Chemistry 3830

Noble Gases

Properties of Noble Gases

Element	Electronic structure	mp, °C	E_{ea}, kJ mol^{-1}	$E_{i,1}$, kJ mol^{-1}	Electronegativity	van der Waals radius, pm
He	$1s^2$	−272	−48	2373	5.5	143
Ne	[He] $2s^2 2p^6$	−249	−116	2080	5.1	160
Ar	[Ne] $3s^2 3p^6$	−189	−96	1520	3.3	190
Kr	[Ar] $3d^{10} 4s^2 4p^6$	−157	−96	1351	3.1	200
Xe	[Kr] $4d^{10} 5s^2 5p^6$	−112	−77	1170	2.4	220
Rn	[Xe] $4f^{14} 5d^{10} 6s^2 6p^6$	−71	?	1036	?	230

Composition of Air

Selected components of air in order of increasing b.p.

	boiling point, °C	percent abundance
He	−269	5.24×10^{-4}
Ne	−246	1.818×10^{-3}
N_2	−196	78.085
Ar	−186	0.934
O_2	−183	20.948
Kr	−153	1.14×10^{-4}
Xe	−108	8.7×10^{-6}

Liquefaction of Air/ Linde Process

- Fractional distillation of liquefied air
  - Air is compressed and cooled. Adiabatic expansion will cool air further
  - Major products: liquid nitrogen and oxygen

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- Helium cannot be produced by the Linde Process

Helium

Need:
- Liquid helium is necessary to cool magnets for NMR and MRI
- Party balloons

Source:

- Helium is present in some natural gases: 0.2 – 7 vol%
  - In the past: He was obtained from American natural gas wells
  - But, the American He-rich natural gas wells are declining
  - Helium prices have gone up in the last 10 years.
  - New He-rich wells have been found in Arabia (Qatar) and Africa (Tanzania)
  - World-largest He plant: in Qatar

- He is non-renewable, therefore, it should be recovered if possible

Discovery of Noble Gas Compounds

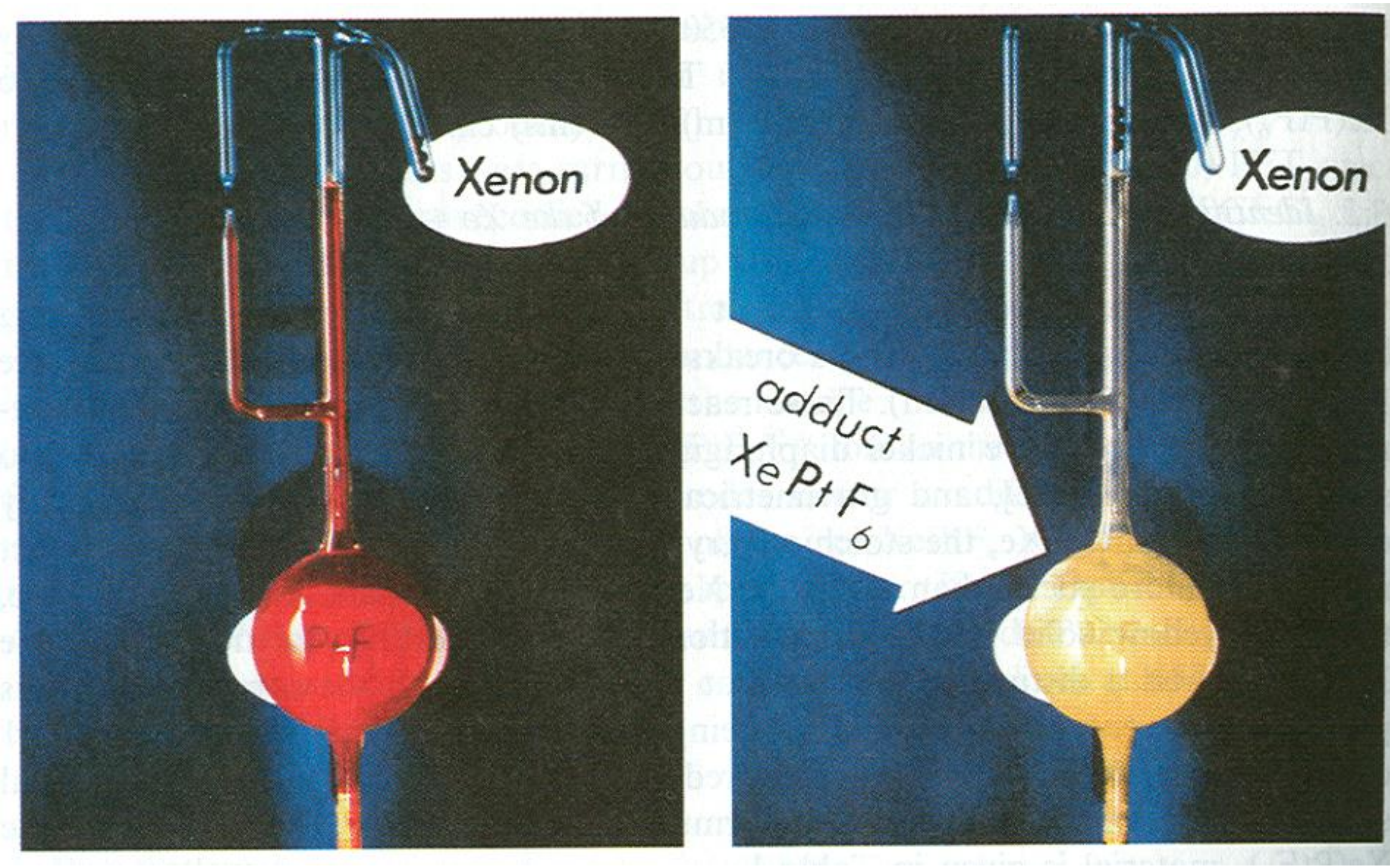
- In 1962: Neil Bartlett at UBC discovered noble gas reactivity

$$O_2 + PtF_6 \rightarrow O_2^+PtF_6^-$$

  - Ionization potential of O_2: 12.2 eV
  - Ionization potential of Xe: 12.13 eV

$$Xe + PtF_6 \rightarrow \text{“}Xe^+PtF_6^-\text{”}$$

Discovery of Noble Gas Compounds



Xenon Fluorides

- In 1962, Hoppe (from Germany) reported the synthesis of XeF_2

XeF_2, $\Delta_f H = -164$ kJ/mol
XeF_4, $\Delta_f H = -284$ kJ/mol   exothermic
XeF_6, $\Delta_f H = -361$ kJ/mol

Synthetic approaches:

$$Xe_{(g)} + F_{2(g)} \rightarrow XeF_2 \text{ (400°C, 1 atm, xenon in excess)}$$

$$Xe_{(g)} + 2F_{2(g)} \rightarrow XeF_4 \text{ (600°C, 6 atm, } Xe : F_2 = 1 : 5\text{)}$$

$$Xe_{(g)} + 3F_{2(g)} \rightarrow XeF_6 \text{ (300°C, 60 atm, } Xe : F_2 = 1 : 20\text{)}$$

- XeF_8 ?

Xenon Fluorides

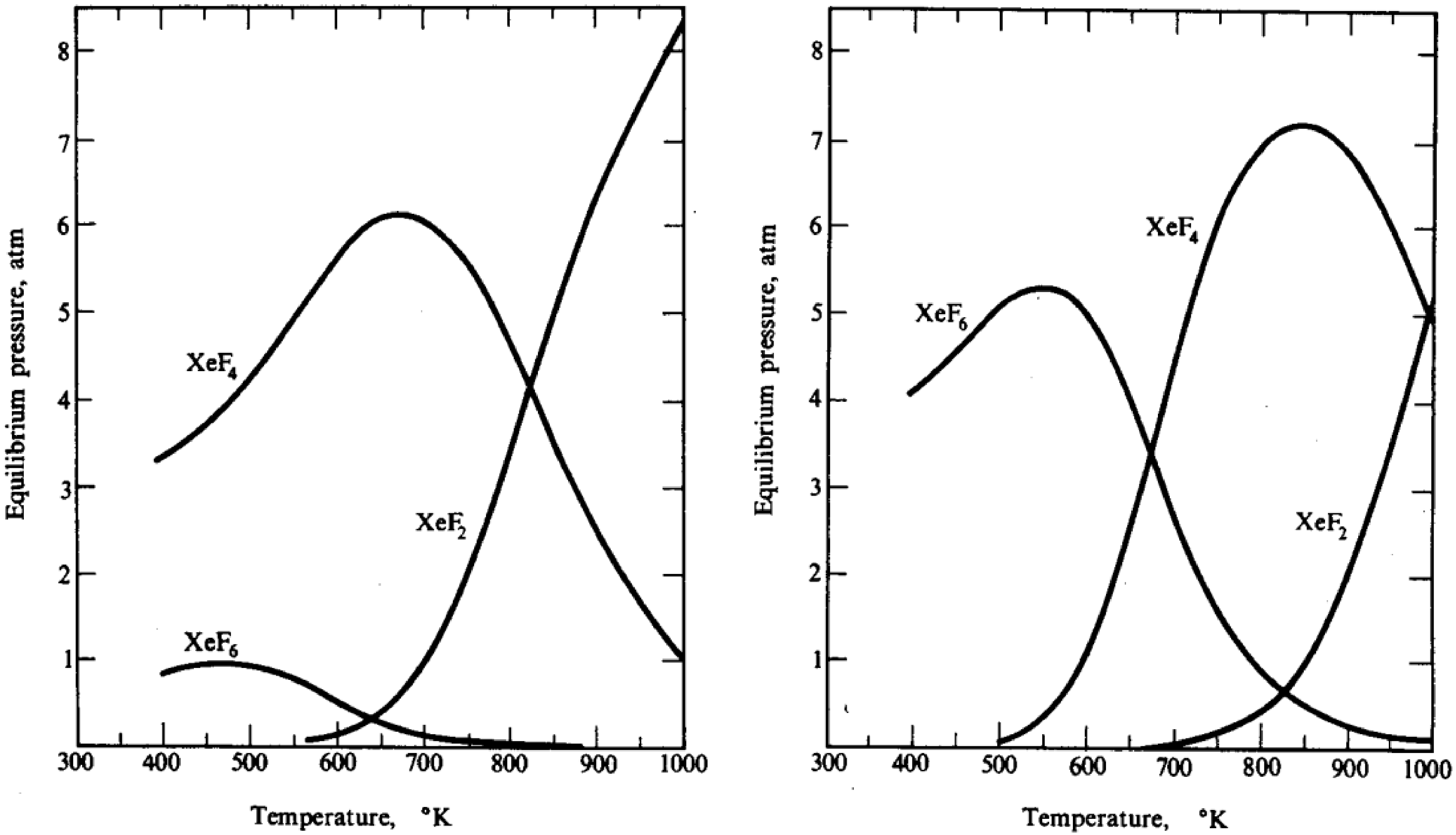


FIG. 15. Pressure and temperature influence on XeF_2, XeF_4, and XeF_6 formation

(a)
Equilibrium pressures of xenon fluorides as a function of temperature.
Initial conditions: 125 mmoles Xe, 275 mmoles F_2 per 1000 ml.

(b)
Equilibrium pressures of xenon fluorides as a function of temperature.
Initial conditions: 125 mmoles Xe, 1225 mmoles F_2 per 1000 ml.

Bonding in Xenon Fluorides

VB

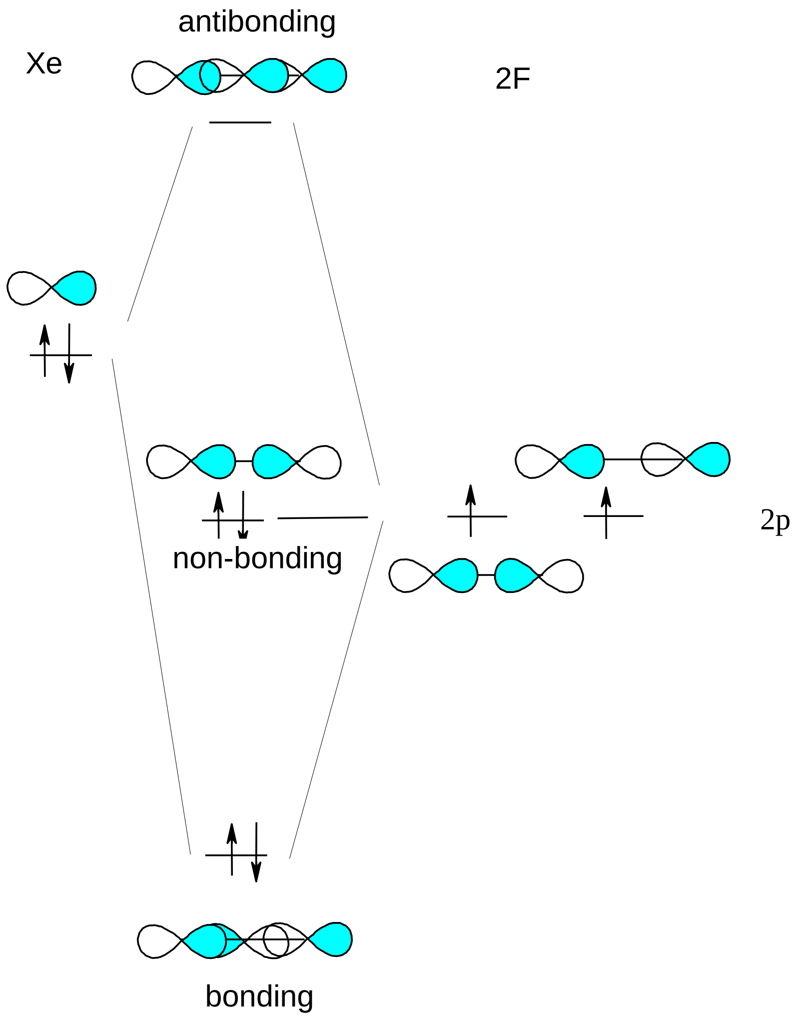
MO

Bonding in Xenon Fluorides

VB

$F{-}Xe^{+}\ F^{-} \leftrightarrow F^{-}\ {}^{+}Xe{-}F$

MO



- 3-centre-4-electron bonding

Structure of XeF_6

Structure: what does it mean?

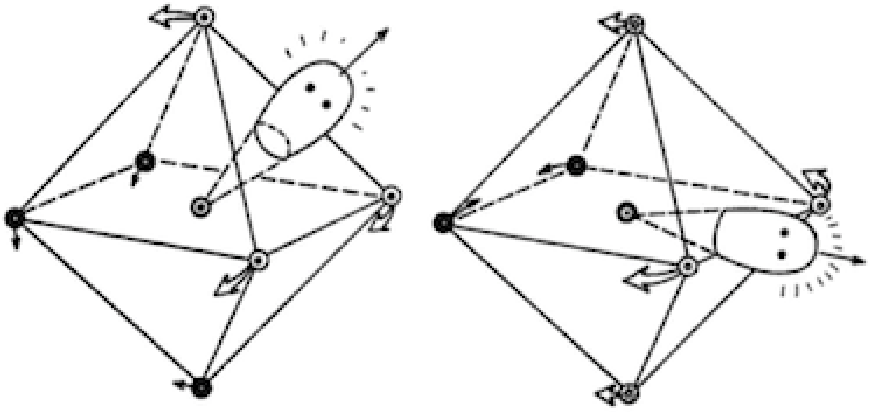
- In the solid
- In the gas phase
- In the liquid
- In solutions (different solvents?)

Structure of Gaseous XeF_6

In the gas-phase:

Monomeric XeF_6:

- Stereochemically active lone pair!
- Non-octahedral
- Fluxional; lone pair going from one face to the next



Characterization methods:

- Vibrational spectroscopy
- NMR spectroscopy
- Gas-phase electron diffraction
- Computational chemistry

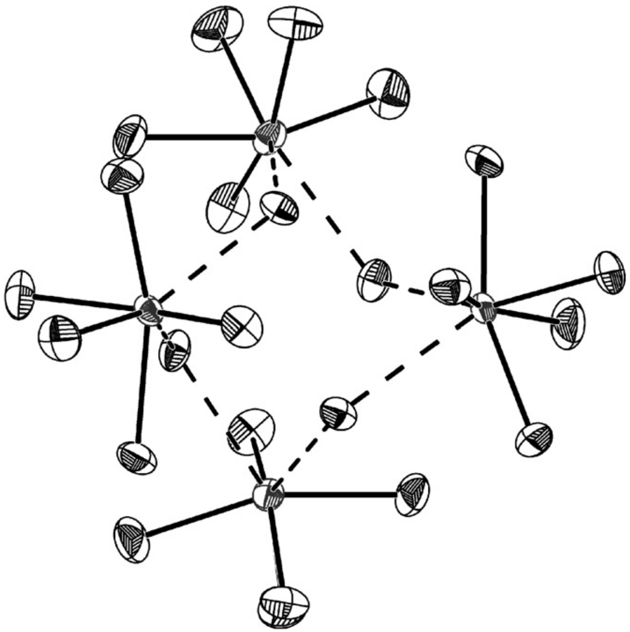
Time Scales of Characterization Tools

EPR	10^{-6} s	
NMR	10^{-3} to 10^{-6} s	
IR/Raman	10^{-12} s	
UV/visible	10^{-15} s	
Mössbauer	10^{-18} s	
X-ray Diffraction	10^{-18} s	Careful: special averaging!

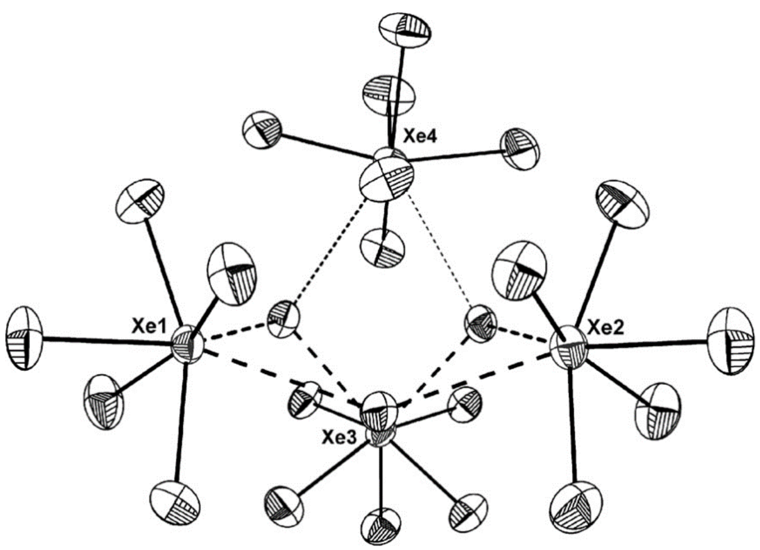
Structure of Solid XeF_6

- Different modifications (different packing and/or different structural units)

modification	structural units	method of crystallization
XeF_6 (*mP32*)	tetramers, $(XeF_5^+F^-)_3\ XeF_6$	sublimation at 30°C
XeF_6 (*mC32*)	tetramers, $(XeF_5^+F^-)_3\ XeF_6$	rapid sublimation above room temperature
XeF_6 (*mP8*)	tetramers????	crystallization from melt
XeF_6 (*cF144*)	tetramers, $(XeF_5^+F^-)_4$ and hexamers $(XeF_5^+F^-)_6$	maintaining sample at 4-18 °C
XeF_6 (*mP16*)	tetramers $(XeF_5^+F^-)_4$	crystallization form solution at −40 to −18°C
XeF_6 (*oP16*)	hexamers $(XeF_5^+F^-)_6$	low-temperature sublimation



tetramers



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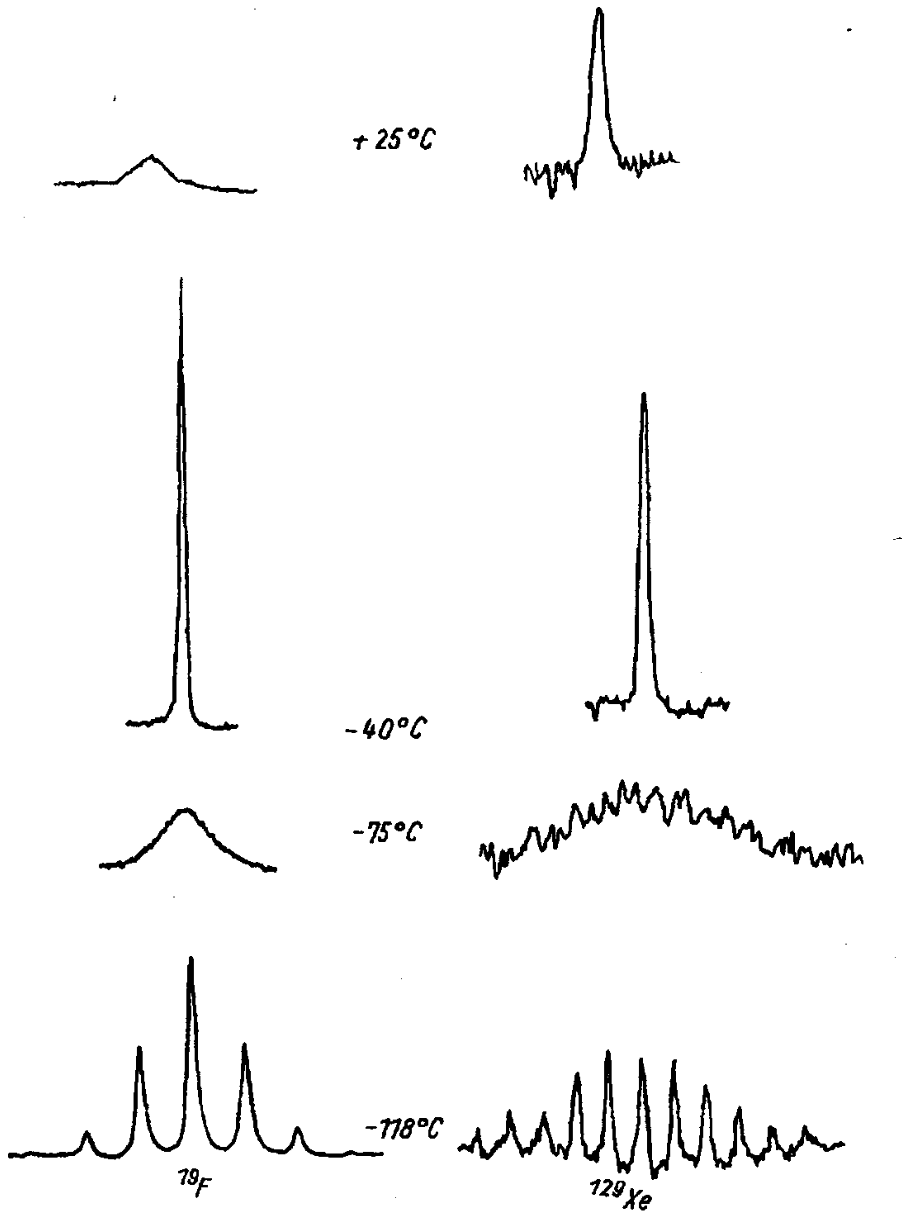
Characterization methods:

- X-ray crystallography
- Vibrational spectroscopy
- Solid-state NMR spectroscopy
- Computational chemistry (not for packing!!!)

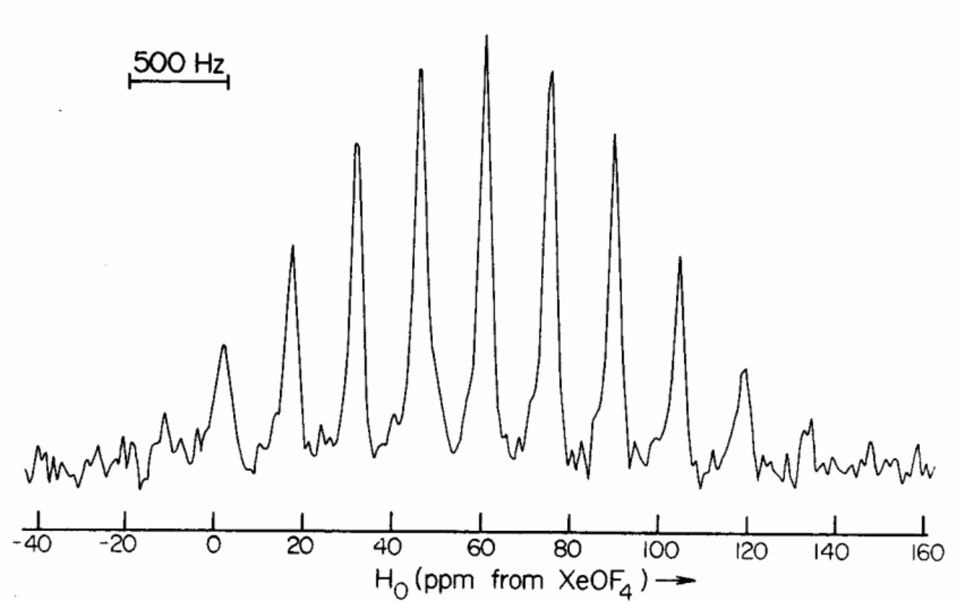
Structure of XeF_6 in Solution

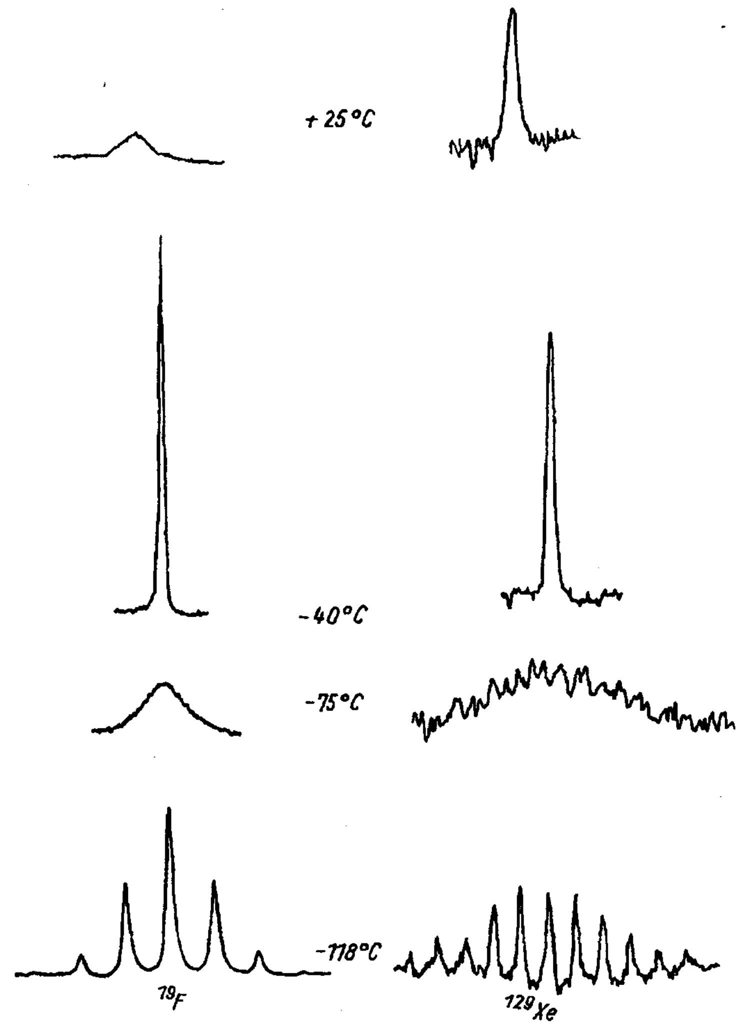


In F_5SOSF_5 solvent

Structure of XeF_6 in Solution

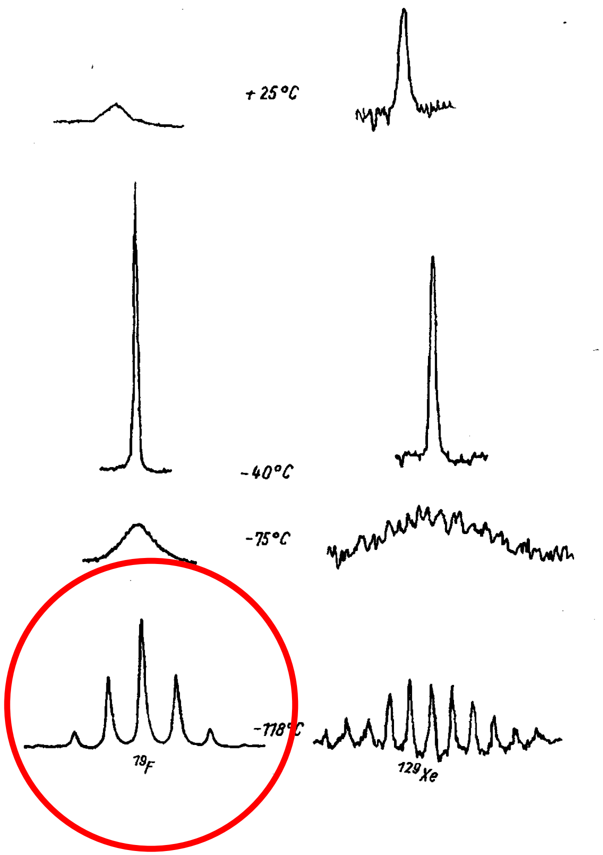
In SO_2ClF/CF_2Cl_2 at h –145 °C:





- Tetrameric structure is consistent with the line intensities: Xe_4F_{24}

Structure of XeF_6 in Solution



- Five different isotopologues with abundances:

Xe_4F_{24}
$(0.7356)^4 = 29.28\%$

$^{129}XeXe_3F_{24}$
$4(0.2644)(0.7356)^3 = 42.10\%$

$^{129}Xe_2Xe_2F_{24}$
$6(0.2644)^2(0.7356)^2 = 22.70\ \%$

$^{129}Xe_3XeF_{24}$
$4(0.7356)(0.2644)^3 = 5.439\ \%$

$^{129}Xe_4F_{24}$
$(0.2644)^4 = 0.4887\ \%$

Sum of abundances = 100 %