Curso :Química Inorgánica Avanzada
Capitulo: Elementos representativos
Profesor: Carlos Díaz

# Gases Nobles

# Propiedades generales de los elementos

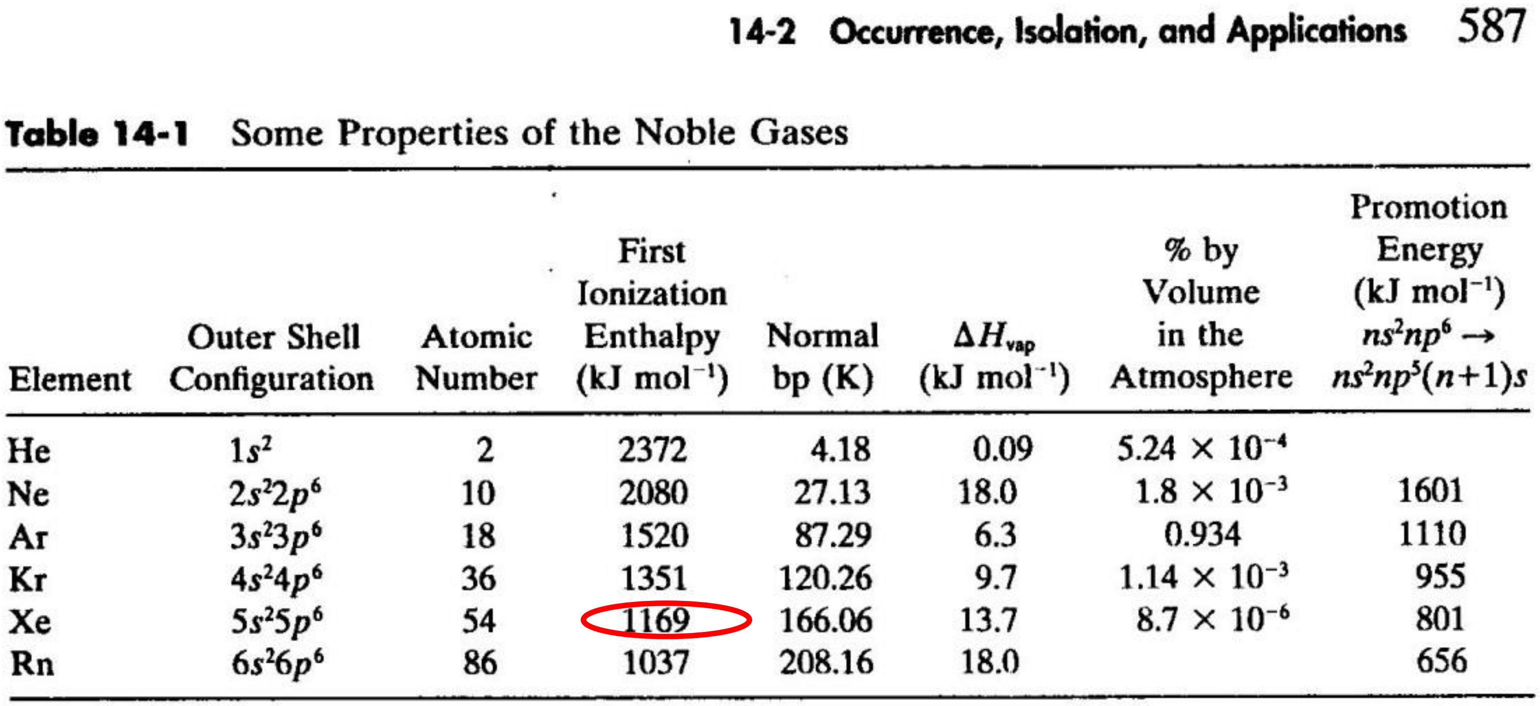


**Table 14-1** Some Properties of the Noble Gases

| Element | Outer Shell Configuration | Atomic Number | First Ionization Enthalpy (kJ mol⁻¹) | Normal bp (K) | $\Delta H_{vap}$ (kJ mol⁻¹) | % by Volume in the Atmosphere | Promotion Energy (kJ mol⁻¹) $ns^2np^6 \rightarrow ns^2np^5(n+1)s$ |
|---|---|---|---|---|---|---|---|
| He | $1s^2$ | 2 | 2372 | 4.18 | 0.09 | $5.24 \times 10^{-4}$ | |
| Ne | $2s^22p^6$ | 10 | 2080 | 27.13 | 18.0 | $1.8 \times 10^{-3}$ | 1601 |
| Ar | $3s^23p^6$ | 18 | 1520 | 87.29 | 6.3 | 0.934 | 1110 |
| Kr | $4s^24p^6$ | 36 | 1351 | 120.26 | 9.7 | $1.14 \times 10^{-3}$ | 955 |
| Xe | $5s^25p^6$ | 54 | 1169 | 166.06 | 13.7 | $8.7 \times 10^{-6}$ | 801 |
| Rn | $6s^26p^6$ | 86 | 1037 | 208.16 | 18.0 | | 656 |

Inerticidad Química : configuración de capa llena

# Compuestos mas comunes y estructura

Xe-F

Xe-O

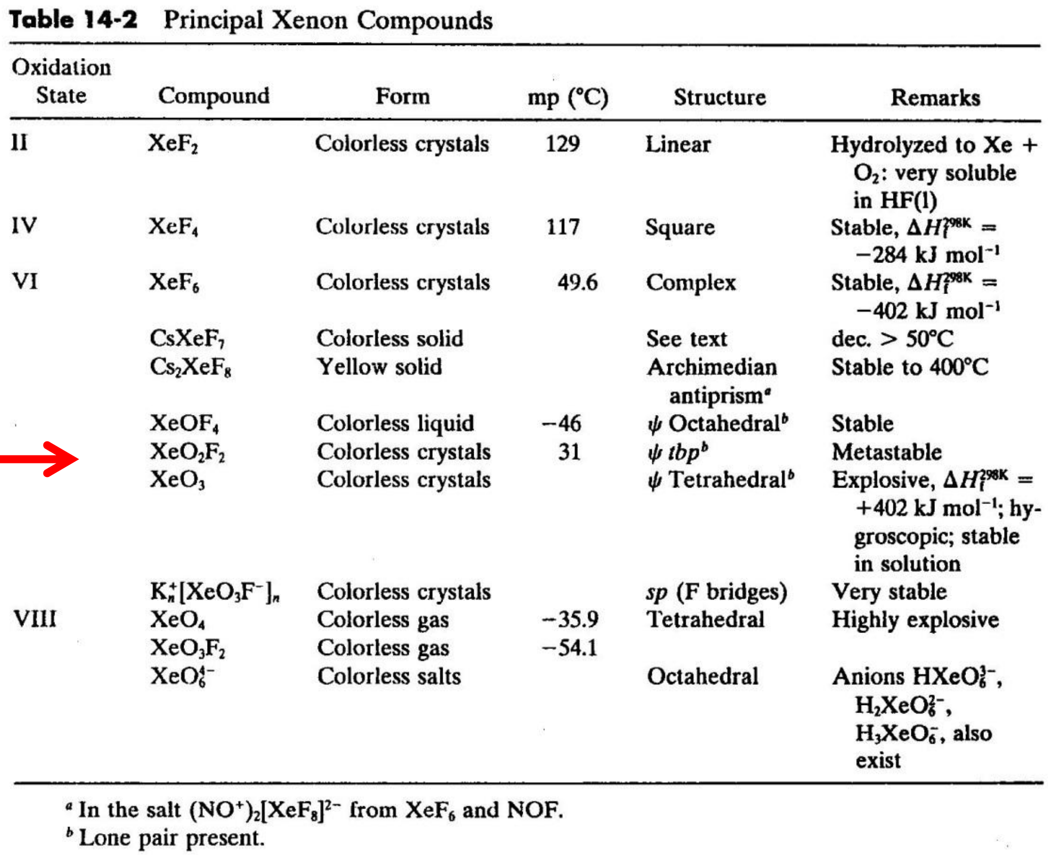


**Table 14-2** Principal Xenon Compounds

| Oxidation State | Compound | Form | mp (°C) | Structure | Remarks |
|---|---|---|---|---|---|
| II | $XeF_2$ | Colorless crystals | 129 | Linear | Hydrolyzed to Xe + $O_2$: very soluble in HF(l) |
| IV | $XeF_4$ | Colorless crystals | 117 | Square | Stable, $\Delta H_f^{298K} = -284$ kJ mol$^{-1}$ |
| VI | $XeF_6$ | Colorless crystals | 49.6 | Complex | Stable, $\Delta H_f^{298K} = -402$ kJ mol$^{-1}$ |
|  | $CsXeF_7$ | Colorless solid |  | See text | dec. > 50°C |
|  | $Cs_2XeF_8$ | Yellow solid |  | Archimedian antiprism[a] | Stable to 400°C |
|  | $XeOF_4$ | Colorless liquid | −46 | $\psi$ Octahedral[b] | Stable |
|  | $XeO_2F_2$ | Colorless crystals | 31 | $\psi$ *tbp*[b] | Metastable |
|  | $XeO_3$ | Colorless crystals |  | $\psi$ Tetrahedral[b] | Explosive, $\Delta H_f^{298K} = +402$ kJ mol$^{-1}$; hygroscopic; stable in solution |
|  | $K_n^+[XeO_3F^-]_n$ | Colorless crystals |  | *sp* (F bridges) | Very stable |
| VIII | $XeO_4$ | Colorless gas | −35.9 | Tetrahedral | Highly explosive |
|  | $XeO_3F_2$ | Colorless gas | −54.1 |  |  |
|  | $XeO_6^{4-}$ | Colorless salts |  | Octahedral | Anions $HXeO_6^{3-}$, $H_2XeO_6^{2-}$, $H_3XeO_6^-$, also exist |

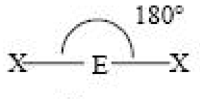
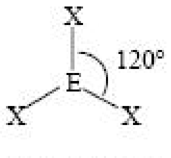
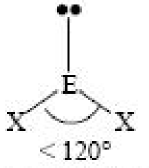
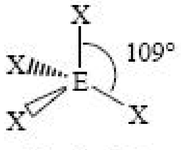
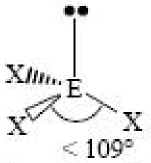
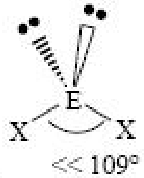
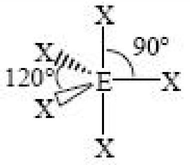
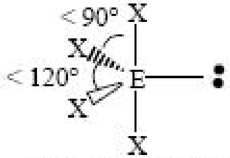
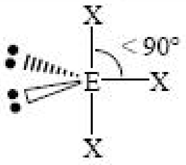
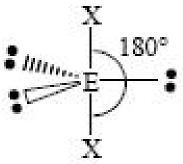
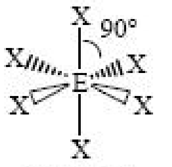
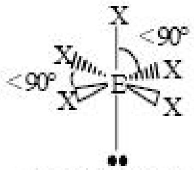
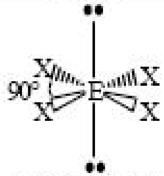
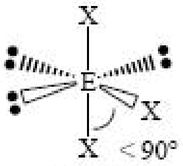
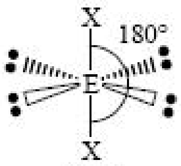
[a] In the salt $(NO^+)_2[XeF_8]^{2-}$ from $XeF_6$ and NOF.

[b] Lone pair present.

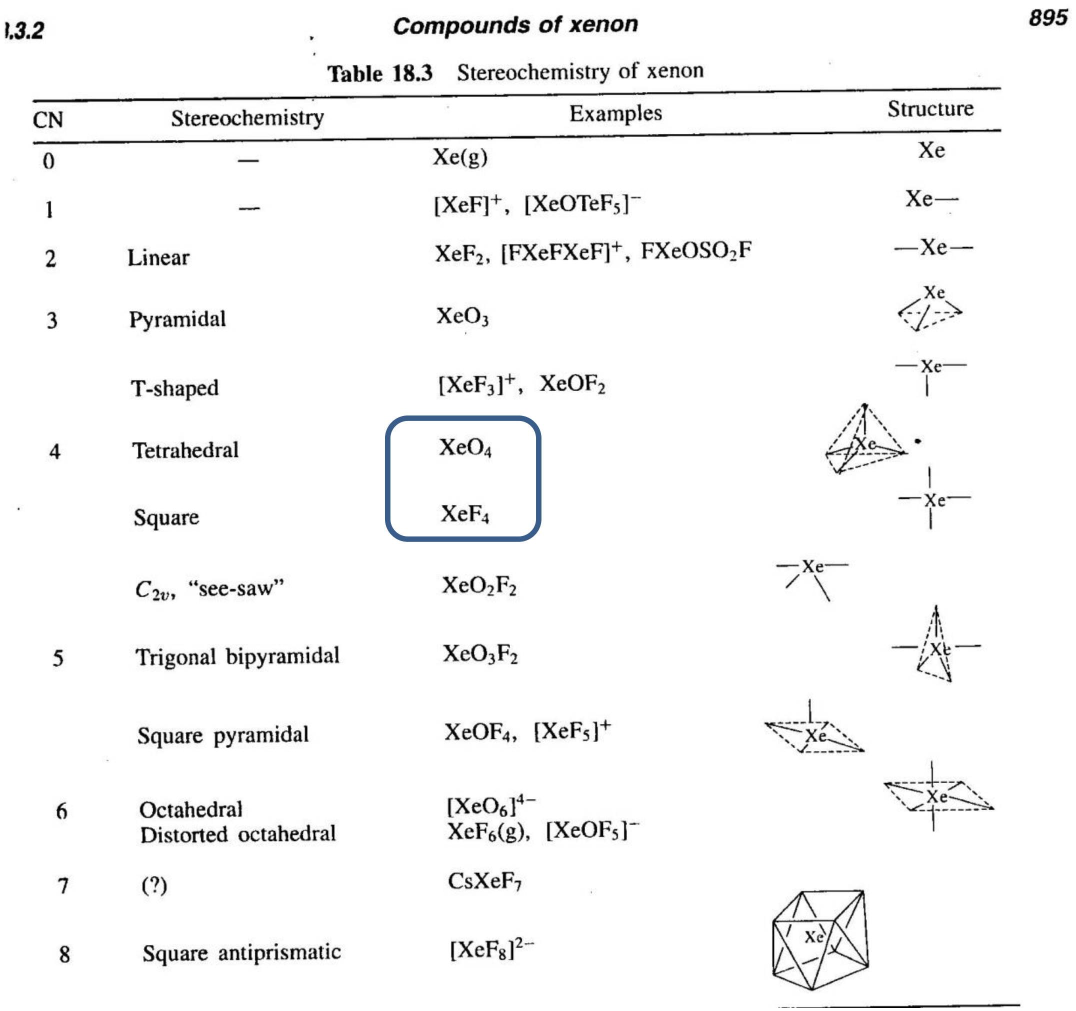
Uno de los aspectos mas interesantes sus múltiples estados de oxidación: (II); (IV) ; (VI) y (VIII) y diversidad estructural

# Tabla de geometrías según el modelo de Gillespie : $EX_n(\bullet\bullet)_m$

**VSEPR Geometries**

| Steric No. | Basic Geometry<br>0 lone pair | 1 lone pair | 2 lone pairs | 3 lone pairs | 4 lone pairs |
|---|---|---|---|---|---|
| 2 |  **Linear** | | | | |
| 3 |  **Trigonal Planar** |  **Bent or Angular** | | | |
| 4 |  **Tetrahedral** |  **Trigonal Pyramid** |  **Bent or Angular** | | |
| 5 |  **Trigonal Bipyramid** |  **Sawhorse or Seesaw** |  **T-shape** |  **Linear** | |
| 6 |  **Octahedral** |  **Square Pyramid** |  **Square Planar** |  **T-shape** |  **Linear** |

# Estereoquímica de compuestos de Gases Nobles :Gillespie



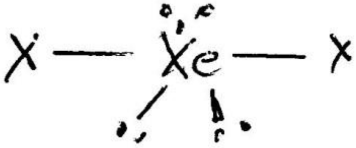
1.3.2 *Compounds of xenon* 895

**Table 18.3** Stereochemistry of xenon

| CN | Stereochemistry | Examples | Structure |
|---|---|---|---|
| 0 | — | Xe(g) | Xe |
| 1 | — | $[XeF]^+$, $[XeOTeF_5]^-$ | Xe— |
| 2 | Linear | $XeF_2$, $[FXeFXeF]^+$, $FXeOSO_2F$ | —Xe— |
| 3 | Pyramidal | $XeO_3$ | Xe |
|  | T-shaped | $[XeF_3]^+$, $XeOF_2$ | Xe |
| 4 | Tetrahedral | $XeO_4$ | Xe |
|  | Square | $XeF_4$ | Xe |
|  | $C_{2v}$, "see-saw" | $XeO_2F_2$ | Xe |
| 5 | Trigonal bipyramidal | $XeO_3F_2$ | Xe |
|  | Square pyramidal | $XeOF_4$, $[XeF_5]^+$ | Xe |
| 6 | Octahedral | $[XeO_6]^{4-}$ | Xe |
|  | Distorted octahedral | $XeF_6(g)$, $[XeOF_5]^-$ |  |
| 7 | (?) | $CsXeF_7$ |  |
| 8 | Square antiprismatic | $[XeF_8]^{2-}$ | Xe |

# Modelo de Gillespie

$XeX_2$



→ lineal

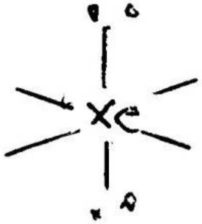
$MX_2E_3$

$XeX_3^+$

→ Forma T

$MX_3\,E_2$

$XeX_4$



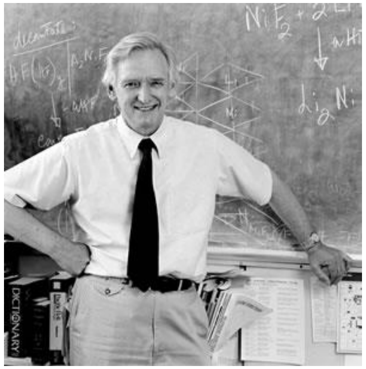
→ Cuadrado Plano

$MX_4E_2$

**X= pares de electrones compartido**

**E= pares de electrones solitarios**

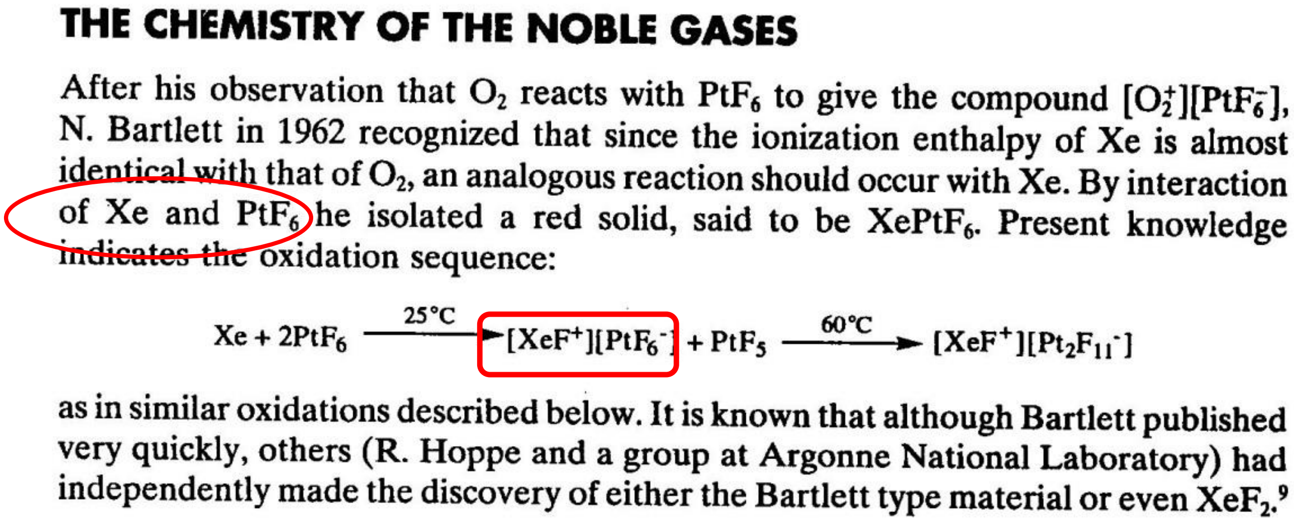
# Reseña histórica: descubrimiento



N. Bartlett

$O_2 \longrightarrow O_2^+$ $P_I = 276$ Kcal/mol

$Xe \longrightarrow Xe^+$ $P_I = 279$ Kcal/mol



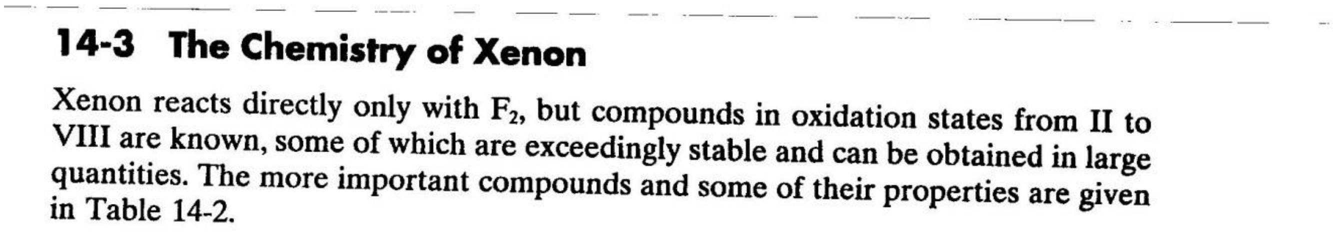
## THE CHEMISTRY OF THE NOBLE GASES

After his observation that $O_2$ reacts with $PtF_6$ to give the compound $[O_2^+][PtF_6^-]$, N. Bartlett in 1962 recognized that since the ionization enthalpy of Xe is almost identical with that of $O_2$, an analogous reaction should occur with Xe. By interaction of Xe and $PtF_6$ he isolated a red solid, said to be $XePtF_6$. Present knowledge indicates the oxidation sequence:

$$Xe + 2PtF_6 \xrightarrow{25°C} \boxed{[XeF^+][PtF_6^-]} + PtF_5 \xrightarrow{60°C} [XeF^+][Pt_2F_{11}^-]$$

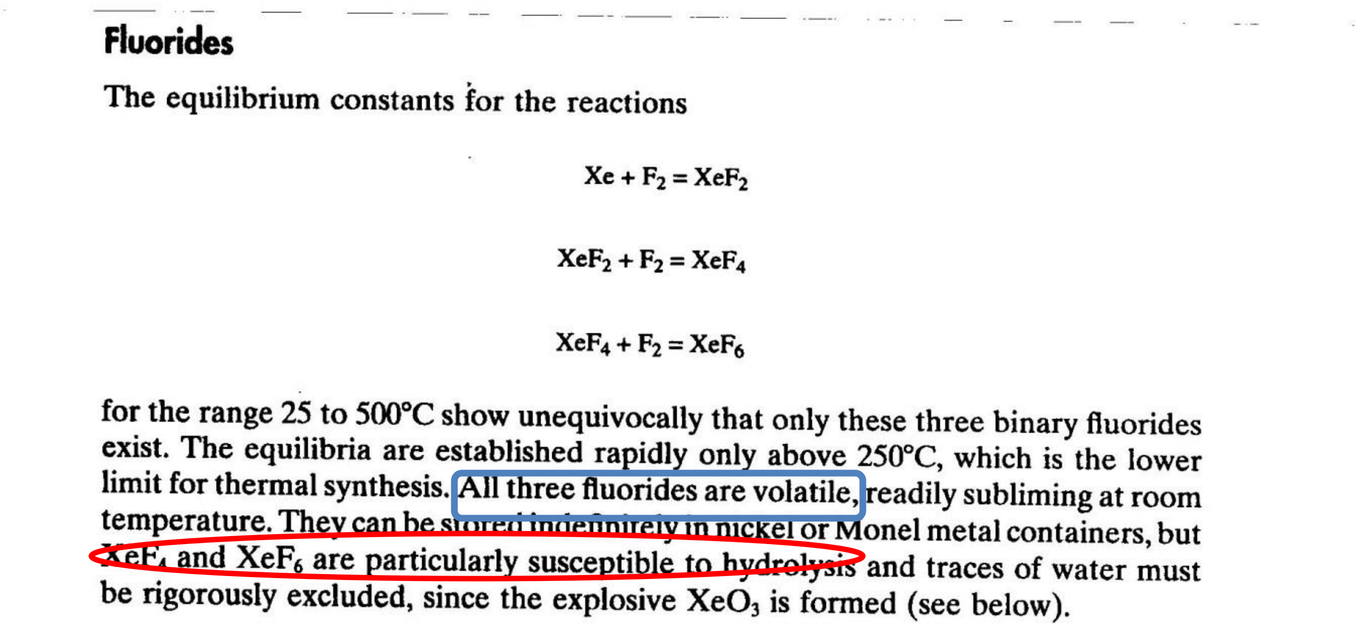
as in similar oxidations described below. It is known that although Bartlett published very quickly, others (R. Hoppe and a group at Argonne National Laboratory) had independently made the discovery of either the Bartlett type material or even $XeF_2$.[9]

# Química del Xenón



## 14-3 The Chemistry of Xenon

Xenon reacts directly only with $F_2$, but compounds in oxidation states from II to VIII are known, some of which are exceedingly stable and can be obtained in large quantities. The more important compounds and some of their properties are given in Table 14-2.



### Fluorides

The equilibrium constants for the reactions

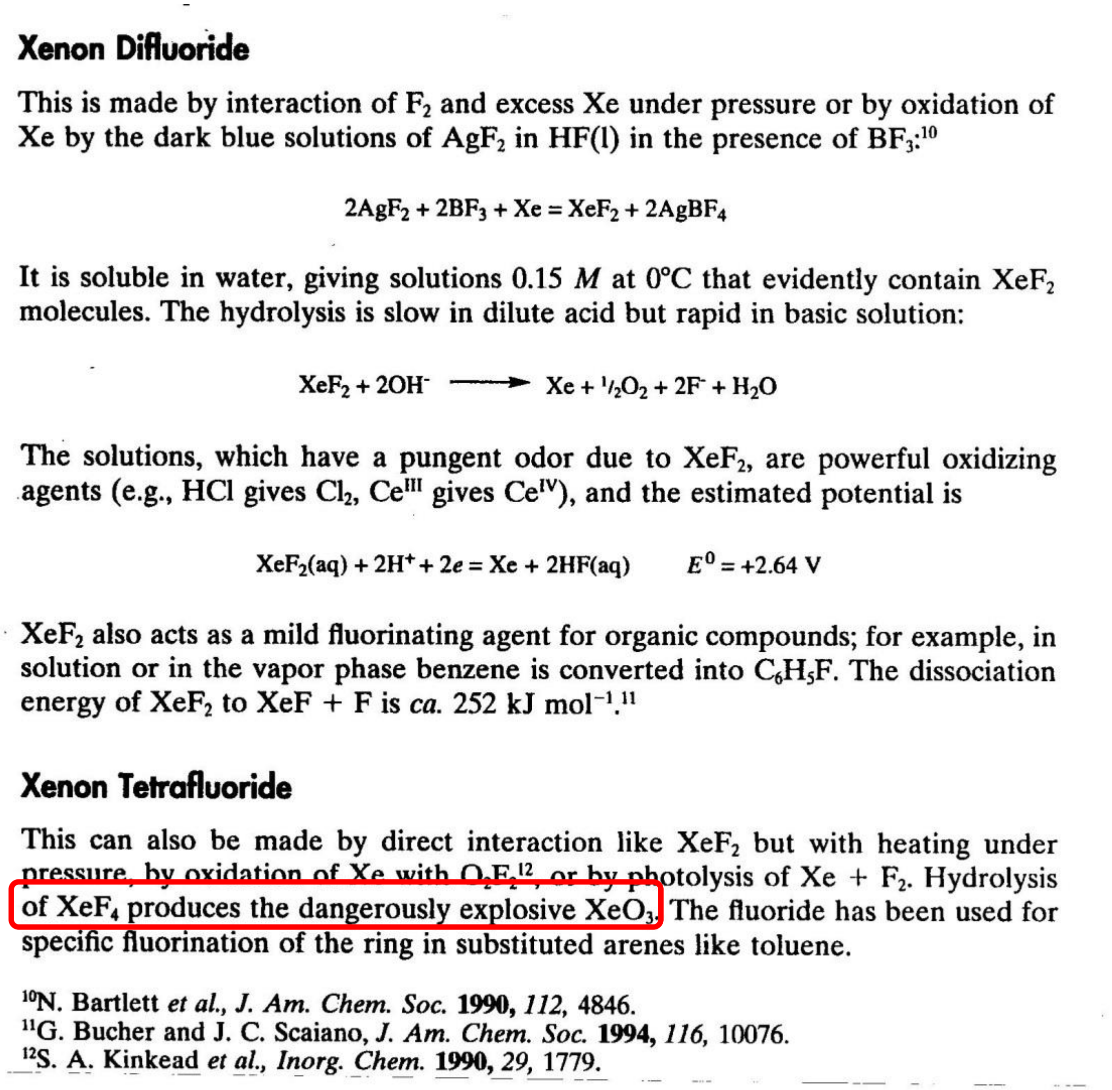
$$Xe + F_2 = XeF_2$$

$$XeF_2 + F_2 = XeF_4$$

$$XeF_4 + F_2 = XeF_6$$

for the range 25 to 500°C show unequivocally that only these three binary fluorides exist. The equilibria are established rapidly only above 250°C, which is the lower limit for thermal synthesis. All three fluorides are volatile, readily subliming at room temperature. They can be stored indefinitely in nickel or Monel metal containers, but $XeF_4$ and $XeF_6$ are particularly susceptible to hydrolysis and traces of water must be rigorously excluded, since the explosive $XeO_3$ is formed (see below).

# Difluoruoro de Xenon



### Xenon Difluoride

This is made by interaction of $F_2$ and excess Xe under pressure or by oxidation of Xe by the dark blue solutions of $AgF_2$ in HF(l) in the presence of $BF_3$:[10]

$$2AgF_2 + 2BF_3 + Xe = XeF_2 + 2AgBF_4$$

It is soluble in water, giving solutions 0.15 *M* at 0°C that evidently contain $XeF_2$ molecules. The hydrolysis is slow in dilute acid but rapid in basic solution:

$$XeF_2 + 2OH^- \longrightarrow Xe + {}^1\!/_2O_2 + 2F^- + H_2O$$

The solutions, which have a pungent odor due to $XeF_2$, are powerful oxidizing agents (e.g., HCl gives $Cl_2$, $Ce^{III}$ gives $Ce^{IV}$), and the estimated potential is

$$XeF_2(aq) + 2H^+ + 2e = Xe + 2HF(aq) \qquad E^0 = +2.64\ V$$

$XeF_2$ also acts as a mild fluorinating agent for organic compounds; for example, in solution or in the vapor phase benzene is converted into $C_6H_5F$. The dissociation energy of $XeF_2$ to XeF + F is *ca.* 252 kJ $mol^{-1}$.[11]

### Xenon Tetrafluoride

This can also be made by direct interaction like $XeF_2$ but with heating under pressure, by oxidation of Xe with $O_2F_2$,[12] or by photolysis of Xe + $F_2$. Hydrolysis of $XeF_4$ produces the dangerously explosive $XeO_3$. The fluoride has been used for specific fluorination of the ring in substituted arenes like toluene.

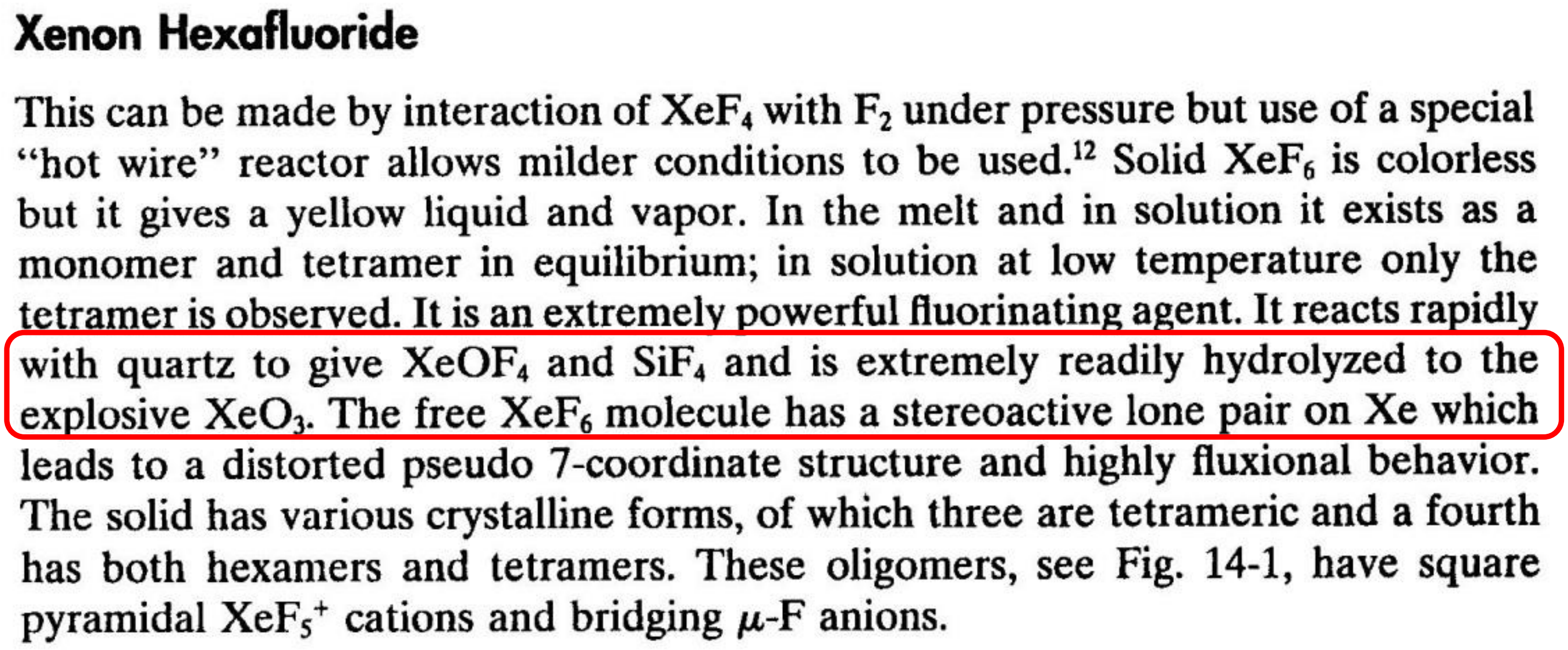
[10] N. Bartlett *et al.*, *J. Am. Chem. Soc.* **1990,** *112,* 4846.
[11] G. Bucher and J. C. Scaiano, *J. Am. Chem. Soc.* **1994,** *116,* 10076.
[12] S. A. Kinkead *et al.*, *Inorg. Chem.* **1990,** *29,* 1779.

hidrolisis

Agente oxidante

Uso en Química Orgánica

# Hexafluoruro de Xenón



## Xenon Hexafluoride

This can be made by interaction of $XeF_4$ with $F_2$ under pressure but use of a special "hot wire" reactor allows milder conditions to be used.[12] Solid $XeF_6$ is colorless but it gives a yellow liquid and vapor. In the melt and in solution it exists as a monomer and tetramer in equilibrium; in solution at low temperature only the tetramer is observed. It is an extremely powerful fluorinating agent. It reacts rapidly with quartz to give $XeOF_4$ and $SiF_4$ and is extremely readily hydrolyzed to the explosive $XeO_3$. The free $XeF_6$ molecule has a stereoactive lone pair on Xe which leads to a distorted pseudo 7-coordinate structure and highly fluxional behavior. The solid has various crystalline forms, of which three are tetrameric and a fourth has both hexamers and tetramers. These oligomers, see Fig. 14-1, have square pyramidal $XeF_5^+$ cations and bridging $\mu$-F anions.

# Estructura de algunos compuestos

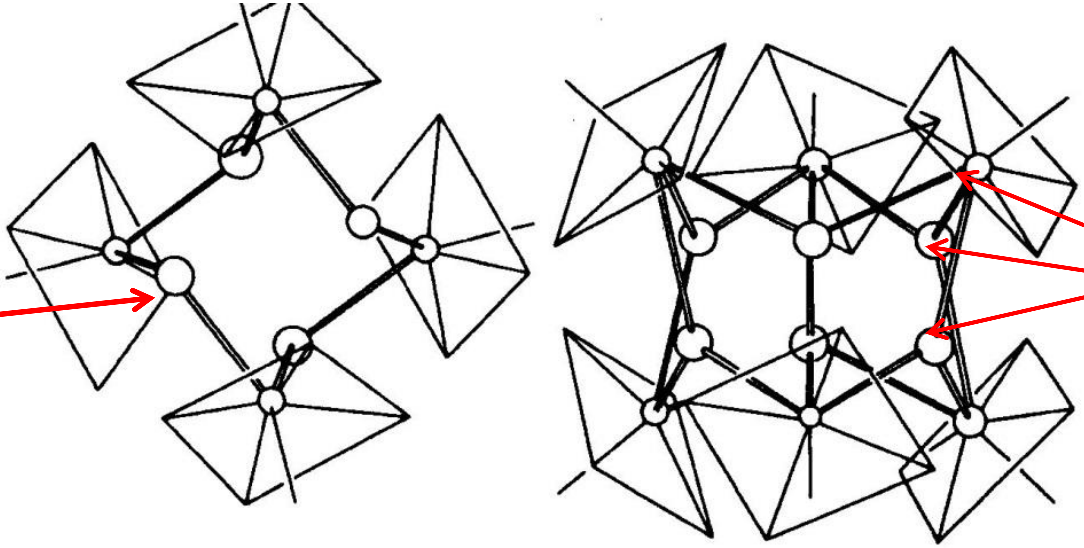


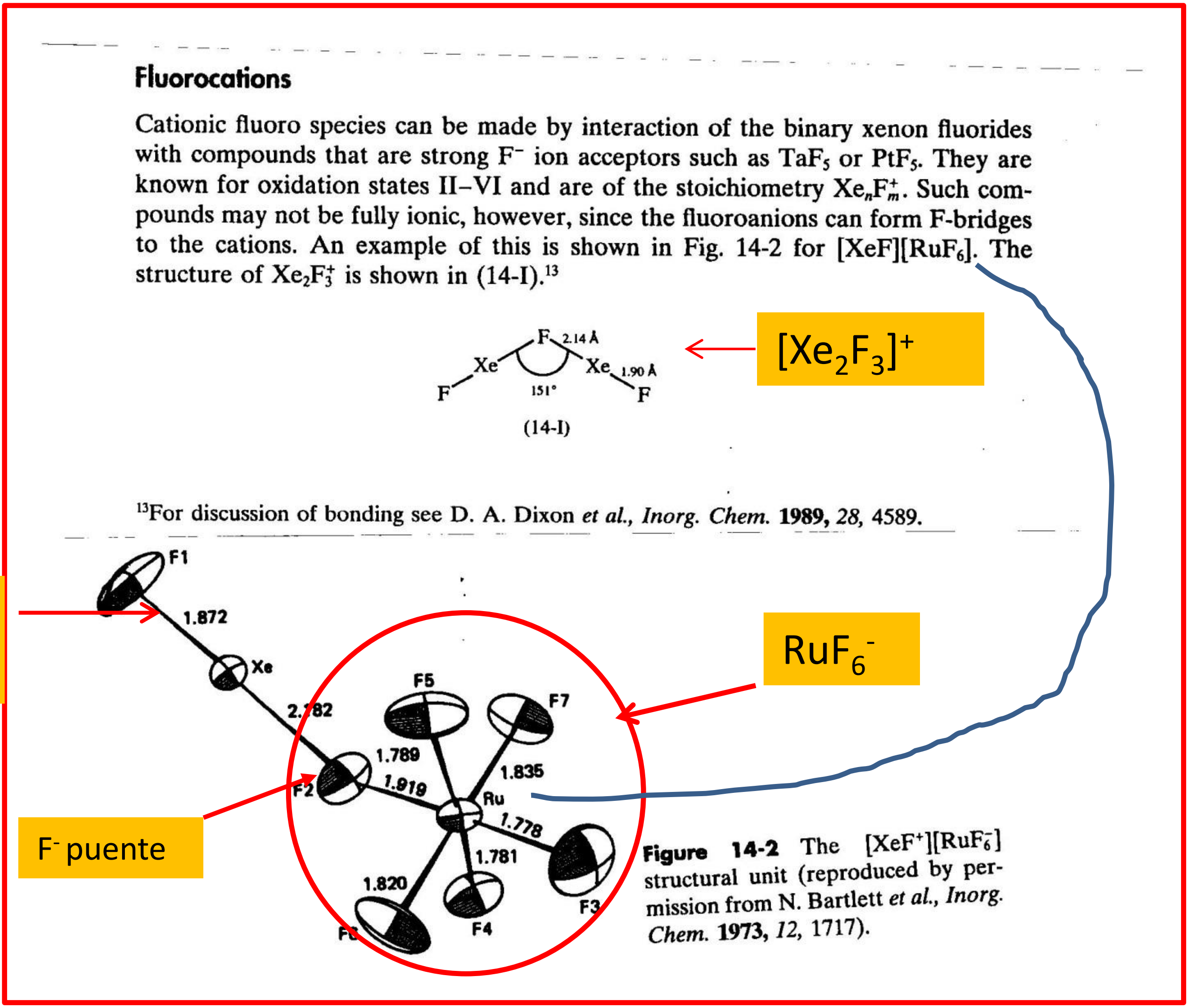
**Figure 14-1** The tetrameric and hexameric units in one of the crystal forms of $XeF_6$.

$F^-$

Puentes Xe-F-Xe

$XeF_5$ — $F^-$ — $XeF_5$

# Quimica: Fluorocationes



**Fluorocations**

Cationic fluoro species can be made by interaction of the binary xenon fluorides with compounds that are strong $F^-$ ion acceptors such as $TaF_5$ or $PtF_5$. They are known for oxidation states II–VI and are of the stoichiometry $Xe_nF_m^+$. Such compounds may not be fully ionic, however, since the fluoroanions can form F-bridges to the cations. An example of this is shown in Fig. 14-2 for $[XeF][RuF_6]$. The structure of $Xe_2F_3^+$ is shown in (14-I).[13]

(14-I)

---

[13] For discussion of bonding see D. A. Dixon *et al.*, *Inorg. Chem.* **1989,** *28,* 4589.

**Figure 14-2** The $[XeF^+][RuF_6^-]$ structural unit (reproduced by permission from N. Bartlett *et al.*, *Inorg. Chem.* **1973,** *12,* 1717).

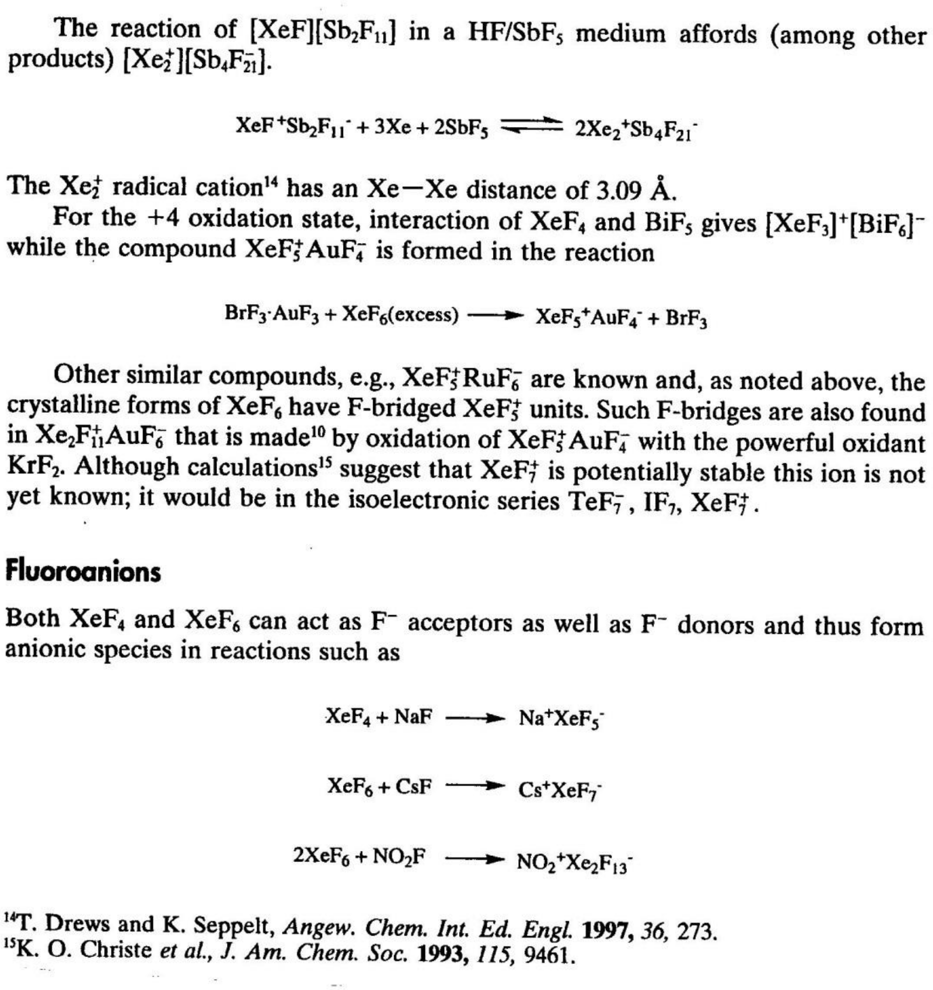
$[Xe_2F_3]^+$

$[XeF]^+$

$RuF_6^-$

$F^-$ puente

# Fluoraniones



The reaction of [XeF][$Sb_2F_{11}$] in a HF/$SbF_5$ medium affords (among other products) [$Xe_2^+$][$Sb_4F_{21}^-$].

$$XeF^+Sb_2F_{11}^- + 3Xe + 2SbF_5 \rightleftharpoons 2Xe_2^+Sb_4F_{21}^-$$

The $Xe_2^+$ radical cation[14] has an Xe—Xe distance of 3.09 Å.

For the +4 oxidation state, interaction of $XeF_4$ and $BiF_5$ gives $[XeF_3]^+[BiF_6]^-$ while the compound $XeF_5^+AuF_4^-$ is formed in the reaction

$$BrF_3\cdot AuF_3 + XeF_6(\text{excess}) \longrightarrow XeF_5^+AuF_4^- + BrF_3$$

Other similar compounds, e.g., $XeF_5^+RuF_6^-$ are known and, as noted above, the crystalline forms of $XeF_6$ have F-bridged $XeF_5^+$ units. Such F-bridges are also found in $Xe_2F_{11}^+AuF_6^-$ that is made[10] by oxidation of $XeF_5^+AuF_4^-$ with the powerful oxidant $KrF_2$. Although calculations[15] suggest that $XeF_7^+$ is potentially stable this ion is not yet known; it would be in the isoelectronic series $TeF_7^-$, $IF_7$, $XeF_7^+$.

### Fluoroanions

Both $XeF_4$ and $XeF_6$ can act as $F^-$ acceptors as well as $F^-$ donors and thus form anionic species in reactions such as

$$XeF_4 + NaF \longrightarrow Na^+XeF_5^-$$

$$XeF_6 + CsF \longrightarrow Cs^+XeF_7^-$$

$$2XeF_6 + NO_2F \longrightarrow NO_2^+Xe_2F_{13}^-$$

---

[14] T. Drews and K. Seppelt, *Angew. Chem. Int. Ed. Engl.* **1997,** *36,* 273.
[15] K. O. Christe *et al.*, *J. Am. Chem. Soc.* **1993,** *115,* 9461.

$XeF_2$

$XeF_4$

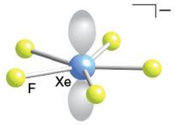
$XeF_6$

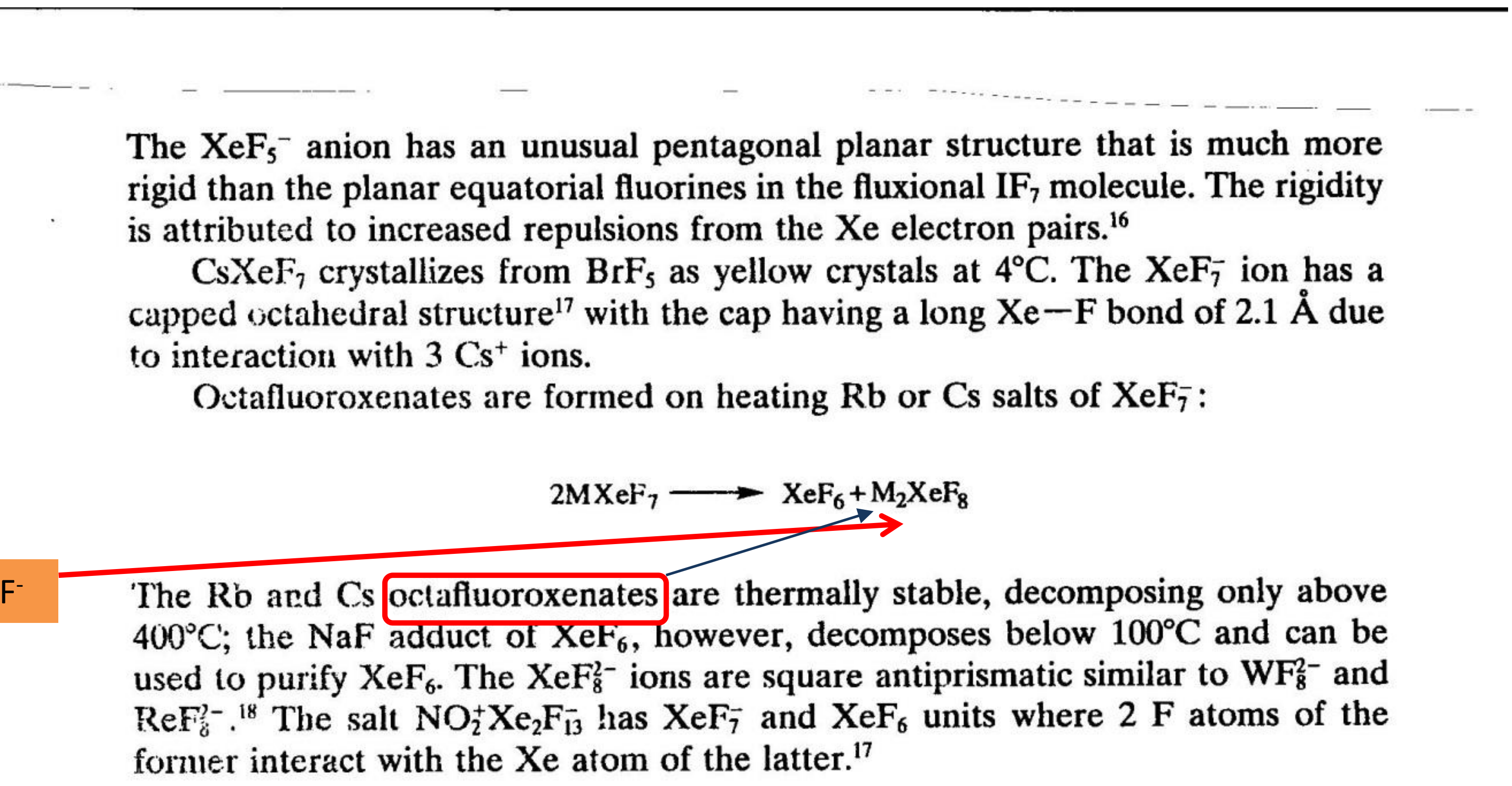
$BiF_5$ ,$SbF_5$ y $AuF_3$ como aceptores

$XeF_4$ y $XeF_6$

Sales MF y $NO_2F$ como dadores de $F^-$

# Otros aniones





The $XeF_5^-$ anion has an unusual pentagonal planar structure that is much more rigid than the planar equatorial fluorines in the fluxional $IF_7$ molecule. The rigidity is attributed to increased repulsions from the Xe electron pairs.[16]

$CsXeF_7$ crystallizes from $BrF_5$ as yellow crystals at 4°C. The $XeF_7^-$ ion has a capped octahedral structure[17] with the cap having a long Xe—F bond of 2.1 Å due to interaction with 3 $Cs^+$ ions.

Octafluoroxenates are formed on heating Rb or Cs salts of $XeF_7^-$:

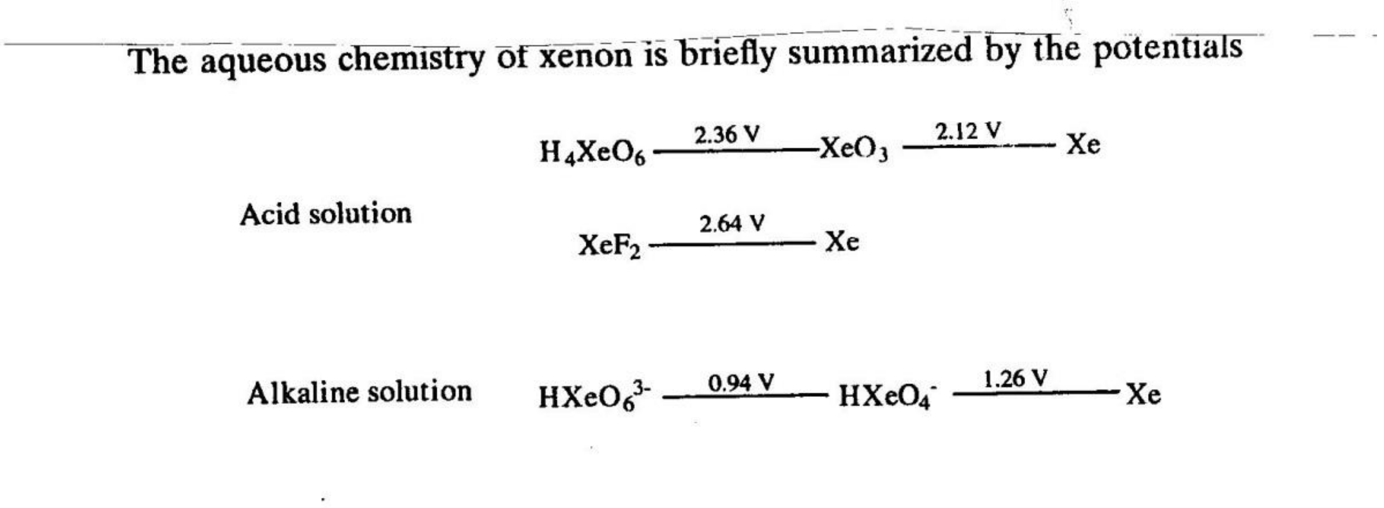
$$2MXeF_7 \longrightarrow XeF_6 + M_2XeF_8$$

Aceptor de dos $F^-$

The Rb and Cs octafluoroxenates are thermally stable, decomposing only above 400°C; the NaF adduct of $XeF_6$, however, decomposes below 100°C and can be used to purify $XeF_6$. The $XeF_8^{2-}$ ions are square antiprismatic similar to $WF_8^{2-}$ and $ReF_8^{2-}$.[18] The salt $NO_2^+Xe_2F_{13}^-$ has $XeF_7^-$ and $XeF_6$ units where 2 F atoms of the former interact with the Xe atom of the latter.[17]

# Química en agua: potenciales redox principales

## Potenciales de reducción



The aqueous chemistry of xenon is briefly summarized by the potentials

Acid solution

$$H_4XeO_6 \xrightarrow{2.36\ V} XeO_3 \xrightarrow{2.12\ V} Xe$$

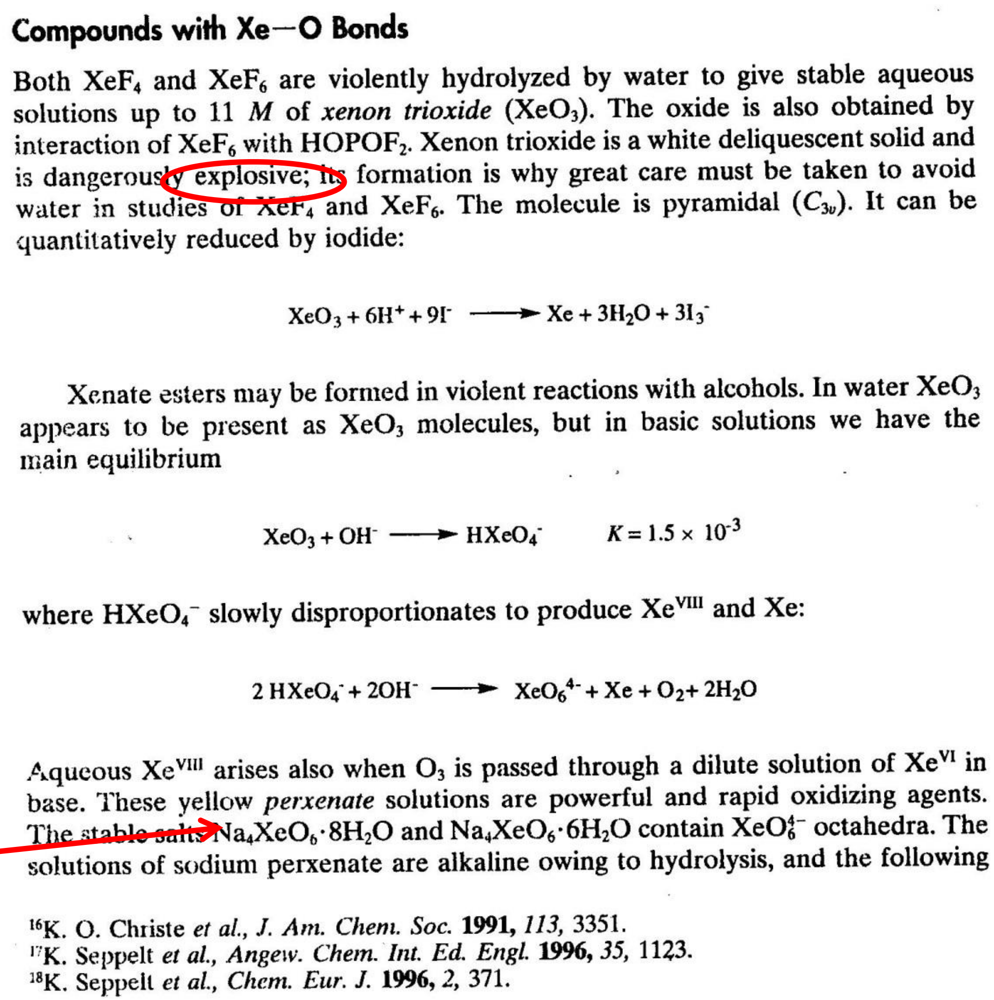
$$XeF_2 \xrightarrow{2.64\ V} Xe$$

Alkaline solution

$$HXeO_6^{3-} \xrightarrow{0.94\ V} HXeO_4^{-} \xrightarrow{1.26\ V} Xe$$

La tendencia de compuestos de Xe es como oxidante : altos potenciales de reducción

# Compuestos con enlaces Xe-O



## Compounds with Xe—O Bonds

Both $XeF_4$ and $XeF_6$ are violently hydrolyzed by water to give stable aqueous solutions up to 11 *M* of *xenon trioxide* ($XeO_3$). The oxide is also obtained by interaction of $XeF_6$ with $HOPOF_2$. Xenon trioxide is a white deliquescent solid and is dangerously explosive; its formation is why great care must be taken to avoid water in studies of $XeF_4$ and $XeF_6$. The molecule is pyramidal ($C_{3v}$). It can be quantitatively reduced by iodide:

$$XeO_3 + 6H^+ + 9I^- \longrightarrow Xe + 3H_2O + 3I_3^-$$

Xenate esters may be formed in violent reactions with alcohols. In water $XeO_3$ appears to be present as $XeO_3$ molecules, but in basic solutions we have the main equilibrium

$$XeO_3 + OH^- \longrightarrow HXeO_4^- \qquad K = 1.5 \times 10^{-3}$$

where $HXeO_4^-$ slowly disproportionates to produce $Xe^{VIII}$ and Xe:

$$2\,HXeO_4^- + 2OH^- \longrightarrow XeO_6^{4-} + Xe + O_2 + 2H_2O$$

Aqueous $Xe^{VIII}$ arises also when $O_3$ is passed through a dilute solution of $Xe^{VI}$ in base. These yellow *perxenate* solutions are powerful and rapid oxidizing agents. The stable salts $Na_4XeO_6 \cdot 8H_2O$ and $Na_4XeO_6 \cdot 6H_2O$ contain $XeO_6^{4-}$ octahedra. The solutions of sodium perxenate are alkaline owing to hydrolysis, and the following

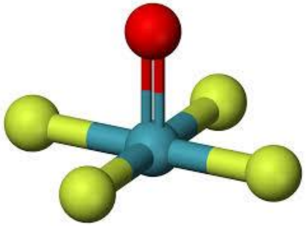
[16] K. O. Christe *et al.*, *J. Am. Chem. Soc.* **1991,** *113,* 3351.
[17] K. Seppelt *et al.*, *Angew. Chem. Int. Ed. Engl.* **1996,** *35,* 1123.
[18] K. Seppelt *et al.*, *Chem. Eur. J.* **1996,** *2,* 371.

Perxenatos

# Dentro de los compuestos Xe-O estan tambien los oxofluoruros

## Oxofluorides

Several of these are known. Representative syntheses are



$$XeF_6 + NaNO_3 \longrightarrow XeOF_4 + FNO_2 + NaF$$

$$XeF_6 + OPF_3 \longrightarrow XeOF_4 + PF_5$$

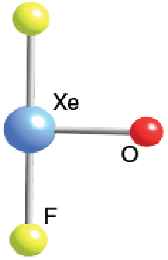
$$XeF_6 + 2XeO_3 \longrightarrow 3XeO_2F_2$$

Xe$^{+6}$ no hay cambio de estado de oxidación

$XeOF_4$

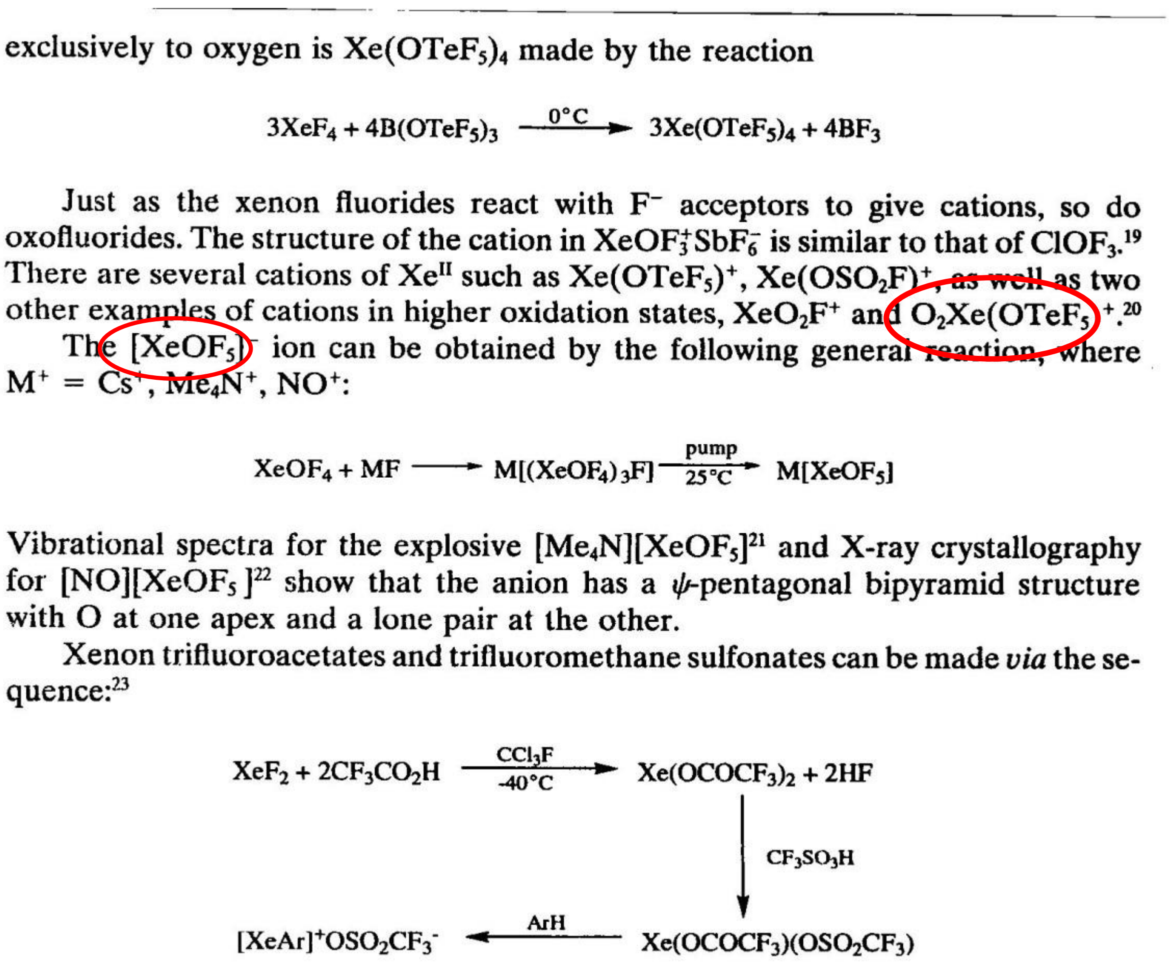
Xenon oxotetrafluoride has a square pyramidal structure, whereas $XeO_2F_2$ is like $SF_4$ with F atoms in axial positions ($C_{2v}$). Xenon oxodifluoride ($XeOF_2$) and $XeO_3F_2$ are unstable.

There are also some derivatives of the oxofluorides with the ligand $OTeF_5^-$; these are $XeO(OTeF_5)_4$ and $XeO_2(OTeF_5)_2$. The only compound of Xe$^{IV}$ bound



$XeOF_2$

# Oxofluoruros,continuacion



exclusively to oxygen is $Xe(OTeF_5)_4$ made by the reaction

$$3XeF_4 + 4B(OTeF_5)_3 \xrightarrow{0^\circ C} 3Xe(OTeF_5)_4 + 4BF_3$$

Just as the xenon fluorides react with $F^-$ acceptors to give cations, so do oxofluorides. The structure of the cation in $XeOF_3^+SbF_6^-$ is similar to that of $ClOF_3$.[19] There are several cations of $Xe^{II}$ such as $Xe(OTeF_5)^+$, $Xe(OSO_2F)^+$, as well as two other examples of cations in higher oxidation states, $XeO_2F^+$ and $O_2Xe(OTeF_5)^+$.[20]

The $[XeOF_5]^-$ ion can be obtained by the following general reaction, where $M^+ = Cs^+, Me_4N^+, NO^+$:

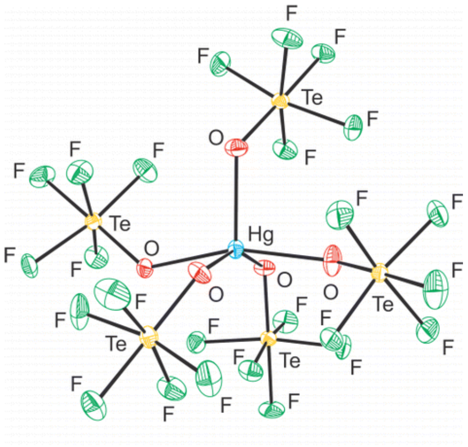
$$XeOF_4 + MF \longrightarrow M[(XeOF_4)_3F] \xrightarrow[25^\circ C]{pump} M[XeOF_5]$$

Vibrational spectra for the explosive $[Me_4N][XeOF_5]$[21] and X-ray crystallography for $[NO][XeOF_5]$[22] show that the anion has a *ψ*-pentagonal bipyramid structure with O at one apex and a lone pair at the other.

Xenon trifluoroacetates and trifluoromethane sulfonates can be made *via* the sequence:[23]

$$\begin{tikzcd}
XeF_2 + 2CF_3CO_2H \arrow[r, "CCl_3F", "-40^\circ C"'] & Xe(OCOCF_3)_2 + 2HF \arrow[d, "CF_3SO_3H"] \\
{[XeAr]^+OSO_2CF_3^-} & Xe(OCOCF_3)(OSO_2CF_3) \arrow[l, "ArH"']
\end{tikzcd}$$

Aniones de $XeOF_4^-$



$[Hg(OTeF_5)_5]^{3-}$

Anión pentafluorooxitelurato: $OTeF_5^-$

# Otras especies Xe-O: fluorsulfonatos

*Other species* with bonds to oxygen are formed when $XeF_2$ reacts with strong oxo acids (e.g., $HSO_3F$) or their anhydrides [e.g., $(F_2OP)_2O$] to give products in which one or both F atoms are replaced. Examples are

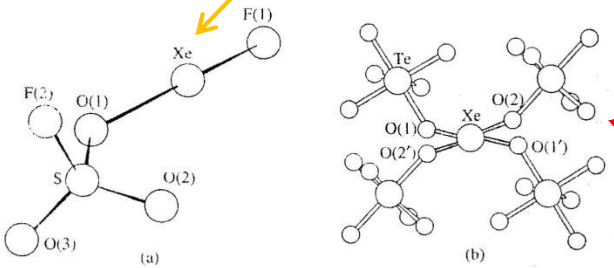
$$XeF_2 + HSO_3F \longrightarrow FXeOSO_2F,\ \ Xe(OSO_2F)_2$$

$$XeF_2 + P_2O_3F_4 \longrightarrow FXe(OPO_2F),\ \ Xe(OPO_2F)_2$$

+ HF

Anión fluorsulfonato: $OSO_2F^-$

Anión fluorfosfonato: $OPO_2F^-$



Xe(OTeF$_5$)$_4$

(a) The molecular structure of FXeOSO$_2$F. Precision of bond lengths is *ca.* 1 pm (uncorrected for thermal motion). The angle F(1)–Xe–O(1) is 177.5 ± 0.4° and angle Xe–O(1)–S is 123.4 ± 0.6°
(b) The molecular structure of $Xe(OTeF_5)_4$ (see text)

These products are unstable at about room temperature and several are highly explosive. Xenon tetrafluoride and $XeF_6$ react with $HSO_3F$ as follows:

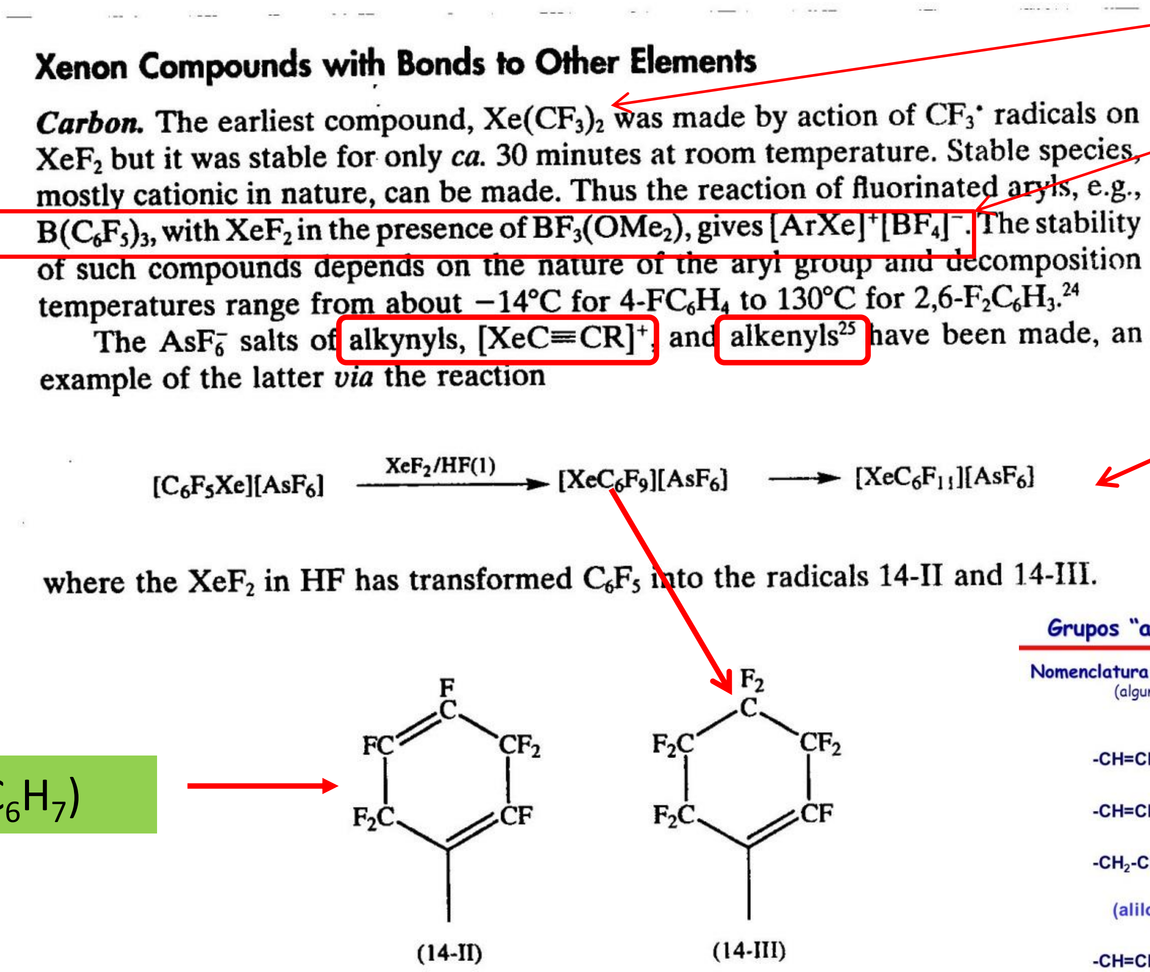
$$XeF_4 + HSO_3F \longrightarrow \boxed{FXe(OSO_2F)}\ \ Xe(OSO_2F)_2 + S_2O_6F_2$$

$$XeF_6 + HSO_3F \longrightarrow F_5Xe(OSO_2F) + HF$$

$F_5Xe(OSO_2F)$ is a white solid, stable at 22°C but decomposing above 73°C.

[19] G. J. Schrobilgen *et al.*, *Inorg. Chem.* **1993,** *32,* 386.
[20] G. J. Schrobilgen *et al.*, *Inorg. Chem.* **1992,** *31,* 3381.
[21] K. O. Christe *et al.*, *Inorg. Chem.* **1995,** *34,* 1868.
[22] A. Ellern and K. Seppelt, *Angew. Chem. Int. Engl.* **1995,** *34,* 1586.
[23] D. Naumann *et al.*, *J. Chem. Soc., Chem. Commun.* **1994,** 2651.

# Compuestos de Xe con enlaces Xe-C



### Xenon Compounds with Bonds to Other Elements

***Carbon.*** The earliest compound, $Xe(CF_3)_2$ was made by action of $CF_3^{\bullet}$ radicals on $XeF_2$ but it was stable for only *ca.* 30 minutes at room temperature. Stable species, mostly cationic in nature, can be made. Thus the reaction of fluorinated aryls, e.g., $B(C_6F_5)_3$, with $XeF_2$ in the presence of $BF_3(OMe_2)$, gives $[ArXe]^+[BF_4]^-$. The stability of such compounds depends on the nature of the aryl group and decomposition temperatures range from about −14°C for $4\text{-}FC_6H_4$ to 130°C for $2,6\text{-}F_2C_6H_3$.[24]

The $AsF_6^-$ salts of alkynyls, $[XeC{\equiv}CR]^+$, and alkenyls[25] have been made, an example of the latter *via* the reaction

$$[C_6F_5Xe][AsF_6] \xrightarrow{XeF_2/HF(l)} [XeC_6F_9][AsF_6] \longrightarrow [XeC_6F_{11}][AsF_6]$$

where the $XeF_2$ in HF has transformed $C_6F_5$ into the radicals 14-II and 14-III.

(14-II)

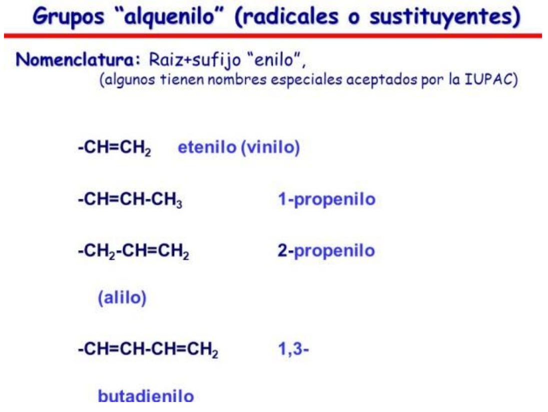
(14-III)

Xe-$CF_3$

Xe-$C_6F_5$

Fluorización sucesiva del anillo

($C_6H_7$)



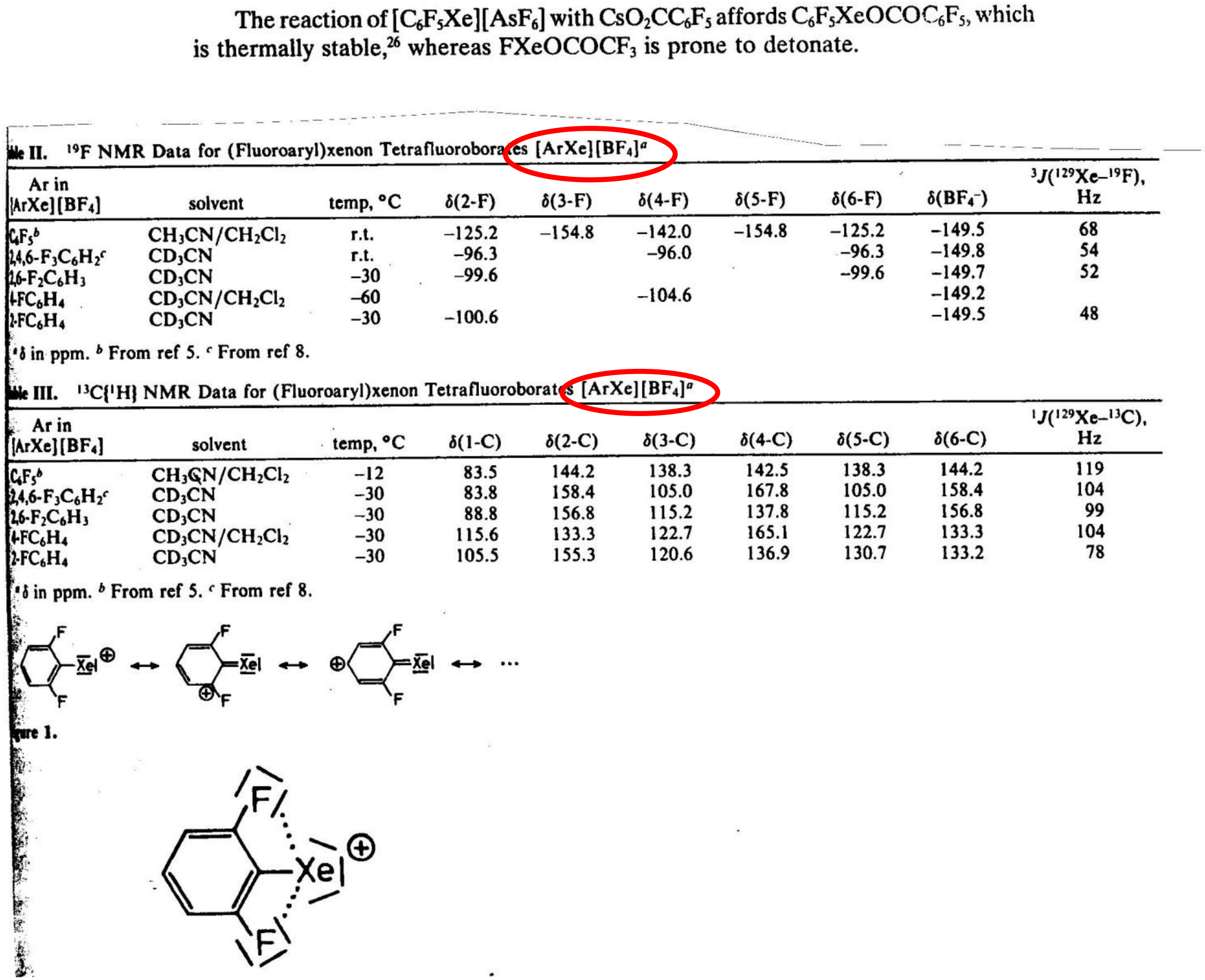
**Grupos "alquenilo" (radicales o sustituyentes)**

**Nomenclatura:** Raiz+sufijo "enilo",
(algunos tienen nombres especiales aceptados por la IUPAC)

| | |
|---|---|
| $-CH{=}CH_2$ | etenilo (vinilo) |
| $-CH{=}CH\text{-}CH_3$ | 1-propenilo |
| $-CH_2\text{-}CH{=}CH_2$ | 2-propenilo<br>(alilo) |
| $-CH{=}CH\text{-}CH{=}CH_2$ | 1,3-<br>butadienilo |

# Caracterización espectroscópica

NMR multinuclear



The reaction of $[C_6F_5Xe][AsF_6]$ with $CsO_2CC_6F_5$ affords $C_6F_5XeOCOC_6F_5$, which is thermally stable,[26] whereas $FXeOCOCF_3$ is prone to detonate.

le II. $^{19}F$ NMR Data for (Fluoroaryl)xenon Tetrafluoroborates $[ArXe][BF_4]$[a]

| Ar in $[ArXe][BF_4]$ | solvent | temp, °C | δ(2-F) | δ(3-F) | δ(4-F) | δ(5-F) | δ(6-F) | δ($BF_4^-$) | $^3J(^{129}Xe-^{19}F)$, Hz |
|---|---|---|---|---|---|---|---|---|---|
| $C_6F_5$[b] | $CH_3CN/CH_2Cl_2$ | r.t. | −125.2 | −154.8 | −142.0 | −154.8 | −125.2 | −149.5 | 68 |
| 2,4,6-$F_3C_6H_2$[c] | $CD_3CN$ | r.t. | −96.3 | | −96.0 | | −96.3 | −149.8 | 54 |
| 2,6-$F_2C_6H_3$ | $CD_3CN$ | −30 | −99.6 | | | | −99.6 | −149.7 | 52 |
| 4-$FC_6H_4$ | $CD_3CN/CH_2Cl_2$ | −60 | | | −104.6 | | | −149.2 | |
| 2-$FC_6H_4$ | $CD_3CN$ | −30 | −100.6 | | | | | −149.5 | 48 |

[a] δ in ppm. [b] From ref 5. [c] From ref 8.

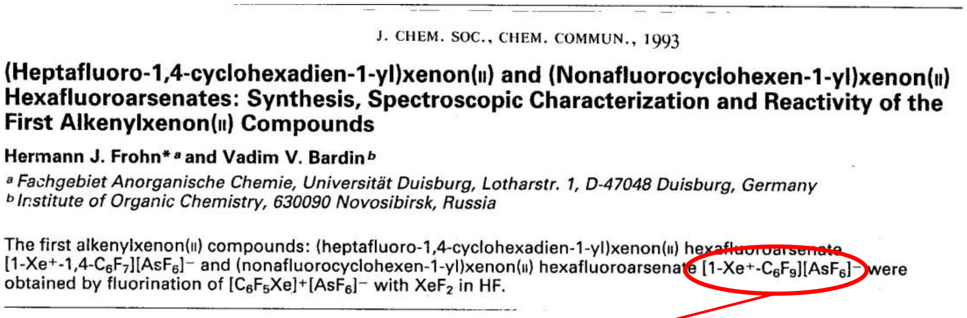
le III. $^{13}C\{^1H\}$ NMR Data for (Fluoroaryl)xenon Tetrafluoroborates $[ArXe][BF_4]$[a]

| Ar in $[ArXe][BF_4]$ | solvent | temp, °C | δ(1-C) | δ(2-C) | δ(3-C) | δ(4-C) | δ(5-C) | δ(6-C) | $^1J(^{129}Xe-^{13}C)$, Hz |
|---|---|---|---|---|---|---|---|---|---|
| $C_6F_5$[b] | $CH_3CN/CH_2Cl_2$ | −12 | 83.5 | 144.2 | 138.3 | 142.5 | 138.3 | 144.2 | 119 |
| 2,4,6-$F_3C_6H_2$[c] | $CD_3CN$ | −30 | 83.8 | 158.4 | 105.0 | 167.8 | 105.0 | 158.4 | 104 |
| 2,6-$F_2C_6H_3$ | $CD_3CN$ | −30 | 88.8 | 156.8 | 115.2 | 137.8 | 115.2 | 156.8 | 99 |
| 4-$FC_6H_4$ | $CD_3CN/CH_2Cl_2$ | −30 | 115.6 | 133.3 | 122.7 | 165.1 | 122.7 | 133.3 | 104 |
| 2-$FC_6H_4$ | $CD_3CN$ | −30 | 105.5 | 155.3 | 120.6 | 136.9 | 130.7 | 133.2 | 78 |

[a] δ in ppm. [b] From ref 5. [c] From ref 8.

ure 1.

# El primer compuesto Xe-C(alquenilo)



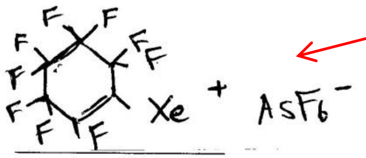
J. CHEM. SOC., CHEM. COMMUN., 1993

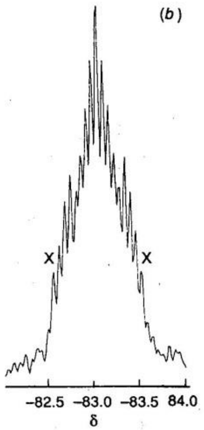
**(Heptafluoro-1,4-cyclohexadien-1-yl)xenon(II) and (Nonafluorocyclohexen-1-yl)xenon(II) Hexafluoroarsenates: Synthesis, Spectroscopic Characterization and Reactivity of the First Alkenylxenon(II) Compounds**

**Hermann J. Frohn***[a] **and Vadim V. Bardin**[b]

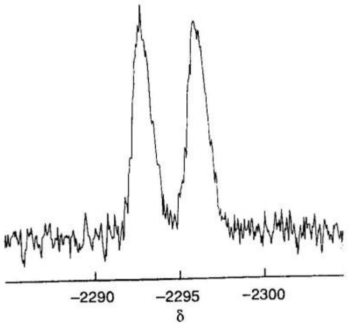
[a] *Fachgebiet Anorganische Chemie, Universität Duisburg, Lotharstr. 1, D-47048 Duisburg, Germany*
[b] *Institute of Organic Chemistry, 630090 Novosibirsk, Russia*

The first alkenylxenon(II) compounds: (heptafluoro-1,4-cyclohexadien-1-yl)xenon(II) hexafluoroarsenate $[1\text{-}Xe^+\text{-}1,4\text{-}C_6F_7][AsF_6]^-$ and (nonafluorocyclohexen-1-yl)xenon(II) hexafluoroarsenate $[1\text{-}Xe^+\text{-}C_6F_9][AsF_6]^-$ were obtained by fluorination of $[C_6F_5Xe]^+[AsF_6]^-$ with $XeF_2$ in HF.



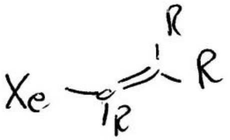


$^{19}$F - NMR



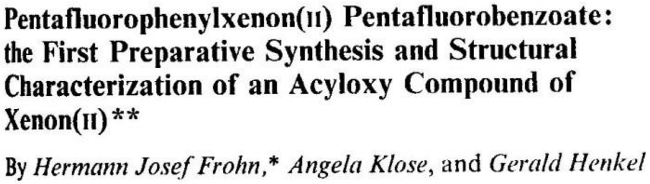
$^{129}$Xe NMR
(HF, −30°C)

**$^{129}$Xe espín nuclear: 1/2**



Alquenilos

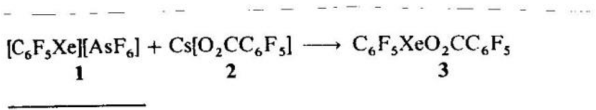
# Compuestos con enlaces Xe-C(aciloxi)



**Pentafluorophenylxenon(II) Pentafluorobenzoate: the First Preparative Synthesis and Structural Characterization of an Acyloxy Compound of Xenon(II)****

By *Hermann Josef Frohn,* Angela Klose*, and *Gerald Henkel*

Síntesis



$$\underset{\mathbf{1}}{[C_6F_5Xe][AsF_6]} + \underset{\mathbf{2}}{Cs[O_2CC_6F_5]} \longrightarrow \underset{\mathbf{3}}{C_6F_5XeO_2CC_6F_5}$$

Caracterización

$C_6F_5XeOCC_6H_5$

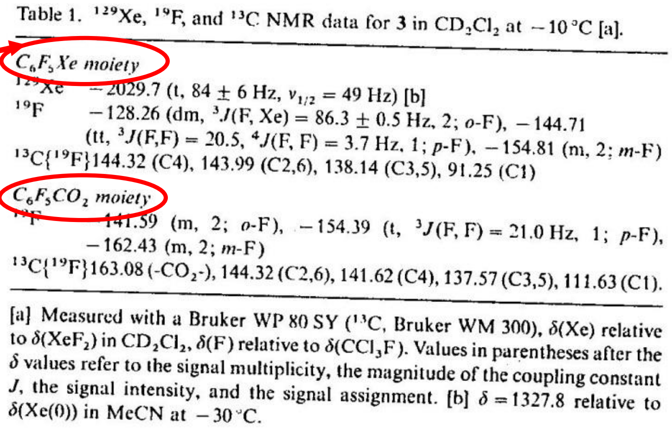


Table 1. $^{129}$Xe, $^{19}$F, and $^{13}$C NMR data for **3** in $CD_2Cl_2$ at −10 °C [a].

| | |
|---|---|
| *$C_6F_5Xe$ moiety* | |
| $^{129}$Xe | −2029.7 (t, 84 ± 6 Hz, $\nu_{1/2} = 49$ Hz) [b] |
| $^{19}$F | −128.26 (dm, $^3J$(F, Xe) = 86.3 ± 0.5 Hz, 2; *o*-F), −144.71 (tt, $^3J$(F,F) = 20.5, $^4J$(F, F) = 3.7 Hz, 1; *p*-F), −154.81 (m, 2; *m*-F) |
| $^{13}$C{$^{19}$F} | 144.32 (C4), 143.99 (C2,6), 138.14 (C3,5), 91.25 (C1) |
| *$C_6F_5CO_2$ moiety* | |
| $^{19}$F | −141.59 (m, 2; *o*-F), −154.39 (t, $^3J$(F, F) = 21.0 Hz, 1; *p*-F), −162.43 (m, 2; *m*-F) |
| $^{13}$C{$^{19}$F} | 163.08 (-$CO_2$-), 144.32 (C2,6), 141.62 (C4), 137.57 (C3,5), 111.63 (C1). |

[a] Measured with a Bruker WP 80 SY ($^{13}$C, Bruker WM 300), δ(Xe) relative to δ($XeF_2$) in $CD_2Cl_2$, δ(F) relative to δ($CCl_3F$). Values in parentheses after the δ values refer to the signal multiplicity, the magnitude of the coupling constant *J*, the signal intensity, and the signal assignment. [b] δ = 1327.8 relative to δ(Xe(0)) in MeCN at −30 °C.

$C_6F_5Xe\text{-}O(O)CC_6CF_5$

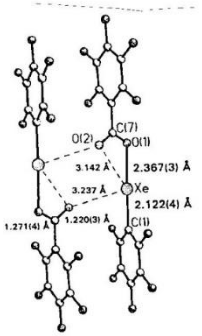
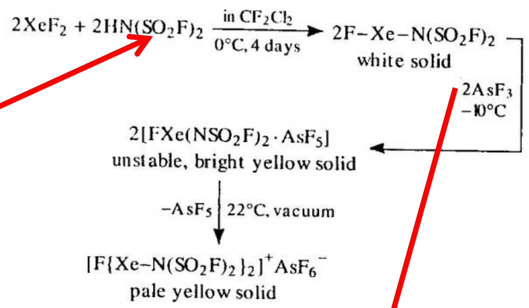


Fig. 1. Crystal structure of **3** with Xe–ligand bond lengths and the relevant intra- and intermolecular Xe–O contact distances. The C–Xe–O bond angle is 178.1(1)°.

RC(O)O-M

# Compuestos con enlaces Xe-N

Amina acidica: sustitución



$$2XeF_2 + 2HN(SO_2F)_2 \xrightarrow[0°C,\ 4\ days]{in\ CF_2Cl_2} 2F{-}Xe{-}N(SO_2F)_2$$

white solid

+ HF

$$\xrightarrow[-10°C]{2AsF_3} 2[FXe(NSO_2F)_2 \cdot AsF_5]$$

unstable, bright yellow solid

$$\xrightarrow[22°C,\ vacuum]{-AsF_5} [F\{Xe{-}N(SO_2F)_2\}_2]^+AsF_6^-$$

pale yellow solid

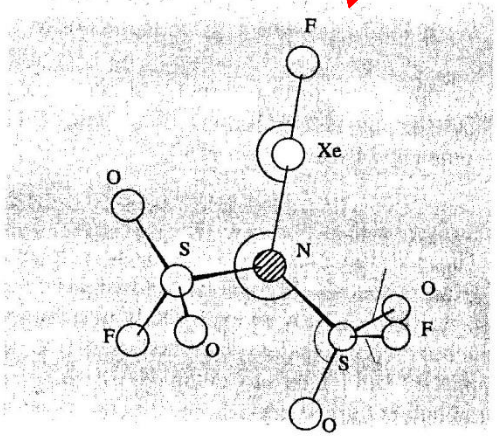
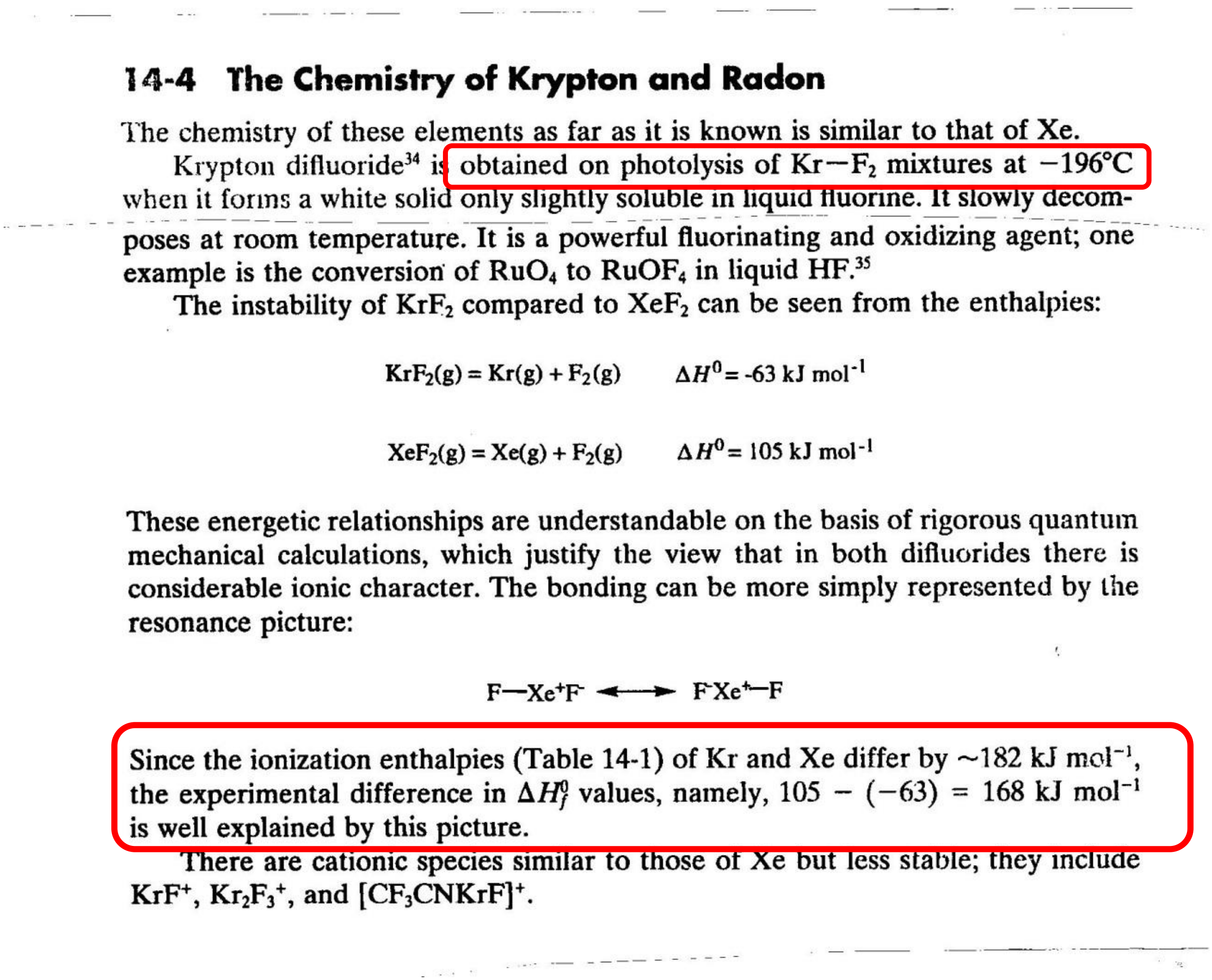


**Figure 18.4** The structure of $FXeN(SO_2F)_2$ ($C_2$ symmetry) showing essentially linear Xe and planar N. Other bond angles are OSO 122.6°, OSF 106.3°, NSO 107.2° and 111.2°, NSF 101.2°.

# La química del Kriptón y Radón



## 14-4 The Chemistry of Krypton and Radon

The chemistry of these elements as far as it is known is similar to that of Xe.

Krypton difluoride[34] is obtained on photolysis of Kr—$F_2$ mixtures at −196°C when it forms a white solid only slightly soluble in liquid fluorine. It slowly decomposes at room temperature. It is a powerful fluorinating and oxidizing agent; one example is the conversion of $RuO_4$ to $RuOF_4$ in liquid HF.[35]

The instability of $KrF_2$ compared to $XeF_2$ can be seen from the enthalpies:

$$KrF_2(g) = Kr(g) + F_2(g) \qquad \Delta H^0 = -63 \text{ kJ mol}^{-1}$$

$$XeF_2(g) = Xe(g) + F_2(g) \qquad \Delta H^0 = 105 \text{ kJ mol}^{-1}$$

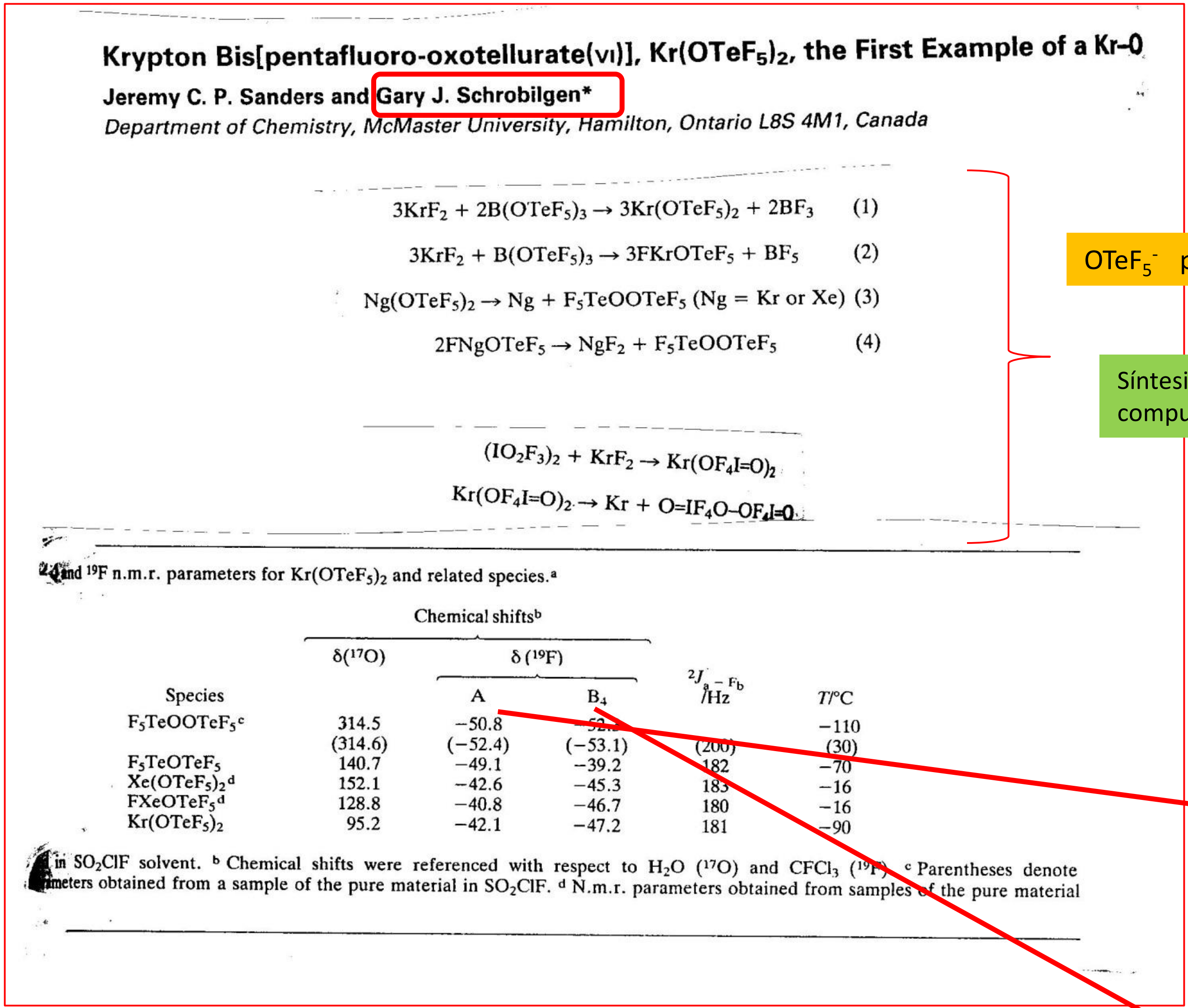
These energetic relationships are understandable on the basis of rigorous quantum mechanical calculations, which justify the view that in both difluorides there is considerable ionic character. The bonding can be more simply represented by the resonance picture:

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

Since the ionization enthalpies (Table 14-1) of Kr and Xe differ by ~182 kJ $mol^{-1}$, the experimental difference in $\Delta H_f^0$ values, namely, 105 − (−63) = 168 kJ $mol^{-1}$ is well explained by this picture.

There are cationic species similar to those of Xe but less stable; they include $KrF^+$, $Kr_2F_3^+$, and $[CF_3CNKrF]^+$.

# El primer ejemplo de compuestos Kr-O



**Krypton Bis[pentafluoro-oxotellurate(VI)], $Kr(OTeF_5)_2$, the First Example of a Kr–O**

**Jeremy C. P. Sanders and Gary J. Schrobilgen***
*Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada*

$$3KrF_2 + 2B(OTeF_5)_3 \rightarrow 3Kr(OTeF_5)_2 + 2BF_3 \quad (1)$$

$$3KrF_2 + B(OTeF_5)_3 \rightarrow 3FKrOTeF_5 + BF_5 \quad (2)$$

$$Ng(OTeF_5)_2 \rightarrow Ng + F_5TeOOTeF_5 \ (Ng = Kr \text{ or } Xe) \quad (3)$$

$$2FNgOTeF_5 \rightarrow NgF_2 + F_5TeOOTeF_5 \quad (4)$$

$$(IO_2F_3)_2 + KrF_2 \rightarrow Kr(OF_4I{=}O)_2$$

$$Kr(OF_4I{=}O)_2 \rightarrow Kr + O{=}IF_4O{-}OF_4I{=}O$$

and $^{19}F$ n.m.r. parameters for $Kr(OTeF_5)_2$ and related species.[a]

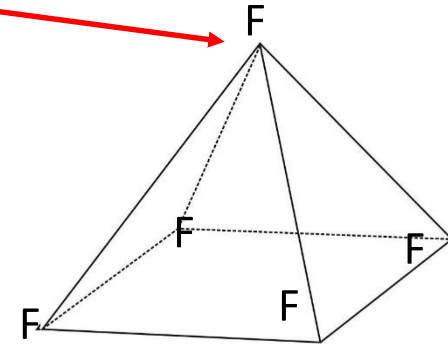
| Species | Chemical shifts[b] $\delta(^{17}O)$ | $\delta(^{19}F)$ A | $\delta(^{19}F)$ $B_4$ | $^2J_{F_a-F_b}$/Hz | T/°C |
|---|---|---|---|---|---|
| $F_5TeOOTeF_5$[c] | 314.5 | −50.8 | −52.[illegible] | | −110 |
| | (314.6) | (−52.4) | (−53.1) | (200) | (30) |
| $F_5TeOTeF_5$ | 140.7 | −49.1 | −39.2 | 182 | −70 |
| $Xe(OTeF_5)_2$[d] | 152.1 | −42.6 | −45.3 | 183 | −16 |
| $FXeOTeF_5$[d] | 128.8 | −40.8 | −46.7 | 180 | −16 |
| $Kr(OTeF_5)_2$ | 95.2 | −42.1 | −47.2 | 181 | −90 |

in $SO_2ClF$ solvent. [b] Chemical shifts were referenced with respect to $H_2O$ ($^{17}O$) and $CFCl_3$ ($^{19}F$). [c] Parentheses denote meters obtained from a sample of the pure material in $SO_2ClF$. [d] N.m.r. parameters obtained from samples of the pure material

$OTeF_5^-$ pentafluorooxitelurato

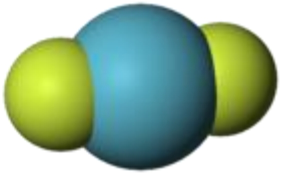
Síntesis de varios compuestos Kr-O

Caracterización por NMR multinuclear



# Una gran Contribución la Química de gases nobles :Gary Schrobilgen

Mc Master University, Canadá



# El primer compuesto Kr-N

CHEM. SOC., CHEM. COMMUN., 1988

## The Fluoro(hydrocyano)krypton(II) Cation $[HC{\equiv}N{-}Kr{-}F]^+$; the First Example of a Krypton–Nitrogen Bond

**Gary J. Schrobilgen**
*Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada*

The first example of krypton bonded to an element other than fluorine has been provided by the synthesis of the novel $[HC{\equiv}N{-}Kr{-}F]^+$ cation, prepared as its $AsF_6^-$ salt by low-temperature reaction of $HC{\equiv}NH^+AsF_6^-$ with $KrF_2$ in HF or $BrF_5$ as solvent, and characterized by low-temperature Raman spectroscopy and $^1H$, $^{13}C$, $^{15}N$, and $^{19}F$ n.m.r. spectroscopy.

Sintesis

$$KrF_2 + HC{\equiv}NH^+AsF_6^- \rightarrow [HC{\equiv}N{-}Kr{-}F]^+AsF_6^- + HF$$

PI HCN 13.59 eV
EA XeF+ 10.9 eV
EA KrF+ 13.2 eV

$^{19}F$ $^{1}H$ $^{15}N$

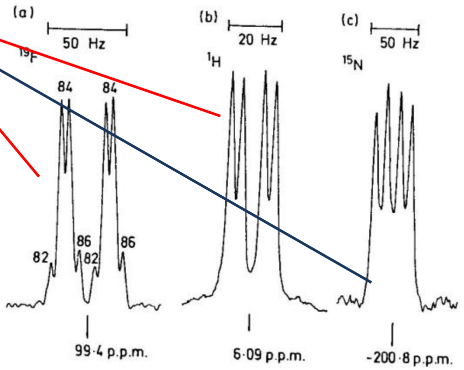


**Figure 1.** N.m.r. spectra of the $[HC{\equiv}N{-}Kr{-}F]^+$ cation enriched to 99.5% with $^{15}N$, in $BrF_5$ as solvent at −57 °C. (a) $^{19}F$ Spectrum (235.36 MHz) depicting $^2J(^{19}F{-}^{15}N)$ and $^4J(^{19}F{-}^1H)$ and krypton isotope shifts. Lines assigned to fluorine bonded to $^{82}Kr$ (11.56%), $^{84}Kr$ (56.90%), and $^{86}Kr$ (17.37%) are denoted by the krypton mass number. The innermost lines of the $^{82}Kr$ and $^{86}Kr$ doublets overlap their corresponding $^{84}Kr$ doublets. The isotopic shift arising from $^{83}Kr$ (11.53%) is not resolved; those of $^{78}Kr$ (0.35%) and $^{80}Kr$ (2.27%) are too weak to be observed. (b) $^1H$ Spectrum (80.02 MHz) depicting $^2J(^{15}N{-}^1H)$ and $^4J(^{19}F{-}^1H)$. (c) $^{15}N$ Spectrum (50.70 MHz) depicting $^2J(^{19}F{-}^{15}N)$ and $^2J(^{15}N{-}^1H)$.

# Caracterización espectroscópica

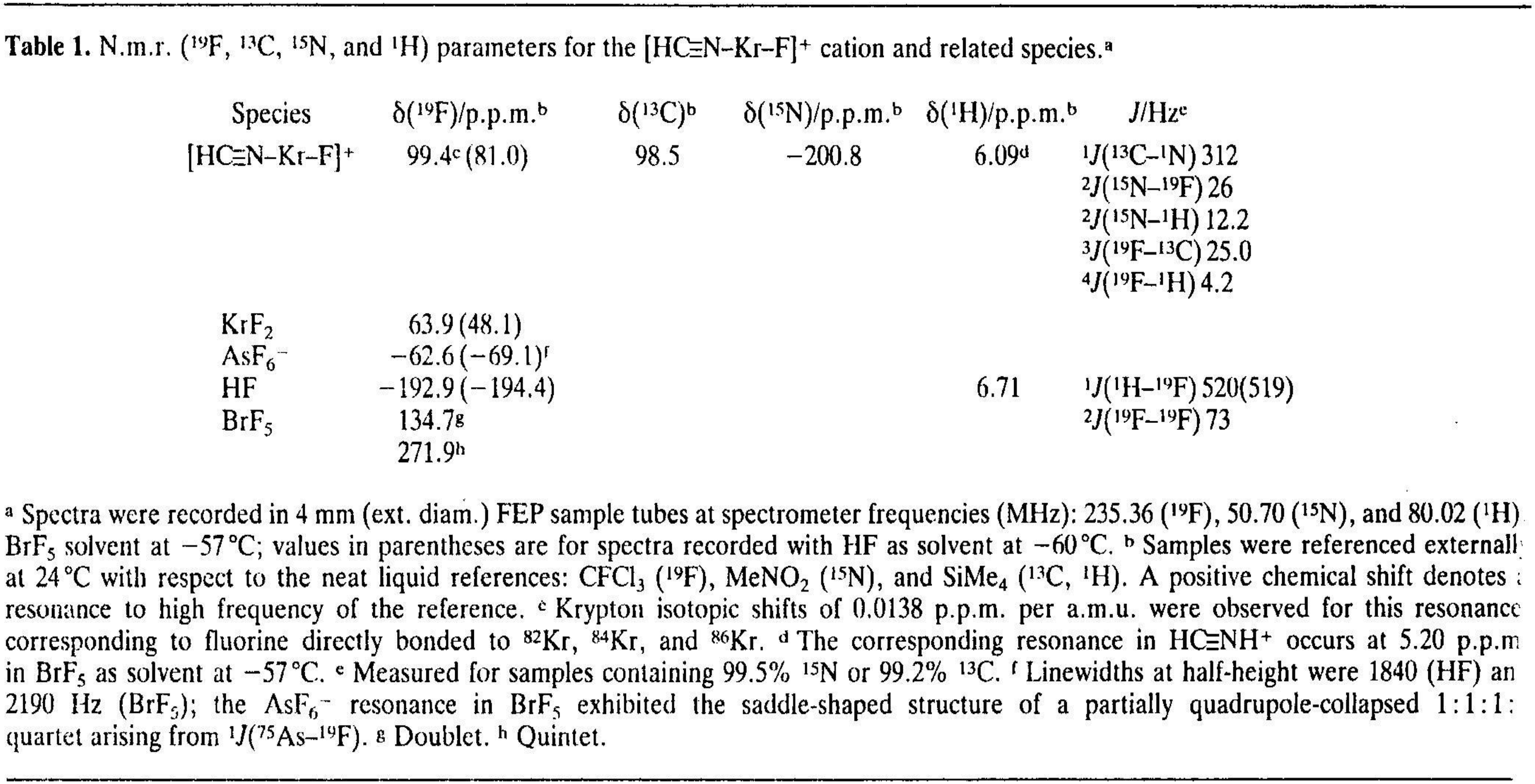
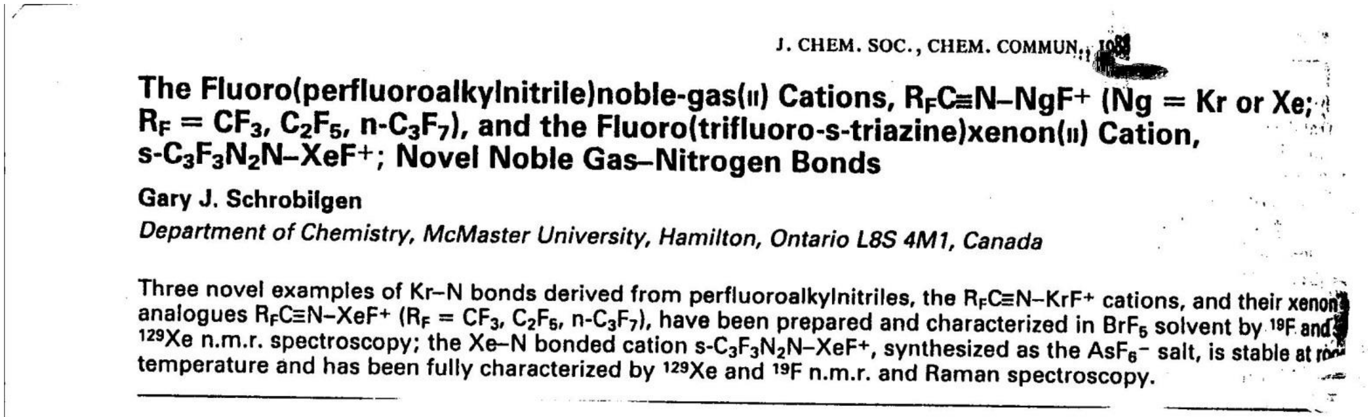


**Table 1.** N.m.r. ($^{19}F$, $^{13}C$, $^{15}N$, and $^{1}H$) parameters for the $[HC{\equiv}N{-}Kr{-}F]^+$ cation and related species.[a]

| Species | $\delta(^{19}F)$/p.p.m.[b] | $\delta(^{13}C)$[b] | $\delta(^{15}N)$/p.p.m.[b] | $\delta(^{1}H)$/p.p.m.[b] | $J$/Hz[e] |
|---|---|---|---|---|---|
| $[HC{\equiv}N{-}Kr{-}F]^+$ | 99.4[c] (81.0) | 98.5 | −200.8 | 6.09[d] | $^{1}J(^{13}C{-}^{1}N)$ 312<br>$^{2}J(^{15}N{-}^{19}F)$ 26<br>$^{2}J(^{15}N{-}^{1}H)$ 12.2<br>$^{3}J(^{19}F{-}^{13}C)$ 25.0<br>$^{4}J(^{19}F{-}^{1}H)$ 4.2 |
| $KrF_2$ | 63.9 (48.1) | | | | |
| $AsF_6^-$ | −62.6 (−69.1)[f] | | | | |
| HF | −192.9 (−194.4) | | | 6.71 | $^{1}J(^{1}H{-}^{19}F)$ 520(519) |
| $BrF_5$ | 134.7[g]<br>271.9[h] | | | | $^{2}J(^{19}F{-}^{19}F)$ 73 |

[a] Spectra were recorded in 4 mm (ext. diam.) FEP sample tubes at spectrometer frequencies (MHz): 235.36 ($^{19}F$), 50.70 ($^{15}N$), and 80.02 ($^{1}H$) $BrF_5$ solvent at −57 °C; values in parentheses are for spectra recorded with HF as solvent at −60 °C. [b] Samples were referenced externall at 24 °C with respect to the neat liquid references: $CFCl_3$ ($^{19}F$), $MeNO_2$ ($^{15}N$), and $SiMe_4$ ($^{13}C$, $^{1}H$). A positive chemical shift denotes resonance to high frequency of the reference. [c] Krypton isotopic shifts of 0.0138 p.p.m. per a.m.u. were observed for this resonance corresponding to fluorine directly bonded to $^{82}Kr$, $^{84}Kr$, and $^{86}Kr$. [d] The corresponding resonance in $HC{\equiv}NH^+$ occurs at 5.20 p.p.m in $BrF_5$ as solvent at −57 °C. [e] Measured for samples containing 99.5% $^{15}N$ or 99.2% $^{13}C$. [f] Linewidths at half-height were 1840 (HF) an 2190 Hz ($BrF_5$); the $AsF_6^-$ resonance in $BrF_5$ exhibited the saddle-shaped structure of a partially quadrupole-collapsed 1:1:1: quartet arising from $^{1}J(^{75}As{-}^{19}F)$. [g] Doublet. [h] Quintet.

# Compuestos Xe(Kr)-N



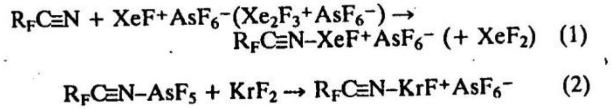
J. CHEM. SOC., CHEM. COMMUN., 198

### The Fluoro(perfluoroalkylnitrile)noble-gas(II) Cations, $R_FC{\equiv}N{-}NgF^+$ (Ng = Kr or Xe; $R_F$ = $CF_3$, $C_2F_5$, n-$C_3F_7$), and the Fluoro(trifluoro-s-triazine)xenon(II) Cation, s-$C_3F_3N_2N{-}XeF^+$; Novel Noble Gas–Nitrogen Bonds

**Gary J. Schrobilgen**
*Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada*

**Three novel examples of Kr–N bonds derived from perfluoroalkylnitriles, the $R_FC{\equiv}N{-}KrF^+$ cations, and their xenon analogues $R_FC{\equiv}N{-}XeF^+$ ($R_F$ = $CF_3$, $C_2F_5$, n-$C_3F_7$), have been prepared and characterized in $BrF_5$ solvent by $^{19}F$ and $^{129}Xe$ n.m.r. spectroscopy; the Xe–N bonded cation s-$C_3F_3N_2N{-}XeF^+$, synthesized as the $AsF_6^-$ salt, is stable at ro temperature and has been fully characterized by $^{129}Xe$ and $^{19}F$ n.m.r. and Raman spectroscopy.**

Síntesis



$$R_FC{\equiv}N + XeF^+AsF_6^-(Xe_2F_3^+AsF_6^-) \rightarrow R_FC{\equiv}N{-}XeF^+AsF_6^- \; (+ XeF_2) \qquad (1)$$

$$R_FC{\equiv}N{-}AsF_5 + KrF_2 \rightarrow R_FC{\equiv}N{-}KrF^+AsF_6^- \qquad (2)$$

Síntesis a dos pasos

| | | |
|---|---|---|
| PI | $CF_3CN$ | 13.90 eV |
| EA | $XeF^+$ | 10.9 eV |
| EA | $KrF^+$ | 13.2 eV |
| PI | HCN | 13.59 eV |

# Caracterización

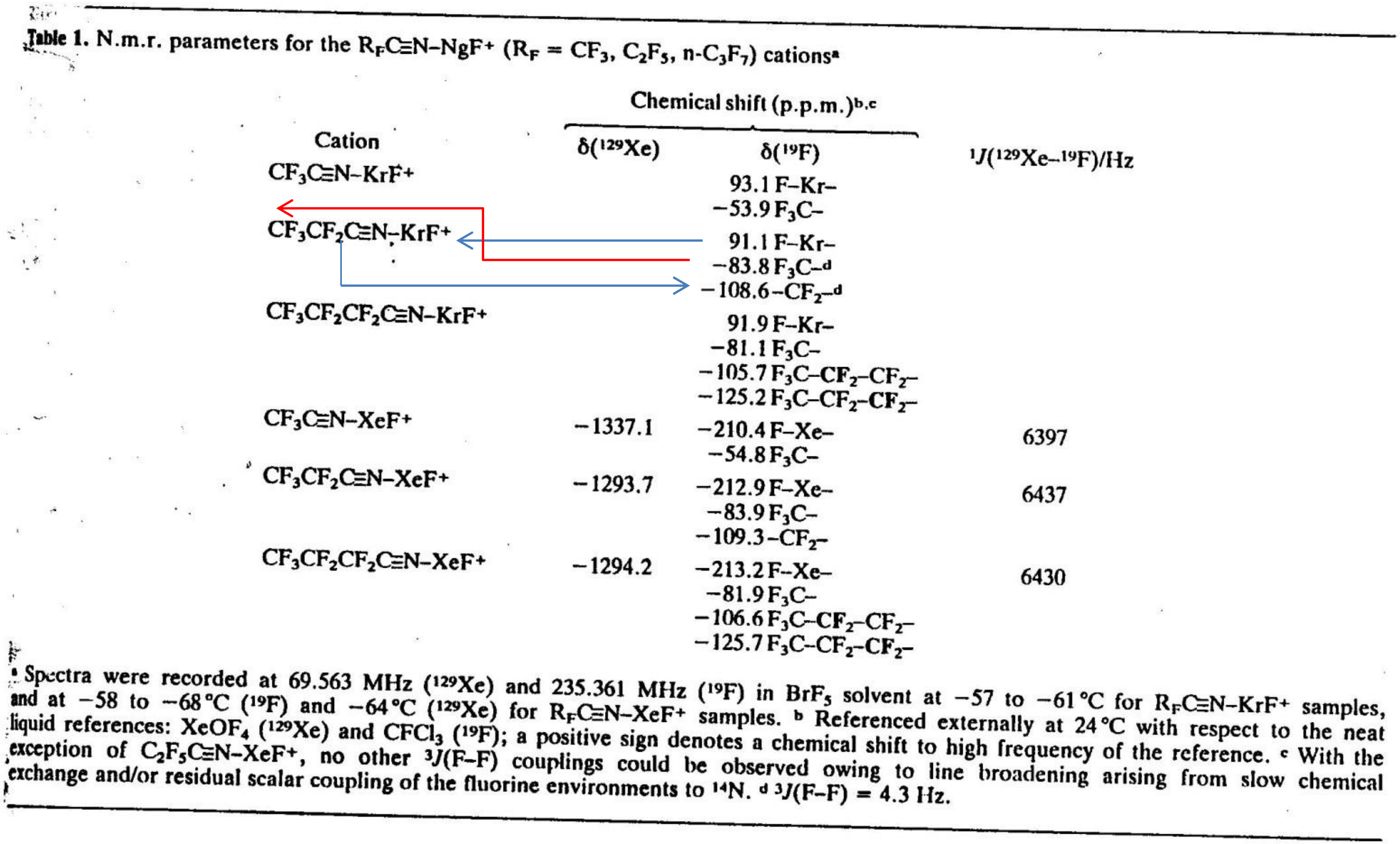
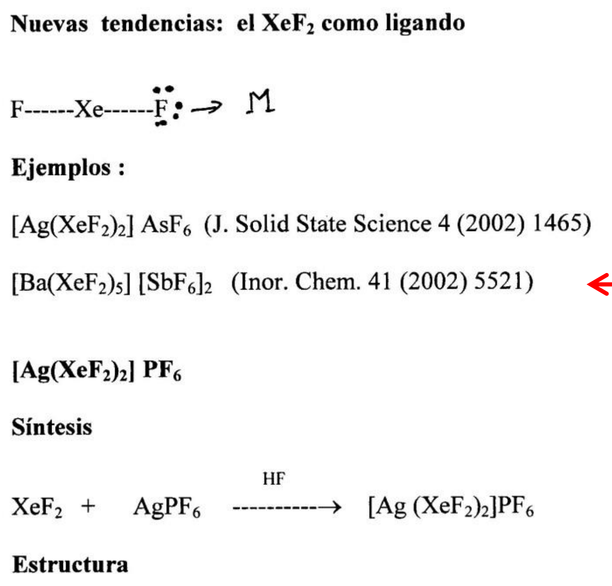


**Table 1.** N.m.r. parameters for the $R_FC{\equiv}N{-}NgF^+$ ($R_F = CF_3$, $C_2F_5$, n-$C_3F_7$) cations[a]

| Cation | Chemical shift (p.p.m.)[b,c] $\delta(^{129}Xe)$ | Chemical shift (p.p.m.)[b,c] $\delta(^{19}F)$ | $^1J(^{129}Xe{-}^{19}F)$/Hz |
|---|---|---|---|
| $CF_3C{\equiv}N{-}KrF^+$ | | 93.1 F–Kr–<br>−53.9 $F_3C-$ | |
| $CF_3CF_2C{\equiv}N{-}KrF^+$ | | 91.1 F–Kr–<br>−83.8 $F_3C-$[d]<br>−108.6 $-CF_2-$[d] | |
| $CF_3CF_2CF_2C{\equiv}N{-}KrF^+$ | | 91.9 F–Kr–<br>−81.1 $F_3C-$<br>−105.7 $F_3C{-}\mathbf{CF_2}{-}CF_2-$<br>−125.2 $F_3C{-}CF_2{-}\mathbf{CF_2}-$ | |
| $CF_3C{\equiv}N{-}XeF^+$ | −1337.1 | −210.4 F–Xe–<br>−54.8 $F_3C-$ | 6397 |
| $CF_3CF_2C{\equiv}N{-}XeF^+$ | −1293.7 | −212.9 F–Xe–<br>−83.9 $F_3C-$<br>−109.3 $-CF_2-$ | 6437 |
| $CF_3CF_2CF_2C{\equiv}N{-}XeF^+$ | −1294.2 | −213.2 F–Xe–<br>−81.9 $F_3C-$<br>−106.6 $F_3C{-}\mathbf{CF_2}{-}CF_2-$<br>−125.7 $F_3C{-}CF_2{-}\mathbf{CF_2}-$ | 6430 |

[a] Spectra were recorded at 69.563 MHz ($^{129}Xe$) and 235.361 MHz ($^{19}F$) in $BrF_5$ solvent at −57 to −61 °C for $R_FC{\equiv}N{-}KrF^+$ samples, and at −58 to −68 °C ($^{19}F$) and −64 °C ($^{129}Xe$) for $R_FC{\equiv}N{-}XeF^+$ samples. [b] Referenced externally at 24 °C with respect to the neat liquid references: $XeOF_4$ ($^{129}Xe$) and $CFCl_3$ ($^{19}F$); a positive sign denotes a chemical shift to high frequency of the reference. [c] With the exception of $C_2F_5C{\equiv}N{-}XeF^+$, no other $^3J(F{-}F)$ couplings could be observed owing to line broadening arising from slow chemical exchange and/or residual scalar coupling of the fluorine environments to $^{14}N$. [d] $^3J(F{-}F)$ = 4.3 Hz.

# $XeF_2$ como ligante



**Nuevas tendencias: el $XeF_2$ como ligando**

F------Xe------$\underset{..}{\ddot{F}}$: → M

**Ejemplos :**

$[Ag(XeF_2)_2]\ AsF_6$ (J. Solid State Science 4 (2002) 1465)

$[Ba(XeF_2)_5]\ [SbF_6]_2$ (Inor. Chem. 41 (2002) 5521)

**$[Ag(XeF_2)_2]\ PF_6$**

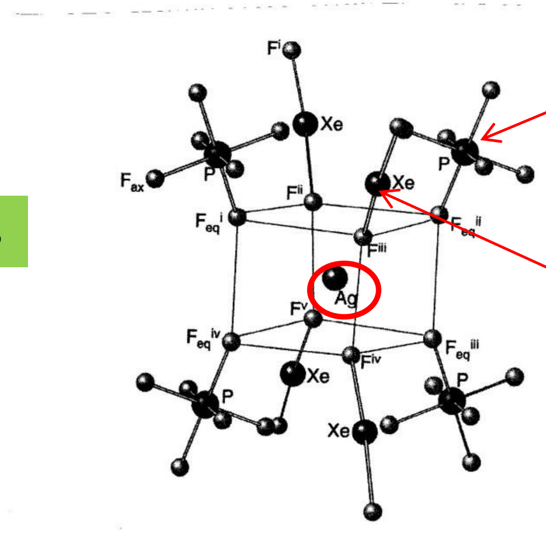
**Síntesis**

$$XeF_2 + AgPF_6 \xrightarrow{HF} [Ag\,(XeF_2)_2]PF_6$$

**Estructura**

Ag-F

Ba-F



$PF_6^-$

$XeF_2$

$Ag^+$ coordinación 8

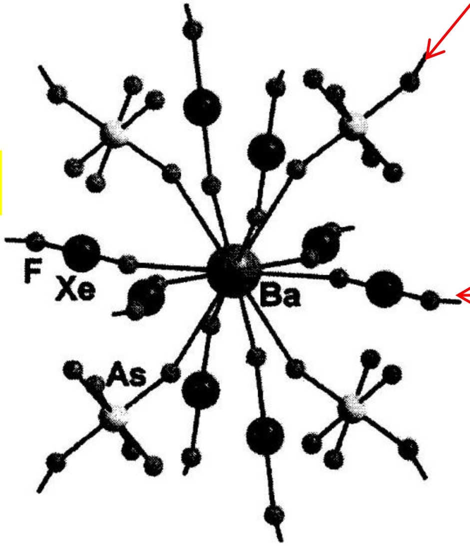
# Otro ejemplo

**$[Ba(XeF_2)_5]\ [SbF_6]_2$**

**Síntesis :**

$$Ba(SbF_6)_2 + XeF_2 \xrightarrow{HF} [Ba(XeF_2)_5][(SbF_6)_2$$

**Estructura:**



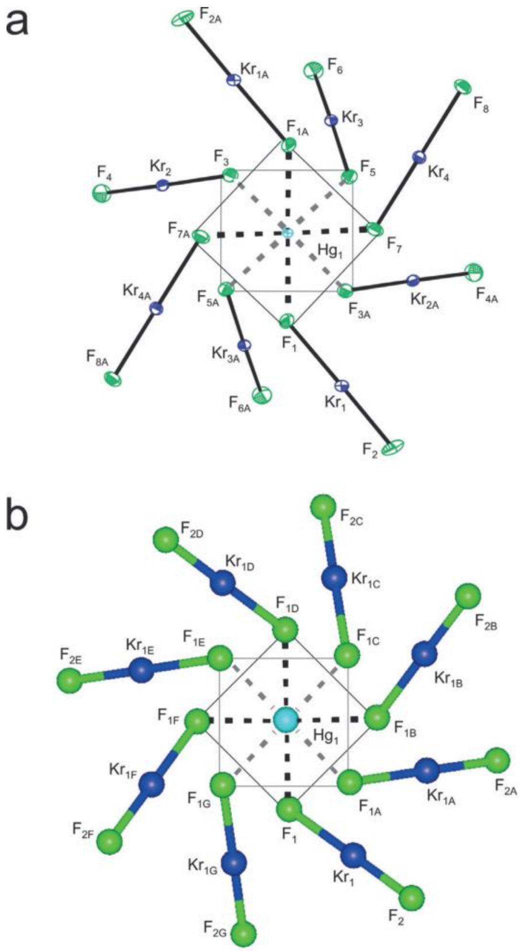
$SbF_6^-$

$Ba^{+2}$ coordinación 12

$XeF_2$

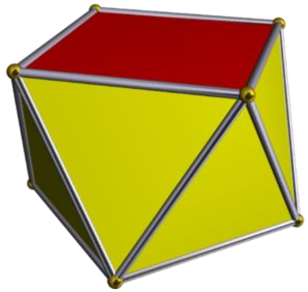
# Síntesis y Caracterización de $[Hg(KrF_2)_8][AsF_6]2 \cdot 2HF$

$$Hg(AsF_6)_2 + 8\,KrF_2 \xrightarrow{HF} [Hg(KrF_2)_8][AsF_6]_2 \cdot 2\,HF$$



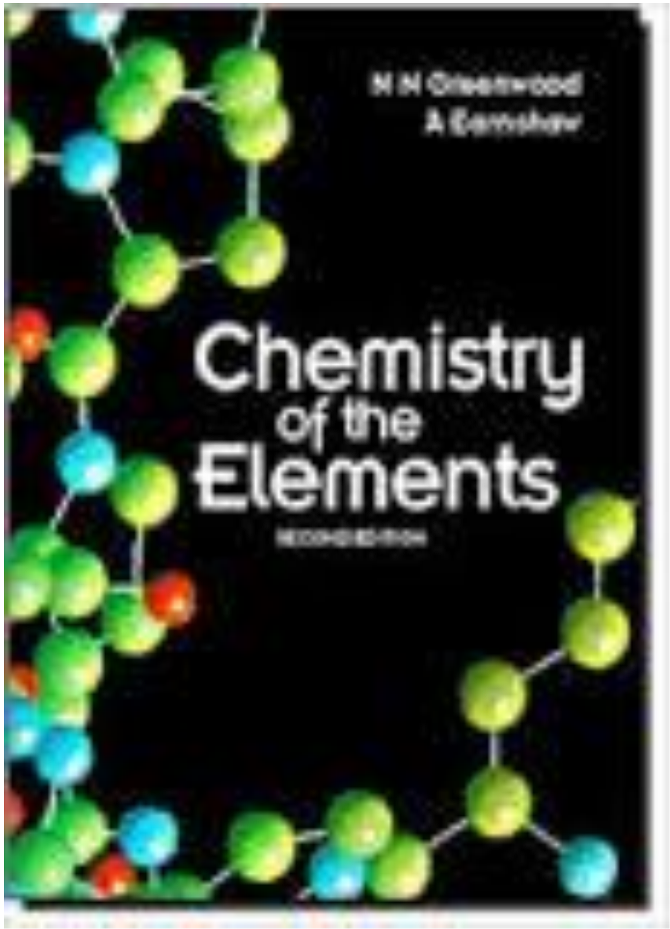
El primer compuesto de coordinación homoléptico : solo $KrF_2$ como ligante

Hg coordinación 8



John R. DeBackere and Gary J. Schrobilgen Angew.Chemie Int. Ed.(2018), 57, 13167.

# Referencia base



**Chemistry of the Elements**
**(Second Edition)**
*Author(s):*
***A. Earnshaw and Norman Greenwood***