Adsorption of small molecules on amorphous ice: Volumetric and FT-IR isotherm co-measurements II. The case of carbon monoxide

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Methods :

experimental :

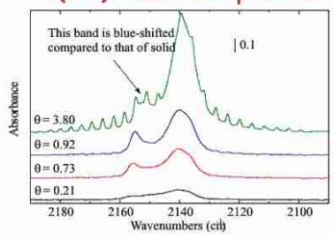
• combination of volumetric and infrared measurements to plot «IR isotherms» and to get additional information

theoretical :

• DFT calculations using Plane-Wave ultrasoft Pseudopotential to deal with large systems

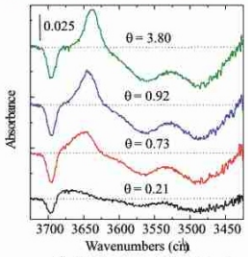
Experimental study

ν(CO) infrared spectra



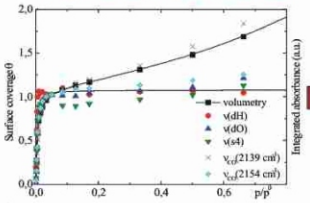
2 bands grow **simultaneously**
• blue shift ⇒ H bond

Surface modes of ice



3 interactions : dH, s4 and dO

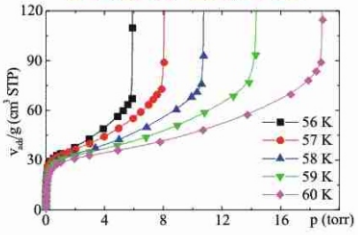
Plot of IR isotherms



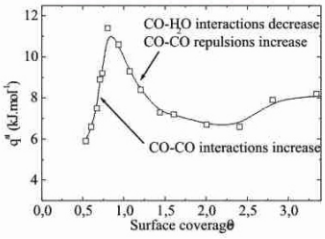
For CO :
• ν_{CO} (2154 cm^{-1}) ⇔ **CO above dH**
• ν_{CO} (2139 cm^{-1}) ⇔ monolayer + multilayer

For ice :
• **3 surface modes with similar evolution**

Series of isotherms



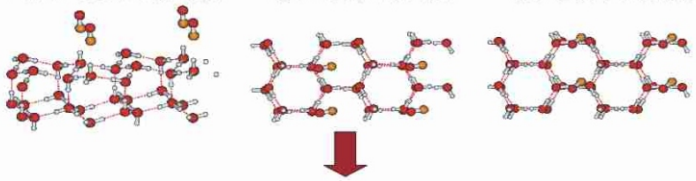
Heat of adsorption



Quantum study

One CO per cell

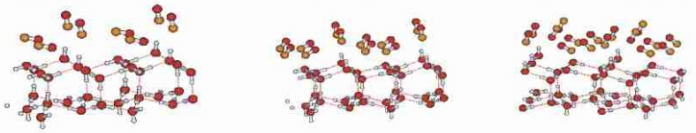
CO interacting with :
• dH : **11.4 kJ/mol**
• s4 : **9.6 kJ/mol**
• dO: **10.4 kJ/mol**



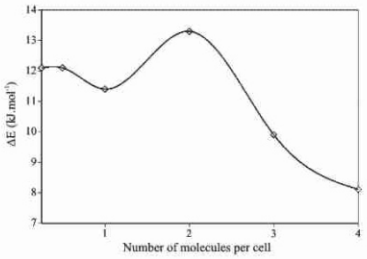
Low surface coverage : 3 equivalent adsorption sites

Higher surface coverage

2 CO per cell (dH,s4): **13.3 kJ/mol**
3 CO per cell: **9.9 kJ/mol**
4th CO above the canal: **8.1 kJ/mol**

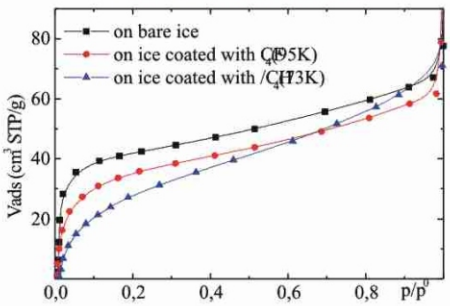


Adsorption energy depends on the number of molecules per cell



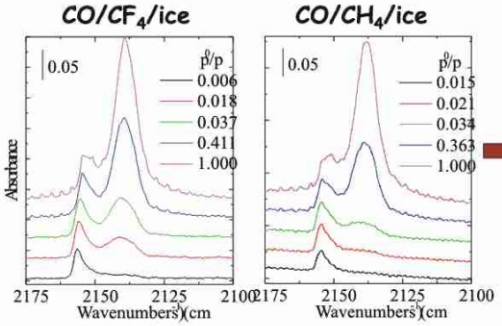
Successive adsorptions : CO/CF_4/Ice and CO/CH_4/Ice

Volumetric isotherms



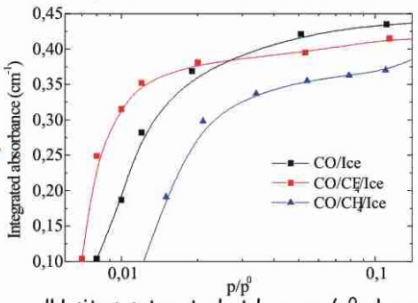
• CO adsorption disturbed by the pre-adsorbates
• Greater influence of CH_4 compared to CF_4

ν(CO) infrared spectra



• The 2 bands **do not grow simultaneously**: ν_{CO} (2154 cm^{-1}) grows alone at the beginning

ν_{CO}(2154 cm^{-1}) IR isotherms



• dH sites saturated at lower p/p^0 when CF_4 is pre-adsorbed ⇒ CF_4 lets them free
• Weaker dH-CH_4 affinity than dH-CO

Conclusions

- **Good agreement between experiment and theory**
- **Weak interaction between CO and ice**
- **At least 3 sorts of adsorption sites, but no evidence for site selectivity**
- **Lateral interactions are likely to stabilize**
- **Successive adsorptions reveal enhanced dH-CO affinity compared to dH-CF_4 and dH-CH_4**