Bulgarian Academy of Sciences

Institute of General and Inorganic Chemistry

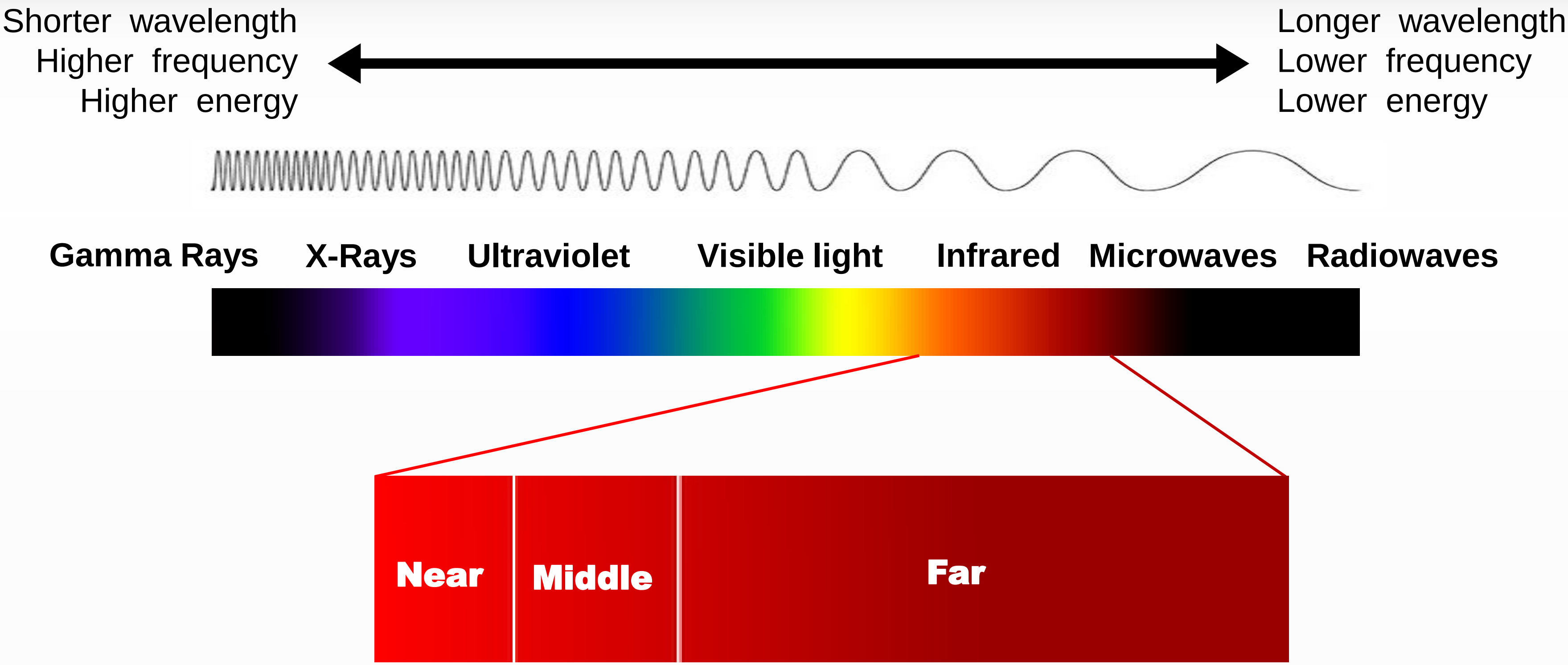
BAS-IGIC

Characterization of solid surfaces using IR spectroscopy of probe molecules

Laboratory
“Reactivity of solid surfaces”
IGIC-BAS

Kristina Chakarova

Infrared radiation



Shorter wavelength
Higher frequency
Higher energy

Longer wavelength
Lower frequency
Lower energy

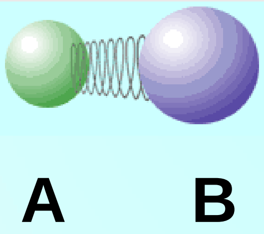
Gamma Rays **X-Rays** **Ultraviolet** **Visible light** **Infrared** **Microwaves** **Radiowaves**

Near **Middle** **Far**

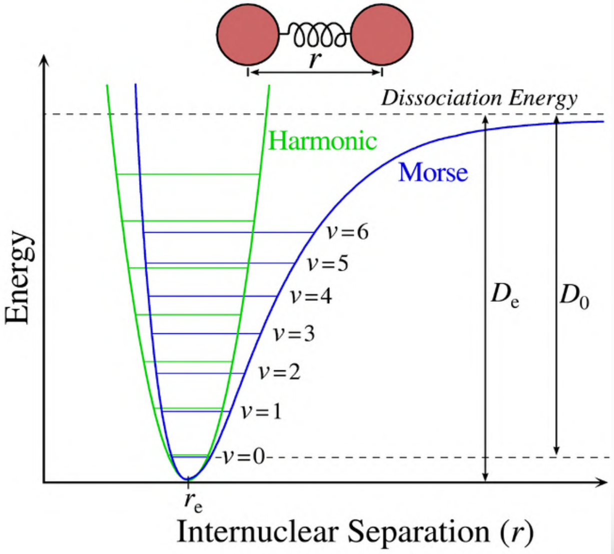
	Wavenumber, cm^{-1}	Wavelength, μm
Near-IR	14000 – 4000	0.7 – 2.5
Mid-IR	4000 – 400	2.5 – 25
Far-IR	400 – 10	25 – 1000

Vibrational spectroscopy

The stretching frequency, ν, of a diatomic molecule AB depends on the force constant (k) and the reduced mass (μ) of the two atoms:



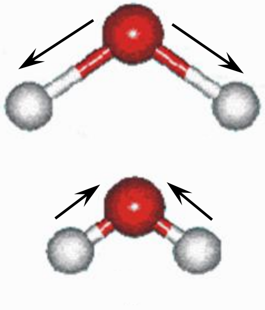
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{M_A M_B}{M_A + M_B}$$



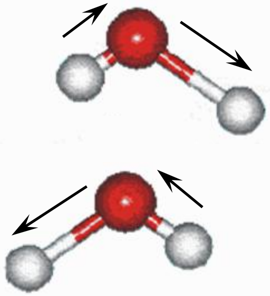
In theory, there is no difference between practice and theory. In practice, there is.

A. Einstein

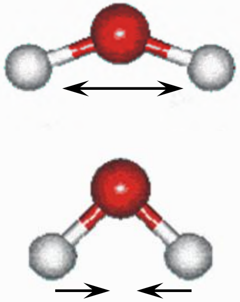
Different vibrational modes



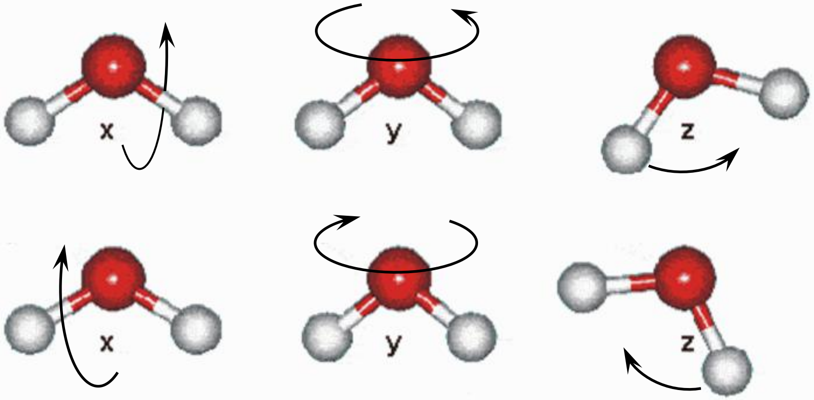
Symmetric stretchings



Antisymmetric stretchings



Deformation modes



Libraions

IR spectroscopy in surface chemistry

- It is inexpensive, highly sensitive and selective technique.
- Gives some direct information about the surface species (OH groups, stable surface species, impurities, etc.)

However…

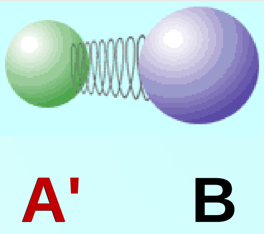
- Brings only little information on the surface properties.
- Gives poor information about the acidity of the surface OH groups.
- It is "blind" to the presence of coordinatively unsaturated surface ions.
- No discrimination between bulk and surface species can be made.

Some requirements for probe molecules

- The functional group or atom with which the molecule is coordinated to the surface should be well known.
- The molecule should have a pronounced acidic or basic character, it should occupy the same type of adsorption sites and the formed surface complexes should have the same structure.
- Adsorption complexes should be stable enough to allow characterization and their adsorption bands should have sufficiently high intensity.
- The spectral parameters of the molecule should fall within the area where the sample is transparent and should be sensitive to the state of the surface sites on which they are adsorbed.
- The molecule should not cause chemical modification of the surface.

Isotopic exchange

The stretching frequency, ν, of a diatomic molecule AB depends on the force constant (k) and the reduced mass (μ) of the two atoms:



$$\nu_{A'B} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{A'B}}}$$

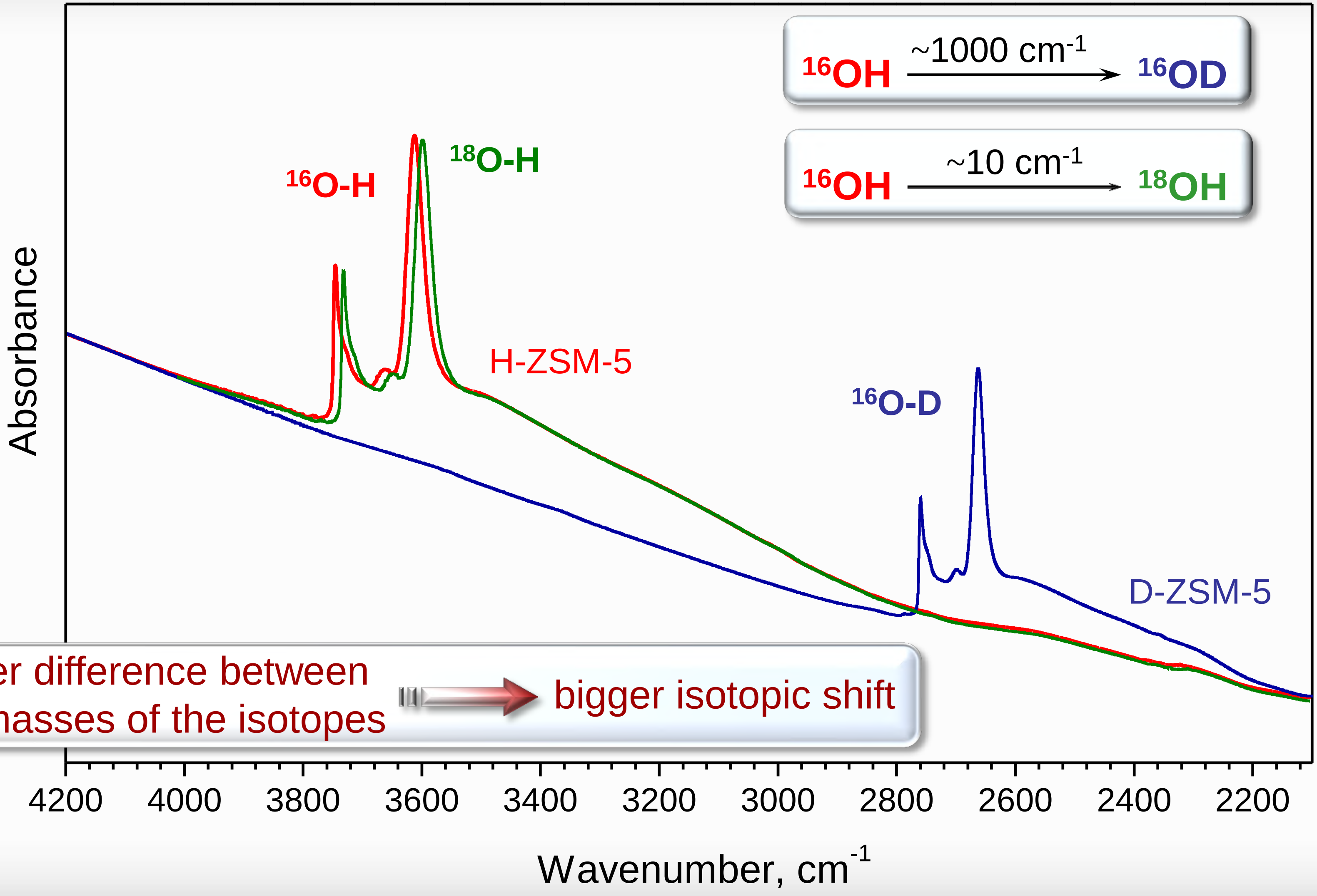
$$\mu_{A'B} = \frac{M_{A'}M_B}{M_{A'}+M_B}$$

The ν(AB) will be changed after replacement of atom A by its isotope A′ and the corresponding IR band will be shifted.

isotopic shift factor ←

$$i = \frac{\nu_{AB}}{\nu_{A'B}} = \sqrt{\frac{\mu_{A'B}}{\mu_{AB}}}$$

Isotopically labelled molecules

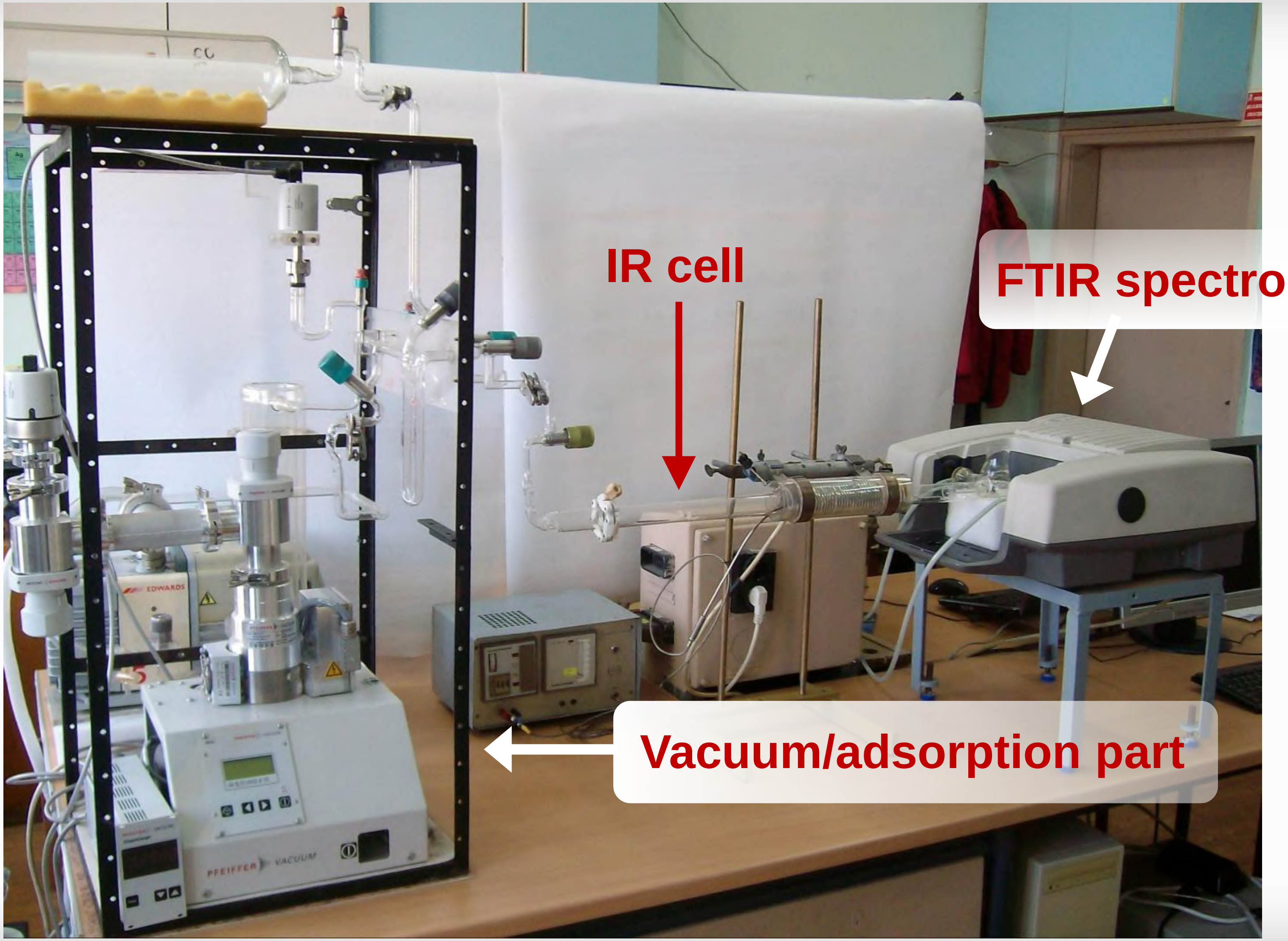


$$^{16}\mathrm{OH} \xrightarrow{\sim 1000\ \mathrm{cm}^{-1}} {}^{16}\mathrm{OD}$$

$$^{16}\mathrm{OH} \xrightarrow{\sim 10\ \mathrm{cm}^{-1}} {}^{18}\mathrm{OH}$$

bigger difference between the masses of the isotopes → bigger isotopic shift

IR adsorption system



IR cell

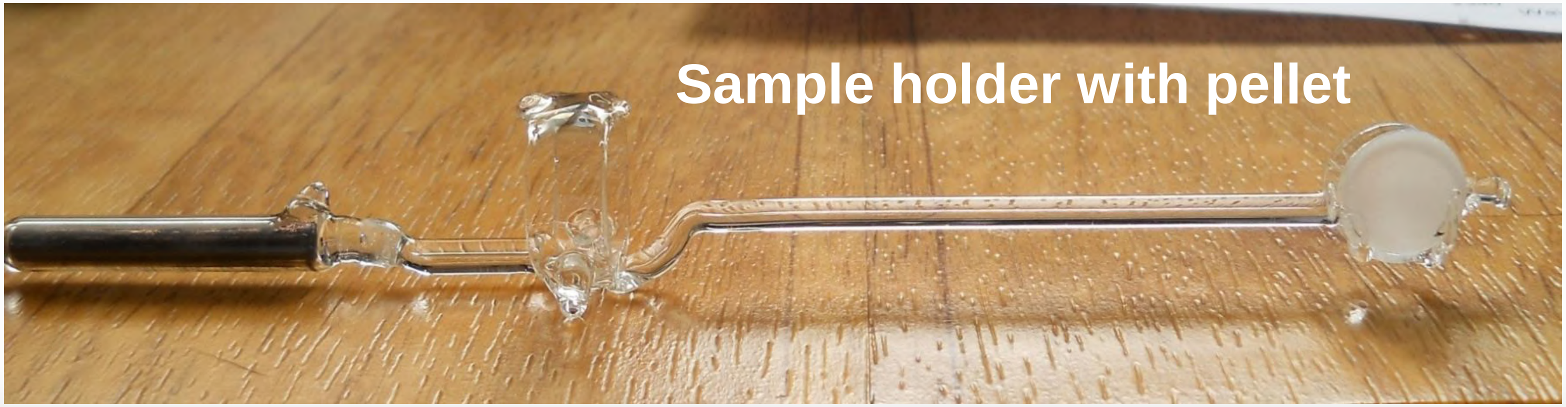
FTIR spectrometer

Vacuum/adsorption part

Making self-supporting pellets

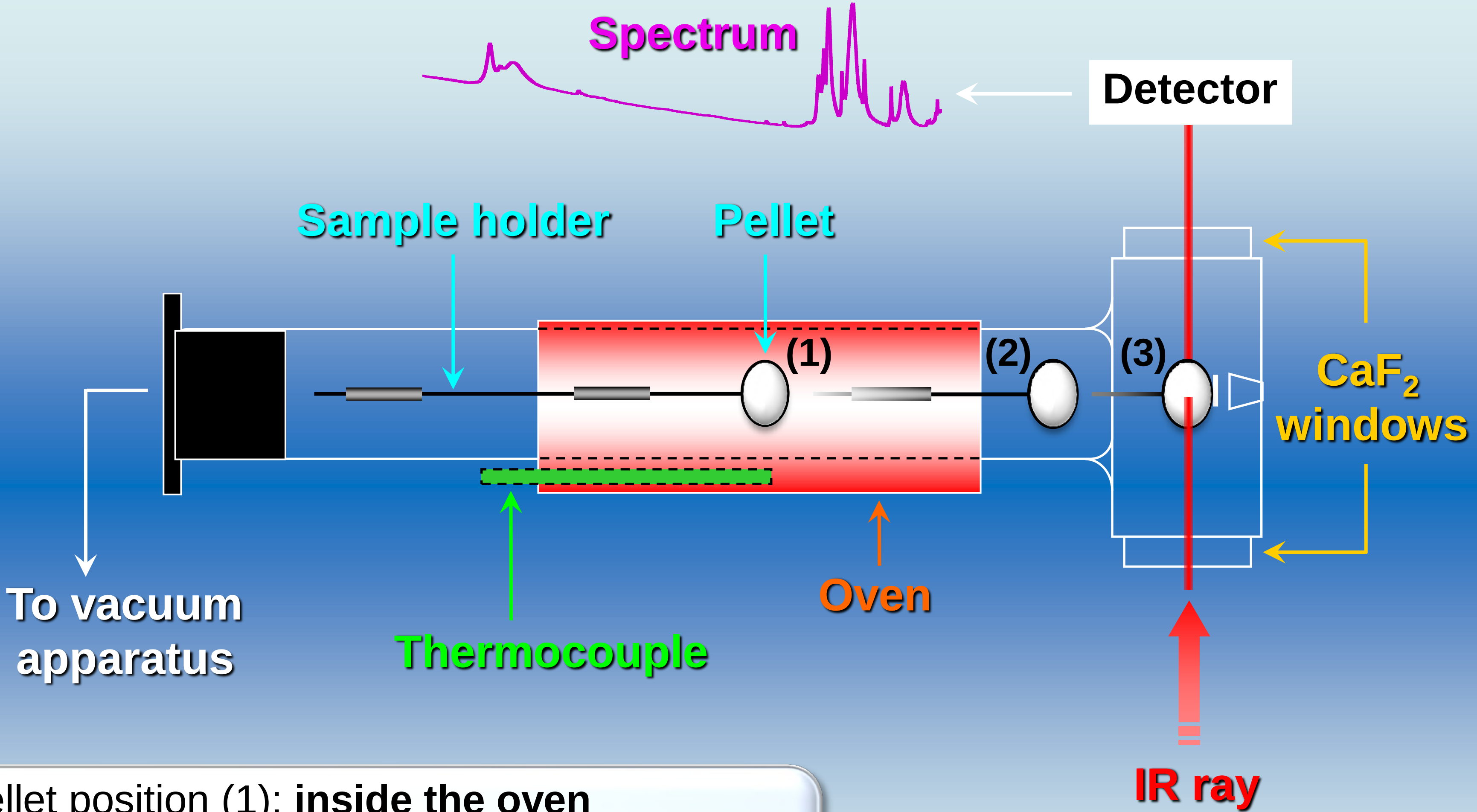
Hydraulic press

Round pellet die set



Sample holder with pellet

IR cell for adsorption studies



Pellet position (1): **inside the oven**

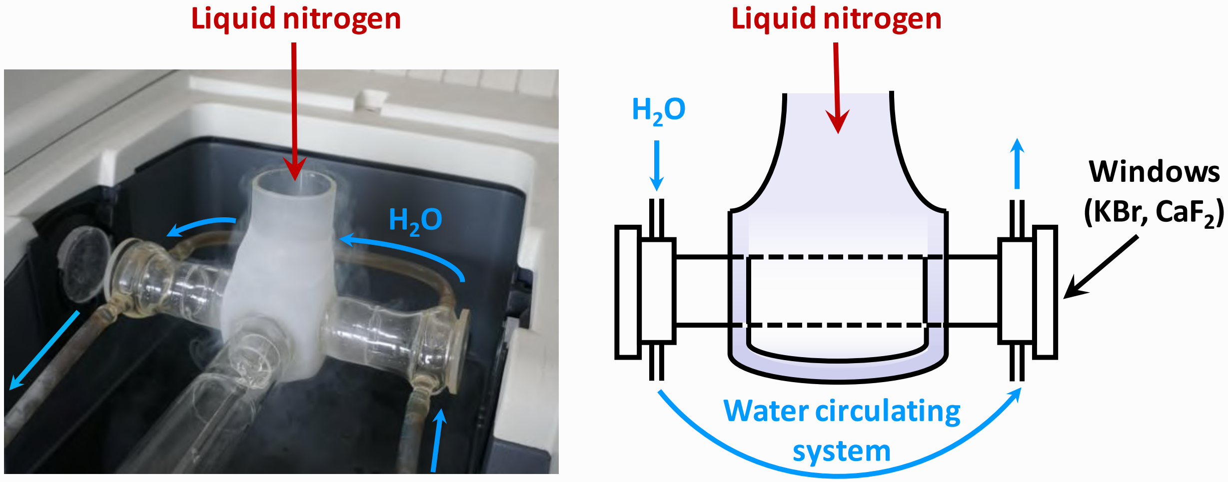
Pellet position (2): **intermediate**

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

IR cells for adsorption studies at different temperatures

IR cell for adsorption studies at ambient temperature

IR cell for adsorption studies at low temperature (100 K)



More details on our experimental protocol

jove Journal of Visualized Experiments www.jove.com

Video Article

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

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DOI: doi:10.3791/60285

Keywords: Chemistry, Issue 156, Adsorption, Brønsted acidity, CO_2 capture, FTIR spectroscopy, Lewis acidity, Metal-organic frameworks, Probe molecules, Surface characterization, UiO-66

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Abstract

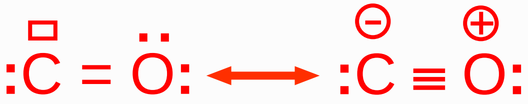
In situ infrared spectroscopy is an inexpensive, highly sensitive, and selective valuable tool to investigate the interaction of polycrystalline solids with adsorbates. Vibrational spectra provide information on the chemical nature of adsorbed species and their structure. Thus, they are very useful for obtaining molecular level understanding of surface species. The IR spectrum of the sample itself gives some direct information about the material. General conclusions can be drawn concerning hydroxyl groups, some stable surface species and impurities. However, the spectrum of the sample is "blind" with respect to the presence of coordinatively unsaturated ions and gives rather poor information about the acidity of surface hydroxyls, species decisive 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, substances that interact specifically with the surface;

CO as a probe molecule

- The vibrational spectrum of CO is simple.
- The *v*(C−O) stretching vibration is sensitive to the nature and the strength of the bond formed with the surface.
- The extinction coefficient of CO is high.
- The CO molecule is small and its adsorption is not hindered by steric interactions.

Bonding of CO to surface

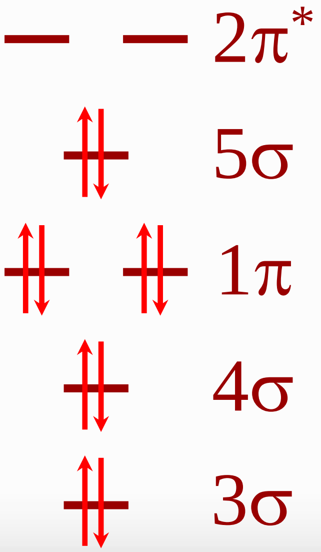
CO structure

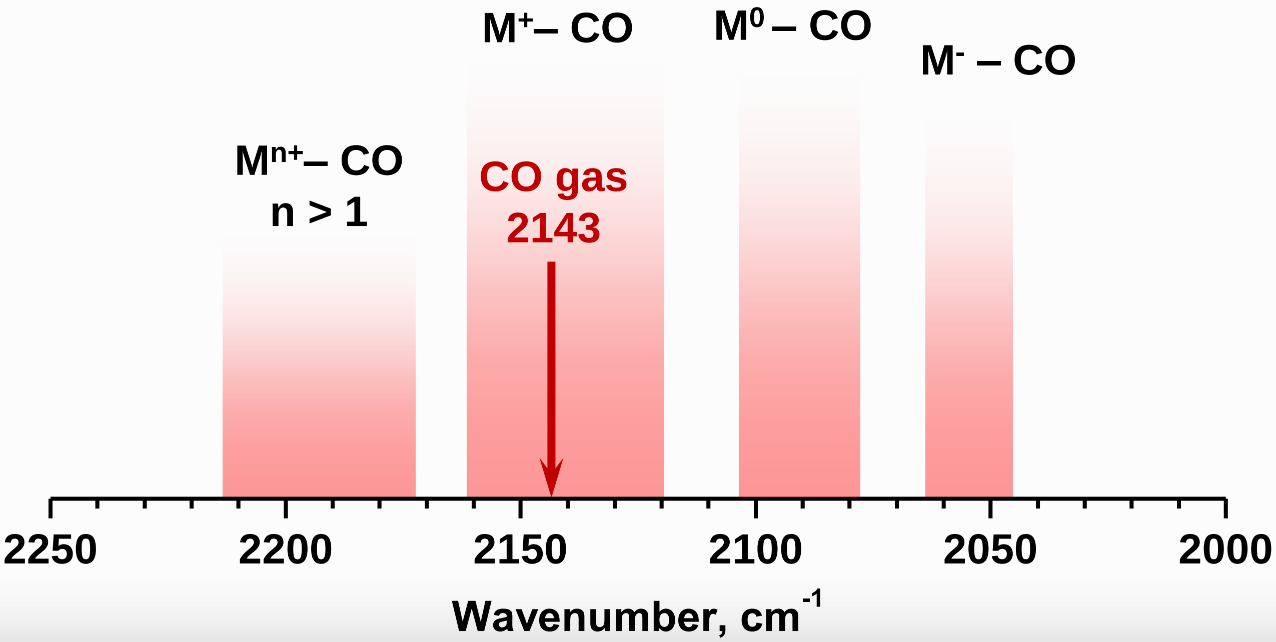


$$:\overset{\square}{C} = \overset{\cdot\cdot}{O}: \longleftrightarrow :\overset{\ominus}{C} \equiv \overset{\oplus}{O}:$$

The lower the oxidation state of a given metal cation, the lower the frequency of the corresponding carbonyl band.

Molecular orbitals of CO



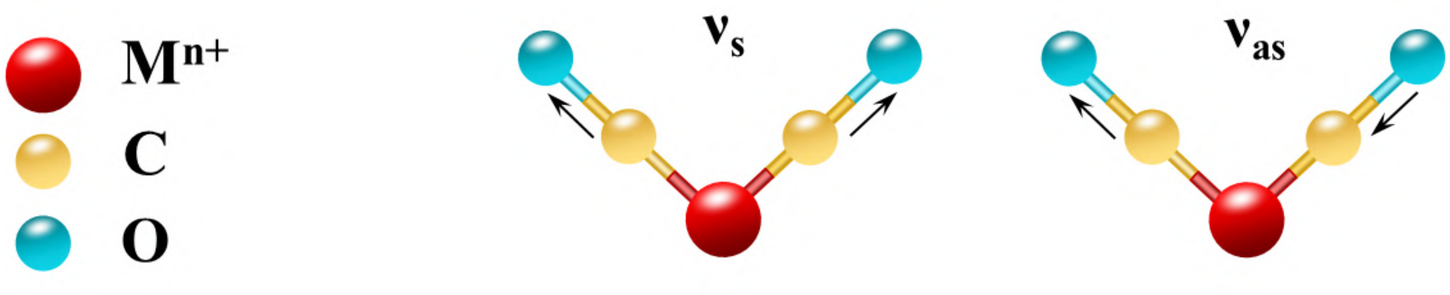


Coordination state of cations

CO molecules coordinated simultaneously to one cation = number of effective coordination vacancies

Exceptions: complex-specified polycarbonyls of Rh^{n+}, Ru^{n+}, Os^{n+} and Ir^{n+} ions.

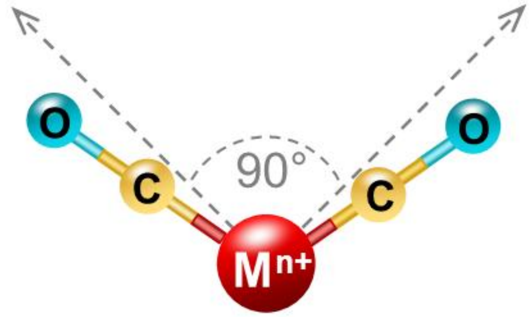
Dicarbonyls

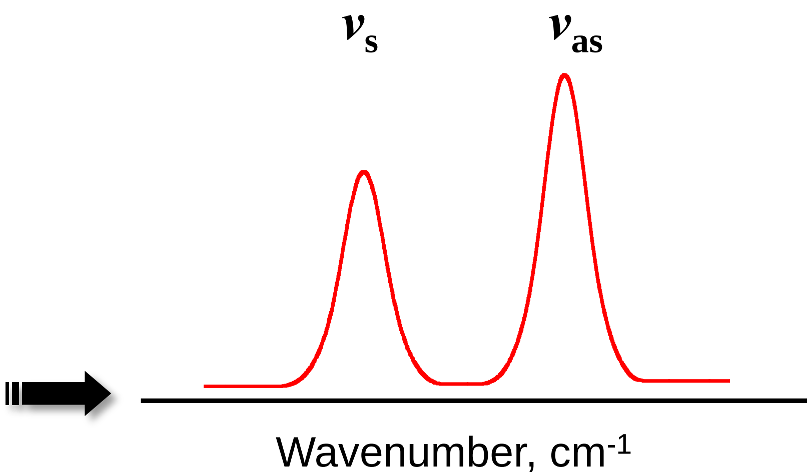


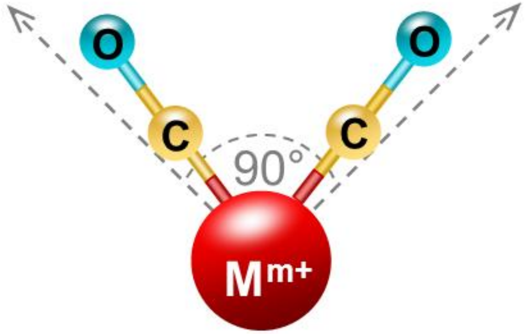
Symmetric stretching mode

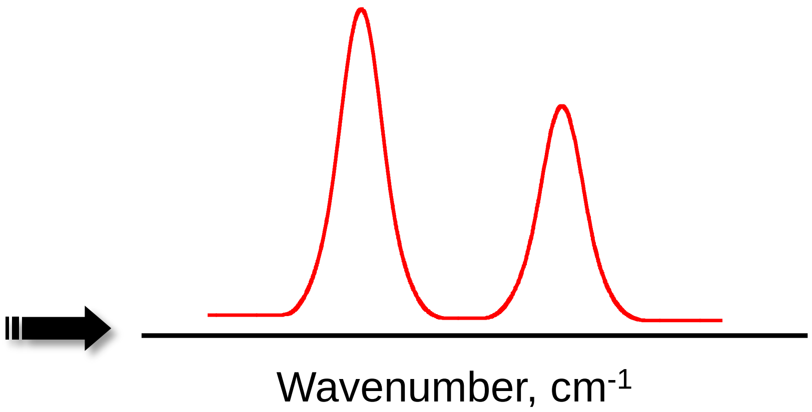
Antisymmetric stretching mode

Dicarbonyls

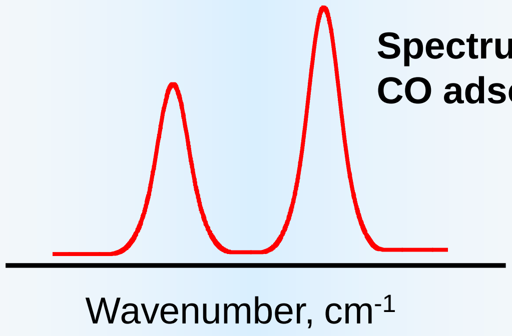




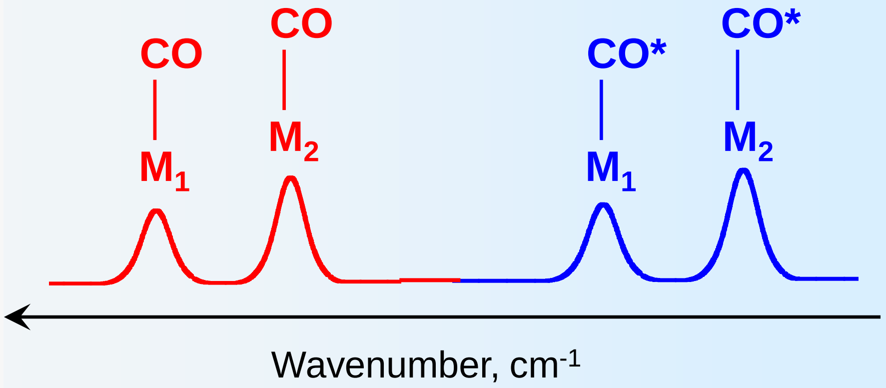




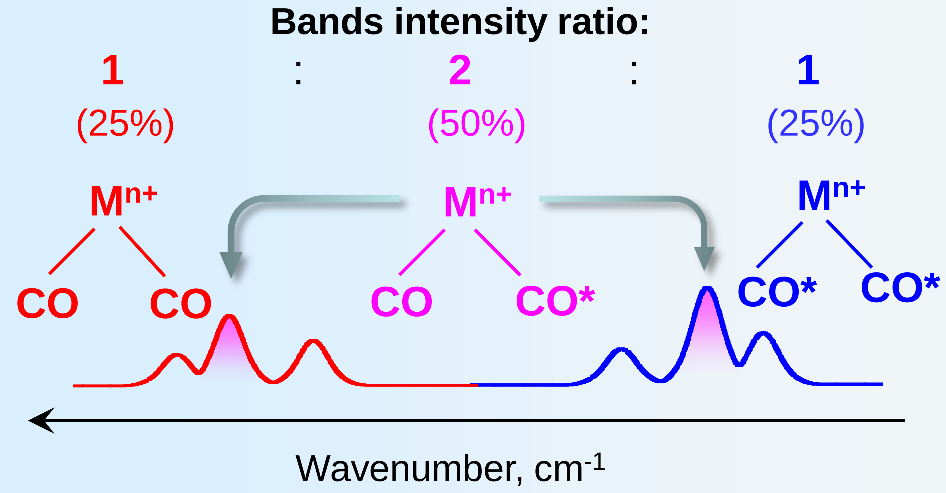
Dicarbonyls: adsorption of CO isotopic mixtures



Spectrum after CO adsorption



Spectrum after adsorption of isotopic mixture if the bands are due to monocarbonyls



Spectrum after adsorption of isotopic mixture if the bands are due to dicarbonyls

CO isotopic mixtures

- Isotopologues: **CO, ^{13}CO, C^{18}O, ^{13}C^{18}O**

- Isotopic mixtures:

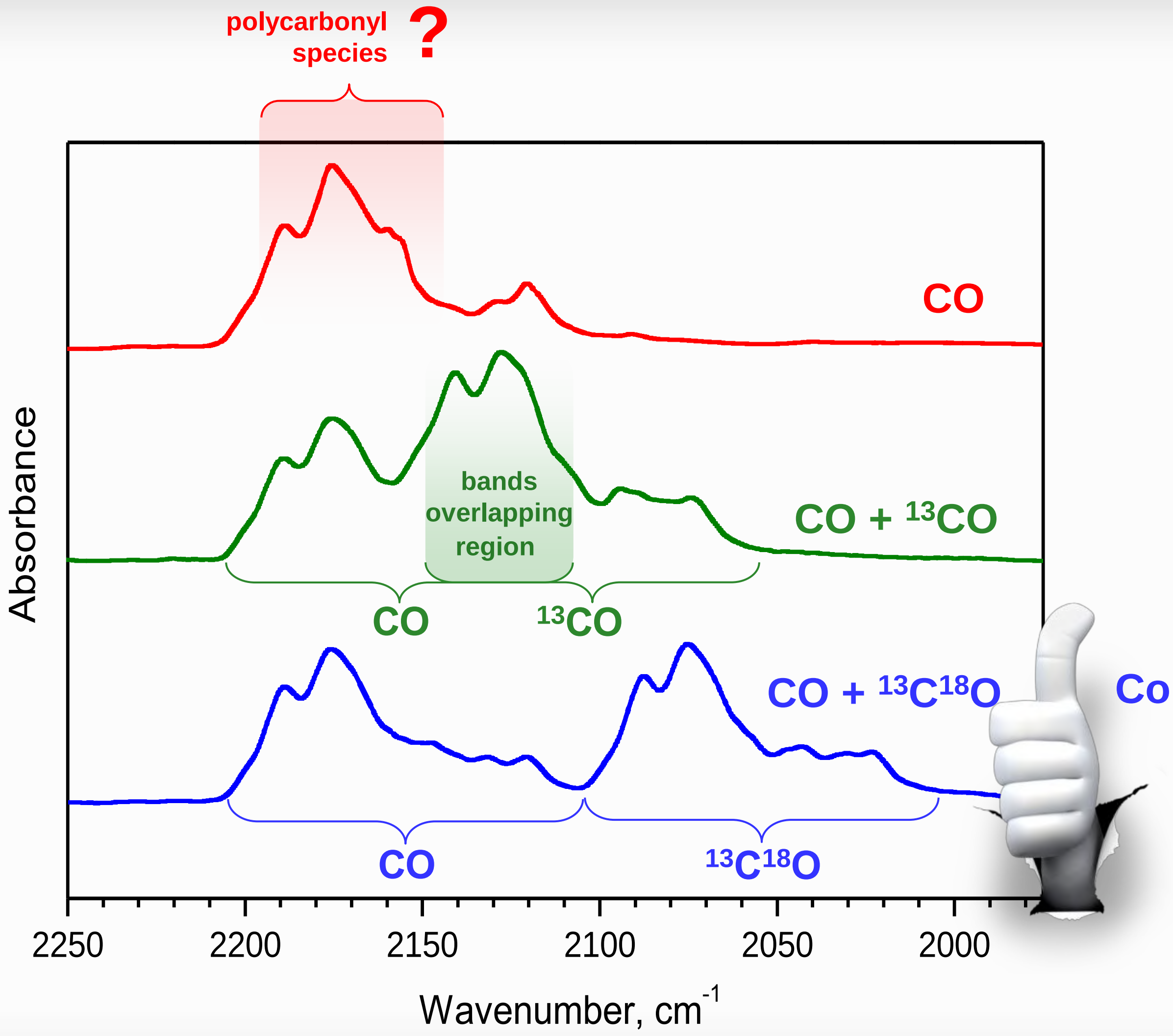
CO + ^{13}CO conventional mixture (spectral separation ~ **50 cm^{-1}**)

CO + C^{18}O (spectral separation ~ **50 cm^{-1}**)

^{13}CO + C^{18}O (spectral separation ~ **0 cm^{-1}**)

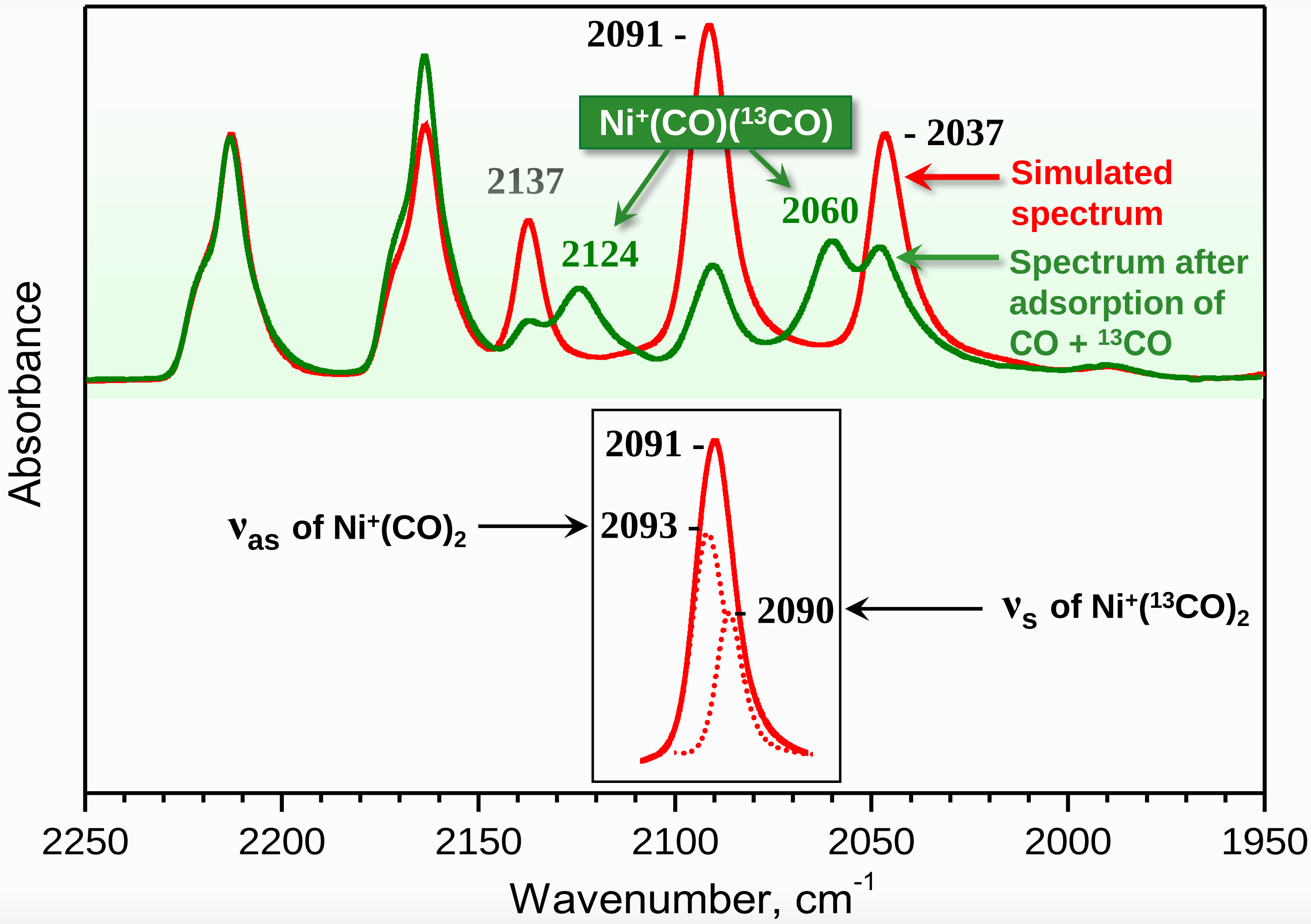
CO + ^{13}C^{18}O heavy mixture (spectral separation ~ **100 cm^{-1}**)

Low-temperature adsorption of CO and CO+CO* isotopic mixtures on reduced Fe-BEA

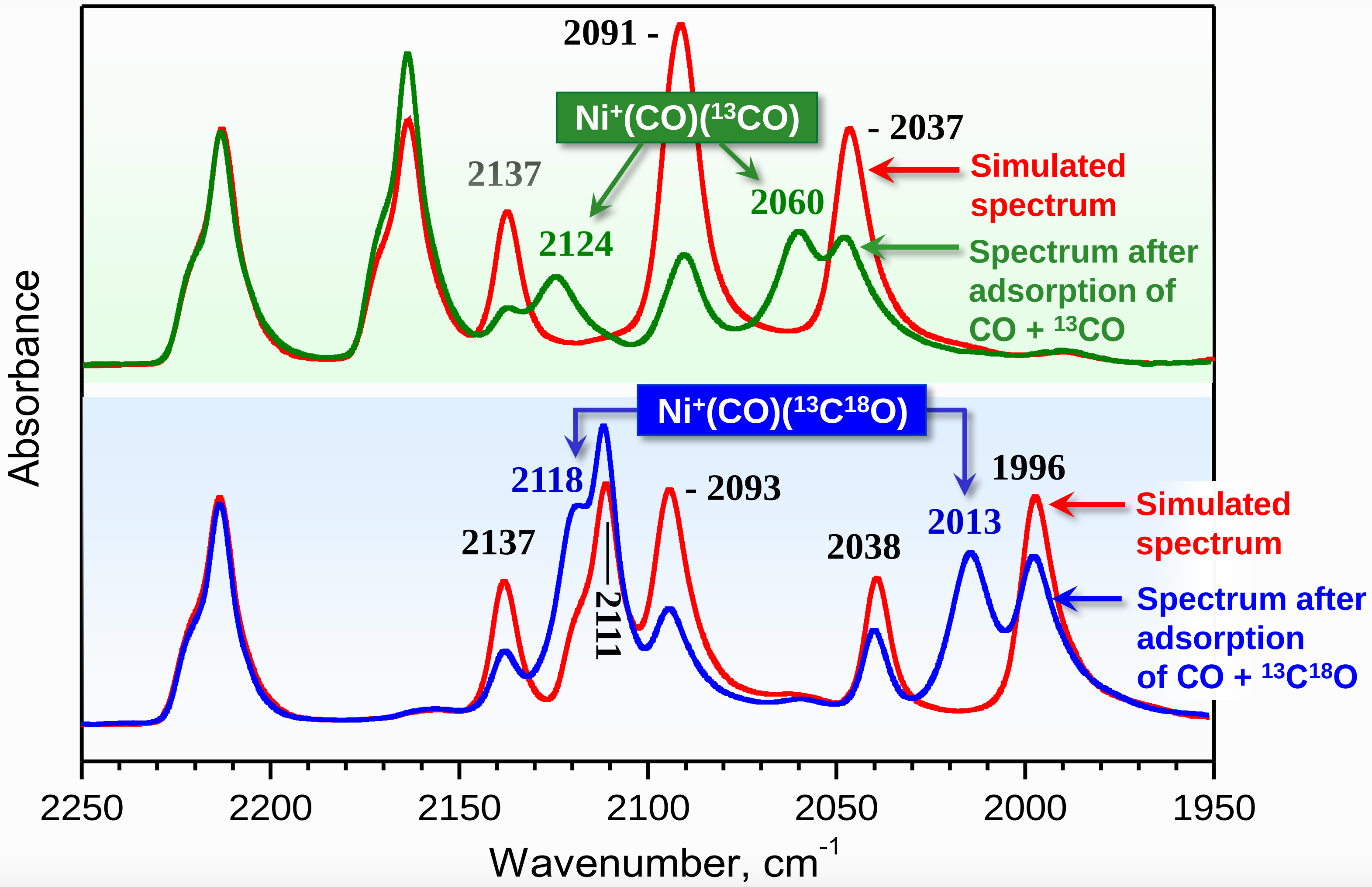


Complete separation of the bands

Low-temperature adsorption of CO and CO+CO* isotopic mixtures on partially reduced Ni-ZSM-5



Low-temperature adsorption of CO and CO+CO* isotopic mixtures on partially reduced Ni-ZSM-5



Tricarbonyl complexes

- Tricarbonyls with C_{3v} symmetry:
  - Characterized by two (symmetric and antisymmetric) bands
  - After adsorption of CO + CO* isotopic mixtures:

$M^{n+}(CO)_3 \rightarrow$ *2 bands* $M^{n+}(CO)_2(CO^*) \rightarrow$ *3 bands*

$M^{n+}(CO^*)_3 \rightarrow$ *2 bands* $M^{n+}(CO)(CO^*)_2 \rightarrow$ *3 bands*

- Tricarbonyls with lowered symmetry:
  - Characterized by three bands
  - 12+ bands after adsorption of isotopic mixtures

Di- and tricarbonyl complexes

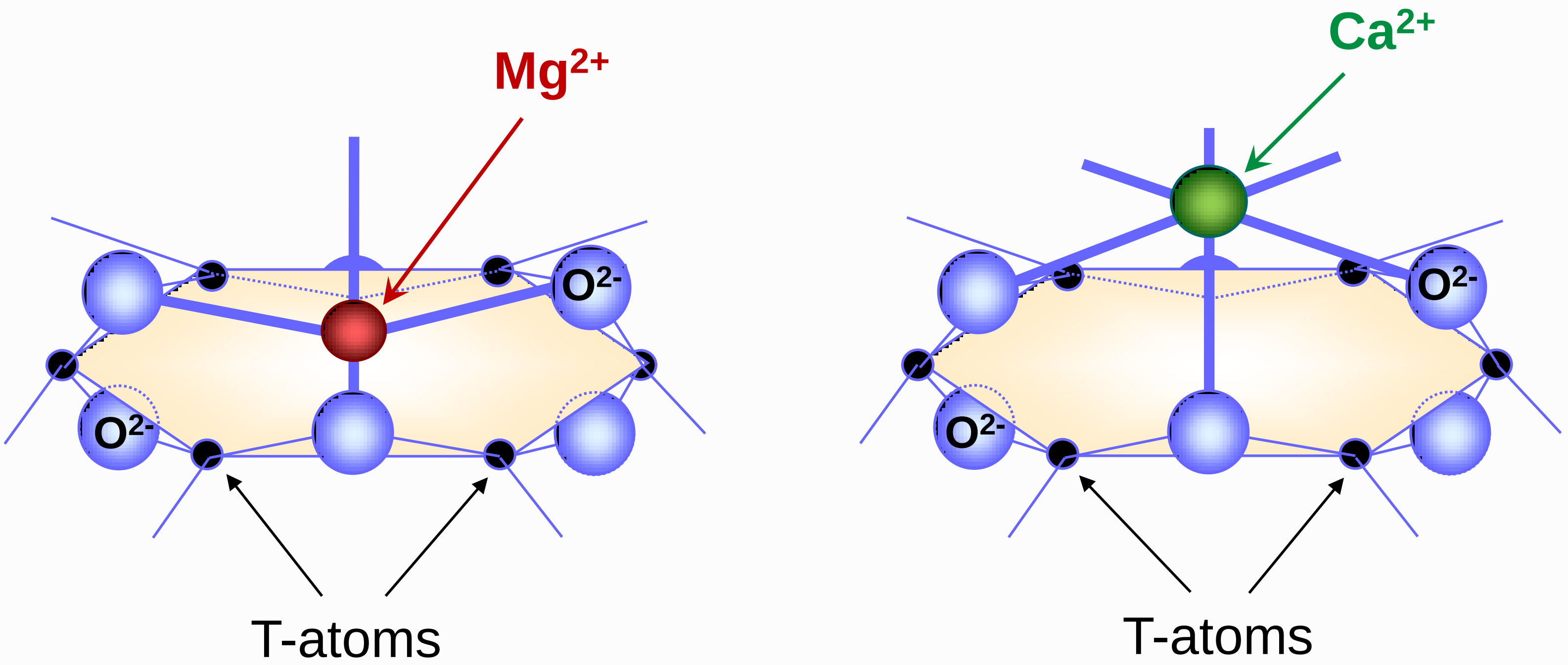
Concentration (% of total) of ***dicarbonyl species*** *having different numbers of labelled CO ligands (CO*) at two different CO : CO* isotopic ratios.*

CO : CO* ratio	$M(CO)_2$	$M(CO)(CO^*)$	$M(CO^*)_2$
1 : 1	25	50	25
3 : 1	56.25	37.5	6.25

Concentration (% of total) of ***tricarbonyl species*** *having different numbers of labelled CO ligands (CO*) at two different CO : CO* isotopic ratios.*

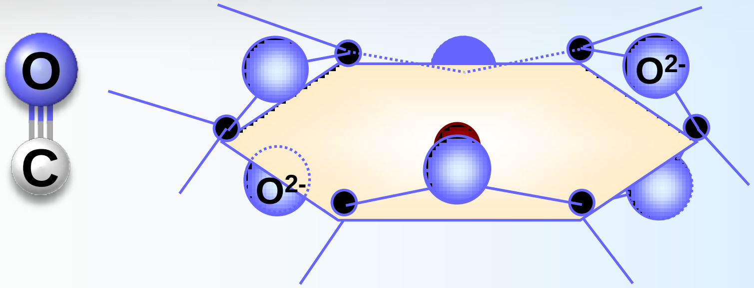
CO : CO* ratio	$M(CO)_3$	$M(CO)_2(CO^*)$	$M(CO)(CO^*)_2$	$M(CO^*)_3$
1 : 1	12.5	37.5	37.5	12.5
3 : 1	42.2	42.2	14	1.6

Effect of the cationic radius



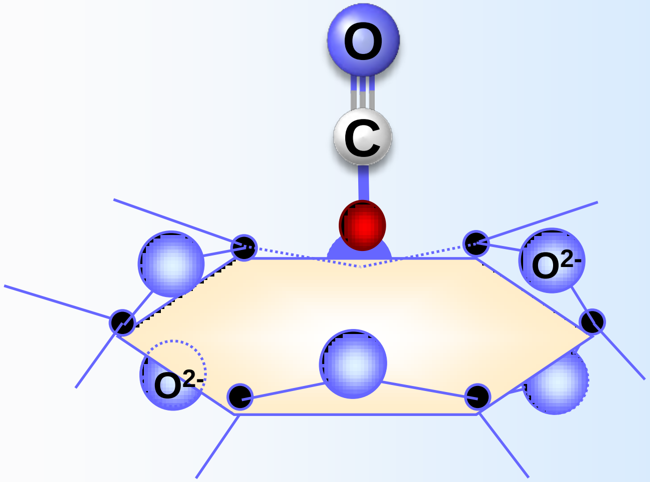
Twin species are formed only if the cationic radius is higher than the critical value for the given support.

Effect of the cationic radius: Carbonyls in Au^{3+}/NaY

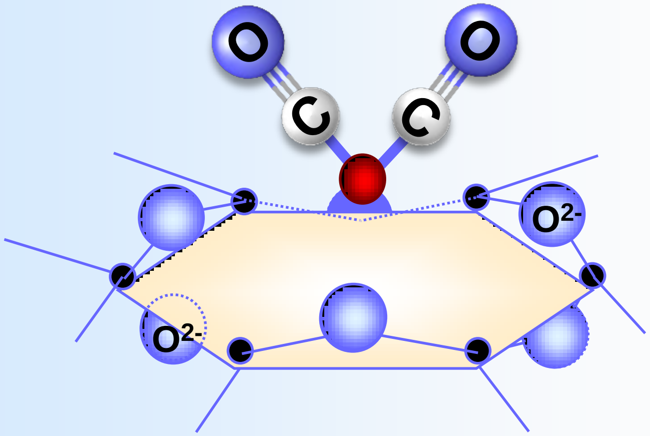


CO ads. at 85 K → No carbonyls of Au^{3+}

T > 220 K → Au^{3+}– CO



T lowered to 85 K in presence of CO → $Au^{3+}(CO)_2$



When the cationic radius is around the critical one, the formation of dicarbonyls could depend on the adsorption temperature.

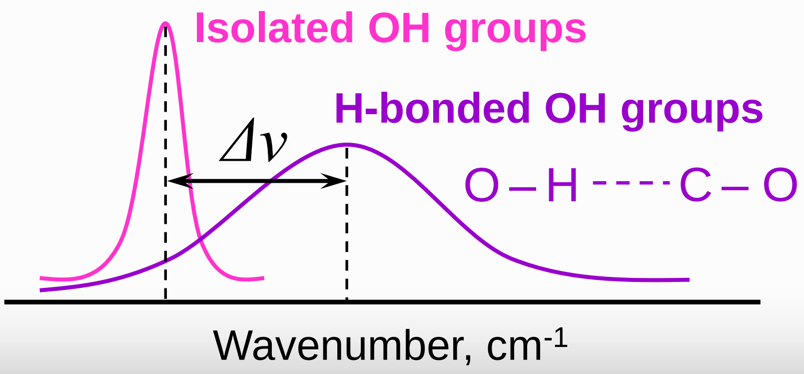
Acidity of surface OH groups: IR approaches

Ion-pair method

- Based on the interaction of hydroxyls with strong bases like pyridine or ammonia;
- Gives information on the presence of Brönsted acid sites but does not give direct results on the acidity strength;
- Adsorption of pyridine and ammonia is not specific to acidic sites and they can also be dissociatively adsorbed on basic sites.

H-bond method

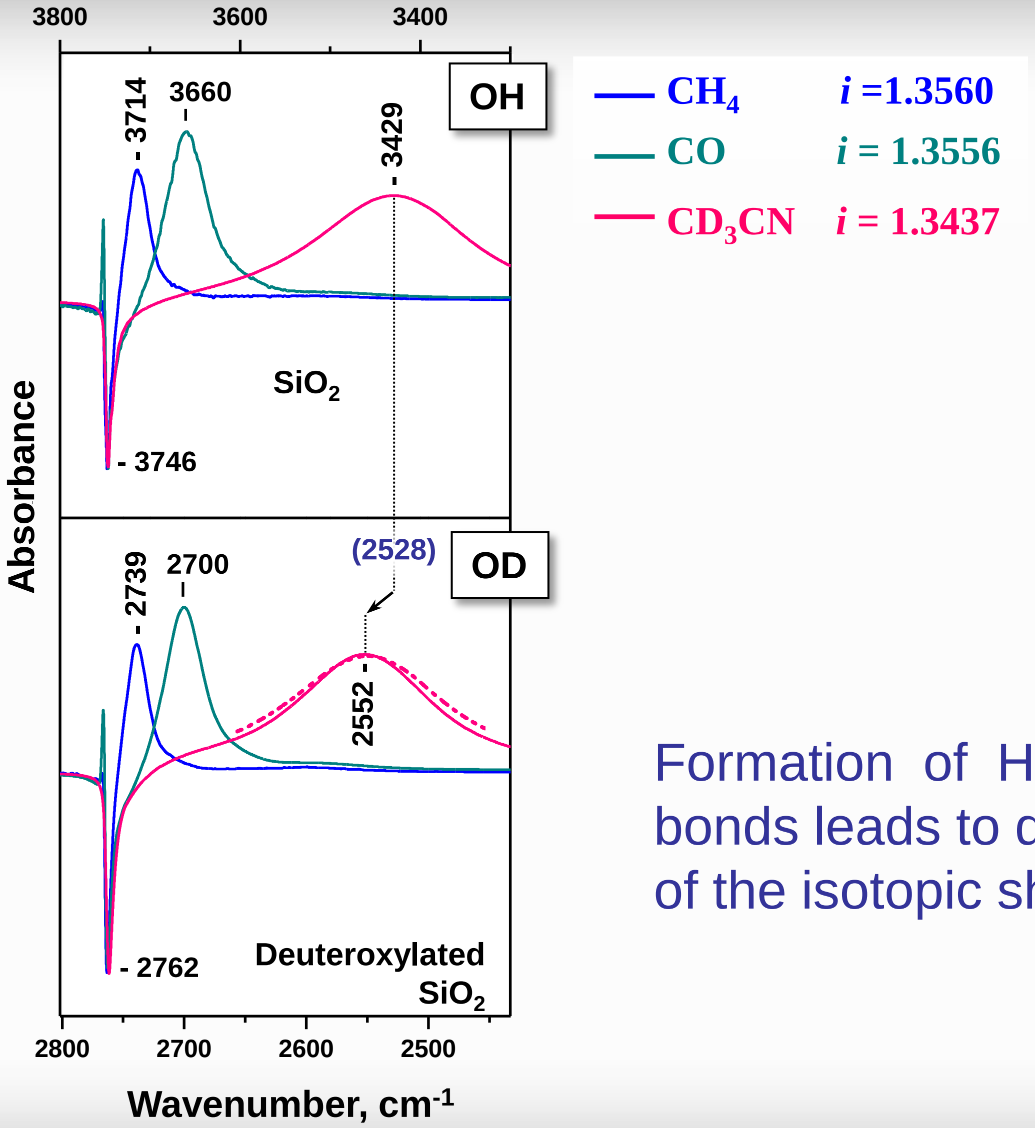
- Based on the interaction of hydroxyls with weak bases;
- Gives direct values on the OH acidity;
- The acidity is proportional to the adsobate-induced red shift $\Delta\nu$ of the OH modes.



OH → OD exchange

- To identify if a given vibration involves hydrogen
- To establish the accessibility of the OH groups
- To obtain high quality spectra
- To check for existence of spectral phenomena

Acidity of OH and OD groups

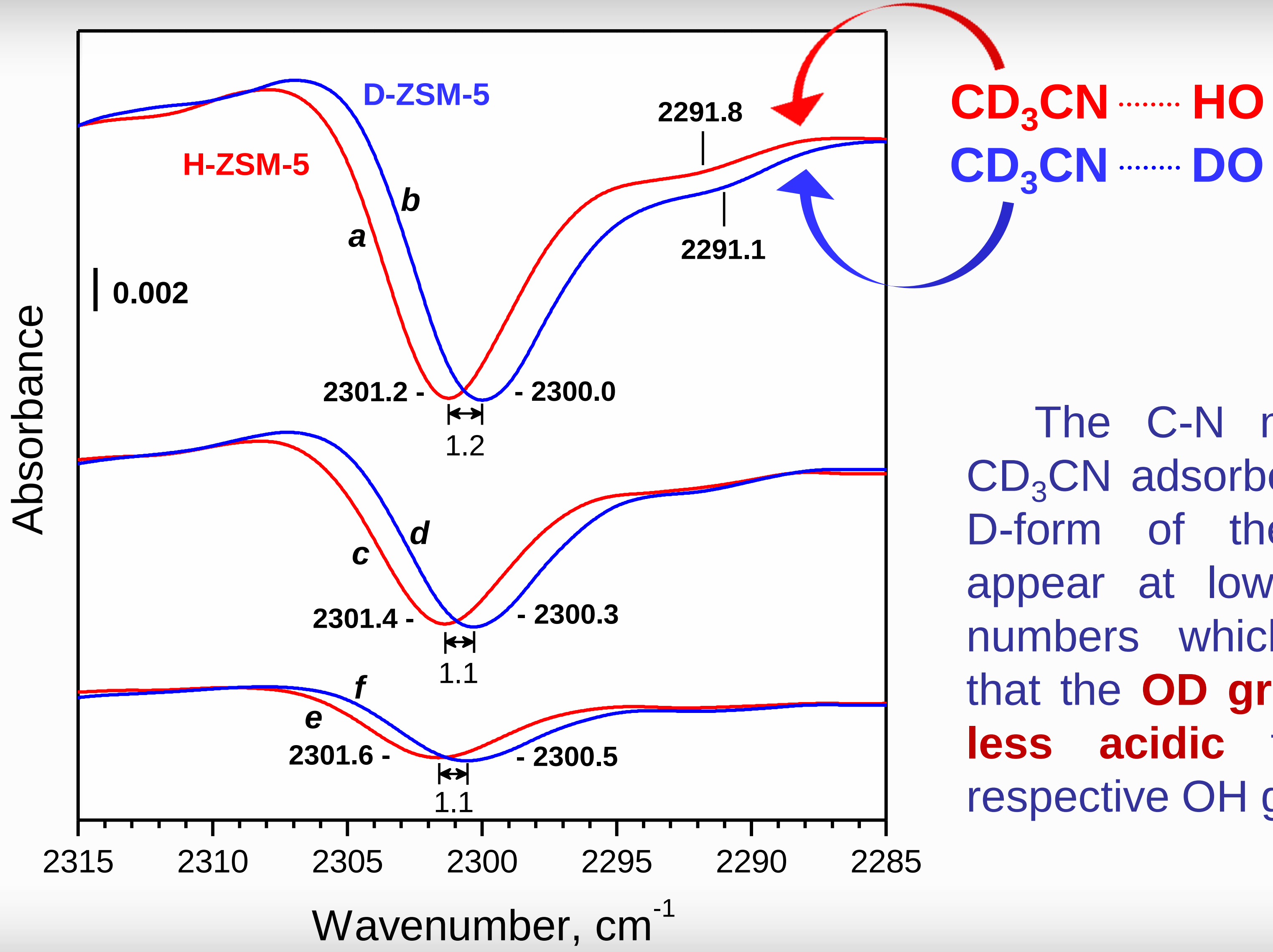


Formation of H- and D-bonds leads to decrease of the isotopic shift factor

OH *vs.* OD groups

- The drastic difference between the masses of H_2 and D_2 leads to measurable differences in their chemical properties.
- The O–D bonds are more harmonic as compared to the OH bonds.
- The O–D bonds are stronger than the respective O–H bonds.
- The OD groups have lower acidity than the corresponding OH groups.

Acidity of OH and OD groups



The C-N modes of CD_3CN adsorbed on the D-form of the zeolite appear at lower wave-numbers which proves that the **OD groups are less acidic** than the respective OH groups.

NO isotopologues

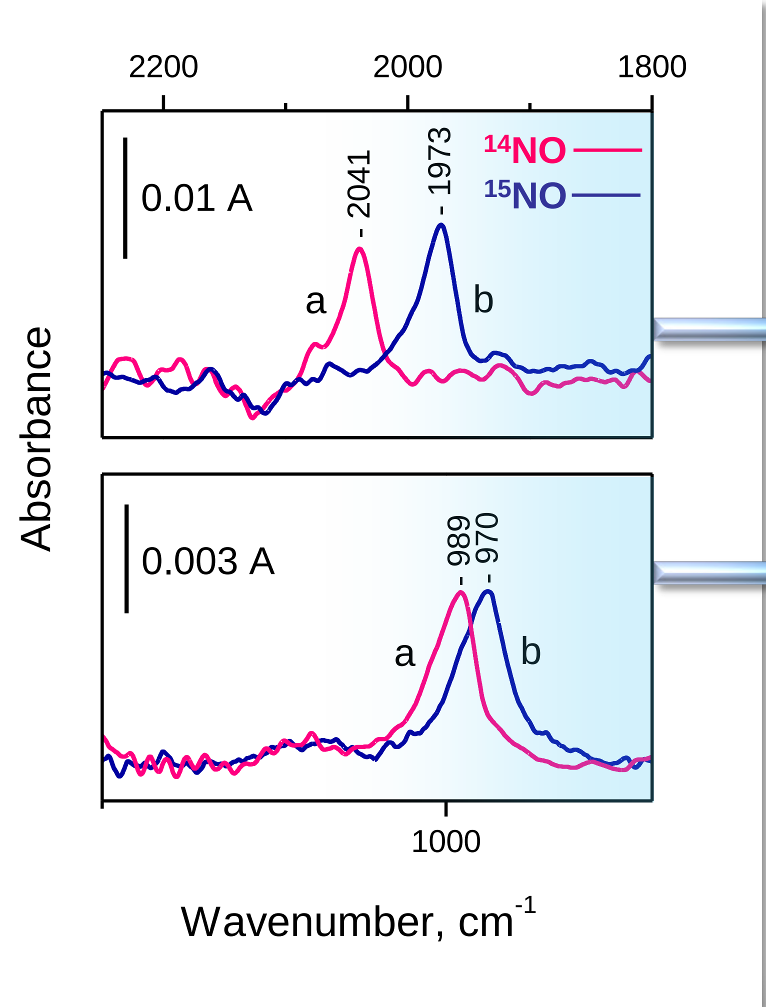
$^{14}\mathrm{NO}$ → most frequently used

$^{15}\mathrm{NO}$ → provides additional information

$^{15}\mathrm{N}^{18}\mathrm{O}$ → difficulties in delivery

Conversion of NO on CeO$_2$

IR bands sensitive to the ^{14}N/^{15}N substitution: 2041 and at 989 cm^{-1}



i = **1.034** → N–N vibration

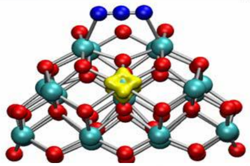
i = **1.019** → N–O vibration
(*cis*-hyponitrite species)

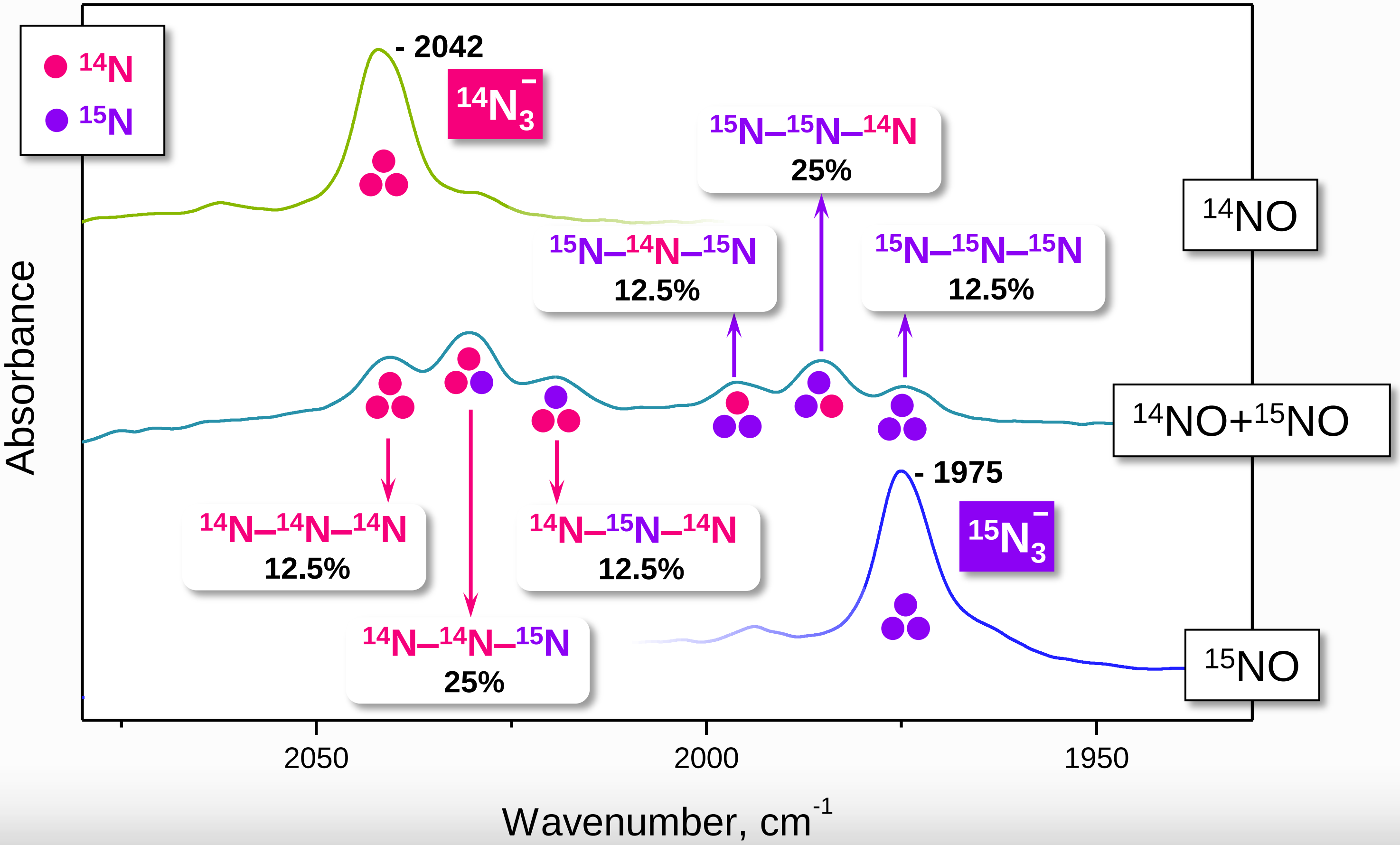
i_{theor} = **1.035** for ν(^{14}N–^{14}N) / ν(^{15}N–^{15}N)

i_{theor} = **1.018** for ν(^{14}N–O) / ν(^{15}N–O)

Azides on reduced CeO_2

^{15}N-substituted azides





Thank you for your attention!

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