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Blue-Shifting Hydrogen Bonds

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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.

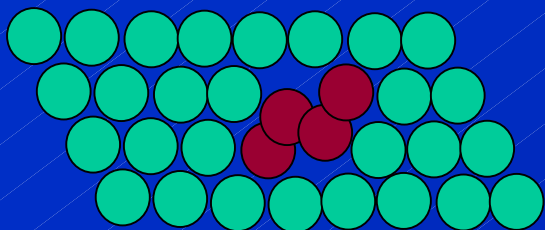
B.J. van der Veken, W.A. Herrebout, R. Szostak, D.N. Shchepkin, Z. Havlas, P. Hobza, J. Am. Chem. Soc. 123 (2001) 12290

SUMMARY

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

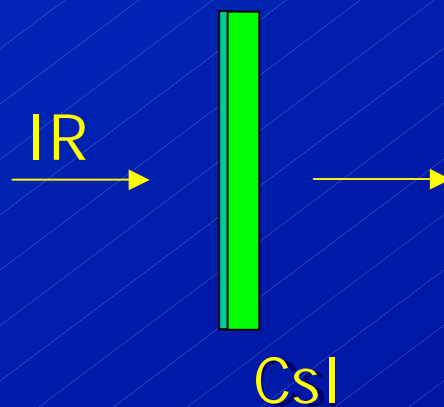
FTIR SPECTROSCOPY OF CRYOSOLUTIONS

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

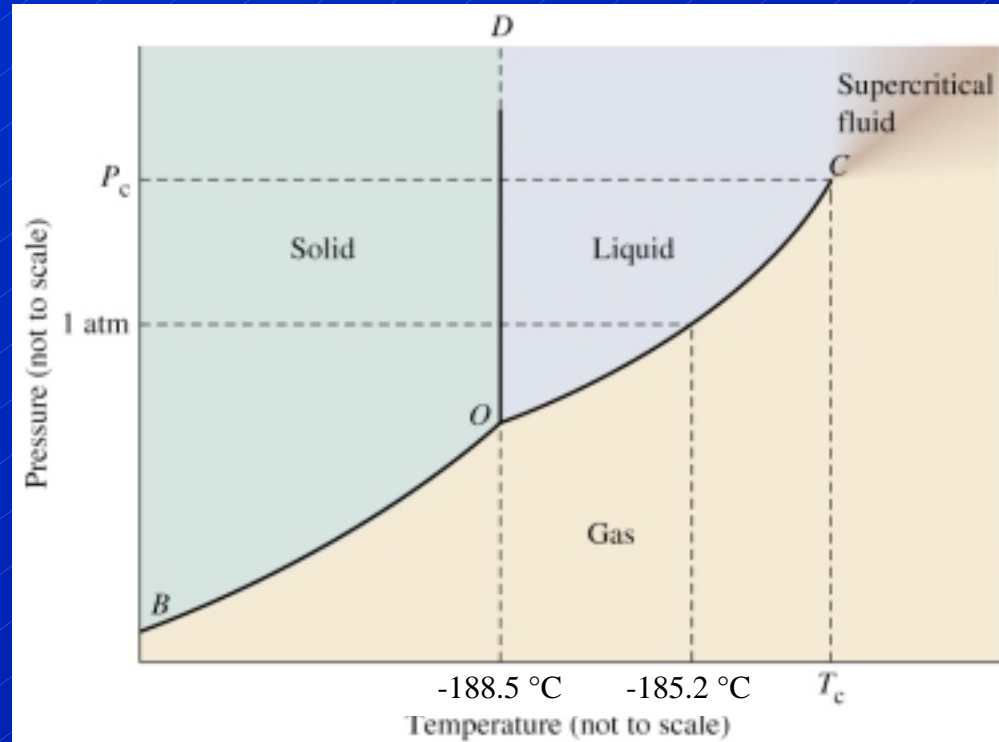
advantages :

- relatively low temperatures
- weak solute-solvent interactions
- chemical equilibrium
- transparent 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

$-188.5\text{ }^{\circ}\text{C}$

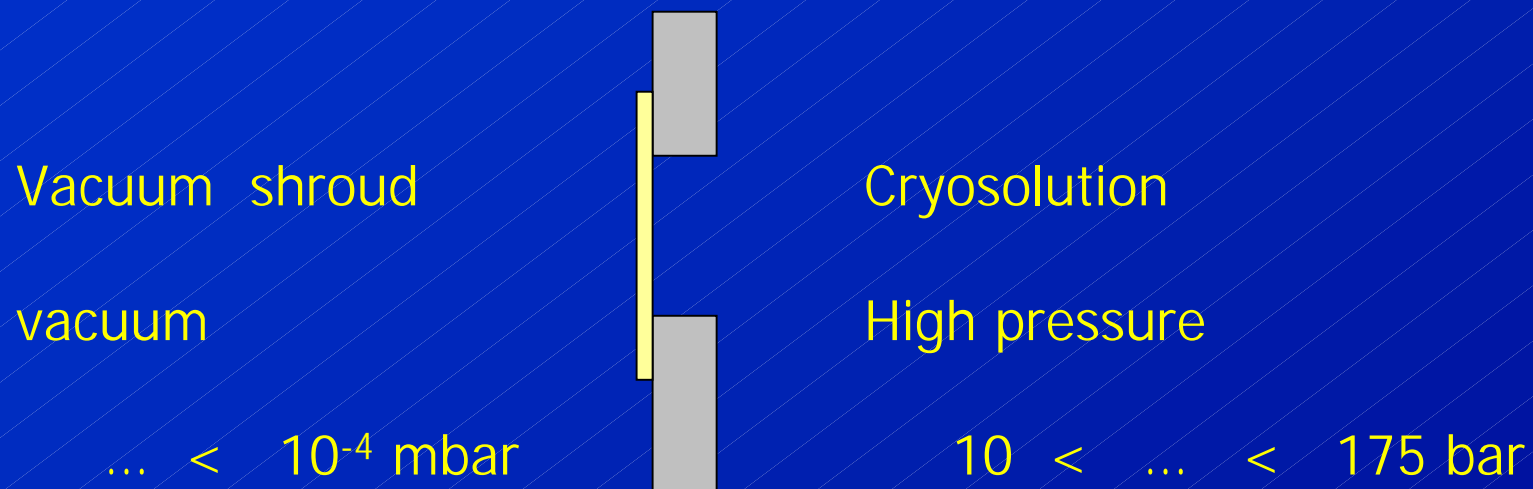
$-185.2\text{ }^{\circ}\text{C}$

15 atm

$-188.5\text{ }^{\circ}\text{C}$

$-150.3\text{ }^{\circ}\text{C}$

experimental set-up is not straightforward !



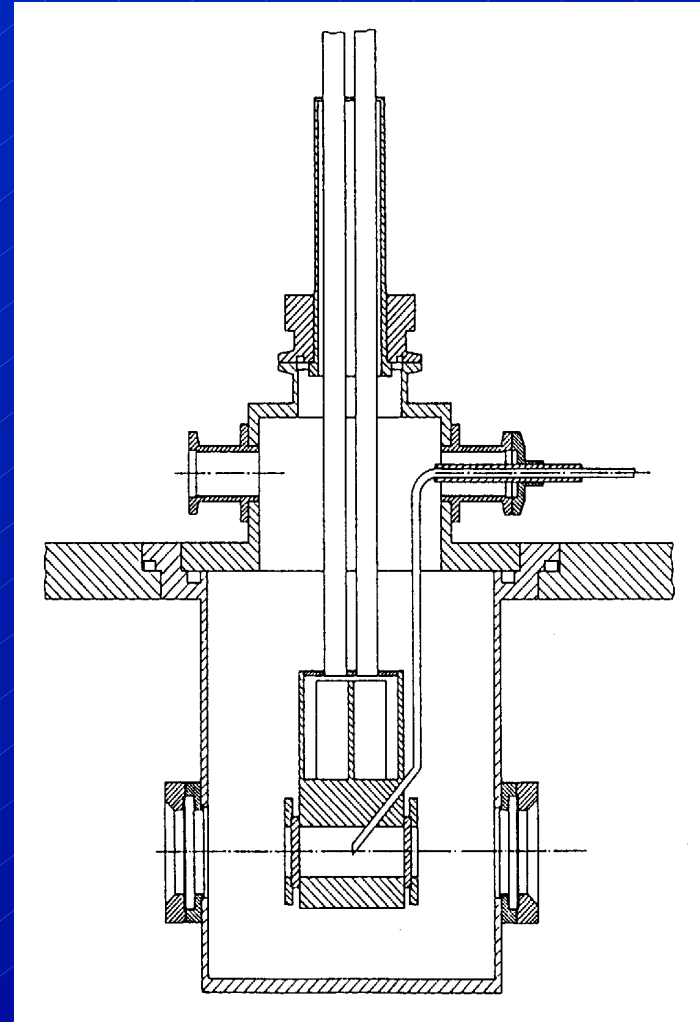
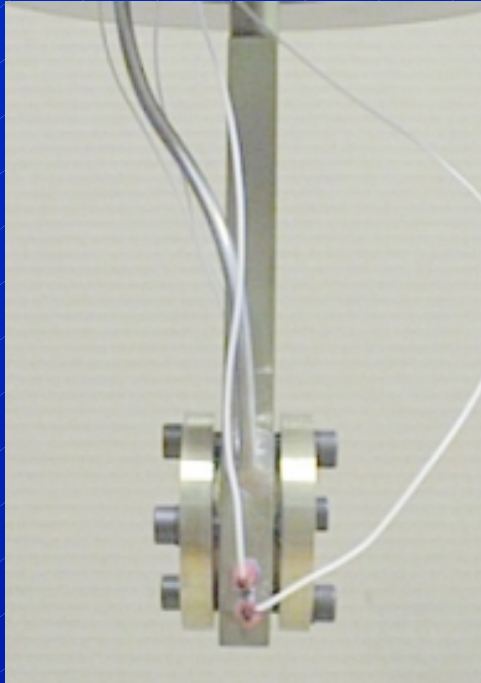
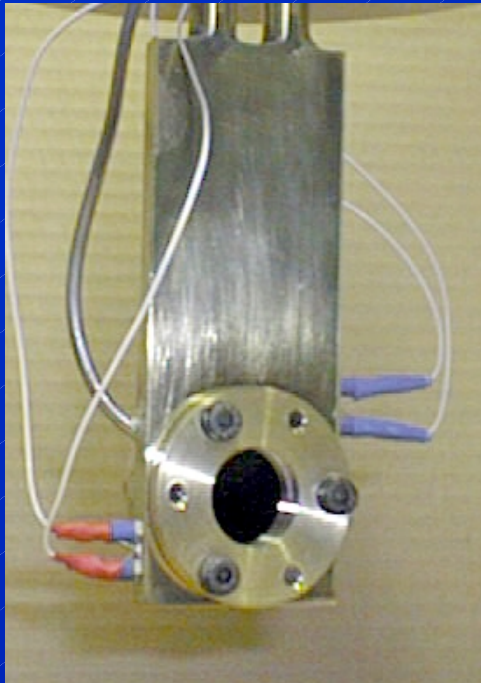
No leaks at room temperature and at lower temperatures !!

$$25 \text{ K} < T < 300 \text{ K}$$

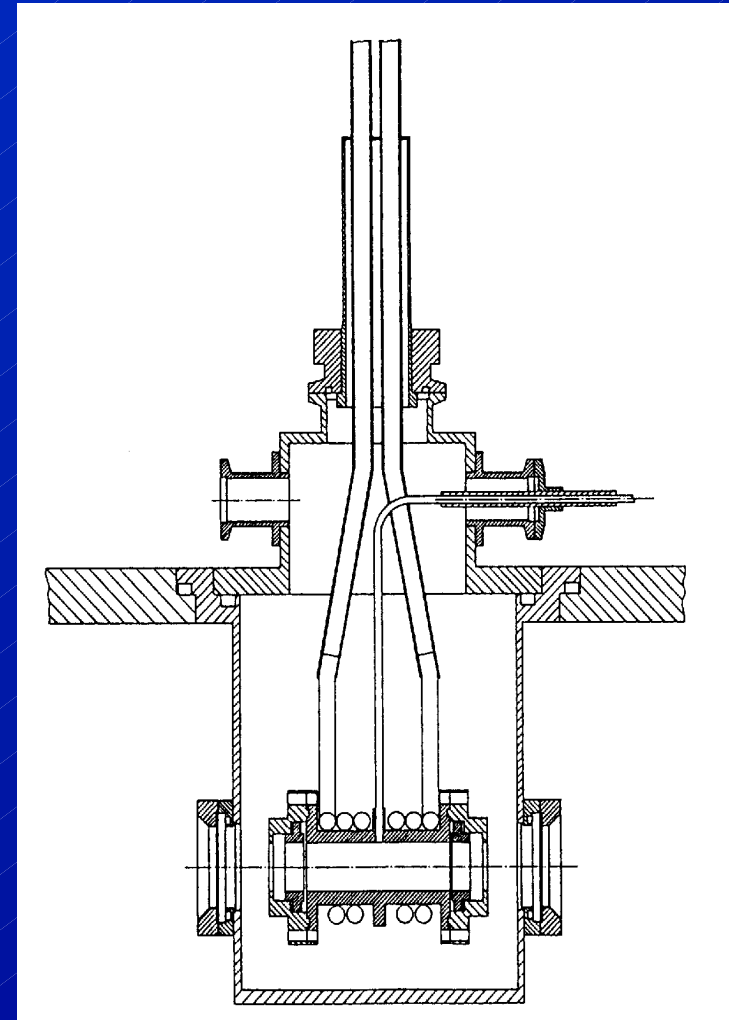
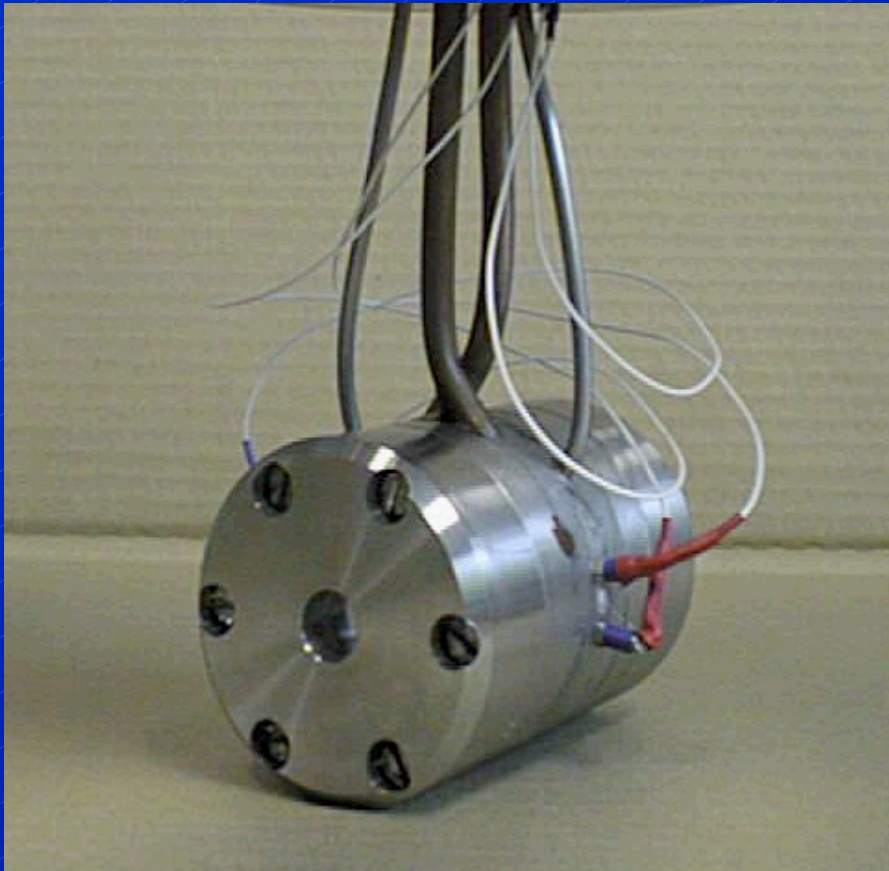
M.O. Bulanin, In: Handbook of Vibrational Spectroscopy; J.M. Chalmers and P.R. Griffiths, Eds.; J; Wiley & Sons: Chichester, 2002; Vol. 2, p 1329.



liquid cell : low-pressure design ($l = 10.0\text{ mm}$)

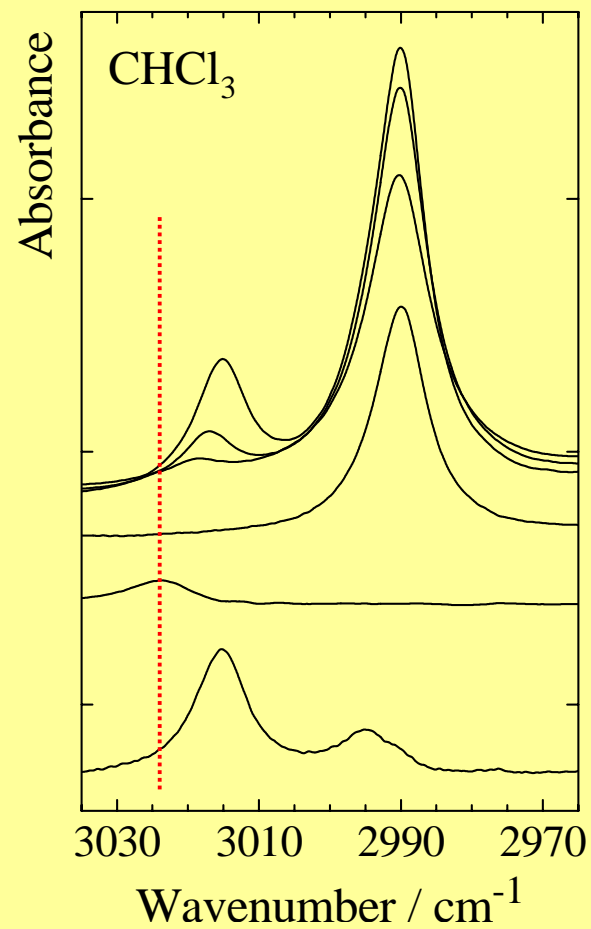
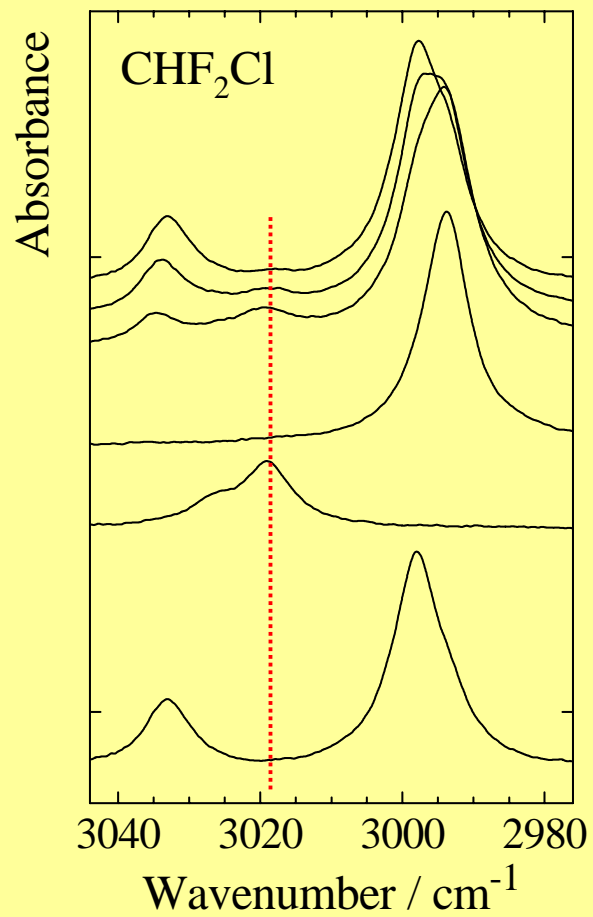


liquid cell : high-pressure design ($l = 70 \text{ mm}$)



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

Complexes of Dimethyl Ether with CHCl_xF_y



<i>Experiment</i>	HCF ₃	HCClF ₂	HCCl ₂ F	HCCl ₃
$\Delta\nu_{\text{C-H}} / \text{cm}^{-1}$	17.7	14.0	4.8	-8.3

<i>Ab initio</i>	HCF ₃	HCClF ₂	HCCl ₂ F	HCCl ₃
$\Delta\nu_{\text{C-H}} / \text{cm}^{-1}$	40.8	21.9	8.2	-4.1

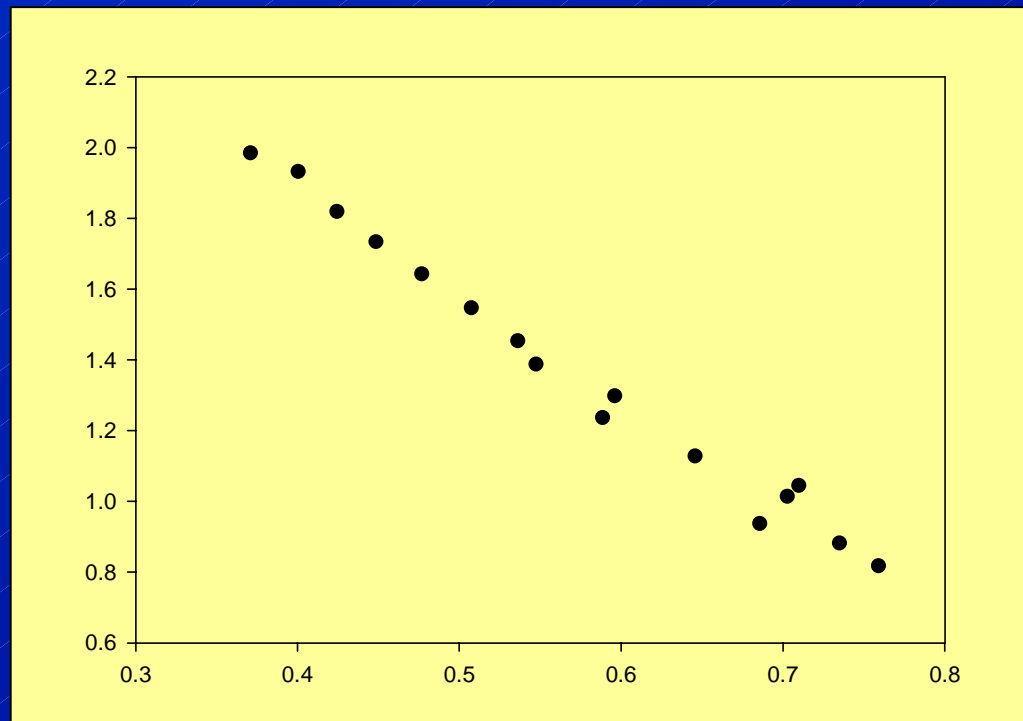
B.J. van der Veken, W.A. Herrebout, R. Szostak, D.N. Shchepkin, Z. Havlas, P. Hobza, *J. Am. Chem. Soc.* 123 (2001) 12290.

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

What happens with the infrared intensity ?

$$I_{\text{complex}}^{\text{corr}} = -\frac{\epsilon_{\text{complex}}}{\epsilon_{\text{monomeer}}} I_{\text{monomeer}}^{\text{corr}} + c$$

$$I_i^{\text{corr}}(T) = I_i(T) \frac{\rho(T_R)}{\rho(T)}$$

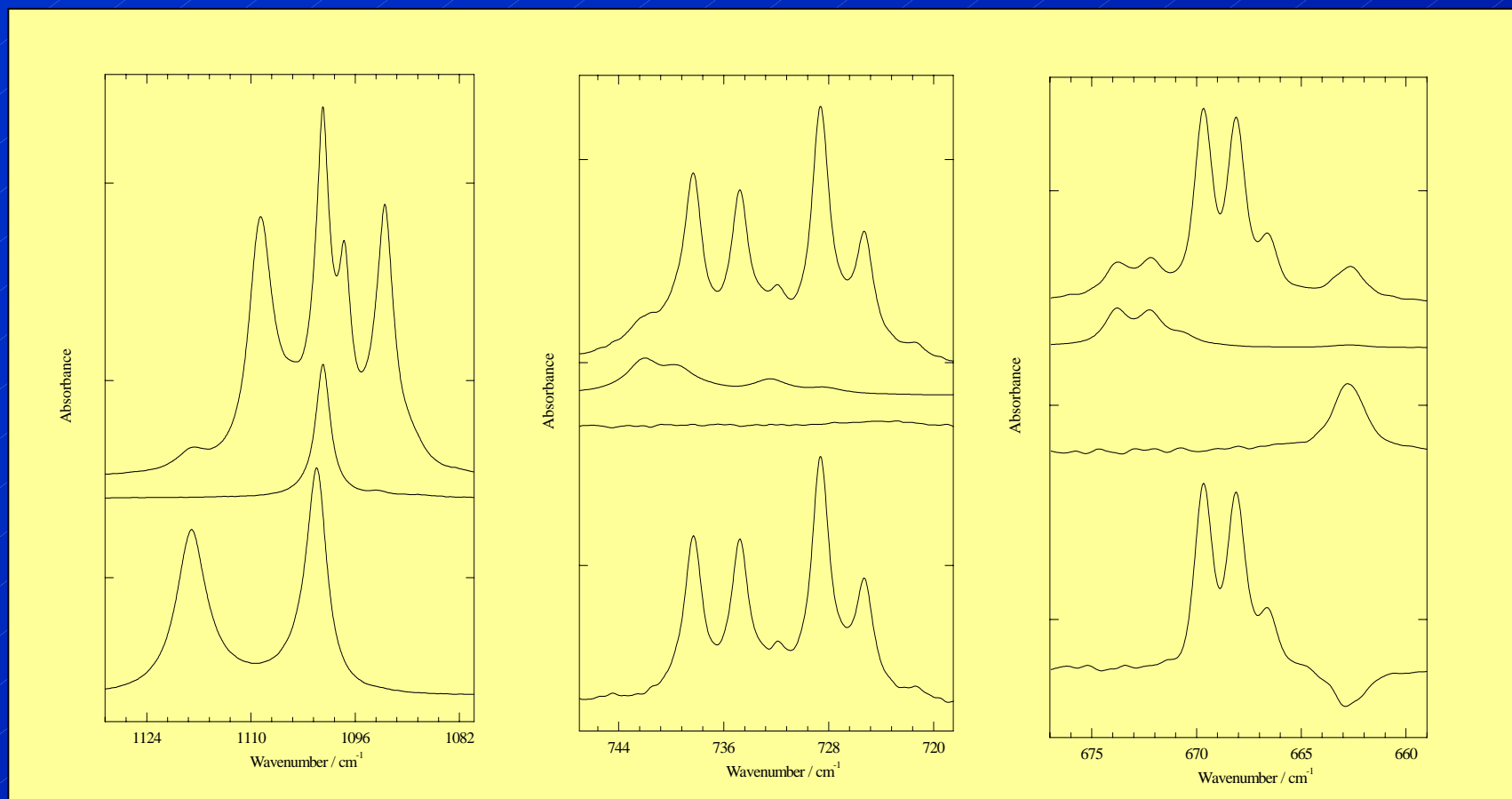


	HCF ₃	HCClF ₂	HCCl ₂ F	HCCl ₃
$\epsilon_{\text{complex}} / \epsilon_{\text{monomeer}}$	0.09(2)	0.89(6)	26(1)	56(3)

	HCF ₃	HCClF ₂	HCCl ₂ F	HCCl ₃
$\Delta\nu_{\text{C-H}} / \text{cm}^{-1}$	17.7	14.0	4.8	-8.3

What happens with the other modes ?

C-Cl and C-F stretching fundamentals

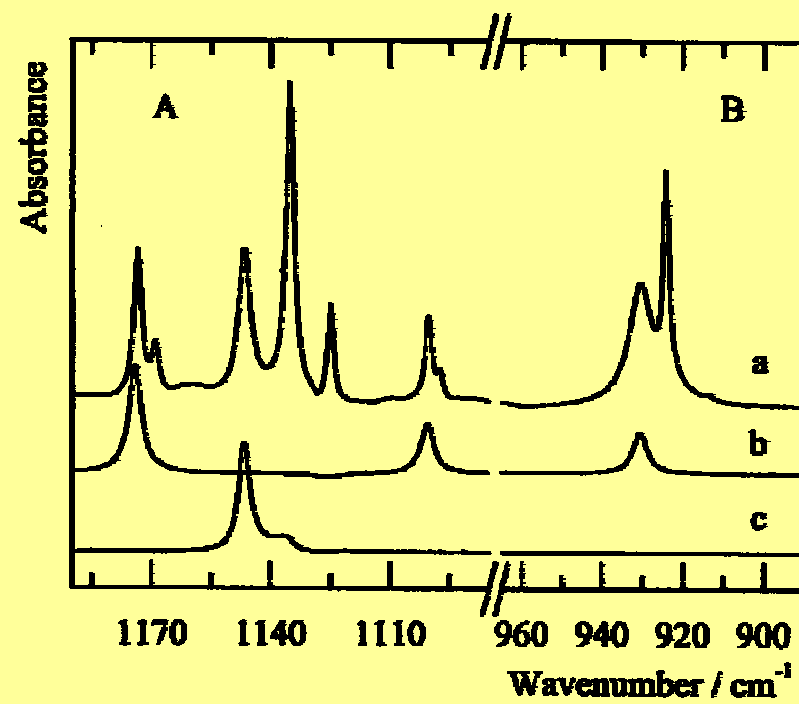
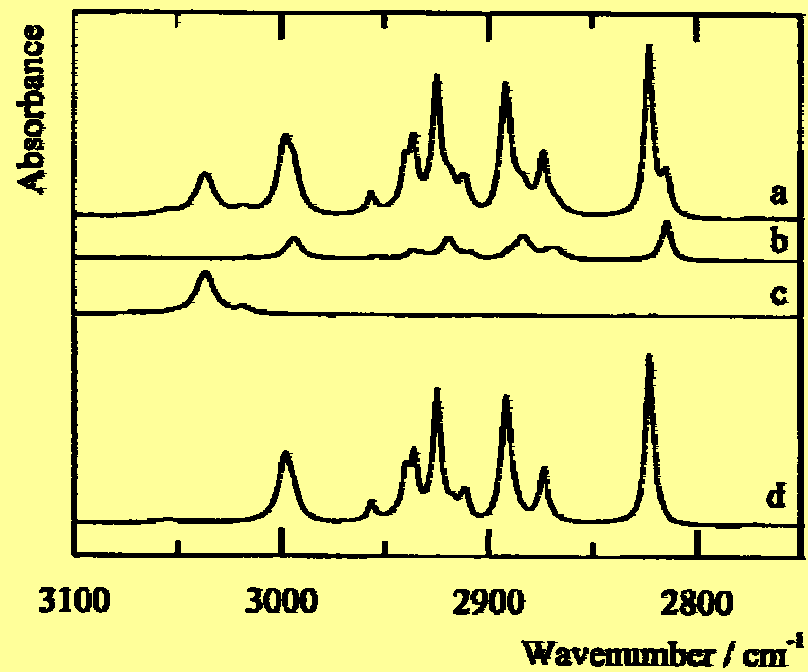


CHF_2Cl

CHFC1_2

CHCl_3

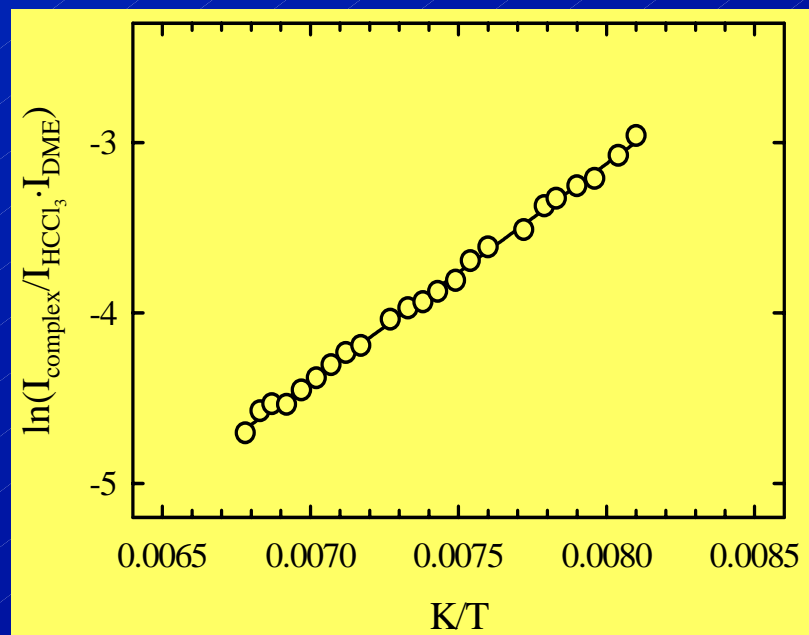
other modes



What about the relative stability ?

determination of the complexation enthalpy

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



resulting complexation enthalpies (LKr)

	HCF ₃	HCClF ₂	HCCl ₂ F	HCCl ₃
ΔH° / 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 : $\Delta_{\text{sol}}G$, $\Delta_{\text{sol}}H$ and $\Delta_{\text{sol}}S$

Monte Carlo / Free Energy Perturbation Theory

resulting complexation energies

	HCF ₃	HCCIF ₂	HCCl ₂ F	HCCl ₃
$\Delta E_{\text{exp}} / \text{kJ mol}^{-1}$	-19.5(10)	-20.8(9)	-23.2(8)	-24.3(5)

MP2/aug-cc-PVTZ calculations including CP corrections

	HCF ₃	HCCIF ₂	HCCl ₂ F	HCCl ₃
$\Delta E / \text{kJ mol}^{-1}$	-17.9	-18.9	-20.0	-21.2(5)

Similar results are obtained for acetone and oxirane

acetone	HCF ₃	HCClF ₂	HCCL ₂ F	HCCl ₃
$\Delta\nu_{\text{C-H}} / \text{cm}^{-1}$	26.7	24.1	15.5	0.6
$\epsilon_{\text{complex}} / \epsilon_{\text{monomer}}$	0.08(1)	0.61(3)	3.8(2)	58(8)

oxirane	HCF ₃	HCClF ₂	HCCL ₂ F	HCCl ₃
$\Delta\nu_{\text{C-H}} / \text{cm}^{-1}$	24.1	20.7	14.2	1.3
$\epsilon_{\text{complex}} / \epsilon_{\text{monomer}}$	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 ₂ F	HCCl ₃
$\Delta E_{\text{exp}} / \text{kJ mol}^{-1}$	-19.1 (6)	-22.1 (4)	-24.3 (5)	-26.0 (6)
$\Delta E / \text{kJ mol}^{-1}$	-18.6	-19.6	-20.4	-22.6

complexation energies for oxirane

	HCF ₃	HCClF ₂	HCCl ₂ F	HCCl ₃
$\Delta E_{\text{exp}} / \text{kJ mol}^{-1}$	-20.4 (6)	-21.2 (8)	-23.0 (6)	-23.2(4)
$\Delta E / \text{kJ mol}^{-1}$	-18.2	-19.6	-20.4	-21.4

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

Some questions remain :

Can we obtain supplementary data by using Raman Spectroscopy ?

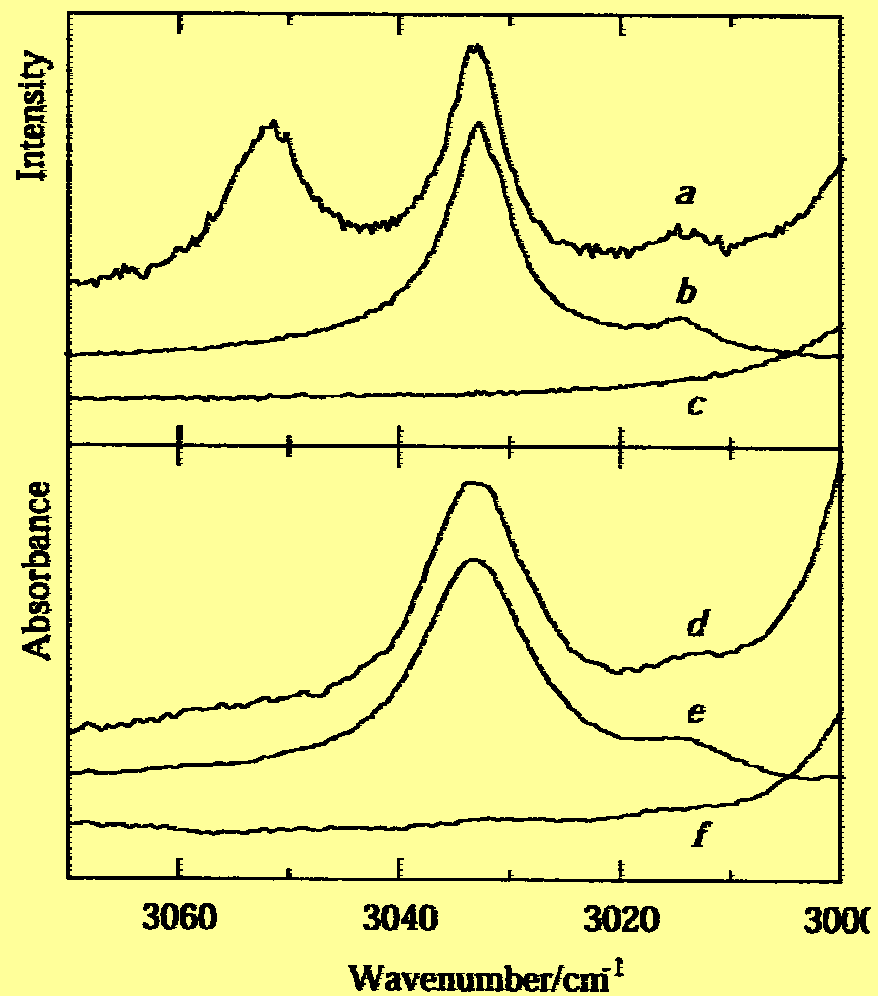
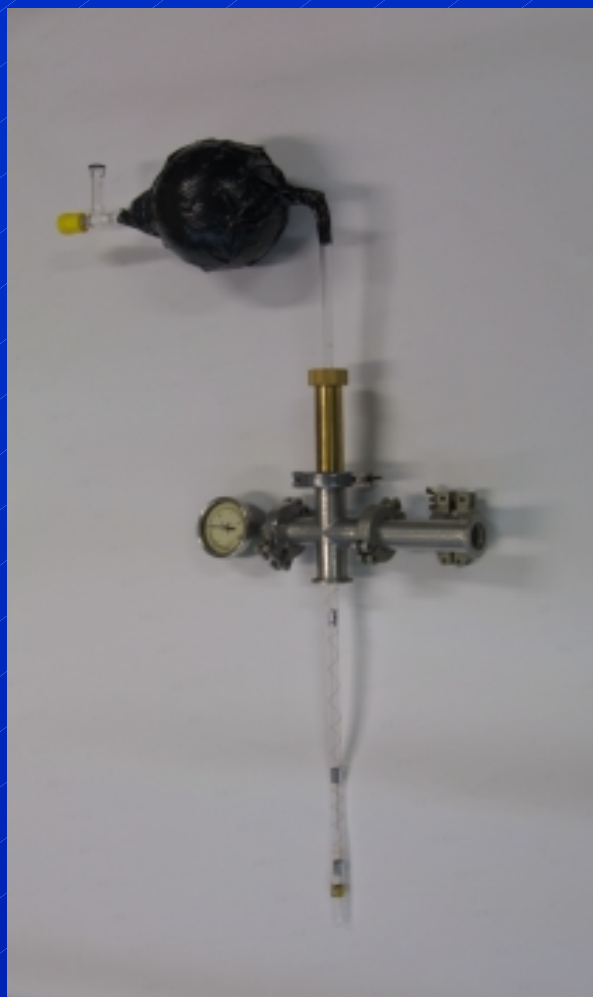
Can we expand the series of proton donors with other species such as CH_2Cl_2 , CH_2F_2 , CH_3F , ?

Can we obtain additional information by using Raman Spectroscopy ?

MP2/6-311++G(d,p) ab initio calculations for DME-CHF₃

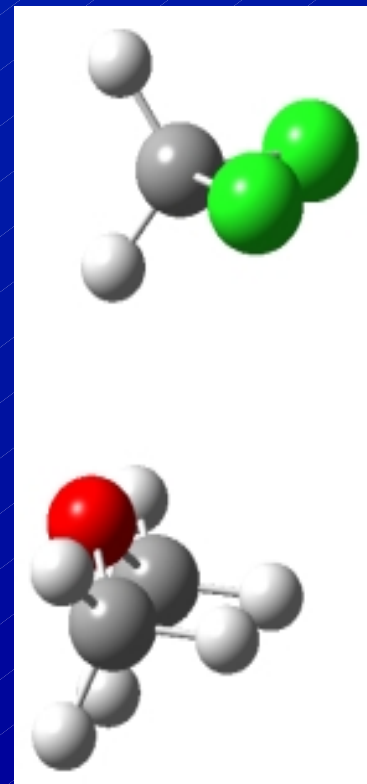
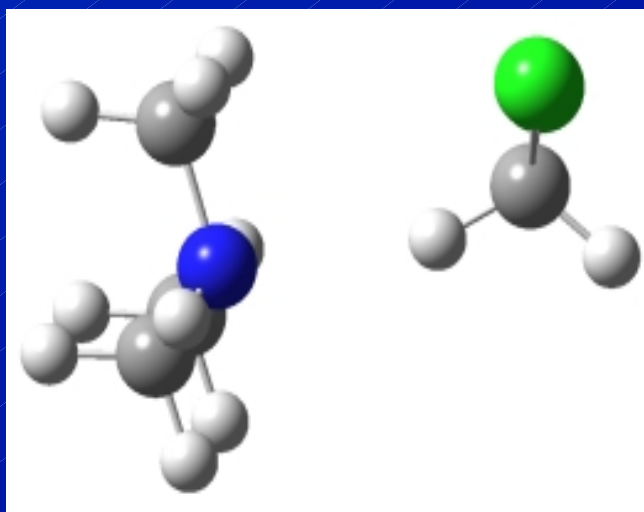
	monomer	complex
$\Delta\nu_{\text{CH}} / \text{cm}^{-1}$	3228.7	3251.1
IR intensity / km mol ⁻¹	34.3	2.3
Raman scattering activity / Å ⁴ amu	66.1	94.6

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

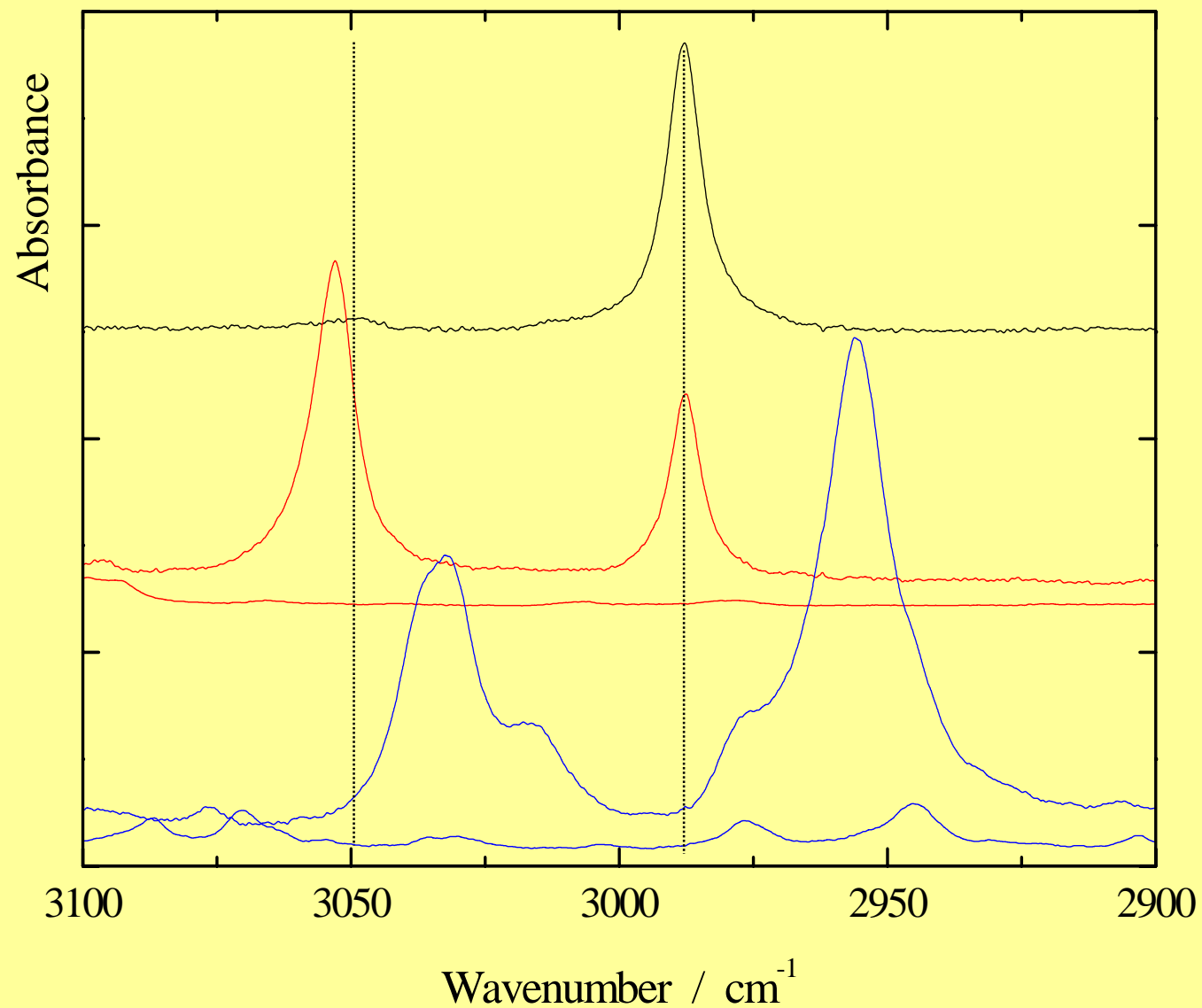


Can we expand the series of proton donors with other species such as CH_2Cl_2 , CH_2F_2 , CH_3F , ?

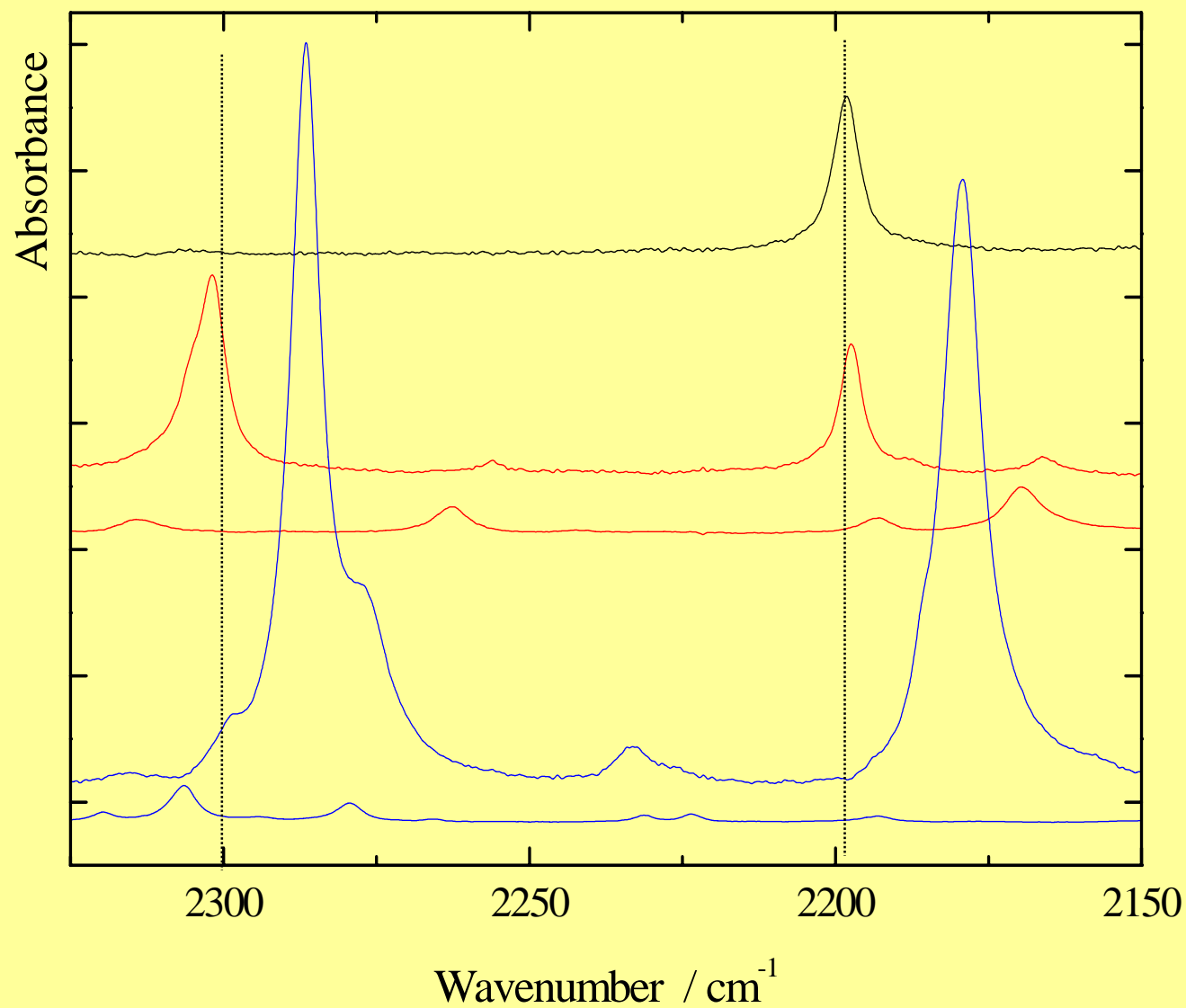
CH...O and CH...N hydrogen bonded complexes of CH_2Cl_2 with Dimethyl Ether and Trimethyl Amine



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



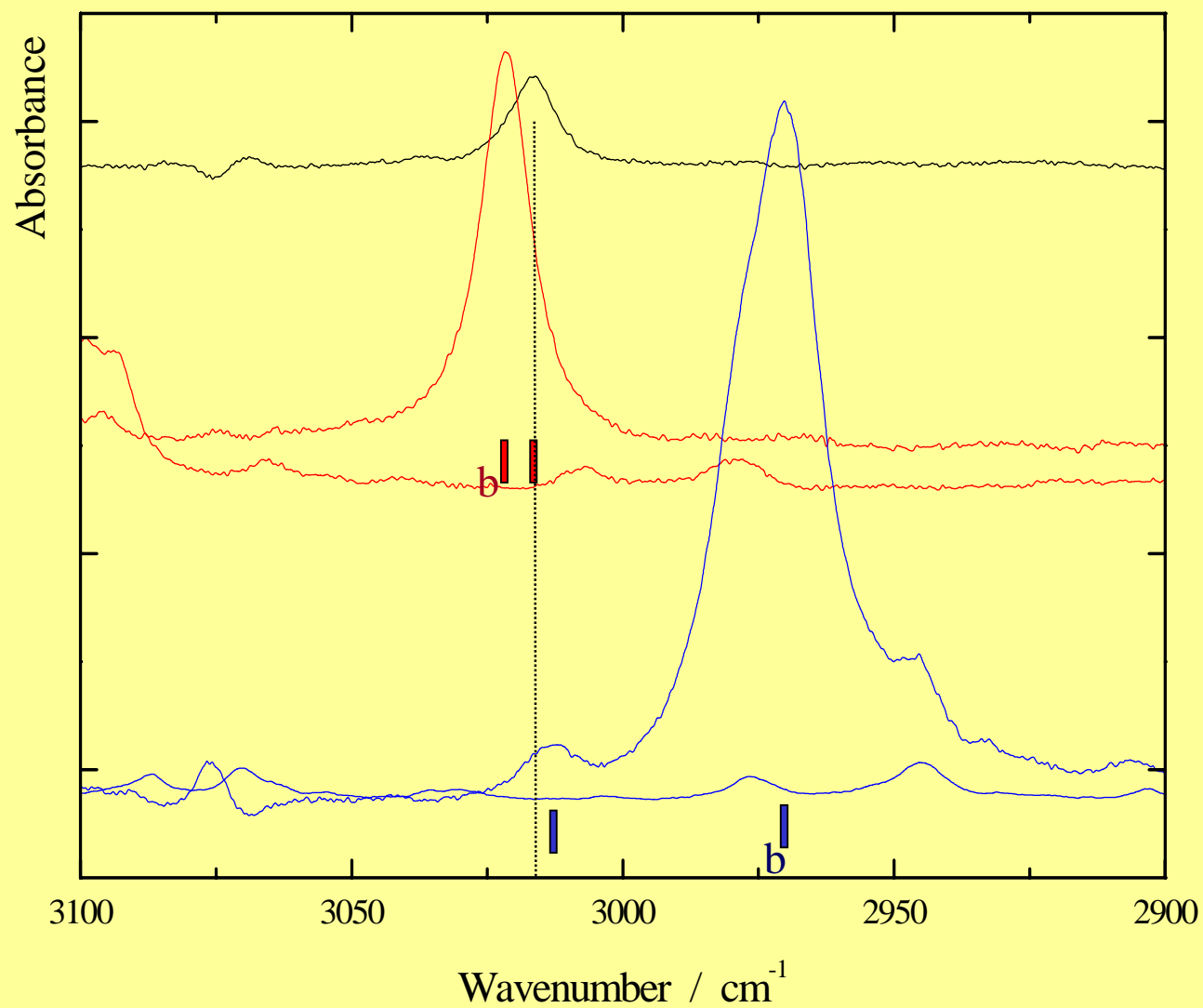
The results obtained for CH_2Cl_2 and CD_2Cl_2 are in excellent agreement with the data reported in

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

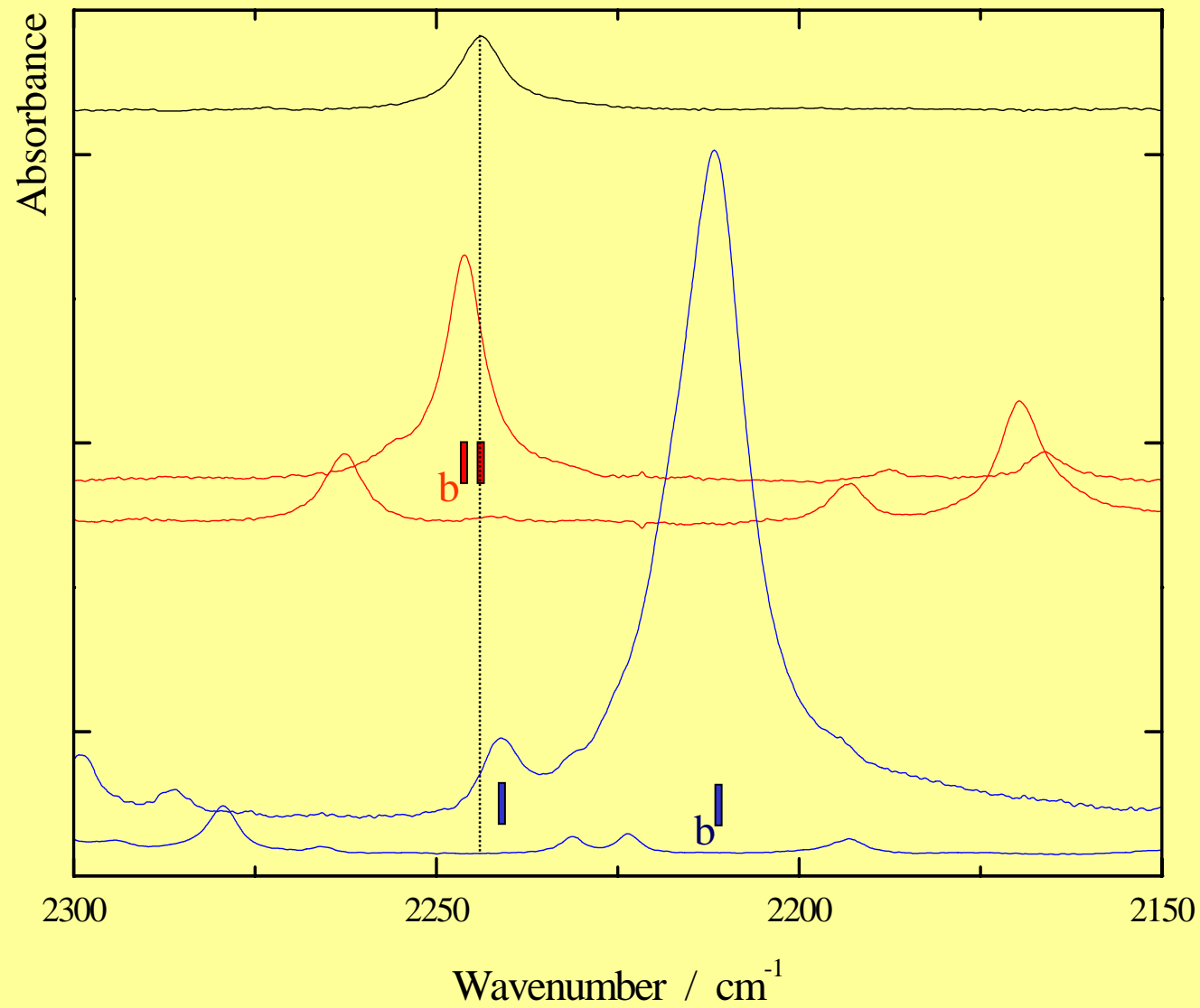
Unfortunately, no separate information on the hydrogen bonded C-H bond and on the 'free' C-H bond is available. These data can be obtained by using the partially deuterated species CHDCl_2 .



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

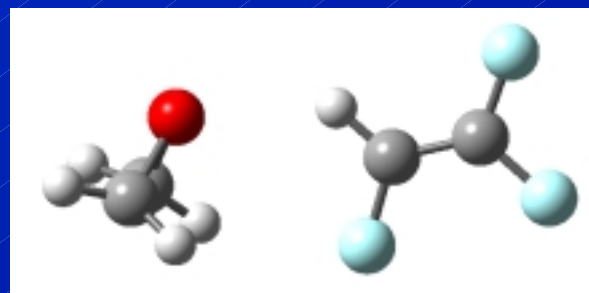
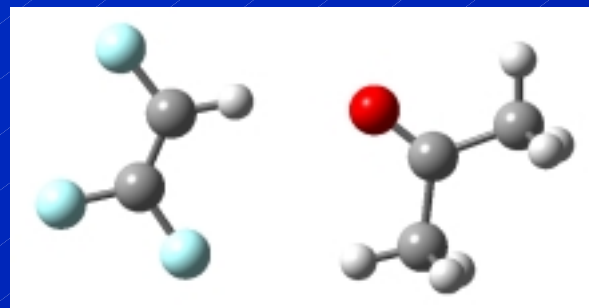
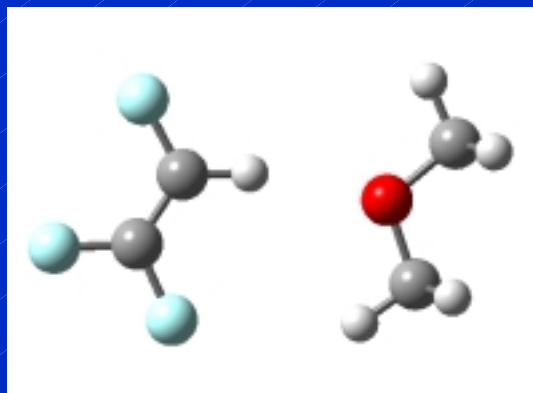
Preliminary data are available for some complexes with CH_3F , CHDF_2 and CH_2DF

Can we trust our experimental data ?

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

$\text{CH}\cdots\text{X}$ bonded complexes involving C_2HF_3

Equilibrium geometries and predicted frequency shifts *



dimethyl ether

$$\Delta\nu_{\text{CH}} = -35 \text{ cm}^{-1}$$

acetone

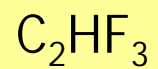
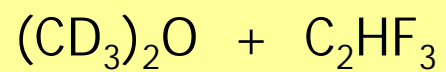
$$\Delta\nu_{\text{CH}} = -16 \text{ cm}^{-1}$$

oxirane

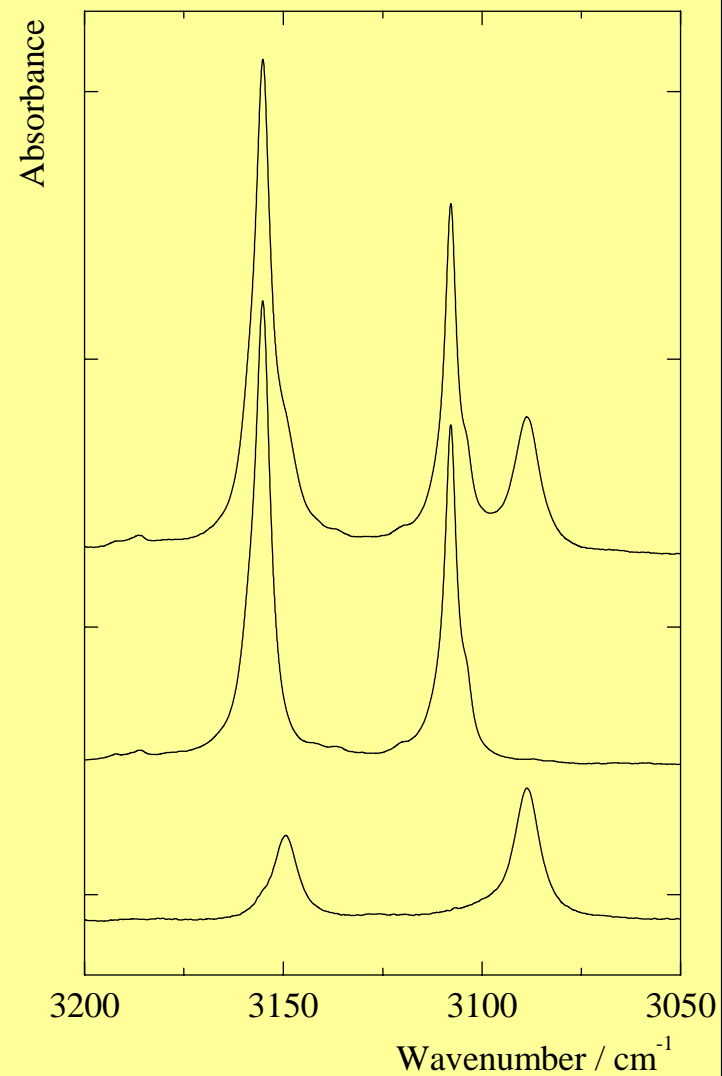
$$\Delta\nu_{\text{CH}} = -11 \text{ cm}^{-1}$$

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

Vibrational Spectra [LKr , -150 °C]



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')

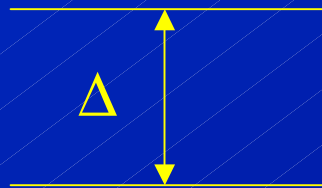
Accurate analysis of the $\nu_1 \sim \nu_2 + \nu_3$ Fermi dyad in monomer trifluoroethylene and in the complexes requires knowledge of the corresponding cubic force constant α_{123}

FERMI RESONANCE :

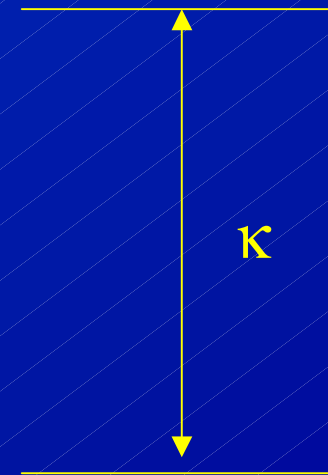
Interaction between two or more energy levels which have identical symmetry

fundamental

*overtone or
combination band*

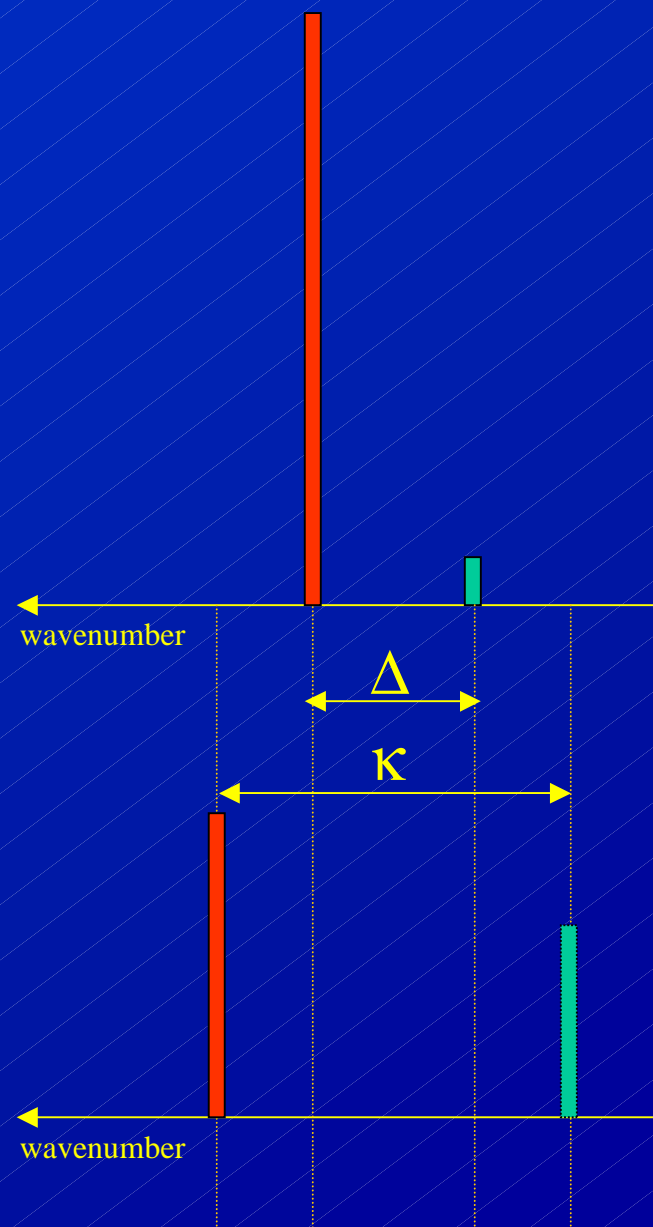
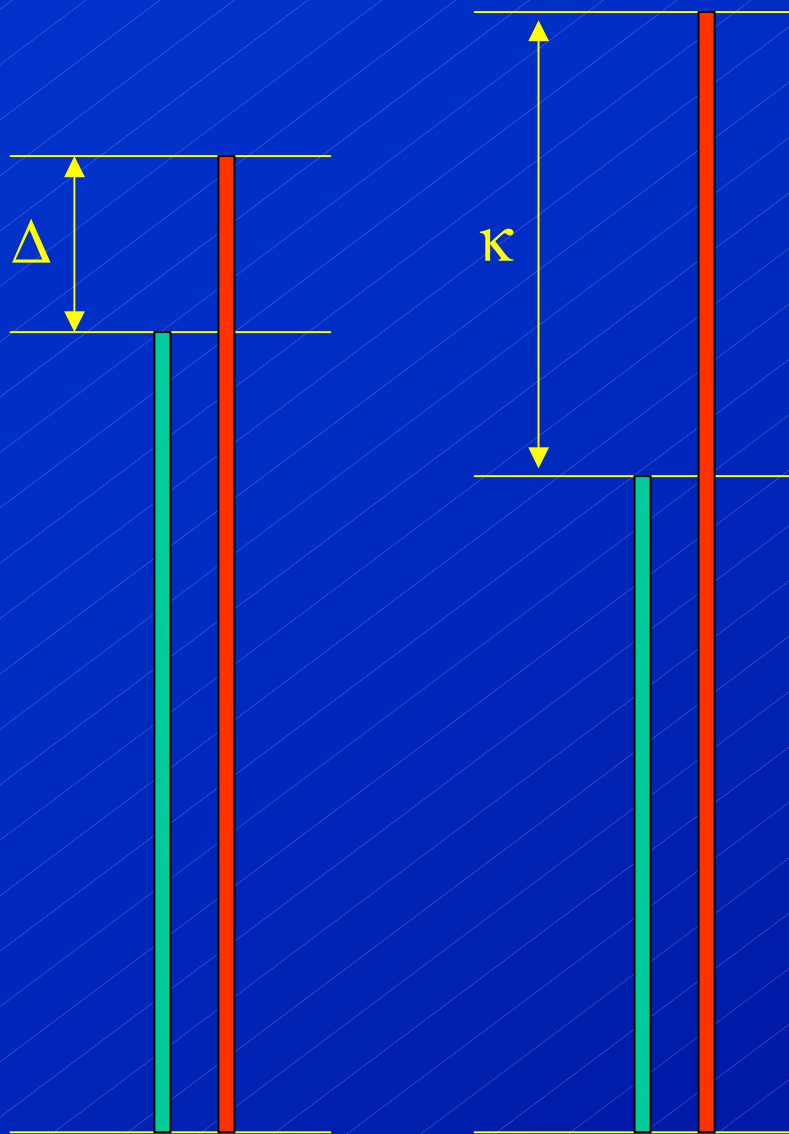


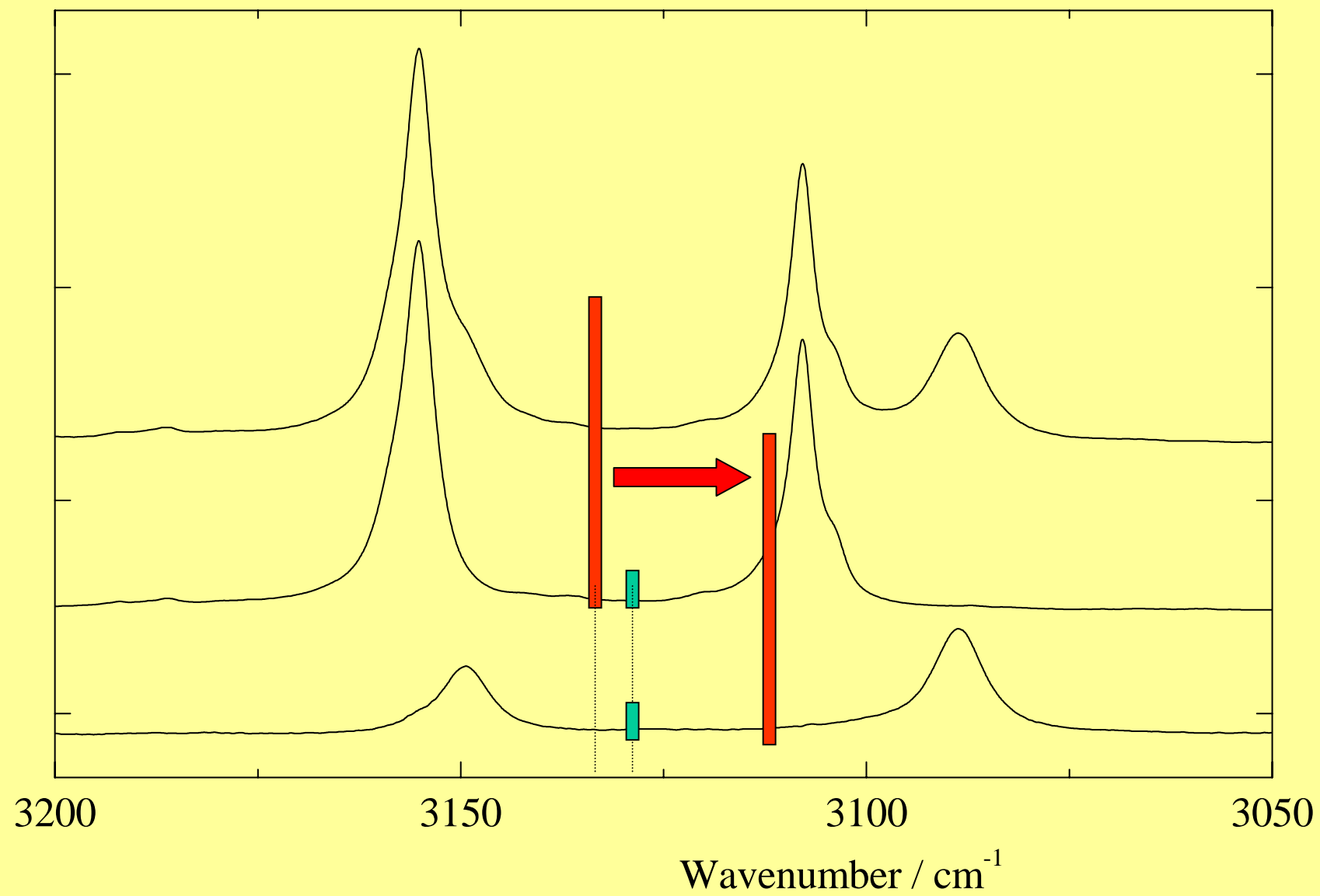
unperturbed



perturbed

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





Comparison with calculated values

	MP2/6-31++G(d,p)	Liquid Krypton
dimethyl ether	$\Delta\nu_{\text{CH}} = -35 \text{ cm}^{-1}$	$\Delta\nu_1^0 = -26.3 \text{ cm}^{-1}$
acetone	$\Delta\nu_{\text{CH}} = -16 \text{ cm}^{-1}$	$\Delta\nu_1^0 = -14.7 \text{ cm}^{-1}$
oxirane	$\Delta\nu_{\text{CH}} = -11 \text{ cm}^{-1}$	$\Delta\nu_1^0 = -16.9 \text{ cm}^{-1}$

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

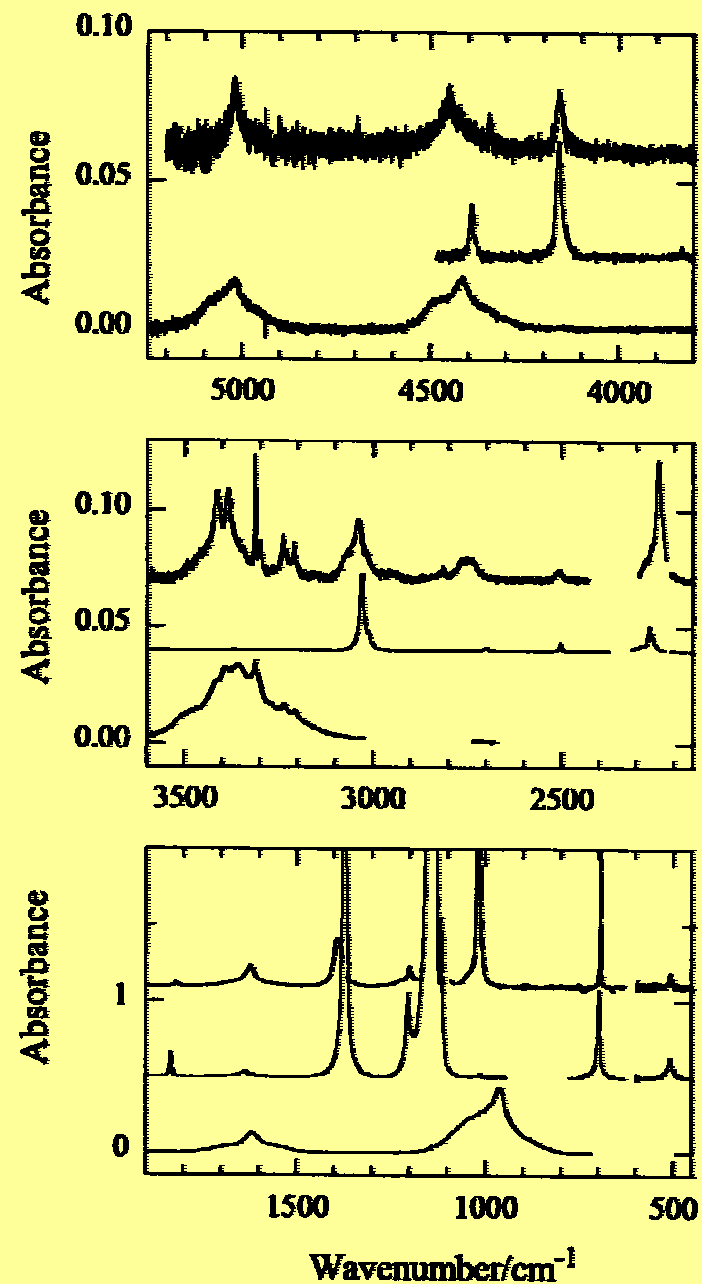
Infrared spectra and relative stability of the CHF_3 / NH_3 hydrogen bonded complex in liquefied xenon

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

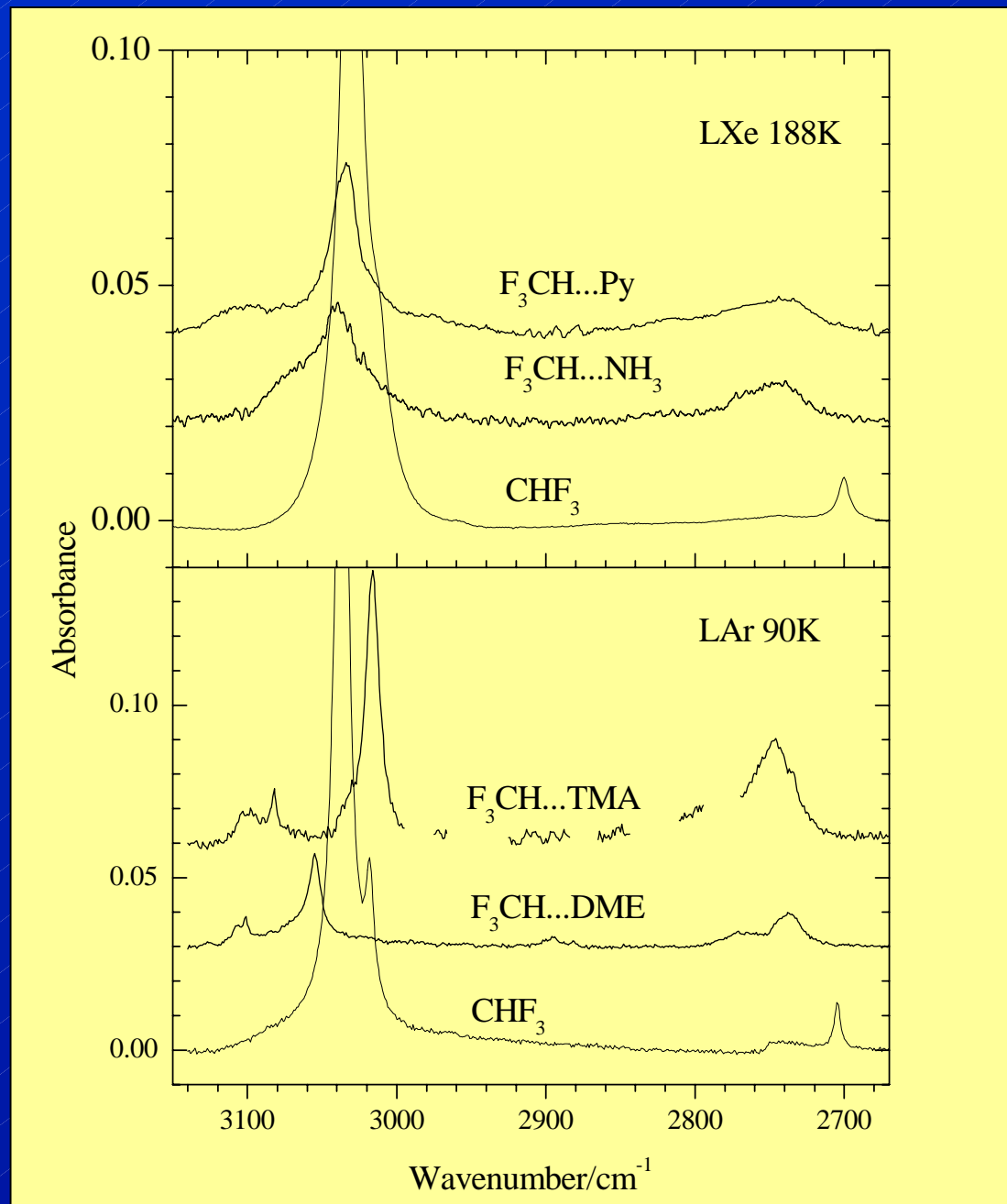
W. A. Herrebout, S.M. Melikova, S.N. Delanoye, K.S. Rutkowski, D.N. Shchepkin, B.J. van der Veken, J. Phys. Chem. A 109 (2005) 3038-3044

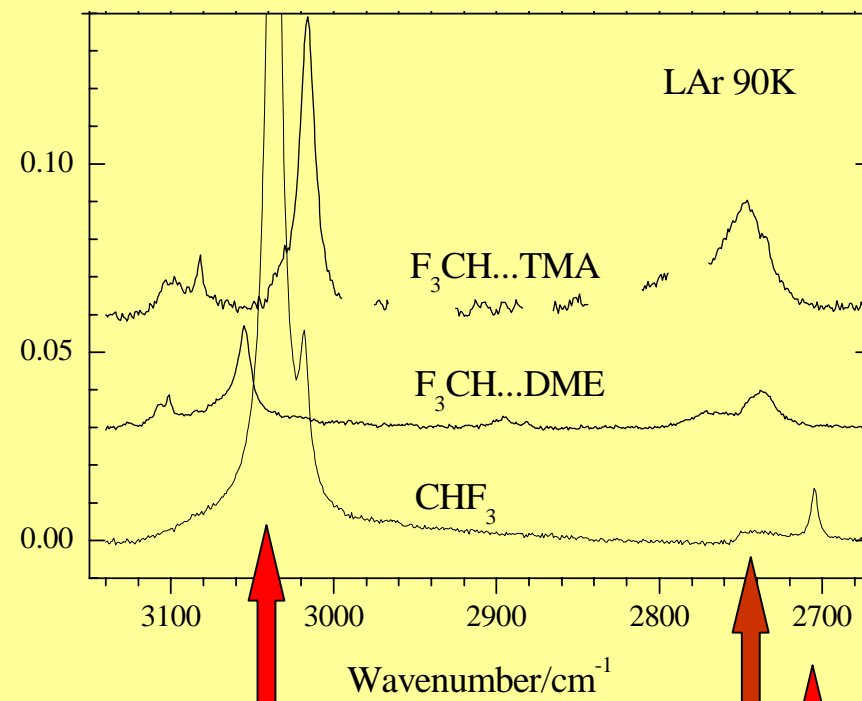
Survey infrared spectra of $\text{CHF}_3\text{-NH}_3$ (top), CHF_3 (middle) and NH_3 (bottom) in LXe, at 172K.



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

Reason ??





$\nu_1 (A_1)$

$2\nu_4 (E)$

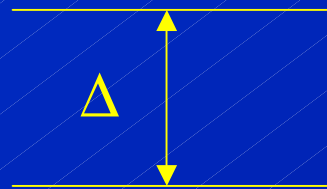
$2\nu_4 (A_1)$

FERMI RESONANCE

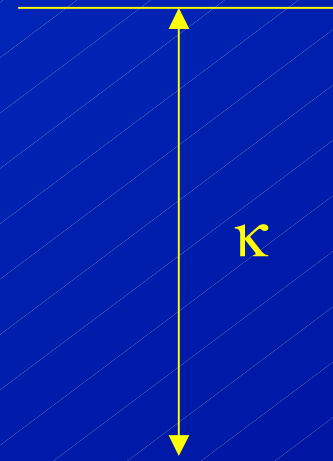
FERMI RESONANCE in monomer CHF_3

$\nu_1 (A_1)$

$2\nu_4 (A_1)$



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

$$V/hc = \frac{1}{2}\omega_1 Q_1^2 + \frac{1}{2}\omega_4 (X_4^2 + Y_4^2) + \alpha_{111} Q_1^3 + \alpha_{144} Q_1 (X_4^2 + Y_4^2) \\ + \beta_{1111} Q_1^4 + \beta_{1144} Q_1^2 (X_4^2 + Y_4^2) + \beta_{4444} (X_4^2 + Y_4^2)^2 + \dots$$

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

$$\nu_1 (A_1) \quad 2\nu_4 (A_1)$$

How does the $\nu_1 / 2\nu_4$ 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_1^0 and $2\nu_4^0$ if the cubic force constant α_{144} is known accurately.

monomer

ν_1
 $2\nu_4$



ν_1^0
 $2\nu_4^0$

$\downarrow \Delta\nu_1$

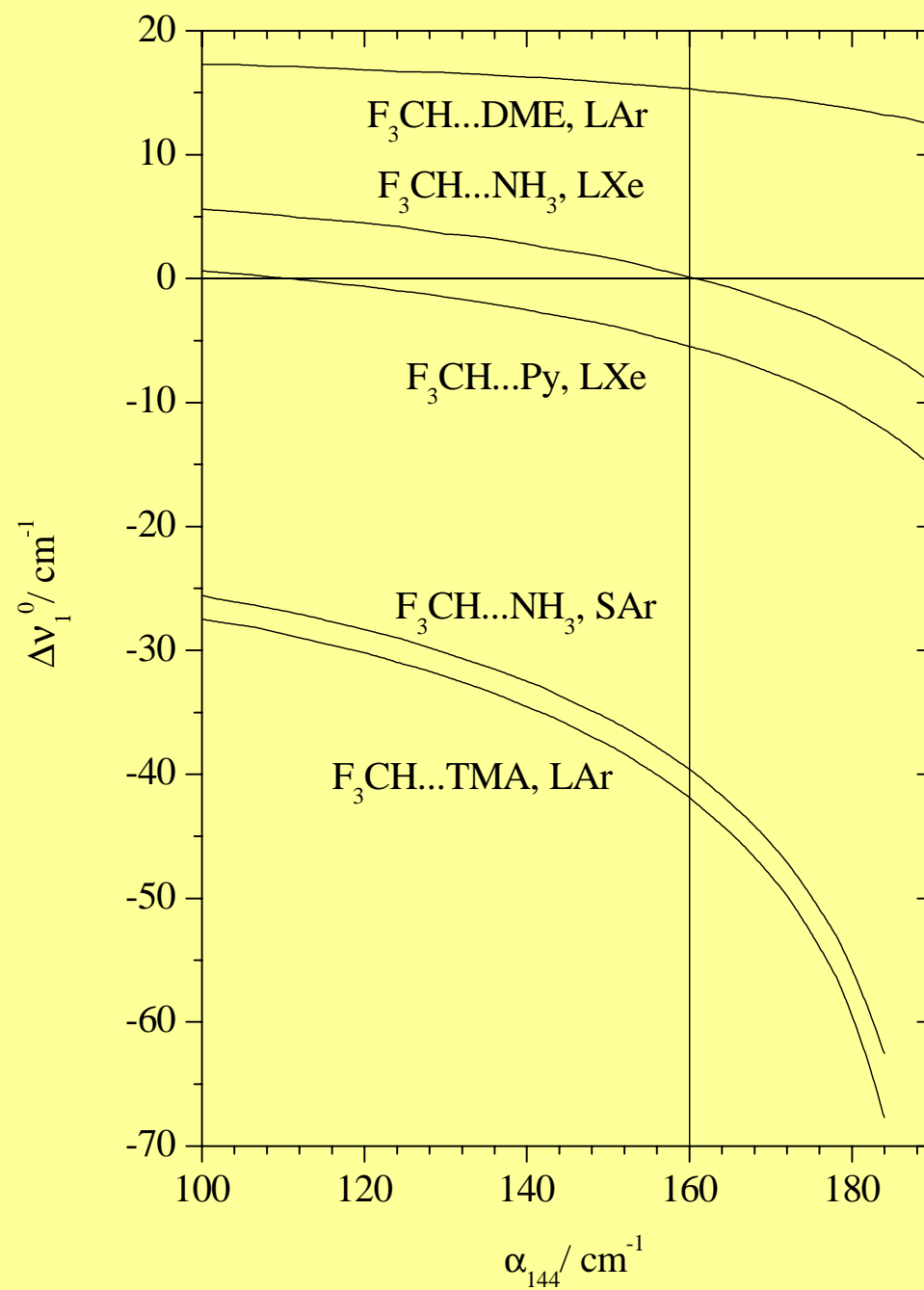
$\downarrow \Delta\nu_1^0$

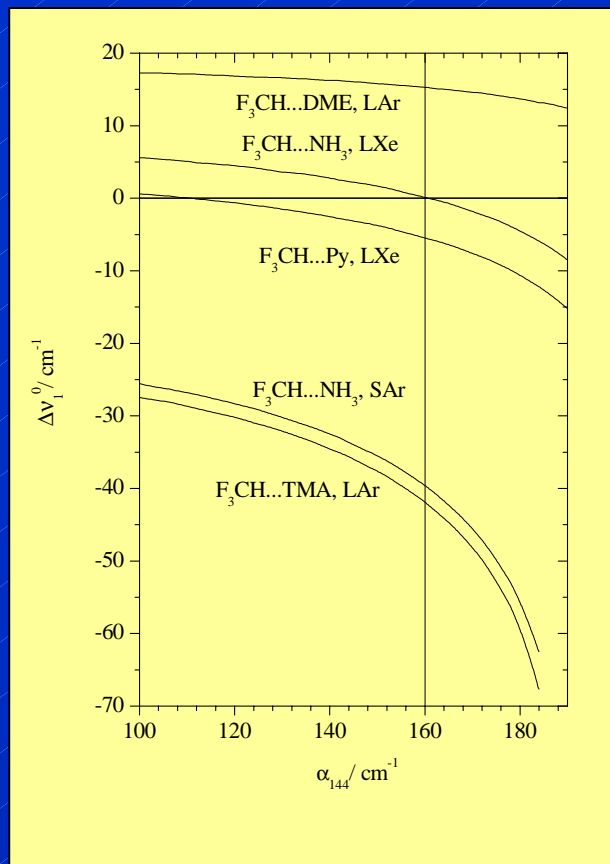
complex

ν_1
 $2\nu_4$



ν_1^0
 $2\nu_4^0$





ammonia – fluoroform

$$\Delta v_1 = + 7.6 \text{ cm}^{-1}$$

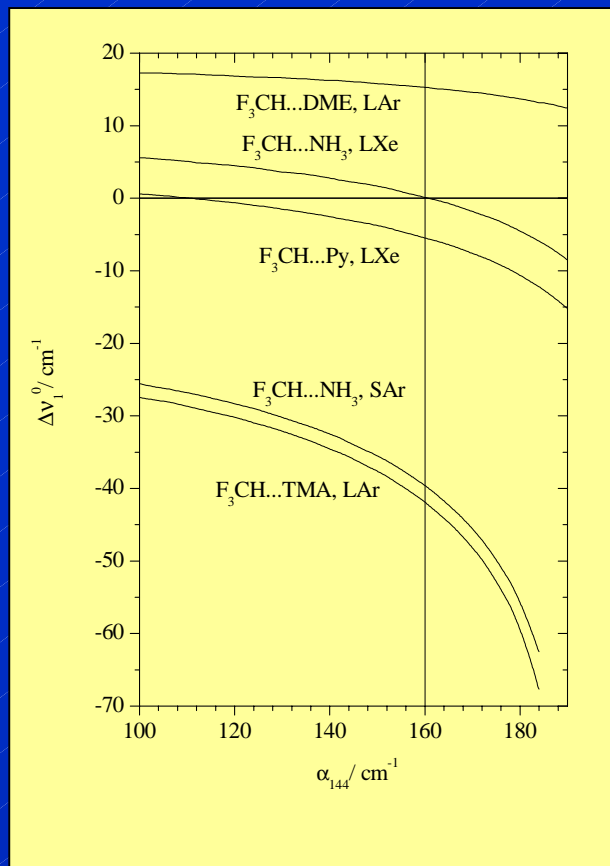
$$\Delta v_1^0 = -0.3 (6) \text{ cm}^{-1}$$

pyridine – fluoroform

$$\Delta v_1 = + 3.0 \text{ cm}^{-1}$$

$$\Delta v_1^0 = -6.0 (6) \text{ cm}^{-1}$$

pseudo - blue-shifting hydrogen bond



dimethyl ether – fluoroform

$$\Delta v_1 = +18.1 \text{ cm}^{-1}$$

$$\Delta v_1^0 = +15.1 (4) \text{ cm}^{-1}$$

trimethyl amine – fluoroform

$$\Delta v_1 = -22.8 \text{ cm}^{-1}$$

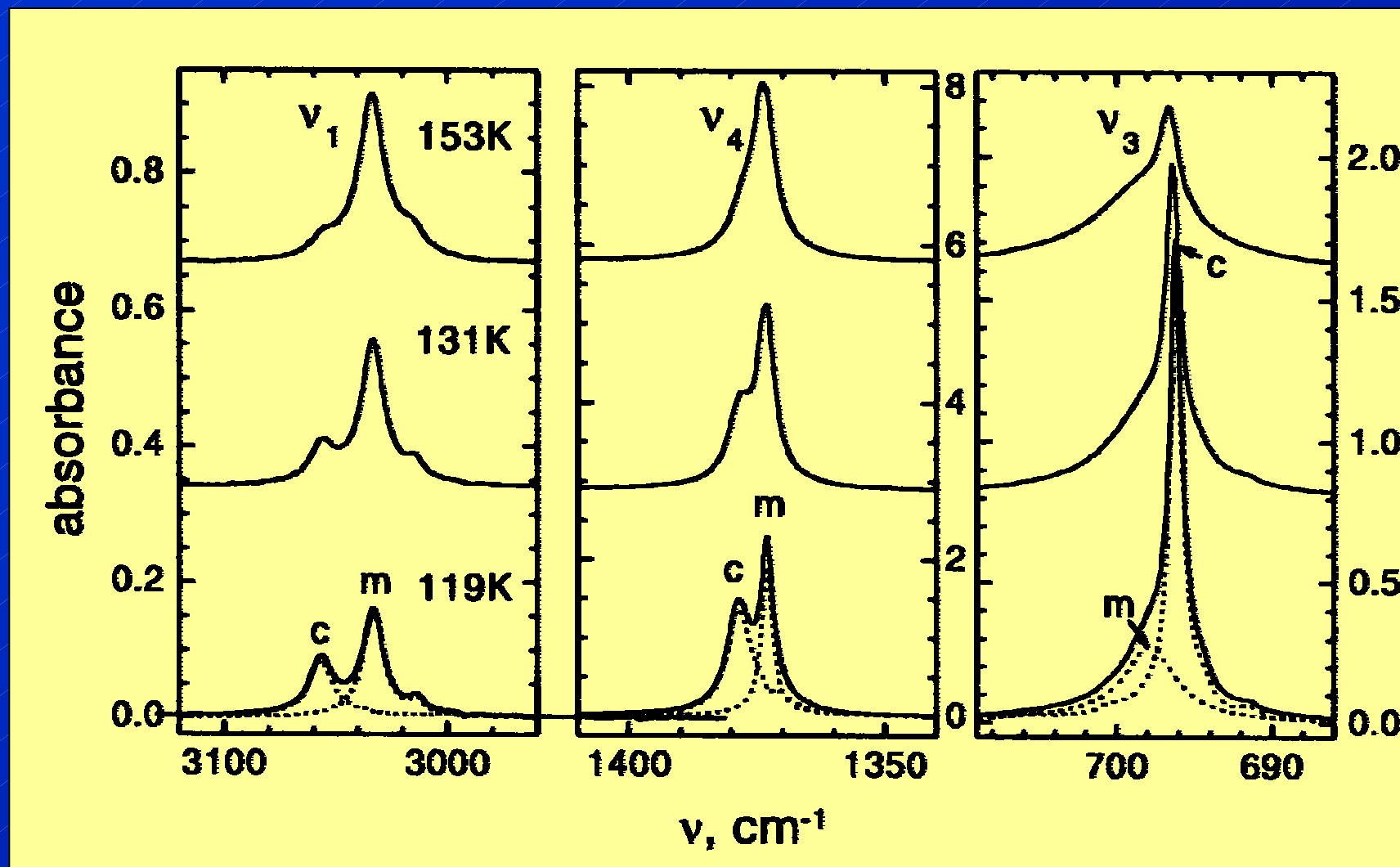
$$\Delta v_1^0 = -43.5 (6) \text{ cm}^{-1}$$

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

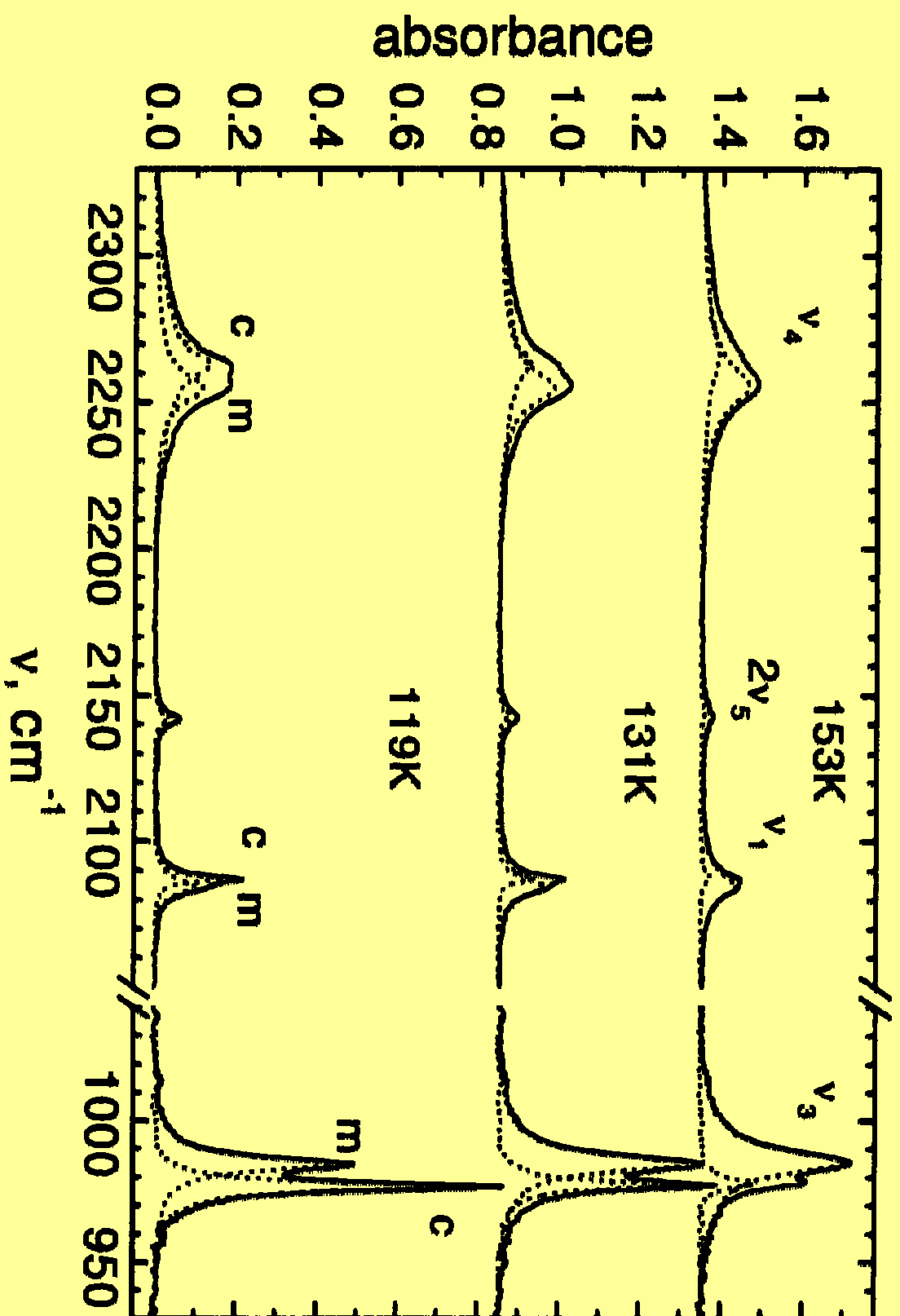
CAN SIMILAR DATA BE OBTAINED
FOR OTHER CH...X INTERACTIONS?

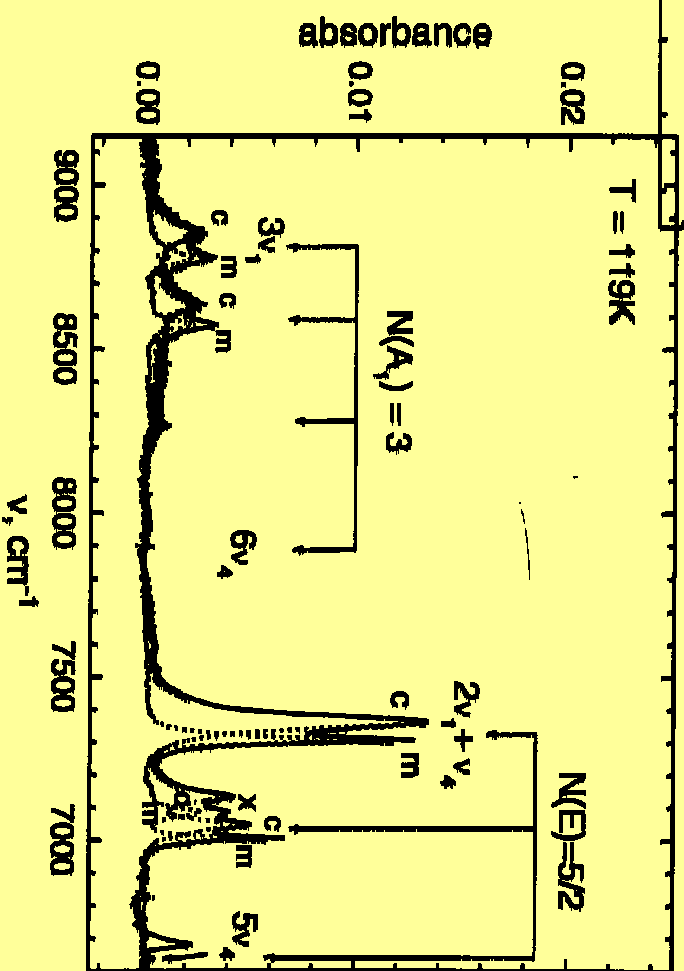
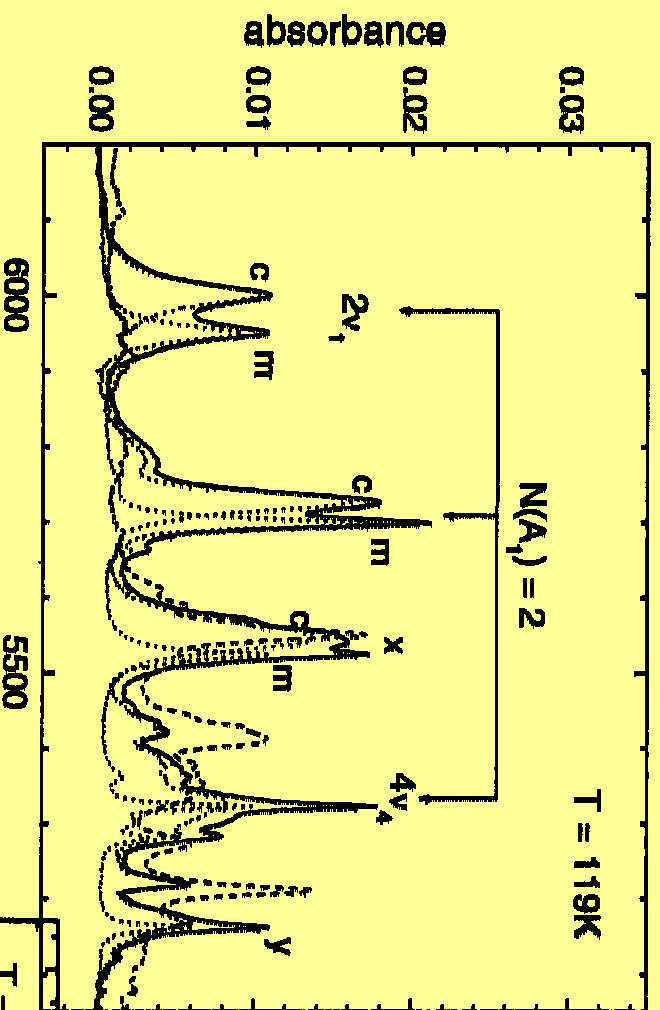
CAN WE INCLUDE DATA FROM THE
NEAR INFRARED?

Complexes of Fluoroform with CD_3F

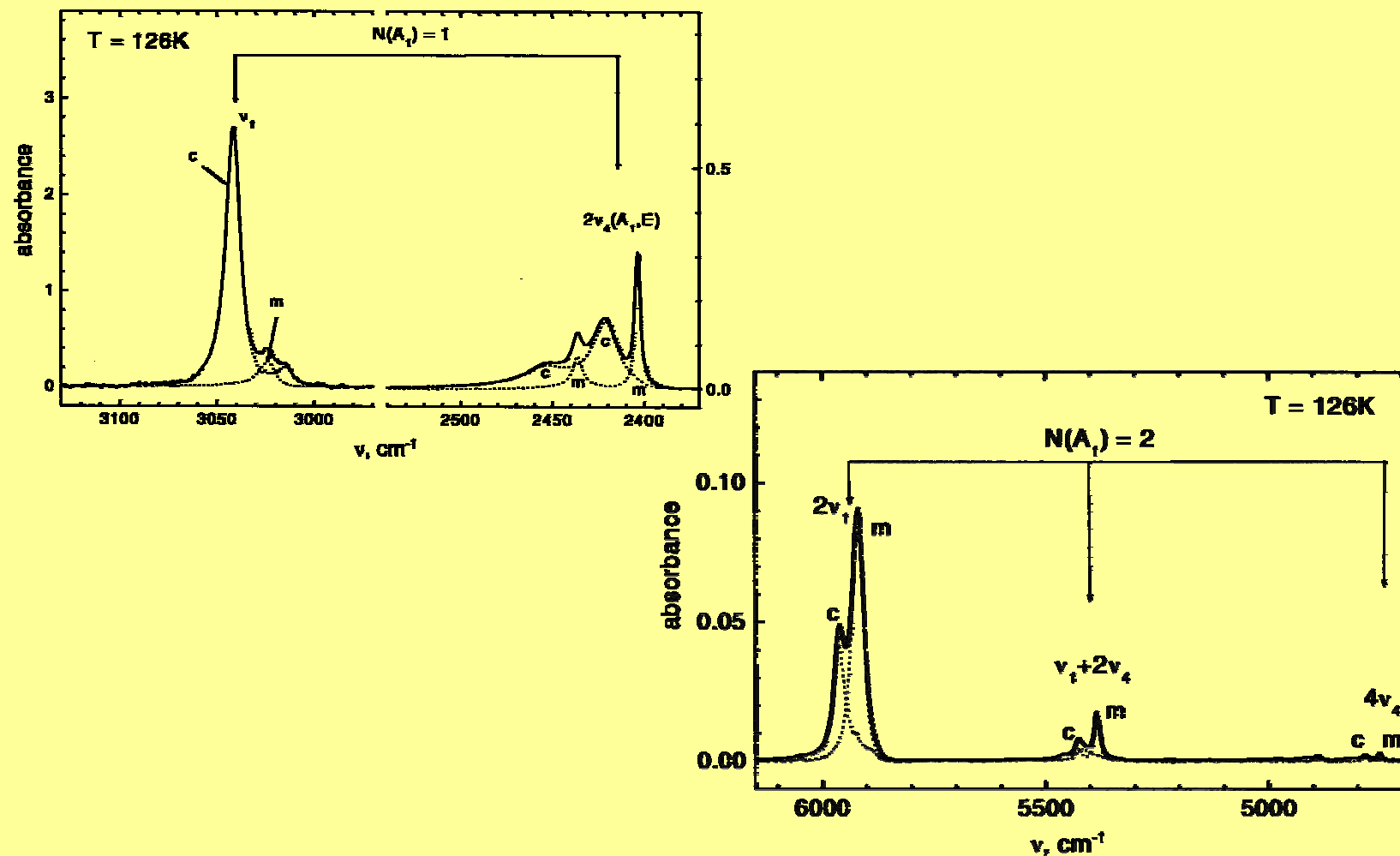


K.S. Rutkowski, P. Rodziewicz, S.M. Melikova, W.A. Herrebout, B.J. van der Veken, A. Koll, *Chem. Phys.* 313 (2005) 225-243.

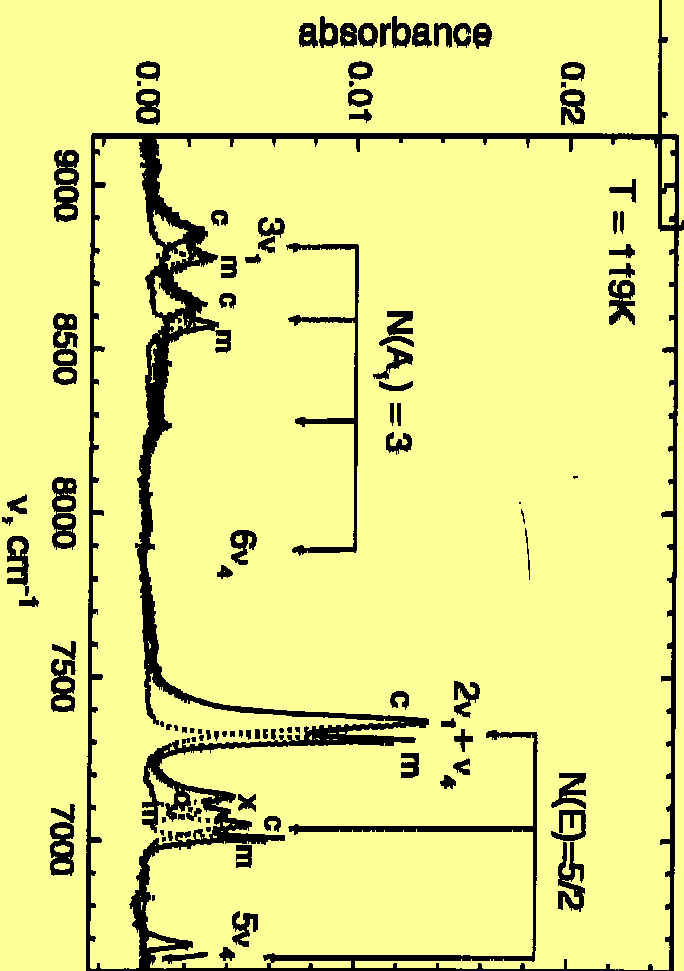
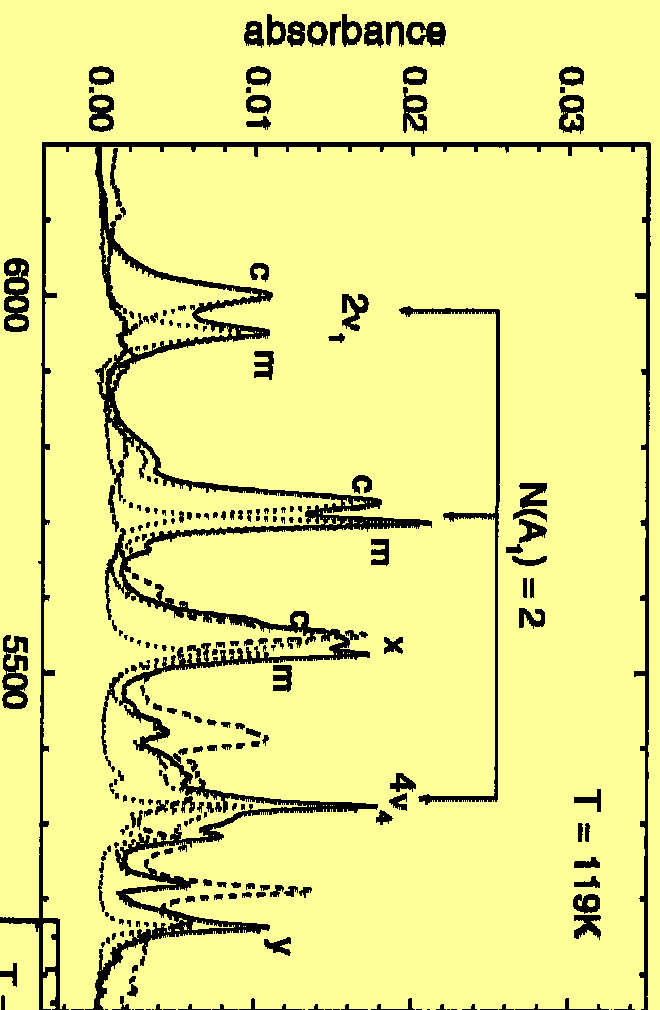




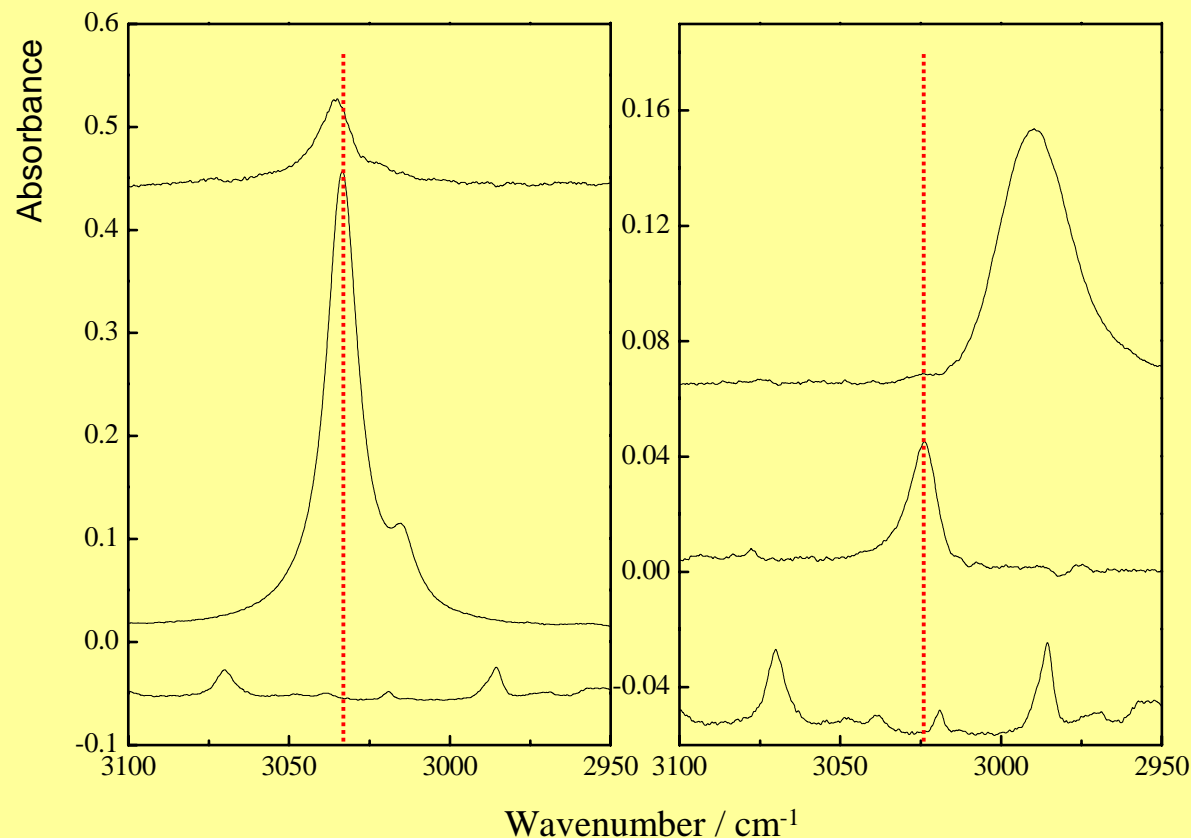
Complexes of Chloroform with CD_3F



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



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 $\text{CH}\cdots\text{S}$ hydrogen bond ??

So far, the experimental data for DMS-CHF₃ 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 CHF₃.

The experimental data obtained for DMS-CHF₃ and DMS-CHCl₃ are in line with preliminary data obtained for the mixed haloforms CHF₂Cl and CHFCl₂

	before correction	after correction
DMS-CHF ₃	+3.8 cm ⁻¹	-3 (1) cm ⁻¹
DMS-CHF ₂ Cl	-4.4 cm ⁻¹	
DMS-CHFCl ₂	-15.6 cm ⁻¹	
DMS-CHCl ₃	-32.8 cm ⁻¹	-34 (1) cm ⁻¹

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KLEINE PROJECTEN