Laboratory Studies of Astrophysical Ices in the Near- and Mid-Infrared

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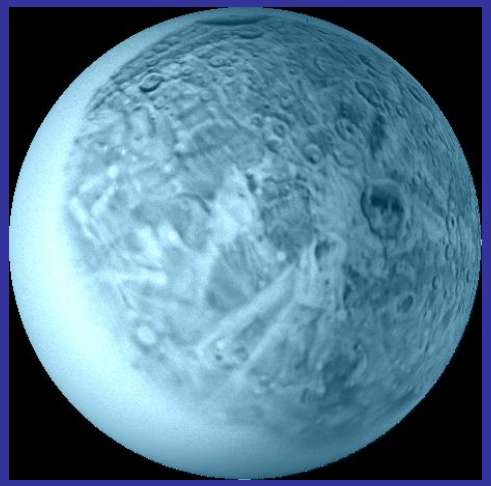
"Understanding the Universe through IR and Submillimeter Astrophysics"

Condensed volatiles (“ices”) are present in many Astrophysical Environments

Comets

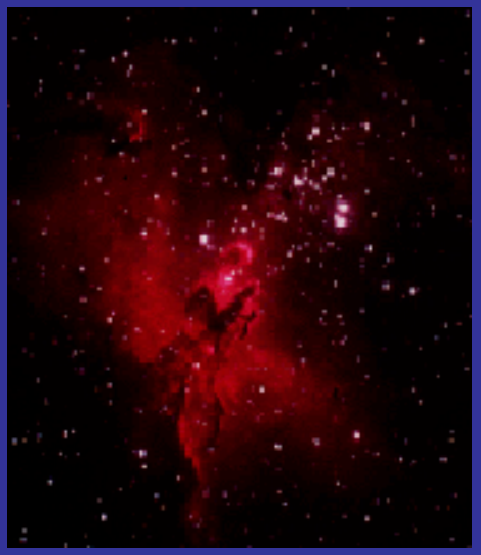
Comet Hale-Bopp,
as seen in 1996
H_2O, CO, NH_3, ...

Icy Moons



Oberon,
moon of Uranus,
N_2, CH_4, ...

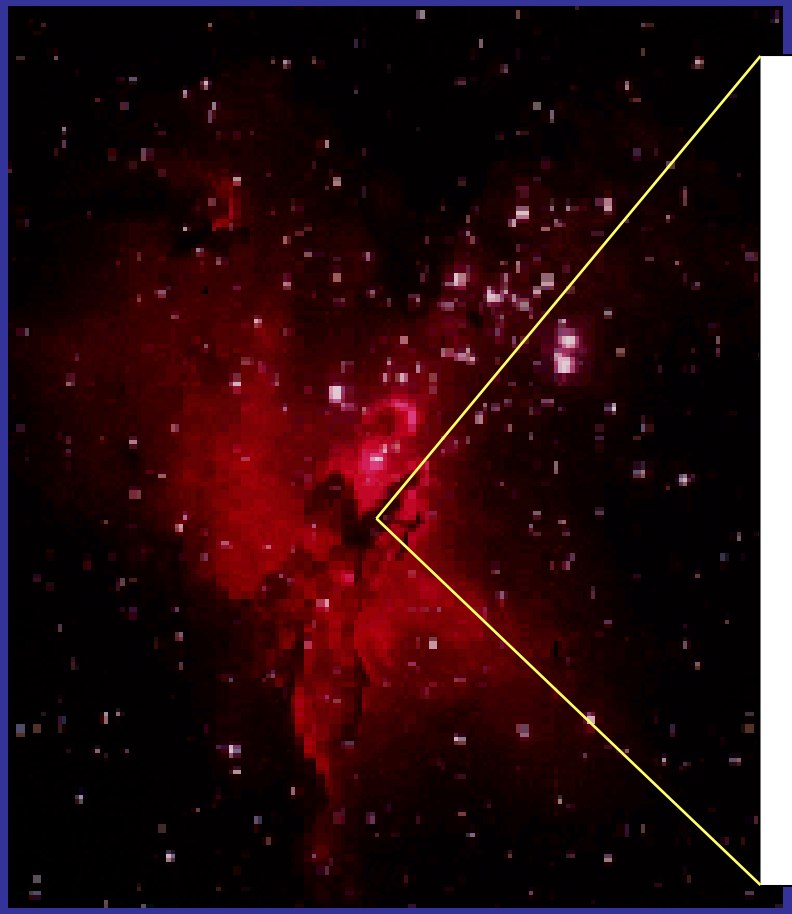
Dense Interstellar Clouds

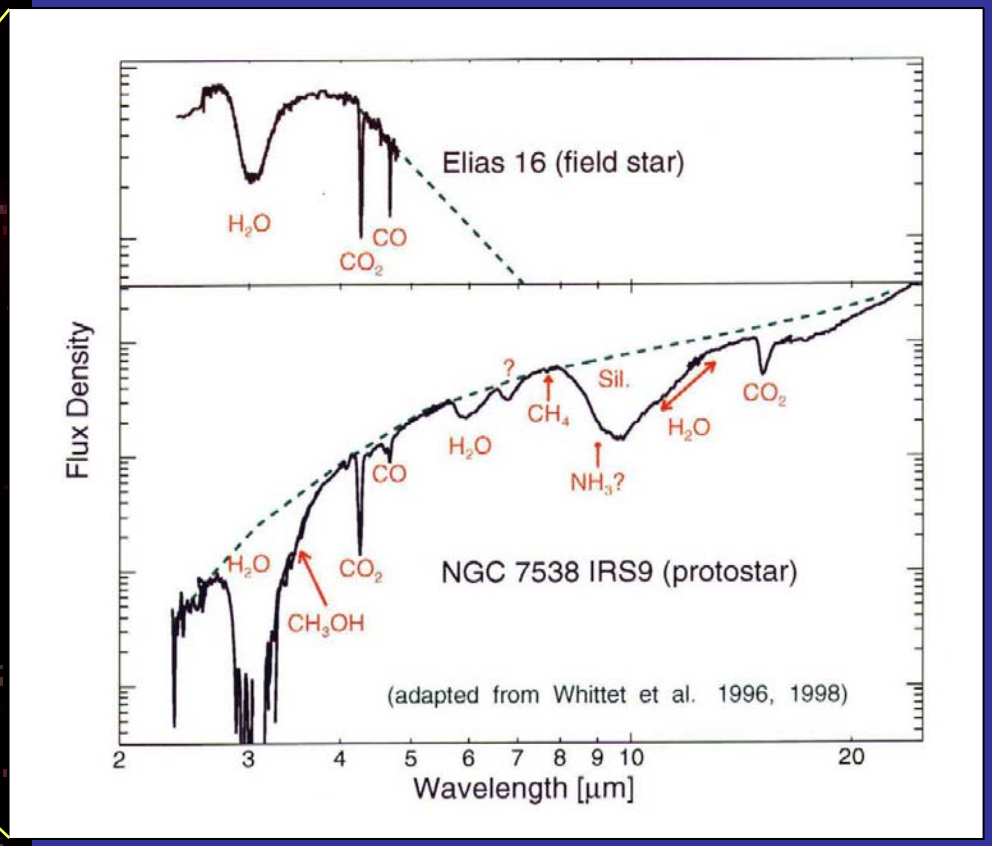


M16- Eagle Nebula
H_2O, CO, CO_2, ...

Spectroscopy of dense interstellar clouds

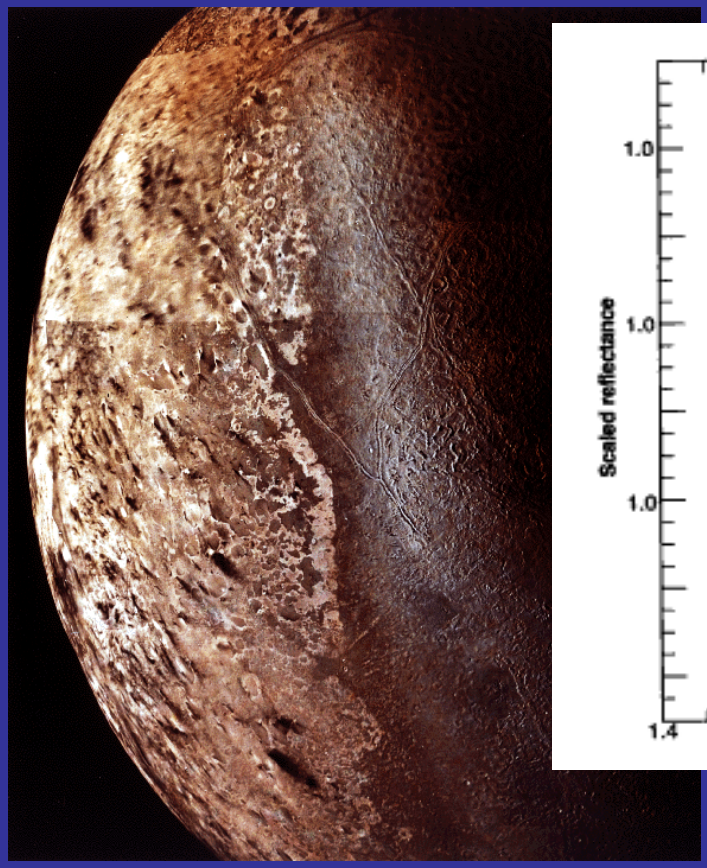
absorption features due to molecules in the solid phase at low T (10-50 K)

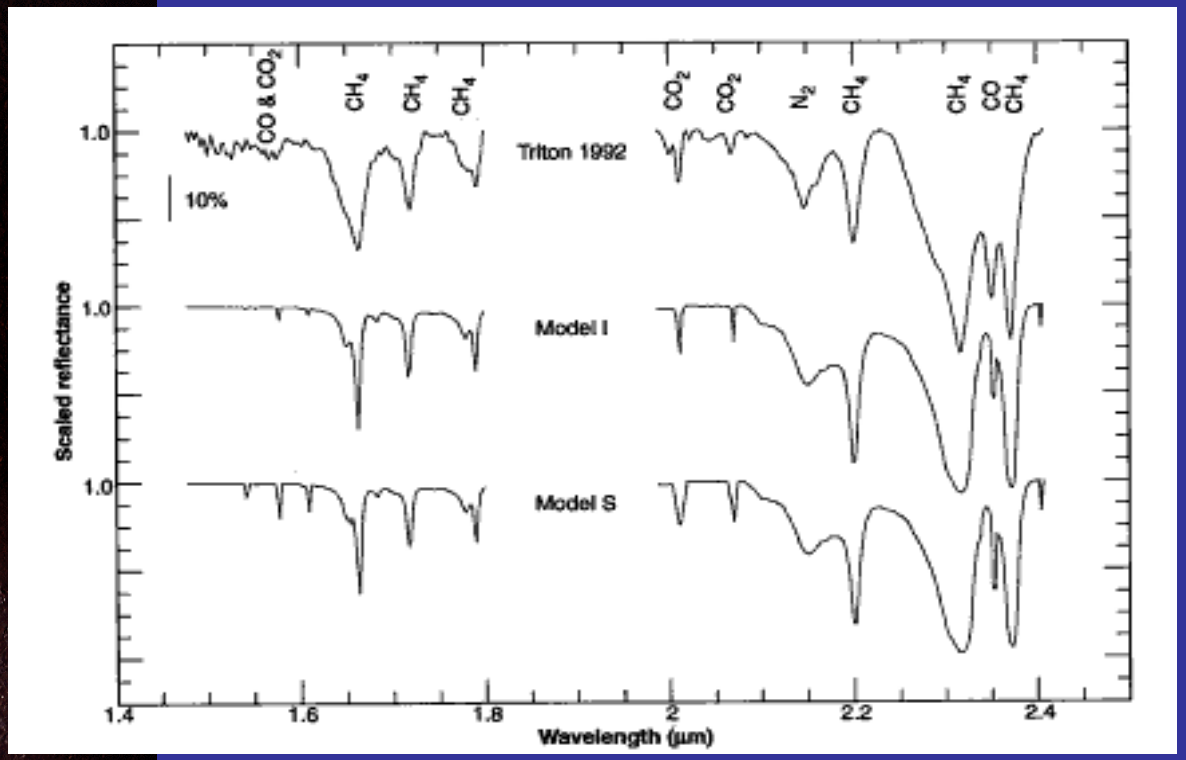




Infrared reflectance spectrum of Triton

N_2, CO, CO_2, CH_4, T=40K



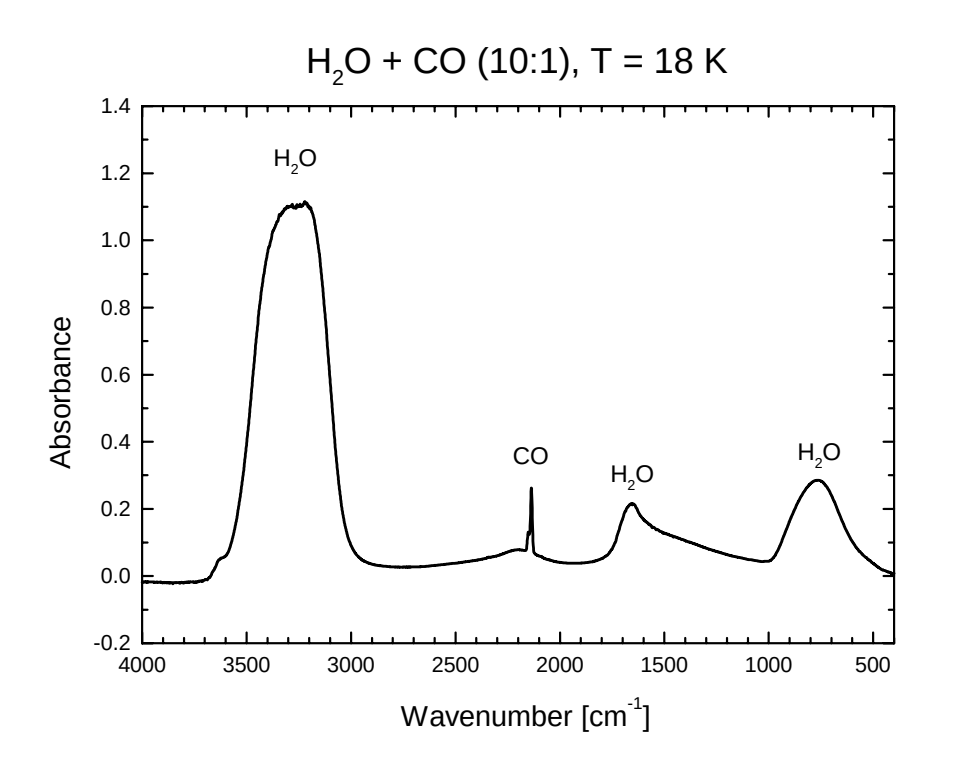


Cruikshank et al. (1993)

How can laboratory work shed light on these environments?

Identifications of solid-phase absorption features based on comparisons to laboratory data

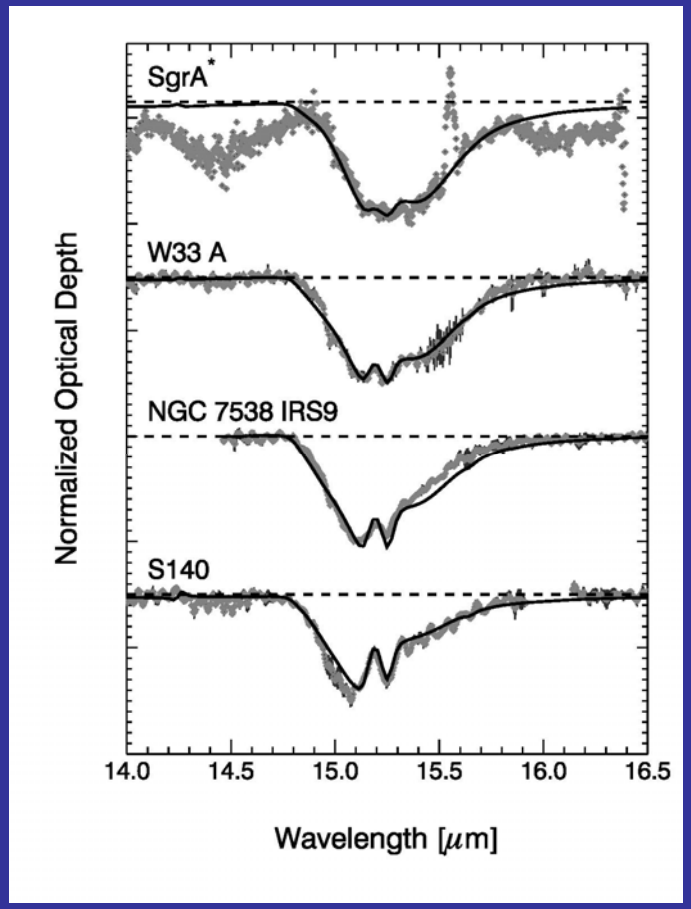
e.g., a laboratory spectrum of H_2O + CO at 18 K displays the vibrational modes of these molecules



Detailed laboratory fits to ice spectra

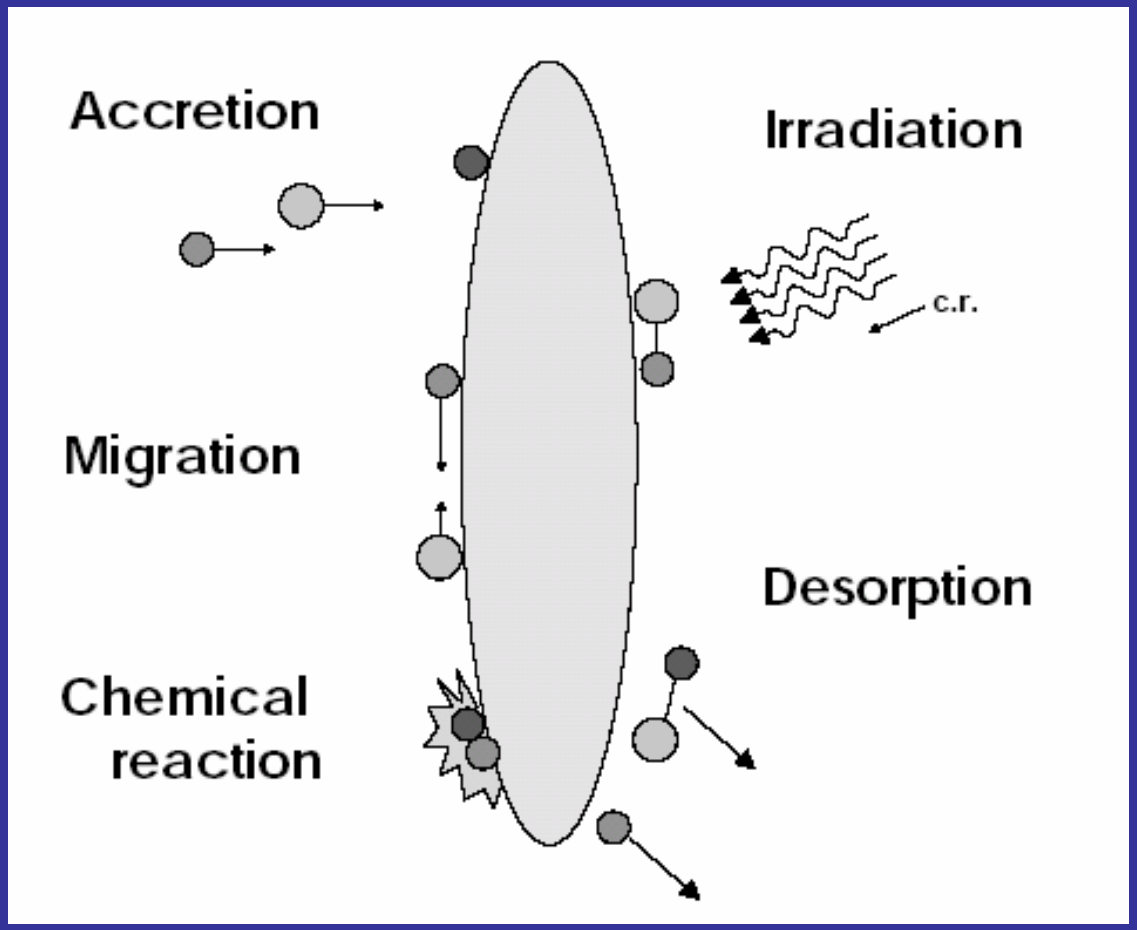
Information about ice composition, temperature, structure, and chemical environment

e.g., interstellar solid CO_2 as observed by ISO compared to laboratory spectra of $H_2O+CO_2+CH_3OH$ at various temperatures



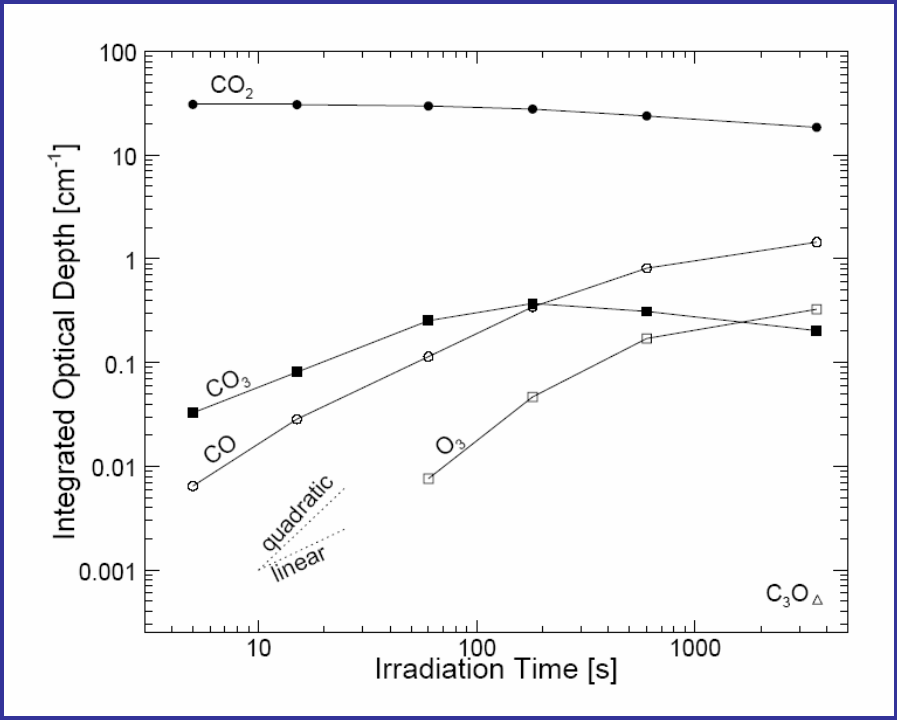
Gerakines et al. (1999)

Simulations of physical and chemical processes…



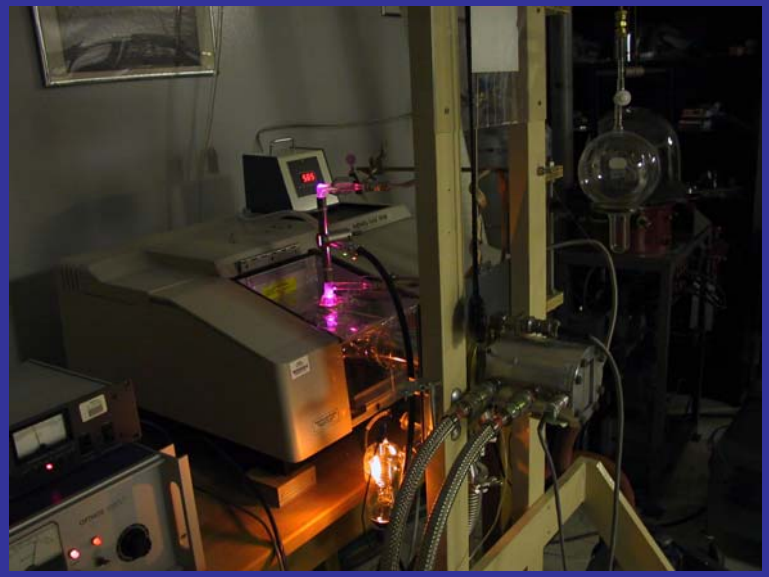
… lead to predictions about ice chemistry

e.g., lab-measured photo-production rates of molecules lead to predictions about molecular abundances in astrophysical environments



Gerakines et al. (1996)

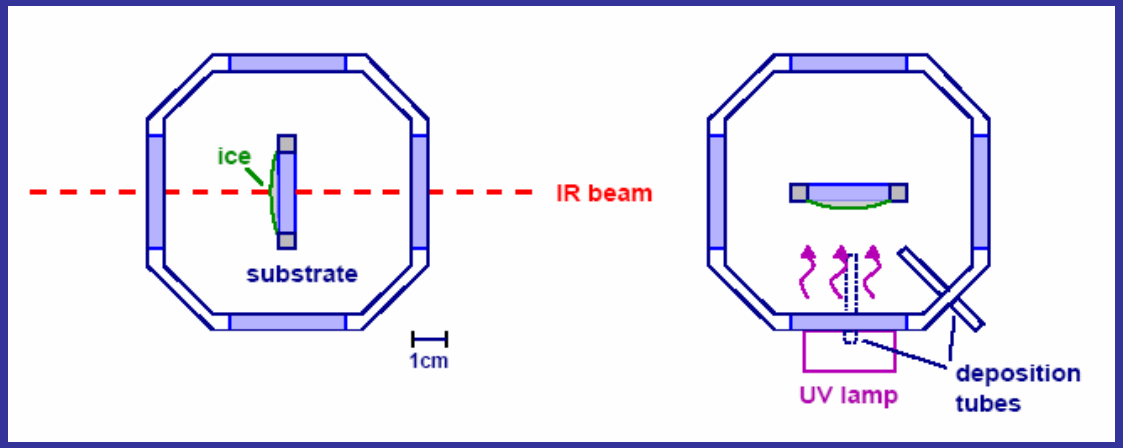
Interstellar/Planetary Ice Laboratory at UAB



IR Spectra from 1-25 µm

Spectra measured in transmission

UV photolysis lamp

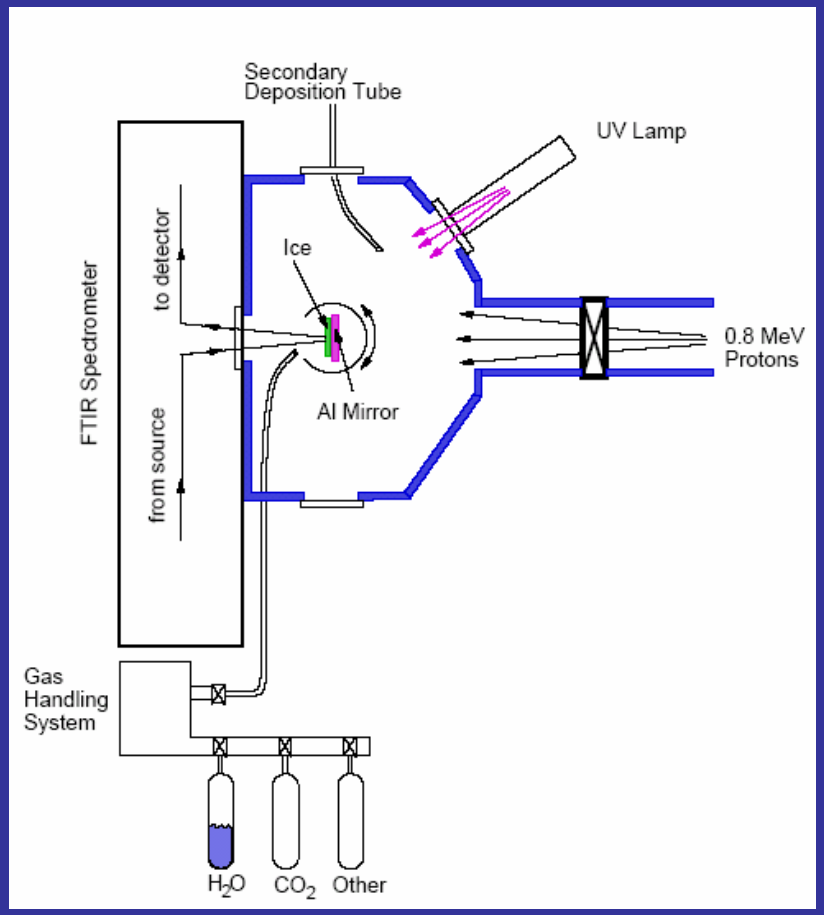


Cosmic Ice Laboratory at NASA/GSFC

Ices created as thin films (0.1 - 50 μm) on cold substrate (10 - 300 K) inside vacuum chamber

IR spectra obtained by FTIR spectrometer coupled to vacuum system

Ports allow access to sources of energetic photons or ions for photolysis and irradiation studies



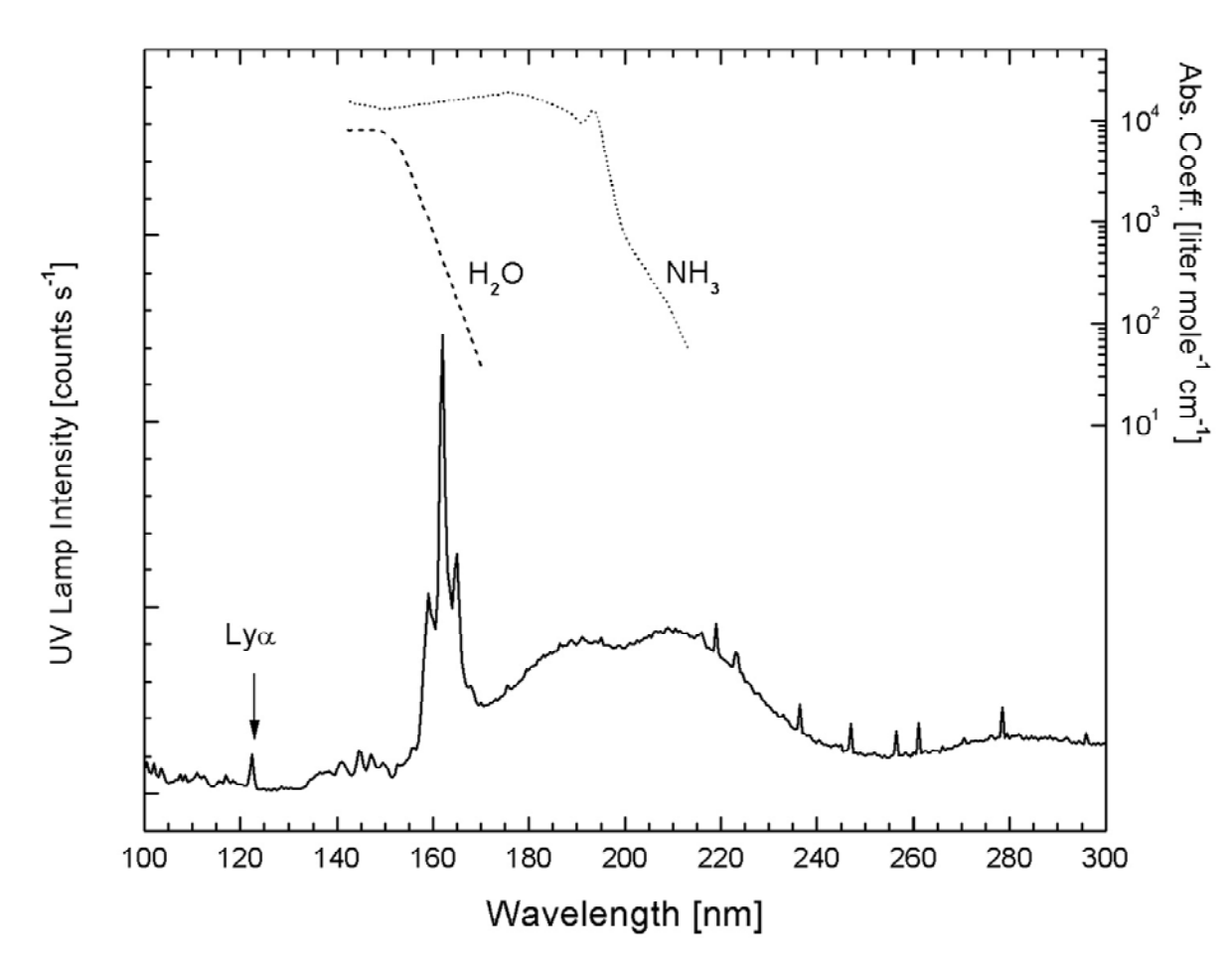
Spectrum of UV Photolysis Lamp at NASA/GSFC and UAB

<E> = 7.4 eV

Flux peak at 160 nm

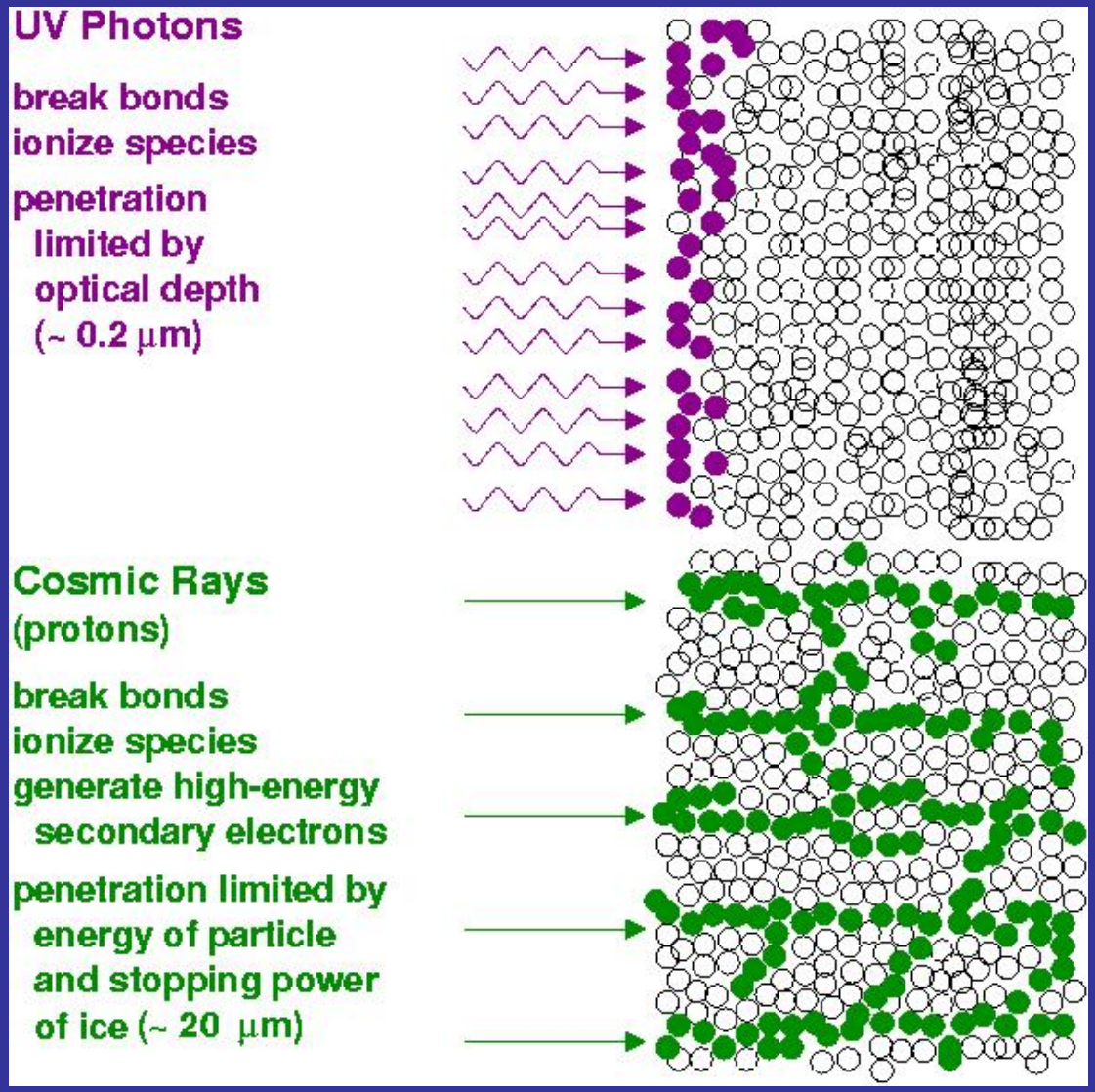
Highest flux in the range of strong ice absorptions

$\phi \sim 10^{14}$ cm^{-2} s^{-1}



Gerakines & Moore (2001)

Forms of Ice Processing in Space



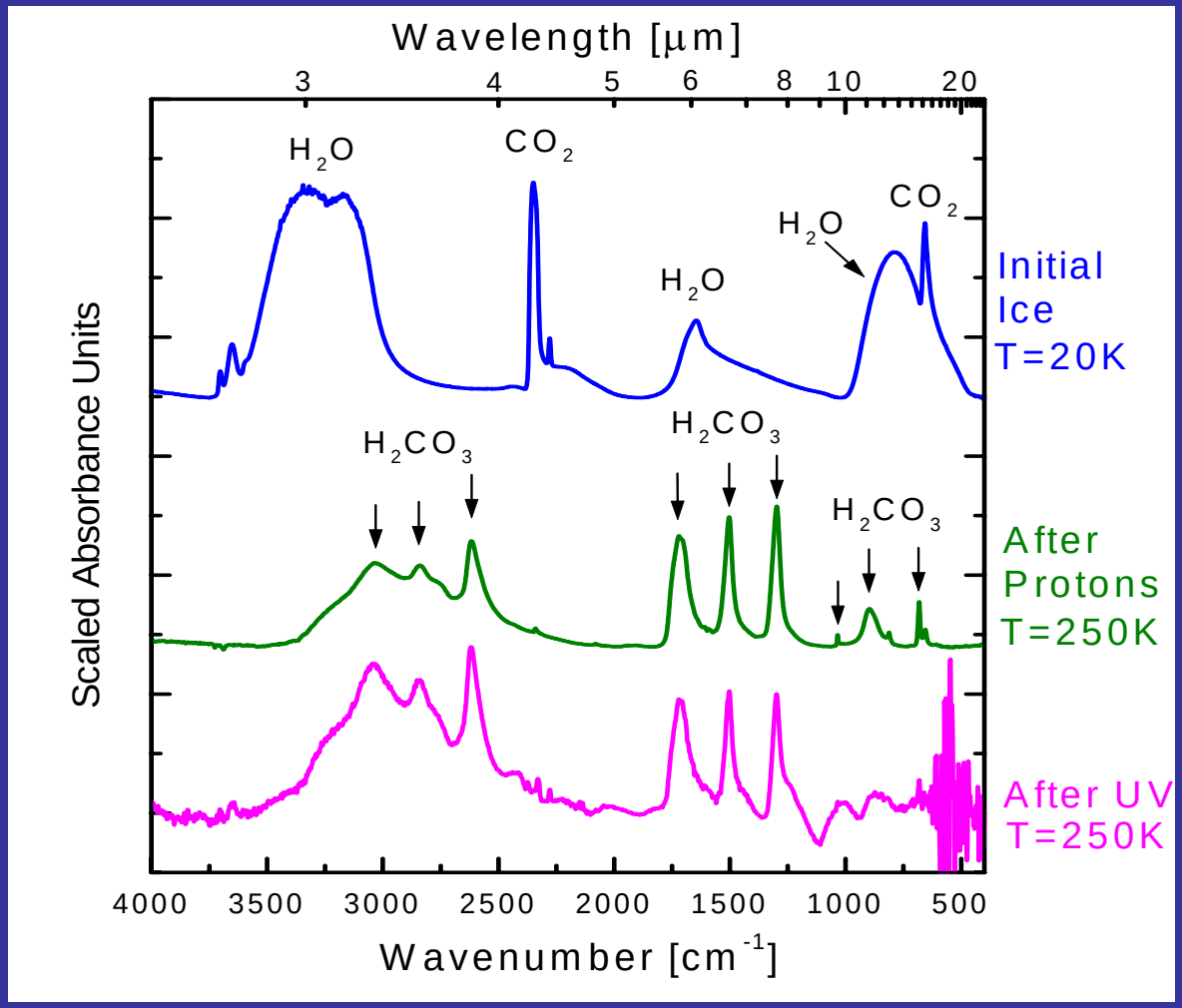
Is there a way to distinguish between ices processed by UV and those processed by cosmic rays?

Carbonic Acid Formation from $H_2O + CO_2$ Ice
(Relevant to ISM, Icy Moons)

$H_2O + CO_2$ (1:1) ice deposited at 20K

Residue at 250 K after exposure to 0.8 MeV protons

Residue at 250 K after exposure to 7.4 eV UV photons



Gerakines, Moore, & Hudson (2000)

Product formation rates in $H_2O + CO_2$ (1:1) Ice

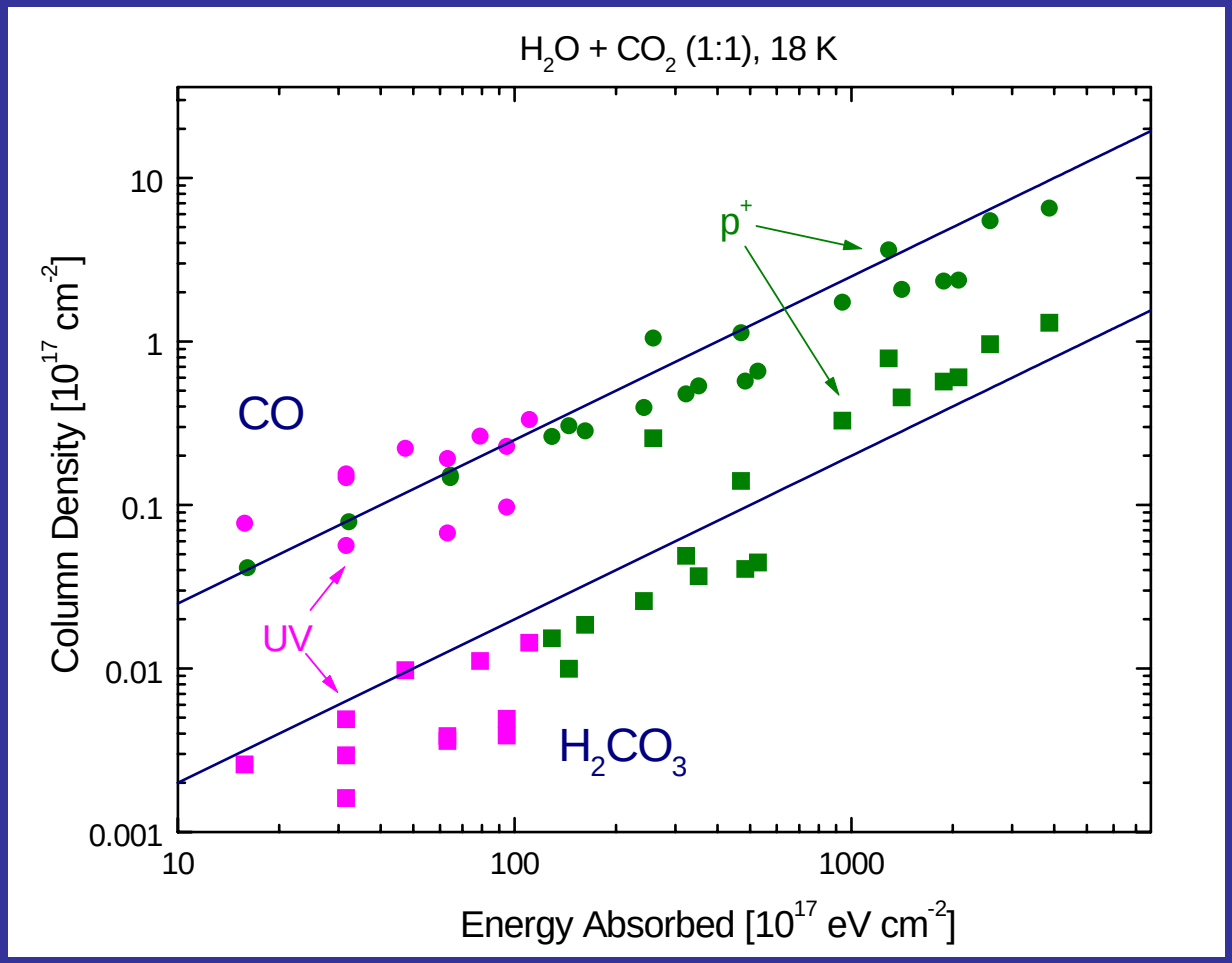
Rates independent of the nature of the processing

CO:
G= 0.25 molec / 100eV

H_2CO_3:
G= 0.03 molec / 100eV

Only dependent on the total amount of energy absorbed by the ice sample

Expect ~ 1% rel. to CO2 In astrophysical environ-ments.



Gerakines, Moore, & Hudson (2000)

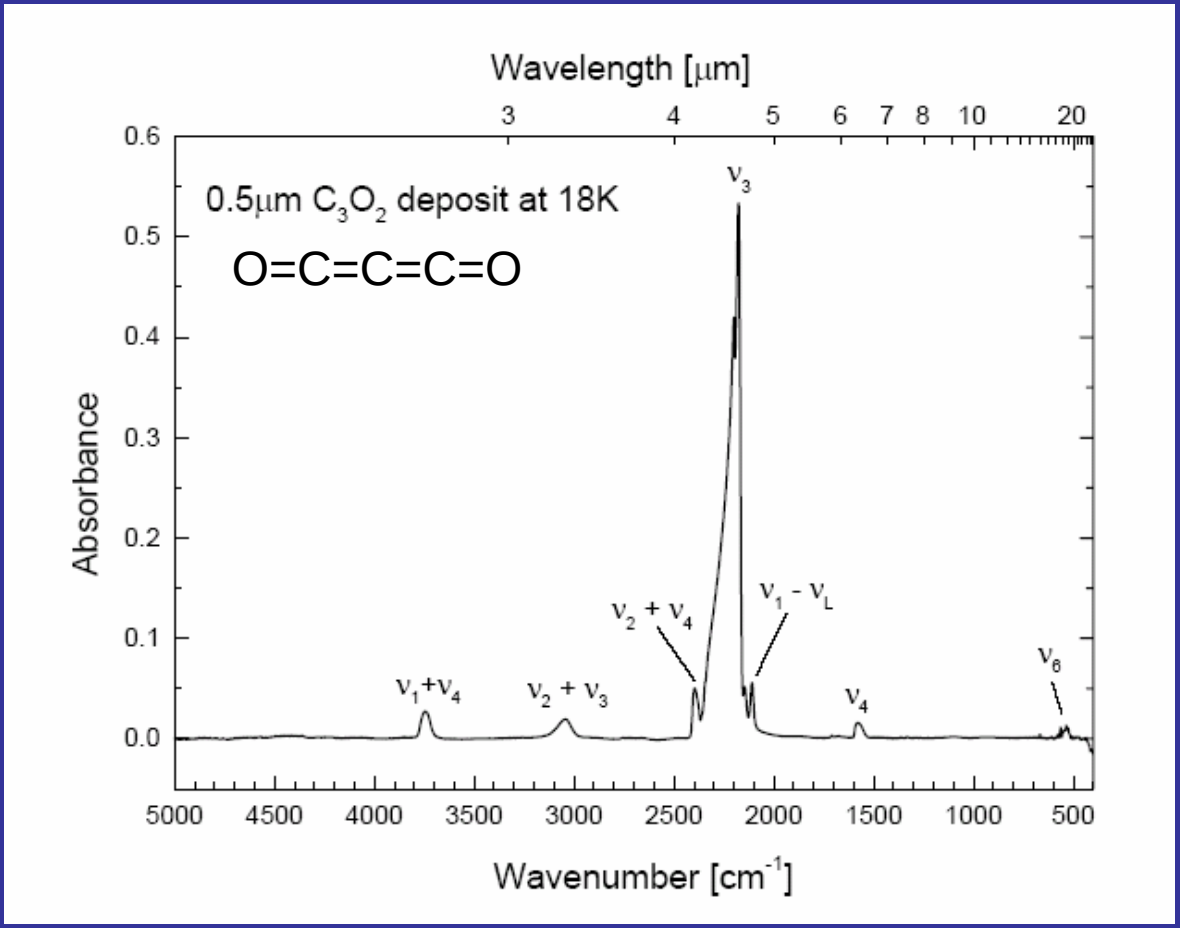
Mid-IR spectrum of carbon suboxide (C_3O_2) at 18K

Studied in CO discharge experiments since the mid-1800's

Polymers vary in color from red to brown

Suggested by Kuiper (1957) as source of yellow clouds on Venus

Suggested by Huntress et al. (1991) as source of low cometary albedo



Gerakines & Moore (2001)

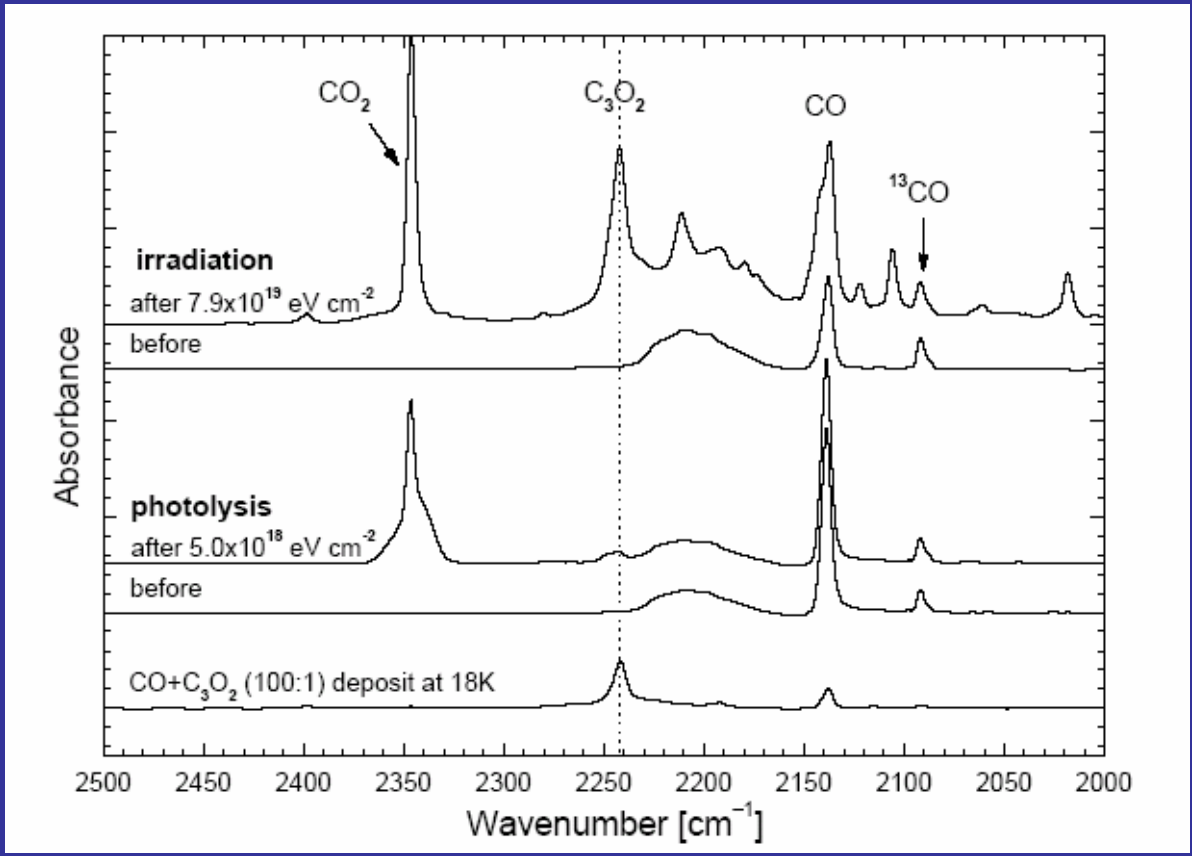
Carbon suboxide (C_3O_2) formation in CO-containing ices

Processing of pure CO at 18 K…

… by 0.8 MeV Protons

… by UV Photolysis

$CO+C_3O_2$ (100:1) at 18K for comparison



Gerakines & Moore (2001)

Suboxide production rates for CO processing at 18 K

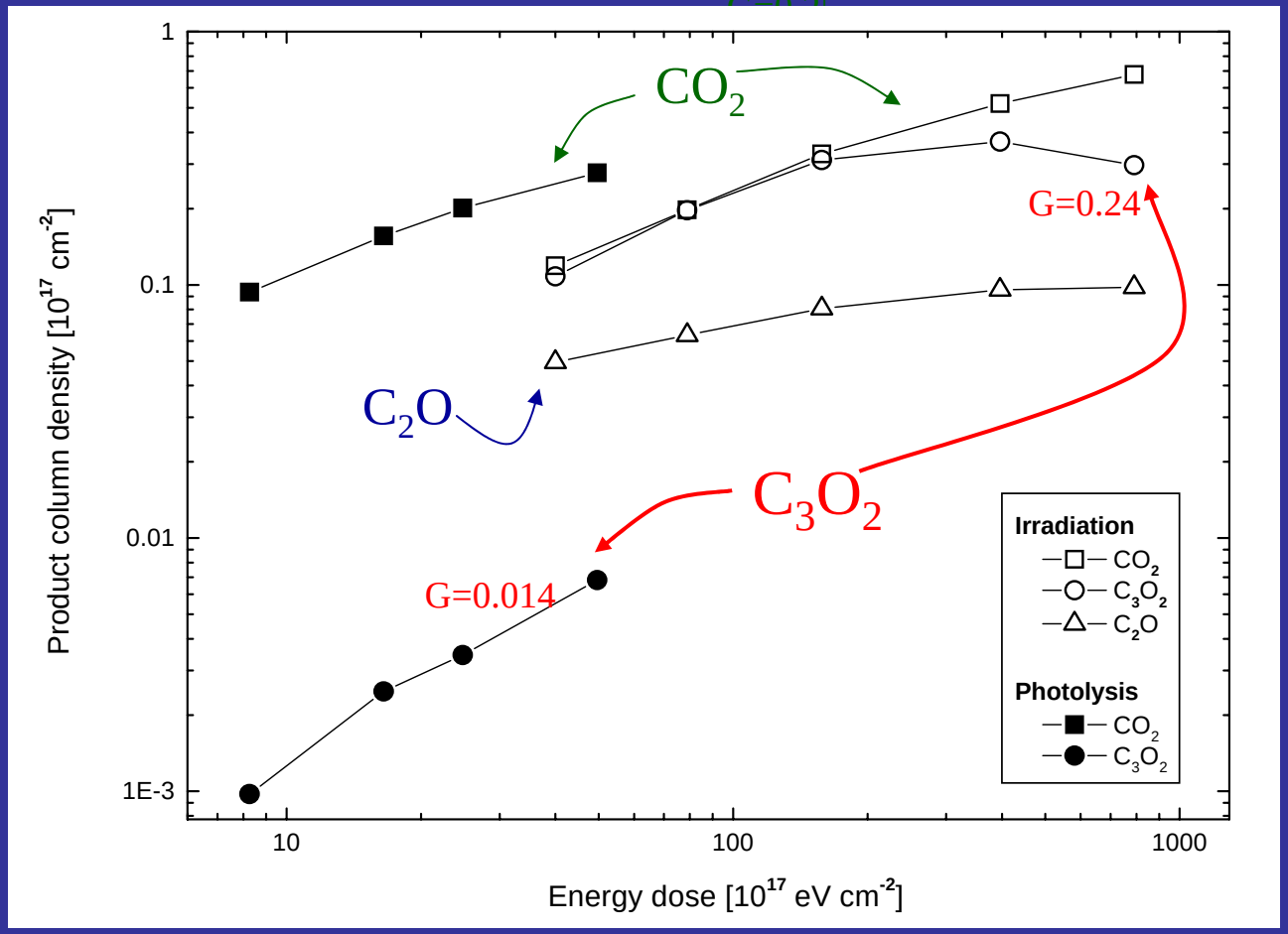
Large differences in formation rates, dependent on form of energy

C_3O_2:

G = 0.24 (irradiation)

G= 0.014 (photolysis)

Due to high dissociation energy of CO molecule (11eV)

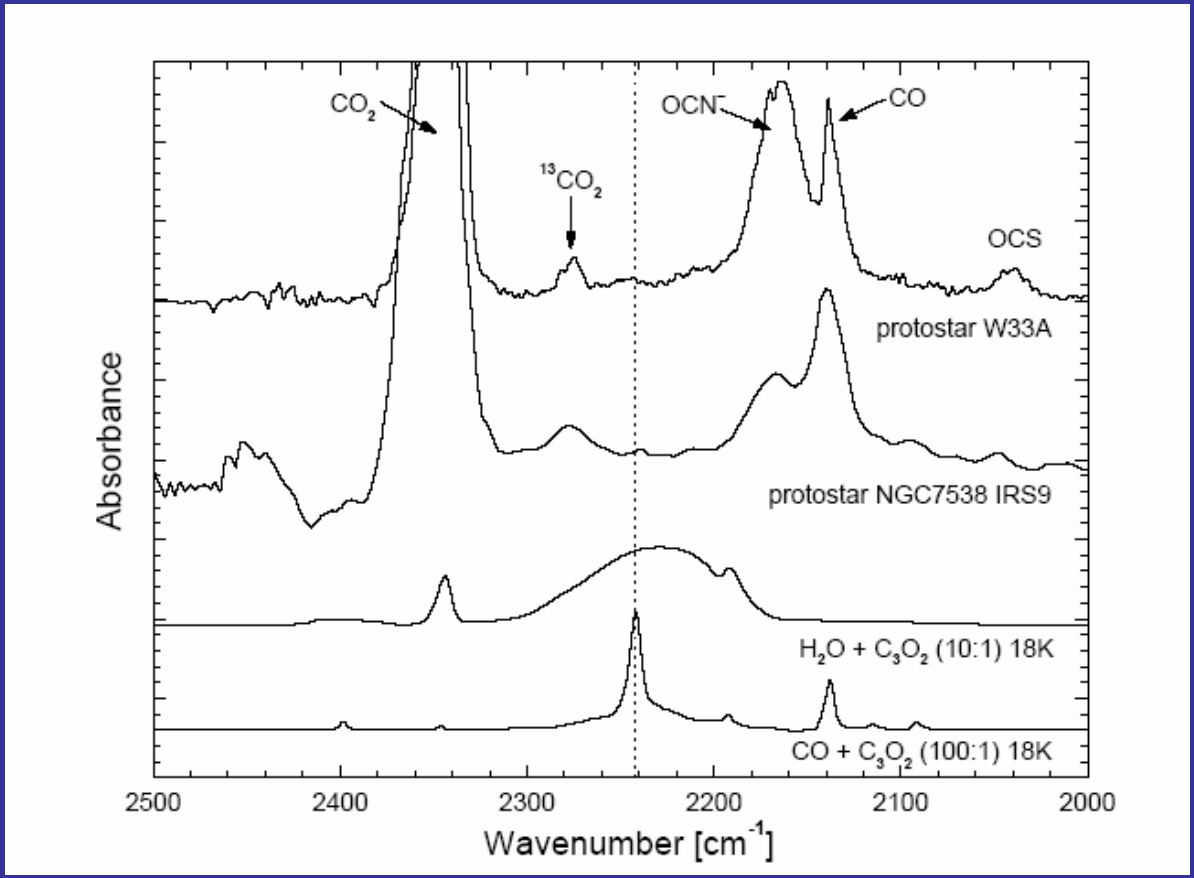


Gerakines & Moore (2001)

Could C_3O_2 be found in the ISM?

High band strength of 1.3×10^{-16} cm/molec would allow detection of low C_3O_2 abundances

Upper limits from ISO spectra < 0.05 % of H_2O



Gerakines & Moore (2001)

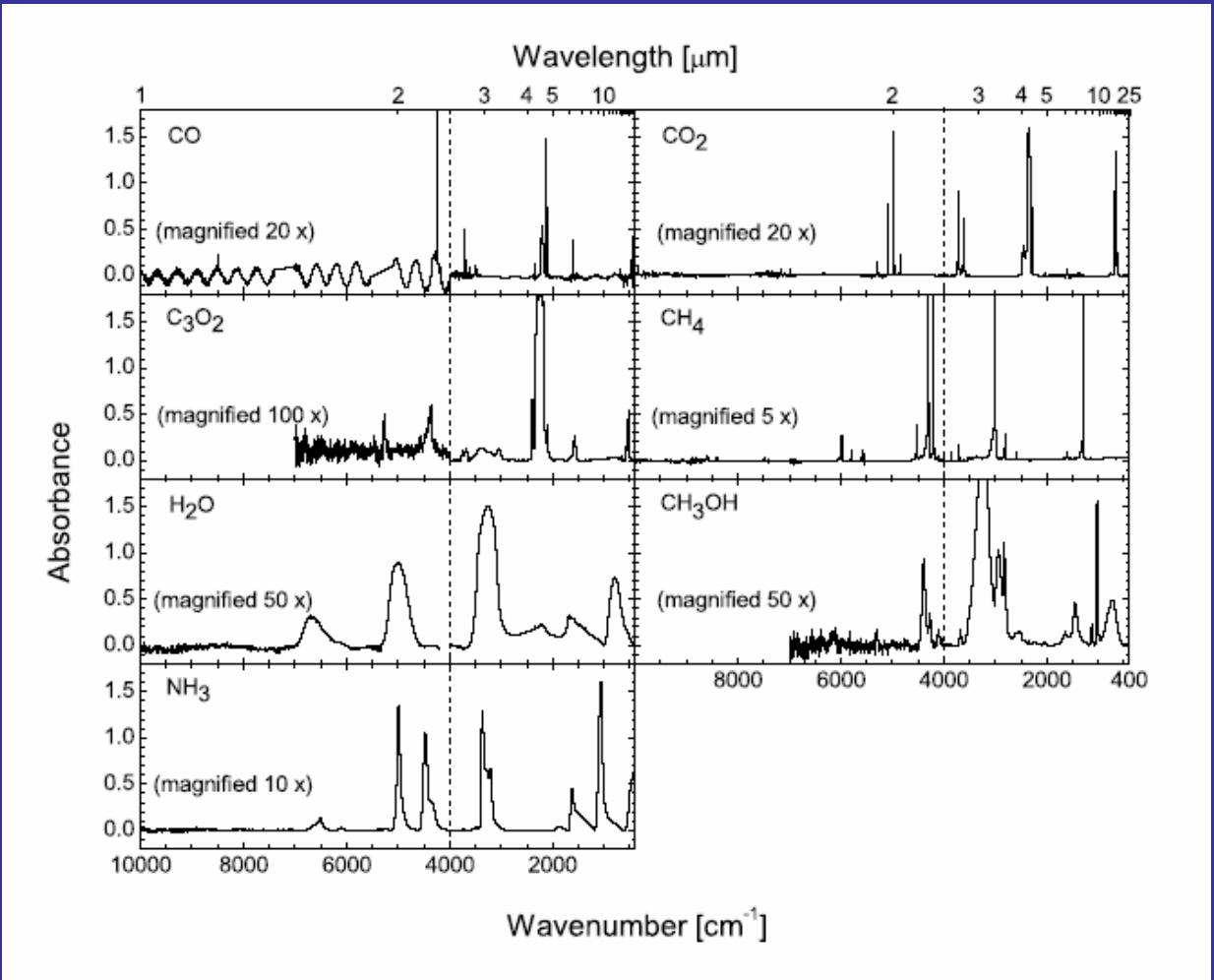
Studies of Ice Overtone Features in Near-IR

Relevant to studies of planetary ices

Some observations of the ISM in Near-IR (Pontoppidan et al.)

Overtone features 10-100 times weaker than fundamentals in Mid-IR

Thick ices required:
For Mid-IR, 0.1-1μm
For Near-IR, 5-50μm



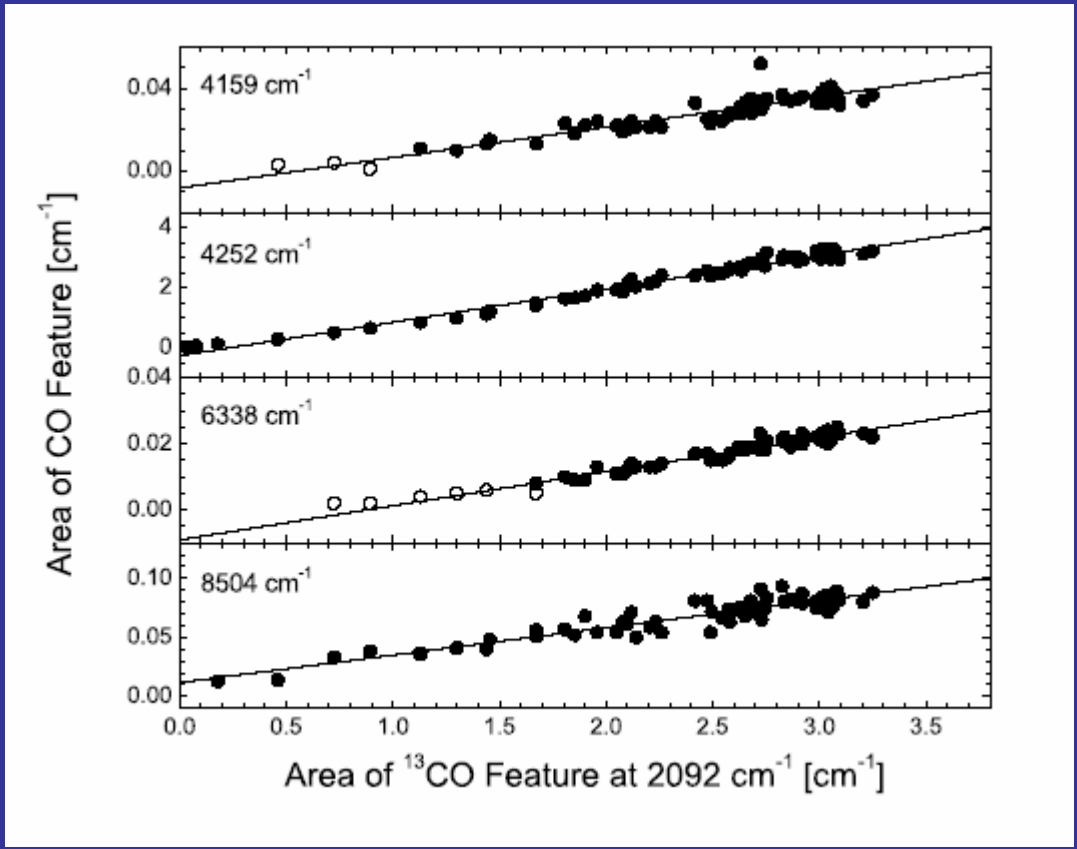
Studies of Ice Overtone Features in Near-IR

Long deposits (1-3 days) were monitored by FTIR spectroscopy in both Mid- and Near-IR

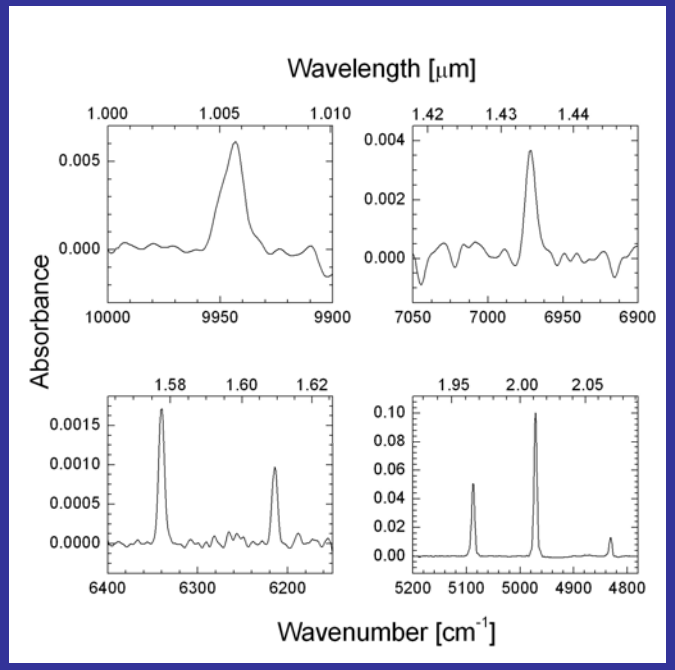
Areas of Near-IR features plotted vs. area of well-studied Mid-IR feature

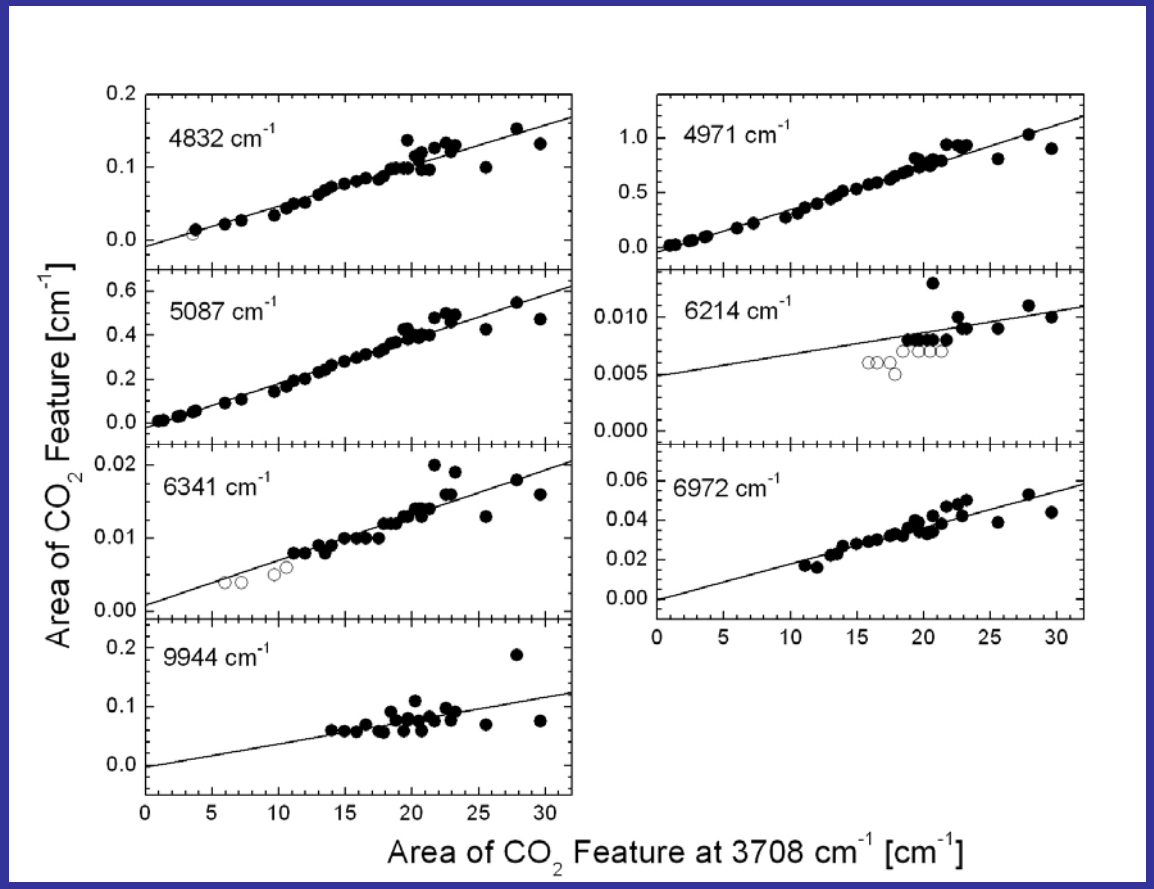
Slope of trends used as scaling factor to determine band strengths

Results for CO

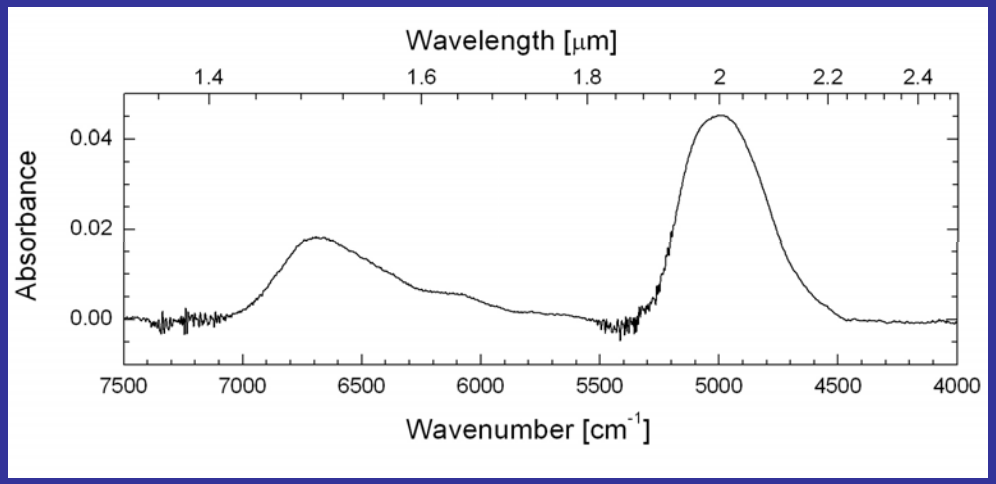


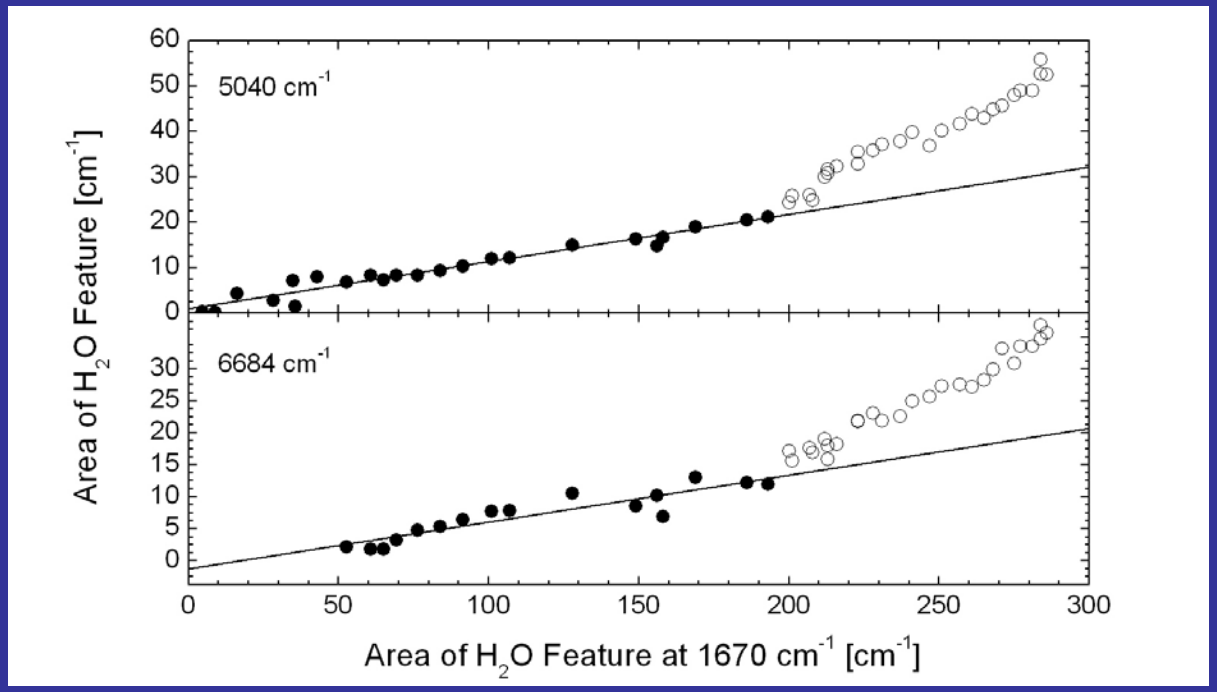
Results for CO_2



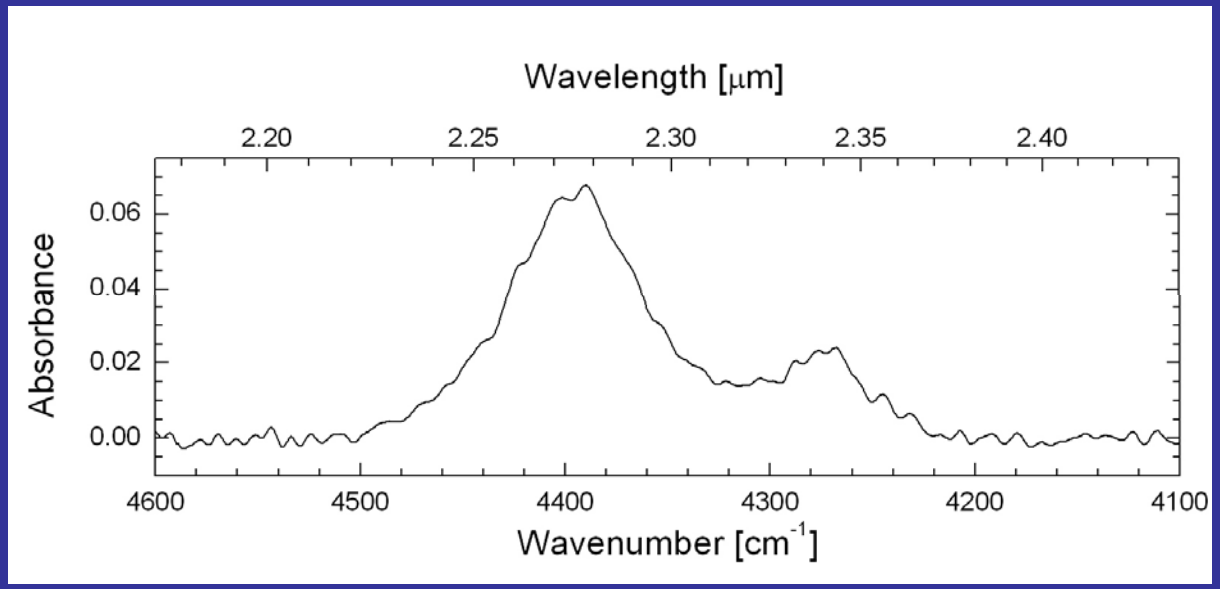


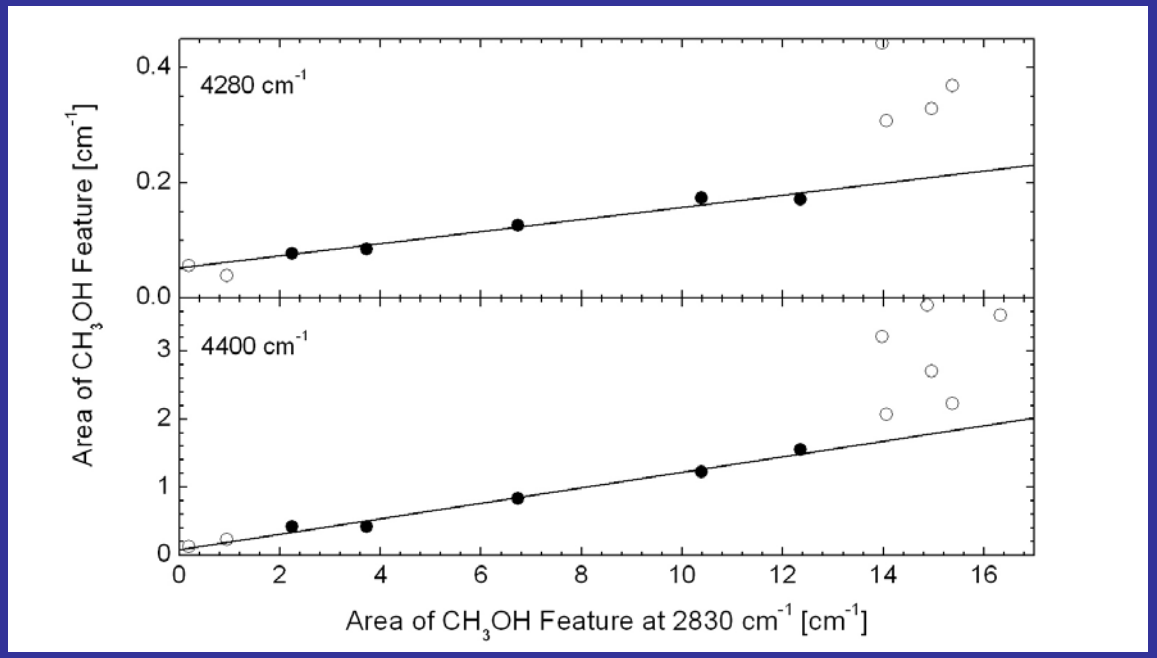
Results for H_2O



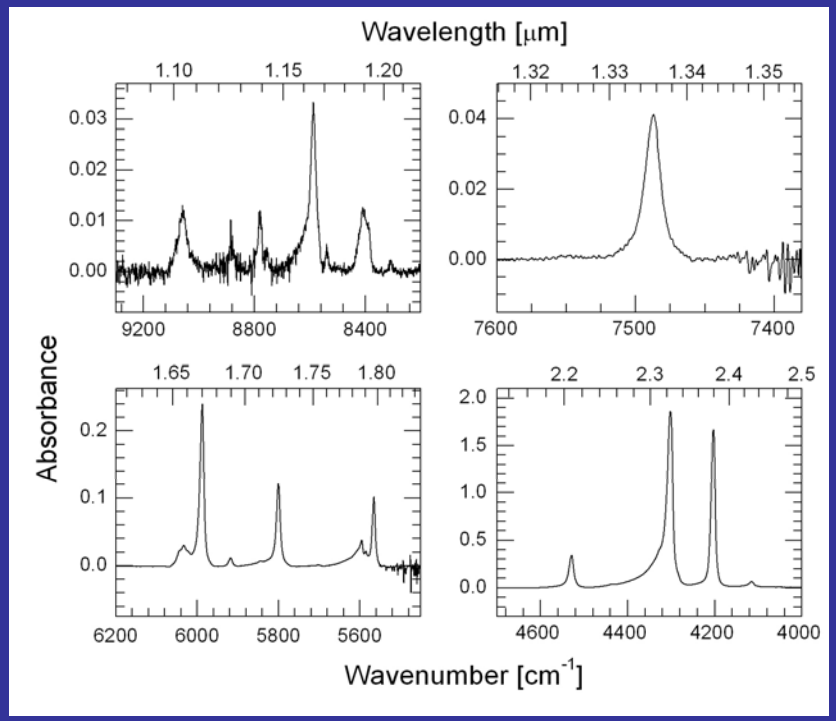


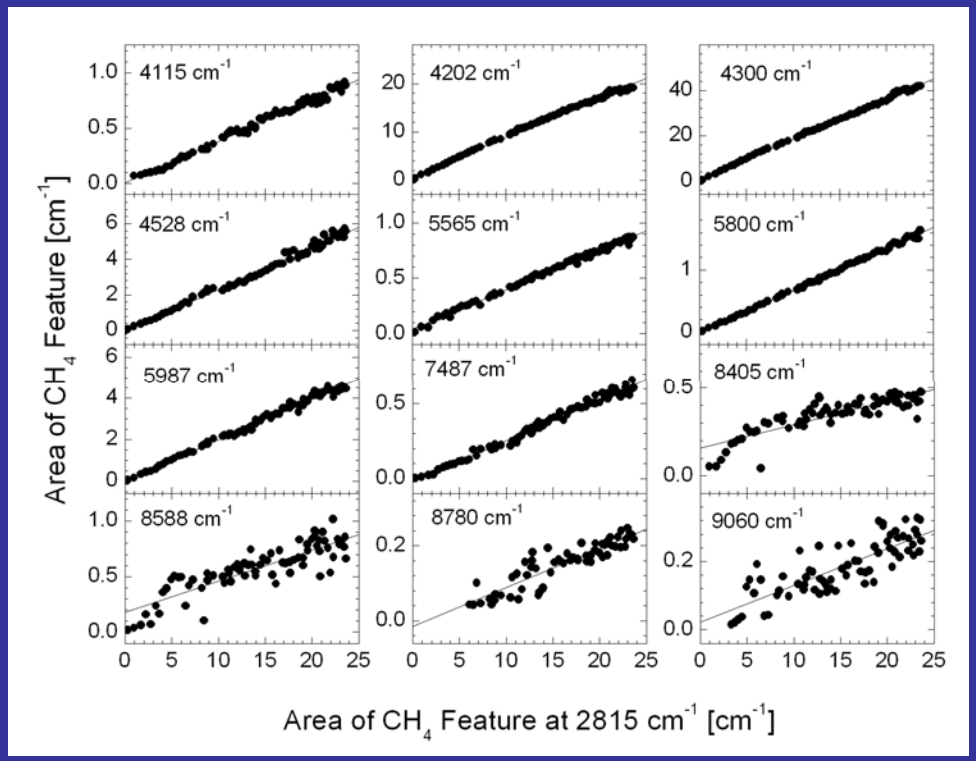
CH_3OH


Wavelength [μm]
2.20
2.25
2.30
2.35
2.40
Absorbance
0.06
0.04
0.02
0.00
4600
4500
4400
4300
4200
4100
Wavenumber [cm-1]


4280 cm-1
4400 cm-1
Area of CH3OH Feature [cm-1]
0.4
0.2
0.0
3
2
1
0
0
2
4
6
8
10
12
14
16
Area of CH3OH Feature at 2830 cm-1 [cm-1]

CH_4


Wavelength [μm]
1.10
1.15
1.20
1.32
1.33
1.34
1.35
1.65
1.70
1.75
1.80
2.2
2.3
2.4
2.5
Absorbance
Wavenumber [cm-1]


4115 cm-1
4202 cm-1
4300 cm-1
4528 cm-1
5565 cm-1
5800 cm-1
5987 cm-1
7487 cm-1
8405 cm-1
8588 cm-1
8780 cm-1
9060 cm-1
Area of CH4 Feature [cm-1]
Area of CH4 Feature at 2815 cm-1 [cm-1]

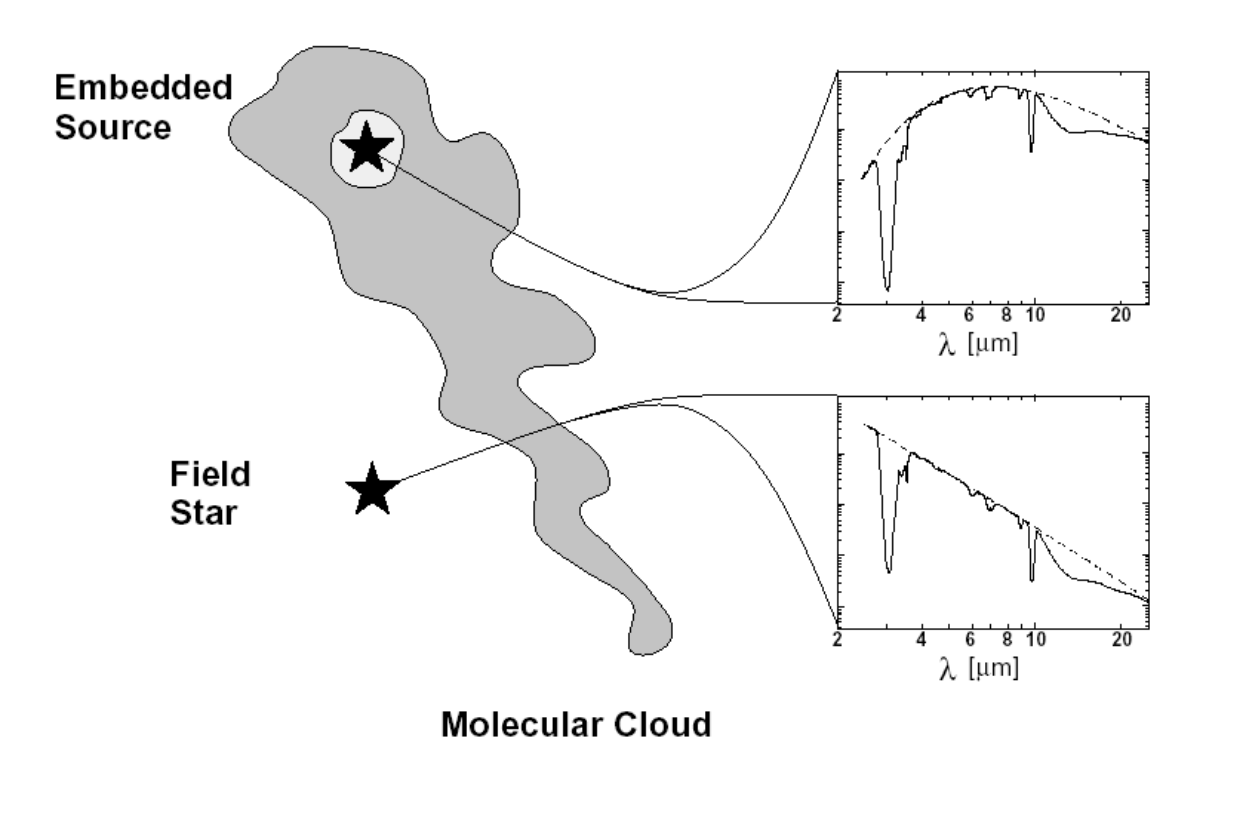
Studies of Ice Overtone Features in Near-IR

Peak Position $\tilde{\nu}$ [cm^{-1}]	Peak Position λ [μm]	FWHM, $\Delta\tilde{\nu}$ [cm^{-1}]	Vibration Mode	Strength, A [cm molec^{-1}]	Notes
CO[a]					
4159	2.404	3	2ν ^{13}CO	$(2.1 \pm 0.1) \times 10^{-21}$	1
4252	2.352	3	2ν ^{12}CO	$(1.6 \pm 0.1) \times 10^{-19}$	1
6338	1.578	4	3ν ^{12}CO	$(1.5 \pm 0.1) \times 10^{-21}$	1
8504	1.176	8	?	$(3.4 \pm 0.2) \times 10^{-21}$	
CO_2					
4832	2.070	6	$4\nu_2 + \nu_3$	$(7.8 \pm 0.5) \times 10^{-21}$	1
4971	2.012	7	$\nu_1 + 2\nu_2 + \nu_3$	$(5.4 \pm 0.2) \times 10^{-20}$	1
5087	1.966	7	$2\nu_1 + \nu_3$	$(2.8 \pm 0.1) \times 10^{-20}$	1
6214	1.609	7	$\nu_1 + 4\nu_2 + \nu_3$	$(2.6 \pm 1.8) \times 10^{-22}$	1
6341	1.577	7	$2\nu_1 + 2\nu_2 + \nu_3$	$(8.6 \pm 1.1) \times 10^{-22}$	1
6972	1.434	8	$3\nu_3$	$(2.6 \pm 0.3) \times 10^{-21}$	1
9944	1.006	12	$4\nu_3 + \nu_2$ (?)	$(5.6 \pm 1.9) \times 10^{-21}$	1
C_3O_2					
4370	2.288	78	$2\nu_3$ (?)	$(1.7 \pm 0.2) \times 10^{-19}$	
4570	2.188	37	$\nu_2 + \nu_3 + \nu_4$ (?)	$(1.7 \pm 0.2) \times 10^{-20}$	
5270	1.898	48	$\nu_2 + 2\nu_3$ (?)	$(5.0 \pm 0.9) \times 10^{-20}$	
CH_4					
4115	2.430	14	$\nu_2 + 2\nu_4$	$(7.2 \pm 0.1) \times 10^{-20}$	1
4202	2.380	9	$\nu_1 + \nu_4$	$(1.6 \pm 0.1) \times 10^{-18}$	1
4300	2.326	7	$\nu_3 + \nu_4$	$(3.4 \pm 0.1) \times 10^{-18}$	1
4528	2.208	9	$\nu_2 + \nu_3$	$(4.5 \pm 0.1) \times 10^{-19}$	1
5565	1.797	5	$\nu_3 + 2\nu_4$	$(6.8 \pm 0.1) \times 10^{-20}$	1
5800	1.724	8	$\nu_2 + \nu_3 + \nu_4$	$(1.3 \pm 0.1) \times 10^{-19}$	1
5987	1.670	7	$2\nu_3$	$(3.8 \pm 0.1) \times 10^{-19}$	1
7487	1.336	11	$\nu_2 + 2\nu_3$	$(5.3 \pm 0.1) \times 10^{-20}$	1
8405	1.190	30	$[\nu_1] + [\nu_1] + [\nu_4] + [\nu_4]$	...	2
8588	1.164	42	$2\nu_3 + 2\nu_4$	$(5.4 \pm 0.1) \times 10^{-20}$	1
8780	1.139	17	$\nu_2 + 2\nu_3 + \nu_4$	$(2.0 \pm 0.1) \times 10^{-20}$	1
9060	1.104	28	$3\nu_3$	$(2.1 \pm 0.2) \times 10^{-20}$	3

Peak Position $\tilde{\nu}$ [cm^{-1}]	Peak Position λ [μm]	FWHM, $\Delta\tilde{\nu}$ [cm^{-1}]	Vibration Mode	Strength, A [cm molec^{-1}]	Notes
H_2O					
5040	1.984	408	$\nu_2 + \nu_3$	$(1.2 \pm 0.1) \times 10^{-18}$	
6684	1.496	520	$2\nu_3$	$(8.8 \pm 1.0) \times 10^{-19}$	
CH_3OH					
4280	2.336	34	?	$(8.0 \pm 0.9) \times 10^{-20}$	
4400	2.273	72	?	$(8.7 \pm 0.7) \times 10^{-19}$	
NH_3					
4474	2.235	94	$\nu_1 + \nu_2$ (?)	$(8.7 \pm 0.3) \times 10^{-19}$	
4993	2.002	68	$\nu_1 + \nu_4$ (?)	$(8.1 \pm 0.4) \times 10^{-19}$	
6099	1.640	107	$\nu_1 + \nu_2 + \nu_4$ (?)	$(2.8 \pm 0.5) \times 10^{-20}$	
6515	1.535	118	$2\nu_1$ (?)	$(3.9 \pm 0.3) \times 10^{-20}$	

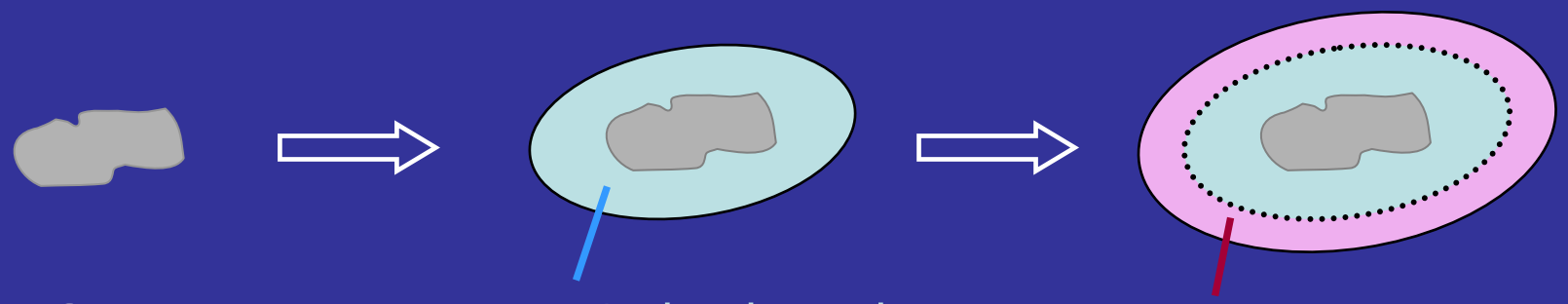
[a]All ^{12}CO and ^{13}CO band strengths are expressed in units of cm per ^{12}CO molecule.

Investigating the Origins of Interstellar CO_2 with the Spitzer Space Telescope



ISO SWS observed ice features in luminous YSOs, but background field stars were generally too faint.

Models predict that ice mantles contain at least two distinct phases with different volatilities (and hence different extinction thresholds)



$O \rightarrow OH \rightarrow H_2O$

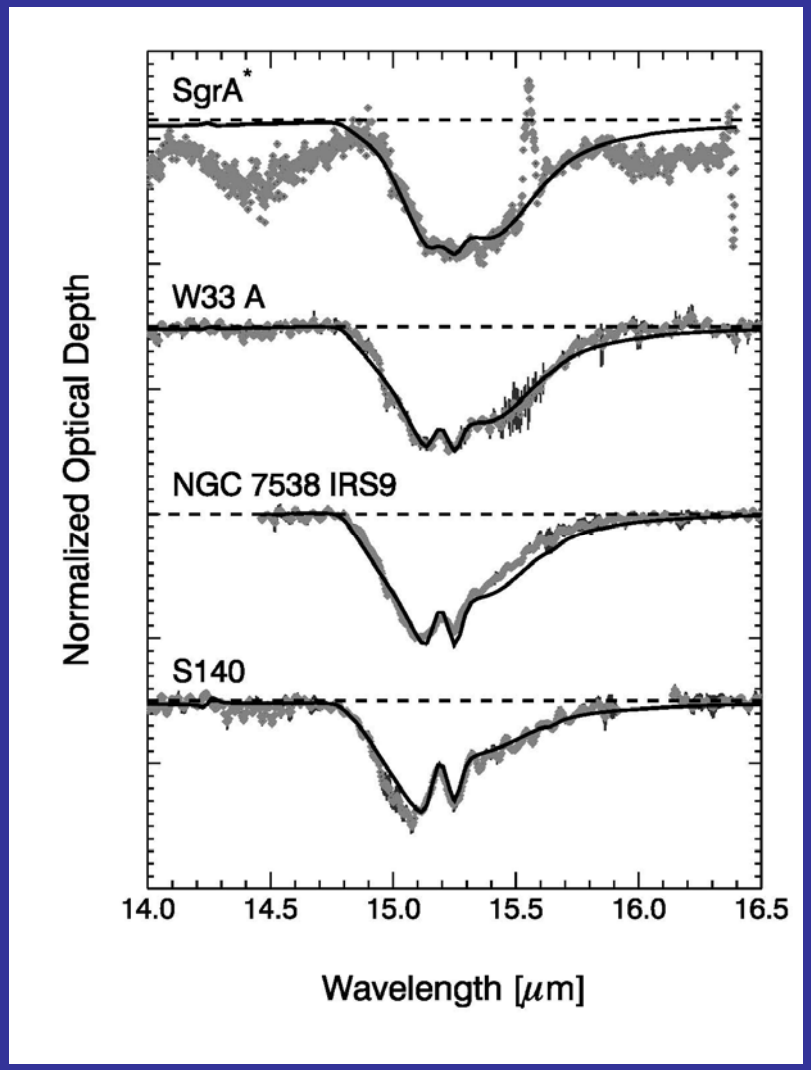
$CO_{gas} \rightarrow CO_{ice}$

An intermediate phase?

$4\ H + CO \rightarrow CH_3OH$?

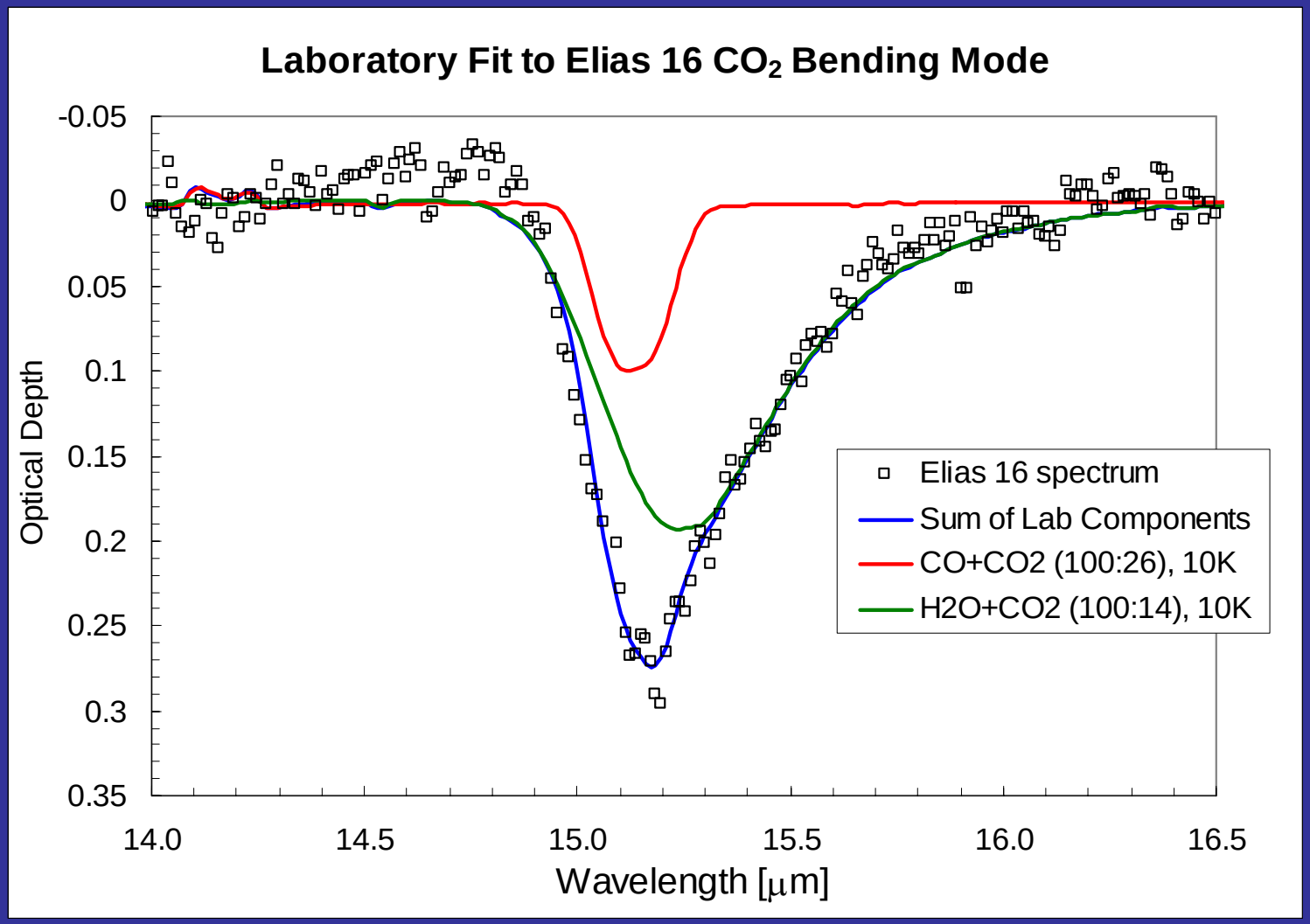
$O + CO \rightarrow CO_2$?

Why is the CO_2 bending mode important?



ISO-SWS data and fits from Gerakines et al. (1999). Fits use lab data for ice mixtures with temperature increasing from top to bottom.

- The narrow sub features are temperature-sensitive
- CO_2 and CH_3OH may form linked complexes that produce a long-wavelength shoulder



Bergin et al. (2005, submitted)

Systematic study of CO_2 bending mode

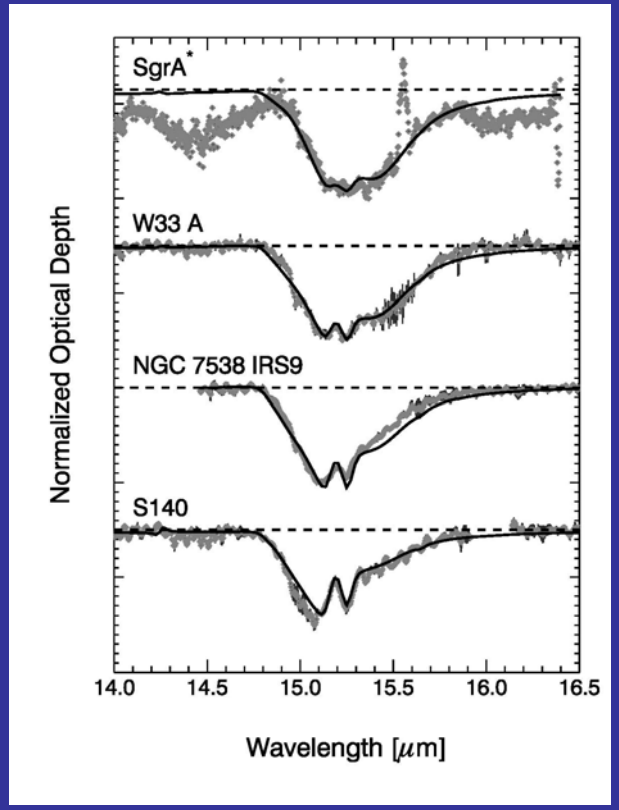


Table 2. Proposed list of 47 ice compositions—combinations of H_2O, CH_3OH, and CO_2—to be systematically studied in this research program.

Mixture	Compositions to be studied
$CH_3OH + CO_2$	(0.1, 0.5, 1, 1.5, 2, 5, 10) : 1
$H_2O + CO_2$	(1, 2, 5, 10, 100) : 1
$H_2O + CH_3OH + CO_2$	(1,2,5,10,100) : (0.1,0.5,1,1.5,2,5,10) : 1

Table 3. Thermal history experiments to be studied in the research program. The ices listed will be annealed at durations from 30 s to 1 h at each temperature listed. Annealing temperatures were chosen based upon the temperatures at which ices showed segregation in Ehrenfreund *et al.* (1999).

Mixture	Compositions	Annealing Temperatures (K)
$CH_3OH + CO_2$	(0.1, 1, 10):1	50, 75, 90, 100, 110, 115, 120, 125, 130, 150
$H_2O + CO_2$	(1, 10):1	50, 75 90, 100, 110, 115, 120, 125, 130, 150
$H_2O + CH_3OH + CO_2$	(1, 10, 100) : (0.1, 1, 10):1	50, 75 90, 100, 110, 115, 120, 125, 130, 150
$H_2O + CH_3OH + CH_4 + CO_2$	10:1:1:1	50, 75, 90, 100, 110, 115, 120, 125, 130, 150
$H_2O + CH_3OH + NH_3 + CO_2$	10:1:1:1	50, 75, 90, 100, 110, 115, 120, 125, 130, 150

Results of SST study so far

- CO_2 displays a threshold extinction in Taurus similar to that of H_2O – it will be important to confirm and compare other clouds

- The CO_2 profile is well matched by a combination of polar (H_2O-dominated) and non-polar (CO-dominated) ice components at 10 K

- There is no evidence for thermal or photolytic processing of ices within the dark cloud

Photolysis of Planetary Ices

Planetary ices identified by vibrational overtones in near-IR

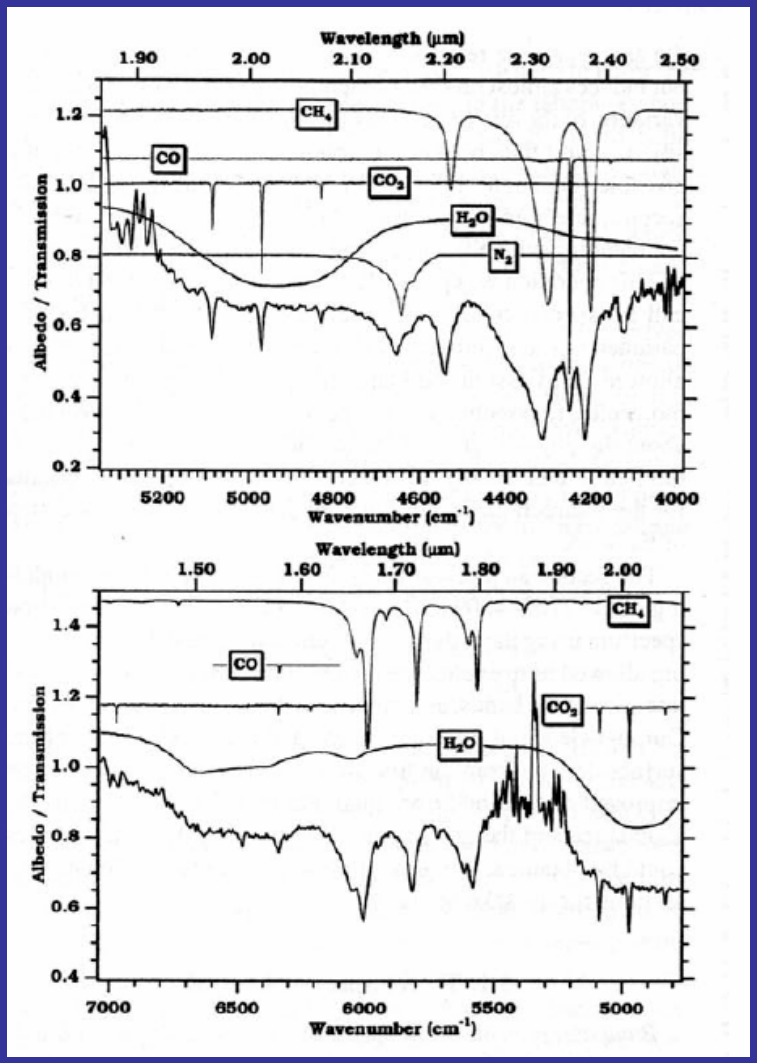
Laboratory spectra of samples created by closed-cell technique used in identification process

Spectra of UV photolyzed ices have never been used in the process

Why?

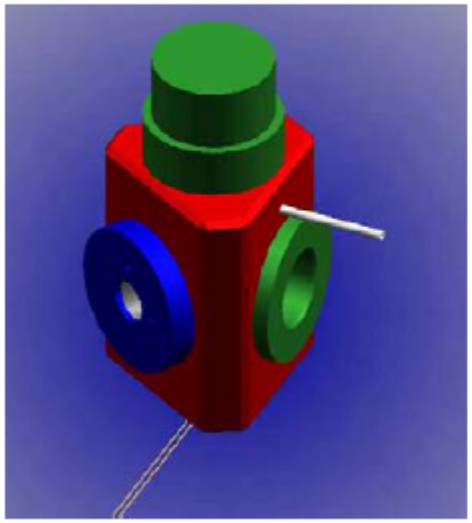
Overtone features are intrinsically weak

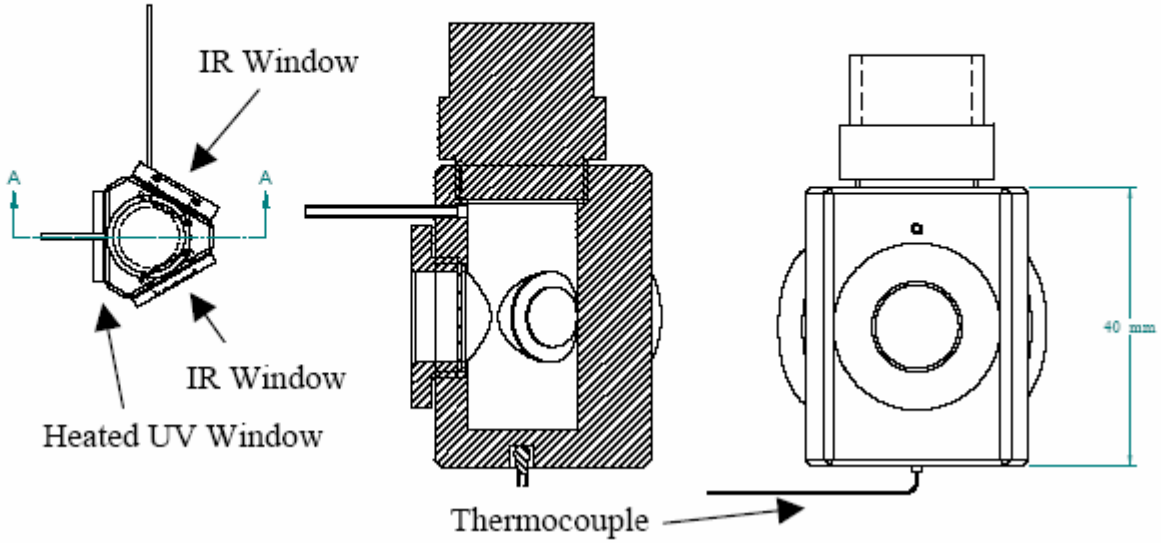
Thick ices difficult to photolyze effectively



Quirico et al. (1999)

Closed Cell for Photolysis of Planetary Ices





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