WEAK HYDROGEN BONDS AND EXPERIMENTAL BLUE SHIFTS

W.A. HERREBOUT
UNIVERSITY OF ANTWERP

BLUE – SHIFTING HYDROGEN BONDS

PAVEL HOBZA , ZDENEK HAVLAS

CHEMICAL REVIEWS

2000, VOL **100**, *PAGE 4253*

The nature of the blue shift has been the subject of intense debate.

Surprisingly little experimental information on C-H...X bonded complexes was available

N.S. Golubev, T.D. Kolomiitsova, S.M. Melikova, D.N. Shchepkin, in: 18th Conference on Spectroscopy, Technical Digest, Gorki, Russia, 1977, p. 78.

(Teor. Spektrosk., Izv. Akad. Nauk. SSSR)

G. Trudeau, J.M. Dumas, P. Dupuis, M. Guerin, C. Sandorfy, Topics in Current Chemistry, 93 (1980) 91.

I.E. Boldeskul, I.F. Tsymbal, E.V. Ryltsev, Z. Latajka, A.J. Barnes, J. Mol. Struct. 436 (1997) 167.

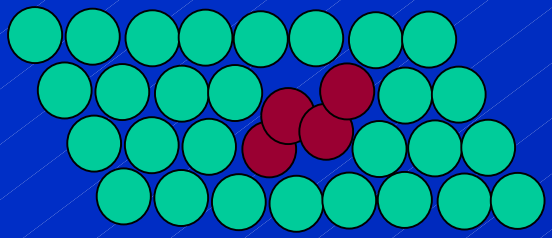
B.J. van der Veken, W.A. Herrebout, R. Szostak, D.N. Shchepkin, Z. Havlas, P. Hobza, J. Am. Chem. Soc. 123 (2001) 12290

SUMMARY

1. CRYOSPECTROSCOPY
2. CH..O AND CH..N HYDROGEN BONDED COMPLEXES
3. PSEUDO-BLUE SHIFTING CH..N HYDROGEN BONDS
4. CH..F AND CH..S HYDROGEN BONDED COMPLEXES

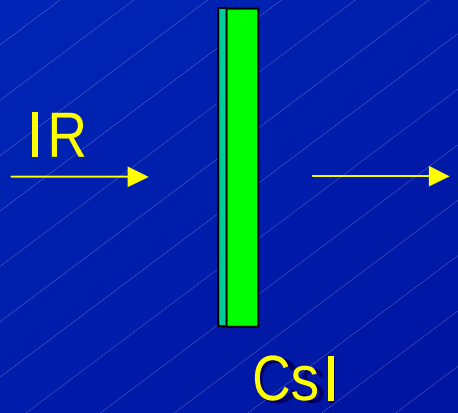
FTIR SPECTROSCOPY OF CRYOSOLUTIONS

matrix – isolation infrared spectroscopy



low temperature : 10 – 35 K

inert environment : Ne, Ar, ...



matrix-isolation remains unsurpassed in a variety of studies including, for example, the study of free radicals and other unstable species

disadvantages :

- strong scattering of the infrared beam by thicker matrices
- spectra are often complicated by site-effects :

  rotation of the solute molecule in its trapping site

  presence of different trapping sites in the matrix

  aggregation of solute molecules

- no thermodynamic properties can be derived

replacing the solid matrices by solutions in liquefied inert gases

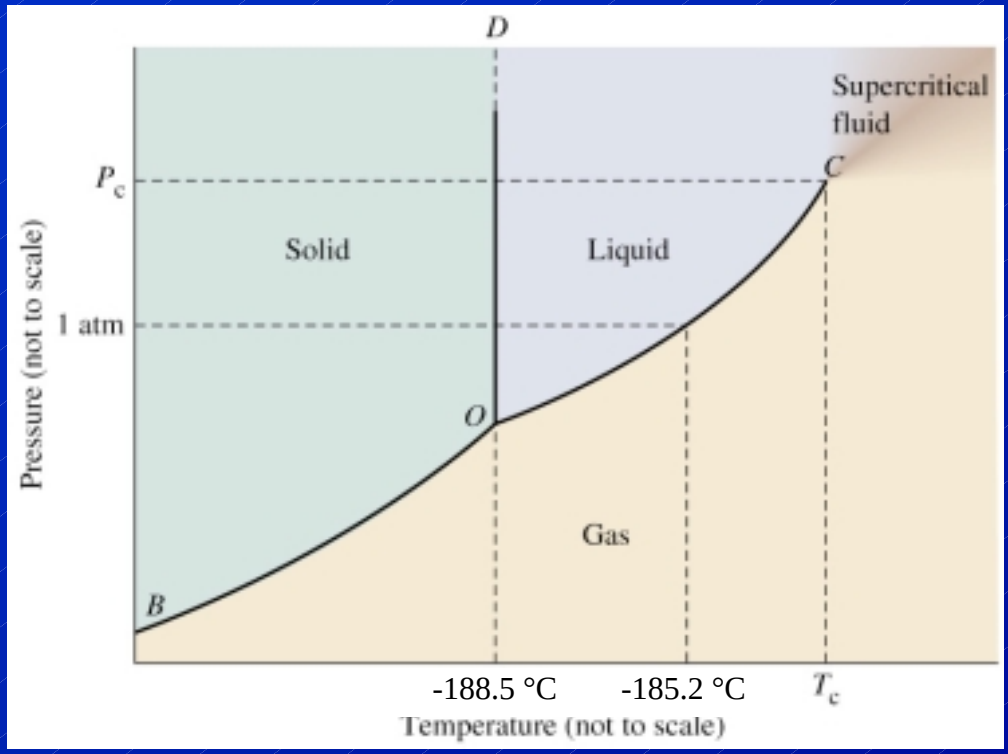
advantages :

- relatively low temperatures
- weak solute-solvent interactions
- chemical equilibrium
- transparant in a broad spectral range : far-IR to UV

disadvantages :

- solubility : typical concentration of 1 – 100 ppm
- limited temperature interval at 1 bar

Phase-diagram for Argon



	mp	bp
1 atm	-188.5 °C	-185.2 °C
15 atm	-188.5 °C	-150.3 °C

experimental set-up is not straightforward !

Vacuum shroud

vacuum

... < 10^{-4} mbar

Cryosolution

High pressure

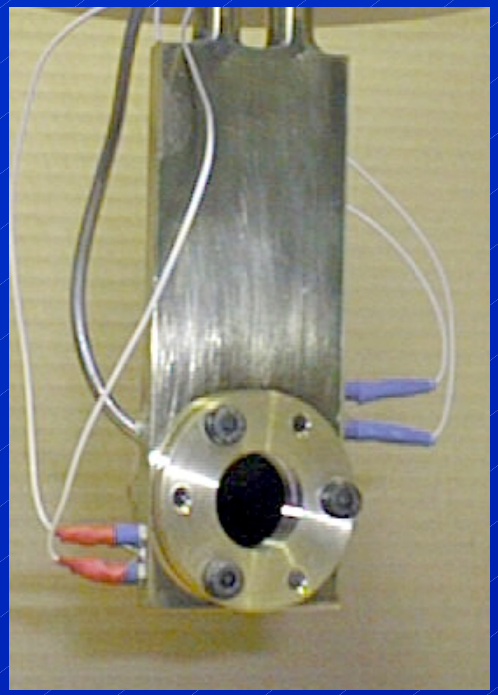
10 < ... < 175 bar

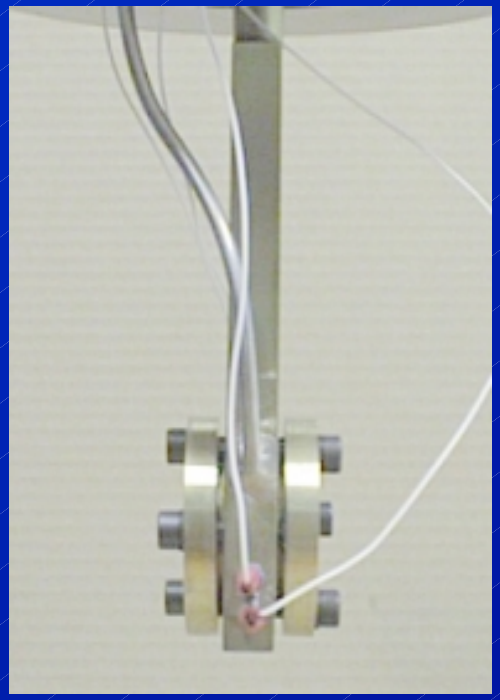
No leaks at room temperature and at lower temperatures ! !

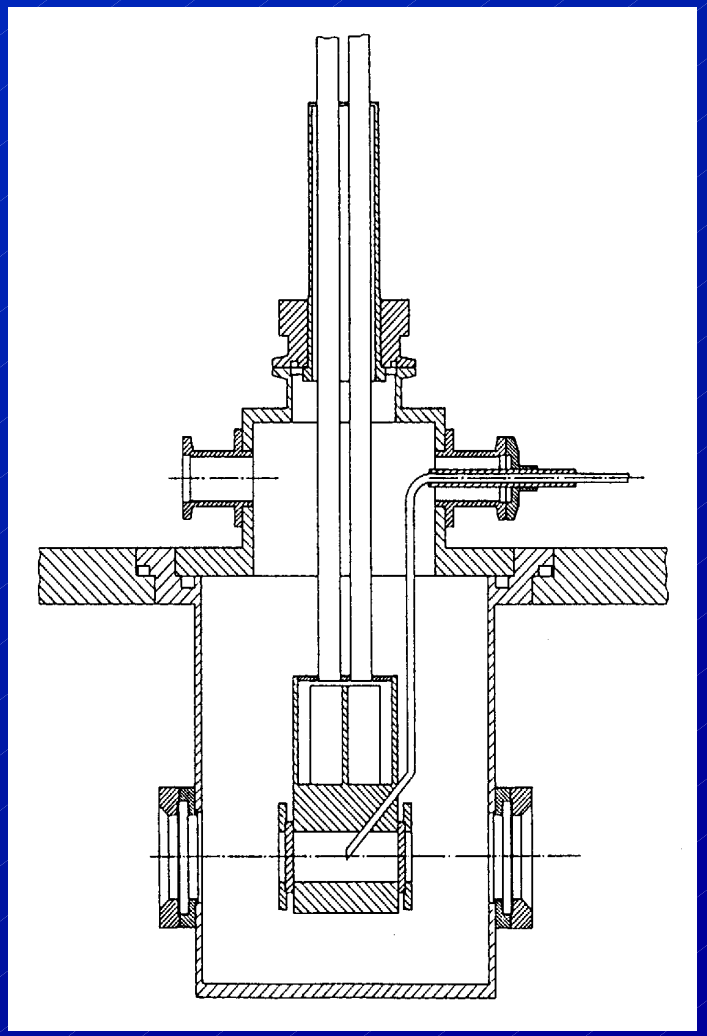
25 K < T < 300 K

M.O. Bulanin, In: Handbook of Vibrational Spectroscopy; J.M. Chalmers and P.R. Griffiths, Eds.; J; Wiley & Sons: Chichester, 2002; Vol. 2, p 1329.

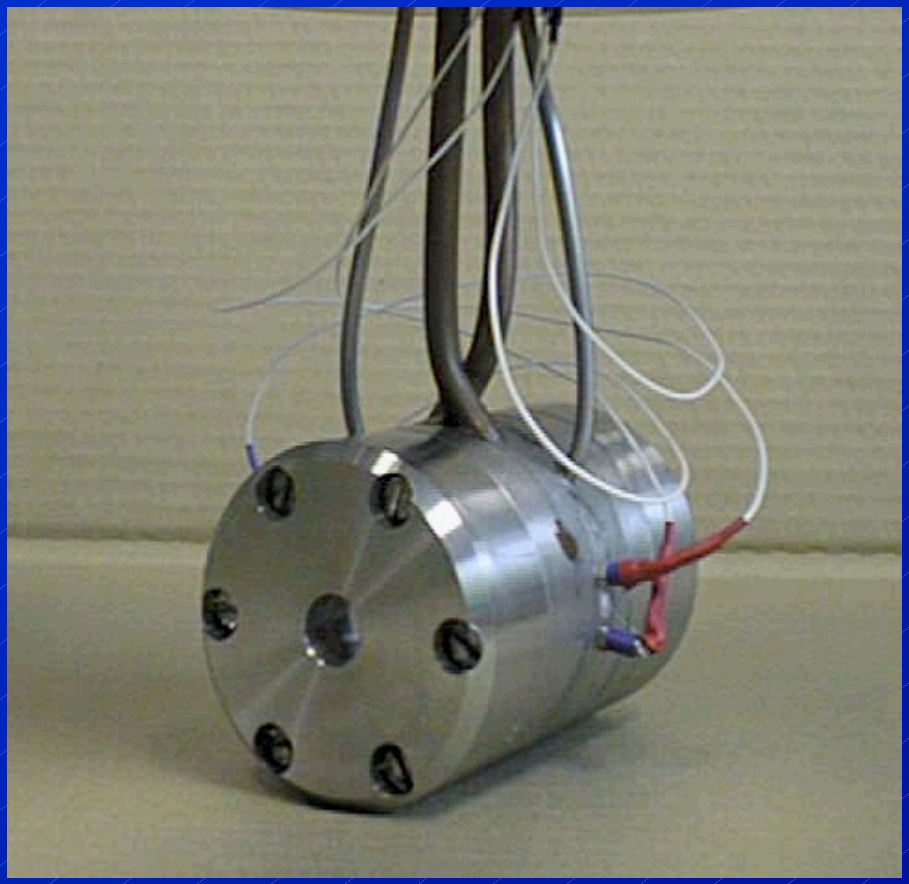
liquid cell : low-pressure design (l = 10.0 mm)

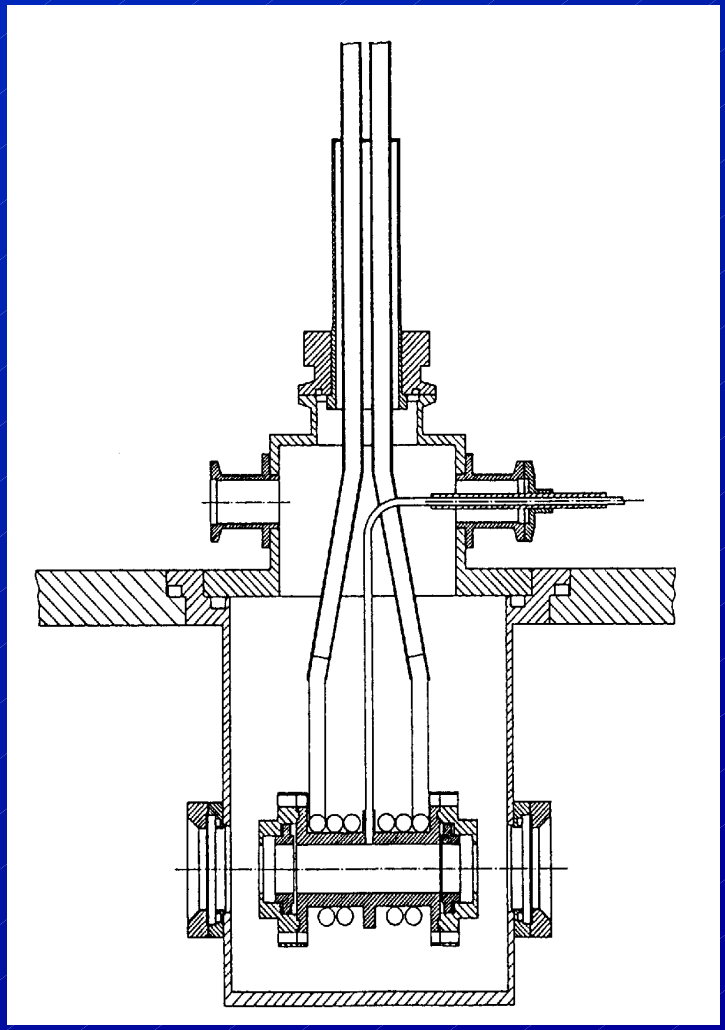






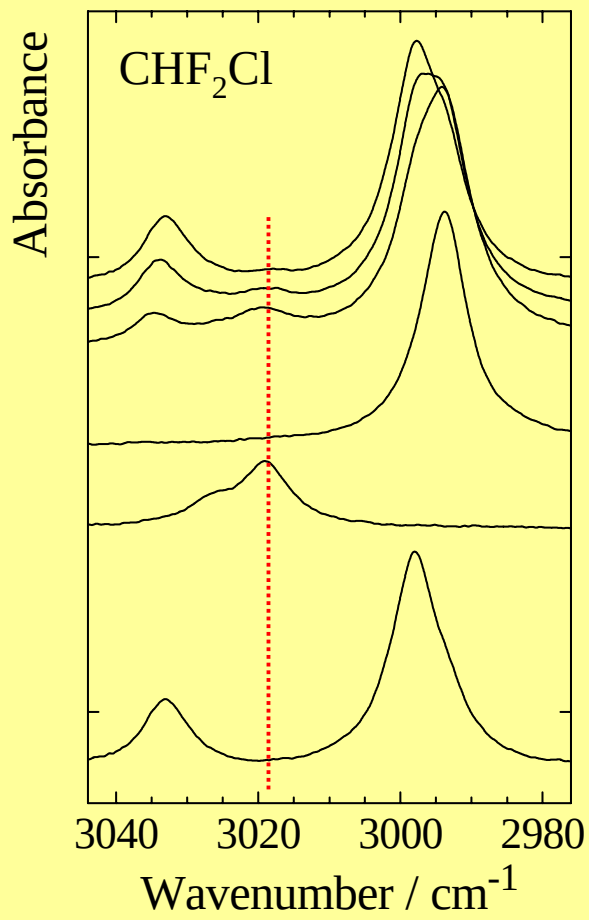
liquid cell : high-pressure design (l = 70 mm)

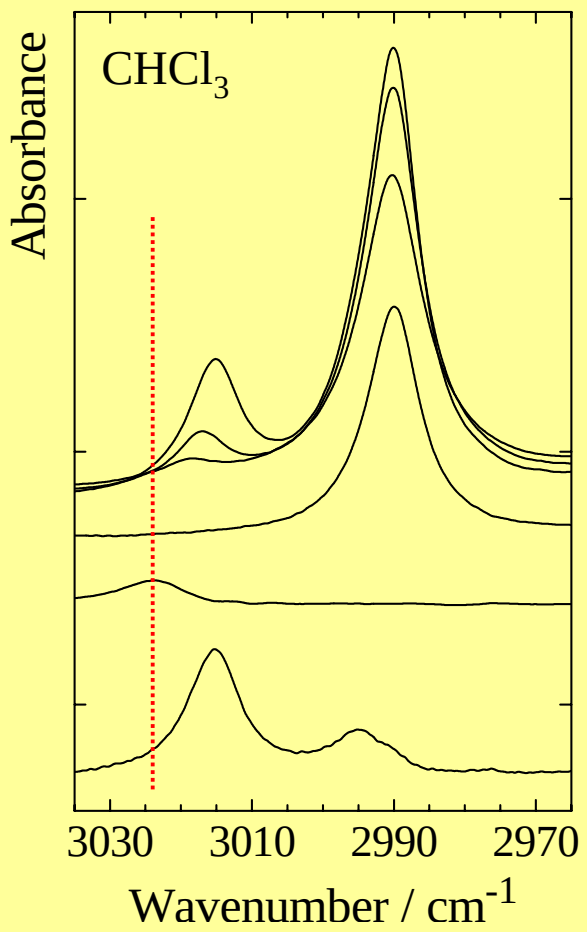




CH..O AND CH..N HYDROGEN BONDED COMPLEXES

Complexes of Dimethyl Ether with $CHCl_xF_y$





Experiment	HCF_3	$HCClF_2$	$HCCl_2F$	$HCCl_3$
$\Delta\nu_{C\text{-}H}$ /cm^{-1}	17.7	14.0	4.8	-8.3

Ab initio	HCF_3	$HCClF_2$	$HCCl_2F$	$HCCl_3$
$\Delta\nu_{C\text{-}H}$ /cm^{-1}	40.8	21.9	8.2	-4.1

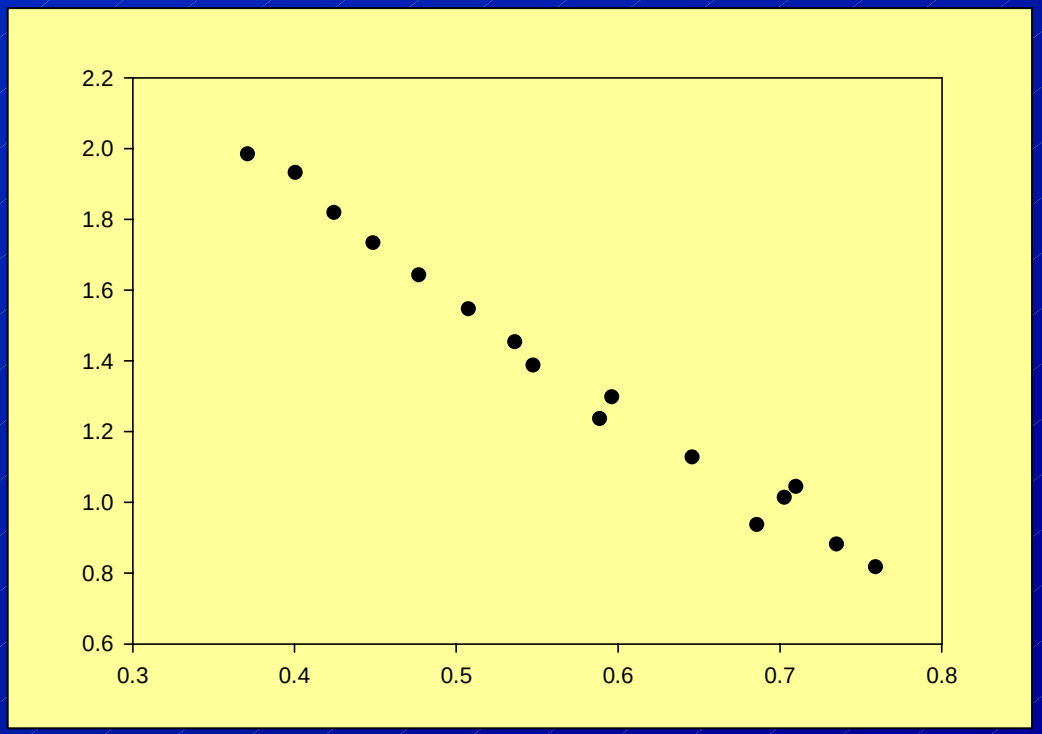
B.J. van der Veken, W.A. Herrebout, R. Szostak, D.N. Shchepkin, Z. Havlas, P. Hobza, *J. Am. Chem. Soc. 123* (2001) 12290.

S.N. Delanoye , W.A. Herrebout , B.J. van der Veken , *J. Am. Chem. Soc. 124* (2002) 7490.

What happens with the infrared intensity ?

$$I^{corr}_{complex} = -\frac{\varepsilon_{complex}}{\varepsilon_{monomeer}} I^{corr}_{monomeer} + c$$

$$I^{corr}_{i}(T) = I_i(T)\,\frac{\rho(T_R)}{\rho(T)}$$

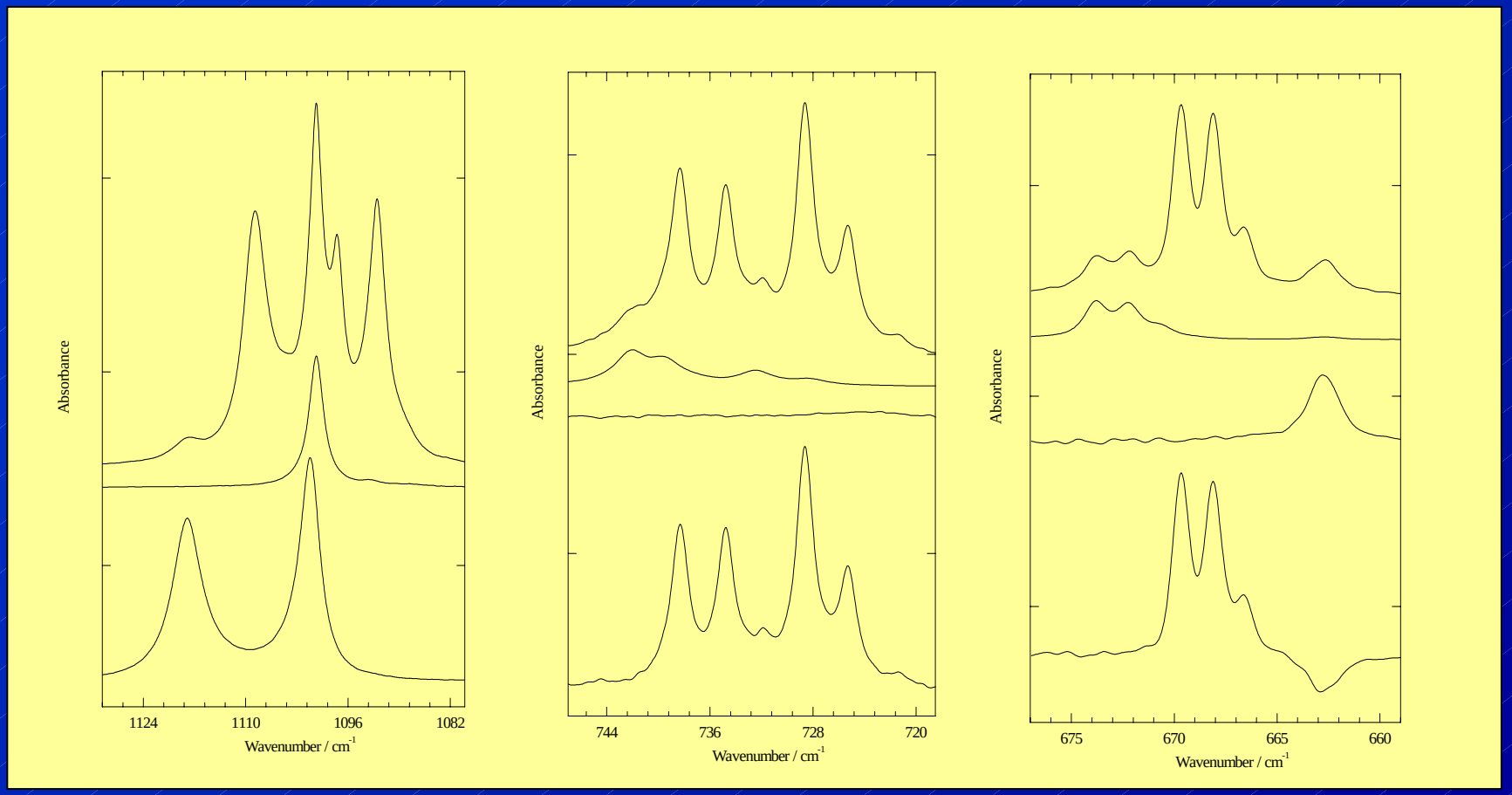


	HCF_3	$HCClF_2$	$HCCl_2F$	$HCCl_3$
$\varepsilon_{complex}/\varepsilon_{monomeer}$	0.09(2)	0.89(6)	26(1)	56(3)

	HCF_3	$HCClF_2$	$HCCl_2F$	$HCCl_3$
$\Delta\nu_{C\text{-}H}/cm^{-1}$	17.7	14.0	4.8	-8.3

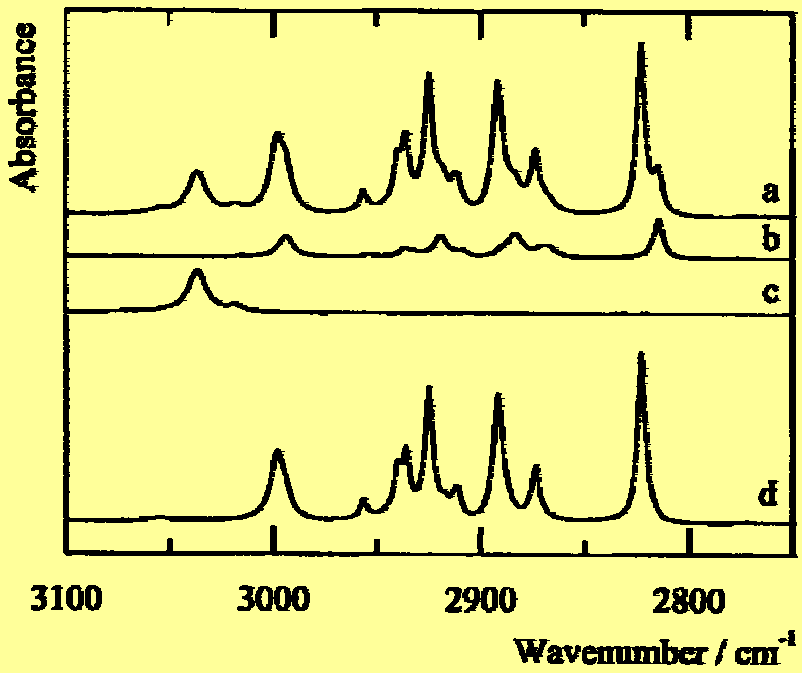
What happens with the other modes ?

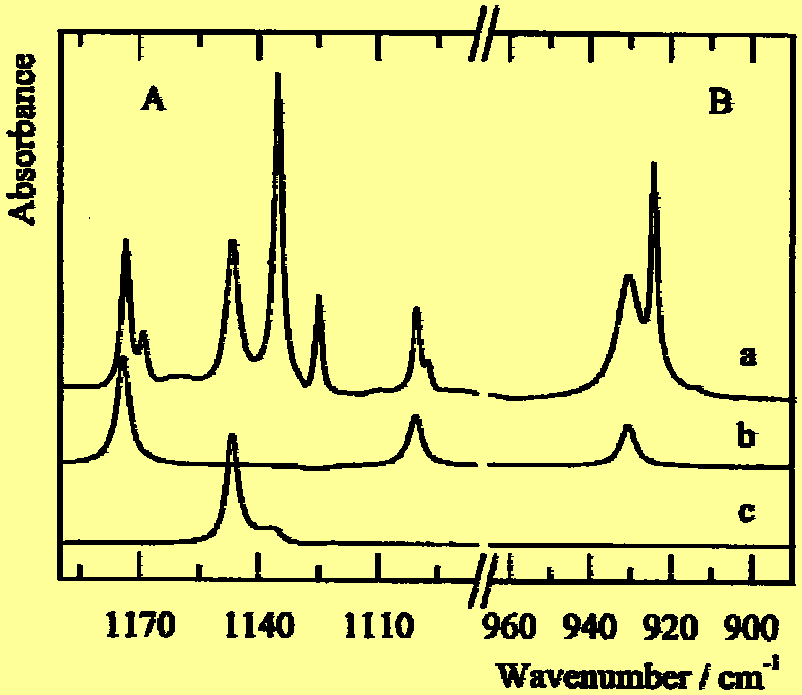
C-Cl and C-F stretching fundamentals



CHF_2Cl $CHFCl_2$ $CHCl_3$

other modes

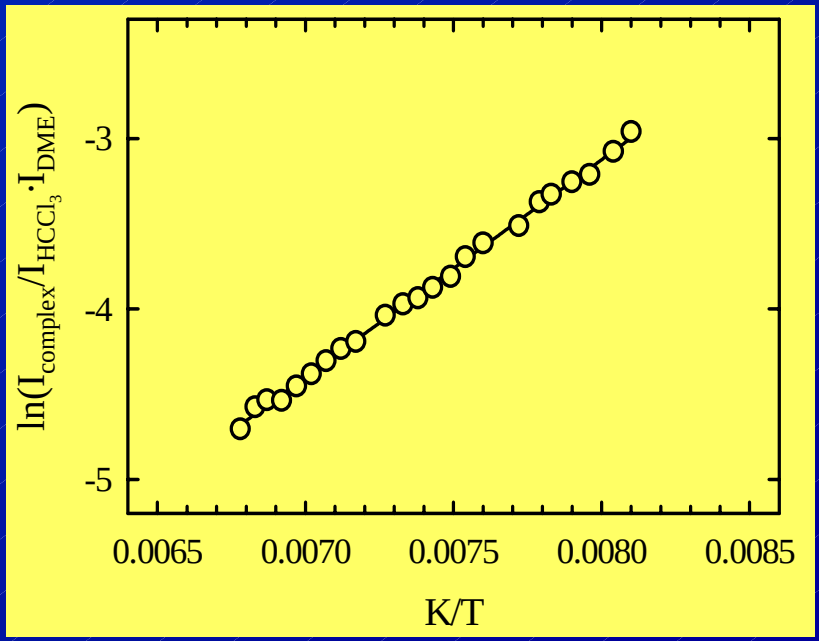

Absorbance
a
b
c
d
3100
3000
2900
2800
Wavenumber / cm-1


Absorbance
A
B
a
b
c
1170
1140
1110
960
940
920
900
Wavenumber / cm-1

What about the relative stability ?

determination of the complexation enthalpy

$$\ln\left[\frac{I_{A_mB_n}}{I_A^{\,m} \times I_B^{\,n}}\right] = -\frac{\Delta H^o}{RT} + c^{st}$$



resulting complexation enthalpies (LKr)

	HCF_3	$HCClF_2$	$HCCl_2F$	$HCCl_3$
$\Delta H°$ / kJ mol^{-1}	-12.5(2)	-12.4(1)	-12.0(2)	-11.1(1)

what do these numbers mean ?

can we convert the complexation enthalpies into complexation energies ?

thermal and zero-point vibrational contributions

Statistical Thermodynamics

solvent effects : $\Delta_{sol}G$, $\Delta_{sol}H$ and $\Delta_{sol}S$

Monte Carlo / Free Energy Perturbation Theory

resulting complexation energies

	HCF_3	$HCClF_2$	$HCCl_2F$	$HCCl_3$
ΔE_{exp} /kJ mol^{-1}	-19.5(10)	-20.8(9)	-23.2(8)	-24.3(5)

MP2/aug-cc-PVTZ calculations including CP corrections

	HCF_3	$HCClF_2$	$HCCl_2F$	$HCCl_3$
ΔE /kJ mol^{-1}	-17.9	-18.9	-20.0	-21.2(5)

W.A. Herrebout, S.N. Delanoye, B.J. van der Veken, *J. Phys. Chem. B, submitted*

Similar results are obtained for acetone and oxirane

acetone	HCF_3	$HCClF_2$	$HCCl_2F$	$HCCl_3$
$\Delta\nu_{C\text{-}H}$ /cm^{-1}	26.7	24.1	15.5	0.6
$\varepsilon_{complex}$ /$\varepsilon_{monomer}$	0.08(1)	0.61(3)	3.8(2)	58(8)

oxirane	HCF_3	$HCClF_2$	$HCCl_2F$	$HCCl_3$
$\Delta\nu_{C\text{-}H}$ /cm^{-1}	24.1	20.7	14.2	1.3
$\varepsilon_{complex}$ /$\varepsilon_{monomer}$	0.13(1)	0.48(2)	4.5(1)	69(14)

S.N. Delanoye , W.A. Herrebout , B.J. van der Veken , *J. Am. Chem. Soc.* 124 (2002) 11854.

complexation energies for acetone

	HCF_3	$HCClF_2$	$HCCl_2F$	$HCCl_3$
ΔE_{exp} /kJ mol^{-1}	-19.1 (6)	-22.1 (4)	-24.3 (5)	-26.0 (6)
ΔE /kJ mol^{-1}	-18.6	-19.6	-20.4	-22.6

complexation energies for oxirane

	HCF_3	$HCClF_2$	$HCCl_2F$	$HCCl_3$
ΔE_{exp} /kJ mol^{-1}	-20.4 (6)	-21.2 (8)	-23.0 (6)	-23.2(4)
ΔE /kJ mol^{-1}	-18.2	-19.6	-20.4	-21.4

W.A. Herrebout, S.N. Delanoye, B.J. van der Veken, *J. Phys. Chem. B, submitted*

Similar results are obtained for CHF_2CF_3 , CHF_2Br , CHF_2I , ...

Some questions remain :

Can we obtain supplementary data by using Raman Spectroscopy ?

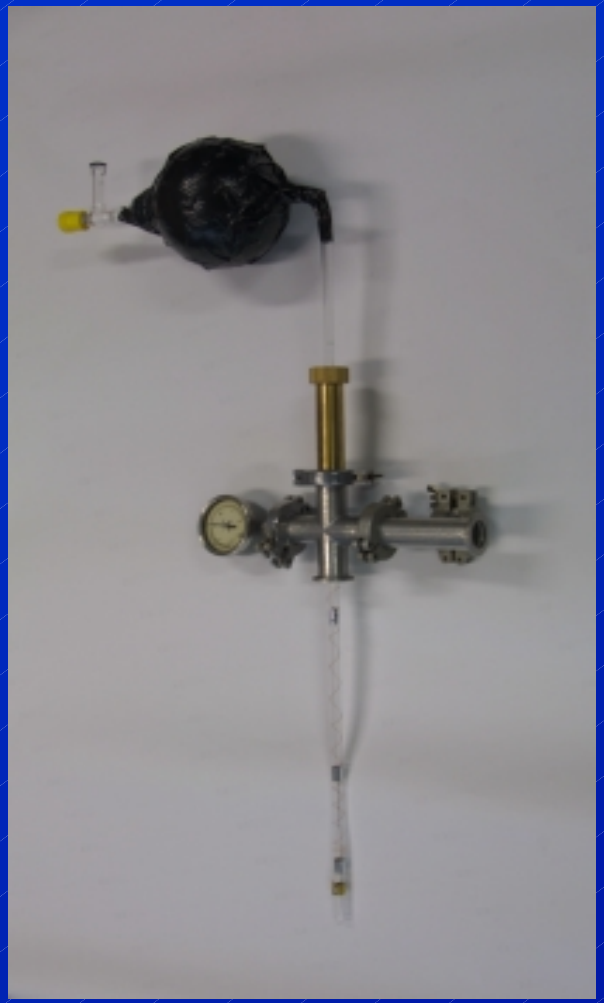
Can we expand the series of proton donors with other species such as CH_2Cl_2, CH_2F_2, CH_3F , ... ?

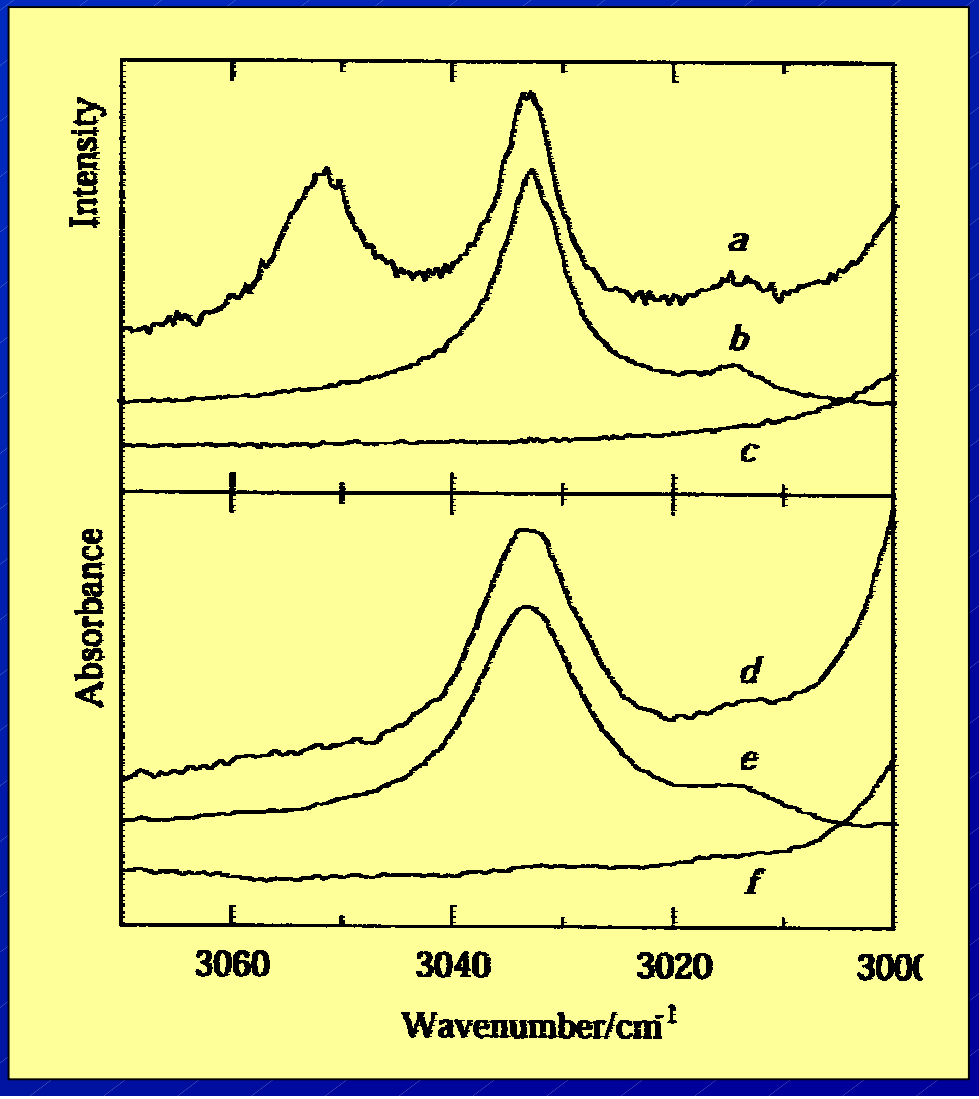
Can we obtain additional information by using Raman Spectroscopy ?

MP2/6-311++G(d,p) ab initio calculations for DME-CHF_3

	monomer	complex
$\Delta\nu_{CH}$ / cm^{-1}	3228.7	3251.1
IR intensity / km mol^{-1}	34.3	2.3
Raman scattering activity / $Å^4$ amu		
	66.1	94.6

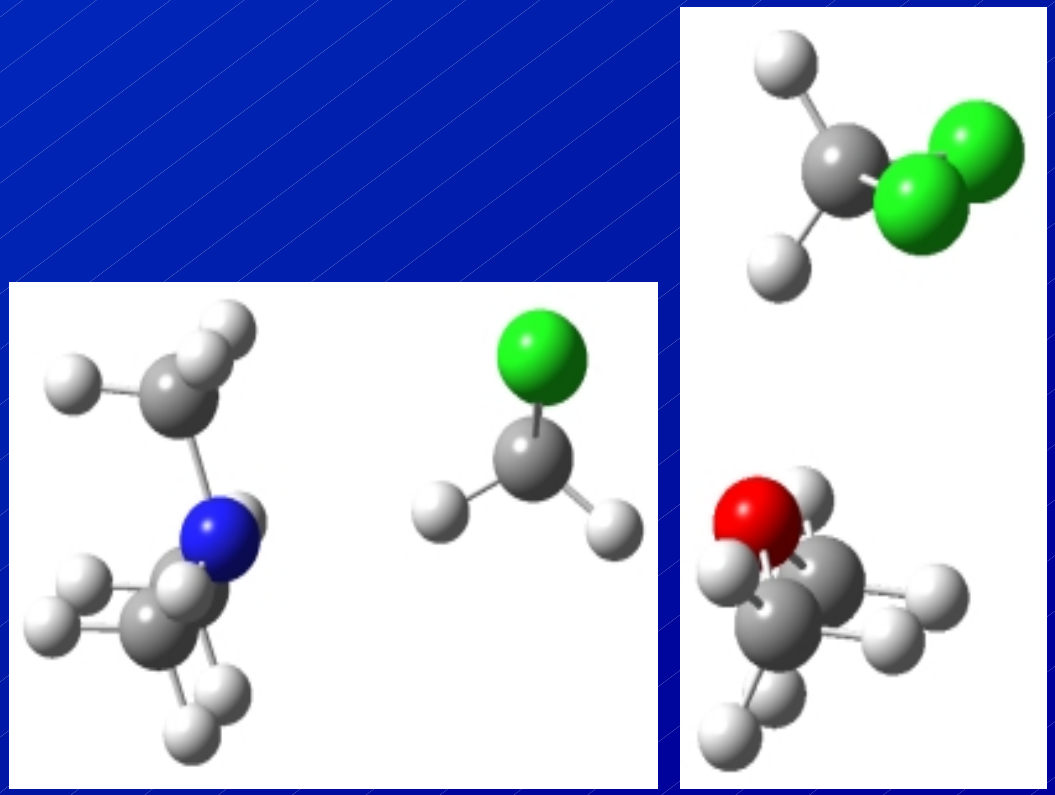
Experimental data obtained for a solution in LKr, at 131 K, containing mole fractions of 0.0008 of DME and CHF_3



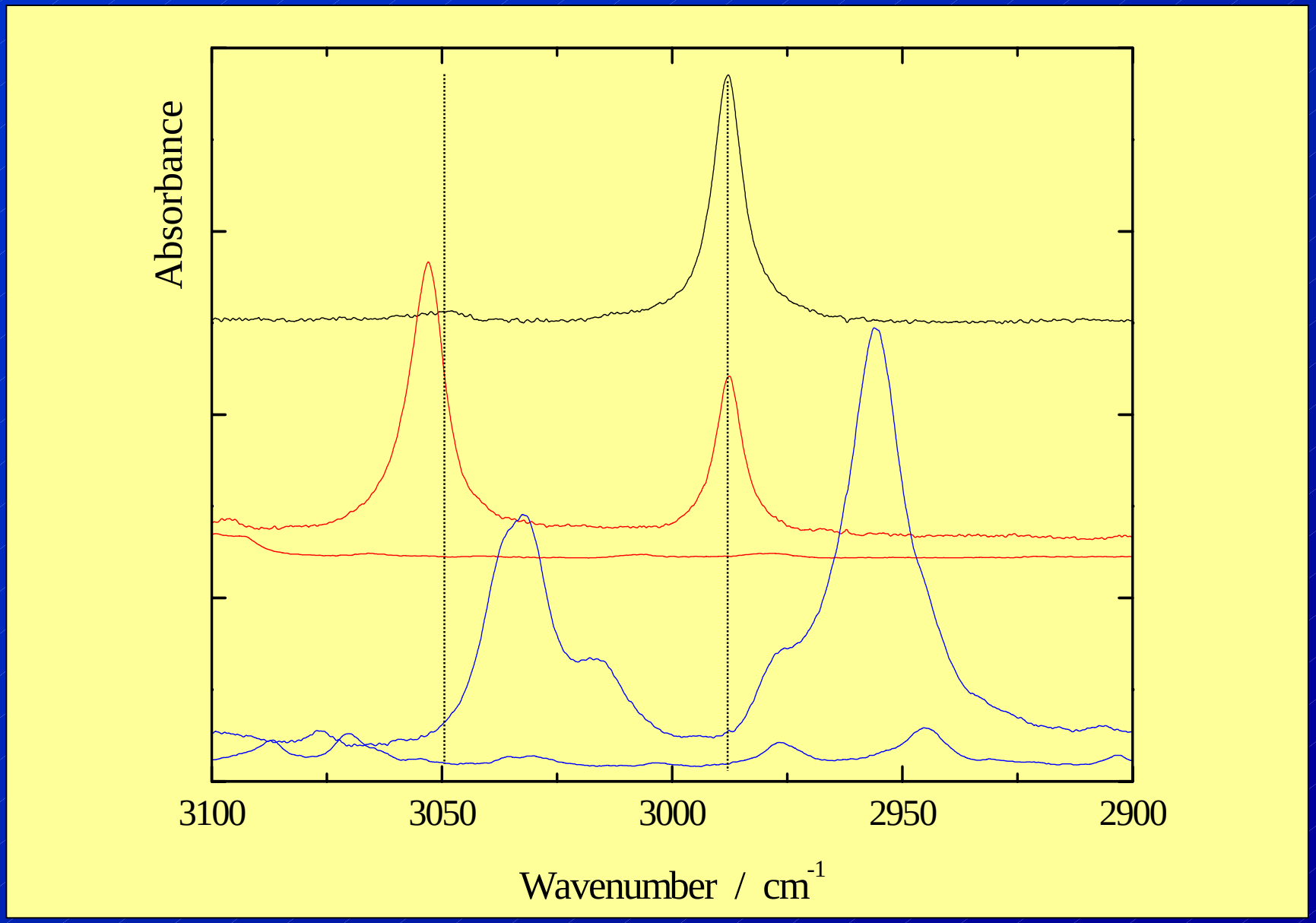


Can we expand the series of proton donors with other species such as CH_2Cl_2, CH_2F_2, CH_3F , …. ?

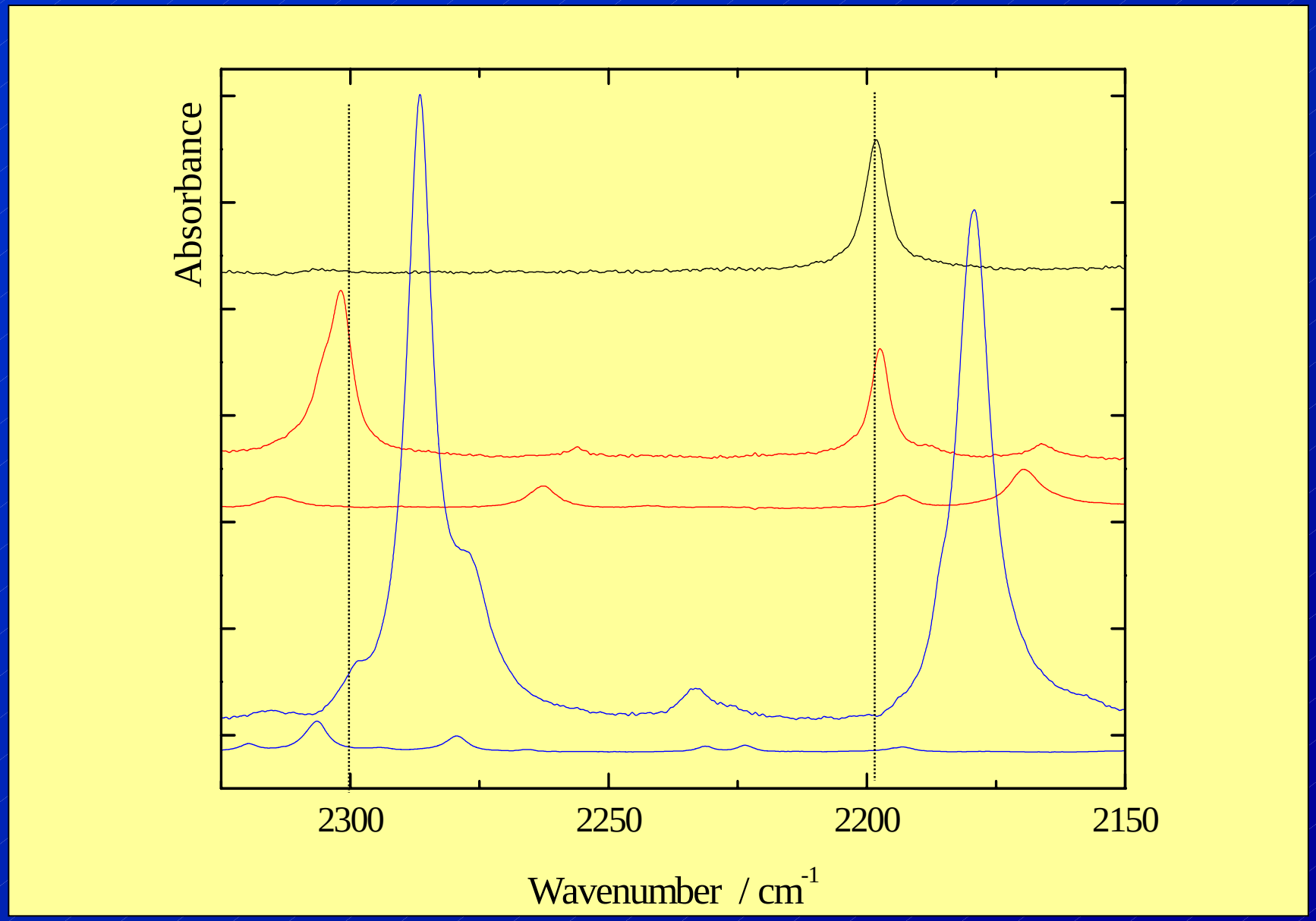
CH...O and CH...N hydrogen bonded complexes of CH_2Cl_2 with Dimethyl Ether and Trimethyl Amine



Solutions in liquid krypton : CH_2Cl_2 with DME-d_6 and TMA-d_9



Solutions in liquid krypton : CD_2Cl_2 with DME and TMA



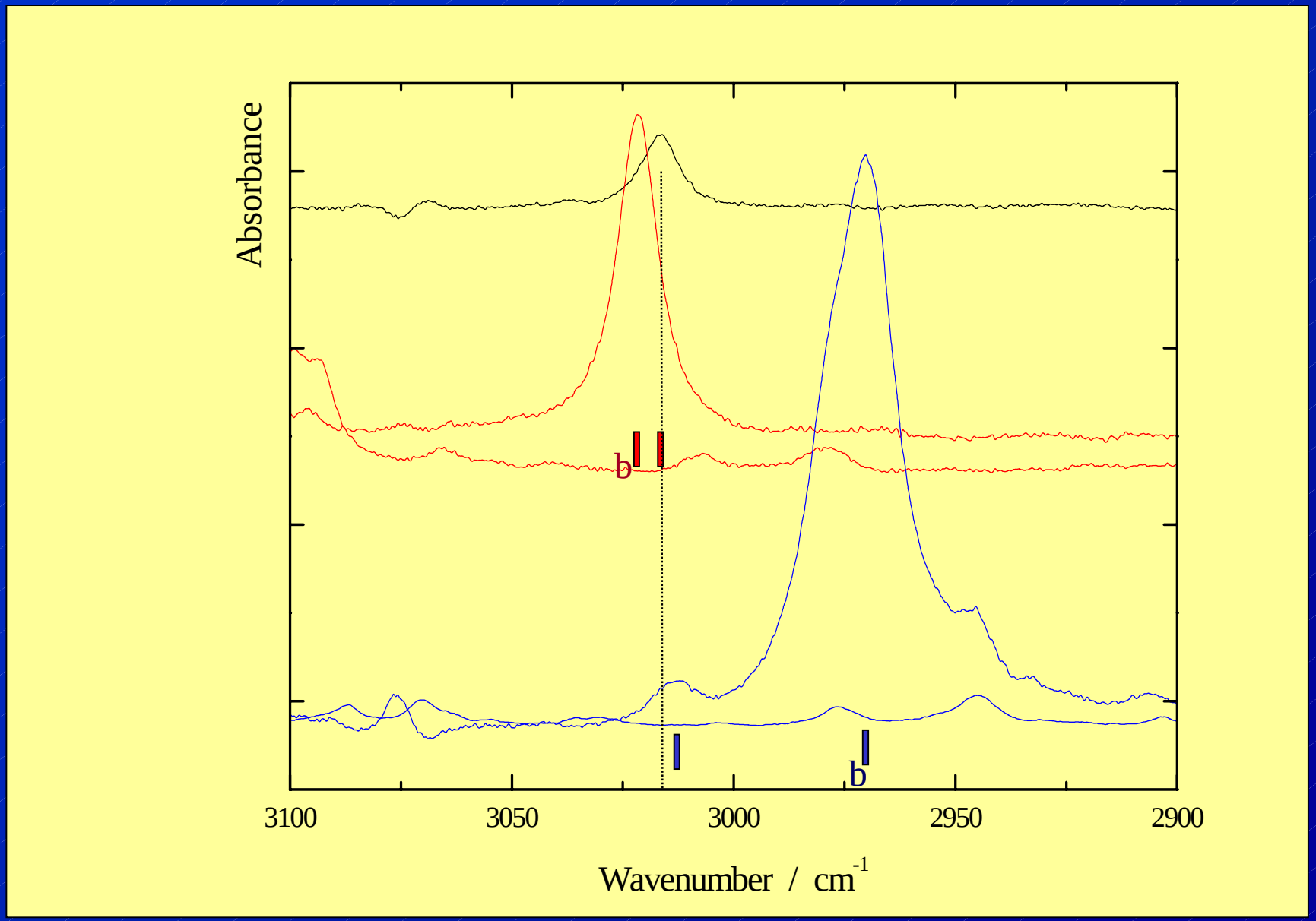
The results obtained for CH_2Cl_2 and CD_2Cl_2 are in excellent agreement with the data reported in

G. Trudeau, J.M. Dumas, P. Dupuis, M. Guerin, C. Sandorfy, Topics in Current Chemistry, 93 (1980) 91.

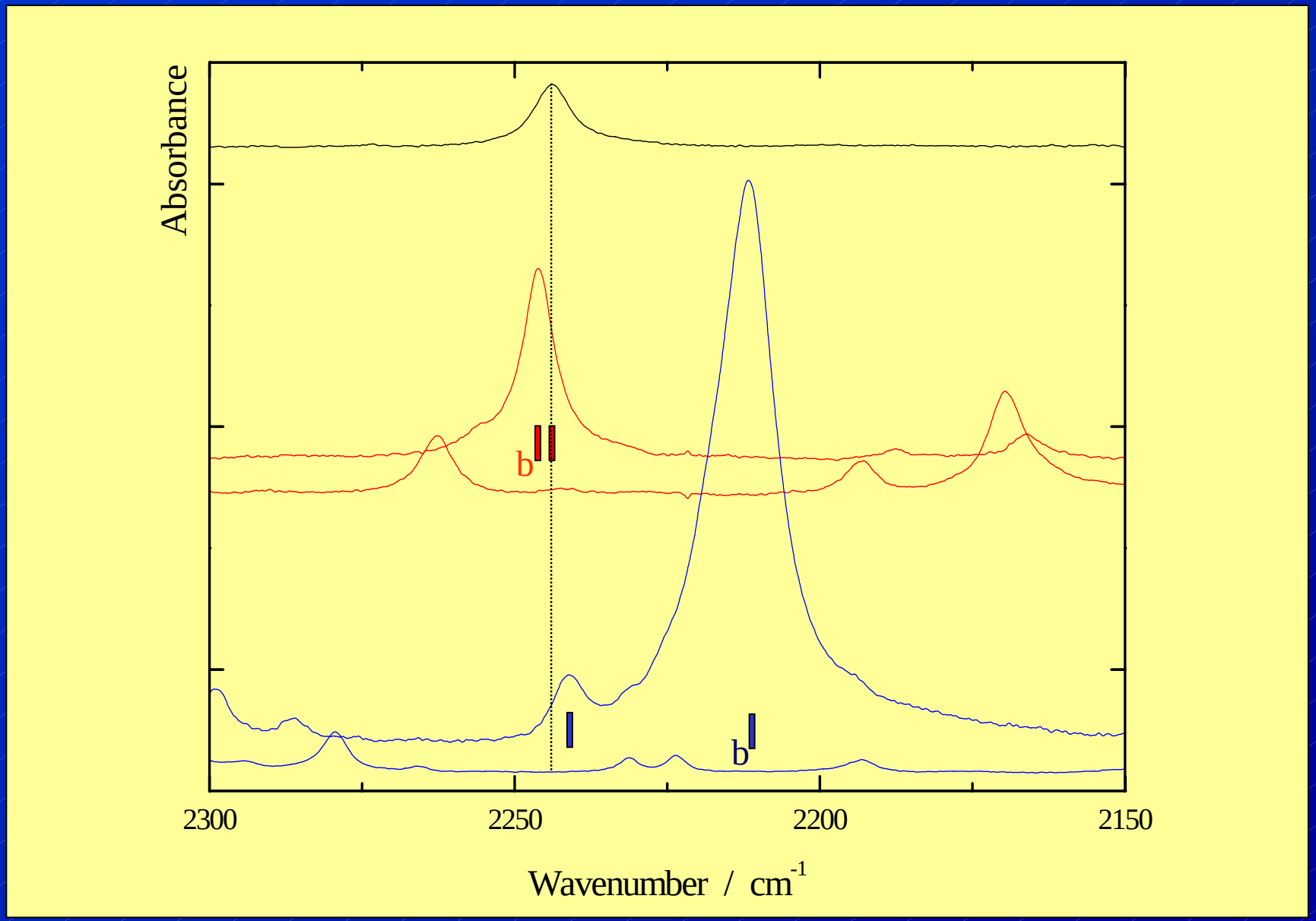
Unfortunately, no separate information on the hydrogen bondend C-H bond and on the 'free' C-H bond is available. These data can be obtained by using the partially deuterated species $CHDCl_2$.

$$CDCl_3 + Zn + \text{concentrated acetic acid} \xrightarrow{-50\ ^\circ C} CHDCl_2$$

Solutions in liquid krypton : isolated CH stretches



Solutions in liquid krypton : isolated CD stretches



Similar results are obtained for the complexes of CH_2F_2 and $CHDF_2$ with Dimethyl ether and Trimethyl amine

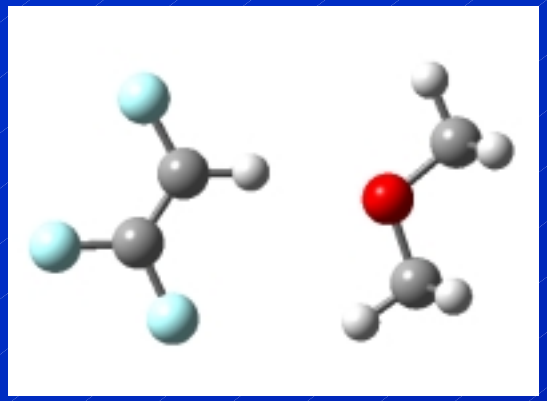
Preliminary data are available for some complexes with CH_3F , $CHDF_2$ and CH_2DF

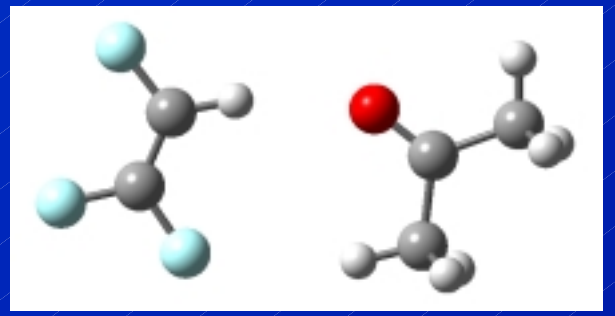
Can we trust our experimental data ?

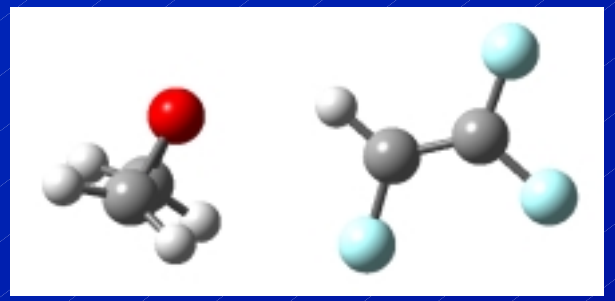
Is a blue shift always caused by a bond strengthening or can other factors interfere ?

$CH\cdots X$ bonded complexes involving C_2HF_3

Equilibrium geometries and predicted frequency shifts *







dimethyl ether	$\Delta\nu_{CH}$ = - 35 cm^{-1}
acetone	$\Delta\nu_{CH}$ = - 16 cm^{-1}
oxirane	$\Delta\nu_{CH}$ = - 11 cm^{-1}

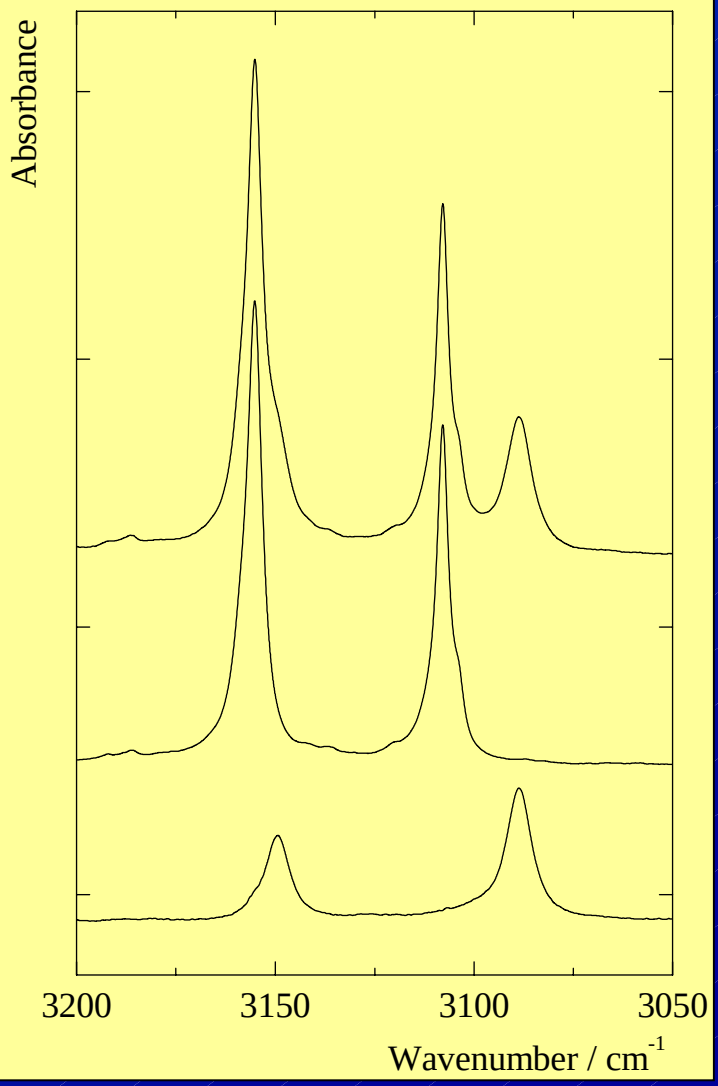
* Obtained using BSSE-corrected gradient techniques, at the MP2/6-31++G(d,p) level

Vibrational Spectra [LKr , -150 °C]

$(CD_3)_2O$ + C_2HF_3

C_2HF_3

complex



Fermi resonance interaction in monomer trifluoroethylene

D.C. McKean [Spectrochimica Acta A, vol. 31, p. 1167]

... a close Fermi resonance dyad 3170 and 3120 cm^{-1}, one component of which is the combination 1362 + 1788 = 3150. The maximum shift possible is 25 cm^{-1}, the most likely one is about 20 cm^{-1} ...

ν_1 CH stretch (A')

ν_2 CC stretch (A') , ν_3 CF stretch (A')

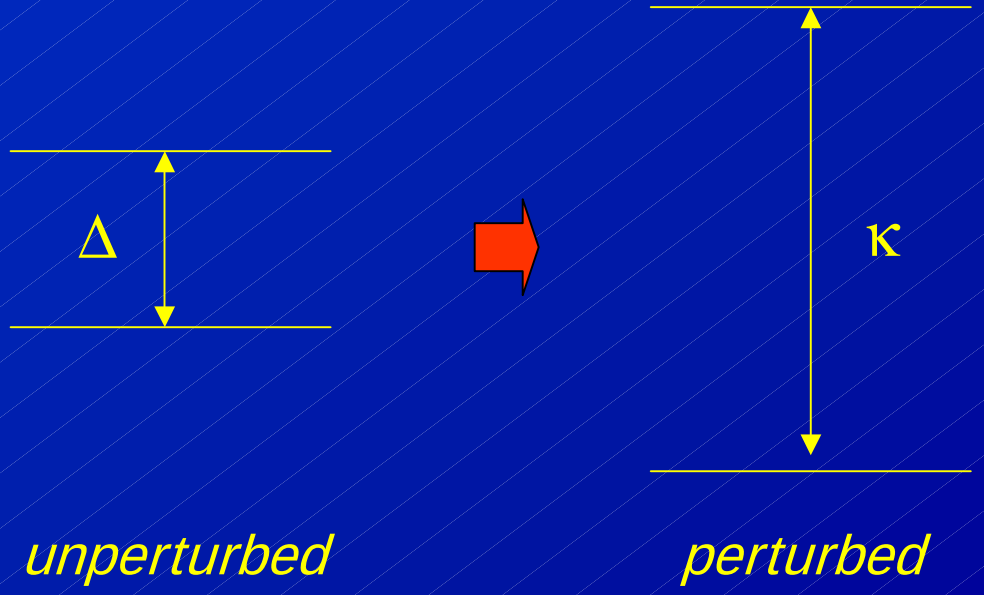
Accurate analysis of the $\nu_1 \sim \nu_2+\nu_3$ Fermi dyad in monomer trifluoroethylene and in the complexes requires knowledge of the corresponding cubic force constant α_{123}

FERMI RESONANCE :

Interaction between two or more energy levels which have identical symmetry

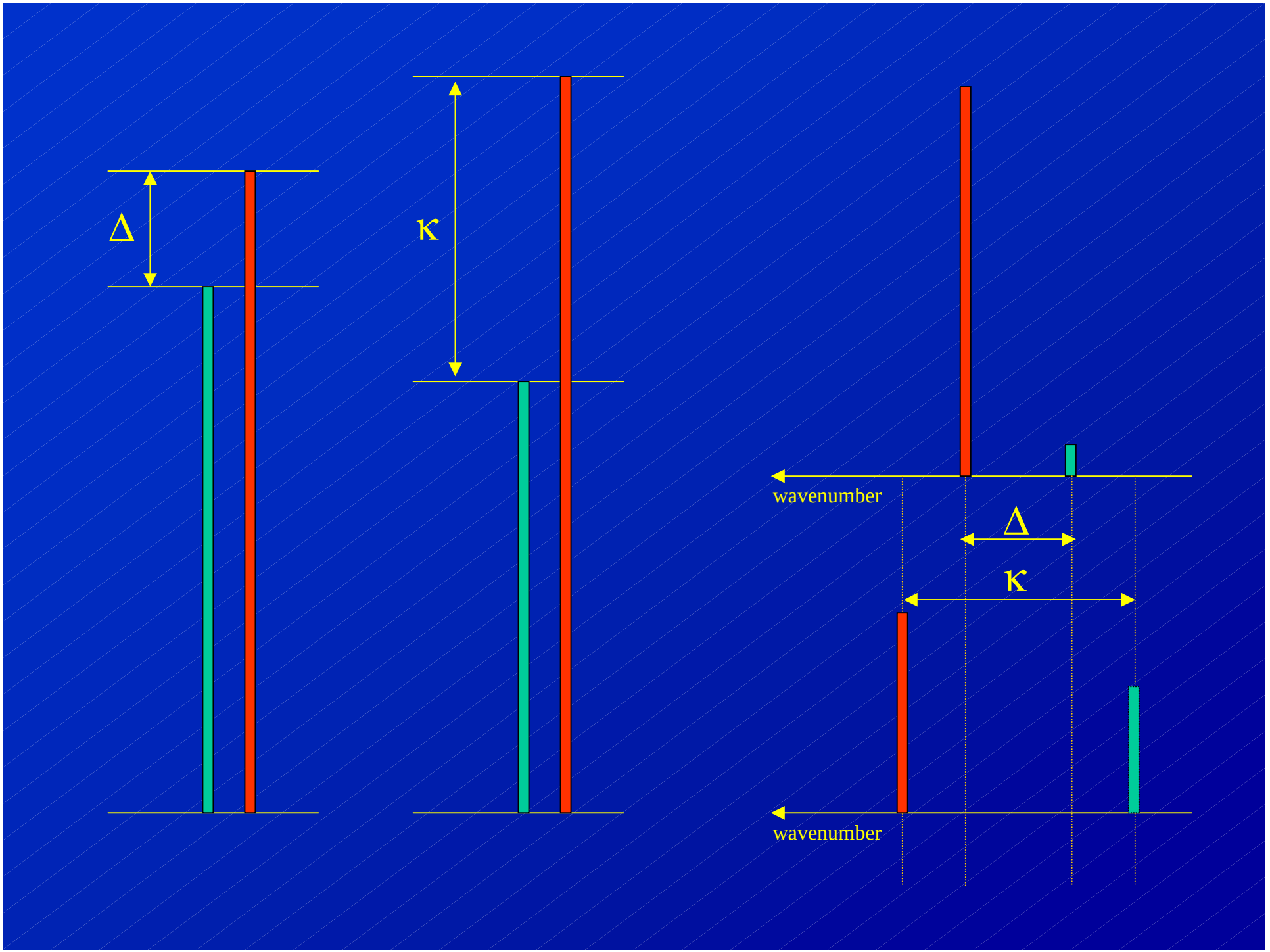
fundamental

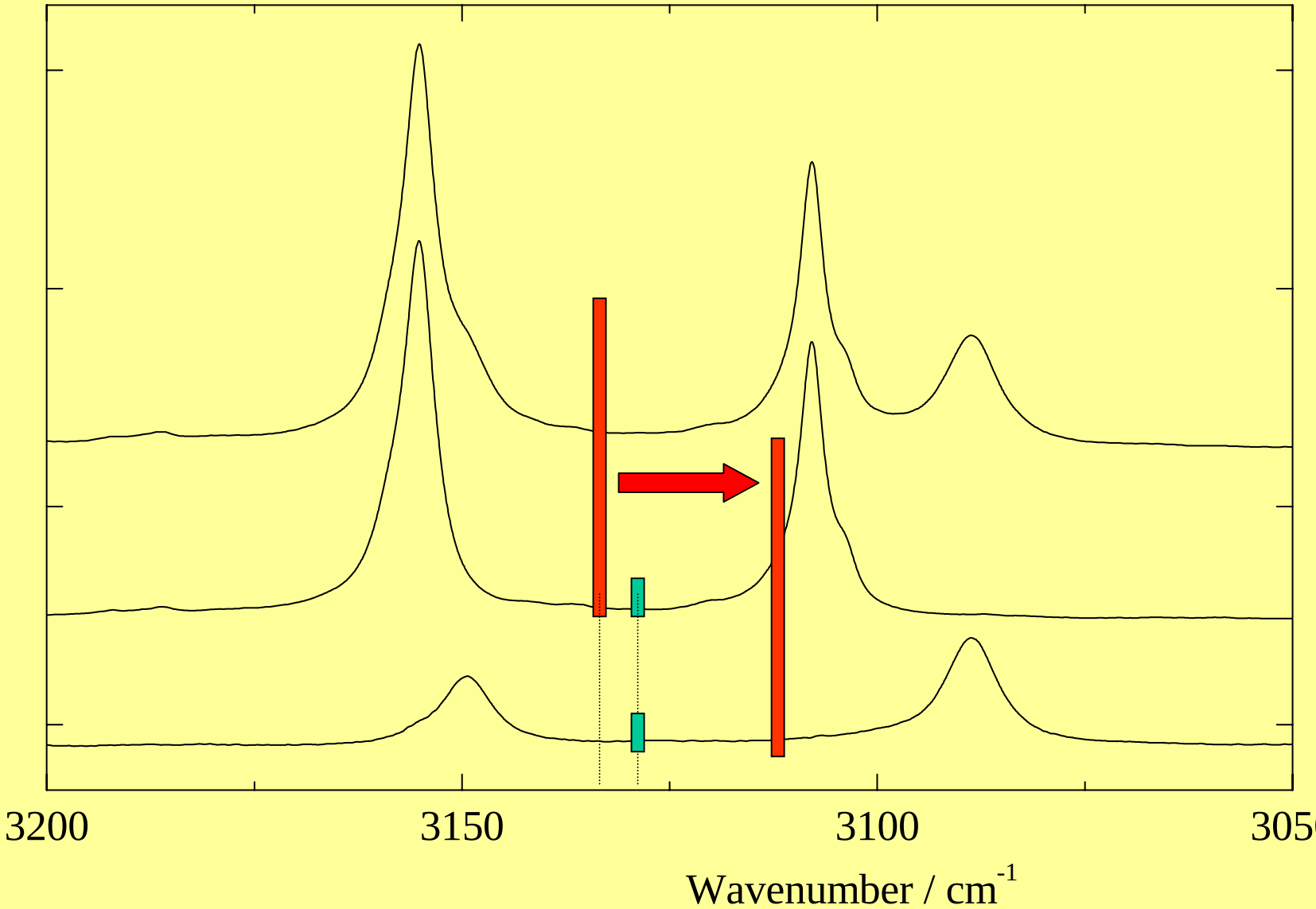
overtone or combination band



unperturbed *perturbed*

$$\Delta^2 = \kappa^2 - 4W^2$$


Δ
κ
wavenumber
Δ
κ
wavenumber


3200
3150
3100
3050
Wavenumber / cm-1

Comparison with calculated values

	MP2/6-31++G(d,p)	Liquid Krypton
dimethyl ether	$\Delta\nu_{CH}$ = - 35 cm^{-1}	$\Delta\nu_1^o$ = -26.3 cm^{-1}
acetone	$\Delta\nu_{CH}$ = - 16 cm^{-1}	$\Delta\nu_1^o$ = -14.7 cm^{-1}
oxirane	$\Delta\nu_{CH}$ = - 11 cm^{-1}	$\Delta\nu_1^o$ = -16.9 cm^{-1}

PSEUDO BLUE-SHIFTING HYDROGEN BONDS

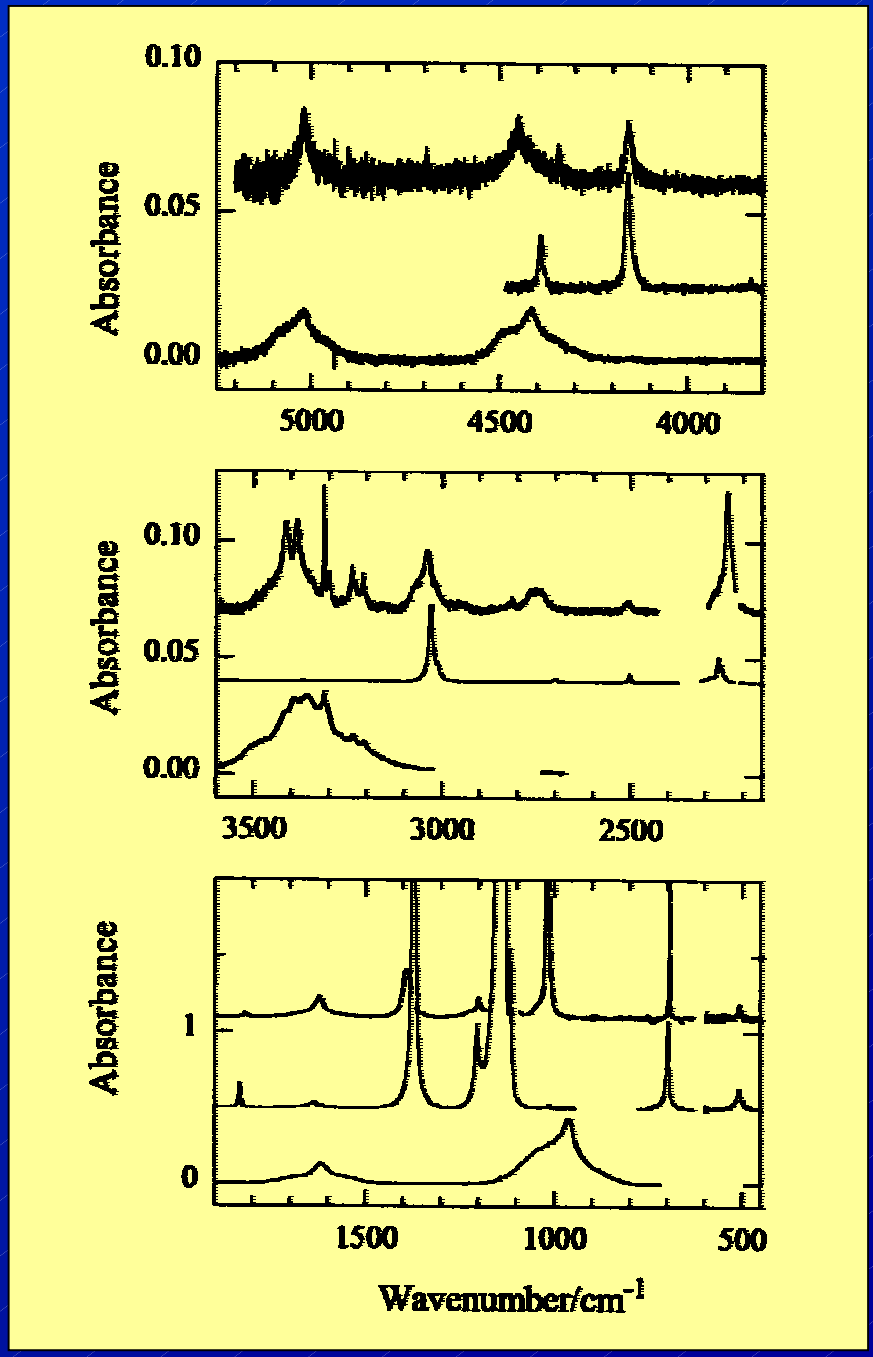
The complex between ammonia and fluoroform has been the subject of many experimental and theoretical studies.

Experimental details obtained for solutions in LXe are described in

Infrared spectra and relative stability of the CHF_3 / NH_3 hydrogen bonded complex in liquefied xenon
K.S. Rutkowski, W.A. Herrebout, S.M. Melikova, P. Rodziewicz, B.J. van der Veken, A. Koll, Spectrochimica Acta part A 61 (2005) 1595-1602

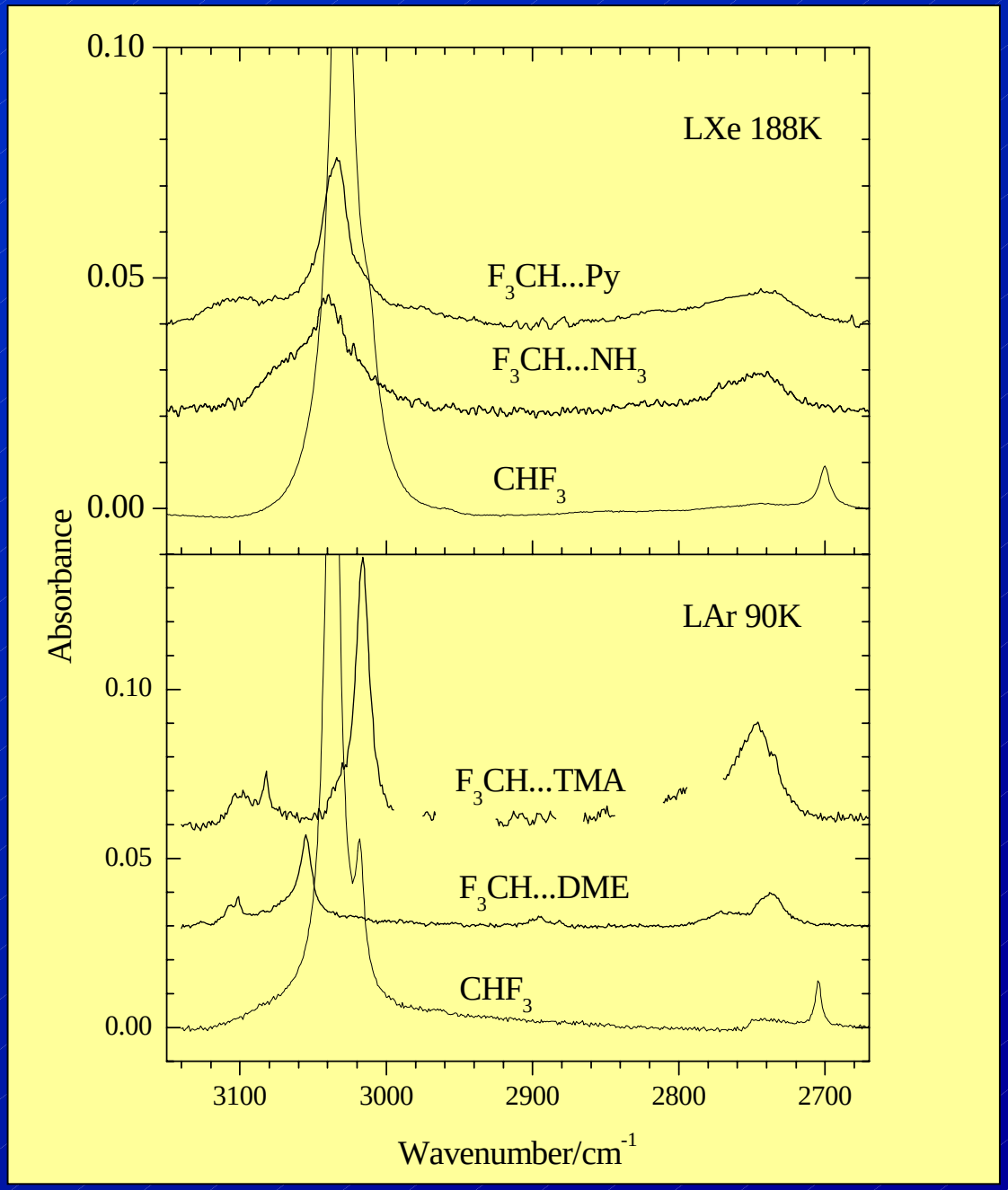
A cryosolution infrared study of the complexes of fluoroform with ammonia and pyridine : Evidence for a C-H...N pseudo blue-shifting hydrogen bond
W. A. Herrebout, S.M. Melikova, S.N. Delanoye, K.S. Rutkowski, D.N. Shchepkin, B.J. van der Veken, J. Phys. Chem. A 109 (2005) 3038-3044

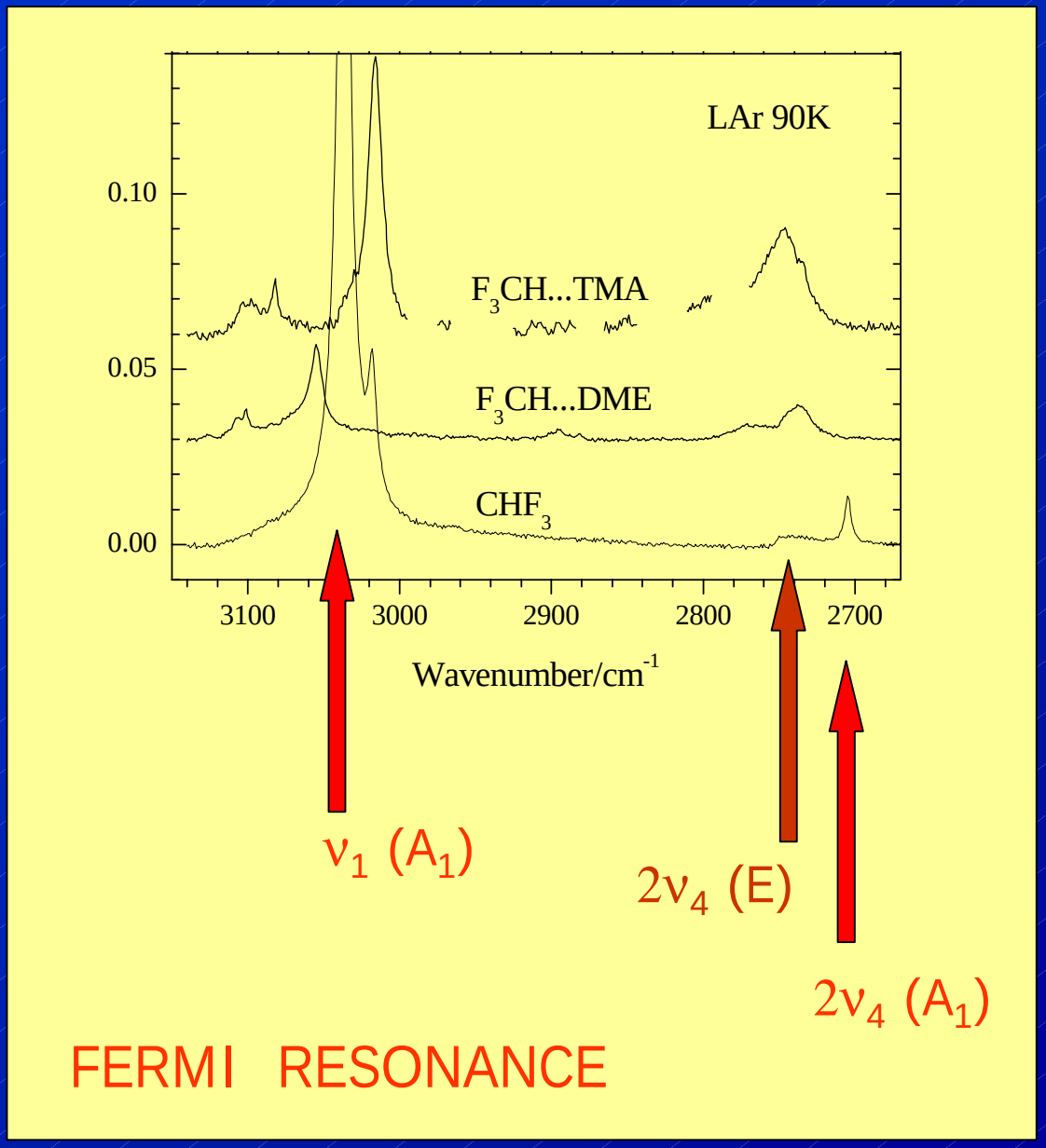
Survey infrared spectra of CHF_3-NH_3 (top), CHF_3 (middle) and NH_3 (bottom) in LXe, at 172K.



For the complexes with NH_3 and pyridine-d_5 a blue shift is observed !

Reason ??

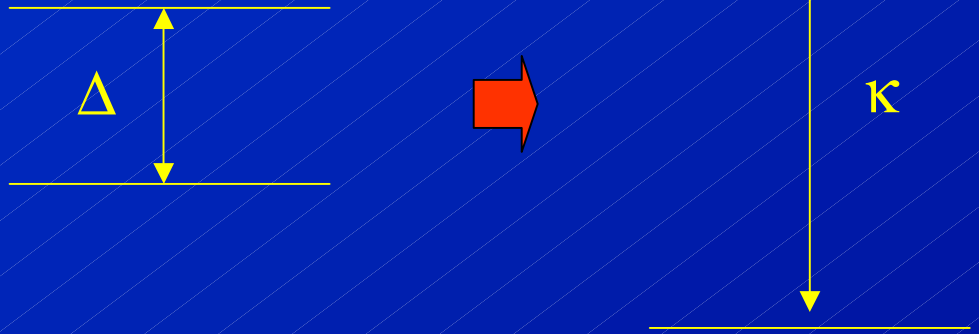



LAr 90K
0.10
0.05
0.00
F3CH...TMA
F3CH...DME
CHF3
3100
3000
2900
2800
2700
Wavenumber/cm-1
ν1 (A1)
2ν4 (E)
2ν4 (A1)
FERMI RESONANCE

FERMI RESONANCE in monomer CHF_3

ν_1 (A_1)

$2\nu_4$ (A_1)



unperturbed *perturbed*

coupling parameter W ?

$$\Delta^2 = \kappa^2 - 4W^2$$

The potential energy for CHF_3 as a function of Q_1 , X_4 and Y_4 can be written as

$$V/hc = \frac{1}{2}\omega_1 Q_1^{\,2} + \frac{1}{2}\omega_4 \left(X_4^{\,2} + Y_4^{\,2} \right) + \alpha_{111} Q_1^{\,3} + \alpha_{144} Q_1 (X_4^{\,2} + Y_4^{\,2})$$

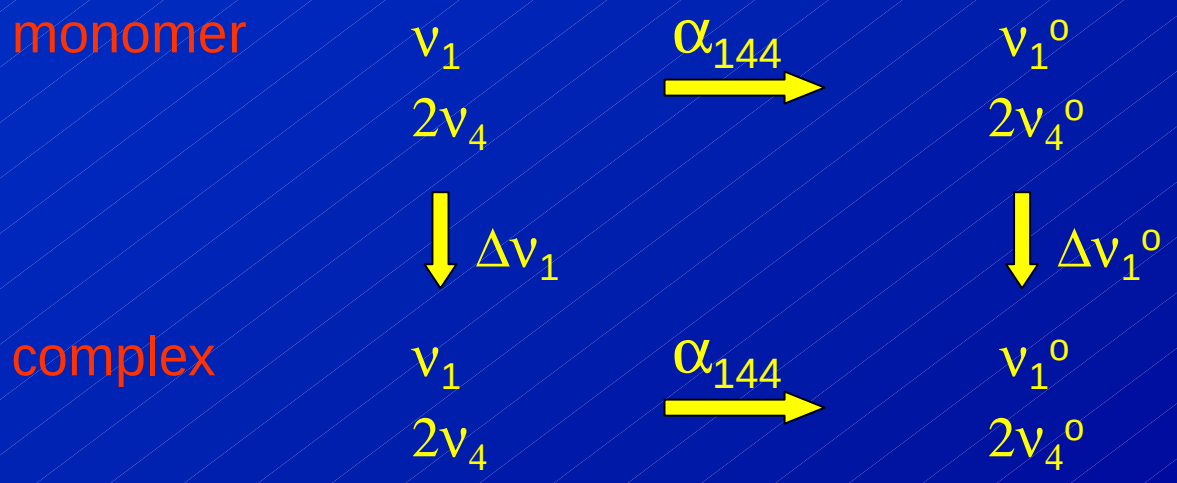
$$+ \beta_{1111} Q_1^{\,4} + \beta_{1144} Q_1^{\,2} (X_4^{\,2} + Y_4^{\,2}) + \beta_{4444} (X_4^{\,2} + Y_4^{\,2})^2 + \ldots$$

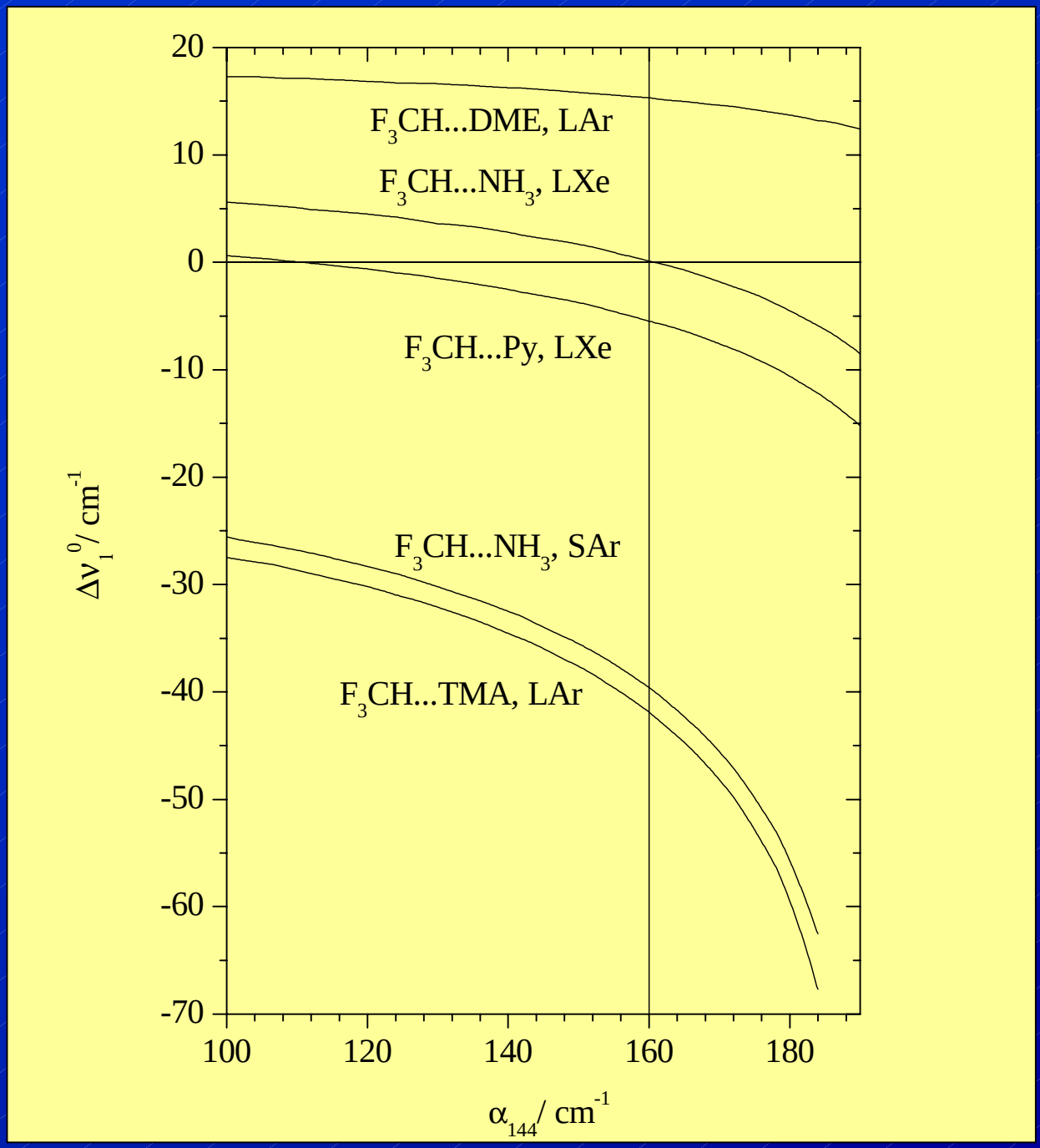
$$W = \left\langle 10 \middle| V \middle| 02^0 \right\rangle = -\frac{1}{\sqrt{2}} \alpha_{144}$$

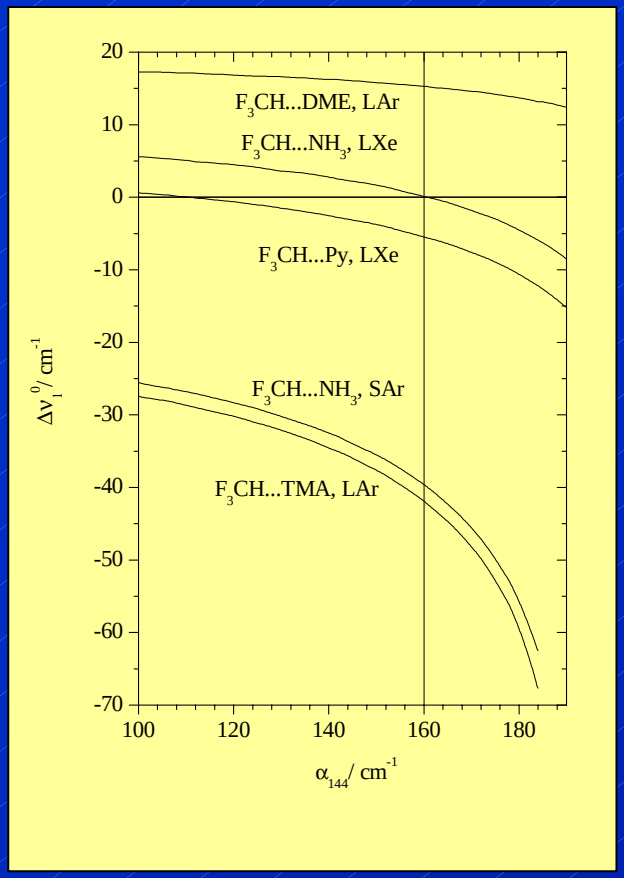
ν_1 (A_1) $\quad$ $2\nu_4$ (A_1)

How does the ν_1 / $2\nu_4$ Fermi resonance influence the red- or blue-shifting properties of ν_1 ?

The perturbed frequencies for ν_1 and $2\nu_4$ observed for monomer CHF_3 and those observed for the complexes can be converted into their unperturbed frequencies ν_1^o and $2\nu_4^o$ if the cubic force constant α_{144} is known accurately.




20
10
0
-10
-20
-30
-40
-50
-60
-70
100
120
140
160
180
$\Delta\nu_1^0$ / cm^{-1}
α_{144} / cm^{-1}
F_3CH...DME, LAr
F_3CH...NH_3, LXe
F_3CH...Py, LXe
F_3CH...NH_3, SAr
F_3CH...TMA, LAr



ammonia – fluoroform

$\Delta\nu_1$ = + 7.6 cm^{-1}

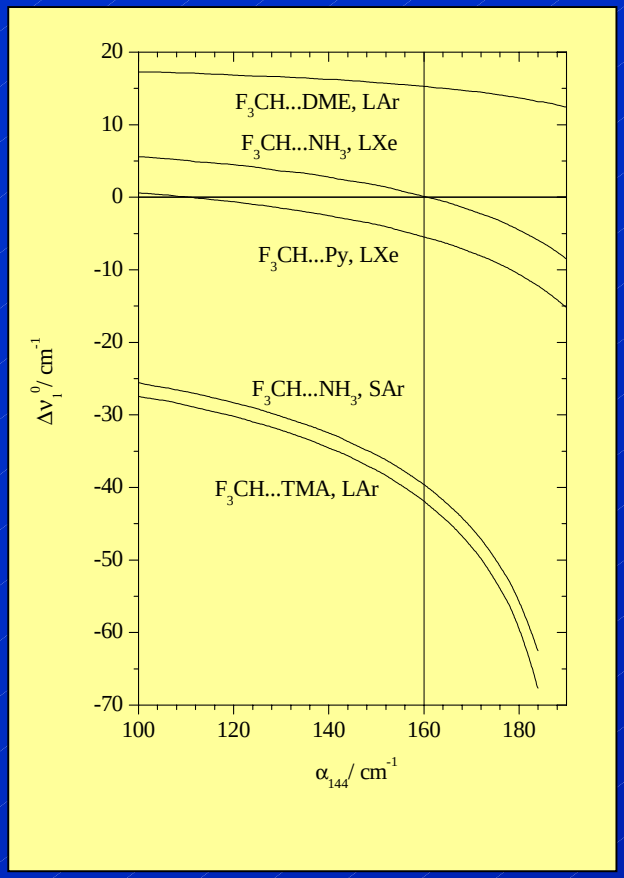
$\Delta\nu_1^0$ = -0.3 (6) cm^{-1}

pyridine – fluoroform

$\Delta\nu_1$ = + 3.0 cm^{-1}

$\Delta\nu_1^0$ = -6.0 (6) cm^{-1}

pseudo - blue-shifting hydrogen bond



dimethyl ether – fluoroform

$\Delta\nu_1$ = + 18.1 cm^{-1}

$\Delta\nu_1^0$ = +15.1 (4) cm^{-1}

trimethyl amine – fluoroform

$\Delta\nu_1$ = -22.8 cm^{-1}

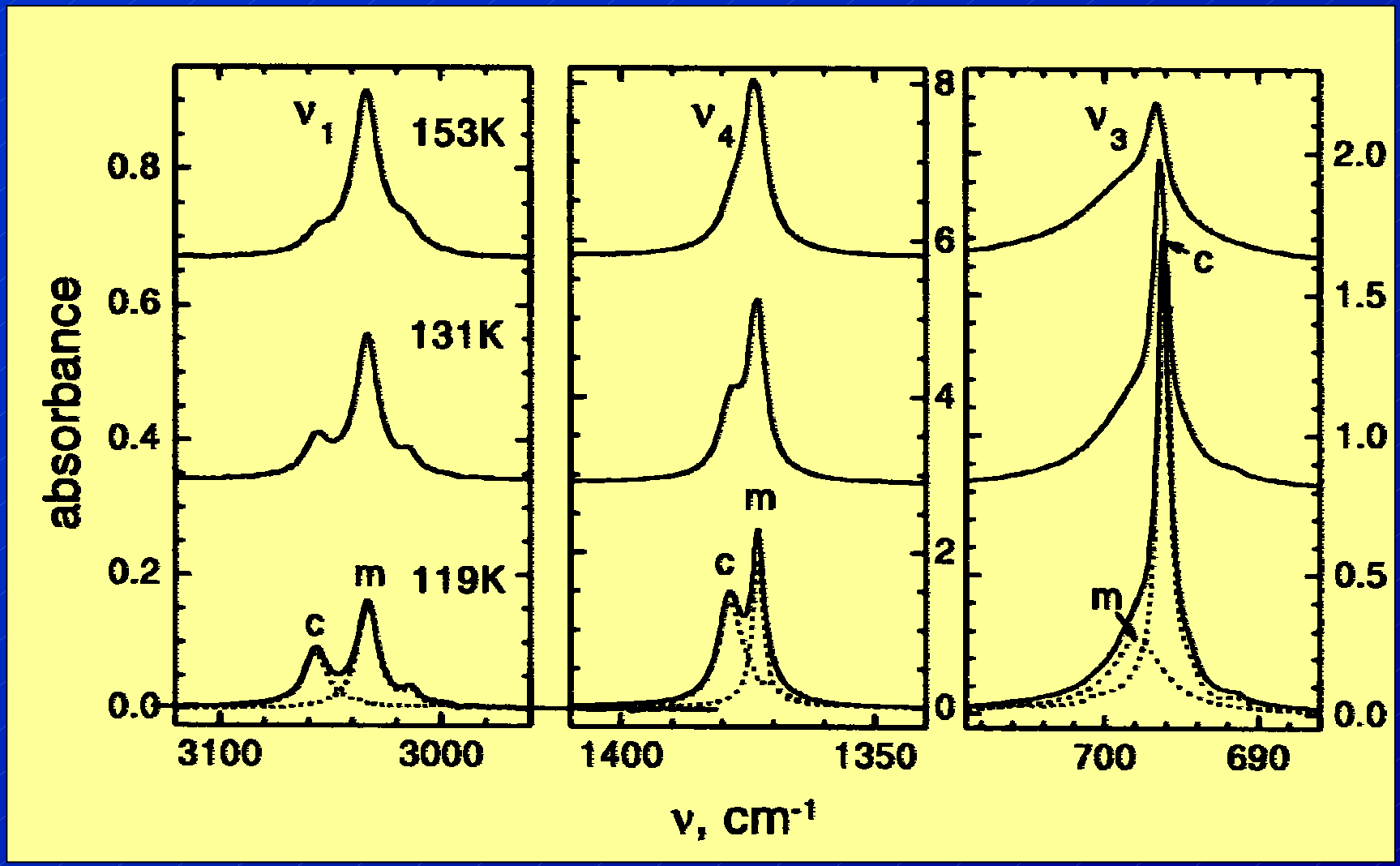
$\Delta\nu_1^0$ = -43.5 (6) cm^{-1}

SO FAR, WE HAVE CONCENTRATED ON CH… O AND CH… N HYDROGEN BONDED SPECIES

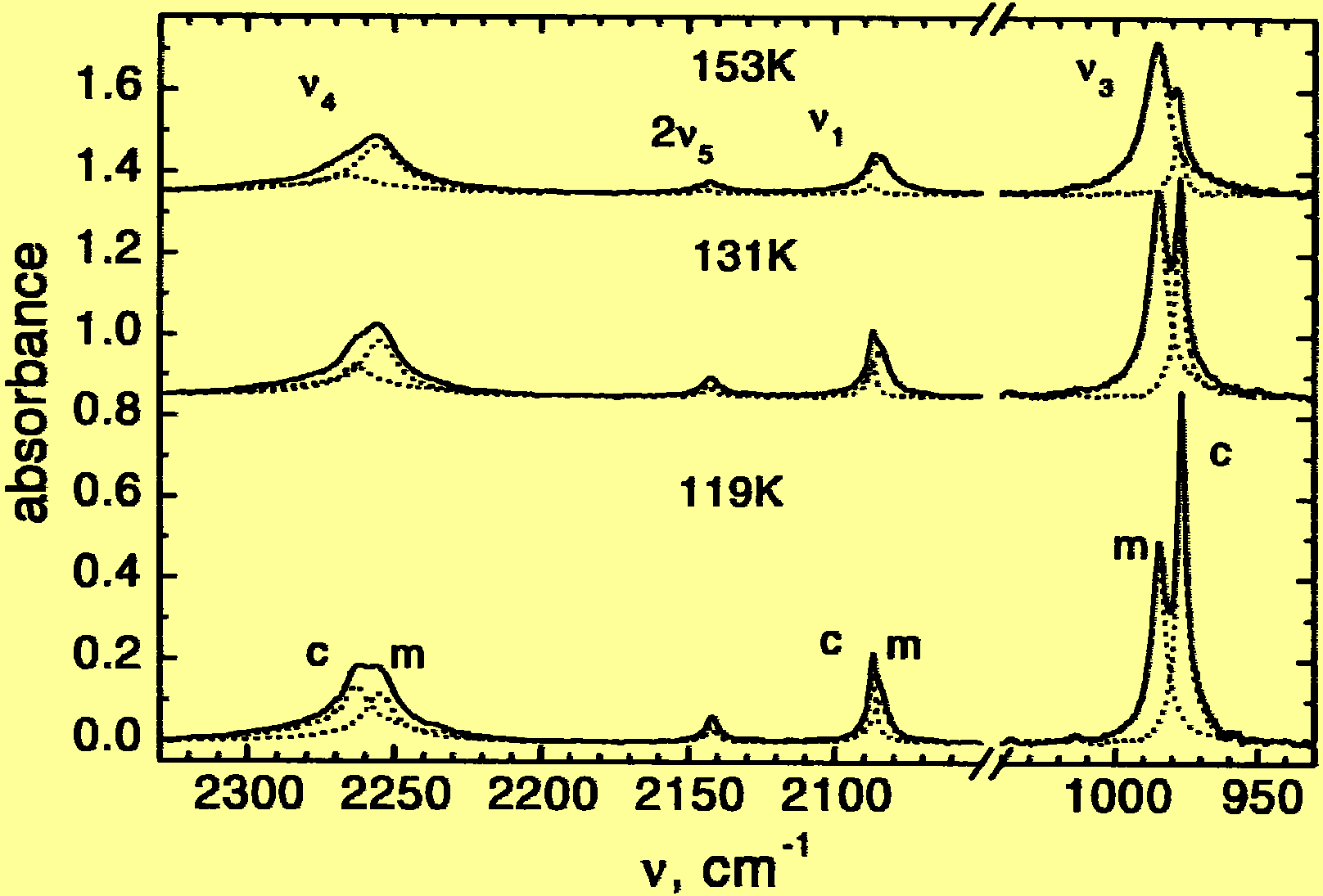
CAN SIMILAR DATA BE OBTAINED FOR OTHER CH… X INTERACTIONS ?

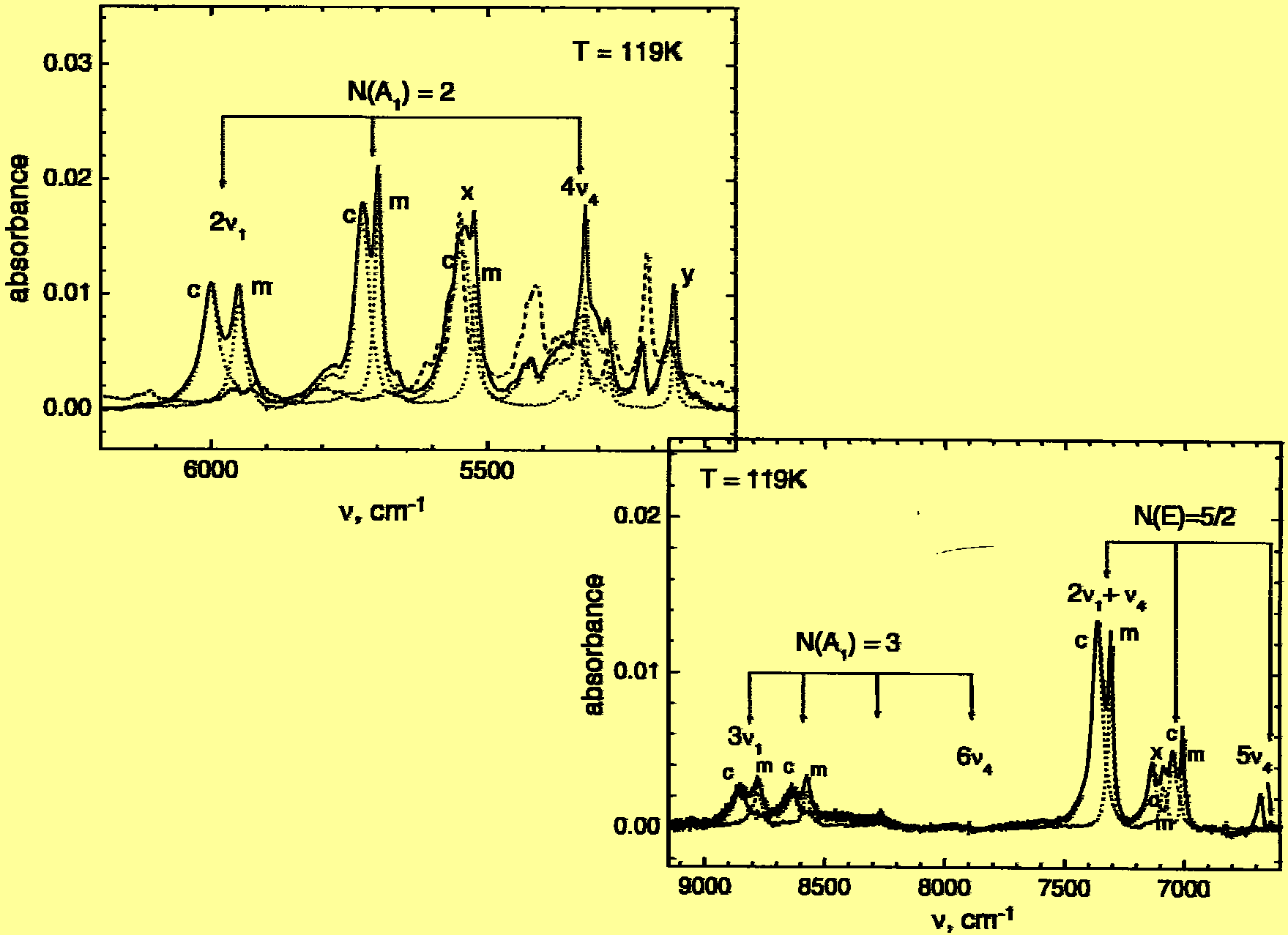
CAN WE INCLUDE DATE FROM THE NEAR INFRARED ?

Complexes of Fluoroform with CD_3F

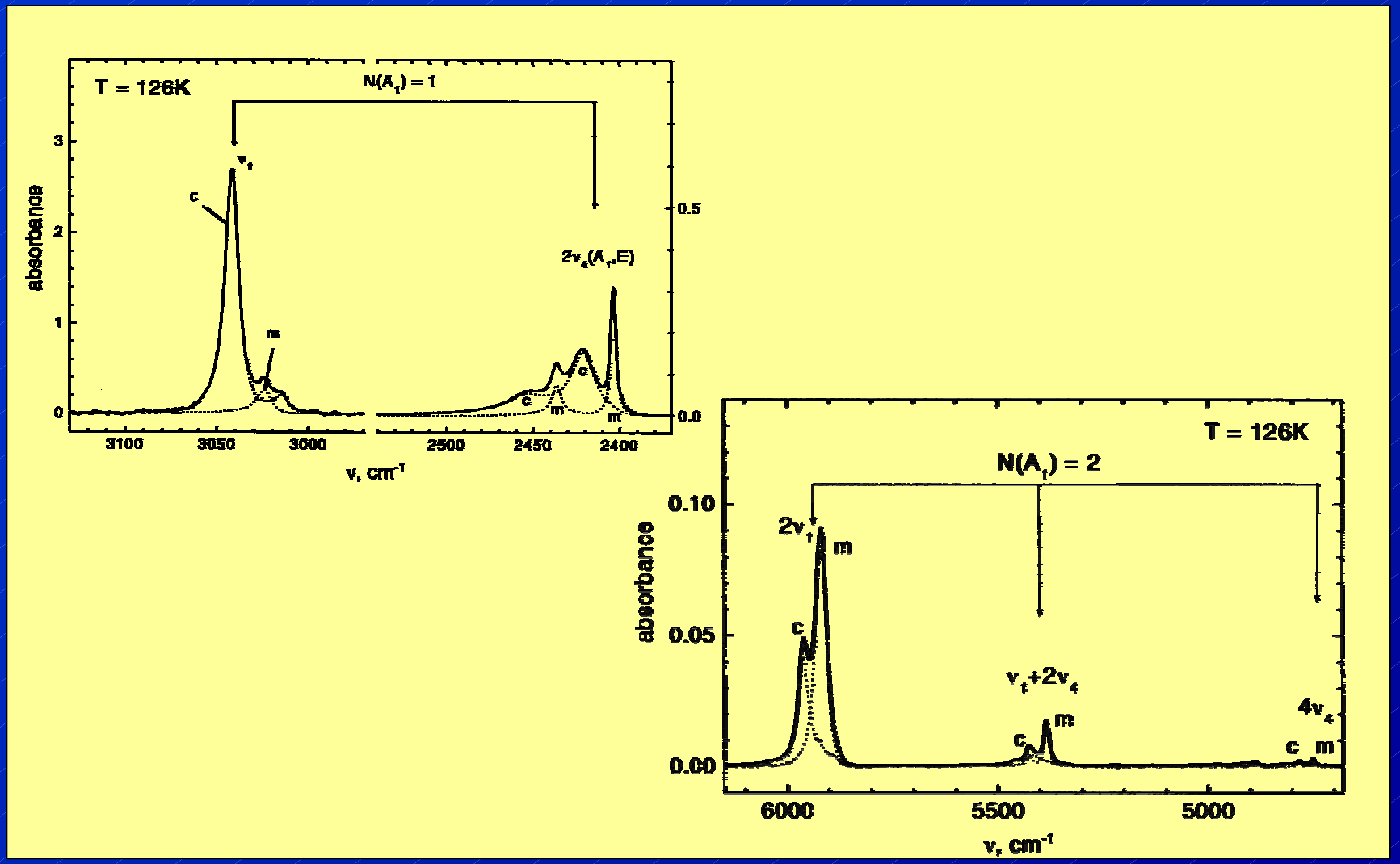


K.S. Rutkowski, P. Rodziewicz, S.M. Melikova, W.A. Herrebout, B.J. van der Veken, A. Koll, *Chem. Phys.* 313 (2005) 225-243.

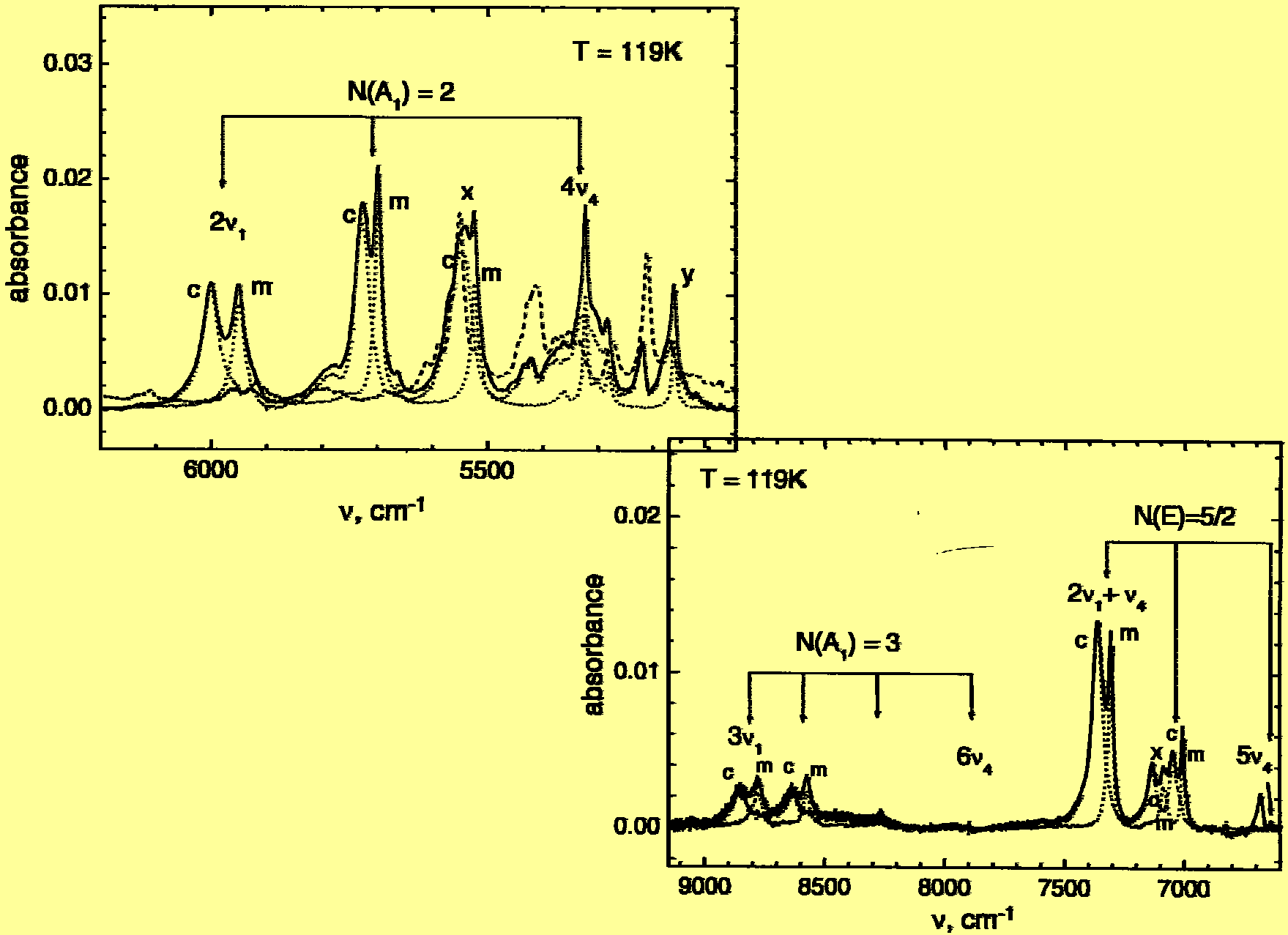

153K
131K
119K
ν_4
$2\nu_5$
ν_1
ν_3
c
m
absorbance
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
2300
2250
2200
2150
2100
1000
950
ν, cm^{-1}


T = 119K
N(A1) = 2
2ν1
4ν4
c
m
x
y
absorbance
0.03
0.02
0.01
0.00
6000
5500
ν, cm-1
T = 119K
N(E)=5/2
N(A1) = 3
3ν1
6ν4
2ν1+ ν4
5ν4
absorbance
0.02
0.01
0.00
9000
8500
8000
7500
7000
ν, cm-1

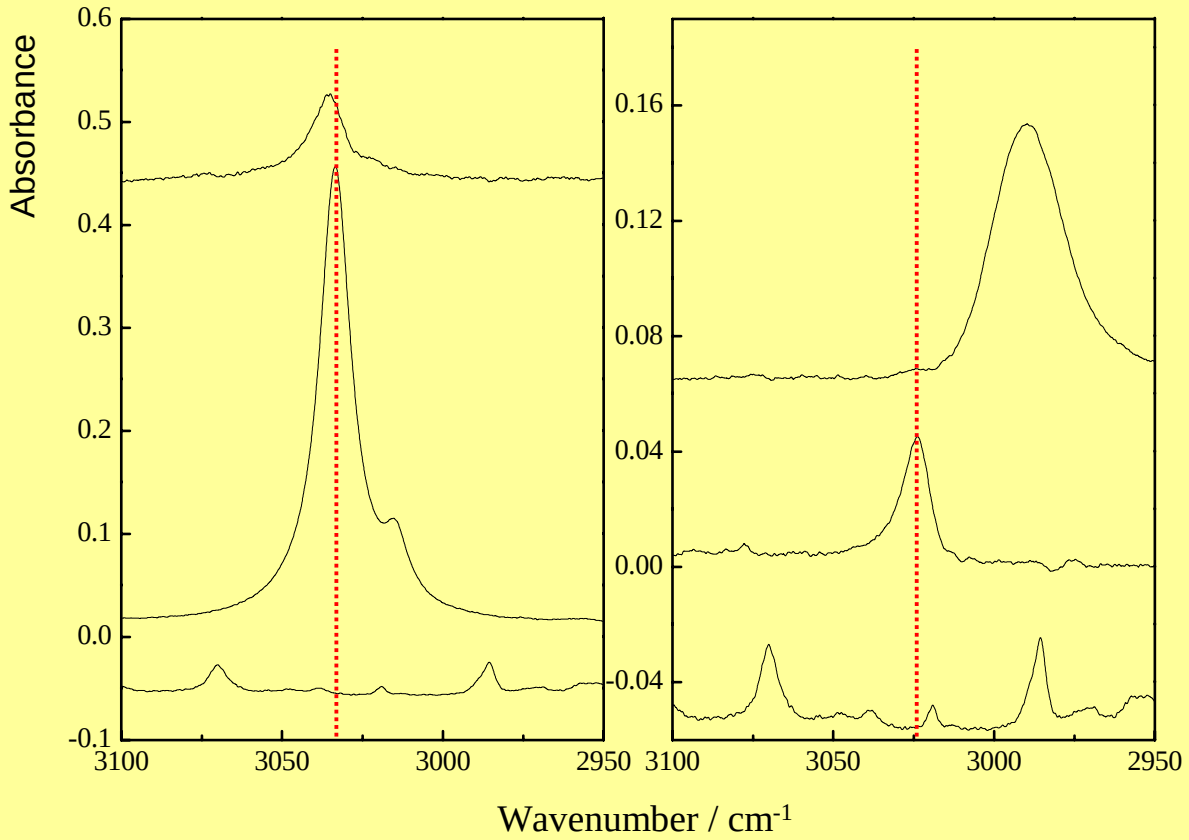
Complexes of Chloroform with CD_3F



K.S. Rutkowski, P. Rodziewicz, S.M. Melikova, W.A. Herrebout, B.J. van der Veken, A. Koll, *Chem. Phys.* 313 (2005) 225-243.


T = 119K
N(A1) = 2
2ν1
4ν4
c
m
x
y
absorbance
0.03
0.02
0.01
0.00
6000
5500
ν, cm-1
T = 119K
N(E)=5/2
N(A1) = 3
3ν1
6ν4
2ν1+ ν4
5ν4
absorbance
0.02
0.01
0.00
9000
8500
8000
7500
7000
ν, cm-1

Complexes of CHF_3 and $CHCl_3$ with CD_3SCD_3



By correcting for the $\nu_1/2\nu_4$ Fermi resonance in CHF_3, the observed blue shift of 3.8 cm^{-1} is converted into a red shift of -3 cm^{-1}

evidence for a pseudo blue shifting CH...S hydrogen bond ??

So far, the experimental data for DMS-CHF_3 strongly contrast with theoretical derived from ab initio calculations

	DMS-CHF_3	DMS-$CHCl_3$
MP2/6-31G(d,p)	+24.4	-12.6
MP2/6-31++G(d,p)	+19.4	-13.7
MP2/6-31++G(2d,2p)	+19.6	-31.7
MP2/6-311G(d,p)	+22.3	-14.6
MP2/6-311++G(d,p)	+21.4	-15.4
MP2/6-311++G(2d,2p)	+15.1	-39.3
Experimental value *	-3 (1)	-34 (1)

* Values obtained after correction for the $\nu_1/2\nu_4$ Fermi resonance in CHF_3.

The experimental data obtained for DMS-CHF_3 and DMS-$CHCl_3$ are in line with preliminary data obtained for the mixed haloforms CHF_2Cl and $CHFCl_2$

	before correction	after correction
DMS-CHF_3	+3.8 cm^{-1}	-3 (1) cm^{-1}
DMS-CHF_2Cl	-4.4 cm^{-1}	
DMS-$CHFCl_2$	-15.6 cm^{-1}	
DMS-$CHCl_3$	-32.8 cm^{-1}	-34 (1) cm^{-1}

ACKNOWLEDGMENT

PROF. DR. BEN VAN DER VEKEN

PROF. DR. BERT MAES

DR. TOM VAN DEN KERKHOF

DR. SOFIE DELANOYE

DR. KOSTIA RUTKOWSKI

DR. SONIA MELIKOVA

JEF VAN GILS

AZAT GATIN

DIETER HAUCHECORNE

BART MICHIELSEN

FUND FOR SCIENTIFIC RESEARCH – FLANDERS (FWO-VLAANDEREN)

FLEMISH COMMUNITY

BIJZONDER ONDERZOEKSFONDS

IMPULSFINANCIERING GROTE APPARATUUR 2004

UNIVERSITY OF ANTWERP

KLEINE PROJECTEN