



**HAL**  
open science

# The advantages of the neon matrix to the vibrational study of van der Waals and hydrogen bonded molecular complexes

Benoît Tremblay, Pascale Soulard

► **To cite this version:**

Benoît Tremblay, Pascale Soulard. The advantages of the neon matrix to the vibrational study of van der Waals and hydrogen bonded molecular complexes. 23rd International conference on "Horizons in hydrogen bond research", Sep 2019, Amsterdam, Netherlands. hal-04019252

**HAL Id: hal-04019252**

**<https://hal.science/hal-04019252>**

Submitted on 8 Mar 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

# The advantages of the neon matrix to the vibrational study of van der Waals and hydrogen bonded molecular complexes

B. Tremblay, P. Soulard

MONARIS, CNRS-Sorbonne Université, Paris FRANCE

The complementarity between experiment and ab initio calculations allow to obtain new data on the n:m L<sub>n</sub>-(H<sub>2</sub>O)<sub>m</sub> complexes



## The neon matrix isolation apparatus coupled with FTIR

Absorption spectra collected on the same sample at 3 K from 80 to 9000 cm<sup>-1</sup> with a Bruker 120 FTIR spectrometer (InSb, MCT, and bolometer detectors)

## Calculated binding energy (kJ/mol) of some 1:1 complexes

	Van der Waals complexes				Hydrogen bonded complexes		
	CO <sub>2</sub>	OCS	N <sub>2</sub> O	H <sub>2</sub> O	H <sub>2</sub> O	(CH <sub>2</sub> ) <sub>2</sub> O	diacetyl
Ne	1.3	0.6	1	0.8			
Ar	2.6	2.1	2.6	1.7			
N <sub>2</sub>	3.8	1.7	3.9	5.4			
H <sub>2</sub> O	12.5	6.6	7.8	-	13	18.8	17.5

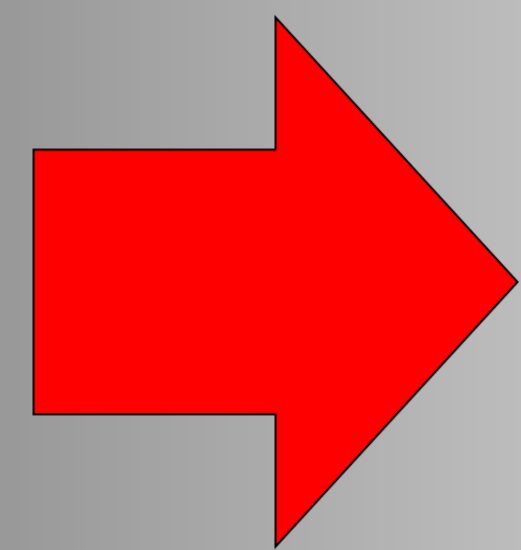
Polarizability	<sup>1</sup> H <sub>2</sub>	<sup>14</sup> N <sub>2</sub>	<sup>20</sup> Ne	<sup>40</sup> Ar
(10 <sup>-24</sup> cm <sup>3</sup> )	0.80	1.71	0.40	1.64

## Vibrational modes for the H<sub>2</sub>O and CO<sub>2</sub> molecules in gas phase and in N<sub>2</sub>, Ar, and Ne matrices

	H <sub>2</sub> O modes						CO <sub>2</sub> modes			
	v <sub>1</sub>	Δv <sup>a</sup>	v <sub>2</sub>	Δv	v <sub>3</sub>	Δv	v <sub>2</sub>	Δv	v <sub>3</sub>	Δv
gas	3656.7		1594.6		3755.8		667.4		2349.1	
N <sub>2</sub>	3634.9	21.8	1597.1	-2.5	3727.4	28.4	662.3	5.1	2349.0	0.1
Ar	3638.4	18.3	1588.7	5.9	3734.1	21.7	663.2	4.2	2339.4 <sup>b</sup>	9.7
Ne	3665.4	-8.7	1595.6	-0.8	3759.5	-3.7	668.0	-0.6	2347.8	1.3

<sup>a</sup> Δv = v<sub>gas</sub> - v<sub>matrix</sub>

<sup>b</sup> In solid argon, the CO<sub>2</sub> v<sub>3</sub> band has two trapping sites



In matrix experiments, the perturbation induced by N<sub>2</sub> and Ar cannot be neglected for a weak binding complex and the use of less perturbing material like neon is essential

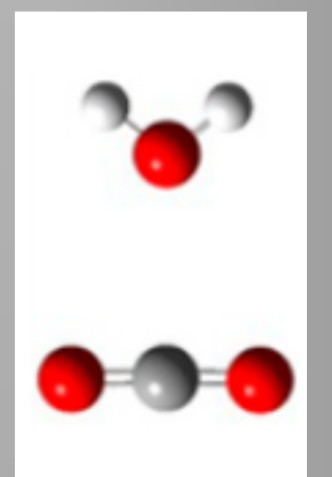
## Hydrated complexes formed with small molecules

- Identification of very weak binding complexes 1:1, 2:1, and 1:2
- Observation of different isomers for n:m complexes
- Observation of inter and intramolecular bands, overtones and combinations (v<sub>intra</sub>+v<sub>inter</sub> and v<sub>intra</sub>+v<sub>intra</sub>)
- Many deduced anharmonic coefficients providing data for anharmonic calculations

## Vibrational modes for the 1:1 H<sub>2</sub>O-CO<sub>2</sub> complex in gas phase and in N<sub>2</sub>, Ar, and Ne matrices

	H <sub>2</sub> O modes			CO <sub>2</sub> modes	
	Δv <sub>1</sub> <sup>a</sup>	Δv <sub>2</sub>	Δv <sub>3</sub>	Δv <sub>2</sub> <sup>b</sup>	Δv <sub>3</sub>
gas		-0.9			
N <sub>2</sub>	2.8	-1.4	1.9	-2.9	-2.0
Ar	0.4	-1.2	1.6	-4.8	-0.8
Ne	0.6	0.4	-0.8	-4.2	-0.4

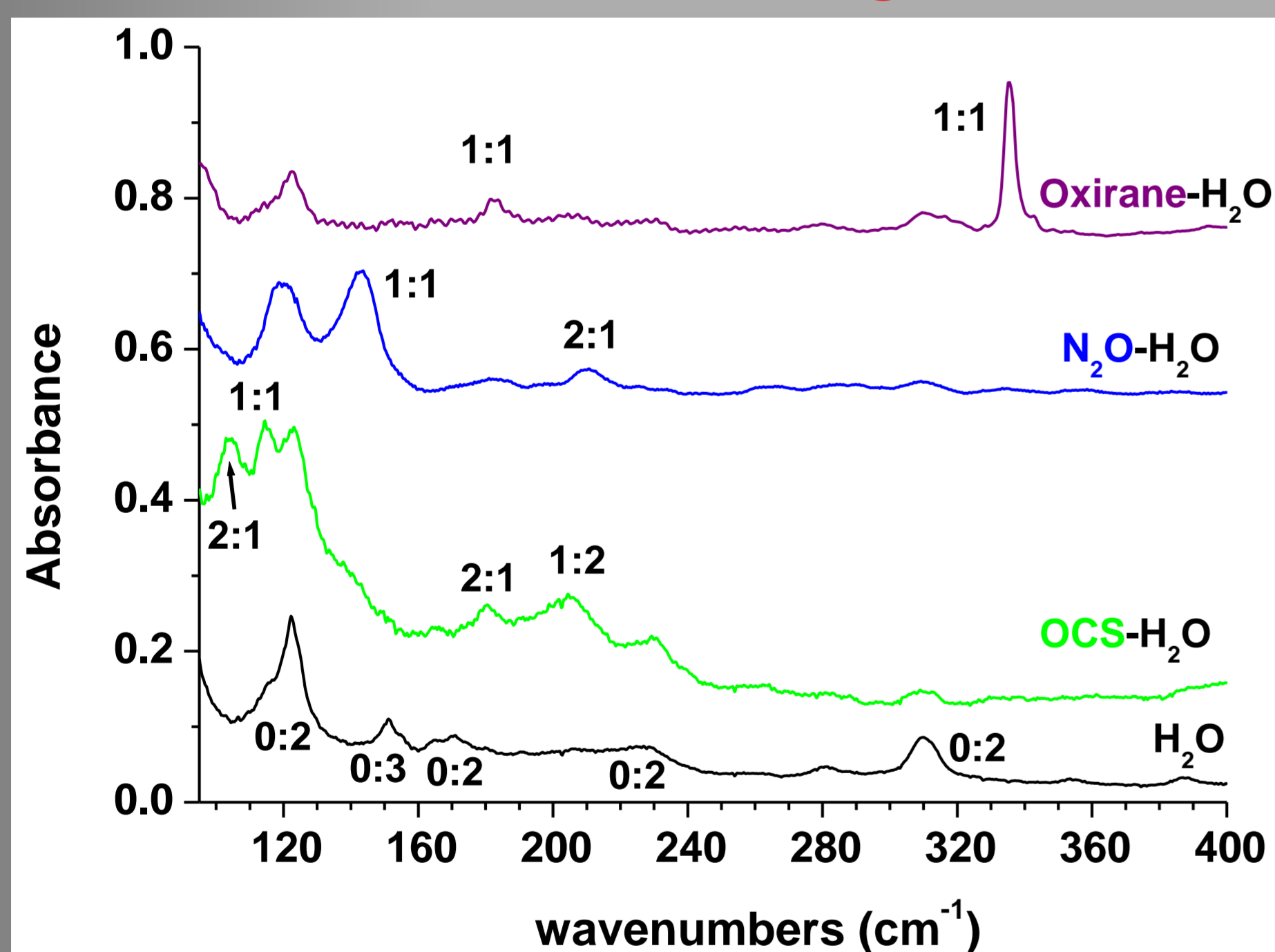
H<sub>2</sub>O-CO<sub>2</sub> complex



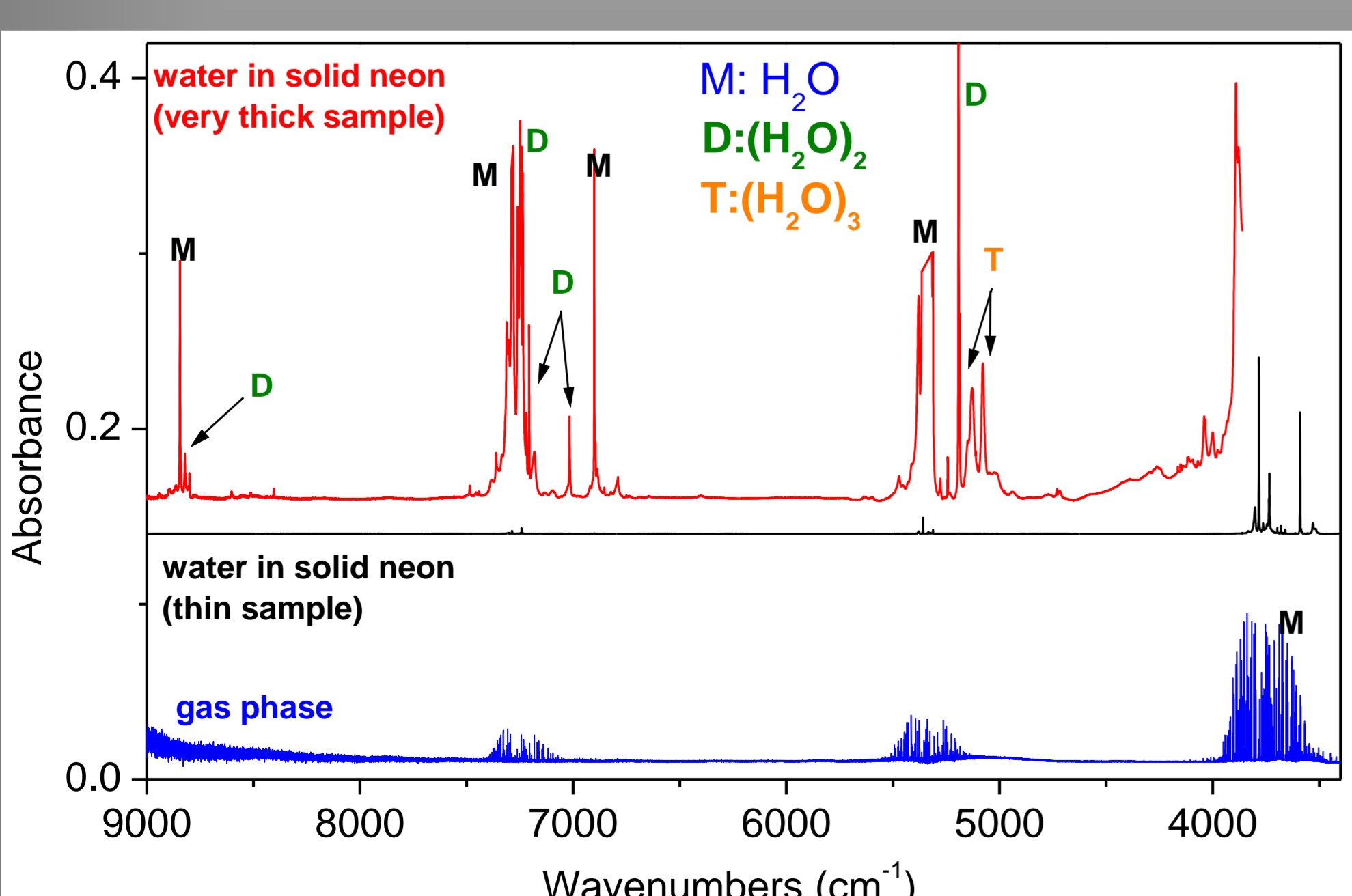
<sup>a</sup> Δv = v<sub>monomer</sub> - v<sub>complex</sub> in the same matrix

<sup>b</sup> the degeneracy of the v<sub>2</sub> mode is broken in the complex

## Far infrared: Intermolecular region



## Near infrared: overtones and combinations region



## Vibrational shifts for molecule-H<sub>2</sub>O complexes in Ne matrices

### Water modes

	Van der Waals complexes			Hydrogen bonded complexes			
	CO <sub>2</sub> -H <sub>2</sub> O	OCS-H <sub>2</sub> O	N <sub>2</sub> O-H <sub>2</sub> O	(H <sub>2</sub> O) <sub>2</sub> <sup>b</sup>	H <sub>2</sub> O-(CH <sub>2</sub> ) <sub>2</sub> O	H <sub>2</sub> O-diacetyl <sup>c</sup>	
1:1	v <sub>1</sub>	0.8	6.0 <sup>a</sup>	1.4	4.8, 74.9	129.6	71.2
	v <sub>2</sub>	-0.4	-2.0	-0.3	-3.6, -20.9	-9.7	-7.6
	v <sub>3</sub>	0.7	7.0	2.0	-2.5, 27.3	42.8	28.3
2:1	v <sub>1</sub>	15	17.4	18.3			
	v <sub>2</sub>	1.0	2.2	-4.6			
	v <sub>3</sub>	9.0	20.0	7.6			
1:2 <sup>b</sup>	v <sub>1</sub>	29.3, 21.6	19, 21	23.6, 18.7			
	v <sub>2</sub>	1.4, 3.2	2.0, 0.9	1.0, no			
	v <sub>3</sub>	24.0, no	22.9, 19.0	22.4, no			

<sup>a</sup> the OCS-H<sub>2</sub>O complex have 2 isomers

<sup>b</sup> the 1:2 and (H<sub>2</sub>O)<sub>2</sub> complexes have PA (proton acceptor) and PD (proton donor) vibrations

<sup>c</sup> the diacetyl-H<sub>2</sub>O complex have 2 isomers

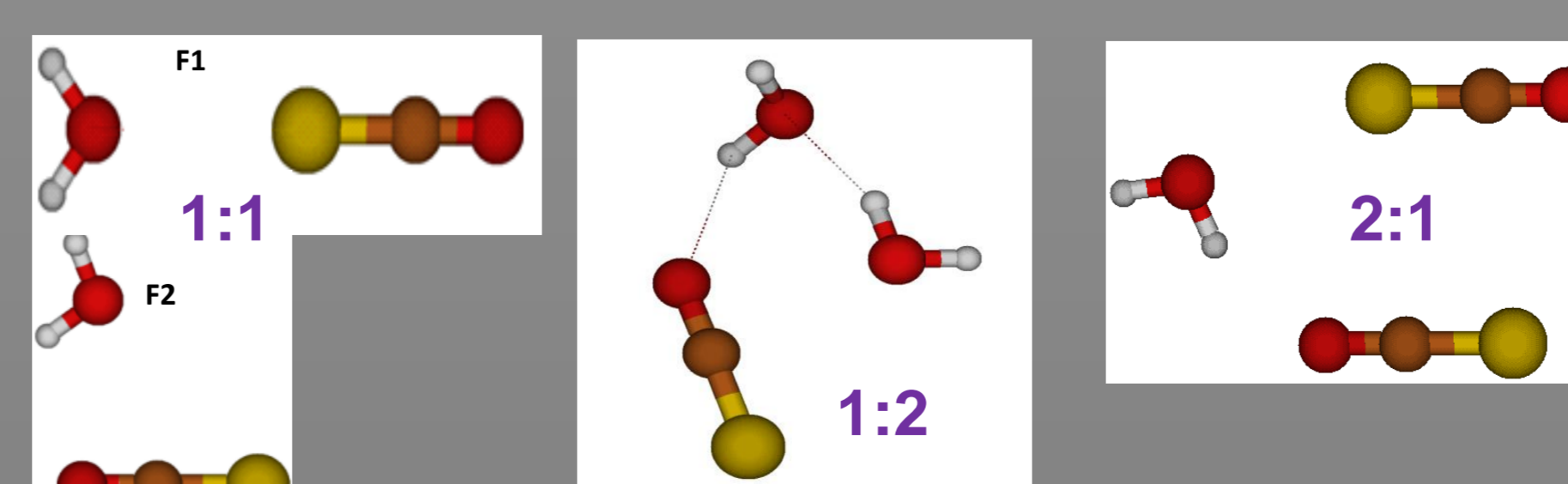
### CO<sub>2</sub>, OCS and N<sub>2</sub>O modes

	Van der Waals complexes				
	CO <sub>2</sub> <sup>a</sup> -H <sub>2</sub> O	OCS-H <sub>2</sub> O	N <sub>2</sub> O-H <sub>2</sub> O		
1:1	v <sub>1</sub>	no	4.0 <sup>b</sup>	2.4	
	v <sub>2</sub>	-4.0, 9.0	-7.5	-7.5	2.3
	v <sub>3</sub>	-0.4	7.0	14.4	-8.9
2:1	v <sub>1</sub>	no	-5.3, 5.7	3.4	
	v <sub>2</sub>	-3.5, 4.5, 12.0	no	-2.8	
	v <sub>3</sub>	-1.5, -2.4	-2.1, 21.2	-12.6	
1:2	v <sub>1</sub>	no	no	-17.4	
	v <sub>2</sub>	-2.6, 14.2	no	-6.0	
	v <sub>3</sub>	-2.4	19.8	-17.4	

<sup>a</sup> the degeneracy of the v<sub>2</sub> mode is broken in the complex

<sup>b</sup> the 1:1 OCS-H<sub>2</sub>O complex have 2 isomers

## Structures for the OCS-H<sub>2</sub>O complexes



## Structure for the 1:1 N<sub>2</sub>O-H<sub>2</sub>O complex

