IUPAC Workshop
"Hydrogen Bonding and Other Molecular Interactions"
Airone Pisa Park Hotel
San Giuliano Terme, Pisa, Italy
5-9 September 2005

a)-Weak Hydrogen Bonding
b)-Proton Transfer and Tunnelling

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KEY WORDS

- ***Hydrogen Bonding***
- *Solvation at a Molecular Level*
- ***Molecular Beams***
- ***Molecular Dynamics***
- ***Molecular Clusters***
- ***Large Amplitude Motions***
- *Molecules of Biological Interest*
- *Conformational Equilibria*
- *Species of Astronomical Interest.*
- *Vibration relaxation in supersonic expansions*

Schedule

1) Description of the Experimental Techniques (skip…)

2) Theoretical models (skip…) .

3) Weak Hydrogen Bonding and not.

a) Features of weak intermolecular hydrogen bonds

- C-H···O - C-H···F

b) Does water prefer F or Cl for Hydrogen Bonding?

Is O-H···Cl or O-H···F favoured?

4) Proton Transfer and Tunnelling

5) H-Bond Isotopomeric Conformational Change

Theoretical Models: we are the seven digits scientists

1) *Interpretation of the rotational spectra with standard deviations of the fits down to a few kHz (10^{-7} cm^{-1}): Watson Hamiltonian, Coupled Hamiltonians..*
2) *Flexible models to handle vibrational and rotational spacings: potential energy surfaces and structural relaxations.*
3) *Distributed polarisability models: economy calculations of conformations and potential energy surfaces of molecular adducts.*
4) *Standard ab initio and DFT calculations (Gaussian and Gamess)*

Features of weak C-H···O and C-H···F intermolecular hydrogen bonds by Fourier transform microwave spectroscopy

“The weak hydrogen bond in structural chemistry and biology” IUCr Monographs on crystallography, Vol. IX (G.R.Desiraju and T.Steiner Ed.s) Oxford University Press, (2001).

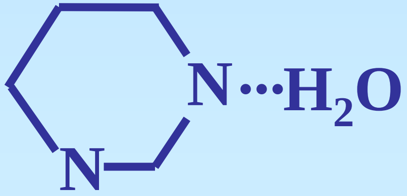
Hobza, P.; Havlas, Z., *Chem. Rev.* 2000, *100*, 4253, and references therein.

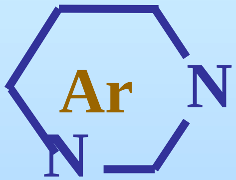
Delanoye, S. N.; Herrebout, W. A.; Van der Veken, B. J., *J.Am.Chem.Soc.*, 2002, *124*, 11854.

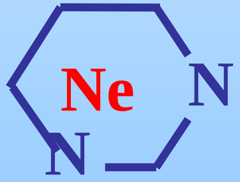
Before of our investigations, data were available only from X-rays diffraction, theoretical calculations, IR measurements in rare gas solution, and non-rotationally resolved spectroscopy

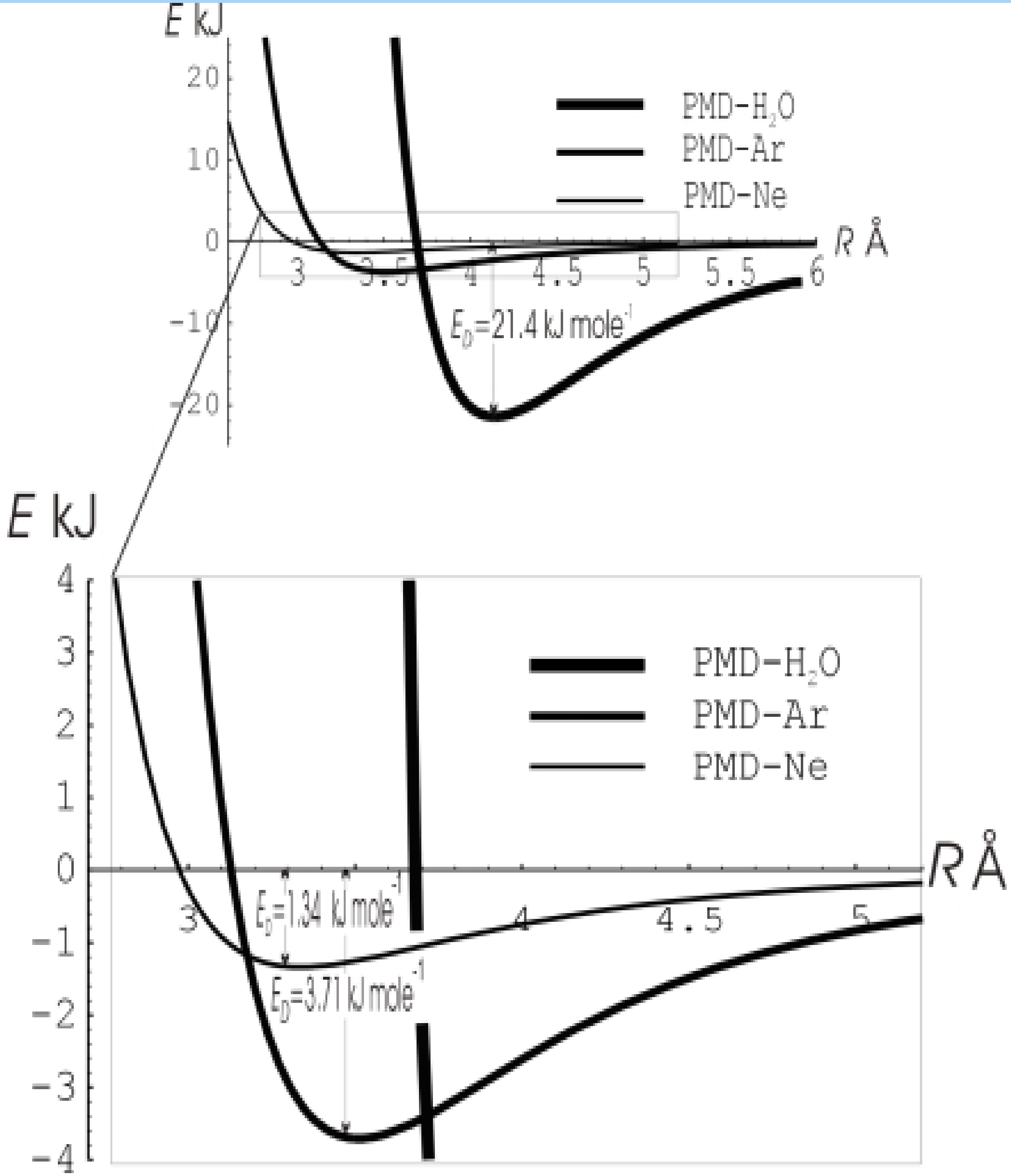
ENERGIE DI DISSOCIAZIONE

Pirimidina···H_2O **Pirimidina···Ar** **Pirimidina···Ne**





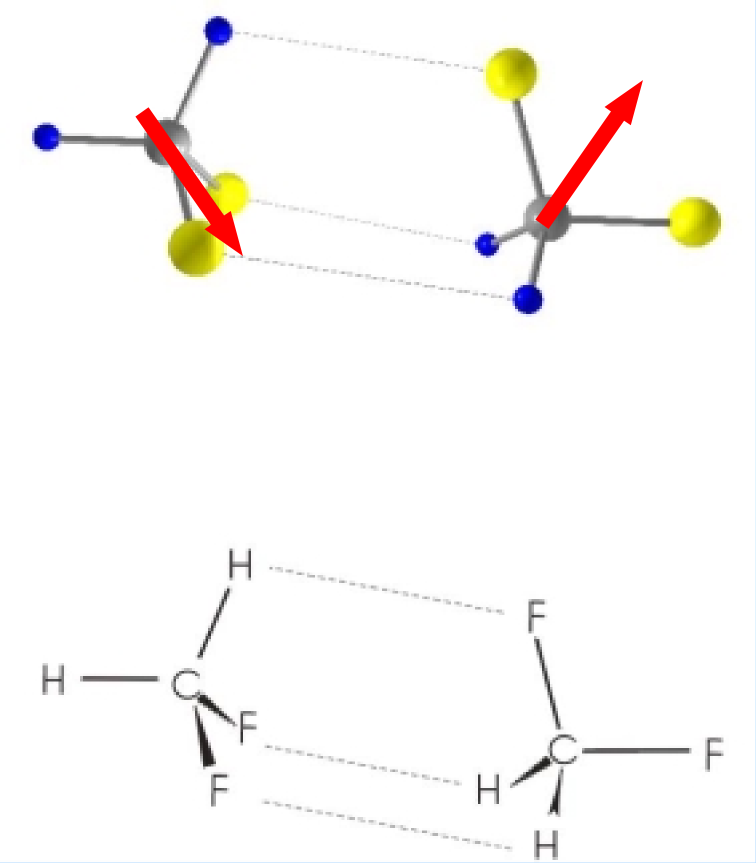




difluoromethane···difluoromethane

$E_D = 6.6$ kJ/mol

2.2 kJ/mol per ogni bond C-H···F-C



W.Caminati, S.Melandri, P.Moreschini and P.G.Favero, *Ang.Chem.Int.Ed.Engl.*, **38** 2924 (1999).

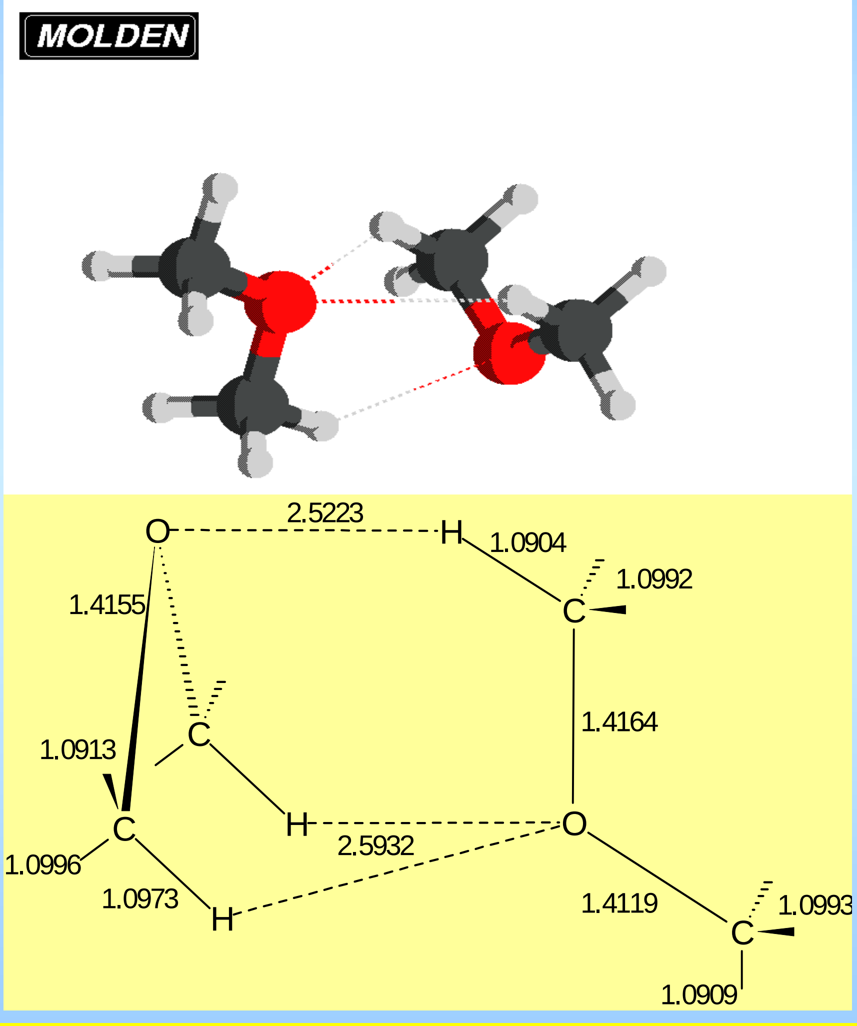
Dimethylether··· Dimethylether

E_D = 6.0 kJ/mol

2.0 kJ/mol

each C-H···O

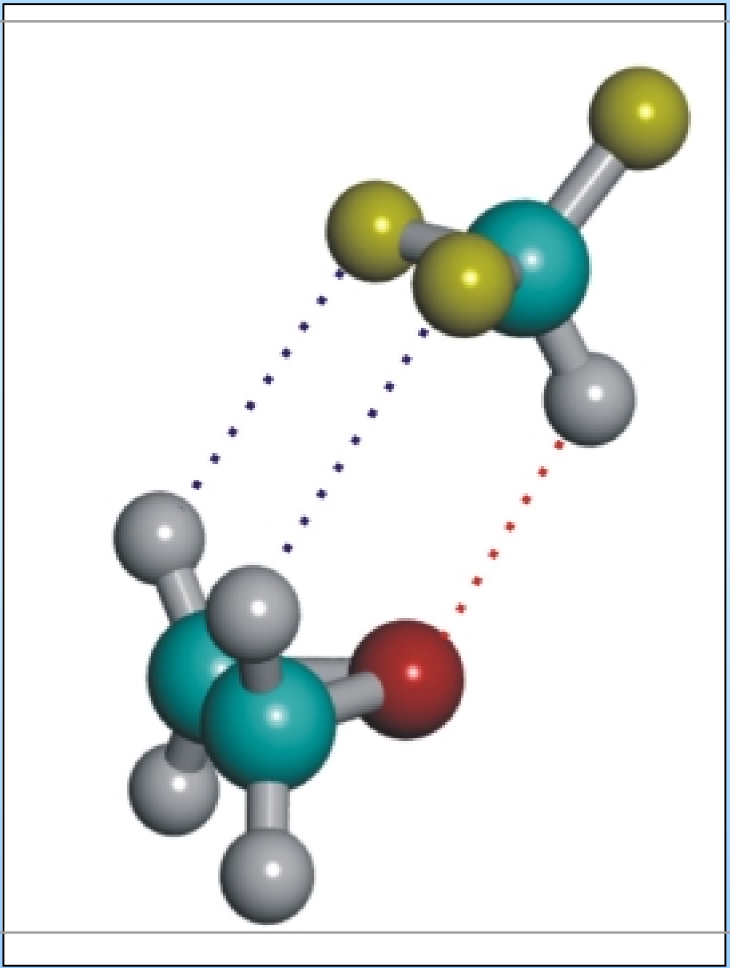
interaction



Tatamitani, Y.; Liu, B.; Shimada, J.; Ogata, T.; Ottaviani, P.; Maris, A.; Caminati, W.; Alonso, J. L., *J. Am. Chem.* Soc. **2002**, *124*, 2739

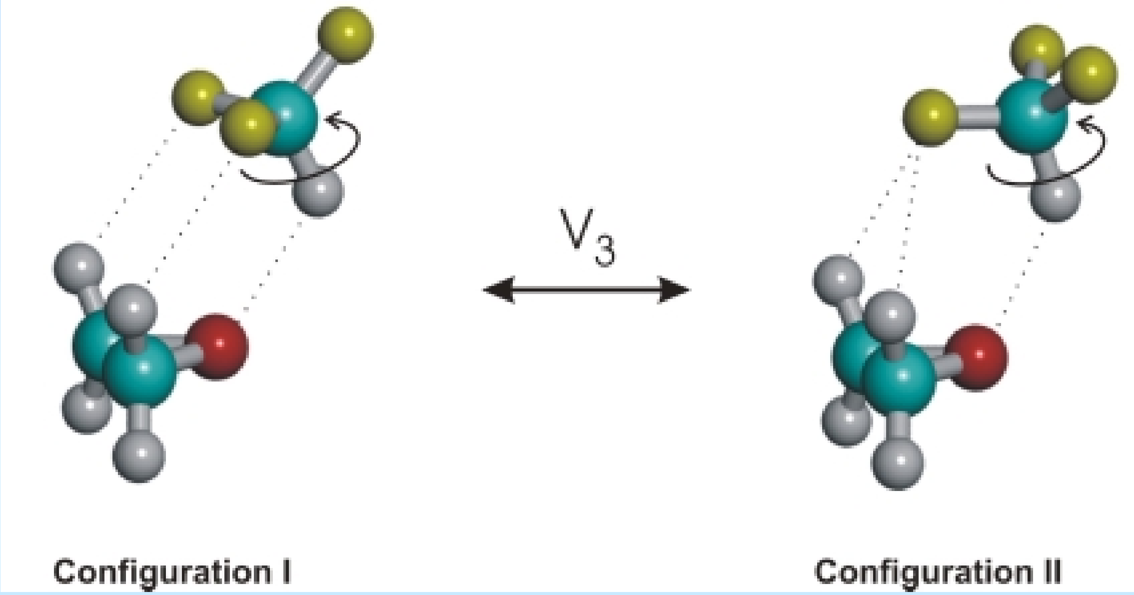
Oxirane-trifluoromethane

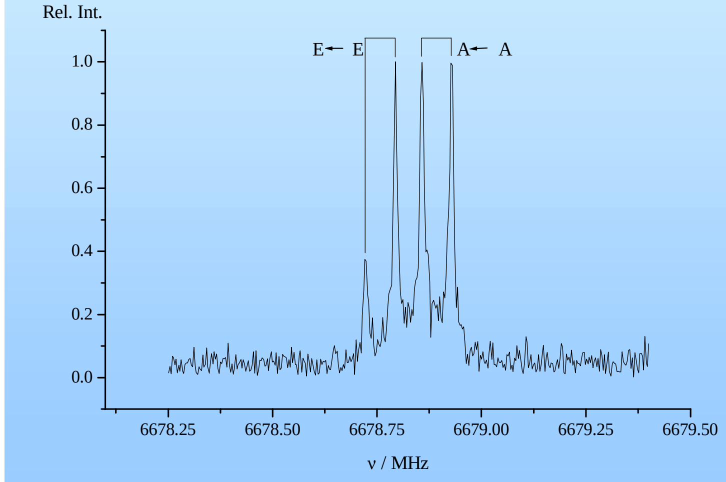
The investigation of the parent and of its two ^{13}C species has been used to establish a C_s geometry, with the two moieties bound by one C-H···O and two C-H···F-C hydrogen bonds. An overall bonding energy of about 6.7 kJ/mol has been derived from the centrifugal distortion analysis. The lengths of the C–H···O and C–H···F hydrogen bonds, *r*(O···H) and *r*(F···H), are 2.37 and 2.68 Å, respectively. The C–H···F–C interactions are at the origin of the HCF_3 internal rotation motion barrier of 0.55(1) kJ/mol giving rise to the A-E splittings observed in the rotational spectra.



J.L.Alonso, S.Antolínez, S.Blanco, A.Lesarri, J.C.López and Walther Caminati, *J.Am.Chem.Soc.*, **126** 3244-3249 (2004)

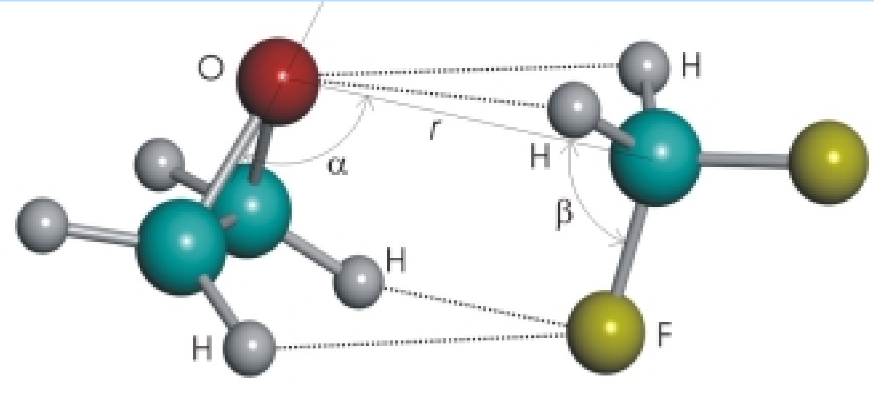
Oxirane-trifluoromethane





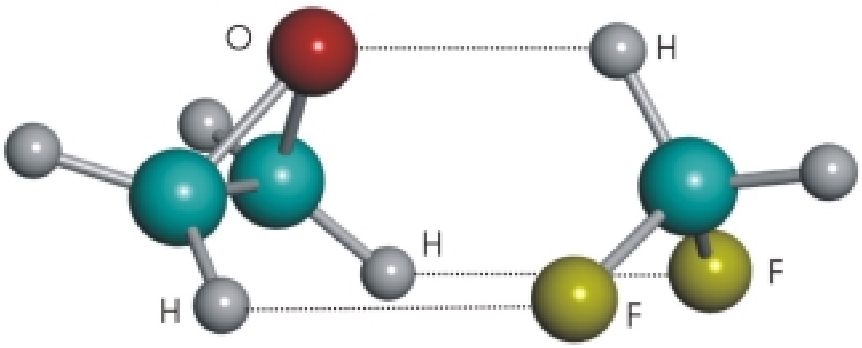
	$C_2H_4O\cdots HCF_3$	$^{13}CCH_4O\cdots HCF_3$	$C_2H_4O\cdots H^{13}CF_3$
I_α / u Å^2	85.73(25)[a]	85.40(27)	84.58(44)
$\angle(a, i)$[b] / deg.	49.31(10)	50.18(18)	49.31(29)
$\angle(b, i)$[b] / deg.	[90.0][c]	[89.6][c]	[90.0][c]
$\angle(c, i)$[b] / deg.	40.69(10)	39.82(18)	40.69(29)
Δ_{AE}[d] / MHz	0.68(1)	0.65(2)	0.69(2)
V_3 / kJ mol^{-1}	0.546(4)	0.541(8)	0.545(8)
σ[e] / kHz	6.7	4.5	3.2

Oxirane-Difluoromethane



I

Observed



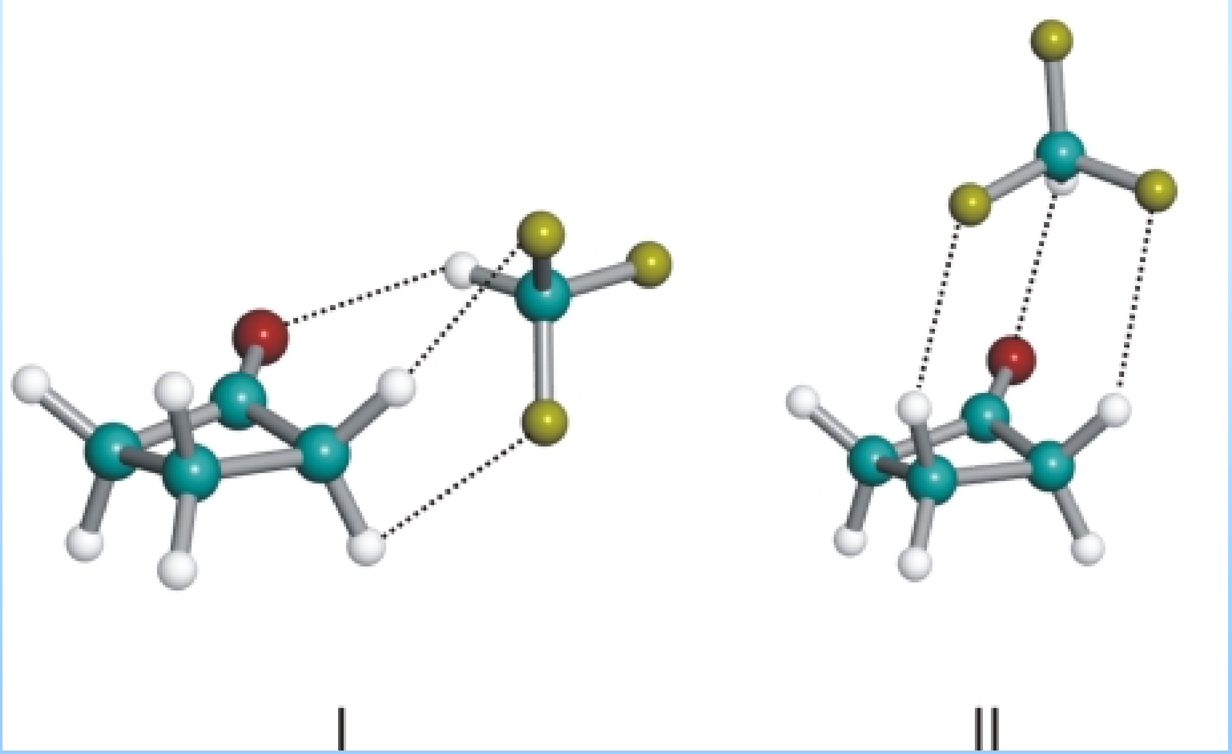
II

The dissociation energy has been estimated 9.6 kJ/mol.

S.Blanco, J.C.López, A.Lesarri, W.Caminati and J.L.Alonso, *ChemPhysChem*, **5** 1779-1782 (2004)

Cyclobutanone-trifluoromethane

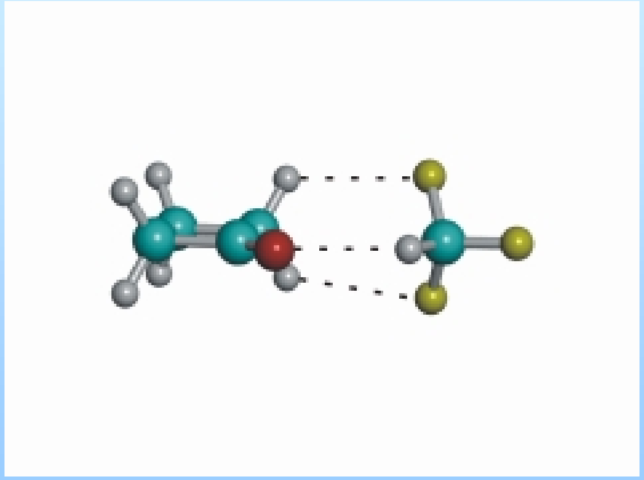
This is the first rotationally resolved investigation of a complex with a C–H···O interaction involving one carbonylic oxygen. This bridge, together with two C–H···F weak hydrogen bonds, can stabilizes the two configurations shown below.



Cyclobutanone-trifluoromethane

The spectroscopic constants, shown aside, can match only the two configurations shown below. The dissociation energy has been estimated 7.5 kJ/mol.

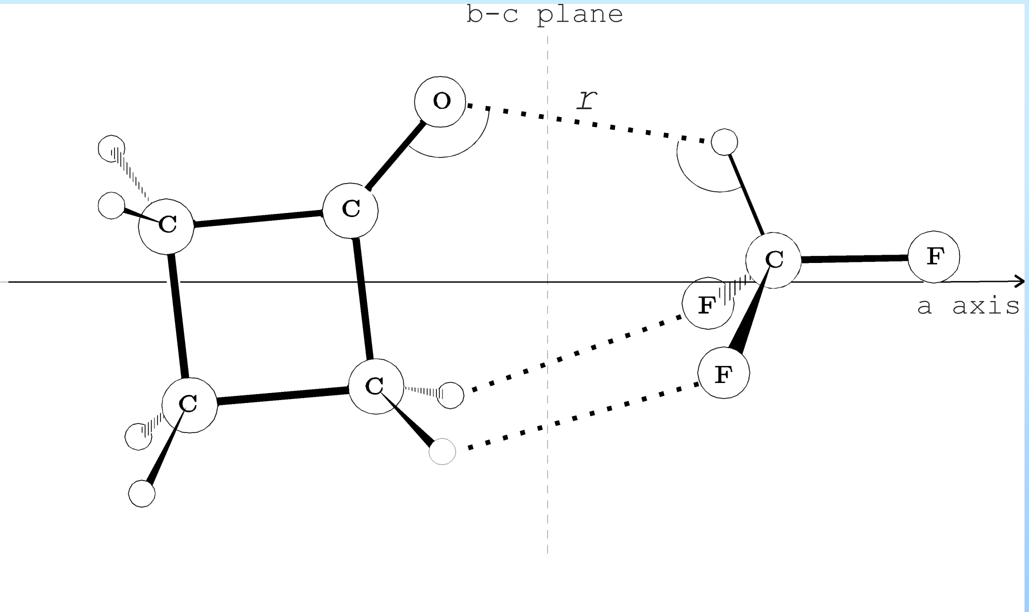
A / MHz	3570.6784(20)[a]
B / MHz	636.00926(10)
C / MHz	604.18927(10)
D_J / kHz	0.36124(20)
D_{JK} / kHz	4.315(8)
D_K / kHz	11.4(4)
d_1 / kHz	-0.01020(24)
d_2 / kHz	0.00938(10)
H_{JK} / Hz	-0.08(2)
H_{KJ} / Hz	-0.9(4)
N[b]	67
J_{max}	12
σ[c]/kHz	1.4



Cyclobutanone-trifluoromethane

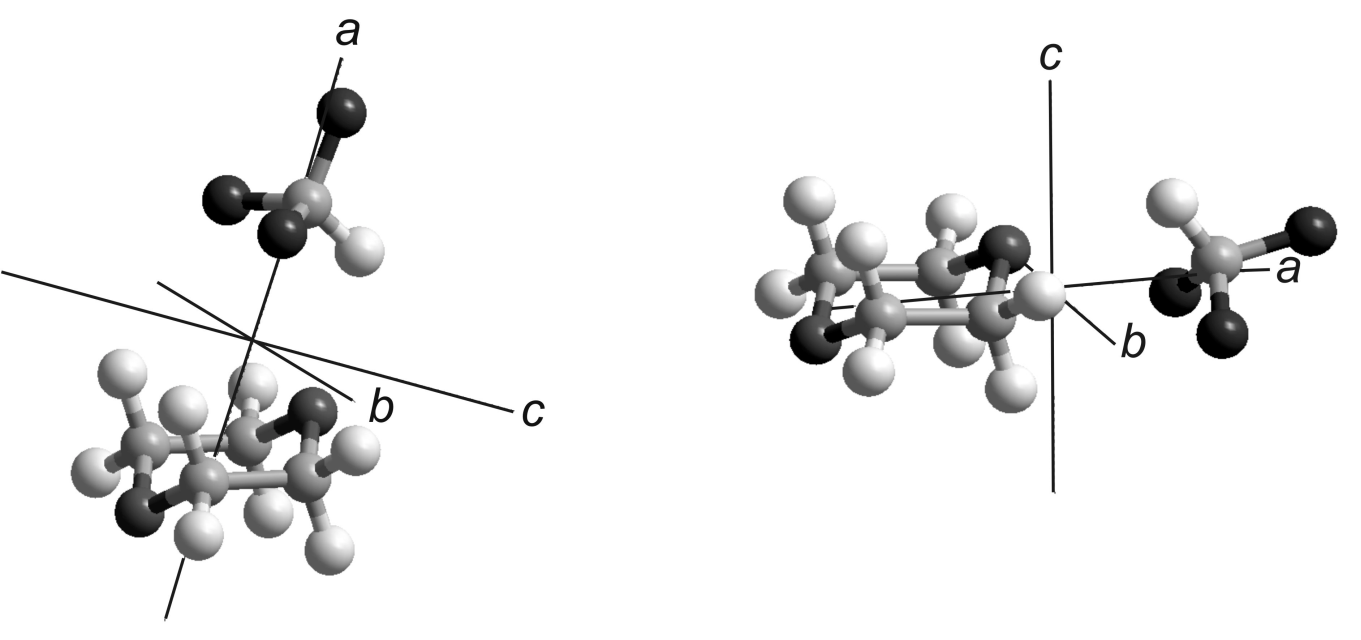
The WHB parameters obtained are shown below.

	r_0 [a]	ab initio [b]
1) r_0 fitted parameters		
r(O ··H)	**2.40(1)^a**	2.39
α	122.4(2)	129.0
β	128.9(4)	118.6
2) Derived WHB parameter		
r(F ··H)	**2.86(1)**	2.87
∠(CHF)	114(1)	112.7



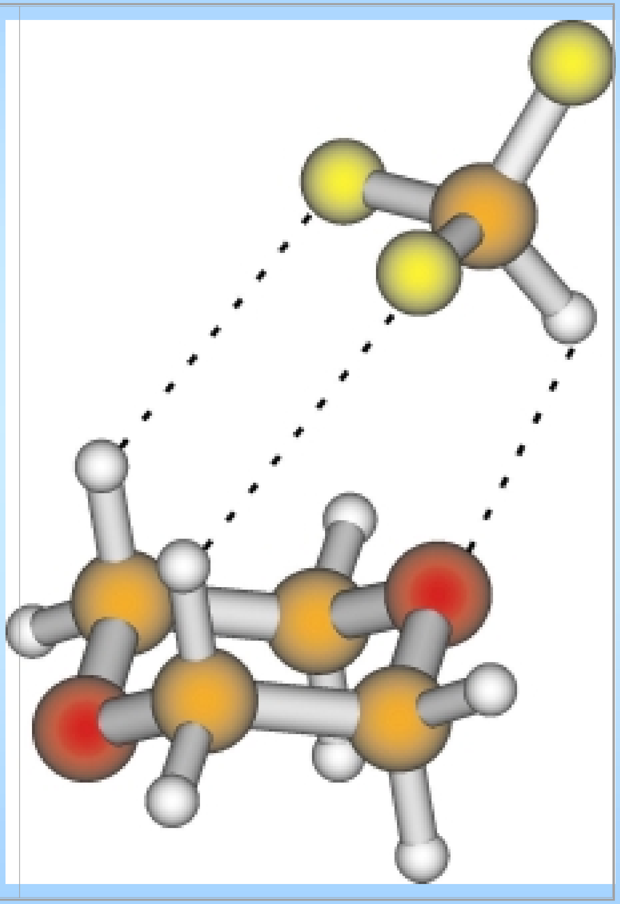
1,4-dioxane-trifluoromethane

In the adduct 1,4-dioxane-trifluoromethane (DXN···CHF_3), the CH···O interaction can take place with the axial or the equatorial lone pair of the ring oxygen, giving rise to the two plausible configurations, axial or equatorial, both with three, CH···O or CH···F WHB linkages, as shown below.



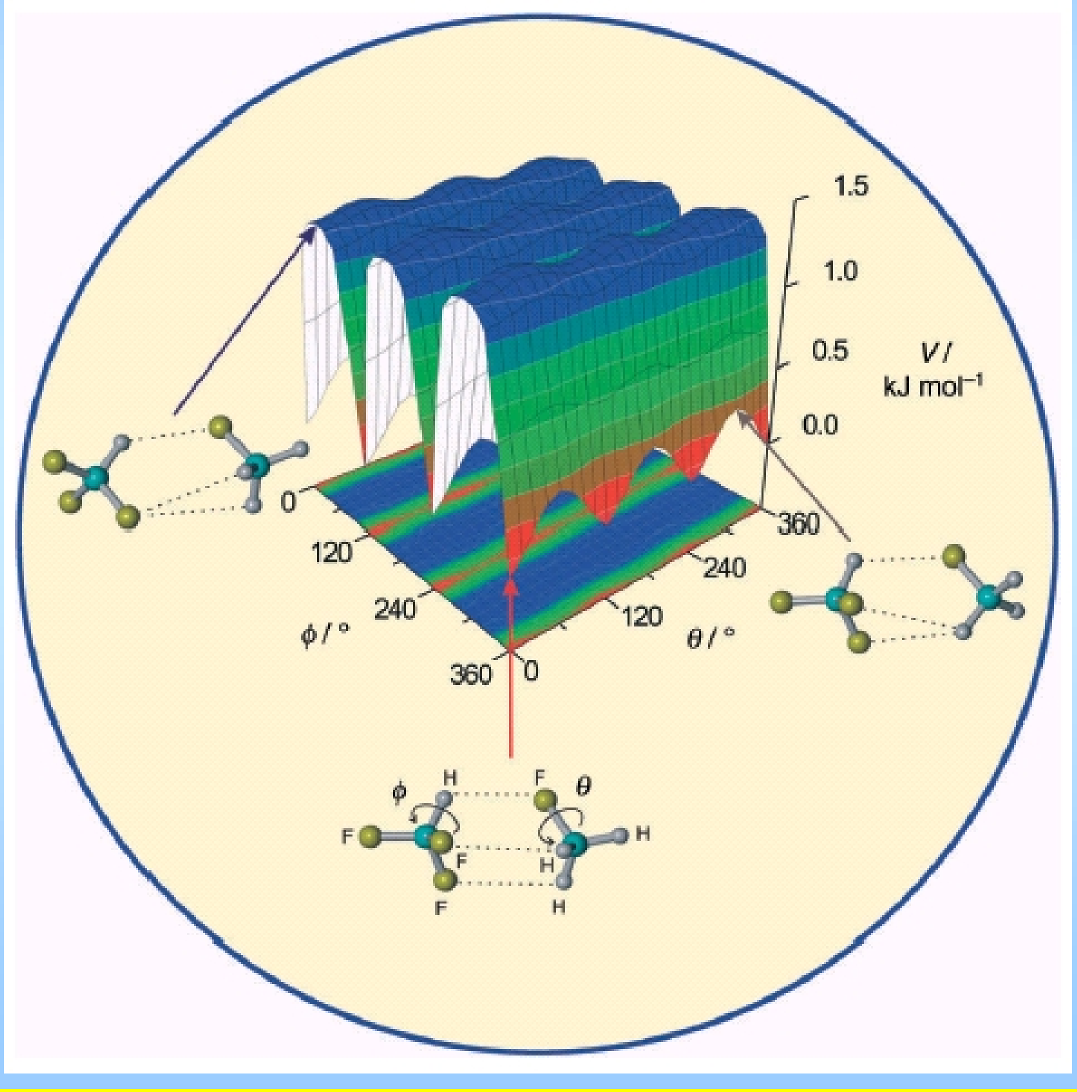
1,4-dioxane-trifluoromethane

The C_s conformation with CHF_3 *axial* with respect to 1,3-dioxane has been assigned. It is stabilized by one C–H···O and two C–H···F weak hydrogen bonds. The dissociation energy has been estimated from the D_J centrifugal distortion parameter to be ca. 6.8 kJ/mol.



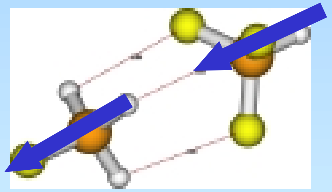
L.B.Favero, B.M.Giuliano, S.Melandri, A.Maris, P.Ottaviani, B.Velino and W.Caminati, *J.Phys.Chem. A*, **109** 7402 (2005).

Fluoromethane-trifluoromethane

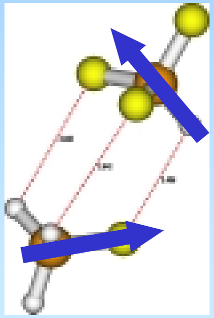


W.Caminati, Juan C. López, José L. Alonso and J.-U.Grabow , *Angew.Chem.Int.Ed.Engl*. **44** 3840-3844 (2005)

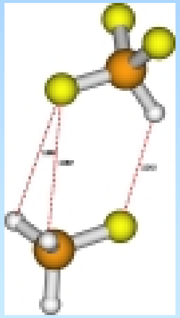
Fluoromethane-trifluoromethane



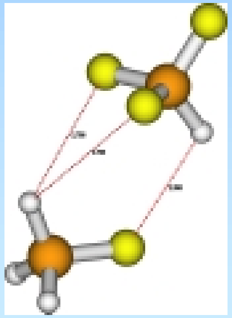
I



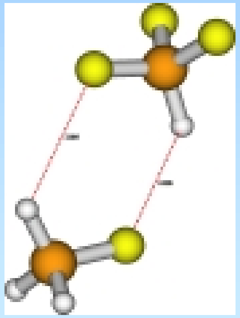
II



III



IV



V

MP2/6-311++G(2df,2p):

ΔE/cm^{-1} **I:**713.8 **II:**0.0 **III:** 29.7 **IV:**113.9 **V:**119.7

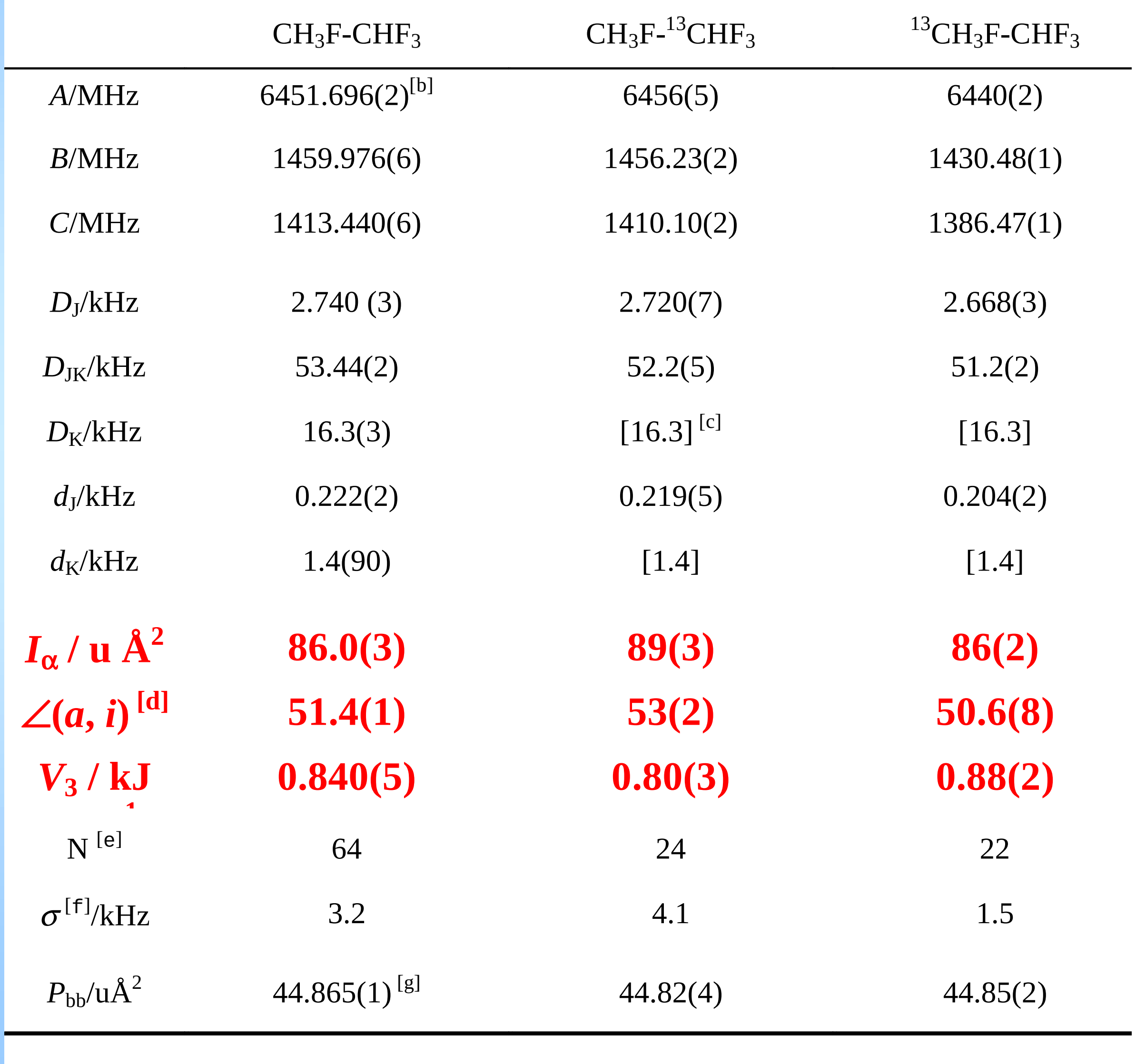
I and **II:** two minima with three WHBs, but differ in dipole-dipole interaction energy.

III - V: saddle points.

Fluoromethane-trifluoromethane

The spectra of three isotopomers, split by the internal rotations of the CH_3 and CF_3 tops, gave the results in the Table.

Lines in red give the internal rotation parameters for the internal rotation of the CF_3 top



	CH_3F-CHF_3	CH_3F-$^{13}CHF_3$	$^{13}CH_3F$-CHF_3
A/MHz	6451.696(2)[b]	6456(5)	6440(2)
B/MHz	1459.976(6)	1456.23(2)	1430.48(1)
C/MHz	1413.440(6)	1410.10(2)	1386.47(1)
D_J/kHz	2.740 (3)	2.720(7)	2.668(3)
D_{JK}/kHz	53.44(2)	52.2(5)	51.2(2)
D_K/kHz	16.3(3)	[16.3] [c]	[16.3]
d_J/kHz	0.222(2)	0.219(5)	0.204(2)
d_K/kHz	1.4(90)	[1.4]	[1.4]
I_α / u Å^2	**86.0(3)**	**89(3)**	**86(2)**
$\angle(a, i)$ [d]	**51.4(1)**	**53(2)**	**50.6(8)**
V_3 / kJ	**0.840(5)**	**0.80(3)**	**0.88(2)**
N [e]	64	24	22
σ [f]/kHz	3.2	4.1	1.5
P_{bb}/uÅ^2	44.865(1) [g]	44.82(4)	44.85(2)

Fluoromethane-trifluoromethane

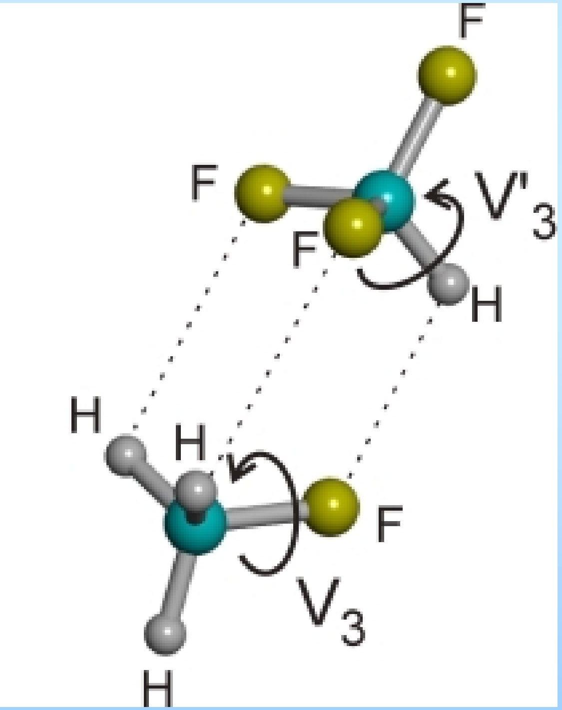
Fluoromethane-trifluoromethane is stabilized by three CH···F weak hydrogen bonds and electrostatic dipole-dipole interaction, and it is internally highly dynamic.

$E_D = 5.3\ \mathrm{kJ\cdot mol^{-1}}$

≈1.8 kJ·mol^{-1}/each C-H···F

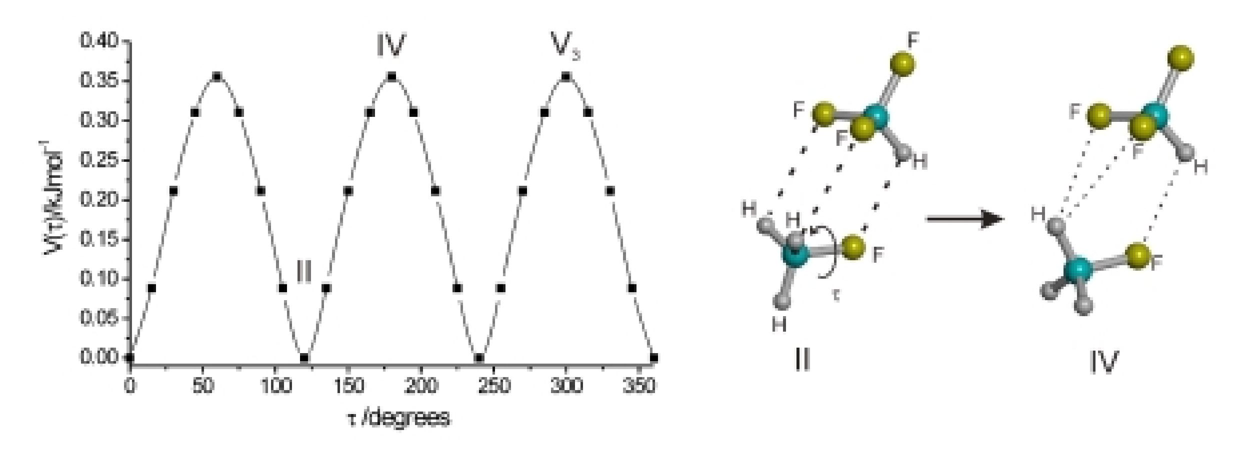
V'_3 (CF_3) = 0.84 kJ·mol^{-1}

V_3 (CH_3) = 0.36 kJ·mol^{-1}

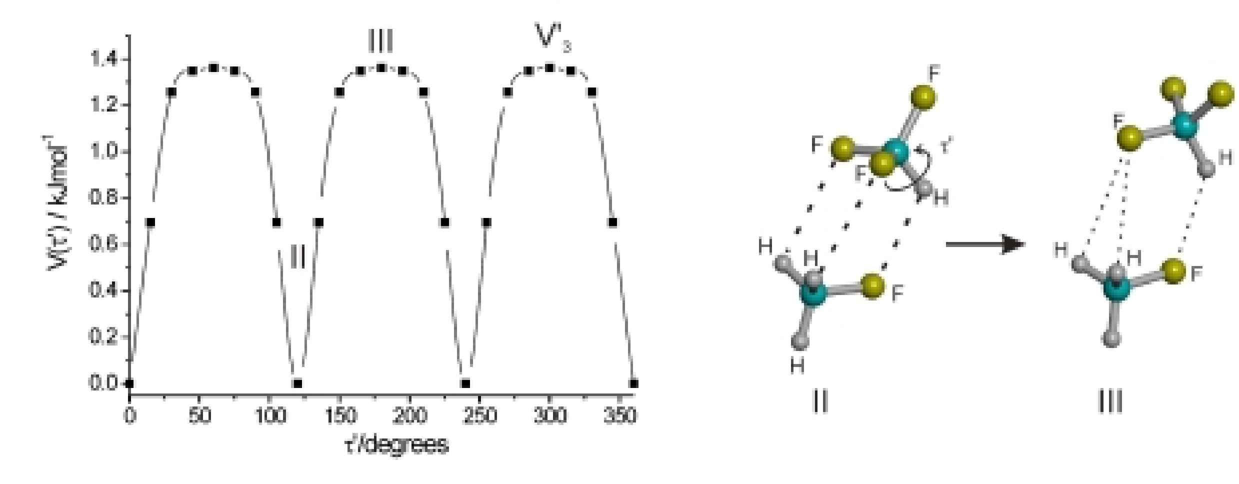


Fluoromethane-trifluoromethane

V_3 (CH_3) = 0.36 kJ/mol



V'_3 (CF_3) = 0.84 kJ/mol



Fluoromethane-trifluoromethane

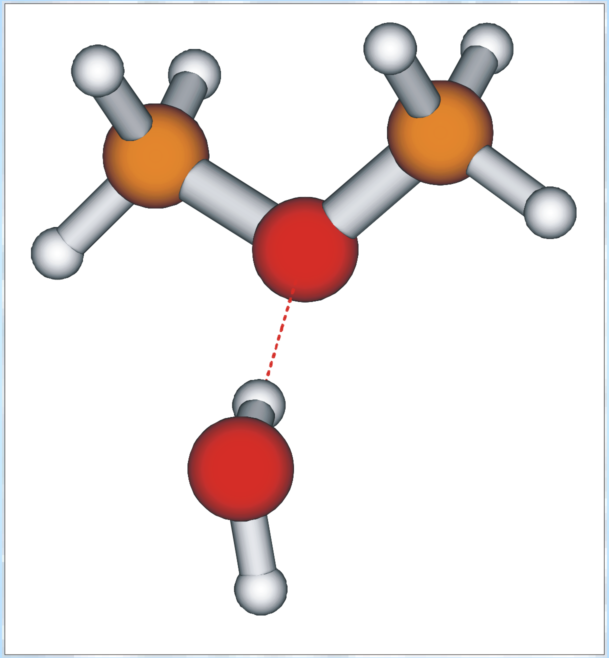
Comparison between the internal rotation parameters for the CF_3 and CH_3 internal rotors of $CH_3F\cdots CHF_3$

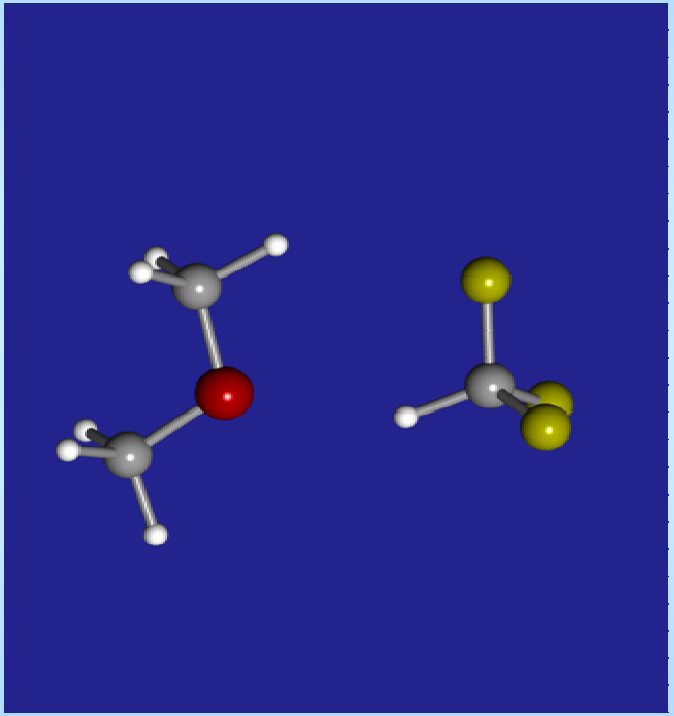
Internal rotor	$\mathbf{CF_3}$	$\mathbf{CH_3}$
I_α / u Å^2	**85.0**	**3.20**
V_3 / kJ mol^{-1}	**0.840**	**0.36**
s	**67.92**	**2.5**
Δ_{AE}[a] / MHz	**$2.6\cdot10^{-1}$**	**$1.2\cdot10^{5}$**
N_{levels}[b]	**12**	**2**

Dynamic and inertial effects

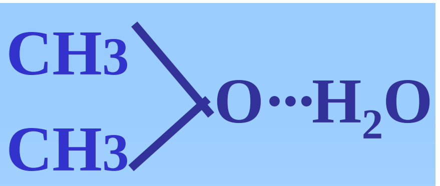
Ratio $\approx 10^6$

Dimethylether-H_2O & Dimethylether-CHF_3

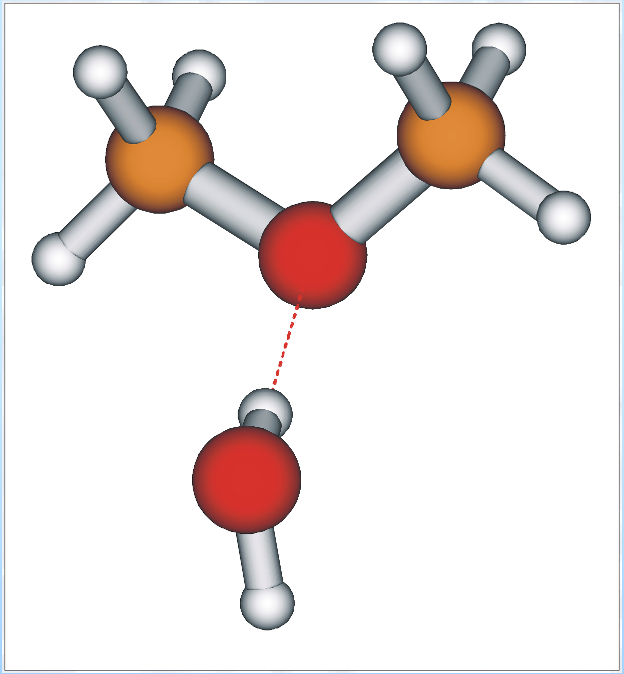


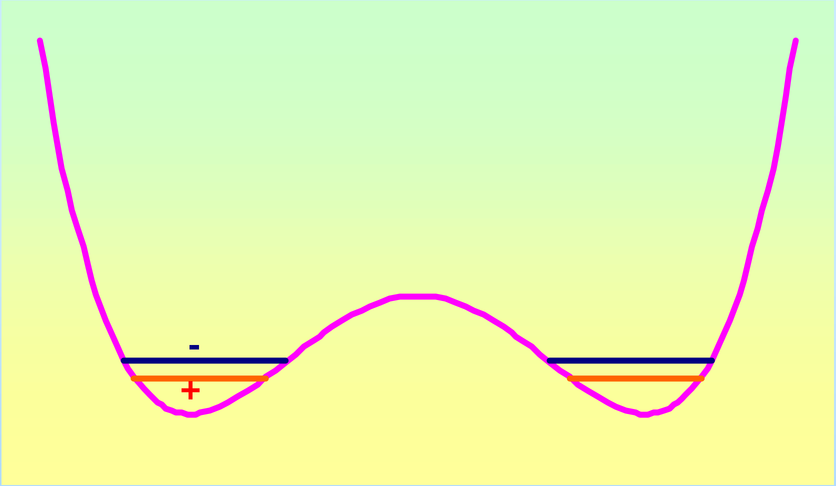


Dimethylether (DME) ···H_2O

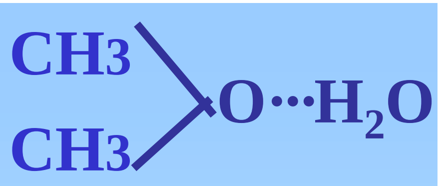


Water is tunnelling from one oxygen lone pair to the other



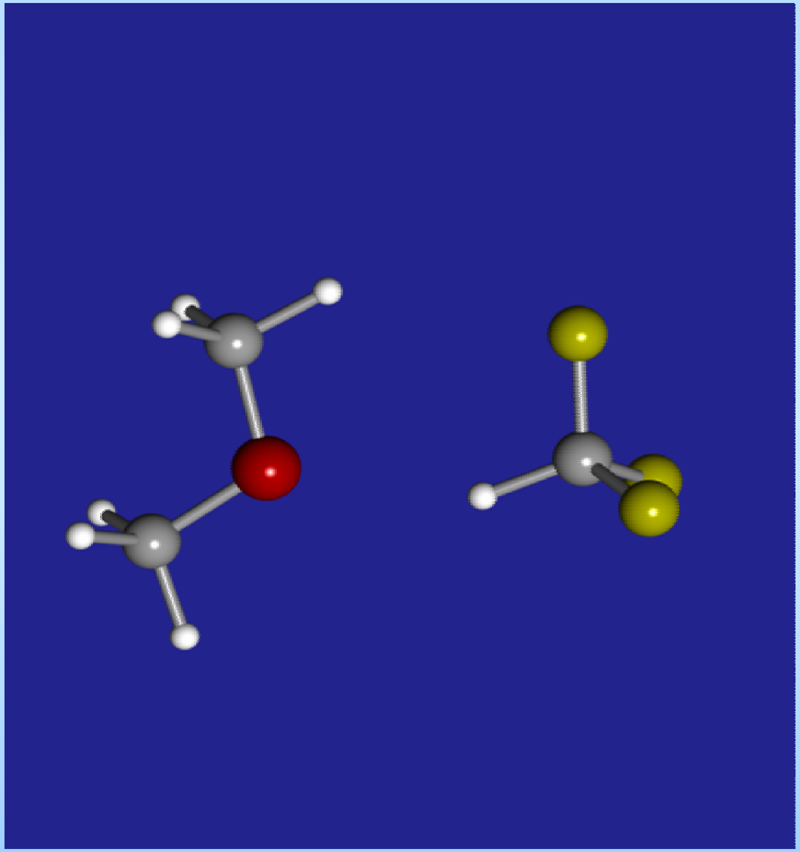


Dimethylether (DME) ···H_2O



	DME···H_2O		DME···$H_2{}^{18}O$		DME···DOH		DME···DOD	
	0^+	0^-	0^+	0^-	0^+	0^-	0^+	0^-
A (MHz)	9412.5(3)	9397.7(3)	9406.5(4)	9392.8(4)	9394.9(4)	9384.0(5)	9310.7(5)	9305.2(6)
B (MHz)	3449.52(6)	3447.66(6)	3220.13(6)	3218.89(7)	3413.53(7)	3412.46(6)	3236.28(4)	3235.85(3)
C (MHz)	2687.9(2)	2689.4(2)	2547.5(3)	2548.8(3)	2668.2(4)	2669.3(4)	2563.9(4)	2564.2(4)
D_J (kHz)	14.78(9)		14.42(13)		14.0(2)		12.2(5)	
D_K (kHz)	-174(18)		-21(23)		-124(20)		-115(16)	
D_{JK} (kHz)	634.8(4)	553.5(6)	567.7(7)	500(1)	564.5(6)	510.2(7)	467(1)	445(1)
d_1 (kHz)	-6.48(5)	-5.80(5)	-5.52(6)	-5.06(7)	-6.15(7)	-5.70(8)	-5.2(2)	-5.0(2)
d_2 (kHz)	-5.74(1)	-4.86(1)	-4.57(1)	-3.91(1)	-4.99(1)	-4.40(2)	-3.666(9)	-3.46(1)
H_{JJK} (Hz)	-151(2)	-117(2)	-135(3)	-99(3)	-125(3)	-88(2)	-86(1)	-75(1)
H_{JKK} (Hz)	916(4)	462(4)	825(6)	383(6)	748(6)	393(4)	506(3)	344(3)
F_{ac} (MHz)	146(5)		159(6)		164(7)		154(9)	
F'_{ac} (kHz)	95(3)		83(4)		94(5)		103(15)	
ΔE (GHz)	2.93(8)		2.36(8)		1.96(8)		0.61(6)	
N	81		70		66		82	
σ (MHz)	0.15		0.12		0.12		0.11	

Dimethylether···CHF_3



A /MHz	3958.0
B / MHz	956.767
C / MHz	896.190
Dist. const....	...
I_α / uÅ^2	85
V_3/ kJ mol^{-1}	0.44

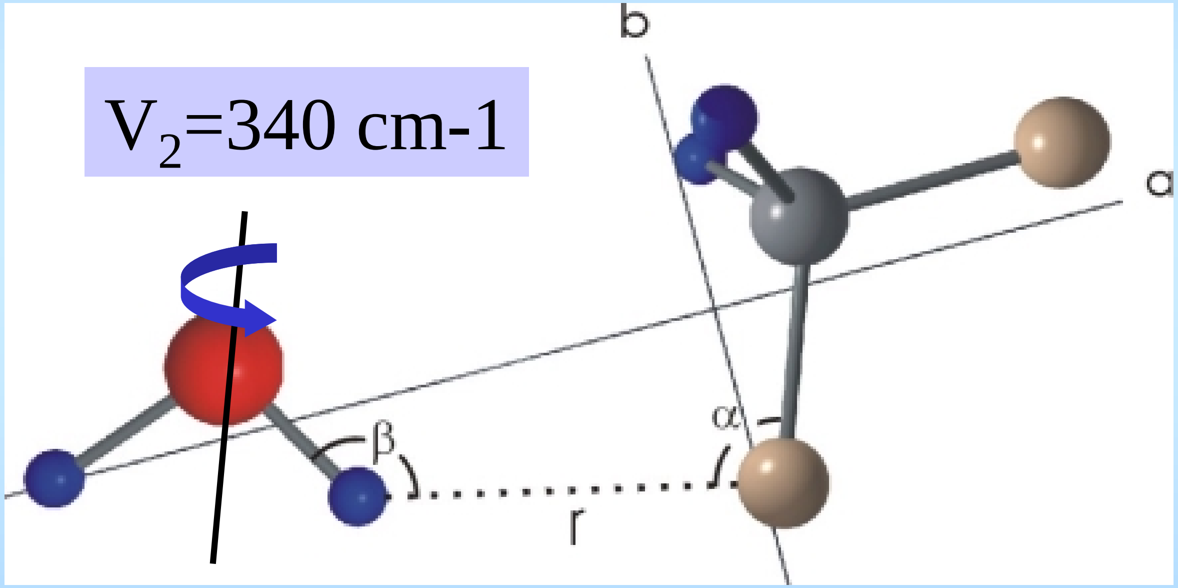
Where Hydrogen bonding?…

Difluorometano···H_2O

r(F···H) = 2.20(1) Å

α = 93(1)º

β = 135(3)º

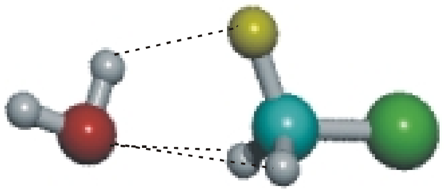


$E_{0,0}$ = 7.5 kJ/mol

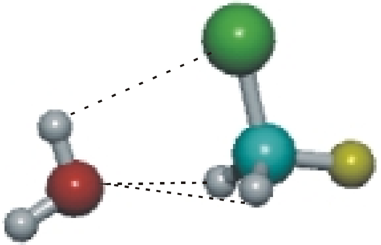
W.Caminati, S.Melandri, I.Rossi and P.G.Favero, *J.Am.Chem.Soc.*, **121** 10098-10101 (1999).
W.Caminati, S.Melandri, M.Schnell, D.Banser, J.-U.Grabow and J.L.Alonso *J.Mol.Struct.*, **742** 87-90 (2005).

CH_2ClF-H_2O & CH_2ClF- CH_2ClF

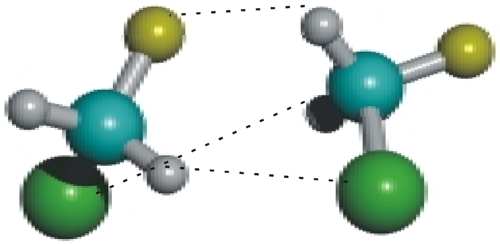
Is O-H···Cl stronger than the O-H···F H-bond?



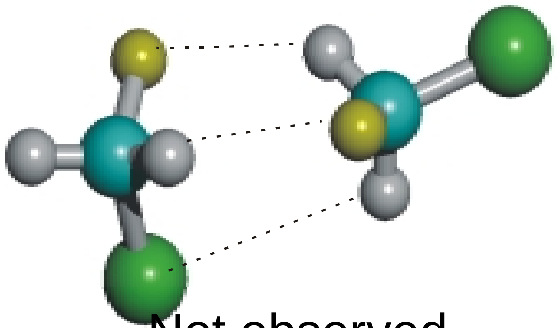
Not observed



Observed



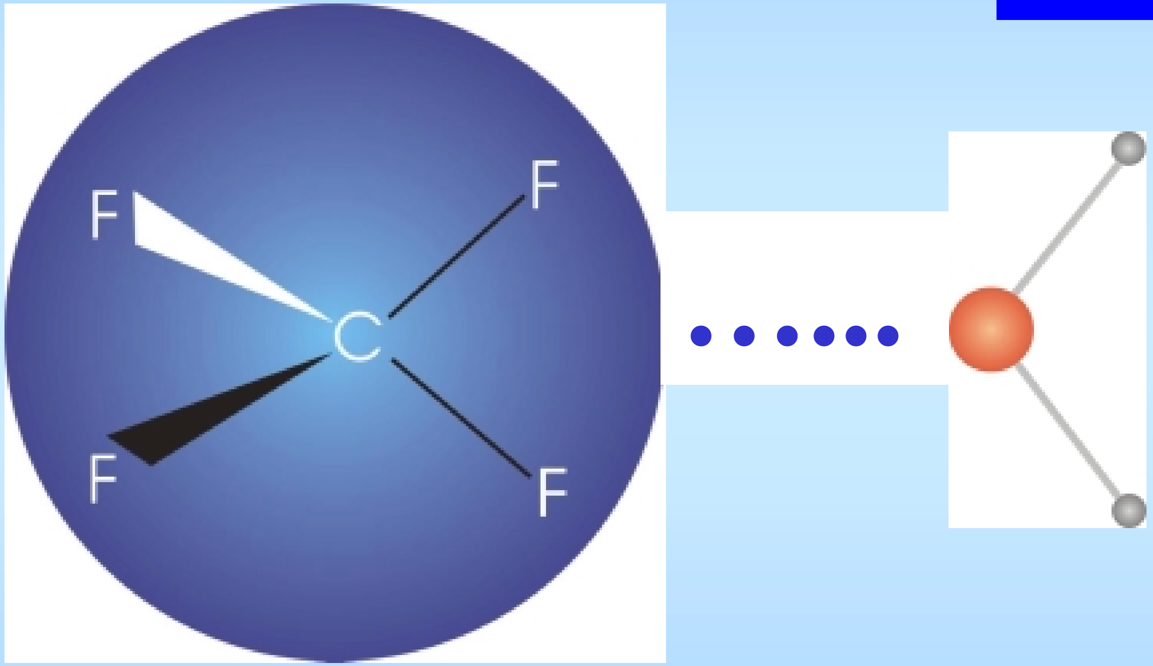
Observed



Not observed

Tetrafluoromethane···H_2O

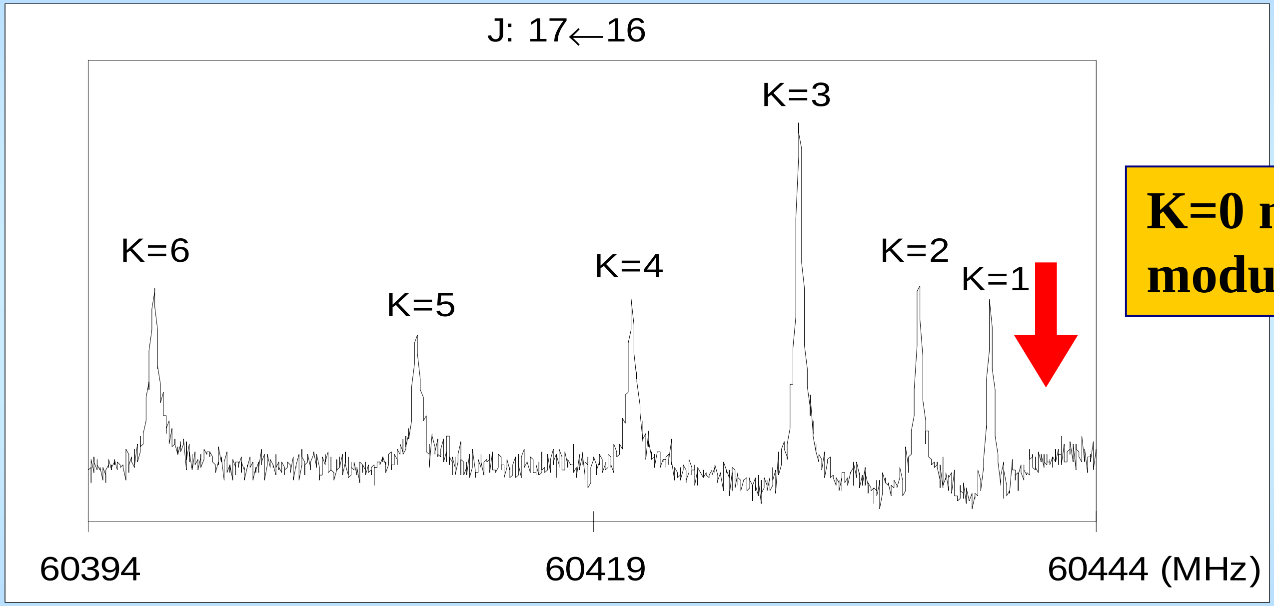
No Hydrogen Bonding



INTERACTION **PLANE-SPHERE**

Tetrafluoromethane···water

Classically an asymmetric top, but…



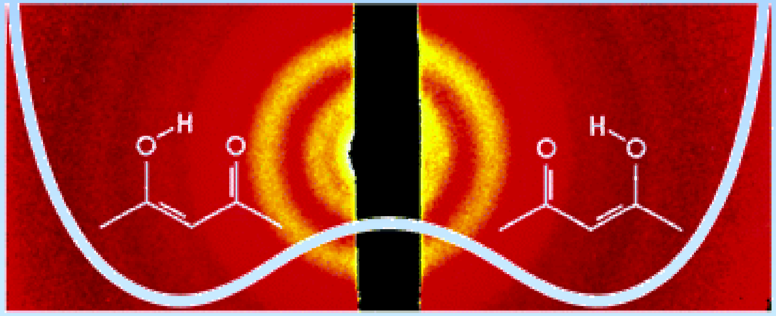
K=0 not Stark modulated

CF_4–D_2O

Proton transfer and tunnelling

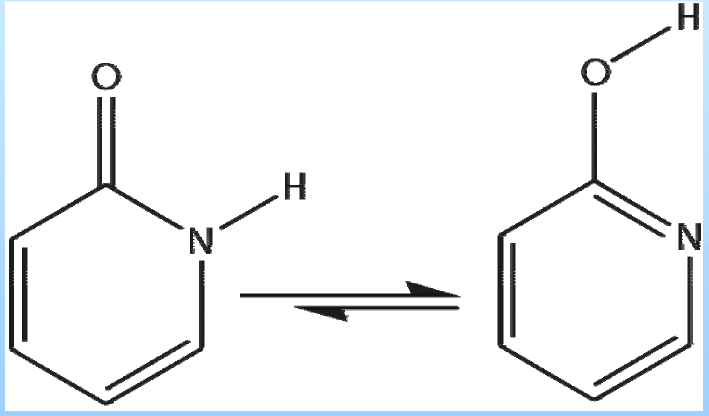
1) Malonaldehyde and acetylacetone

Malonaldehyde and acetylacetone can be considered prototype molecules for studying the keto-enol tautomerization.



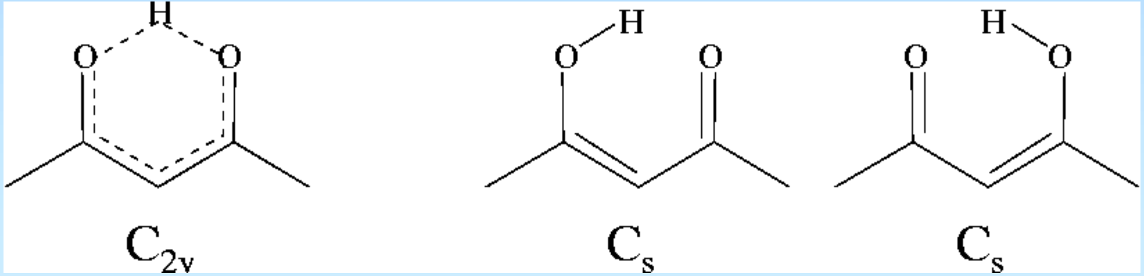
2) 2-Hydroxypyridine/2-Pyridinone

The protomeric tautomerism of PY and HY is frequently considered to be the prototype for the oxo-hydroxy tautomerization process in heterocyclic compounds.



Malonaldehyde and Derivatives

The rotational spectrum of malonaldehyde, characterized by a doubling of the rotational lines corresponding to a W-shaped potential, showed unambiguously that it behaves according to the ***C*s** form below[a]



The same characteristics were found for 2-nitromalonaldehyde[b] and 2-methyl-malonaldehyde.[c]

Combining ab initio and flexible model calculations with the experimental data a barrier to the proton transfer of 3.3 kcal/mol has been determined.[d]

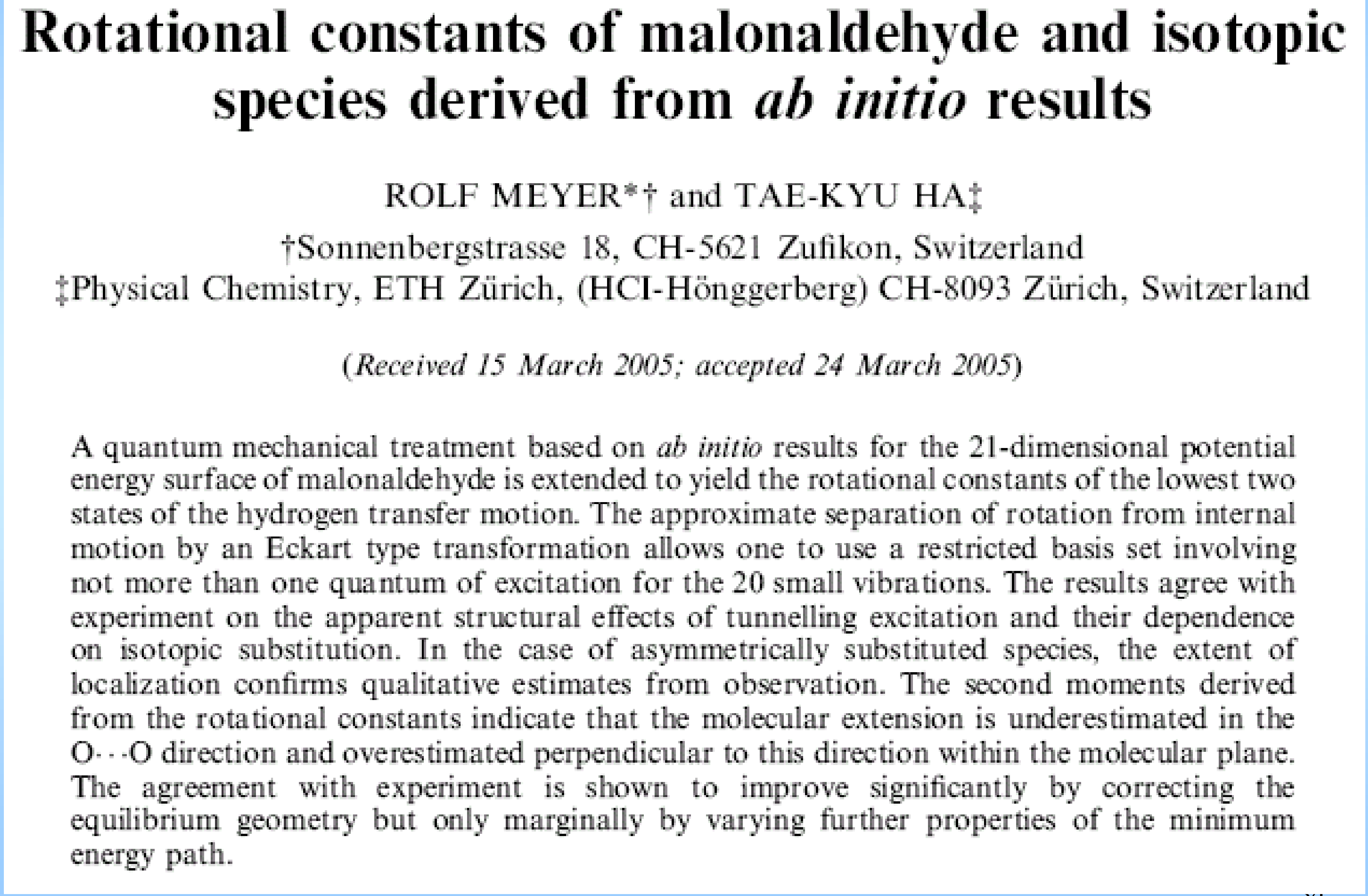
[a] W. F. Rowe, R. W. Duerst, and E. B. Wilson, J. Am. Chem. Soc. 1976, 98, 402; Rowe, W. F.; Duerst, R. W.; Wilson, E. B. *J. Am. Chem. Soc*. **1976**, *98*, 402; Baughcum, S.L.; Duerst, R. W.; Rowe, W. F.; Smith, Z.; Wilson, E. B. *J. Am. Chem. Soc*. **1981**, *103*, 6296; Baughcum, S.L.; Smith, Z.; Wilson, E. B.; Duerst, R. W. *J. Am. Chem. Soc*. **1984**, *106*, 2260.; Turner, P.; Baughcum, S.L.; Coy, S. L.; Smith, Z. *J. Am. Chem. Soc*. **1984**, *106*, 2265.

[b] Sanders, N. D. J. *MolSpectrosc*. **1981**, *86*, 27-42.

[c] Caminati, W. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 825-838.

[d] R. Meyer and T.-K. Ha, Mol. Phys. 2003, 101, 3263.

Malonaldehyde



Rotational constants of malonaldehyde and isotopic species derived from *ab initio* results

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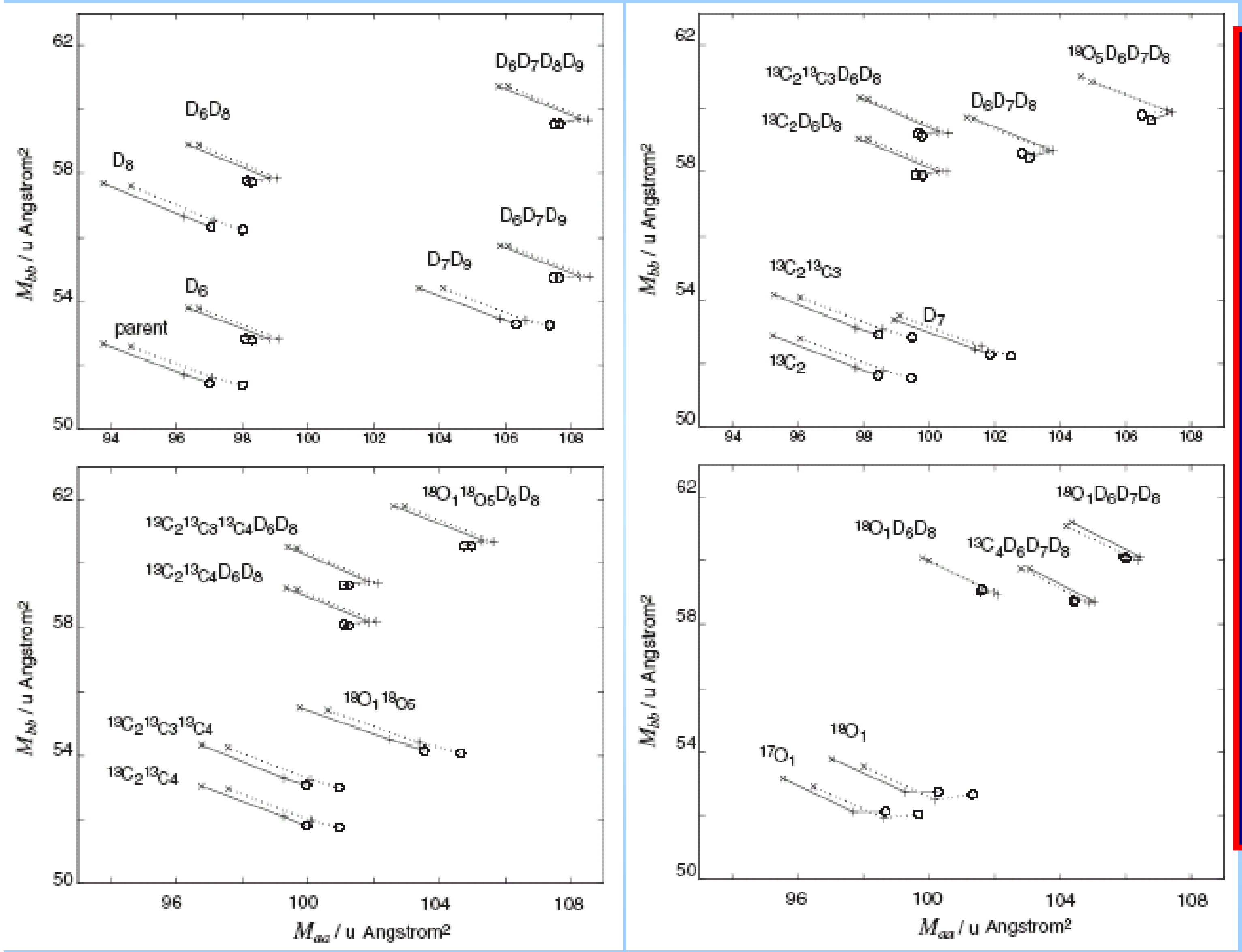
(*Received 15 March 2005; accepted 24 March 2005*)

A quantum mechanical treatment based on *ab initio* results for the 21-dimensional potential energy surface of malonaldehyde is extended to yield the rotational constants of the lowest two states of the hydrogen transfer motion. The approximate separation of rotation from internal motion by an Eckart type transformation allows one to use a restricted basis set involving not more than one quantum of excitation for the 20 small vibrations. The results agree with experiment on the apparent structural effects of tunnelling excitation and their dependence on isotopic substitution. In the case of asymmetrically substituted species, the extent of localization confirms qualitative estimates from observation. The second moments derived from the rotational constants indicate that the molecular extension is underestimated in the O· · ·O direction and overestimated perpendicular to this direction within the molecular plane. The agreement with experiment is shown to improve significantly by correcting the equilibrium geometry but only marginally by varying further properties of the minimum energy path.

[b]R. Meyer and T.-K. Ha, *Mol. Phys*. 2003, 101, 3263; *Mol. Phys* 2005, in press

Malonaldehyde

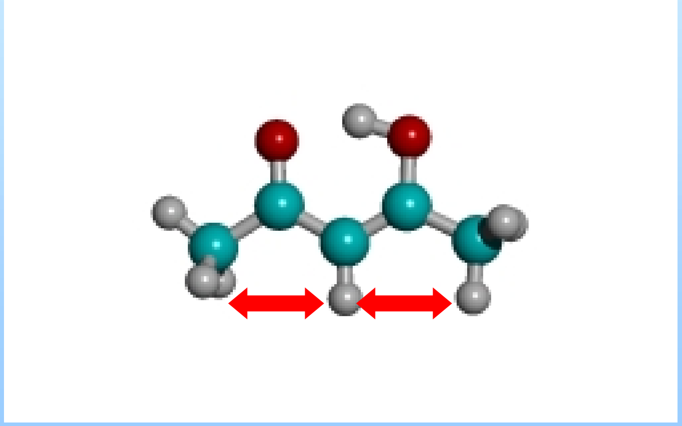


Second moments Maa and Mbb for the parent and symmetrically (left) and asymmetrically (right) substituted species of malonaldehyde,
as obtained from the rotational constants ab initio, after correcting the barrier and the equilibrium structure and from observations. The three points are connected by a full line for the lowest energy level (state 1) and by a dotted line for the second lowest level (state 2) of the hydrogen transfer mode

Acetylacetone

Acetylacetone (AcAc) comprises two tautomeric forms in dynamic equilibrium; together with malonaldheyde it can be considered a prototype molecule for studying the keto-enolic tautomerization.

The two methyl groups makes AcAc a tremendously complicated system. The tautomeric/conformational equilibrium can be understood from the rotational spectrum. We will present here the first step in this direction: the assignment of rotational spectrum of the enolic species.



Acetylacetone: recent literature

(1) Lowrey, A. H.; George, C.; D'Antonio, P.; Karle, J. *J. Am. Chem. Soc*. **1971**, *93*, 6399-6403.
(2) Andreassen, A. L.; Bauer, S. H. *J. Mol. Struct*. **1972**, *12*, 381-403.
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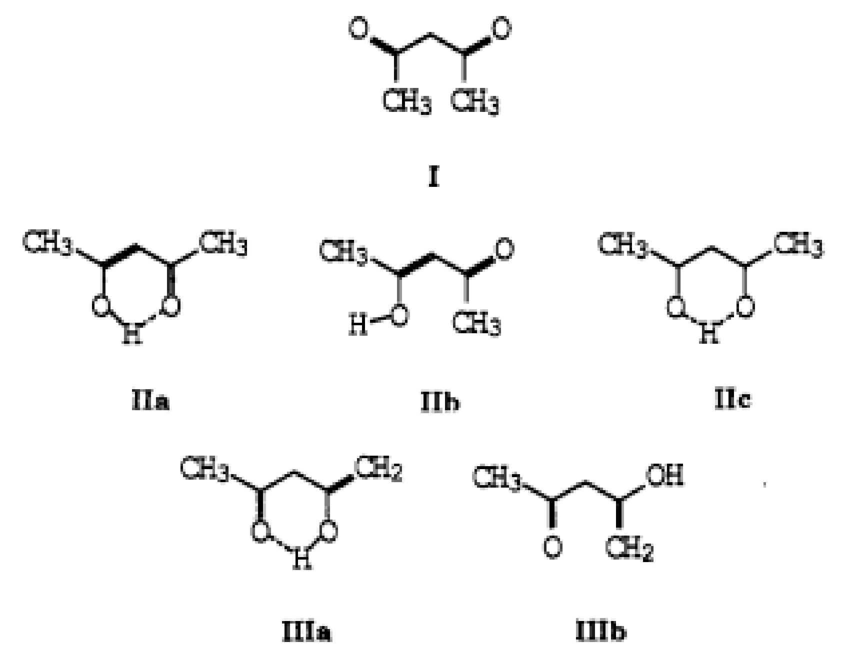
Two gas phase electron diffraction investigations, contrasting results

Acetylacetone: tautomerism



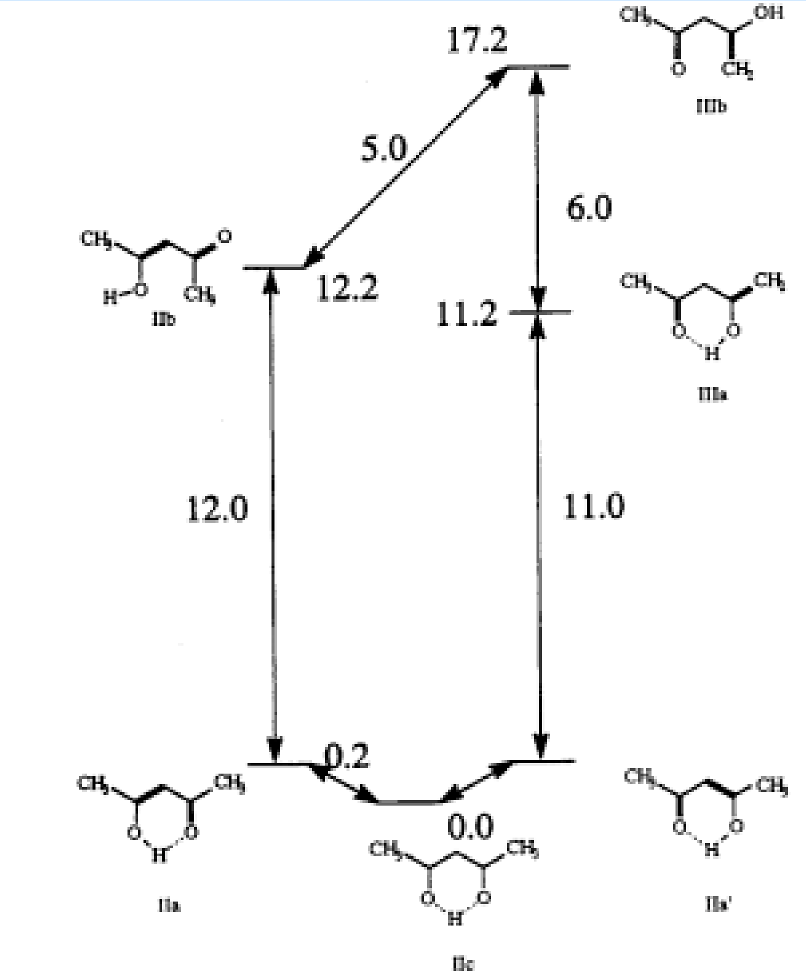
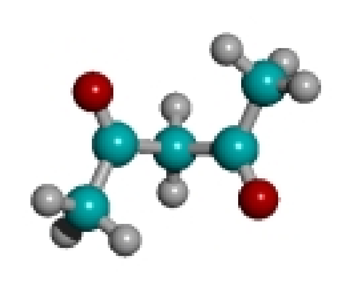
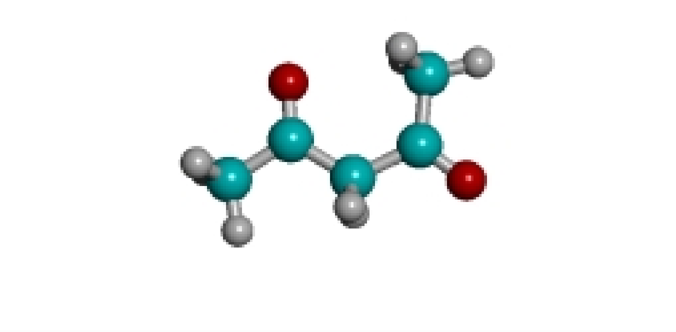


Figure 1. Schematic representation of the energy differences for the different structures of acetylacetone. Energies are taken from MP2/D95** with zero-point vibrational correction (see Table 1).

J.J.Dannenberg and R.Rios, *J.Phys.Chem.*, **98**, 6714-6718 (1994).

Acetylacetone: Conformations of the cheto-form

Species		
Symmetry:	C_2	C_s
Energy(kcal/mol):[a]	**1.9**	**5.8**
Experimental data:	**yes**[b]	**no**

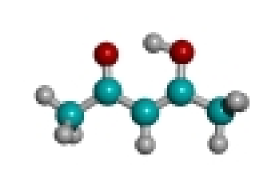
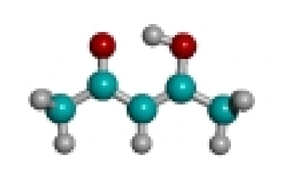
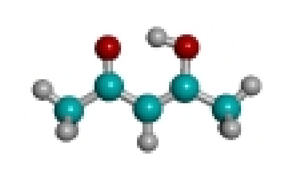
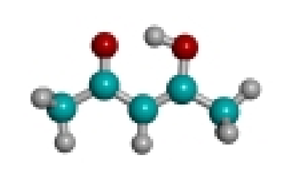
[a] B3LYP/6-311++G**

[b] Gas phase: ED, Ref.s 1) and 2) below

[1] Lowrey, A. H.; George, C.; D'Antonio, P.; Karle, J. *J. Am. Chem. Soc*. **1971**, *93*, 6399-6403.
[2] Srinivasa, R.; Feenstra, J. S.; Park, S. T.; Xu, S.; Zewail, A. H. *J. Am. Chem. Soc*., **2004**, *126*, 2266-2267.

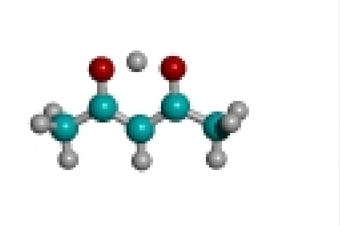
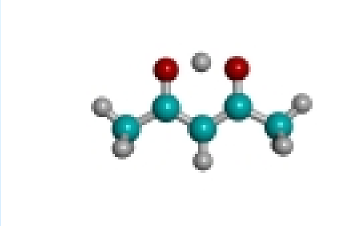
Acetylacetone: Conformations of enolic-forms

C_s Species[1]

E(kcal/mol):[a]	**0.0**	**0.1**	**1.9**	**2.0**

C_{2v} Species[2]

E(kcal/mol):[a]	**3.8**	**5.0**

[a]B3LYP/6-311++G**

[1] Claimed by: Srinivasa, R.; Feenstra, J. S.; Park, S. T.; Xu, S.; Zewail, A. H. *J. Am. Chem. Soc.*, **2004**, *126*, 2266-2267.

[2] Claimed by: Lowrey, A. H.; George, C.; D'Antonio, P.; Karle, J. *J. Am. Chem. Soc.* **1971**, *93*, 6399-6403.

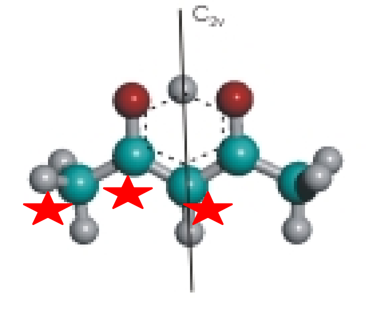
Acetylacetone: Rotational spectrum

Frequencies (ν, MHz) of measured transitions of the AA state of Enol-AcAc

MB-FTMW transitions		Millimeter-wave free jet transitions			
$J'(K_a',K_c')\leftarrow J''(K_a'',K_c'')$	ν	$J'(K_a',K_c')\leftarrow J''(K_a'',K_c'')$	ν	$J'(K_a')\leftarrow J''(K_a'')^{a}$	ν
1(1,1)-0(0,0)	7382.902	7(5,3)-6(4,2)	61975.69	6(6)-5(5)	67878.86
2(1,2)-1(0,1)	10084.243	7(5,2)-6(4,3)	61977.03	7(6)-6(5)	70957.58
2(2,1)-1(1,0)	19447.010	8(5,4)-7(4,3)	65043.75	8(6)-7(5)	74034.29
2(2,0)-1(1,1)	19842.711	8(5,3)-7(4,4)	65048.75	8(8)-8(7)	67327.38
3(1,3)-2(0,2)	12608.377	9(5,5)-8(4,4)	68099.61	9(8)-9(7)	67310.18
3(2,2)-2(1,1)	22148.196	9(5,4)-8(4,5)	68114.58	9(9)-9(8)	76295.47
3(2,2)-3(1,3)	14617.004	9(6,4)-8(5,3)	77107.10	10(8)-10(7)	67287.50
3(2,1)-2(1,2)	23380.963	9(6,3)-8(5,4)	77107.51	10(9)-10(8)	76278.27
3(2,1)-3(1,2)	12497.519	10(4,7)-9(3,6)	61574.48	11(8)-11(7)	67258.16
3(3,1)-3(2,2)	22488.923	10(4,6)-9(3,7)	62432.43	11(9)-11(8)	76256.41
3(3,0)-3(2,1)	22374.759	10(5,6)-9(4,5)	71135.40	12(8)-12(7)	67220.75
4(1,4)-3(0,3)	14985.362	10(5,5)-9(4,6)	71174.53	12(9)-12(8)	76228.85
4(2,3)-3(1,2)	24659.968	11(3,8)-10(2,9)	61398.35	13(8)-13(7)	67173.86
4(2,3)-4(1,4)	15387.585	11(4,8)-10(3,7)	64155.86	13(9)-13(8)	76195.00
4(3,2)-4(2,3)	22550.189	11(4,7)-10(3,8)	65716.64	14(8)-14(7)	67115.79
4(3,1)-4(2,2)	22215.349	11(5,7)-10(4,6)	74139.35	14(9)-14(8)	76153.01
5(1,5)-4(0,4)	17261.716	11(5,6)-10(4,7)	74230.08	15(8)-15(7)	67045.19
5(1,4)-5(0,5)	7893.393	12(3,9)-11(2,10)	66724.68		
5(2,4)-5(1,5)	16359.544	12(4,9)-11(3,8)	66501.36		
5(2,3)-5(1,4)	11574.774	12(4,8)-11(3,9)	69148.17		
5(3,3)-5(2,4)	22671.518	12(5,8)-11(4,7)	77093.74		
5(3,2)-5(2,3)	21917.786	12(5,7)-11(4,8)	77287.12		
6(0,6)-5(1,5)	15387.082	13(3,10)-12(2,11)	72638.69		
6(1,6)-5(0,5)	19494.368	13(4,10)-12(3,9)	68569.23		
6(2,5)-6(1,6)	17534.505	13(4,9)-12(3,10)	72793.15		
6(2,4)-6(1,5)	11289.471	14(4,11)-13(3,10)	70338.27		
6(3,4)-6(2,5)	22878.147	14(4,10)-13(3,11)	76731.35		
6(3,3)-6(2,4)	21448.267	15(4,12)-14(3,11)	71812.14		
7(0,7)-6(1,6)	18662.206	16(4,13)-15(3,12)	73016.43		
7(1,7)-6(0,6)	21739.383	17(4,14)-16(3,13)	73993.16		

Acetylacetone: Rotational spectrum

Frequencies (MHz) of measured transitions of the AA state of the ^{13}C species of Enol-AcAc



Intensity: 2% 2% 1% of normal

$J'(K_a',K_c') \leftarrow J''(K_a'',K_c'')$	$^{13}C_{Me}$	$^{13}C_{CO}$	$^{13}C_{CH}$
1(1,1)-0(0,0)	7311.6708	7375.6940	7334.3564
2(1,2)-1(0,1)	9963.1503	10066.4246	10031.1482
3(1,3)-2(0,2)	12442.7986	12581.4137	12549.7829
3(2,1)-3(1,2)	12479.0692	12520.0777	12358.0508
4(0,4)-3(1,3)	8343.3728	8526.7674	8627.1839
4(1,4)-3(0,3)	14778.8795	14950.1620	14921.0116
5(0,5)-4(1,4)	11705.1352	11938.1686	12046.2933
5(1,5)-4(0,4)	17015.2450	17218.3513	17192.3569
6(0,6)-5(1,5)	15018.8506	15297.5240	15408.5568

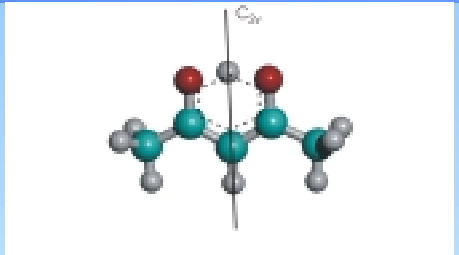
Acetylacetone: Rotational constants

	normal[a]	$^{13}C_{Me}$	$^{13}C_{CO}$	$^{13}C_{CH}$
A/MHz	6032.2431(4)[b]	5985.9431(7)	6030.3379(7)	5985.978(2)
B/MHz	1723.2640(3)	1686.4769(3)	1714.6758(3)	1723.3104(5)
C/MHz	1350.6909(2)	1325.7598(2)	1345.3859(2)	1348.4150(3)
N[c]	79	9	9	9
σ/σ_{exp} [d]	0.47[c]	0.35	0.3	0.71

[a] The following centrifugal distortion constants have been determined for the normal species: D_J = 0.017(3) kHz, D_{JK} = 9.97(1) kHz, D_K = 12.80(4) kHz, d_1 = -0.028(1) kHz, d_2 = -0.0540(6) kHz, H_{JK} = 0.26(9) Hz, H_K = 6.9(3) Hz, H_{KJ} = -15.7(3) Hz. These values have been fixed in the fittings of the less abundant isotopomers. [b] Errors in parenthesis are expressed in units of the last digit. [c] Number of transitions in the fit. [d] Reduced deviation of the fit.

Acetylacetone does have a C_{2v} symmetry

Six factors in support of the C_{2v} symmetry



1) It was possible to fit the observed spectrum in isolation. For a double minimum potential, severe interactions would be expected between the rotational spectra of the two inversion tunnelling states.

2) It was not possible to observe the second low energy inversion state, required in the case of a double minimum potential.

3) The Stark effect of μa overlapped transitions is very hard, corresponding to μa = 0.

4) Rotational constants B of normal and $^{13}C_{CH2}$, specise have the same value: same moment of inertia, this C atom lyes on the b-axis.

5) A 36/28 statistical weight, in favor of the states with an odd value of (K_{+1} + K_{-1}) was observed.
As shown in Fig. 1, the C_{2v} enolic form of AcAc contains three pairs of equivalent methyl hydrogens and than follows the Fermi-Dirac statistics, i.e. the overall wavefunction:

$$\Psi_{tot} = \Psi_e \Psi_v \Psi_R \Psi_s$$

must be anti-symmetric. Both ψ_e and ψ_v are symmetric in the ground state, while the spin function ψ_s (36 A_g; 28 A_u) does have a ratio 9/7 between symmetric and anti-symmetric components; for this reason, the rotational transitions with an anti-symmetric initial state will have a favorable intensity ratio, 9/7, with respect to the symmetric ones. With the C_2 axis lying along the *b*-axis, the even function are characterized by a even value of (K_{+1} + K_{-1}), and vice versa.

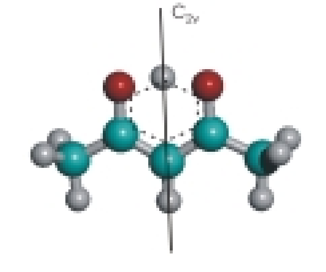
6) Only one isotopomer (with an intensity 2% of that of the normal species) was found for the $^{13}C_{Me}$ and $^{13}C_{CO}$ species

Enolic Acetylacetone: Methyl groups internal rotation

The inertial defect: Expected $\Delta_c = -6.40$ uÅ²

Exprmtl. $\Delta_c = -2.88$ uÅ²

$\Rightarrow$ low V_3



For the AA state of molecules with two almost freely rotating methyl groups, as given in the following Equations:

$$A_{AA} = A_r + 2\,F\,W_{AA}^{(2)}\,\rho_a^{\,2}$$

$$B_{AA} = B_r + 2\,F\,W_{AA}^{(2)}\,\rho_b^{\,2}$$

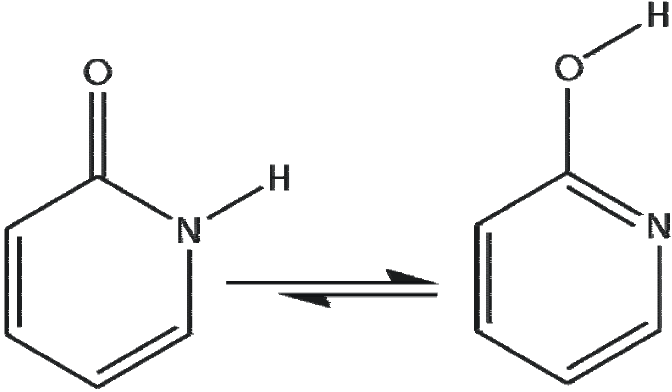
$$C_{AA} = C_r$$

There A_r, B_r and C_r are the “rigid” rotational constants in the limit of the very high barrier. The $W_{AA}^{(2)}$ coefficients are the Hersbach's barrier-dependent perturbation sums relative to the AA sublevels of the ground state, F is the reduced constant of the motion and $\rho_g = \lambda_g I_\alpha / I_g$.

Δ_c reproduced when $W_{AA}^{(2)} = 0.52$, corresponding to a reduced barrier $s = 5$ and to $V_3 = 163$ cal/mol.

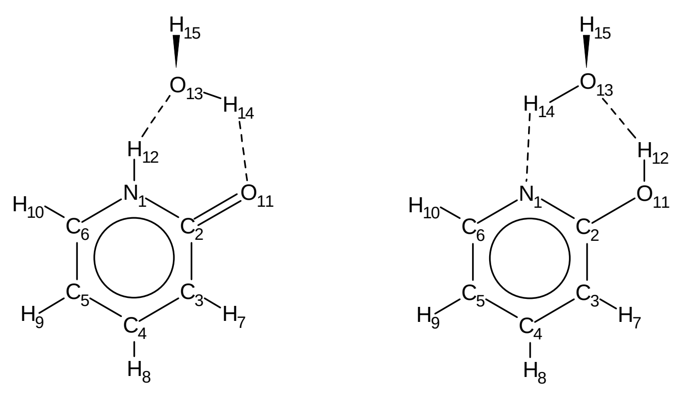
2-Hydroxypyridine/2-Pyridinone (HY/PY)

Several experimental and a myriad of theoretical investigations are available on the HY/PY system. We believe that our data[a] on the relative tautomeric energies are the more reliable ones.



E/kJ/mol	**3.2**	**0.0**

The situation is reversed when moving to the 1:1 complex with water: the complex with the keto form is more stable.[b,c]



PYRIDONE-WATER HYDROXYPYRIDINE-WATER

E/kJ/mol	**0.0**	**1to 4**

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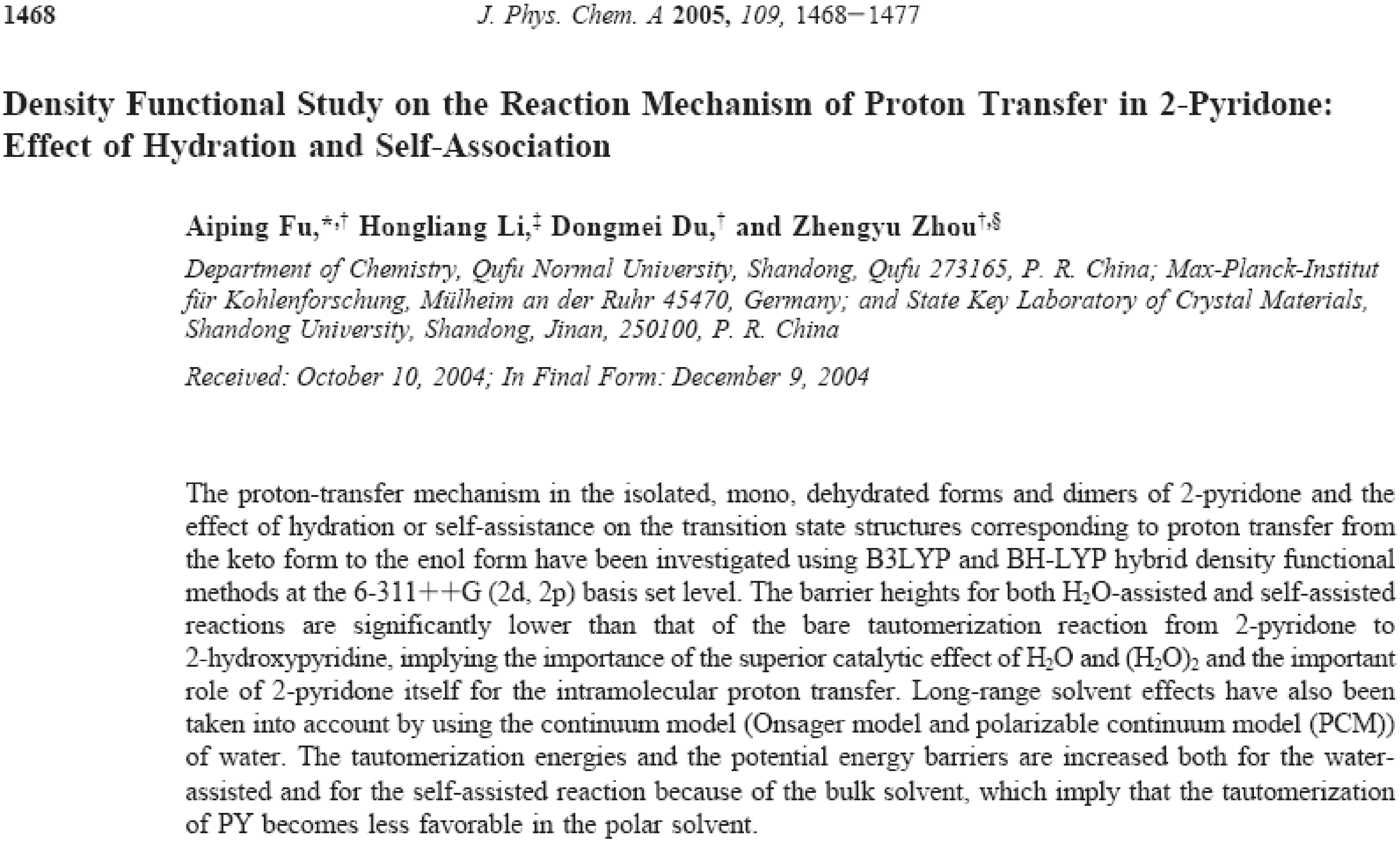
[a] L.D.Haterley, R.D.Brown, P.D.Godfrey, A.P Pierlot, W.Caminati, D.Damiani, S.Melandri, L.B.Favero, *J.Phys.Chem.*, 97 (1993) 46.

[b] Held,A.; Pratt,D.W., *J.Am.Chem.Soc.*, 115 (1993) 9708.

[c] A.Maris, P.Ottaviani and W.Caminati, *Chem.Phys.Letters*, **360** (2002) 155.

2-Hydroxypyridine/2-Pyridinone (HP/PO)



1468 *J. Phys. Chem. A* **2005,** *109,* 1468−1477

Density Functional Study on the Reaction Mechanism of Proton Transfer in 2-Pyridone: Effect of Hydration and Self-Association

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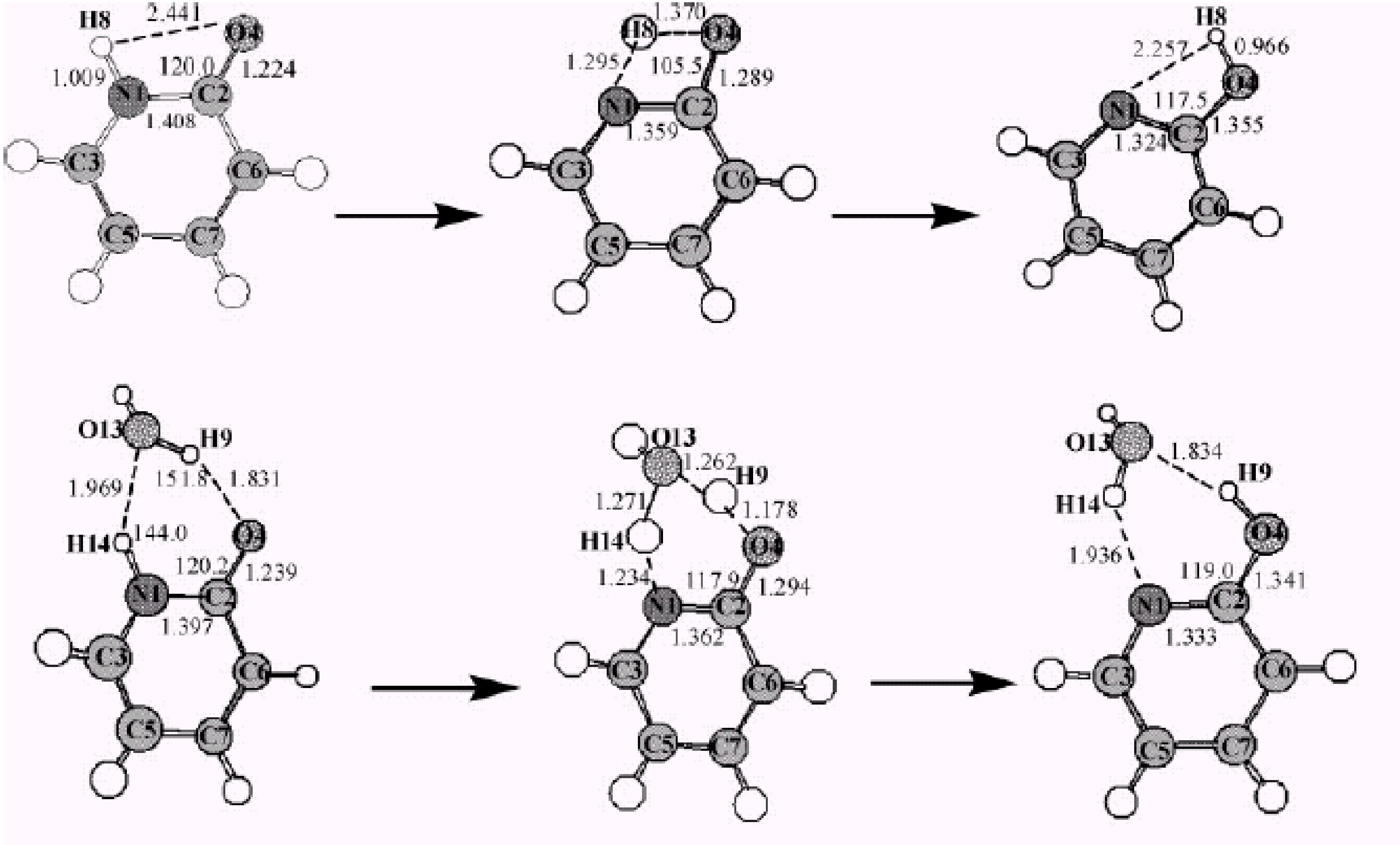
The proton-transfer mechanism in the isolated, mono, dehydrated forms and dimers of 2-pyridone and the effect of hydration or self-assistance on the transition state structures corresponding to proton transfer from the keto form to the enol form have been investigated using B3LYP and BH-LYP hybrid density functional methods at the 6-311++G (2d, 2p) basis set level. The barrier heights for both H_2O-assisted and self-assisted reactions are significantly lower than that of the bare tautomerization reaction from 2-pyridone to 2-hydroxypyridine, implying the importance of the superior catalytic effect of H_2O and $(H_2O)_2$ and the important role of 2-pyridone itself for the intramolecular proton transfer. Long-range solvent effects have also been taken into account by using the continuum model (Onsager model and polarizable continuum model (PCM)) of water. The tautomerization energies and the potential energy barriers are increased both for the water-assisted and for the self-assisted reaction because of the bulk solvent, which imply that the tautomerization of PY becomes less favorable in the polar solvent.

2-Hydroxypyridine/2-Pyridinone (HY/PY)



2-Hydroxypyridine/2-Pyridinone (HY/PY)

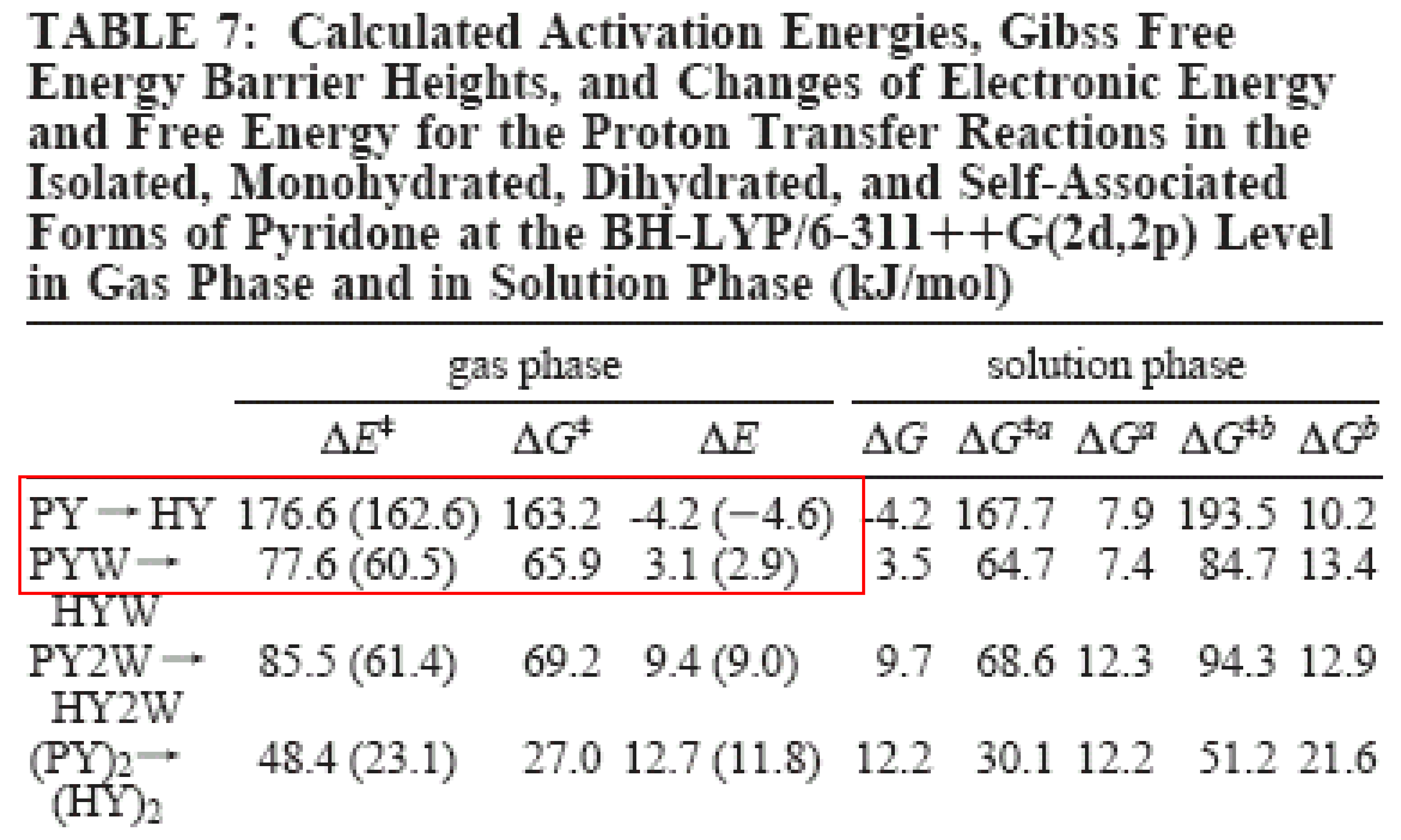
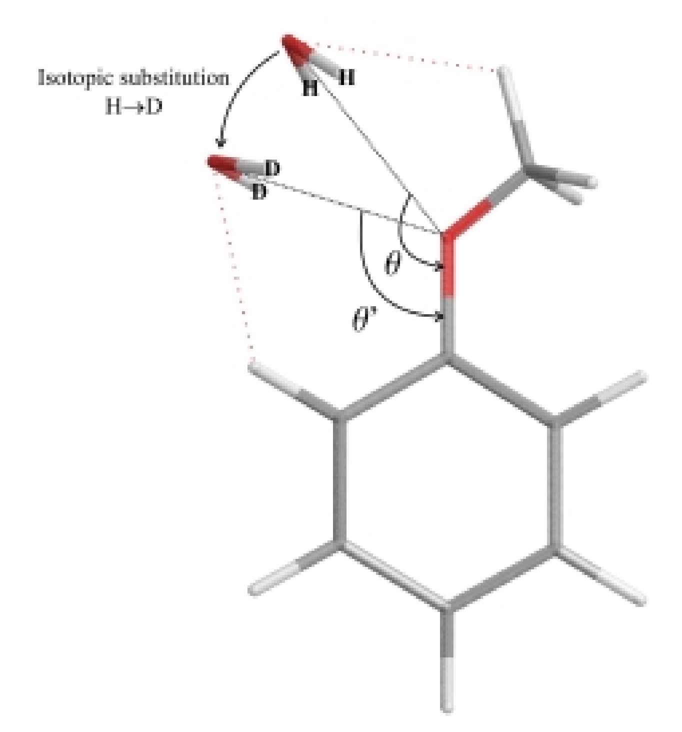


TABLE 7: Calculated Activation Energies, Gibss Free Energy Barrier Heights, and Changes of Electronic Energy and Free Energy for the Proton Transfer Reactions in the Isolated, Monohydrated, Dihydrated, and Self-Associated Forms of Pyridone at the BH-LYP/6-311++G(2d,2p) Level in Gas Phase and in Solution Phase (kJ/mol)

	gas phase			solution phase				
	$\Delta E^{\ddagger}$	$\Delta G^{\ddagger}$	ΔE	ΔG	$\Delta G^{\ddagger a}$	ΔG^{a}	$\Delta G^{\ddagger b}$	ΔG^{b}
PY → HY	176.6 (162.6)	163.2	-4.2 (−4.6)	-4.2	167.7	7.9	193.5	10.2
PYW → HYW	77.6 (60.5)	65.9	3.1 (2.9)	3.5	64.7	7.4	84.7	13.4
PY2W → HY2W	85.5 (61.4)	69.2	9.4 (9.0)	9.7	68.6	12.3	94.3	12.9
$(PY)_2$ → $(HY)_2$	48.4 (23.1)	27.0	12.7 (11.8)	12.2	30.1	12.2	51.2	21.6

Isotopomeric Conformational Change in Anisole-Water

The deuteration of water produces a conformational change in the Anisole···Water complex, as shown by the scheme. The value of the θ angle decreases from 138 to 128°, while the secondary interaction $O\cdots H_{Me}$ is replaced by the $O\cdots H_{\underline{Ph}}$ one.



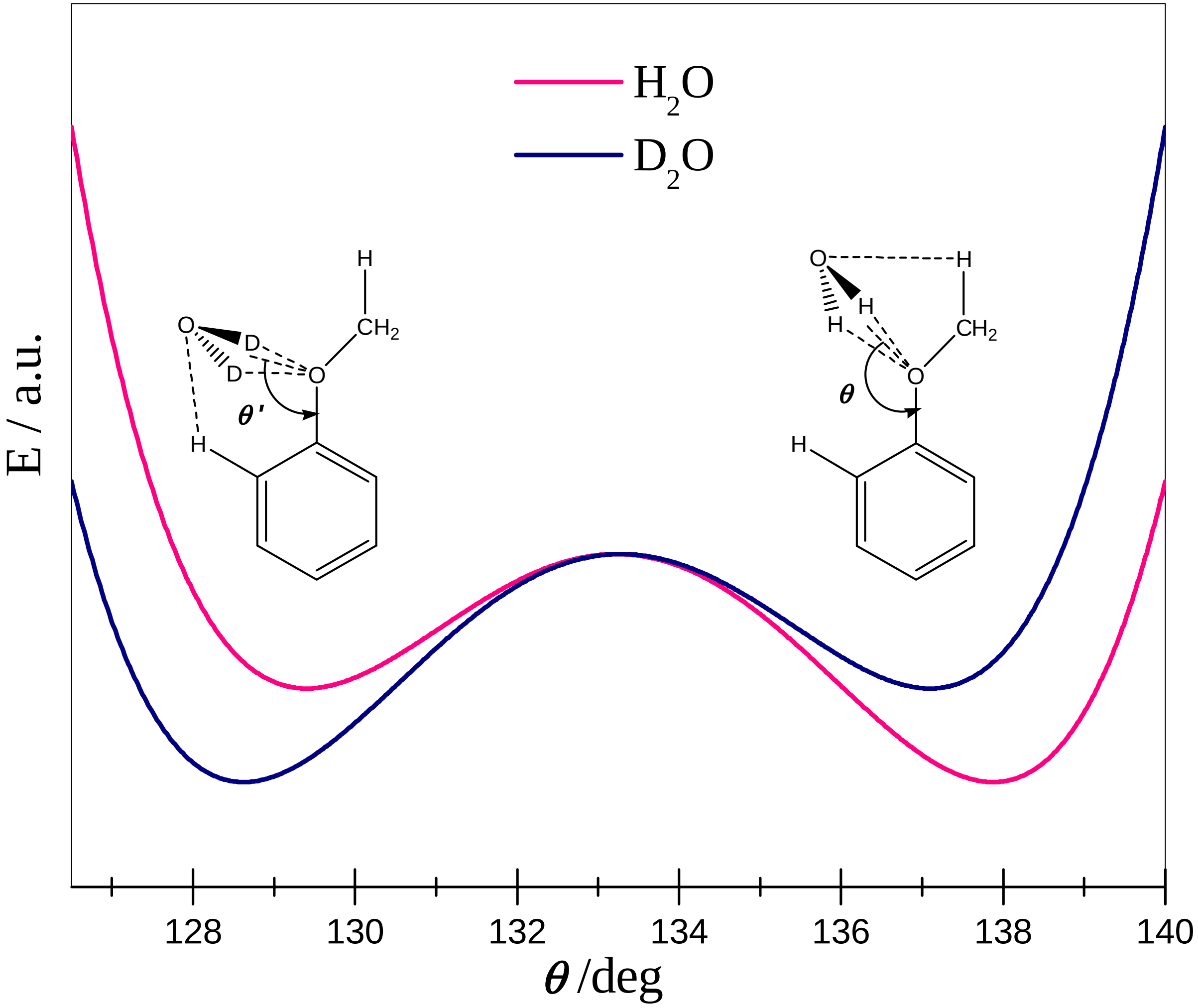
B.M.Giuliano and W.Caminati, *Angew.Chem.Int.Ed.Engl*. **44** 603-605 (2005).

Anisole-Water

Spectroscopic constants

	Anisolo-H_2O		Anisolo-D_2O		Anisolo-DOH	Anisolo-$H_2{}^{18}O$		Anisolo-$D_2{}^{18}O$		Anisolo-$D^{18}OH$
	v=0	v=1	v=0	v=1		v=0	v=1	v=0	v=1	
A/MHz	2943.058(2)	2943.578(2)	2660.639(1)	2660.657(2)	2847.47(1)	2912.223(8)	2912.769(6)	2621.694(9)	2621.80(3)	2813.57(1)
B/MHz	900.1885(9)	900.0276(8)	914.1605(5)	914.1581(6)	907.4638(6)	857.1386(9)	856.9846(7)	876.3307(6)	876.3222(6)	866.2243(2)
C/MHz	694.1488(9)	694.1155(8)	687.0905(3)	687.0900(4)	692.5413(8)	666.5972(7)	666.5624(5)	662.9146(2)	662.9170(9)	666.2012(1)
D_J/kHz	4.25(2)	4.22(2)	4.509(3)	4.510(4)	5.73(1)	4.054(5)	4.029(4)	4.419(7)	4.39(2)	5.789(2)
D_{JK}/kHz	-54.0(1)	-53.8(1)	-54.4(6)	-54.36(5)	-72.3(2)	-52.4(2)	-52.3(1)	-54.6(2)	-56.(1)	-75.5(2)
D_K/kHz	219.0(2)	218.3(2)	202.3(2)	203.5(2)	200(10)	218(1)	218(1)	271(5)	317(9)	196(3)
d_1/kHz	-1.760(2)	-1.751(2)	-1.843(2)	-1.845(3)	-2.394(3)	-1.644(4)	-1.638(3)	-1.802(4)	[-1.845]	[-2.394]
d_2/kHz	-0.108(2)	-0.106(1)	-0.065(2)	-0.064(2)	-0.086(6)	-0.105(3)	-0.106(2)	[-0.065]	[-0.064]	[-0.086]
H_J/Hz	0.7(2)	0.6(1)	-	-	0.14(4)	[0.7]	[0.6]	-	-	[0.14]
H_{JK}/Hz	-15.0(1)	-14.0(9)	-	-	-	-12(2)	-13(2)	-	-	-
H_{KJ}/Hz	85(10)	83(9)	-	-	-	80(10)	78(10)	-	-	-
M_{aa}/uÅ^2	558.8757(8)	558.9585(7)	549.2111(5)	549.2128(5)	554.5879(9)	587.1110(9)	587.2001(7)	573.1450(6)	573.150(2)	581.2018(4)
M_{bb}/uÅ^2	169.1800(8)	169.1322(7)	186.3237(5)	186.3226(5)	175.1577(9)	171.0365(9)	170.9870(7)	189.2141(6)	189.206(2)	177.3964(4)
M_{cc}/uÅ^2	2.5390(8)	2.5565(7)	3.6228(5)	3.6226(5)	2.3258(9)	2.5007(9)	2.5176(7)	3.5540(6)	3.554(2)	2.2256(4)
σ/kHz	5	5	6	6	5	5	5	1	4	3
N	42	42	40	42	35	30	31	12	10	13

Anisole-Water



How I see Hydrogen Bonding

HYDROGEN BONDING: A combination of non-covalent interactions which stabilize, by at least one kcal/mol, a configuration of a molecular system in which an hydrogen atom is in between two (or more) high electronic density sites.

Otherwise:

HYDROGEN CONTACT: Appears in a configuration of a molecular system when an hydrogen atom is in between two (or more) high electronic density sites, but does not bring an appreciable energy stabilization.