



Edelgase

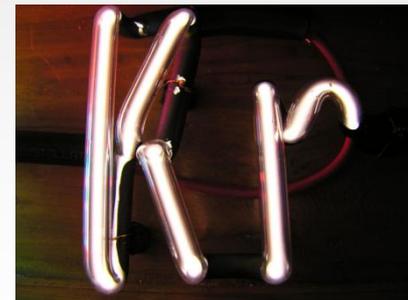
Prof. Dr. Dr. h.c. Thomas M. Klapötke

2. Dezember 2025

Anorganische Experimentalchemie



Edelgase





Helium (griech. Helios: die Sonne)

Neon (das Neue)

Argon (das Träge)

Edelgase

Xenon (das Fremde)

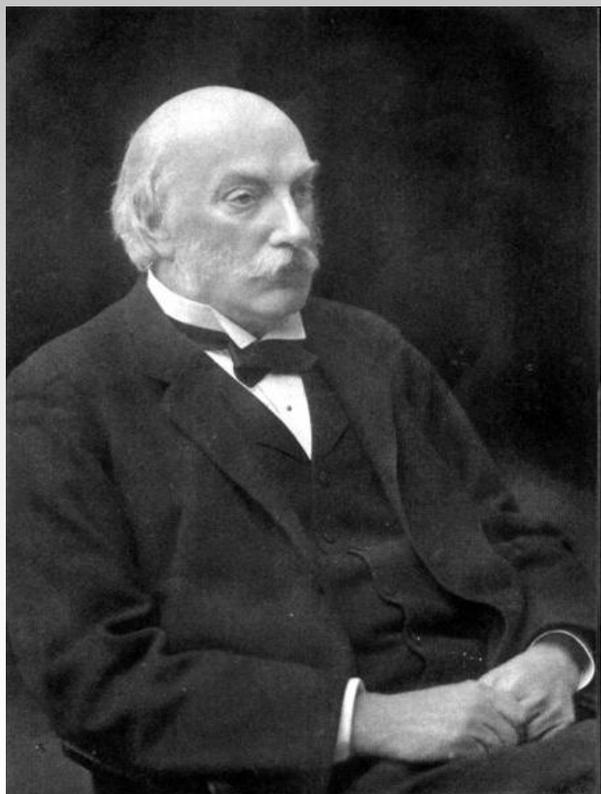
Krypton (das Versteckte)

Radon (das Strahlende)



John William Strutt, 3. Baron Rayleigh

Edelgas Argon (1894)



In Zusammenarbeit mit William Ramsey

Strutt erklärte die blaue Farbe des Himmels anhand der Streuung des Lichtes an kleinen Partikeln (Rayleigh-Streuung).

Nobelpreis Physik 1904

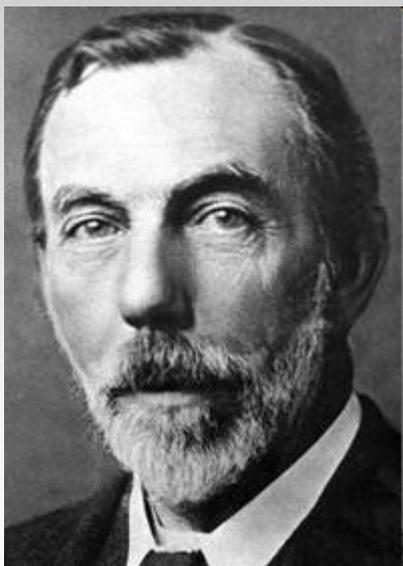
für die Bestimmung der Dichte der wichtigsten Gase und für die Entdeckung des Argons.



Entdeckung

William Ramsey

Entdeckung von Helium (1895), Xeon, Neon und Kryton (1898)



geb. in Glasgow (1852)

Chemiestudium in Tübingen

Professor an der Universität Bristol

Nobelpreis Chemie 1904

"Als Anerkennung des Verdienstes, das er sich durch die Entdeckung der indifferenten gasförmigen Grundstoffe in der Luft und die Bestimmung ihres Platzes im periodischen System erworben hat"

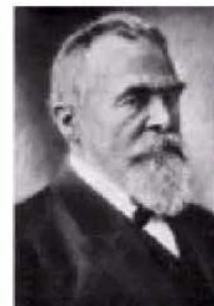
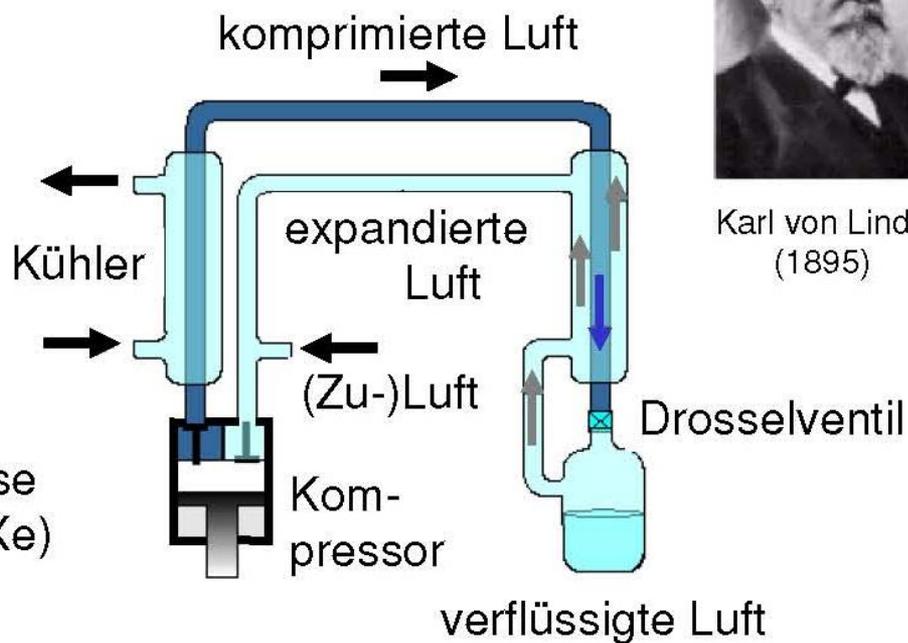
Entdeckung

Luftverflüssigung

Luft:

78,09% N₂
20,95% O₂
0,93% Ar
0,03% CO₂

Rest: Edelgase
(Ne, He, Kr, Xe)

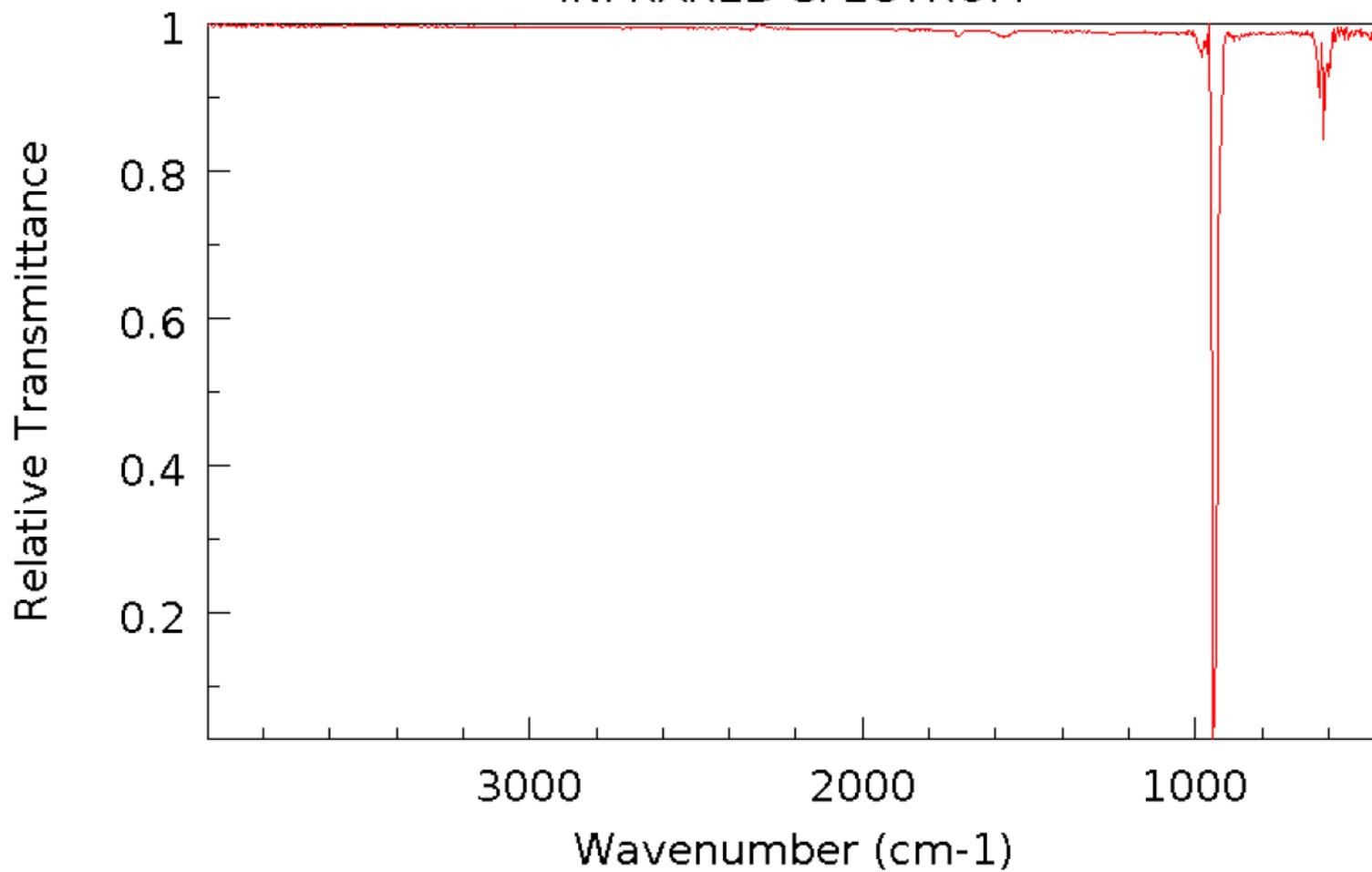


Karl von Linde
(1895)

Eigenschaften

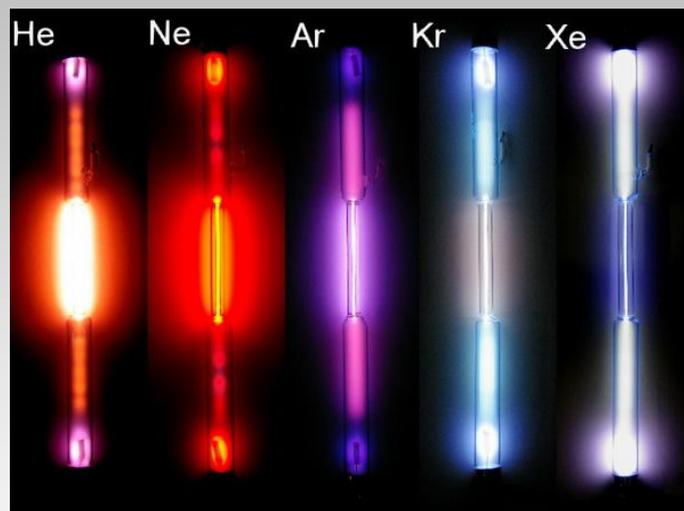
	Helium	Neon	Argon	Krypton	Xenon	Radon
	He	Ne	Ar	Kr	Xe	Rn
Ordnungszahl Z	2	10	18	36	54	86
Elektronenkonfiguration	$1s^2$	[He] $2s^2 2p^6$	[Ne] $2s^2 2p^6$	[Ar] $3d^{10}$ $4s^2 4p^6$	[Kr] $4d^{10}$ $5s^2 5p^6$	[Xe] $4f^{14} 5d^{10}$ $6s^2 6p^6$
Ionisierungsenergie in eV	24,6	21,6	15,8	14,0	12,1	10,7
Promotionsenergie $np \rightarrow (n + 1)s$ in eV	-	16,6	11,5	9,9	8,3	6,8
Schmelzpunkt in °C	-272	-249	-189	-157	-112	-71
Siedepunkt in °C	-269	-246	-186	-153	-108	-62
Kritische Temperatur in °C	-268	-229	-122	-64	17	105
Van der Waals-Radien in pm	120	160	190	200	220	-
Farbe des in Gasentladungsröhren ausgestrahlten Lichts	gelb	rot	rot	gelbgrün	violett	weiss

Sulfur hexafluoride
INFRARED SPECTRUM



Anwendungen

- Edelgase in Gasentladungsröhren



- Argon als Schutzgas (Chemie, Schweißen)

- Technisches Tauchen (Trimix: Helium, Sauerstoff, Stickstoff)

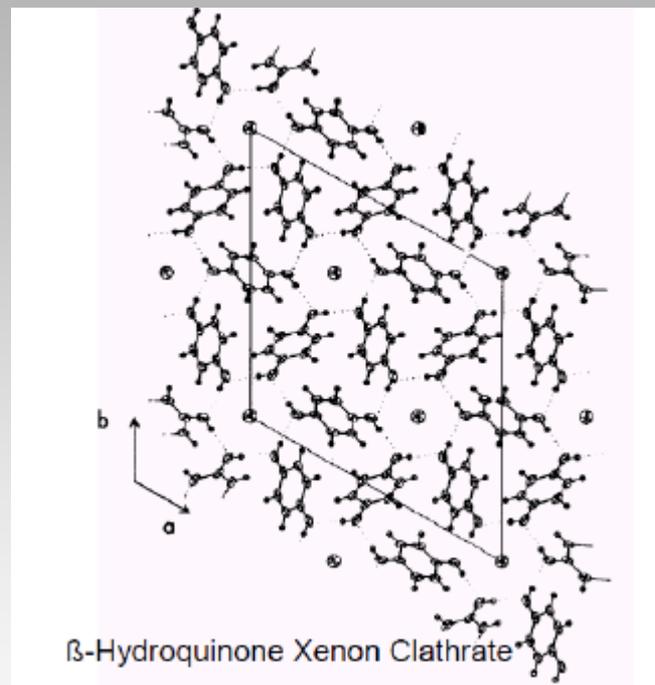
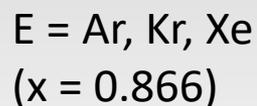
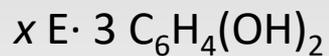
- Helium in Ballons und als Kühlmittel

- Xenon in Ionenantrieben

Edelgas Chemie

1896 Clathrate ($E_8(H_2O)_{46}$)

Später wurden strukturell charakterisierte verwandte Hydrochinon-Komplexe berichtet:



Ruff, Münster





- 1933** L. Pauling
“Xenon sollte Salze der Form Ag_4XeO_6 und AgH_3XeO_6 bilden”
- 1952** L. Pauling
“Edelgase sind völlig unreaktiv und bilden keine Verbindungen”
- 1962** Das Jahr der Edelgase
- $\text{Xe}[\text{PtF}_6]$ (Bartlett, die erste Edelgas Verbindung)
 XeF_2 (Hoppe)
 XeF_4 (Classon)



23rd March 1962.
9 p.m.

The Preparation of Xenon Hexafluoroplatinate (V)

$Xe \rightarrow Xe^+ + 6e$
12.03 eV.

$O_2 \rightarrow O_2^+ + 6e$
12.2 eV.

Prepⁿ of PtF₆.
A sponge (from Min, Pt, F₂) in a nickel boat - ignited in 90% F₂ (lab).
The red vapour was trapped in U traps cooled in liquid oxygen.
When the sponges were platinum ignited/stopped the preparation was
terminated to reduce contamination by SiF₄ to a minimum.

Measurement of PtF₆
The sample of PtF₆ contained with original trap (cooled at -163) was connected
to a Pyrex - silica system as shown. The entire system was evacuated and
flamed then sealed under vacuum at X. The PtF₆ was transferred to the wall of
the bubble gauge (cooled in liq O₂) and the brass valve closed. As the PtF₆
warmed up, the pressure developed was balanced by admitting air to the surround;
chamber. A manometer recorded the pressure of the outer chamber. The vapour
was deep red (only subdued lighting was used during the experiment to reduce photolysis).
Pressure of PtF₆ taken — 45 mm.
Pressure of Xe taken — 95 " "
Residual pressure — 40 " "

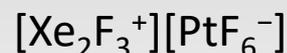
The PtF₆ was condensed in the break seal bottle B which was subsequently
sealed at P.

Meanwhile the Xenon system - isolated by the break seal A had been dried
under vacuum with the tap T open. This system was sealed at X, T closed
and the break-seal on the Xenon bottle broken.

Measurement of Xenon
A was broken and the brass valve opened. Tap T was cautiously opened
and the pressure developed balanced by admitting air to the outer bubble gauge
chamber. T was closed when the pressure developed matched that of the
PtF₆. The brass valve was closed and the tap T closed. The space between
T and the brass valve was pumped out via X, the system again flamed



Xenon hexafluoroplatinat



N. Bartlett,
"Xenon hexafluoroplatinate (V) Xe⁺[PtF₆]⁻".
Proc. Chem. Soc. **1962**, 6, 218.

N. Bartlett, D. H. Lohmann
"Dioxygenyl hexafluoroplatinate (V), O₂⁺[PtF₆]⁻".
Proc. Chem. Soc. **1962**, 3, 115

1962: Die erste Edelgas-Verbindung



1962 Des Jahr des Xenons

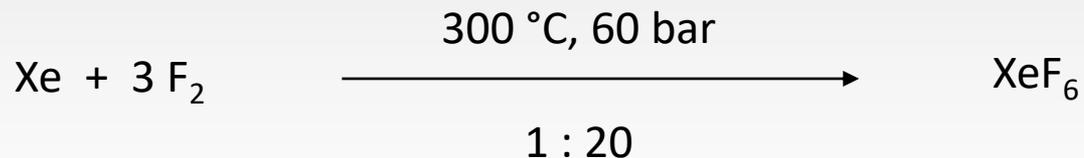
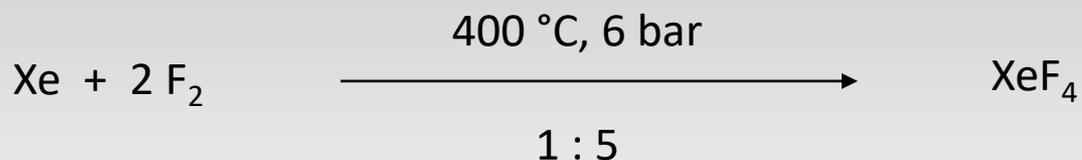
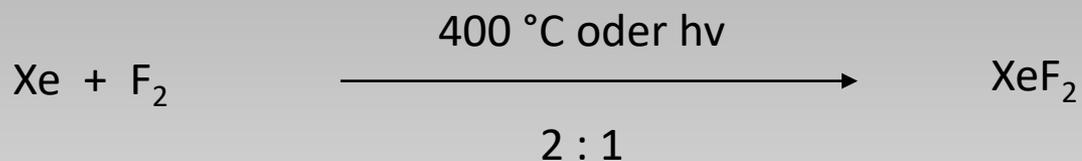
Bartlett: „XePtF₆“ Die erste Edelgas-Verbindung

Hoppe (Münster): Die Synthese von XeF₂

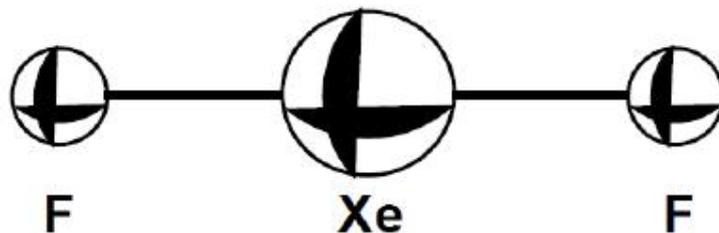
Classon (LANL): Die Synthese von XeF₄



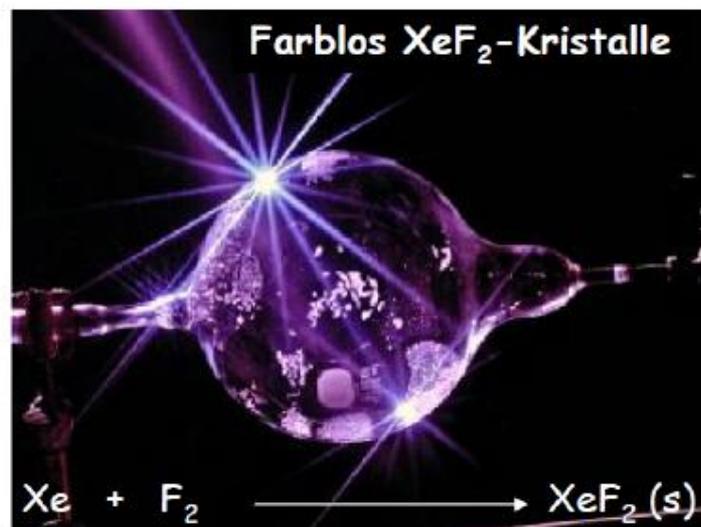
Edelgasfluoride



Ausserdem Kryptonfluorid (KrF_2) und Radonfluorid (RnF_2) bekannt!



Sehr gut löslich in HF
Farblos
Kristallin
Sublimiert bei RT
Wenig H₂O-empfindlich
O₂-stabil
Kristalle durch Sublimation gewonnen
Fp. 140°C

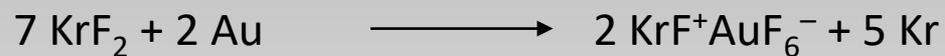


Edelgasfluoride

	XeF ₂	XeF ₄	XeF ₆	KrF ₂
Molekülstruktur (Gas)	D _{∞h}	D _{4h}	C _{3v} (verzerrt oktaedrisch)	D _{∞h}
Fp. (in °C)	129.0	117.1	49.5	metastabil
	120.0 Subl.			
Kp. (in °C)			75.6	
ΔH _f [°] (in kJ mol ⁻¹)	-164	-278	-361	+60
Darstellung	Xe:F ₂ = 2:1, 2 bar, 400 °C	Xe:F ₂ = 1:5, 6 bar, 400 °C	Xe:F ₂ = 1:20, 60 bar, 300 °C	Kr+F ₂ , -183 °C, elektr. Entl.
BDE(Xe-F) (kJ mol ⁻¹)	131	130	126	
Oxidations-stärke	schwach	mittel	stark	sehr stark
Fluorierungs-stärke	schwach	mittel	stark	sehr stark

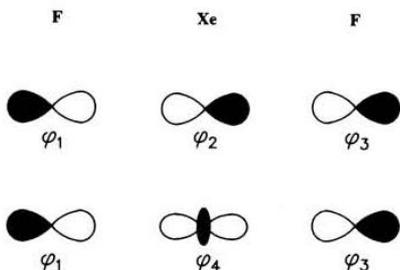


Edelgasfluoride





Bindungsverhältnisse im XeF₂



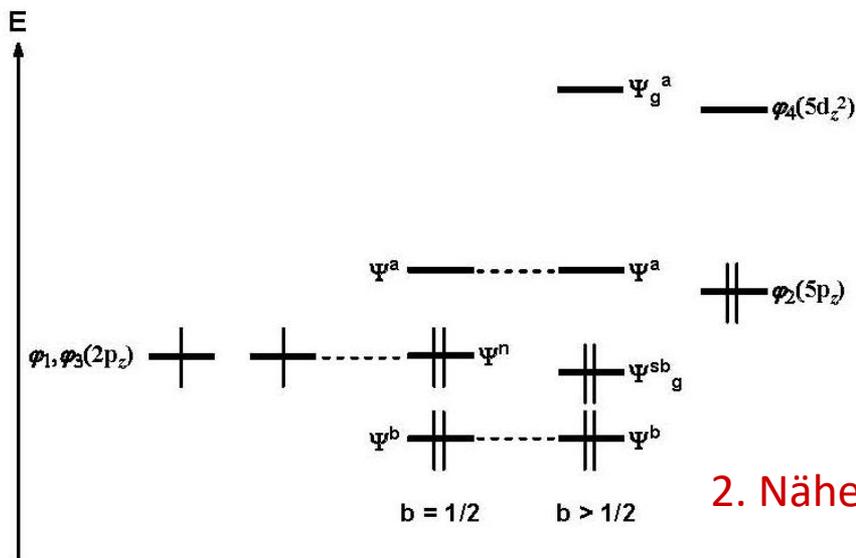
$$\Psi_b = c_1\varphi_2 + c_2(\varphi_1 - \varphi_3)$$

$$\Psi_a = c_1\varphi_2 - c_2(\varphi_1 - \varphi_3)$$

$$\Psi_n = c_2(\varphi_1 + \varphi_3)$$

$$\Psi_g^b = c_3(\varphi_1 + \varphi_3) + c_4\varphi_4$$

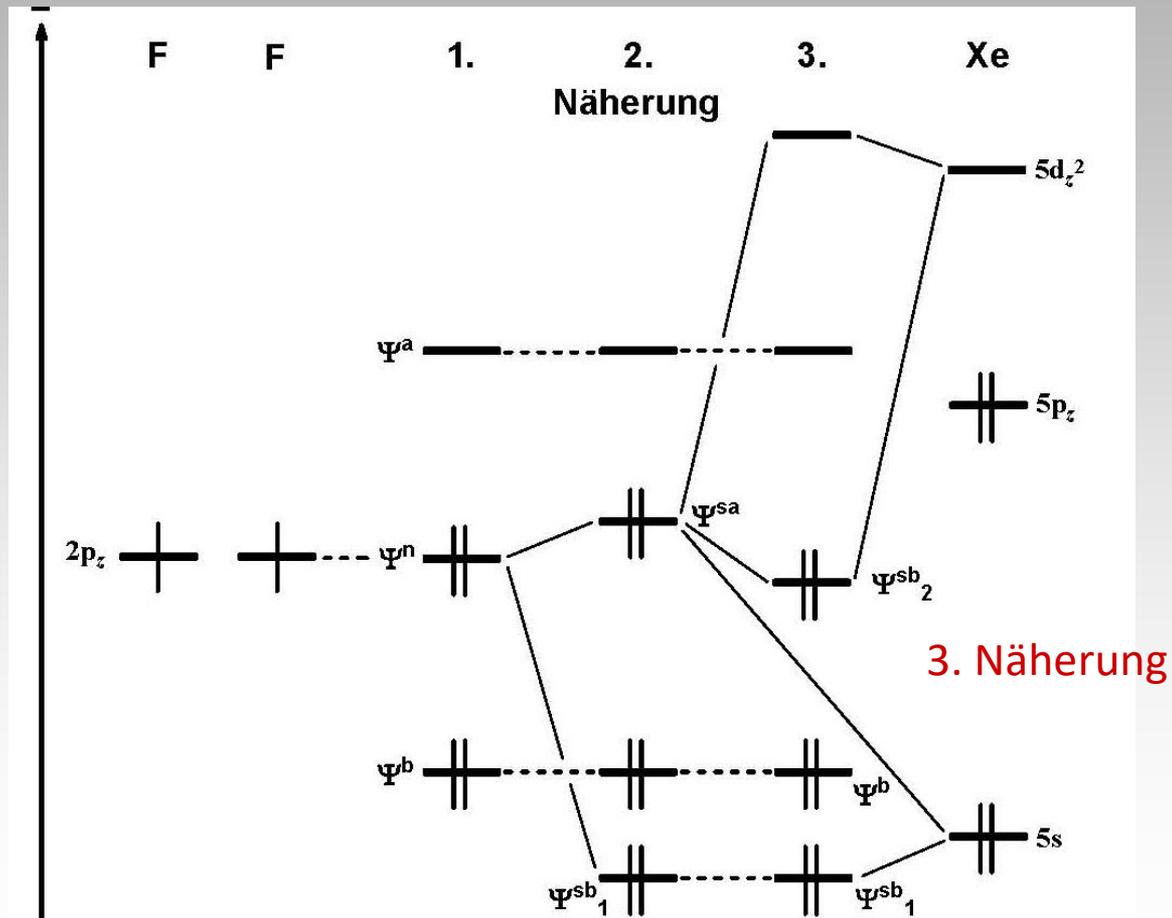
$$\Psi_g^a = c_3(\varphi_1 + \varphi_3) - c_4\varphi_4$$



2. Näherung



Bindungsverhältnisse im XeF₂

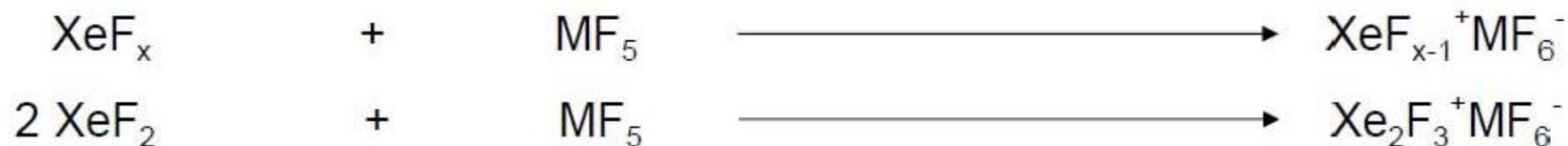


Xenon Verbindungen

Reaktionen:

- (i) Mit F⁻-Akzeptoren unter Bildung von Xe-F-Kationen
- (ii) Mit F⁻-Donatoren unter Bildung von Xe-F-Anionen
- (iii) HF Abspaltung durch Reaktion von XeF_x und wasserfreier Säure
- (iv) Hydrolyse und Bildung von Xenon-Oxofluoriden, Xenon-Oxide, Xenaten

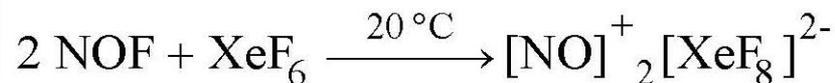
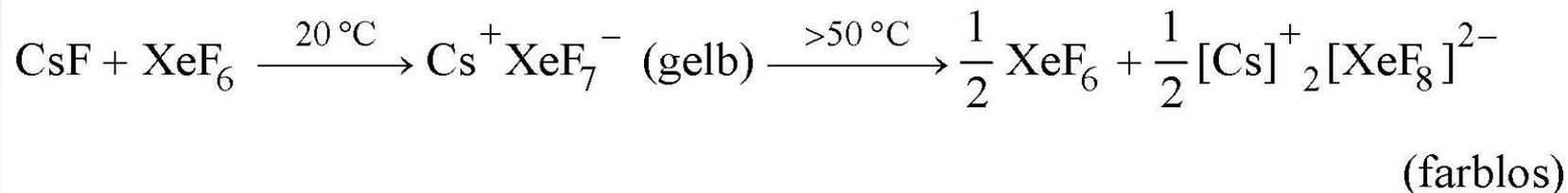
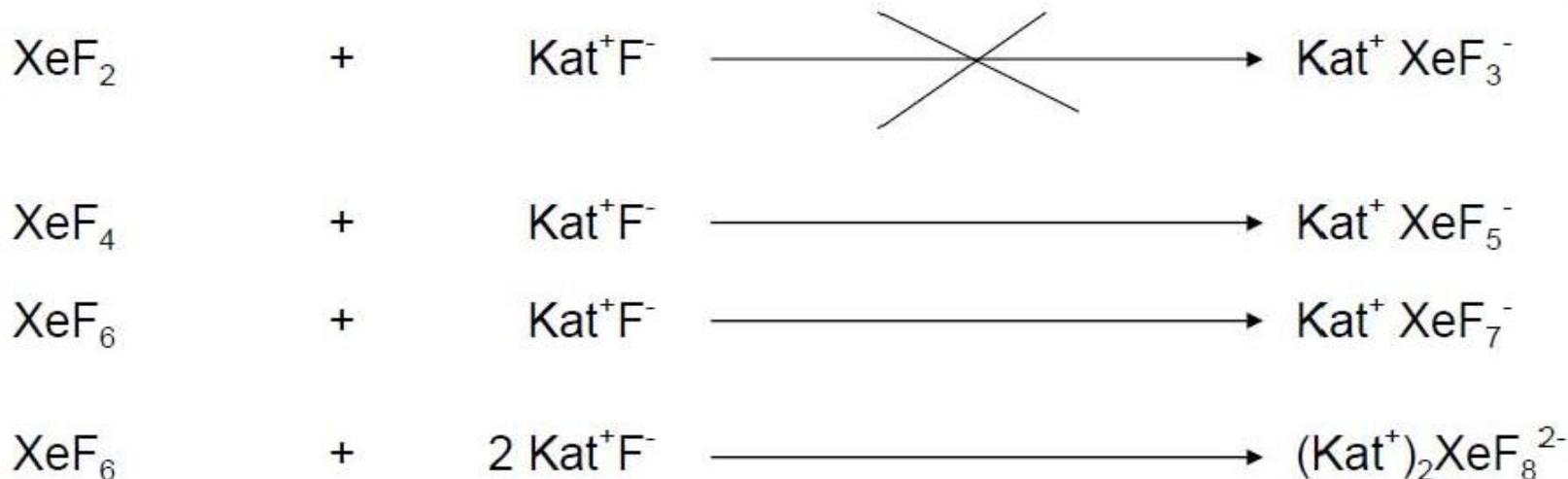
(i) Mit F⁻-Akzeptoren unter Bildung von Xe-F-Kationen



M z.B. PtF₅



(ii) Mit F-Donatoren unter Bildung von Xe-F-Anionen



(iii) HF Abspaltung durch Reaktion von XeF_x und wasserfreier Säure



aber auch:



(iv) Hydrolyse und Bildung von Xenon-Oxofluoriden, Xenon-Oxide, Xenaten

Xenon-Oxofluoride:



Xenon-Oxide:



Perxenate:

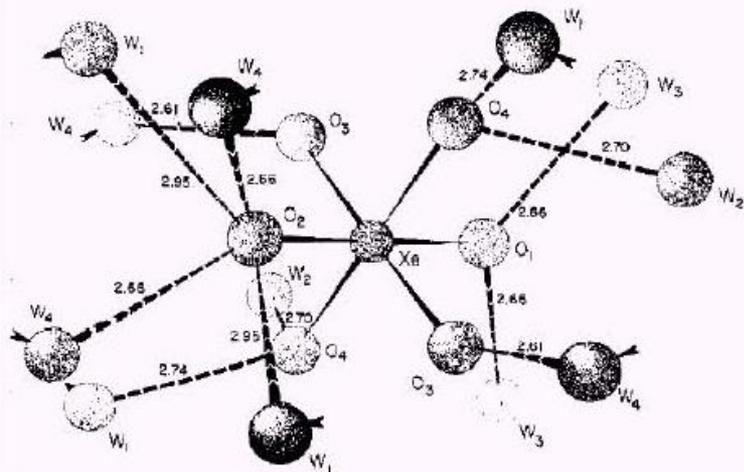




XENON TRIOXIDE

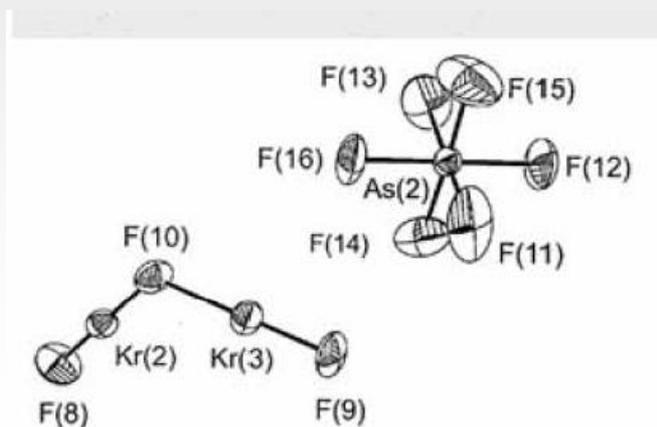
Sir:

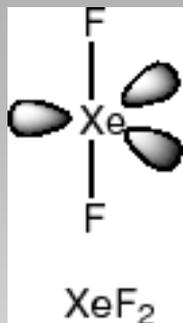
The slow hydrolysis of XeF_6 ¹ has been found to result in a white, transparent, non-volatile crystalline compound that has been identified as XeO_3 . This compound is so very explosive that preparations have been limited in amounts to less than 50 mg. An explosion involving 3 mg. has broken glassware, while an amount less than one milligram has fractured a KBr window. An intentional explosion involving 7.2 mg., in a 25 cc. evacuated infrared cell, seriously deformed and nearly ruptured a 2 mm. thick silver chloride window. Explosions have been produced by rubbing, pressing, or even gentle heating, and have been encountered when manipulating the powder, especially near aqueous solutions. There is some indication that XeO_3 is more unstable when the relative humidity exceeds 20% than in a drier atmosphere.



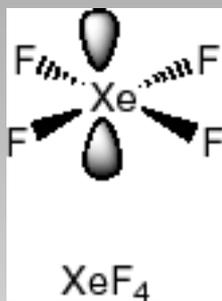
VSEPR Strukturen

Kation	Struktur	Punktgruppe
XeF^+	linear	$C_{\infty v}$
XeF_3^+	T-förmig	C_{2v}
XeF_5^+	quadratisch pyramidal	C_{4v}
Kr_2F_3^+	V-förmig	C_{2v}

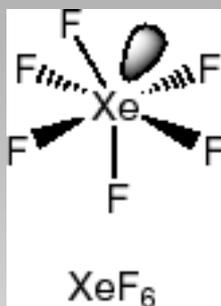




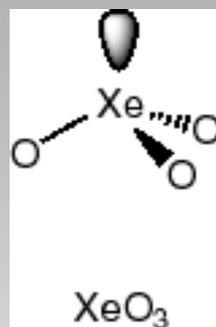
D_{∞h}



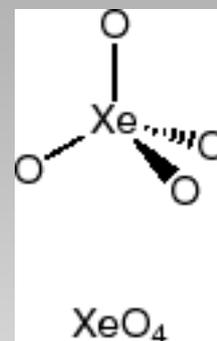
D_{4h}



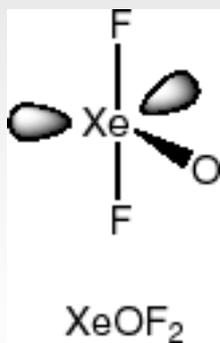
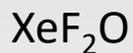
~ O_h



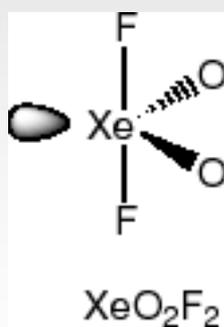
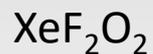
C_{3v}



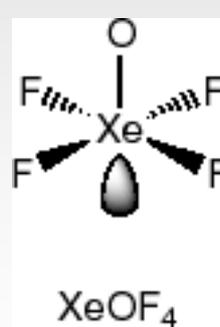
T_d



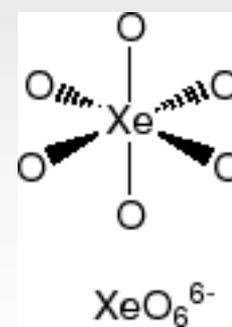
C_{2v}



C_{2v}

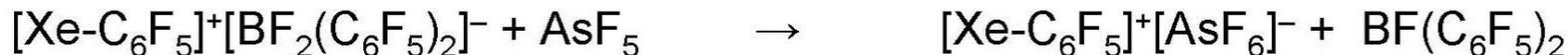
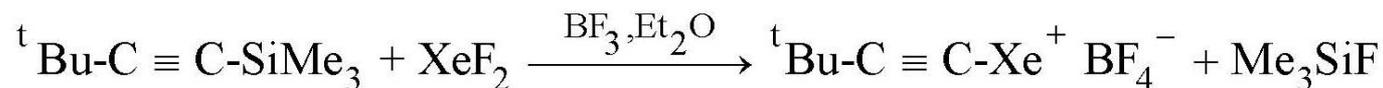
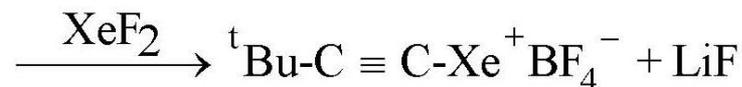
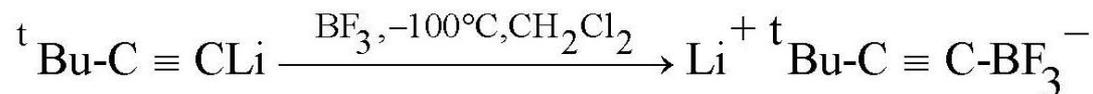
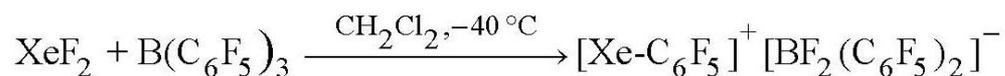


C_{4v}

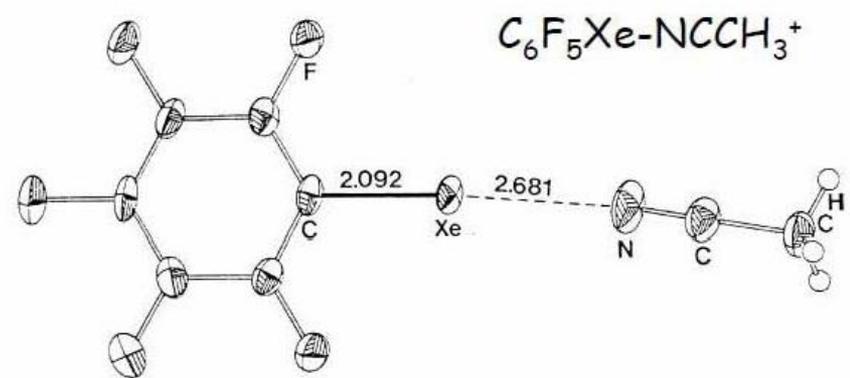
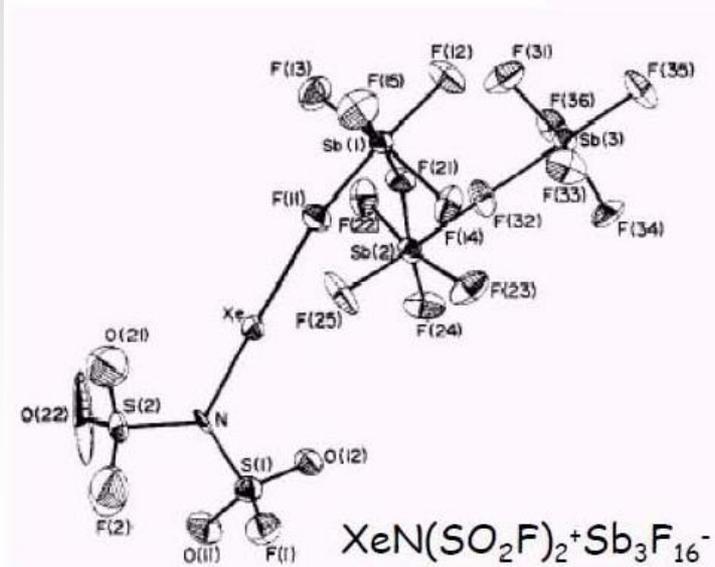
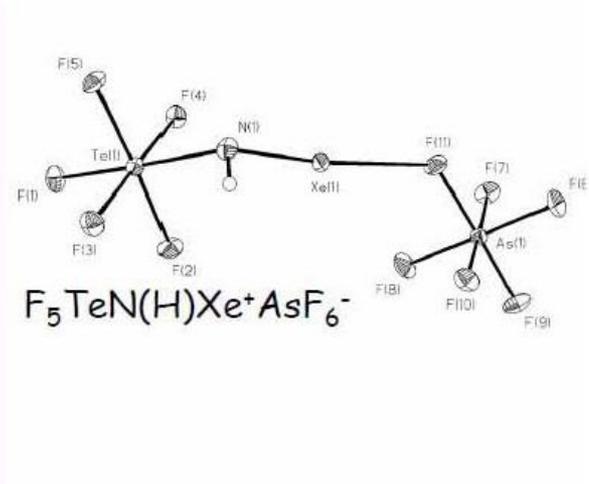
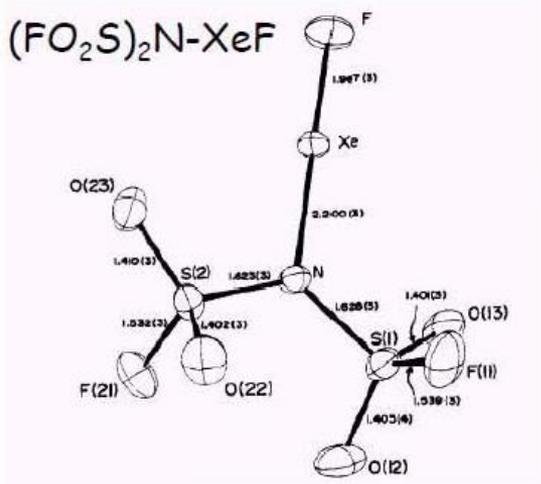
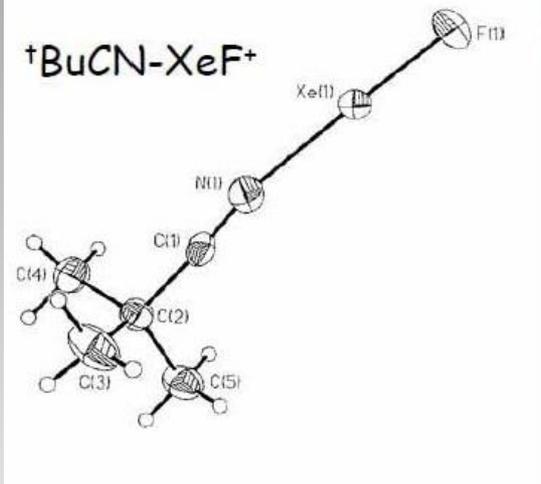


O_h

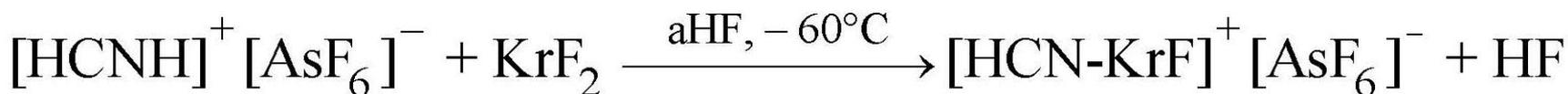
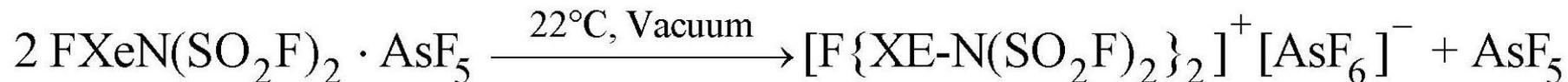
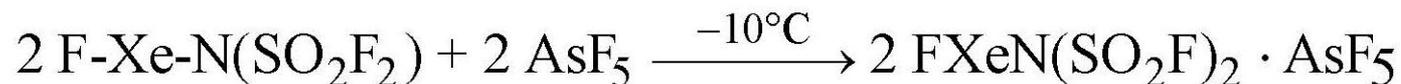
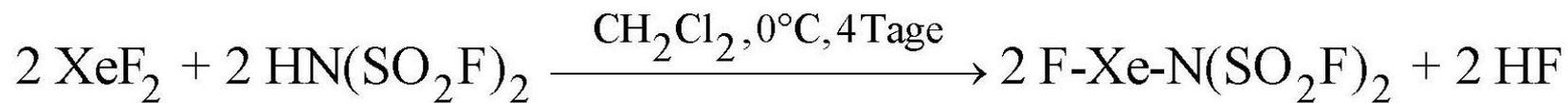
Xenon-C Verbindungen



Xenon-N Verbindungen

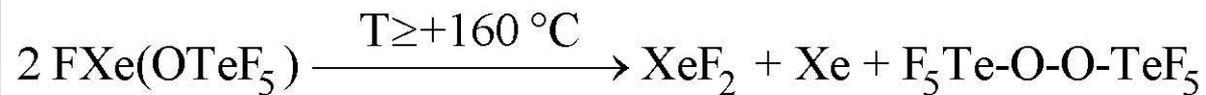
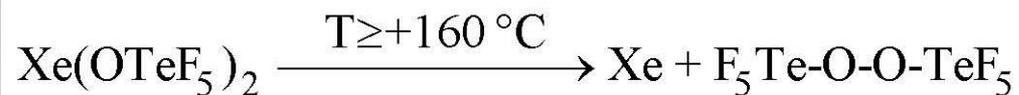
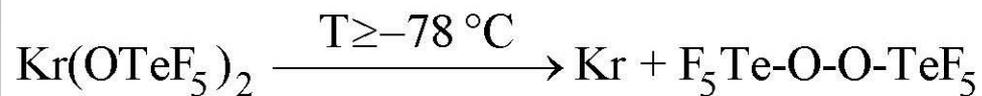


Xenon-N Verbindungen





Edelgas-O Verbindungen



Edelgas-Cl Verbindungen

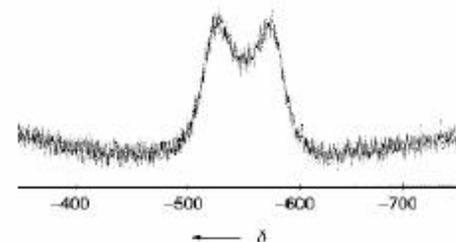
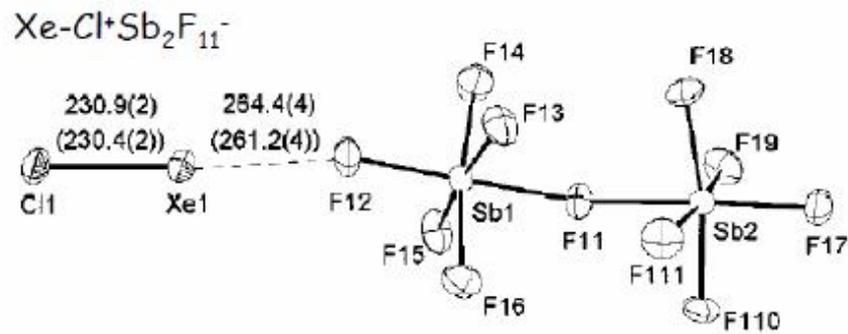
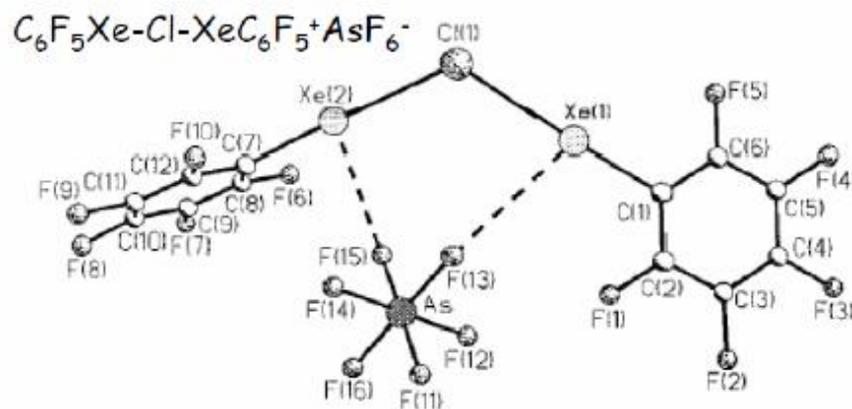
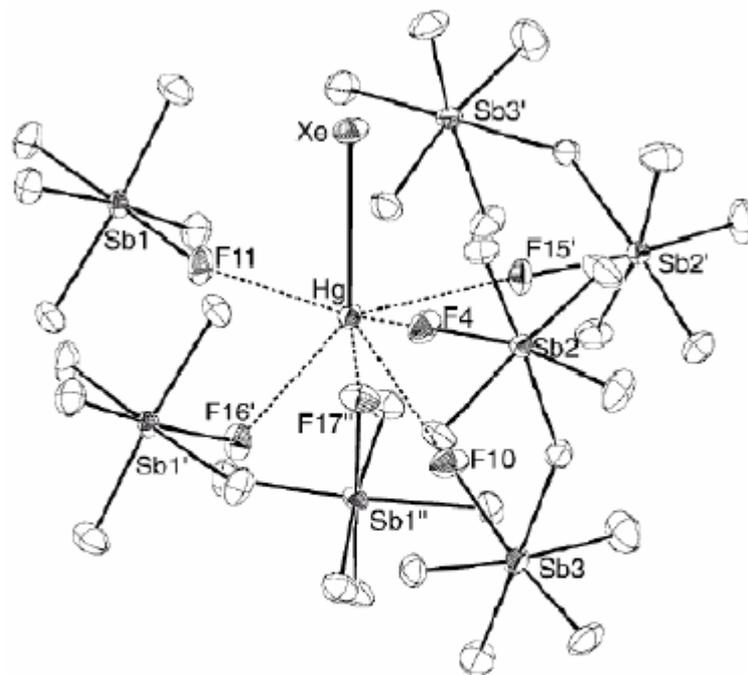
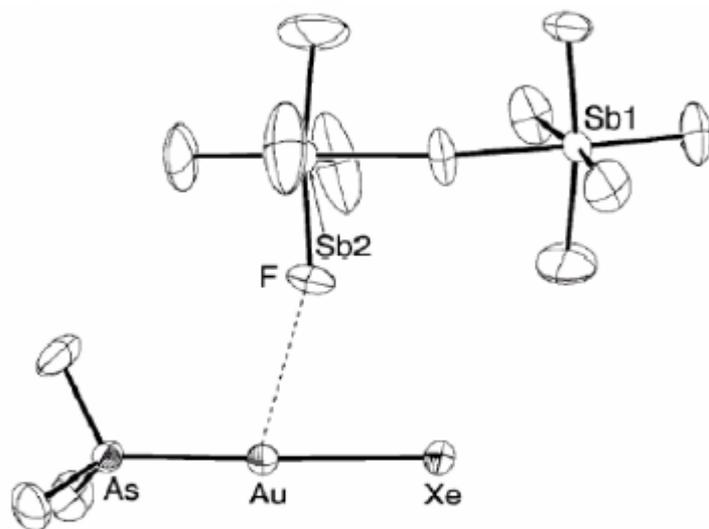


Figure 2. ^{135}Xe NMR spectrum of $[\text{XeCl}]^+ [\text{Sb}_2\text{F}_{11}]^-$ in HF/SbF_5 .

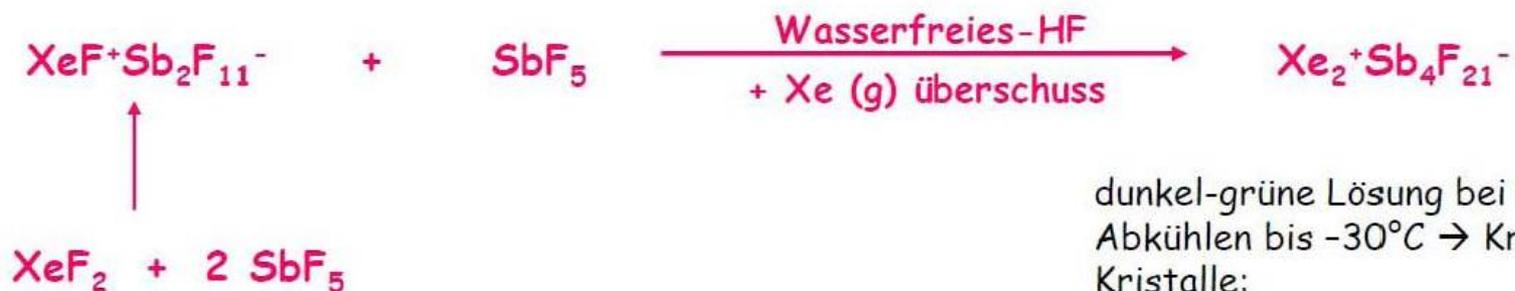
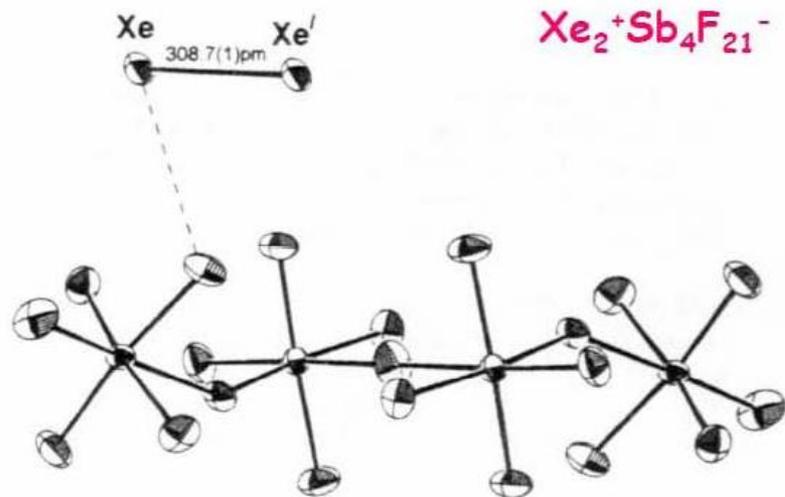
K. Seppelt et al., *Angew. Chem. Int. Ed.*, 40, 2001, 4225

Xe-Bindung zu anderen Metallen ?



K. Seppelt, *Angew. Chem. Int. Ed.*, **42**, 2003.

Das Xe_2^+ Kation

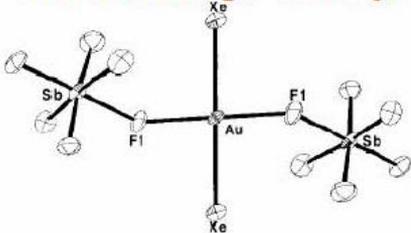
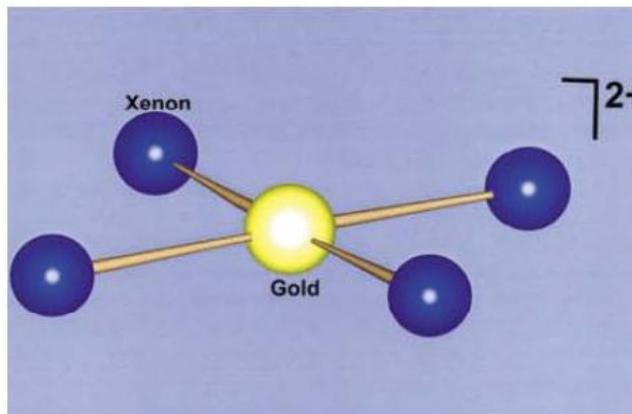
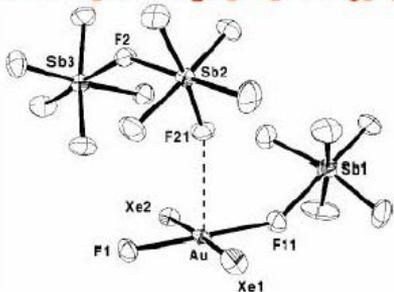
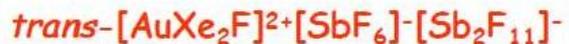


dunkel-gr\u00fcne L\u00f6sung bei 0\u00b0C
 Abk\u00fchlen bis -30\u00b0C \u2192 Kristalle
 Kristalle:

farblose
 gelb
 gr\u00fcn

K. Seppelt, T. Drews, *Angew. Chem.*, **109**, 1997, 264 - 265.

Gold Xenon Verbindungen



K. Seppelt, *Angew. Chem. Int. Ed.*, **41**, 2002, 455.
K. Seppelt, *Science*, **290**, 2000, 117.

