Vibrational study of hydrated methyl formate complexes in solid neon at 3K. Observation for the first time of three isomers for methyl formate-water complex.

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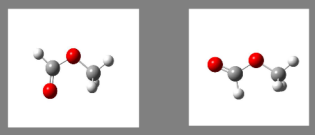
Methyl formate (MF) is an important interstellar medium molecule

Experiments: matrix isolation technique coupled with FTIR

Absorption spectra collected on the same sample from the FIR intermolecular region to NIR combinations and overtones regions (80 to 6000 cm^{-1}) with a Bruker 120 FTIR spectrometer (InSb or MCT or bolometer detectors).

Theoretical details: MP2 aug-cc-pVTZ calculations
D0 kcal/mol

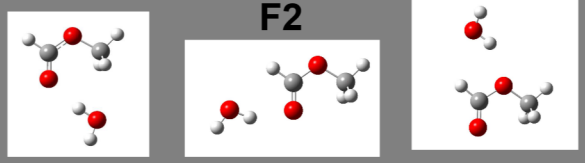
1:0



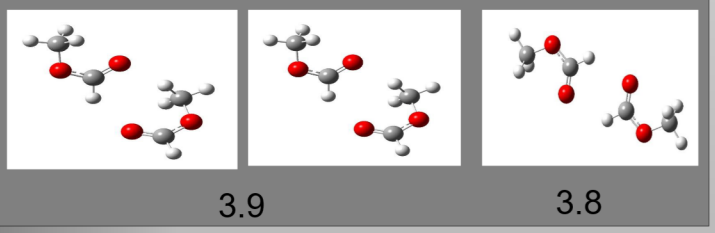
Cis Trans

difference of binding energy of 5.3 kcal/mol
Trans not observable in Ne matrix

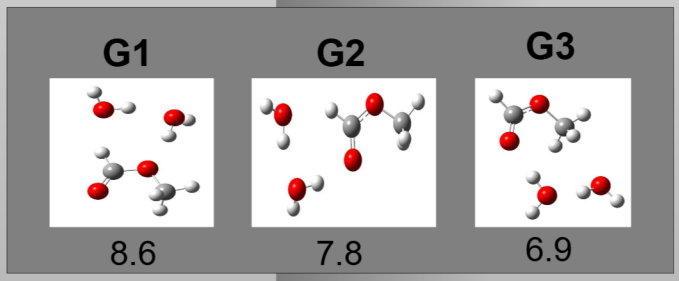
1:1



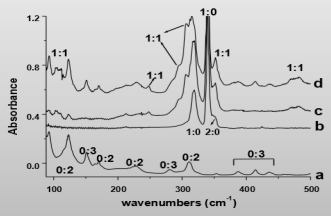
2:0



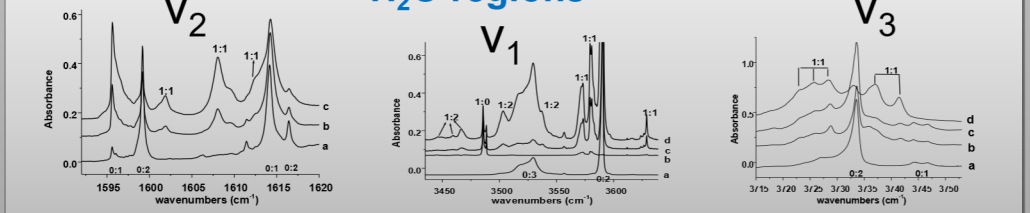
1:2



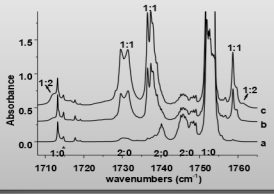
Intermolecular region



H_2O regions



MF CO region



1:1

	Calculated F1		Experimental F2		Isomer F3				
Modes	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	ν	$\Delta\nu$	
H_2O									
$\tilde{\nu}_3$	3912(128)	+36	3917 (128)	+31	3922(147)	+26	3725(350)[c]	+36	F1
							3729(260)	+30	F2
							3740(280)[c]	+20	F3
ν_1	3718(277)	+104	3707(277)	+115	3772(118)	+50	3572(560)[c]	+93	F2
							3580(830)[c]	+85	F1
							3629(100)	+37	F3
ν_2	1649(79)	-21	1643(122)	-15	1633(73)	-5	1602(60)	-5	F3
							1608(170)	-12	F2
							1613(150)	-17	F1
MF									
ν_3	3104(14)	-8	3099(21)	-3	3098(23)	-2	2955(50)	-9	F1
ν_4	1757(331)	+12	1750(289)	+19	1774(268)	-5	1731(700)[c]	+21	F2
							1737(1000)[c]	+15	F1
							1759(270)	-7	F3
ν_5	1516(18)	+3	1518(11)	+1	1520(10)	-1	1462(30)	+5	F1
ν_6	1481(9)	-2	1479(5)	0	1479(2)	0	1443(60)	-3	F1
ν_7	1406(2)	-7	1408(2)	-9	1406(6)	-7	1381(3)	-6	F1 or F2 or F3
ν_8	1272(251)	-25	1265(300)	-18	1230(141)	+17	1222(1000)[c]	-11	F2
							1231(700)	-20	F1
ν_9	1202(41)	-9	1200(49)	-7	1181(176)	+12	1175(600)	-8	F1 or F2
$\tilde{\nu}_{10}$	943(28)	+11	955(27)	-1	949(43)	+5	916(170)[c]	+12	F1
$\tilde{\nu}_{11}$	775(5)	-3	778(7)	-6	768(11)	+4	765(3)	+4	F3
							771(30)	-6	F2
							775(20)	-2	F1
$\tilde{\nu}_{17}$	352 (12)	-5	357(19)	-10	344(35)	+3	352(130)	-12	F2
Inter									
	539(72)		517(71)		443(111)		482(120)		F1
	348(127)		374(130)		274(102)		471(200)		F2
	139(119)		65(113)		84(75)		305(600)		F2
	97(9)		61(15)		40(14)		295(440)		F1
							248(80)		F3
							110(70)		F1
							104(90)		F1

$\Delta\tilde{\nu}=\tilde{\nu}_{monomer} - \tilde{\nu}_{complex}$

1:2

$\Delta\tilde{\nu}=\tilde{\nu}_{monomer} - \tilde{\nu}_{complex}$

	Calculated G1		G2		G3		Exp		Isomer
modes	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	ν	$\Delta\nu$	
H_2O	3639	+80	3576	+143	3580	+139	3448(26)	+143	G2 or G3
ν_1PD	(310)		(430)		(465)		3460(17)	+131	G2 or G3
							3503(1000)	+87	G1
	3694	+120	3627	+187	3620	+194	3460(17)	+201	G2 or G3
ν_1PA	(412)		(789)		(368)		3467(440)	+194	G2 or G3
							3538(250)	+123	G1
MF									
$\tilde{\nu}_9$	1162 (259)	+29	1199 (55)	-6	1200 (96)	-7	1135(110)	+32	G1
ν_4	1770 (183)	-1	1729 (324)	+40	1691 (278)	+78	1712(140) 1761(400)	+40 -9	G2 G1

This vibrational study allows to prove **the existence of several isomers for different 1:1 and 1:2 complexes** involving hydrogen bonding thanks to the contribution of ab initio calculations, showing the importance of the complementarity between theory and experience.
We highlight the presence of **three isomers for the MF dimer** especially by the observation of three signatures for the C=O stretching mode n4.
For the **MF-H2O complex**, we observe without ambiguity **three isomers**
By observing the v1 PD and PA of H2O dimer perturbed by the MF molecule and with the observation of two intense MF modes we conclude that **three isomers of the 1:2 complex** are present in the Ne matrix.

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