分子研研究会「赤外放射光の現状と将来計画」(2002年11月13日～14日)

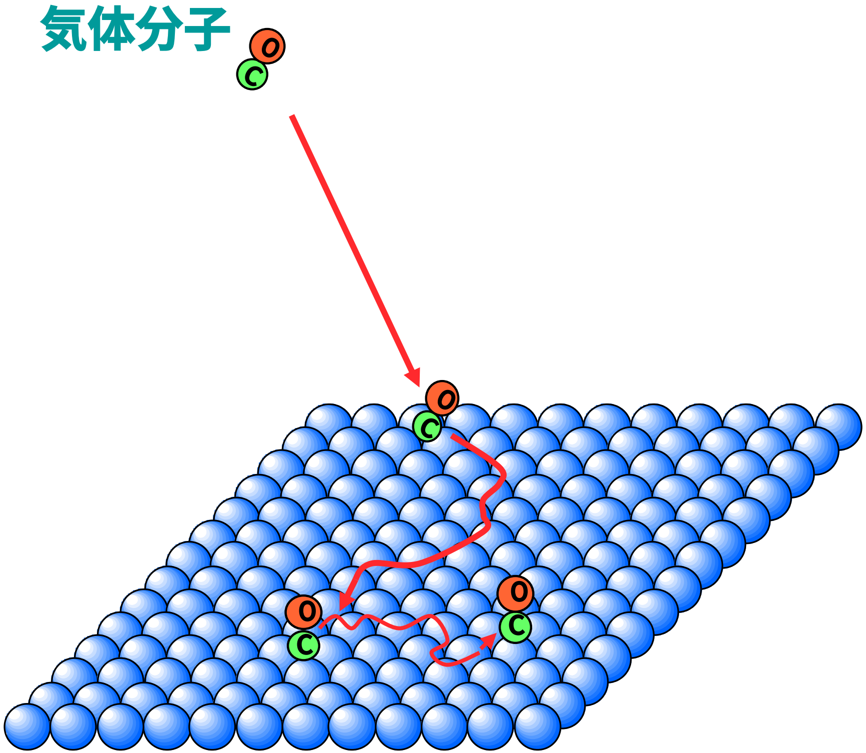
極低温表面における吸着分子の振動分光

－実験室光源を用いたIRAS－

東京大学物性研究所
吉信　淳

共同研究者：山本達 (D1) 塚原規志 (M1) 向井孝三 (技術専門職員) 山下良之 (助手)

Adsorption of molecules on metal surfaces
-elementary processes-



①気体分子の入射

②表面との衝突

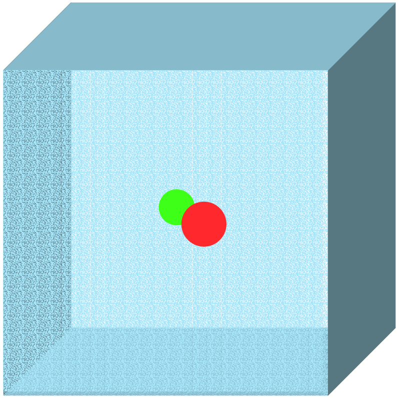
③表面上の過渡的拡散

④表面との結合 (吸着)

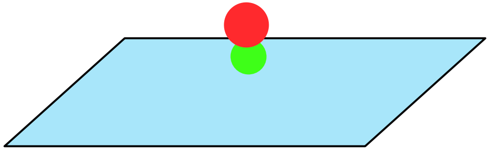
⑤表面の熱的拡散

Vibrational modes of adsorbed CO

–internal stretching and hindered motions–



3次元
自由な配向



2次元
制限された配向

- **分子内振動**
- **並進運動**
- **回転運動**

- **分子内振動**
- **束縛並進運動**
- **束縛回転運動**

振動

分子内伸縮振動

束縛並進運動
(表面垂直方向)
Sモード

束縛並進運動
(表面平行方向)
Tモード

束縛回転運動
Rモード

QuickTimeý Ç²
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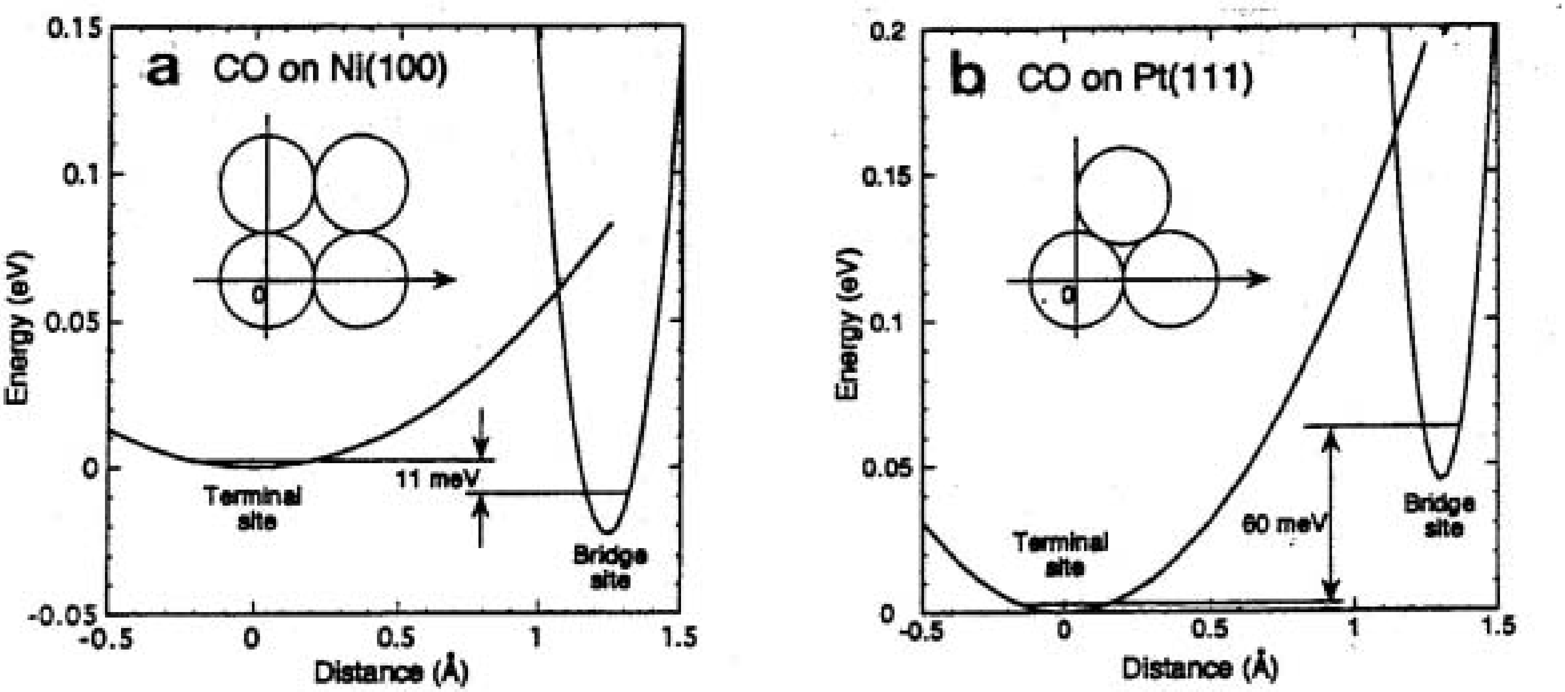
Experimentally determined potential energy surface CO on Ni(100) and CO on Pt(111)



J. Yoshinobu and M. Kawai "Initial adsorption sites of CO on Pt(111) and Ni(100) at low temperature" Surf. Sci., 363,105-111(1996).

Pt(997) surface

QuickTimeý Ç²
ÉtÉHÉg - JPEG êLí£ÉvÉçÉOÉâÉÄ
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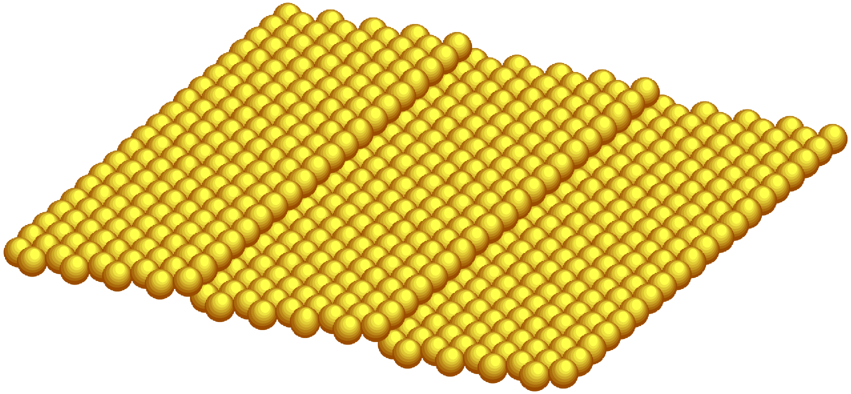
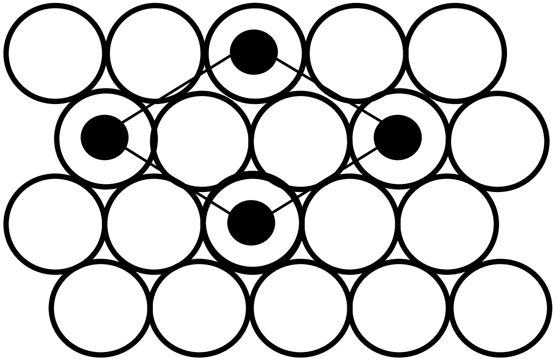


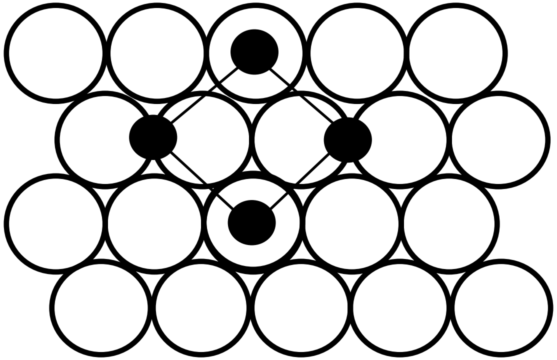
(s)-[9(111)x(111)]

Ep = 170.5 eV

Previous studies
CO/Pt(111)



$(\sqrt{3}\times\sqrt{3})R30°$



c(4×2)

At θ_{CO}=0.33, all CO are located at on-top site.

At θ_{CO}=0.5, a half of CO are adsorbed at on-top site and another half are at bridge sites.

No ordered LEED pattern was observed for CO/Pt(997) at 300K.

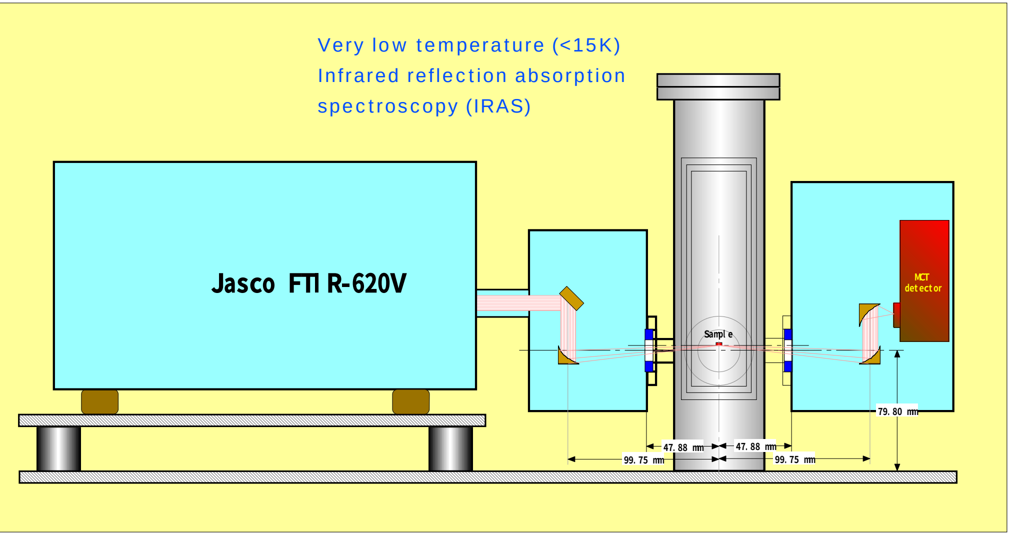
Ref. B. Lang, R. W. Joyner and G. A. Somorjai, Surface Sci. 30 (1972) 454

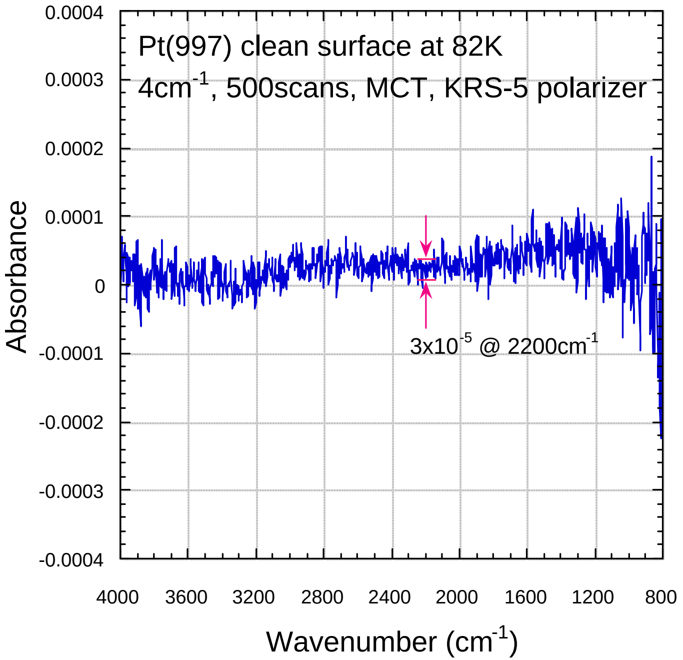
CO diffusion on Pt(111) surfaces

* Using TR-IRAS, J.E.Reutt-Robey et al., PRL61(1988)2778

* Observation at low temperature, J.V.Nekrylova and I.Harrison, JCP101(1994)1730

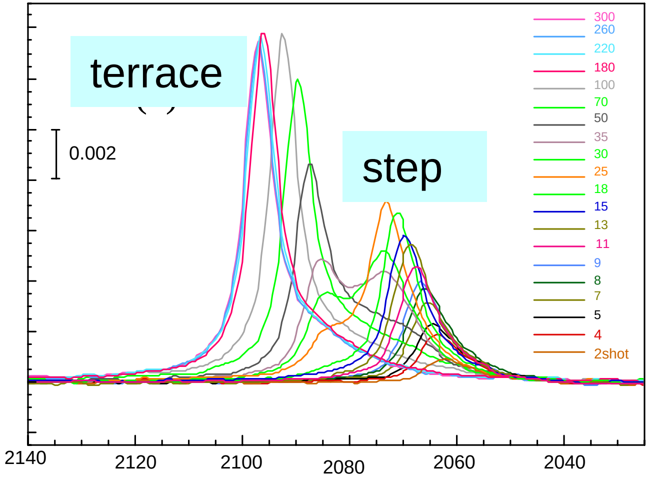
Low temperature IRAS



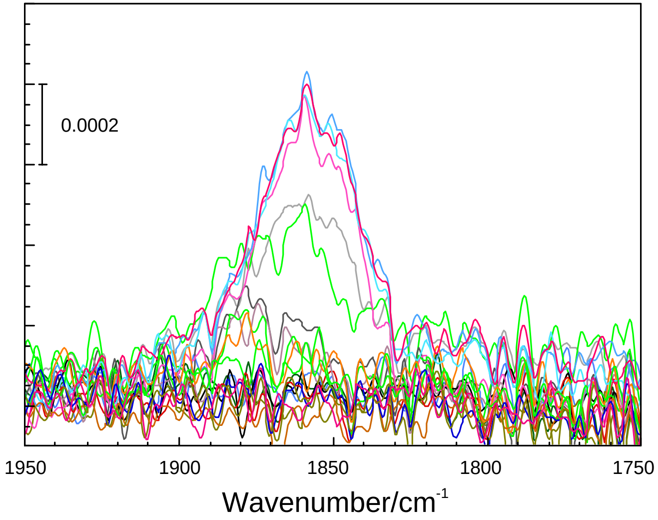


- All optical paths are evacuated (free from water and CO_2 vapor)
- Using liq.He and liq.N_2, the sample can be cooled to 6K (<15K during IRAS)
- Gas is introduced through a palse valve.
- Noise level < 3×10^{-5} absorbance (4 cm^{-1}, 500 scans, @2200 cm^{-1})

Adsorption of CO on Pt(997) at 300K

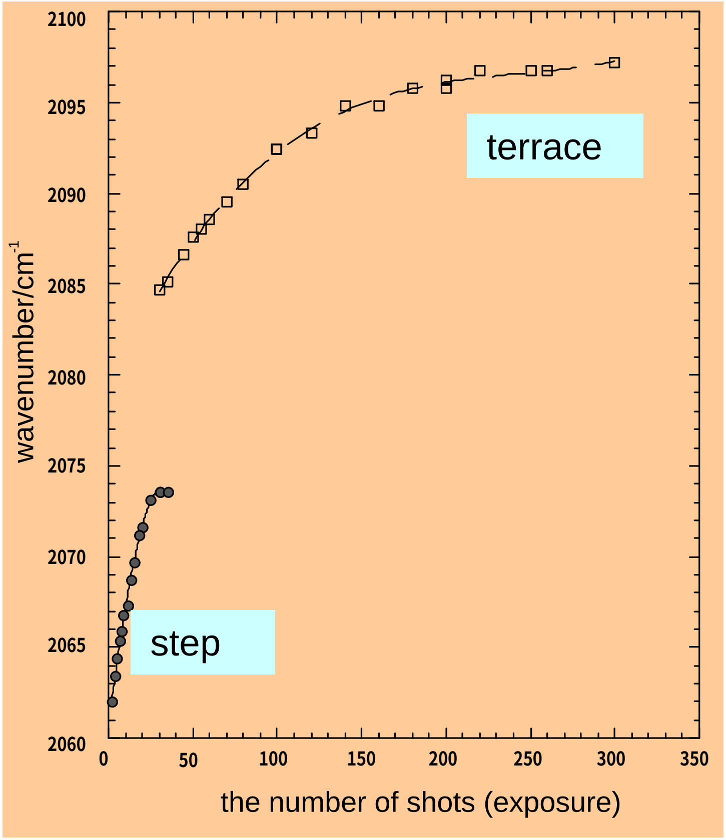


on-top CO

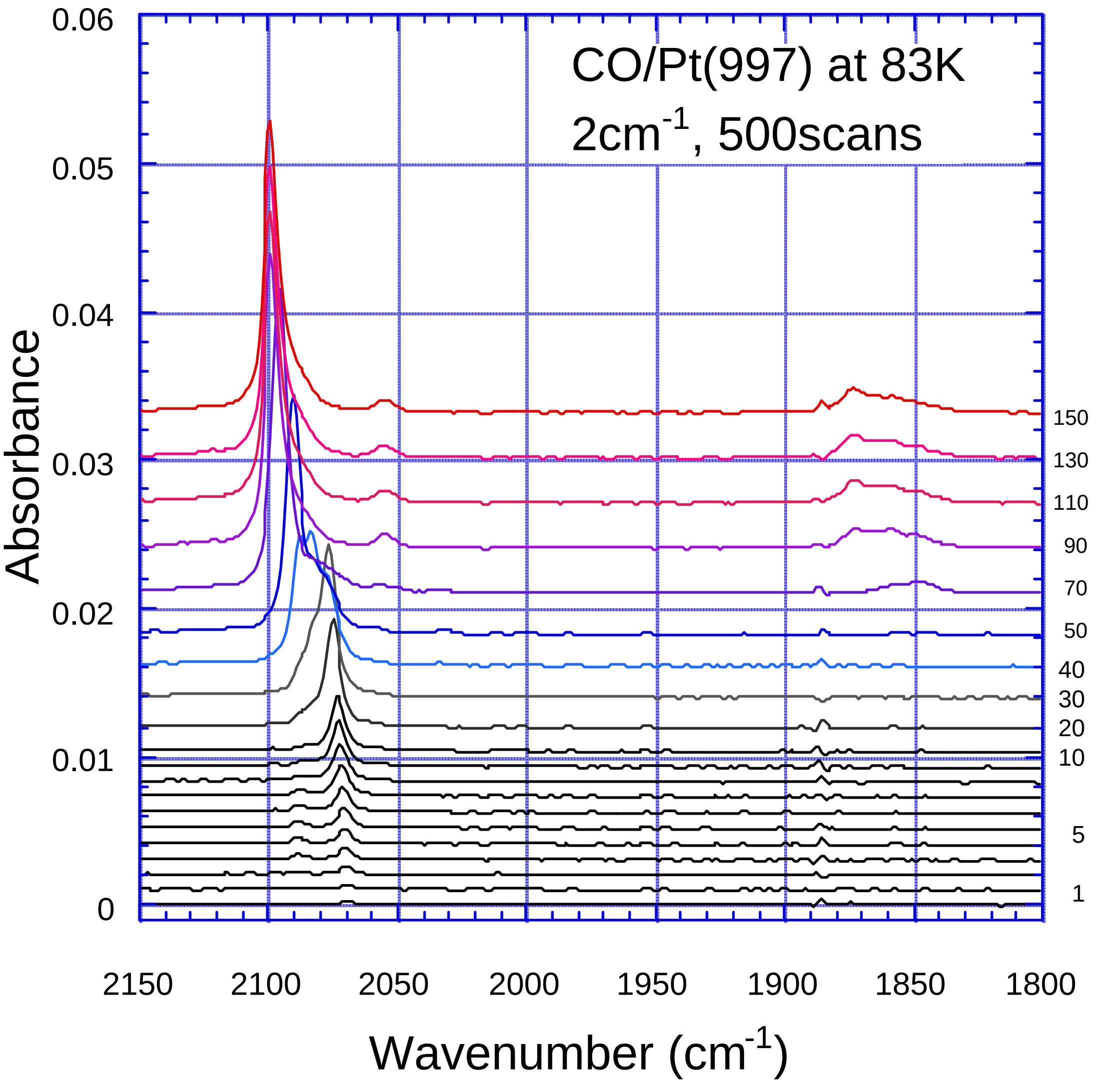


bridge CO

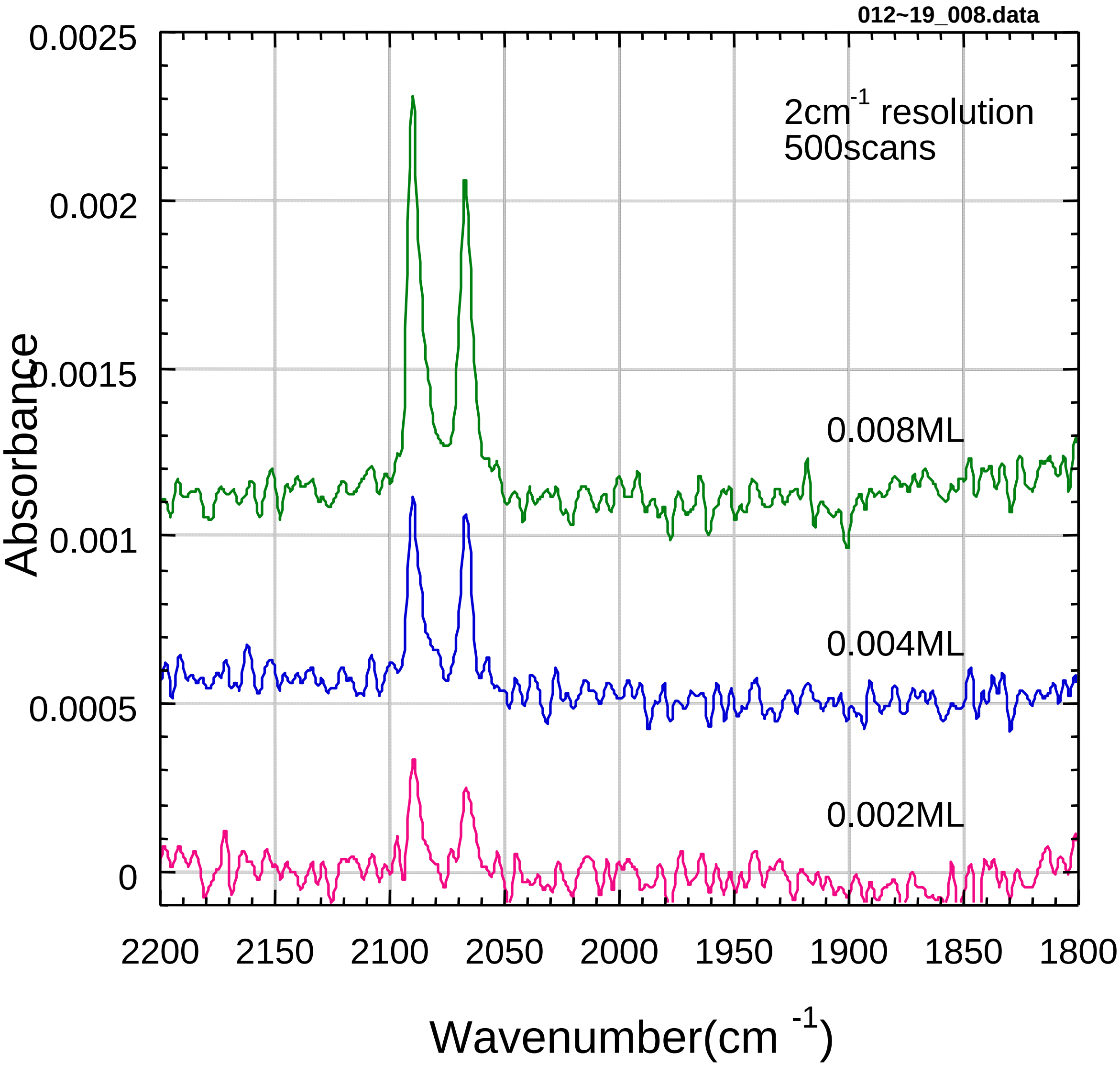
peak position of on-top CO



Adsorption of CO on Pt(997) at 83K



Initial adsorption sites at low temperature
CO on Pt(997) below 20 K

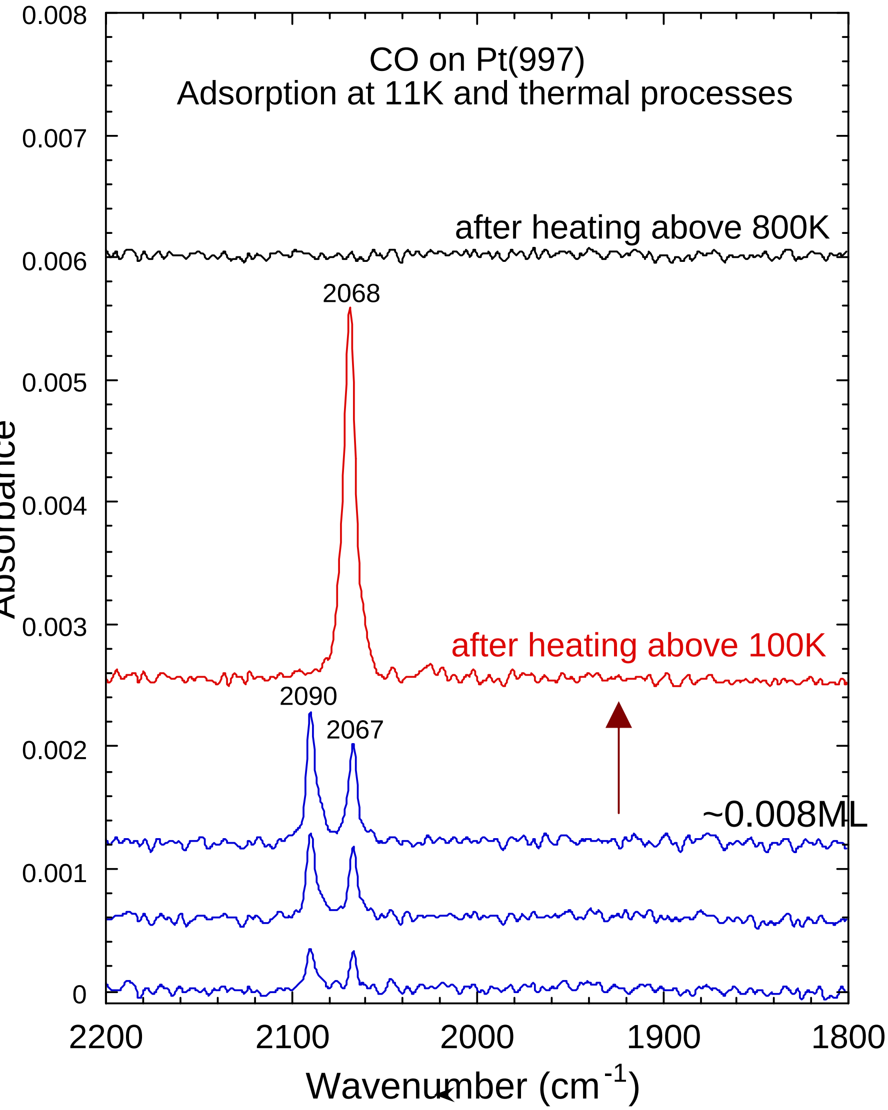


- Peak intensities linearly increase with the exposure.
- Each peak does not shift with the exposure.
- The intensity ratio between two peaks is almost constant.

↓

- Interaction between adsorbed CO is negligible.
- CO molecules are isolated on the surface.

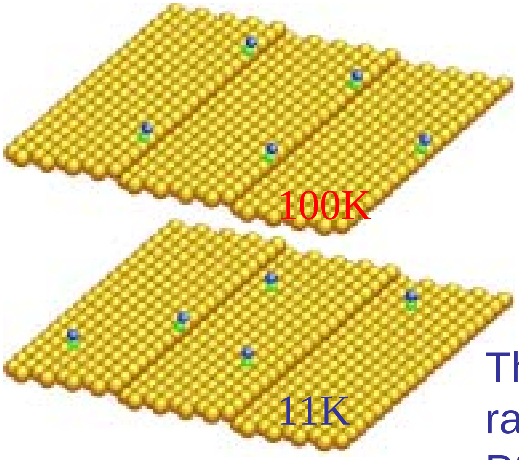
Amount of terrace CO and step CO on Pt(997)



Area intensities of IRAS peaks
At 11K: I_T=0.0086, I_S=0.0065,
After heating: I'_S=0.0296

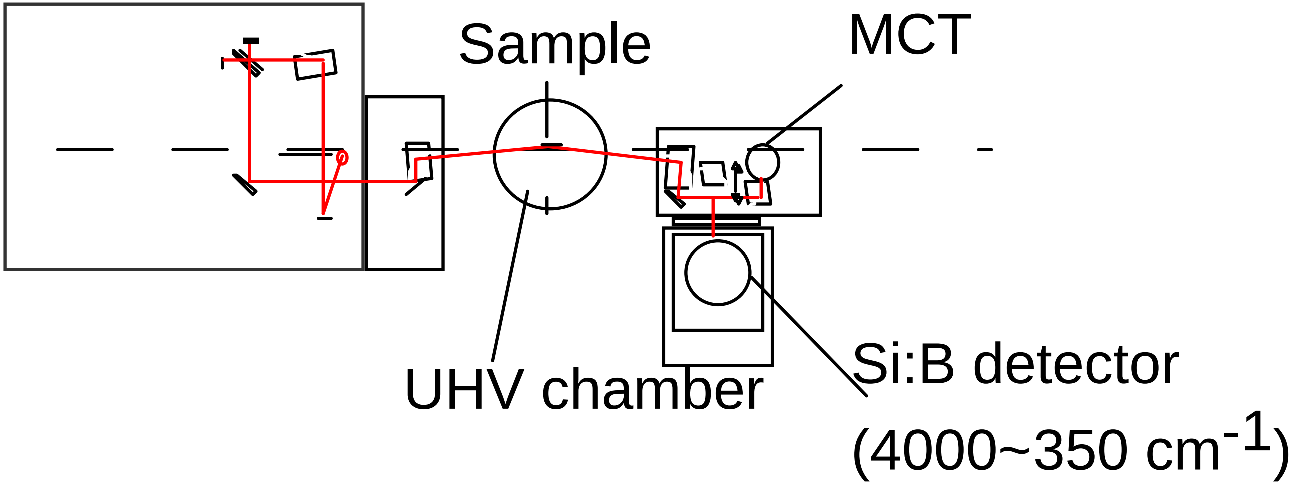
$I_T=\alpha_T n_T$, $I_S=\alpha_S n_S$, where n is the number of molecules and α IR absorbance factor.

Since the total number of adsorbed molecules is conserved, $\Delta n_S=n_T$.
Thus, $n_T=I_T/\alpha_T=\Delta n_S=\Delta I_S/\alpha_S$.
We obtain $\alpha_S=2.7\alpha_T$ and n_T/n_S=3.6.



The initial occupation
ratio of on-top sites o
Pt(997): $n_T:n_S$=3.6:1

Experiments
Infrared reflection absorption spectroscopy (IRAS)



Using an Si:B detector with 4cm^{-1} resolution & 500scans,
noise level : 2~5x10^{-5}abs @2100~2200 cm^{-1}

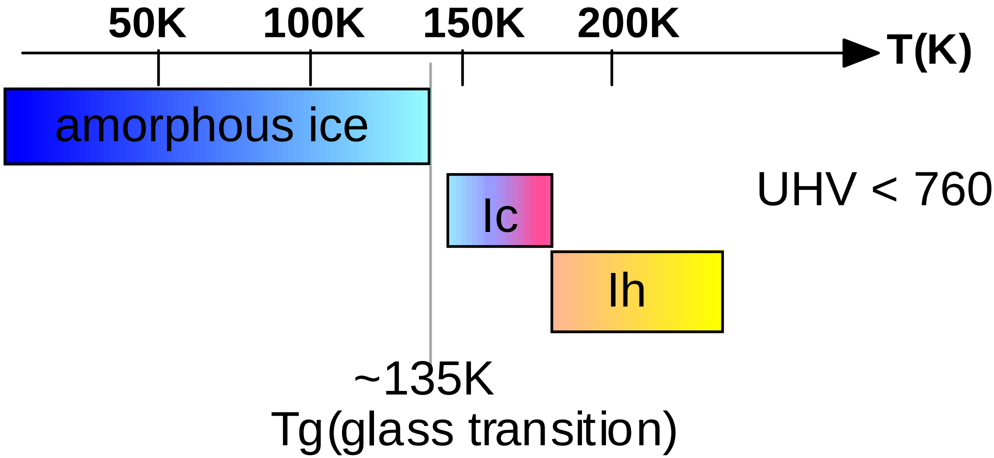
Closed cycle He refrigerator + radiation/electron bombardment heating
→ 25K ~ 1300K

Ice in nature

Ice layers on solid surfaces play an important role in

- astrophysical environments including comets, planetary rings and interstellar clouds
- polar stratospheric clouds (PSCS) on the earth,

etc.



50K **100K** **150K** **200K** **T(K)**

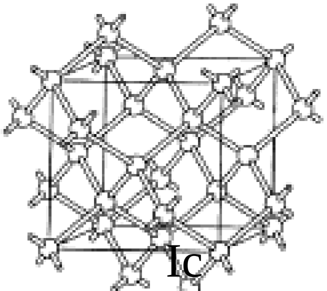
amorphous ice

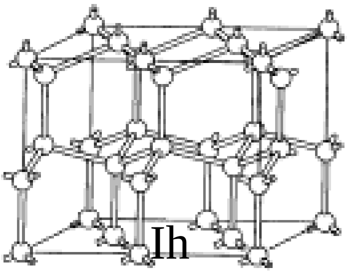
Ic

Ih

UHV < 760torr

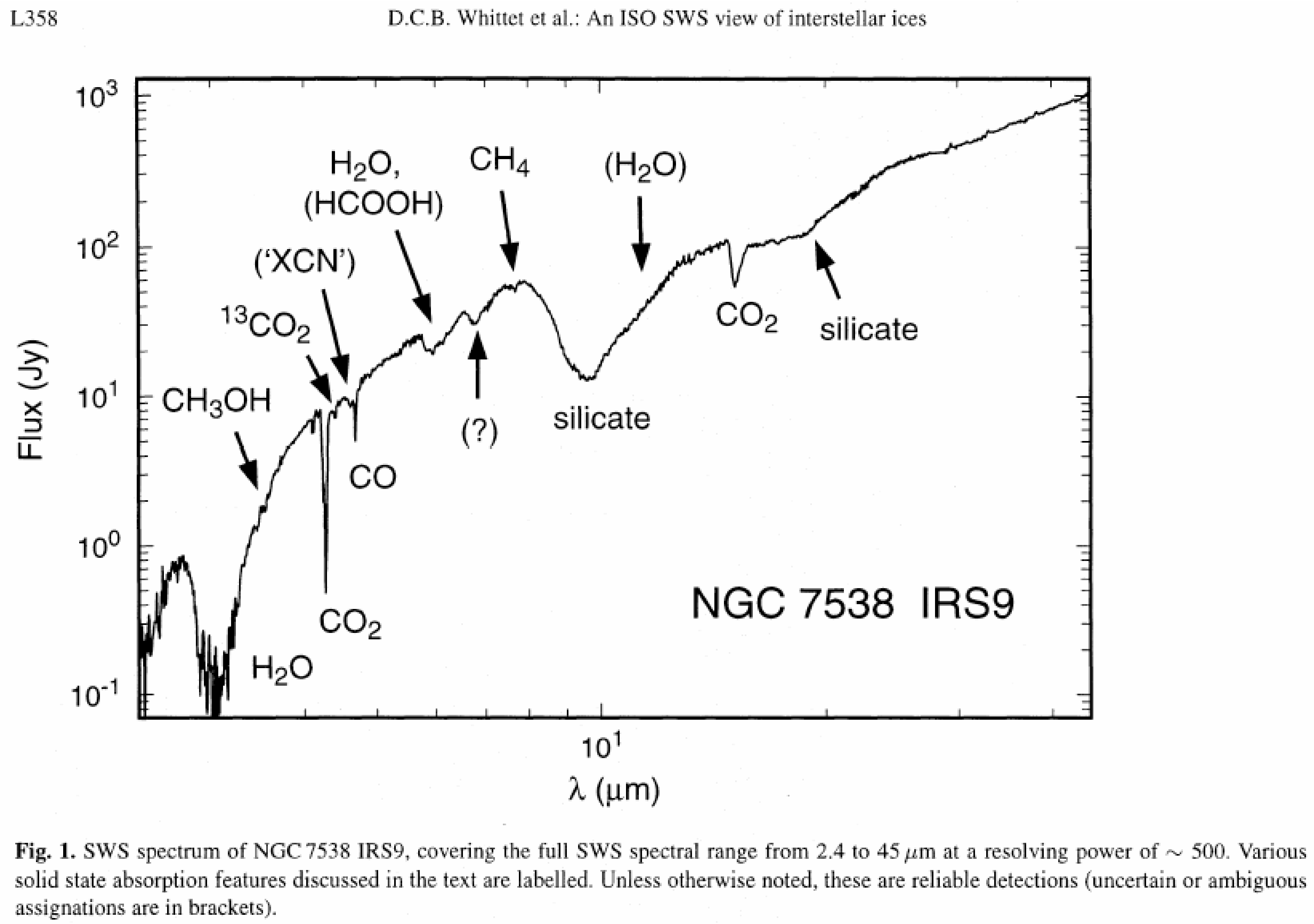
~135K
Tg(glass transition)





The first result of ISO about interstellar ices

Astron.&Astrophys.315L357(1996)



L358 D.C.B. Whittet et al.: An ISO SWS view of interstellar ices

Fig. 1. SWS spectrum of NGC 7538 IRS9, covering the full SWS spectral range from 2.4 to 45 μm at a resolving power of $\sim$ 500. Various solid state absorption features discussed in the text are labelled. Unless otherwise noted, these are reliable detections (uncertain or ambiguous assignations are in brackets).

The abundances of ices in interstellar ice and cometary volatiles

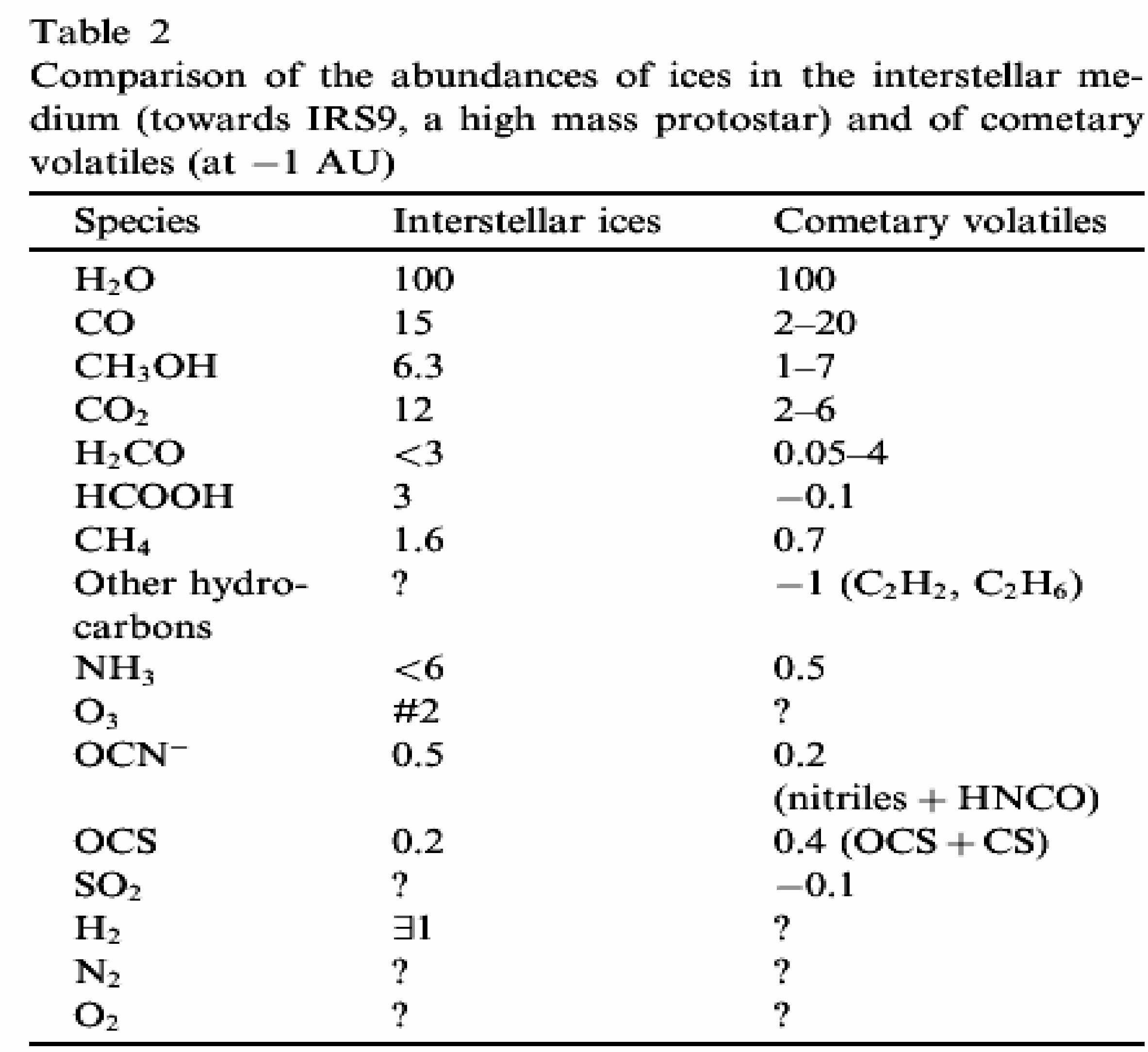


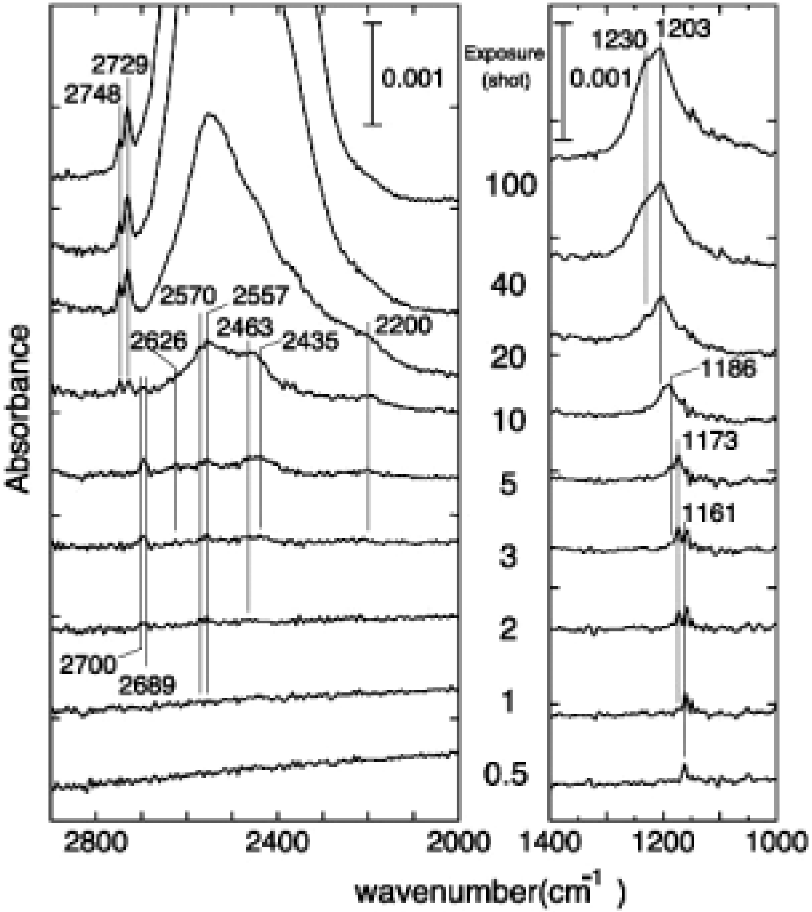
Table 2

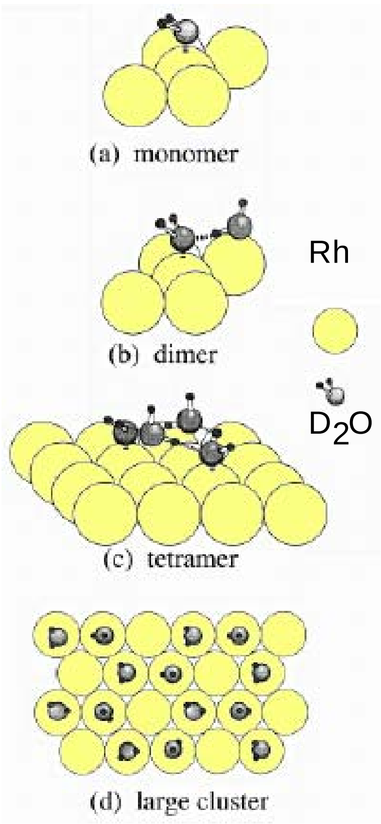
Comparison of the abundances of ices in the interstellar medium (towards IRS9, a high mass protostar) and of cometary volatiles (at −1 AU)

Species	Interstellar ices	Cometary volatiles
H_2O	100	100
CO	15	2–20
CH_3OH	6.3	1–7
CO_2	12	2–6
H_2CO	<3	0.05–4
HCOOH	3	−0.1
CH_4	1.6	0.7
Other hydrocarbons	?	−1 (C_2H_2, C_2H_6)
NH_3	<6	0.5
O_3	#2	?
OCN^-	0.5	0.2 (nitriles + HNCO)
OCS	0.2	0.4 (OCS + CS)
SO_2	?	−0.1
H_2	∃1	?
N_2	?	?
O_2	?	?

J.M.Geenberg,Surf. Sci. 500(2002)793

IRAS of adsorbed D_2O on Rh(111) at 25K

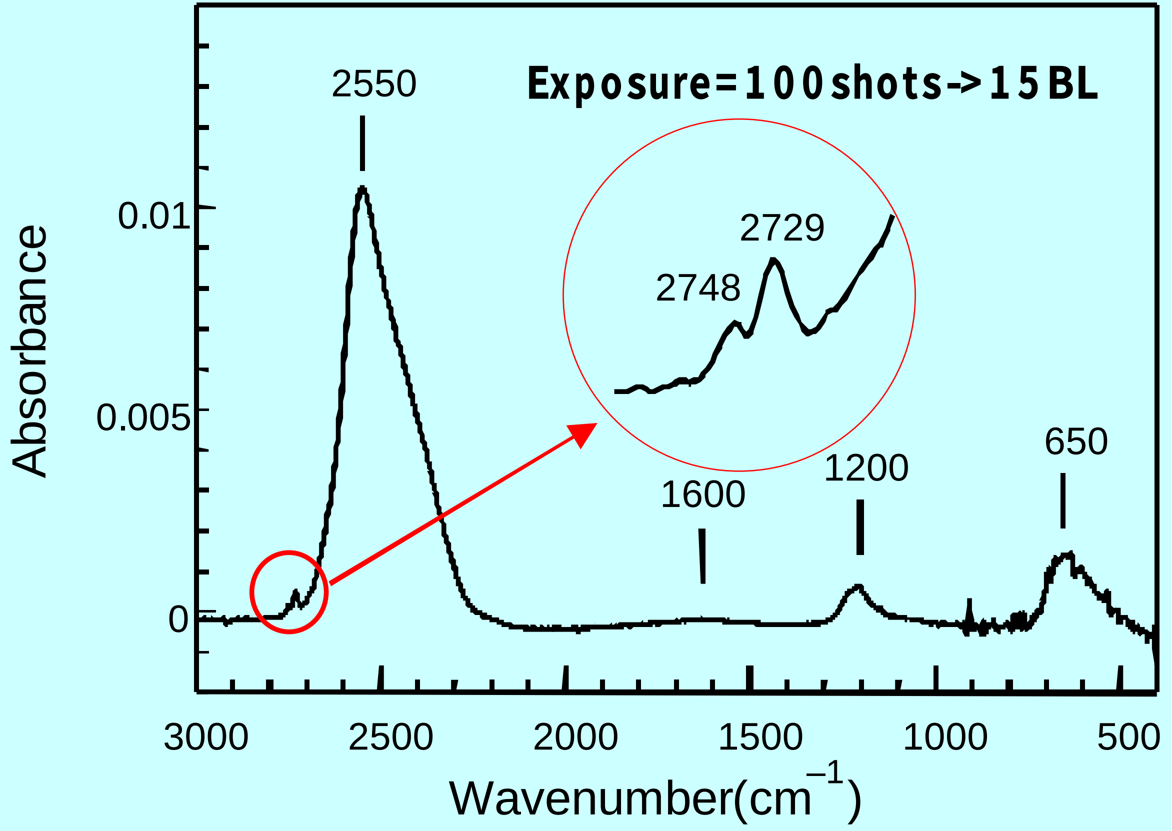




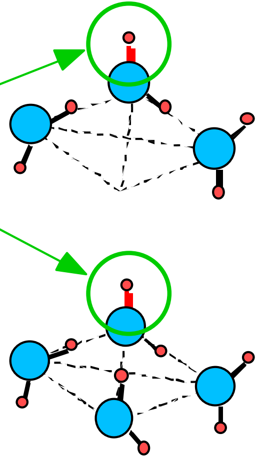
2689~2748cm^{-1}: ν(dangling OD)
2200~2650 cm^{-1}: ν(OD) hydrogen-bonded
1161~1230cm^{-1}: δ(DOD)

- Below monolayer, water molecules are adsorbed as monomer and clusters at 25K
- Amorphous ice is formed after a large amount of exposure.

Amorphous Ice (D_2O) on Rh(111) at 25K



cf.)V. Buch and J. P. Devlin,
J. Chem. Phys. <u>94</u>, 4091(1991



2748 cm^{-1}	**νOD** (dangling OD, 2 coordinated)
2729 cm^{-1}	**νOD** (dangling OD, 3 coordinated)
2550 cm^{-1}	**νOD** (hydrogen bonded) & 2δDOD
1600 cm^{-1}	**association band** 3νL & δDOD+νL
1200 cm^{-1}	**δDOD**& 2νL
650 cm^{-1}	**L** (hindered rotation)

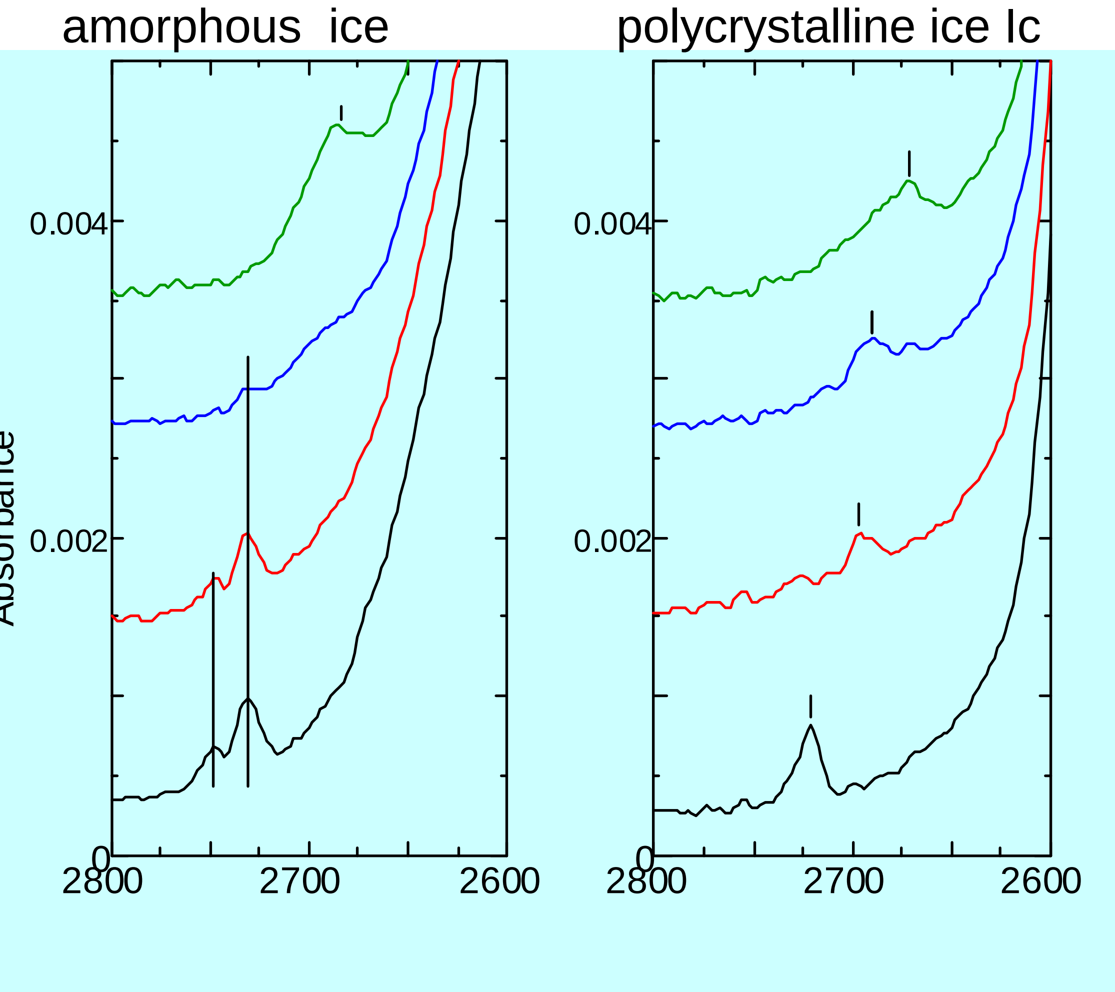
D_2O/Rh(111) -dangling OD- as a function of annealing temperature

Surface water molecules
(2 coordinated) start to relax
at < 80K (below Tg).

ν_{OD} of dangling OD

as a function of exposure

CO / D_2O ice / Rh(111)



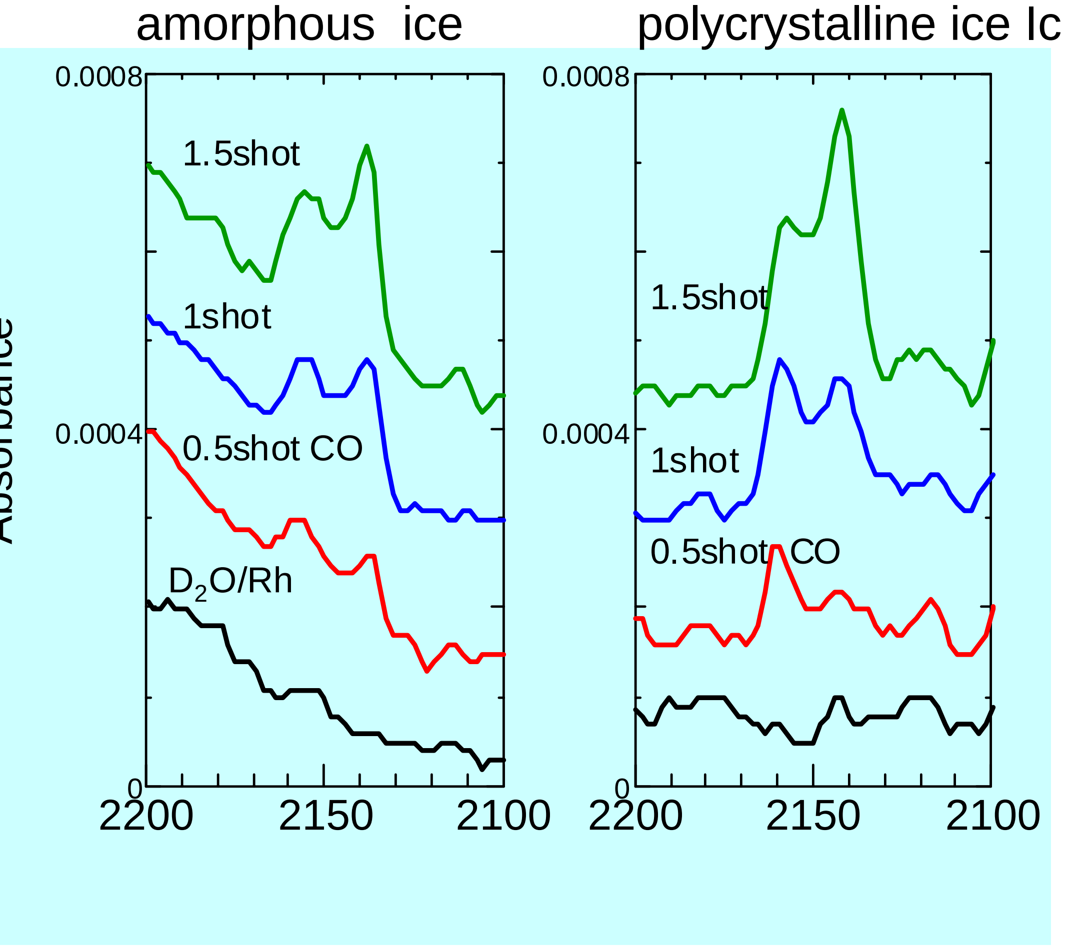
Upon CO adsorption,

- Red shift of ν_{OD}
- Intensity increase for ν_{OD}
- Broadening of ν_{OD}

the hydrogen bonding between dangling OD and adsorbed CO.

ν_{OD}：CO / D_2O ice / Rh(111)

CO as a probe molecule



- 2140 cm^{-1} : multi-layer CO
- 2156~2160 cm^{-1} : CO interacting with dangling OD

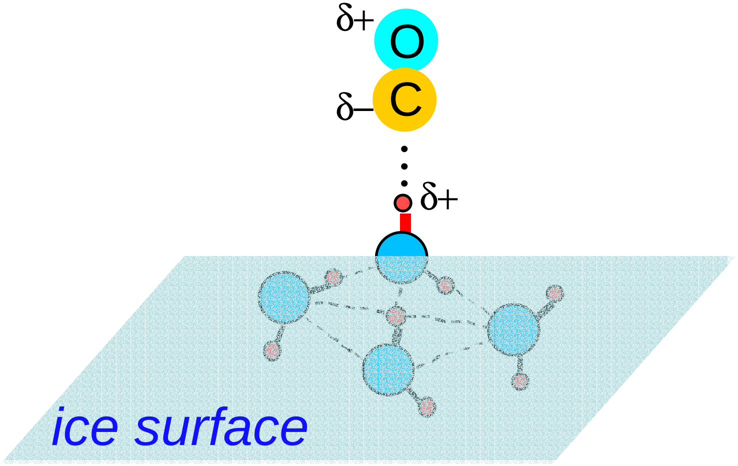
ASW: both CO species develop

Ic ice: the 2154 cm^{-1} peak develops first.

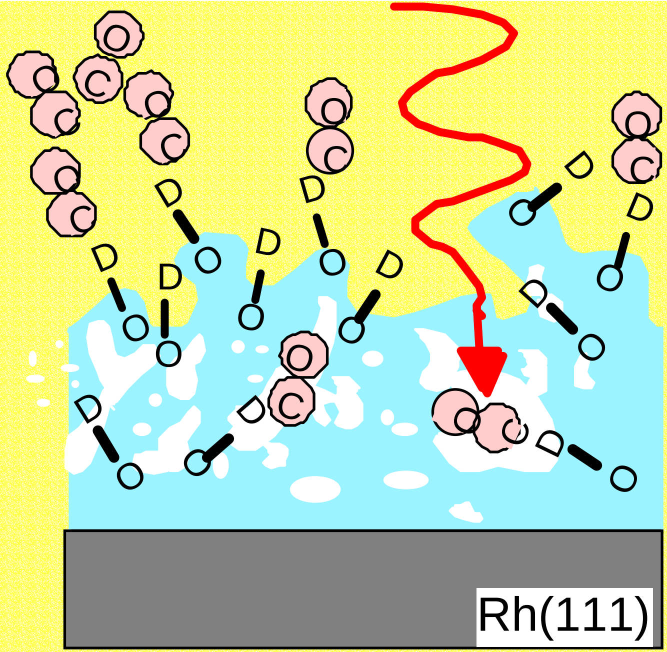
amorphous ice: porous
crystalline ice: the dangling OD exists at outermost surface.

Interaction between dangling OH and CO

1. Adsorbed CO is associated directly with dangling OH on ice surfaces.
2. Blue shift of ν_{CO} indicates the donation from 5σ to the electropositive hydrogen.
3. Red shift of ν_{OH} in dangling OH indicates hydrogen bonding.
4. Broadening of ν_{OH} in dangling OH indicates hydrogen bonding.
5. Intensity increase of ν_{OH} in dangling OH indicates hydrogen bonding.
6. Gas phase CO has a dipole moment 0.112D ($^{\delta-}$CO $^{\delta+}$).

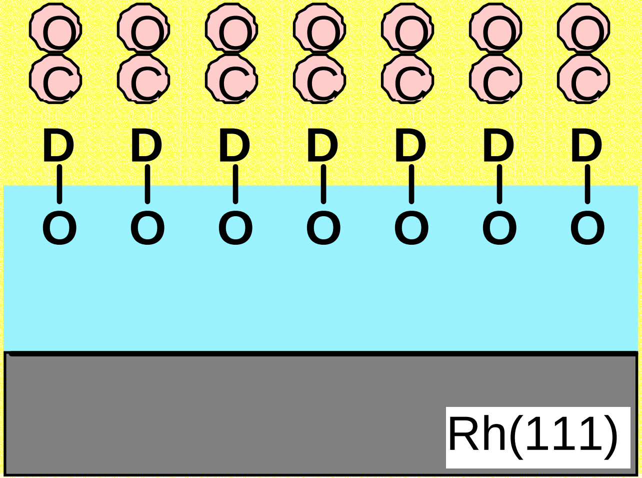


Morphology of ASW and crystalline ice probed by CO adsorption



ASW

two dangling OD species exist on the ASW surfaces



Annealed ASW (polycrystalline ice)

3-coordinated dangling OD species exist on the outermost surface