wall-effect. Briefly, the adsorbate is not
496 uniformly distributed on the sample surface but first saturates the particles from the geometric
497 surface of the pellet. Therefore, the spectra from the desorption experiments are more
498 representative for equilibrium states.

500 A sister technique of the in situ transmission IR spectroscopy is diffuse reflectance spectroscopy
501 (DRIFTS). Although it provides essentially the same information, DRIFTS is not so convenient for
502 quantitative studies. In addition, DRIFTS is usually performed in gas flow. This can be an
503 advantage, because the experiments are performed at conditions similar to the real ones, but
504 also brings the risk of accumulation of impurities on the sample surface. Transmission IR
505 spectroscopy can also be performed in real conditions (e.g. operando spectroscopy).

507 In conclusion, in situ IR spectroscopy provides valuable information on different surfaces and on
508 the nature and properties of the adsorption sites. It can also reveal the method of interaction
509 between the solid and particular gases. However, the technique is often not able to give
510 unambiguous information on some important characteristics, such as the structure of the solid,
511 the location of some sites, etc. This is why combination with other techniques is recommended.
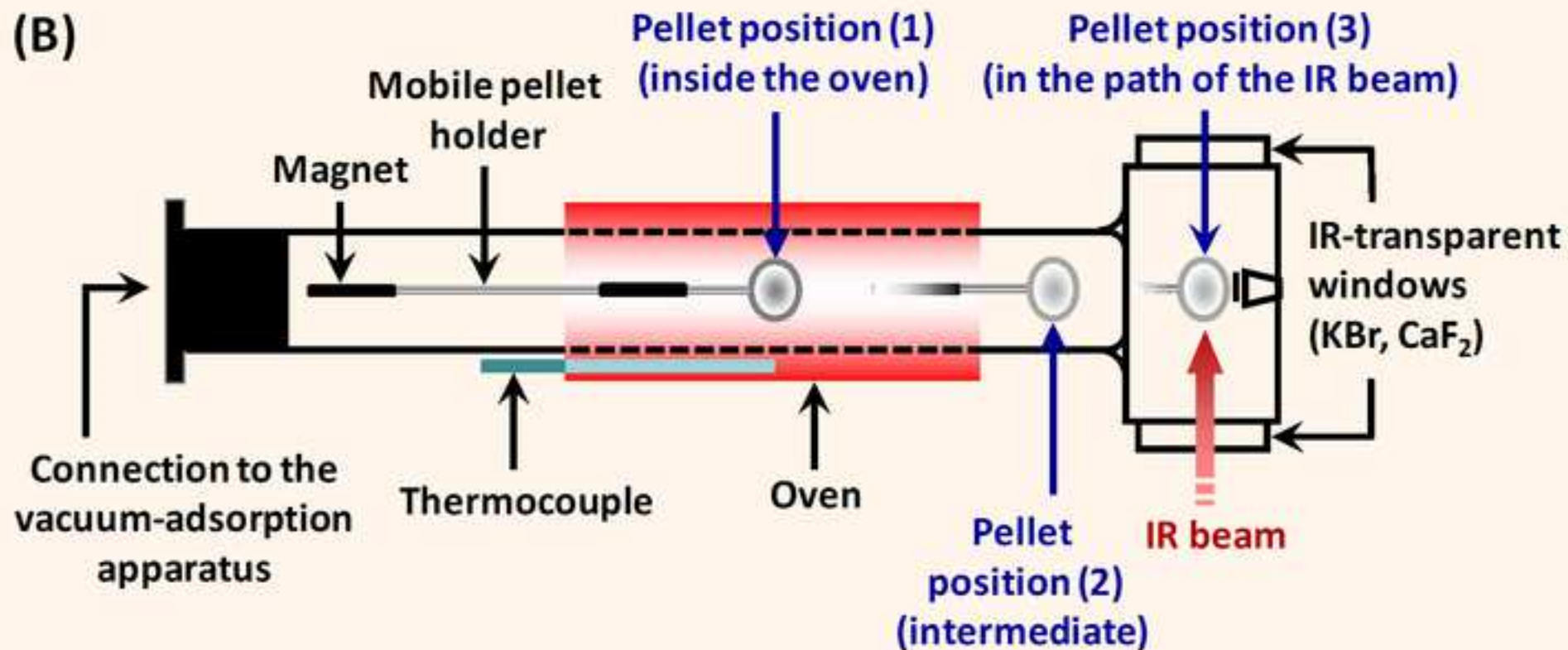
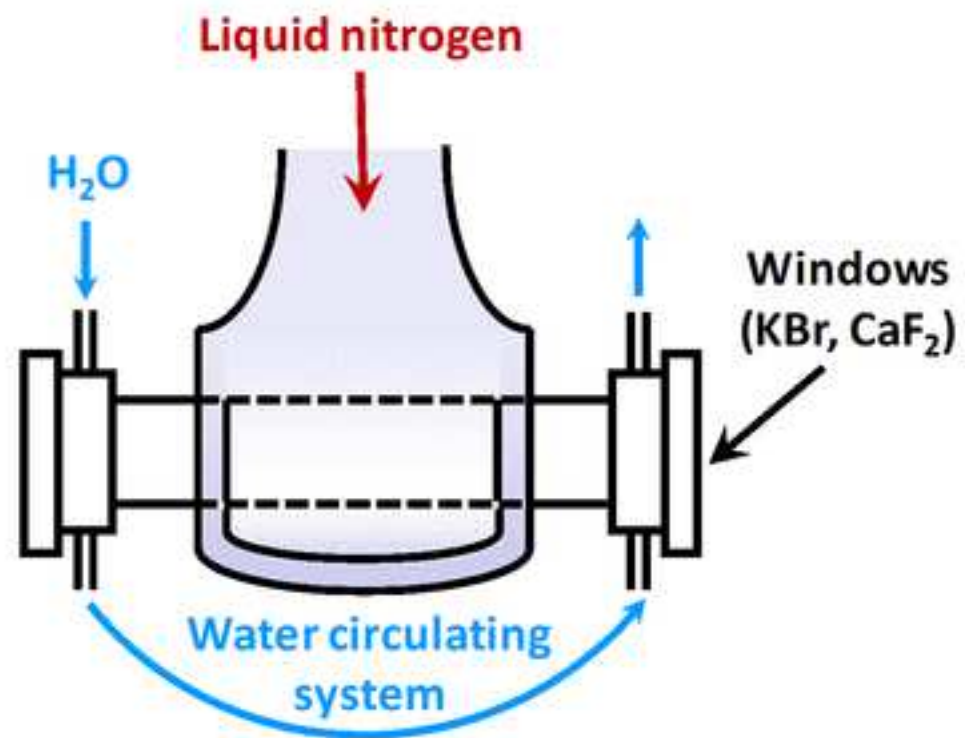519 **DISCLOSURES:**
520 The authors have nothing to disclose.

522 **REFERENCES:**
523 (1)   Ross, J. R. H. *Heterogeneous Catalysis: Fundamentals and Applications.* Elsevier,
524 Amsterdam (2012).
525 (2)   Busca, G. *Heterogeneous Catalytic Materials: Solid State Chemistry, Surface Chemistry,*
526 *Surface Chemistry and Catalytic Behaviour*. Elsevier, Amsterdam (2014).
527 (3)   Davydov, A. A. *Molecular Spectroscopy of Oxide Catalyst Surfaces*. John Wiley & Sons,
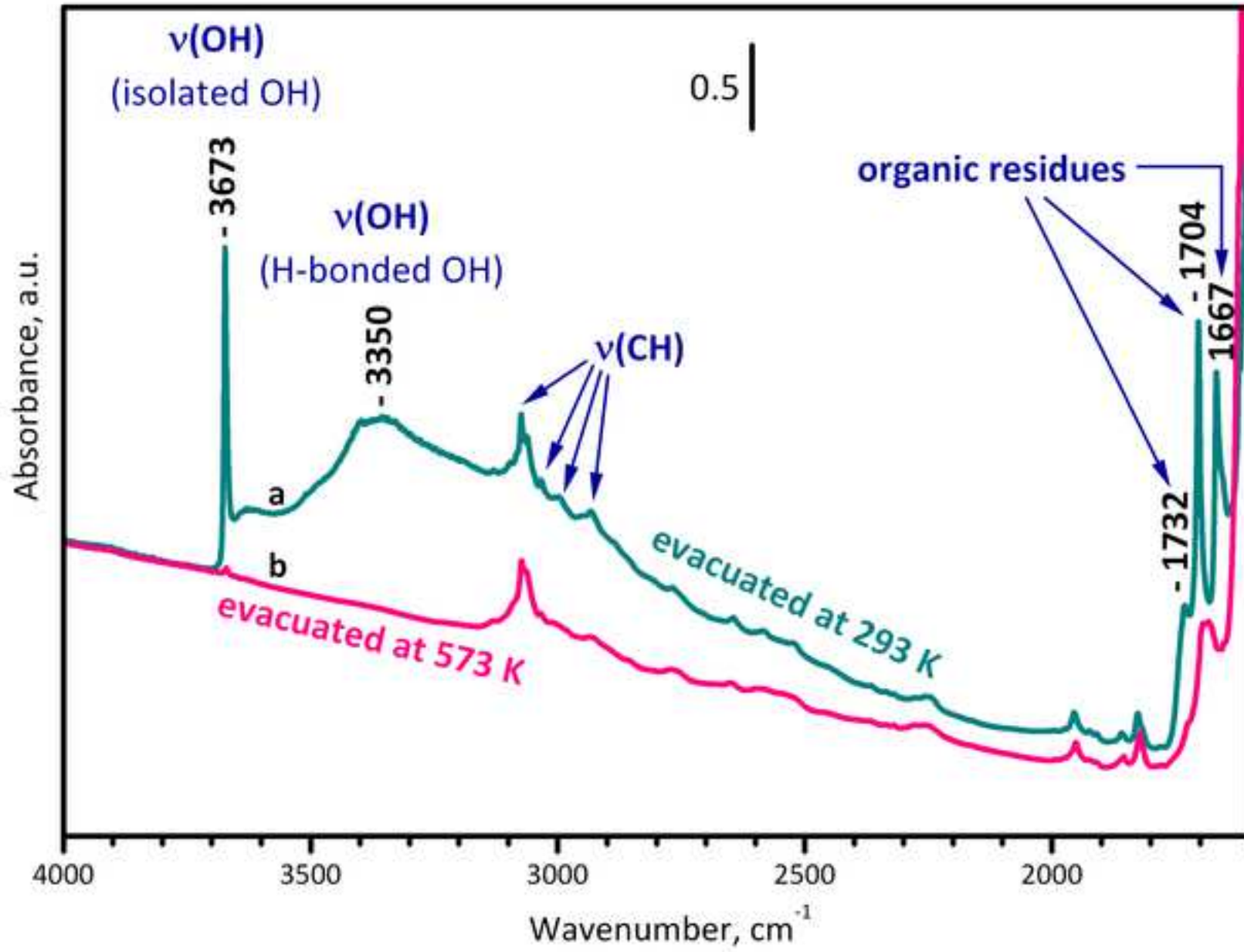528 Hoboken, NJ (2003).

529 (4)   Hadjiivanov, K., Knözinger, H. Characterization of Vacant Coordination Sites of Cations on
530 the Surfaces of Oxides and Zeolites using Infrared Spectroscopy of Adsorbed Probe Molecules.
531 *Surface Science*. **603** (10-12) 1629–1636 (2009).
532 (5)   Knözinger, H., Huber, S. IR Spectroscopy of Small and Weakly Interacting Molecular
533 Probes for Acidic and Basic Zeolites. *Journal of the Chemical Society, Faraday Transaction*. **94** (15),
534 2047–2059 (1998).
535 (6)   Paukshtis, E. A., Yurchenko, E. N. Study of the Acid–Base Properties of Heterogeneous
536 Catalysts by Infrared Spectroscopy, *Russian Chemical Reviews*. **52** (3) 242-258 (1983).
537 (7)   Kustov, L. M. New Trends in IR-Spectroscopic Characterization of Acid and Basic Sites in
538 Zeolites and Oxide Catalysts. *Topics in Catalysis*. **4** (1-2) 131–144 (1997).
539 (8)   Hadjiivanov, K. I. Identification and Characterization of Surface Hydroxyl Groups by
540 Infrared Spectroscopy. *Advances in Catalysis*. **57**, 99-318 (2014).
541 (9)   Hadjiivanov, K. I., Vayssilov, G. N. Characterization of Oxide Surfaces and Zeolites by
542 Carbon Monoxide as an IR Probe Molecule. *Advances in Catalysis*. **47**, 305-511 (2002).
543 (10)   Hadjiivanov, K. Identification of Neutral and Charged N_xO_y Surface Species by IR
544 Spectroscopy. *Catalysis Reviews - Science and Engineering*. **42** (1-2) 71–144 (2000).
545 (11)   Lamberti, C., Zecchina, A., Groppo, E, Bordiga, S. Probing the Surfaces of Heterogeneous
546 Catalysts by *In Situ* IR Spectroscopy. *Chemical Society Reviews*. **39** (12), 4951–5001 (2010).
547 (12)   Meunier, F. C. Pitfalls and Benefits of *In situ* and *Operando* Diffuse Reflectance FT-IR
548 Spectroscopy (DRIFTS) Applied to Catalytic Reactions. *Reaction Chemistry & Engineering*. **1** (2),
549 134–141 (2016).
550 (13)   Ruggeri, M. P., Nova, I., Tronconi, E., Pihl, J. A., Toops, T. J., Partridge, W.P. *In-Situ* DRIFTS
551 Measurements for the Mechanistic Study of NO Oxidation Over a Commercial Cu-CHA Catalyst.
552 *Applied Catalysis B: Environmental*. **166–167**, 181–192 (2015).
553 (14)   Lentz, C. Jand, S. P., Melke, J. Roth, C., Kaghazchi, P. DRIFTS Study of CO Adsorption on Pt
554 Nanoparticles Supported by DFT Calculations. *Journal of Molecular Catalysis A: Chemical*. **426A**,
555 1–9 (2017).
556 (15)   Zhang, W., Liu, X., Dong, X., Dong, F., Zhang, Y. Facile Synthesis of $Bi_{12}O_{17}Br_2$ and $Bi_4O_5Br_2$
557 Nanosheets: In Situ DRIFTS Investigation of Photocatalytic NO Oxidation Conversion Pathway.
558 *Chinese Journal of Catalysis*. **38** (12), 2030–2038 (2017).
559 (16)   Hill, I. M., Hanspal, S., Young, Z. D., Davis, R. J. DRIFTS of Probe Molecules Adsorbed on
560 Magnesia, Zirconia, and Hydroxyapatite Catalysts. *Journal of Physical Chemistry C*. **119** (17),
561 9186–9197 (2015).
562 (17)   Aldana, P.A.U., Ocampo, F.; Kobl, K., Louis, B., Thibault-Starzyk, Daturi, M., Bazin, P.;
563 Thomas, S., Roger, A.C. Catalytic CO_2 Valorization into CH_4 on Ni-Based Ceria-Zirconia. Reaction
564 Mechanism by *Operando* IR Spectroscopy. *Catalysis Today*. **215**, 201–207 (2013).
565 (18)   Bañares, M. A. *Operando* Methodology: Combination of *In Situ* Spectroscopy and
566 Simultaneous Activity Measurements Under Catalytic Reaction Conditions. *Catalysis Today*. **100**
567 (1–2), 71–77 (2005).
568 (19)   Friebe, S., Mundstock, A., Volgmann, K., Caro, J. On the Better Understanding of the
569 Surprisingly High Performance of Metal-Organic Framework-Based Mixed-Matrix Membranes
570 Using the Example of UiO-66 and Matrimid. *ACS Applied Materials Interfaces*. **9** (47), 41553–
571 41558 (2017).
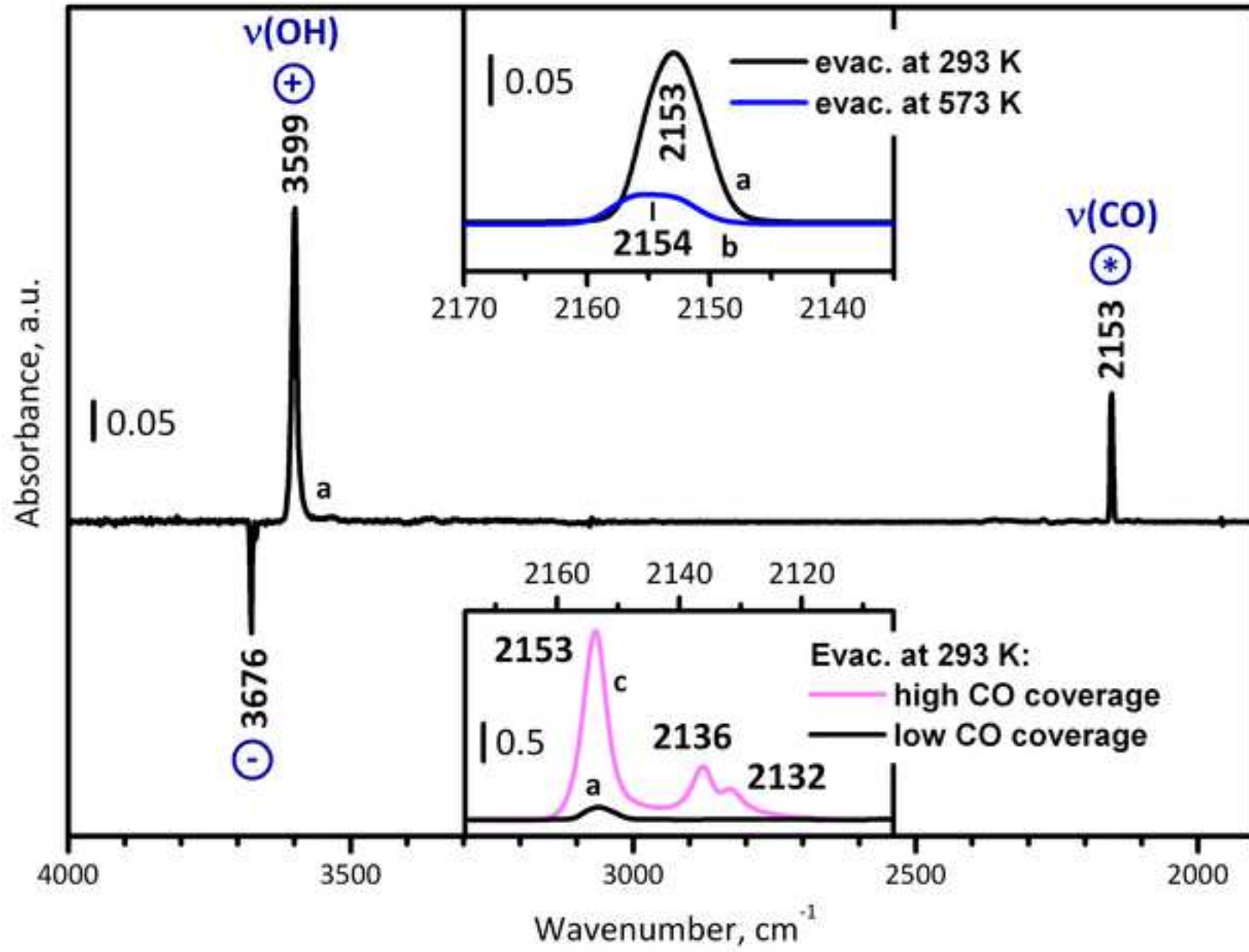572 (20)   Ballinger, Y. H., Wong, J. C. S., Yates, J. T. Jr. Transmission Infrared Spectroscopy of High

573   Area Solid Surfaces. A Useful Method for Sample Preparation. *Langmuir*. **8** (6), 1676–1678 (1992).

574   (21)   Vimont, A. et al. Evidence of CO_2 Molecule Acting as an Electron Acceptor on a
575   Nanoporous Metal–Organic-Framework MIL-53 or $Cr^{3+}(OH)(O_2C–C_6H_4–CO_2)$. *Chemical*
576   *Communications*. **43** (31), 3291–3293 (2007).

577   (22)   Mihaylov, M. et al. Adsorption Forms of CO_2 on MIL-53(Al) and NH_2‑MIL-53(Al) as
578   Revealed by FTIR Spectroscopy. *Journal of Physical Chemistry C*. **120** (41), 23584–23595 (2016).

579   (23)   Chakarova, K., Strauss, I., Mihaylov, M., Drenchev, N., Hadjiivanov, K. Evolution of Acid
580   and Basic Sites in UiO-66 and UiO-66-NH_2 Metal-Organic Frameworks: FTIR Study by Probe
581   Molecules. *Microporous and Mesoporous Materials*. **281**, 110–122 (2019).

582   (24)   Delgado, M. R., Bulánek, R., Chlubná, P., Arean, C. O. Brønsted Acidity of H-MCM-22 as
583   Probed by Variable-Temperature Infrared Spectroscopy of Adsorbed CO and N_2, *Catalysis Today*.
584   **227**, 45–49 (2014).

(A)

(B)

Pellet position (1) (inside the oven)

Pellet position (3) (in the path of the IR beam)

Mobile pellet holder

Magnet

IR-transparent windows (KBr, CaF₂)

Connection to the vacuum-adsorption apparatus

Thermocouple

Oven

Pellet position (2) (intermediate)

IR beam

Liquid nitrogen

H₂O

Liquid nitrogen

Windows (KBr, CaF₂)

Water circulating system

Figure

v(OH)

⊕

3599

| 0.05

evac. at 293 K
evac. at 573 K

2153

a

2154 b

2170   2160   2150   2140

v(CO)

✱

2153

a

| 0.05

— 3676

2160   2140   2120

2153

c

| 0.5

2136

2132

a

Evac. at 293 K:

high CO coverage
low CO coverage

4000   3500   3000   2500   2000

Absorbance, a.u.

Wavenumber, cm⁻¹

Name of Material/ Equipment	Company	Catalog Number	Comments/Description
Acetonitrile-D3	Uvasol, Merck	1.13753.0009	99.69% deuteration degree (for NMR spectroscopy)
Benzoic acid	Sigma Aldrich	242381-500G	C_7H_6O ≥99.5%
Carbon dioxide	Linde Gaz Magyarorszad	GA 473	99.9993% purity
Carbon monoxide	Merck-Schuchardt	823271	99.5% purity
Ethanol	Carl Roth	9065.1	99.8%
Glass sample holder			Self-made
HiCube80 Eco Turbo Pumping Station including HiPace 80 Turbo Pump, MVP 015 Diaphragm Vacuum Pump and DCU 002 Control Unit	Pfeiffer Vacuum	PM S74 150 00	
Horizontal glass IR cells for adsorption studies			Self-made
Methanol	Carl Roth	4627.5	≥99.9%
N,N-Dimethylformamide	Sigma Aldrich	33120-2.5L-M	99.8 %

Nicolet 6700 FTIR spectrometer	Thermo Scientific		USA
Specac Atlas Manual 15T Hydraulic Press	Specac	GS 15011	
Terephthalic acid	Sigma Aldrich	185361-100G	98%
UIO-66			Synthesized at Institute of Physical Chemistry and Electrochemistry, Leibniz Universität Hannover, Germany
Vacuum valve	Ellipse Labo	248.904	90° branches, Ø 0-4 mm
Vacuum valve	Ellipse Labo	248.910	90° branches, Ø 0-10 mm
Zirconium(IV) chloride	Sigma Aldrich	357405-10G	Anhydrous, 98 %

Dear Dr. Steindel,

Re: Submission JoVE60285R3

Please, find uploaded the revised version of our paper:

In situ FTIR Spectroscopy as a Tool for Investigation of Gas/Solid Interaction: Water-Enhanced CO_2 Adsorption in UiO-66 Metal-Organic Framework

We made the following changes according to your requirements:

Req. 1. There are no 'a' or 'b' labels in Figure 3, despite the legend.

Action: Corrected.

Req. 2. Figure 4 and 5 seem to be switched. Additionally, the insets in the current Figure 5 do not seem to be explained in the legend.

Action: Corrected. Explanation of the insets is included in the legend (lines 414-417).

Req. 3. There are no b-d labels in Figure 7. Additionally, further description of the conditions under which these spectra were taken would be useful.

Action: Spectra b-d are labelled. More details on the experimental conditions are provided (lines 430-431).

Req. 4. Please define UiO-66 at first use.

Action: UiO-66 is defined (lines 56-59).

I use the opportunity to wish you Merry Christmas!
Sincerely yours,

Konstantin Hadjiivanov