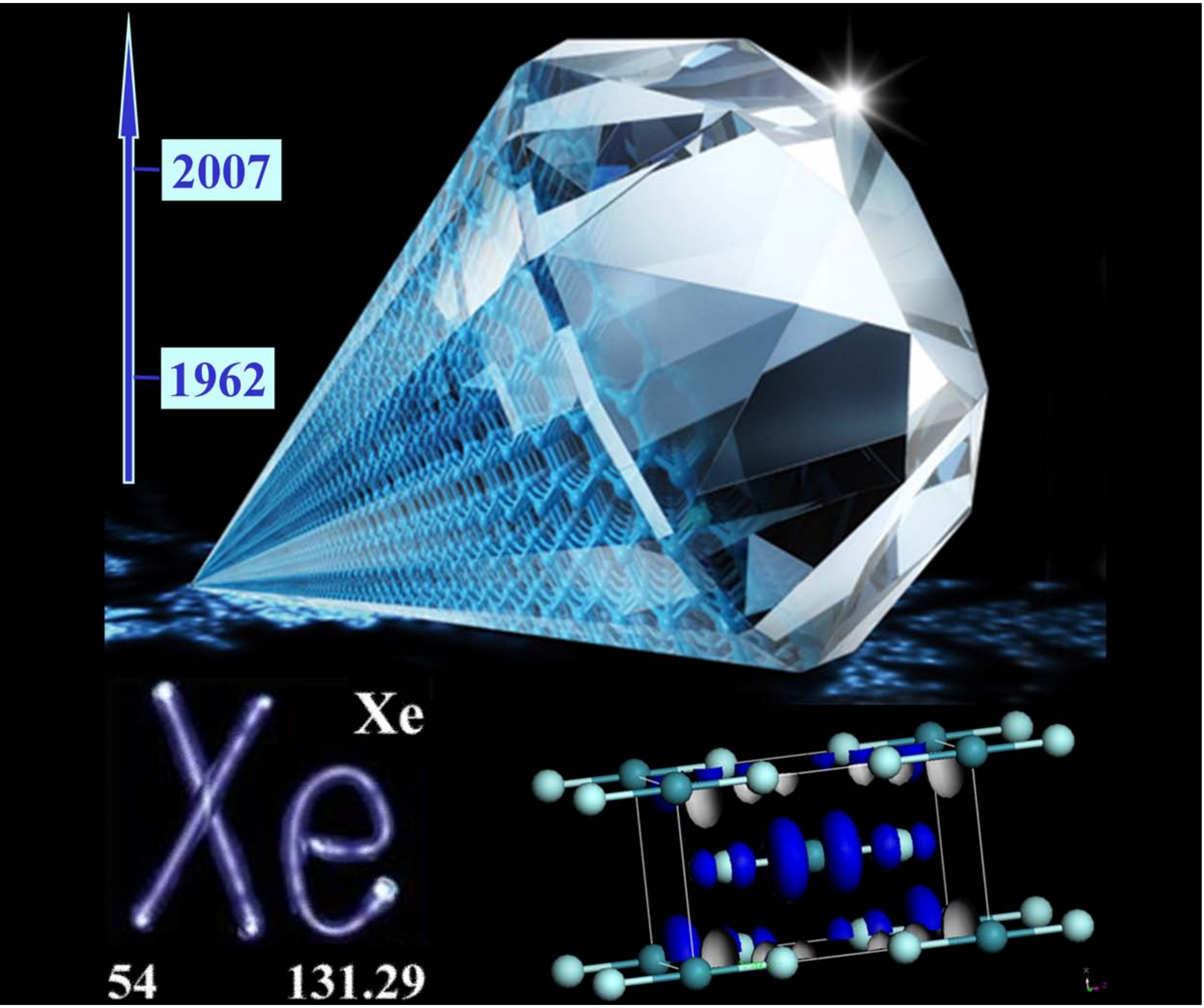
# Chem Soc Rev

Chemical Society Reviews

www.rsc.org/chemsocrev

Volume 36 | Number 10 | October 2007 | Pages 1533 - 1696



ISSN 0306-0012

RSC Publishing

**TUTORIAL REVIEW**
Marc Aucouturier and Evelyne Darque-Ceretti
The surface of cultural heritage artefacts

**CRITICAL REVIEW**
Wojciech Grochala
Atypical compounds of gases, which have been called 'noble'

# Atypical compounds of gases, which have been called 'noble'†

**Wojciech Grochala**[ab]

***Received 12th April 2007***
***First published as an Advance Article on the web 20th June 2007***
**DOI: 10.1039/b702109g**

In this *critical review* I describe fascinating experimental and theoretical advances in 'noble gas' chemistry during the last twenty years, and have taken a somewhat unexpected course since 2000. I also highlight perspectives for further development in this field, including the prospective synthesis of compounds containing as yet unknown Xe–element and element–Xe–element bridging bonds, peroxide species containing Xe, adducts of $XeF_2$ with various metal fluorides, Xe–element alloys, and novel pressure-stabilized covalently bound and host–guest compounds of Xe. A substantial part of the essay is devoted to the—as yet experimentally unexplored—behaviour of the compounds of Xe under high pressure. The blend of science, history, and theoretical predictions, will be valued by inorganic and organic chemists, materials scientists, and the community of theoretical and experimental high-pressure physicists and chemists (151 references).

## 1 Lead-in

They say *noblesse oblige*.[1] Nothing more inaccurate and misleading than that has been said, however, in the context of the heavier gaseous elements of Group 18 (Rn, Xe, Kr), which for a century have been colloquially called 'noble'. Since the discovery of argon ('the lazy one') in 1894 by Rayleigh and Ramsay,[2] and the realisation of the monoatomic and unreactive nature of its homologues, it was long believed that group 18 elements cannot form chemical compounds. And the very concept of the stable 'octet valence configuration', so vital to chemistry, was born.[3] '*Nothing can force a noble gas (Ng) atom into a chemical bonding*' said this new law of nature. But human nature loves challenges. Led by intuition and qualitative considerations, von Antropoff[4a,b] and Pauling[4c] have forseen that heavier Ng's might, in fact, be chemically awaken in powerfully oxidizing conditions while entering the oxide or fluoride environment. Yet nearly forty years were to pass since the apposite predictions saw confirmation in the breakthrough-making 1962 discovery of the first Xe compound.[5,6] In 1989 Xe has completely lost traces of its nobility and inertness when it was turned into metal by use of ultra-high pressure.[7]

About half a thousand compounds of Ng's have been synthesized since 1962.[8] Due to the above mentioned historical reasons and for the purpose of this short essay, we would like draw here the line between 'usual' and 'unusual' compounds. By 'usual' or 'classical', I refer to those compounds predicted by Pauling, *etc.* so long ago. They contain fluoride, oxide and related ligands (such as $SbF_6^-$, $TeOF_5^-$, $IO_2F_4^-$, $WOF_4$, *etc.*) and contain Xe at oxidation states +2, +4, +6, +8 (Fig. 1), or $Kr^{II}$ in fluoride environment; chemistry of 'classical' Ng compounds—also undergoing violent progress[9]—has been reviewed elsewhere[10–12] and only rarely will be mentioned here.[13] Whatever goes beyond that (and *any* chemical bonding involving Ar) will be treated as 'atypical', and described from a chemical perspective to a greater detail, with particular emphasis on chemistry of Xe.

**Wojciech Grochala**

*Wojciech Grochala was born in 1972 in Warsaw, Poland, where he received his MSc, PhD and DSc from the University of Warsaw. He has studied chemistry with Roald Hoffmann in Ithaca (Cornell, USA) and with Peter P. Edwards (then at Birmingham, UK). Inorganic solid state chemistry and mountaineering are Wojciech's real passions. He entered the field of noble gas chemistry through the back door, when studying the most potent oxidizers available to chemistry (higher fluorides of Ag).[144] His scientific interests encompass superconductivity,[145] quantum modelling of solids and molecular materials, hydrogen[37] and energy storage, hydrogen transfer catalysis,[146] applications of high pressures in chemistry,[120] molecular devices, unusual oxidation states of the chemical elements,[147] and more. He now heads the Laboratory of Technology of Novel Functional Materials, a joint enterprise of the ICM and of the Department of Chemistry at Warsaw University.*
*Wojciech is the happy husband of Liliana and father of three kids: Ilona Maria, Oliver Lucian and Leonard Karol.*

## 2 The known Ng–element bonds

### 2.1 The first 'unusual' Ng–nonmetal bonds

Encouraged by fast enriching spectrum of the Xe–F and Xe–O compounds, several groups have tried to break another

---

[a] *Laboratory of Technology of Novel Functional Materials, Interdisciplinary Center for Mathematical and Computational Modeling, University of Warsaw, Pawińskiego 5a, 02106 Warsaw, Poland*
[b] *Laboratory of Intermolecular Interactions, Department of Chemistry, University of Warsaw, Pasteur 1, 02093 Warsaw, Poland*
† This essay is dedicated to Roald Hoffmann, on the occasion of his 70 birthday, who has taught me to feel the pulse of science.

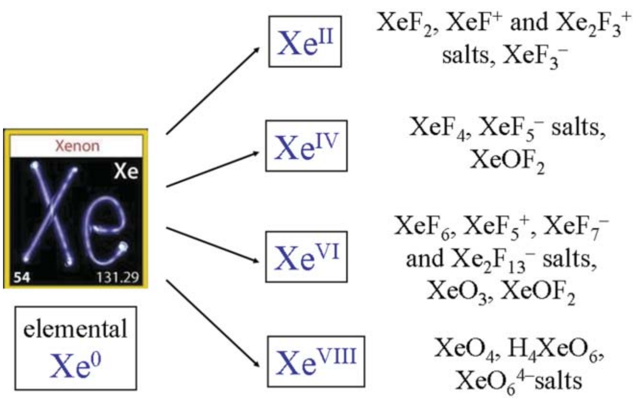


**Fig. 1** Classical chemistry of Xe involving connections to F and O ligands at various oxidation states of a "noble" gas.

paradigm, and to extend bonding to Xe beyond the two most electronegative elements.

The first genuine Xe–N bond saw the daylight in 1974, with the discovery of $(F–Xe^{II})[^-N(SO_2F)_2]$. This new white compound is isolable in gram quantities and is stable to decomposition up to +70 °C (Table 1)! This synthesis paved the road for further developments but these went uphill; during the next 25 years about twenty other compounds have been made in chemists' flasks (including related $Xe^{II}[N(SO_2F)_2^-]_2$, $(RCN–XeF^+)(AsF_6^-)$ where R = H, Me, derivatives of perfluorinated pyridine, perfluoroalkyls, trifluorotriazine *etc.*),[14] $Xe[N(SO_2R)_2^-](2,6\text{-}F_2C_6H_3^-)$ where R = F, $CF_3$,[15] and $[F_3SN–XeF][AsF_6]$.[16] Compounds of $[^-(NH)–TeF_5]$ and related anions[17] have also been made, while some others were suggested as short-lived reaction intermediates.[18] All of them were less thermally stable than the native $F–Xe^{II}–N(SO_2F)_2$.

As time passed by and the knowledge of researchers accumulated, the first examples of the unstable $Xe^{VI}$–N and $Xe^{VIII}$–N bonds were delivered.[19] Finally, Kr has also been linked to N (and to O), but only below −60 °C (for O: −90 °C) in the $BrF_5$ (for O: $SO_2ClF$) solvent.[20,21]

It was also quite difficult to get compounds which have real Xe–C bonds. The precedents, $[(F_5C_6)Xe^+][B(C_6H_5)_3F^-]$ and $[(F_5C_6)Xe^+][B(C_6H_5)F_3^-]$ were synthesized as late as 1988 as colorless solids, and their solutions in acetonitrile proved to be stable at ~0 °C.[22] Soon the preparation method was extended and modified, and new synthetic paths have been invented yielding more related aryl derivatives, the compounds of (partially or entirely fluorinated) unsaturated hydrocarbon groups (*i.e.* alkenyl[23] and alkynyl),[24] and even the first compound with the simultaneous Xe–C and Xe–N bonds.[25] $[(F_5C_6)Xe^+](AsF_6^-)$, which is so thermally stable that it decomposes rapidly only well above its melting temperature ($T_m$ = 102 °C), has become an important reagent in the emerging organoxenon chemistry.[26] It took one decade to synthesize the important siblings $(F_5C_6)XeF$, $Xe(C_6F_5)_2$ and $\{[(F_5C_6)Xe]_2F^+\}(AsF_6^-)$.[27] The electrochemistry of organoxenon(II) derivatives has been explored,[28] and even the first organoxenon(IV) compounds have been prepared ($[(F_5C_6)Xe^{IV}F_2^+](BF_4^-)$ and $Xe^{IV}F_4(CN^-)$).[29]

The formation of the $Xe^{II}$–Cl bond (an analogue of the well-known $Xe^{II}$–F bond) at temperatures close to ambient, was first seen in 1997.[30] This new bond was brought to life in two novel crystalline species, $(F_5C_6)XeCl$ and $\{[(F_5C_6)Xe]_2Cl^+\}(AsF_6^-)$, which showed reasonable kinetic stability at ambient temperature. Since then only one more

**Table 1** Chemical formula and ranking of the thermal decomposition temperature, $T_{dec}$, of selected compounds which exhibit the Xe–E bonds (E = N, C, Cl)

| Chemical formula | $T_{dec}$/°C | Comments |
|---|---|---|
| $F–Xe^{II}–N(SO_2F)_2$ | 70 | Bulk solid |
| $(MeCN–XeF^+)(AsF_6^-)$ | $>-10$ | Solution in anhydrous HF |
| $Xe[N(SO_2F)_2]_2$ | $>-40$ | Solution in $SO_2ClF$ |
| | | |
| $[(F_5C_6)Xe[N(SO_2F)_2]$ | 155 | Bulk solid |
| $[(F_5C_6)Xe[N(SO_2CF_3)_2]$ | 120 | Bulk solid |
| $[(F_5C_6)Xe(NC_5H_3F_2\text{-}2,6)^+](AsF_6^-)$ | $<20$ | Solution in MeCN |
| $[(F_5C_6)Xe(NC–CH_3)^+](F_2B(C_6F_5)^-)$ | 14 | Bulk solid |
| $[(F_5C_6)Xe^+](AsF_6^-)$ | $>130$ | Bulk solid; fast decomp. > 180 °C |
| $[2,6\text{-}(F_2H_3C_6)Xe^+](BF_4^-)$ | 130 | Bulk solid |
| $[2,6\text{-}(F_2H_3C_6)Xe^+][C(SO_2F)_3)$ | 113 | Bulk solid |
| $[(F_5C_6)Xe^+](^-OOC–C_6F_5)$ | 85 | Bulk solid |
| $[(F_5C_6)Xe^+][B(C_6H_5)F_3^-]$ | $<35$ | Solution in MeCN |
| $[(F_5C_6)Xe^+](BF_4^-)$ | $>25$ | Solution in anhydrous HF |
| $[(F_5C_6)Xe^+](BF_4^-)$ | $>25$ | Solution in anhydrous HF |
| $(F_5C_6)_2Xe$ | 20 | Bulk solid, explosive decomposition |
| $[(CF_3C{\equiv}C)Xe^+](BF_4^-)$ | 20 | Stable for at least 2–3 h |
| $[(F_5C_6)Xe^+](HF_2^-)$ | $<20$ | Solution in MeCN |
| $[(F_5C_6)Xe^+][B(C_6H_5)_3F^-]$ | $>0$ | Solution in MeCN |
| $[(4\text{-}ClH_4C_6)Xe^+](BF_4^-)$ | $>-4$ | Bulk solid |
| $[(F_5C_6)Xe^{IV}F_2^+](BF_4^-)$ | $>-20$ | Bulk solid |
| $(F_5C_6)XeF$ | $<-78$ | Solution in $CH_2Cl_2$ |
| $(F_5C_6)Xe(CN)$ | $<-78$ | Solution in $CH_2Cl_2$ |
| | | |
| $\{[(F_5C_6)Xe]_2Cl\}(AsF_6^-)$ | 100 | Bulk solid |
| $(F_5C_6)XeCl$ | 36 | Bulk solid, decomposition with melting |
| $(XeCl^+)(Sb_2F_{11}^-)$ | $-20$ | Bulk solid, decomposition with melting |

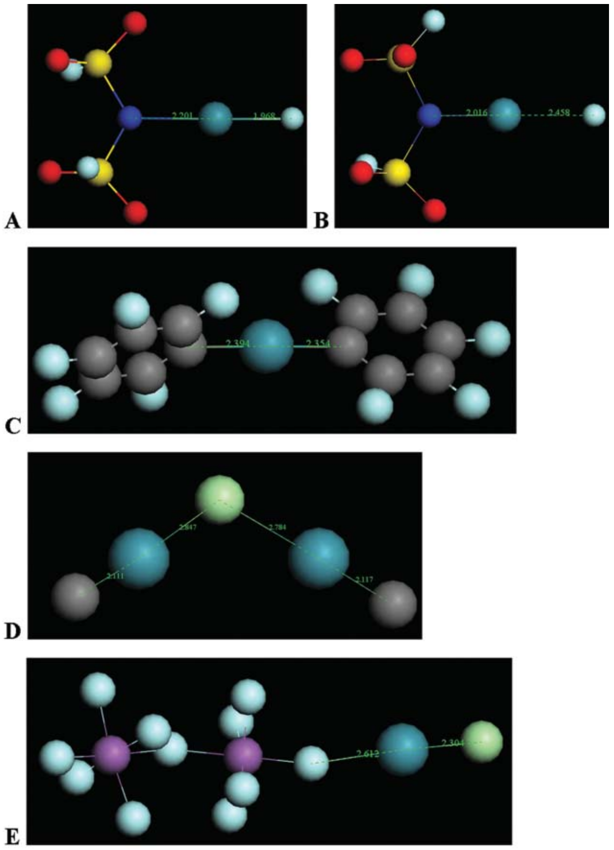


**Fig. 2** Structures of: (A) F–$Xe^{II}$–$N(SO_2F)_2$; (B) $Xe^{II}$–$N(SO_2F)_2(Sb_3F_{16})$; (C) $Xe(C_6F_5)_2$; (D) $\{[(F_5C_6)Xe]_2Cl\}(AsF_6^-)$; (E) $(XeCl^+)(Sb_2F_{11}^-)$. Xe – blue, F – light blue, Cl – green, C – black, N – dark blue, S – yellow, O – red. Molecular units, extracted from full crystal structures, are shown here, except for (D) where only one C atom from each benzene ring is shown.

compound, $(XeCl^+)(Sb_2F_{11}^-)$,[31] has been added to the list of compounds isolable 'in the flask'. The chemistry of the Xe–Cl bond thus remains largely unexplored.

Summarizing this section, we note that close to a hundred organoxenon, Xe–N and Xe–Cl compounds are known up to date.[32] Xenon chemistry finally 'went out from the cold',[33] and started flourishing.

### 2.2 Where are the bonds

Despite the 1974–2006 successes of xenon chemistry, only ~15% of all known solids containing short Xe–C, Xe–N and Xe–Cl contacts have been structurally characterized. Selected structures are shown in Fig. 2.

$Xe^{II}$ is isoelectronic to $I^I$. Not surprisingly, $XeF_2$ is isostructural with the linear symmetric $IF_2^-$ anion (present for example in its $Cs^+$ salt), and all $Xe^{II}$ compounds show two-coordinated Xe in an $E^1\cdots Xe\cdots E^2$ unit ($E^1$, $E^2$ = Lewis base) with its bond angle close to 180° (±10°). Covalent Xe–C bond lengths vary from 2.08 to 2.39 Å, the Xe–N contacts are at 2.02–2.20 Å, while the Xe–Cl bonds are 2.31–2.85 Å long.

Even in the very limited set of experimental data, a clear trend can be perceived, calling for an obvious generalization (Table 2 and Fig. 3).[34] It is clear from Table 2, that for a given $E^1\cdots Ng\cdots E^2$ set of elements (for example: Ng = Xe, $E^1$ = N, $E^2$ = F), a relationship always holds: when $R^1$ becomes longer, $R^2$ becomes shorter, and *vice versa*. Some will attribute it to the varying basicity of one of molecule's counterions, using the following reasoning: since the $(Sb_3F_{16}^-)$ ion is much less basic than $F^-$, the $Xe^{II}\cdots F$ contact must be longer in the $(Sb_3F_{16}^-)\cdots Xe^{II}$–$N(SO_2F)_2$ derivative than in the $(F^-)\cdots Xe^{II}$–$N(SO_2F)_2$ one. In turn, the $Xe^{II}$ center must be more powerful Lewis acid in the former compound, and therefore it is ligated by the $^-N(SO_2F)_2$ base at shorter separation than that found for the latter species.

**Table 2** Chemical formula and the lengths, $R^1$ and $R^2$, of two hypervalent Xe–E bonds (E = N, C, Cl, F) and of two hypervalent Kr–F bonds observed in several compounds of these Ng's.

| Formula | $R^1$/Å | $R^2$/Å | Comment |
|---|---|---|---|
| F–$Kr^{II}$–F | Kr–F: 1.894 | Kr–F: 1.894 | Symmetric |
| $(Kr_2F_3^+)(SbF_6)\cdot KrF_2$ | Kr–F: 1.805 | Kr–F: 2.041 | |
| $(Kr_2F_3^+)(SbF_6)\cdot KrF_2$ | Kr–F: 1.799 | Kr–F: 2.065 | |
| (F–$Kr^{II}$)($BiF_6$) | Kr–F: 1.775 | Kr–F: 2.090 | |
| (F–$Kr^{II}$)($AsF_6$) | Kr–F: 1.765 | Kr–F: 2.131 | |
| (F–$Kr^{II}$)($SbF_6$) | Kr–F: 1.765 | Kr–F: 2.140 | |
| (F–$Kr^{II}$)($AuF_6$) | Kr–F: 1.751 | Kr–F: 2.161 | |
| $(Sb_3F_{16})$–$Xe^{II}$–$N(SO_2F)_2$ | Xe–N: 2.020 | Xe–F: 2.457 | |
| F–$Xe^{II}$–$N(SO_2F)_2$ | Xe–N: 2.200 | Xe–F: 1.967 | |
| $[(F_5C_6)Xe^{II}(NCMe)](F_2B(C_6F_5)^-)$ | Xe–N: 2.681 | Xe–C: 2.092 | |
| $[(F_5C_6)Xe(NC_5H_3F_2\text{-}2,6)^+](AsF_6^-)$ | Xe–N: 2.694 | Xe–C: 2.087 | |
| $[(F_5C_6)Xe^{II}](AsF_6)$ | Xe–C: 2.079 | Xe–F: 2.714 | |
| $[(F_5C_6)Xe^{II}](AsF_6)$ | Xe–C: 2.082 | Xe–F: 2.672 | |
| $[(2,6\text{-}F_2H_3C_6)Xe^{II}](BF_4^-)$ | Xe–C: 2.090 | Xe–F: 2.793 | |
| $[(F_5C_6)Xe(NC_5H_3F_2\text{-}2,6)^+](AsF_6^-)$ | Xe–C: 2.087 | Xe–N: 2.694 | |
| $[(F_5C_6)Xe^{II}(NCMe)](F_2B(C_6F_5)^-)$ | Xe–C: 2.092 | Xe–N: 2.681 | |
| $\{[(F_5C_6)Xe]_2Cl\}(AsF_6^-)$ | Xe–C: 2.111 | Xe–Cl: 2.847 | |
| $\{[(F_5C_6)Xe]_2Cl\}(AsF_6^-)$ | Xe–C: 2.116 | Xe–Cl: 2.784 | |
| $(F_5C_6)_2Xe^{II}$ | Xe–C: 2.350 | Xe–C: 2.394 | Close to symmetric |
| $[(2,6\text{-}F_2H_3C_6)Xe^{II}](^-OSO_2CF_3)$ | Xe–C: 2.079 | Xe–O: 2.687 | |
| | Xe–C: 2.092 | Xe–O: 2.829 | |
| $(XeCl^+)(Sb_2F_{11}^-)$ | Xe–Cl: 2.309 | Xe–F: 2.644 | |
| $XeCl_2$ | Xe–Cl: 2.542 | Xe–Cl: 2.542 | Symmetric (theor. result for solid)[145] |
| $\{[(F_5C_6)Xe]_2Cl\}(AsF_6^-)$ | Xe–Cl: 2.784 | Xe–C: 2.116 | |
| $\{[(F_5C_6)Xe]_2Cl\}(AsF_6^-)$ | Xe–Cl: 2.847 | Xe–C: 2.111 | |

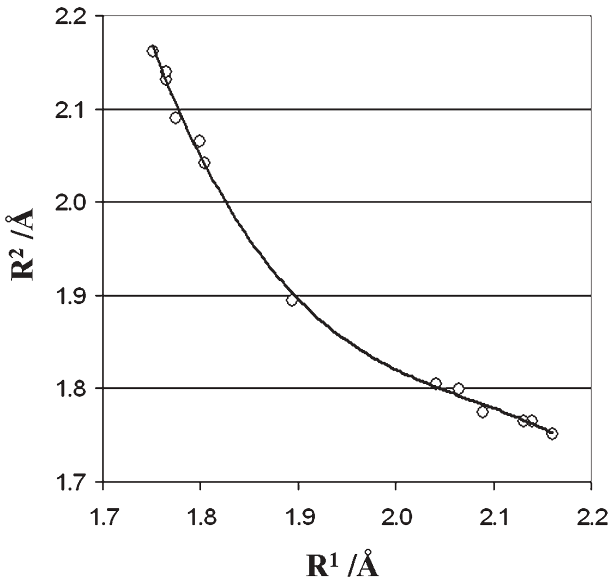


**Fig. 3** Illustration of the nature of a hypervalent bond: the experimental $R^1$ *vs.* $R^2$ dependence for several $F^- \cdots Kr^{II} \cdots F^-$ species.

Others will argue that such asymmetric (long–short) bonding pattern is typical for any hypervalent (here: four-electron–three-center) bonding;[35] it is seen even in a purely fluoride environment for $Kr^{II}$ (compare Fig. 2) and of course for $Xe^{II}$, as well as for many other related species.[36] Notably, the hypervalent E···Xe–C, E···Xe–N and E···Xe–Cl groupings also obey this general relationship.

Coming back to structures: $Xe^{IV}$ resembles $I^{III}$ (or $Br^{III}$) and $Te^{II}$ (or $Se^{II}$), and these species usually appear in a square-planar coordination, as seen for $Xe^{IV}F_4$, $Br^{III}F_4^-$ ion or $L_2Se^{II}Cl_2$ (L = tetrahydrothiophene). Distorted square-planar coordination of $Xe^{IV}$ is also likely to be the case for $[(F_5C_6)Xe^{IV}F_2^+](FBF_3^-)$. A very rare planar pentacoordinated geometry $Xe^{IV}$ is presumably adopted be $Xe^{IV}$ in the $F_4Xe(CN^-)$ anion. These are the only organoxenon(IV) compounds synthesized so far.

### 2.3 Combatting against auto–redox reactions

The chemistry of nonmetal–Xe connections is fascinating but quite difficult to do. There are many reactions possible which may hinder formation and limit stability of Xe–N, Xe–C, Xe–Cl and related bonds, and, indeed, unwanted redox processes are a major headache of researchers of Xe chemistry. Some such processes are illustrated in eqn (1)–(3) for three prototypical Xe–N, Xe–Cl and Xe–C compounds:

$$2\ F\text{–}Xe^{II}\text{–}N(SO_2F)_2 \rightarrow Xe^0 + XeF_2 + [N(SO_2F)_2]_2 \quad (1)$$

$$(F_5C_6)Xe^{II}Cl \rightarrow C_6F_5Cl + Xe^0 \quad (2)$$

$$(F_5C_6)_2Xe^{II} \rightarrow (C_6F_5)_2 + Xe^0 \quad (3)$$

If one considers the limiting ionic Lewis formulas of the native $Xe^{II}$ compounds, in which both ligands are negatively charged, then processes described by eqn (1)–(3) are nothing but 'simple' redox reactions: $Xe^{II}$ is (partially or completely) reduced in a (formally) $2e^-$ process, while two nonmetal–based ligands $L^-$ are oxidized in two $1e^-$ processes, and then they form the L–L bond. Thus stability of nonmetal–Xe bonds is essentially governed by the electron transfer reactions, just as in the case of hydrides,[37] oxides, and many other families of compounds with high oxidation states of chemical elements. In practice, these and similar reactions are most troublesome in the synthesis of new compounds, forcing chemists to carry out their preparations at relatively low temperatures, down to −70 °C; once prepared, the Xe–N, Xe–C and Xe–Cl bonds may be quite stable kinetically and thermally (Table 1).

The occurrence of redox reactions analogous to those of eqn (1)–(3) (and the natural preference of $Xe^{II}$ for only two coordinating Lewis bases) results in an *inherent* instability of Xe bonds to elements that are any less electronegative than those discussed above, such as Si, P, As, S, Se, Br and I. Here, a spontaneous depopulation of the nonmetal's orbital (lone pair) takes place; electrons are transferred for good to $Xe^{II}$. Compounds which contain bonds between the above-mentioned elements and Xe, have never been prepared in large amounts in a chemist's flask (despite numerous attempts...), and their existence is limited to low concentrations of molecules embedded in the noble gas matrices, at very low temperatures. We will describe this exotic chemistry in the present contribution, but first let us show several representative examples of old reaction types for new compounds.

### 2.4 Exploring new chemistry

It turns out that when an additional reducing agent (like metallic mercury or $C_6F_5I$, which are poor reducers, indeed) or an oxidizing one (like $I_2$) are added to selected organoxenon species, electron-transfer reactions proceed even easier at very low temperatures (sometimes vigorously even below −80 °C!) (eqn (4) and (5)), and with nearly quantitative yields:

$$(F_5C_6^-)_2Xe^{II} + I_2 \rightarrow 2\ C_6F_5I + Xe^0 \quad (4)$$

$$(F_5C_6)_2Xe^{II} + Hg^0 \rightarrow (C_6F_5)_2Hg^{II} + Xe^0 \quad (5)$$

$$\begin{gathered}[(F_5C_6^-)Xe^+](BF_4^-) + C_6F_5I \rightarrow \\ [(F_5C_6^-)_2I^+](BF_4^-) + Xe^0\end{gathered} \quad (6)$$

More complex redox reactions (eqn (7)), are also possible:

$$\begin{gathered}[(F_5C_6^-)Xe^+](AsF_6^-) + C_6H_5CF_3 + Me\text{–}C{\equiv}N \rightarrow \\ F_5C_6\text{–}C_6H_4(CF_3) + Xe^0 + (Me\text{–}C{\equiv}NH^+)(AsF_6^-)\end{gathered} \quad (7)$$

The majority of reactions involving Xe–nonmetal compounds exemplify a 'simple' Lewis acid–base chemistry (eqn (8)):

$$\begin{gathered}[(F_5C_6^-)Xe^+](AsF_6^-) + Me\text{–}C{\equiv}N \rightarrow \\ [(F_5C_6^-)Xe^+(N{\equiv}C\text{–}Me)](AsF_6^-)\end{gathered} \quad (8)$$

including metathetic reactions (eqn (9)):

$$\begin{gathered}2\ (F_5C_6^-)Xe^{II}(F^-) + Cd(C_6F_5)_2 \rightarrow \\ 2\ (F_5C_6^-)_2Xe^{II} + CdF_2,\end{gathered} \quad (9)$$

but sometimes they may take much less expected course, like in the following group-transfer and hydrogenation reactions (eqn (10) and (11)):

$$\begin{gathered}[(\text{cyclo-1,4-}C_6F_7)Xe^+](AsF_6^-) + NaF \rightarrow \\ (\text{cyclo-}F_6C_5){=}CF_2 + Xe^0 + NaAsF_6\end{gathered} \tag{10}$$

$$\begin{gathered}[(CF_3C{\equiv}C)Xe^+](BF_4^-) + 3\ HF \rightarrow \\ CF_3CH{=}CHF + XeF_2 + [HBF_4]\end{gathered} \tag{11}$$

New chemistry (and particularly when it's originating from the formation of *new types of chemical bonds*) is always great experience...!

### 2.5 Is white stable? *i.e.* prospect for colourful compounds

All Xe–C and Xe–N compounds synthesized so far are white or (seldomly) slightly yellowish. This indicates that the first allowed electronic transition corresponds to UV or deep violet radiation, and thus requires at least 3 eV. Only $(XeCl^+)(Sb_2F_{11}^-)$ and $[F_5TeN(H)Xe][AsF_6]$[38] break this monotony: they are orange, so should absorb in the blue ($\sim$2.5 to 2.9 eV). Taking into account the products of the thermal decomposition reactions for a variety of Xe–C and Xe–N compounds, and applying chemical intuition to redox reactions, one might anticipate that the lowest energy electronic transition corresponds to the vertical (nonmetal-to-Xe or Lewis base-to-acid) charge–transfer (CT) excitation. Such an electronic transition would thus be a herald of the 'full' redox reaction which takes place if the temperature is raised.

However, analysis of the electronic structure of $Xe^{II}$ derivatives (exemplified here by the quite stable, colourless $XeF_2$, Fig. 4 and Table 3) suggests that situation is more complex. Calculations show three spin-forbidden transitions to the triplet states and two transitions to singlet states (the longer wavelength one is symmetry-forbidden) in the photon energy range from 0 to 6 eV. Thus, $XeF_2$ does not get the chance for colour: the first allowed transition is at 5.64 eV. Nevertheless, the lowest energy transition to $^3\Pi_g$ is at energy as small as 3.56 eV. This indicates that:

- thermal decomposition of $XeF_2$ to Xe and $F_2$ may occur through the bending of an isolated molecule ($\pi_u$ mode), through the coupling between HOMO−1 ($\pi_g$*) and LUMO ($\sigma_u$*);

- the white color of $XeF_2$ is delusive, as the only potentially colour-providing spin- and symmetry-allowed transition is well above the lowest energy excitation (the one which may be activated thermally, leading to decomposition).

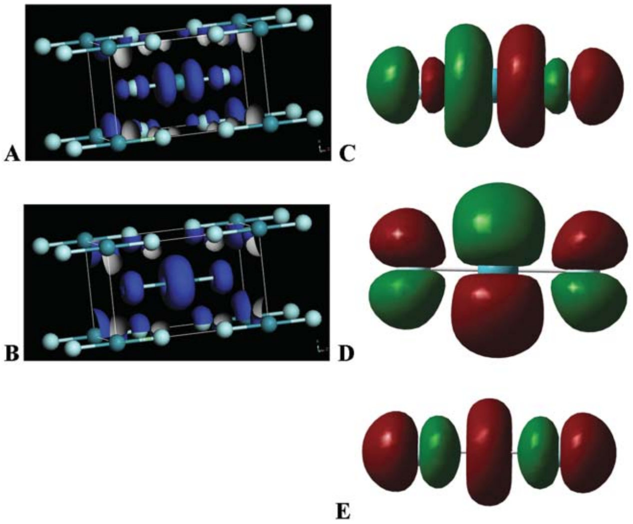


**Fig. 4** Electron density integrated over (A) the first unoccupied, (B) the uppermost occupied, band of solid $XeF_2$ (cell with $Z = 2$), which correspond, respectively, to (C) $\sigma_u$* LUMO and (D) $\pi_u$* HOMO of an isolated $XeF_2$ molecule. Note, HOMO is doubly degenerate, and only one orbital is shown here. (E) $\sigma_g$ HOMO−2 of $XeF_2$ molecule. Note, HOMO−2 is more F- and less Xe-based than LUMO, therefore the allowed HOMO−2 → LUMO ($\sigma_g \rightarrow \sigma_u^*$) electronic excitation has F-to-Xe charge transfer character. DFT calculations for solid and molecular $XeF_2$.

For $Kr^{II}$ compounds, of course, the $F^-$-to-$Kr^{II}$ charge transfer process occurs much more easily than for $Xe^{II}$ (and even in the fluoride environment): yet $KrF_2$ is still colourless.[39] Lack of colour is premonitory here, as it warns of the presence of an 'invisible' singlet → triplet transition at the low energy of 2.9 eV. This excitation testifies to a significant fragility of the thermodynamically unstable $KrF_2$.

Fortunately, the large energies of the *vertical* CT transitions indicate that *barriers* for the Xe–nonmetal bond rupture (in a redox fashion) are not as small as one might think. Indeed, as we have seen from Table 1, some Xe–nonmetal compounds are surprisingly kinetically stable. Hypothetically new bonds of even less electronegative elements to Xe might treat our eye to a palette of colors, but they will be more unstable thermally—and difficult to synthesize. Despite this danger—and as long as events reside in the imaginative minds and skillful hands of an excellent pedigree of synthetic fluorine chemists—compounds containing new Xe–nonmetal bonds, such as Xe–Br, Xe–S, Xe–P, Xe–Si, are just a matter of time.[40]

**Table 3** List of the lowest energy electronic excitations for the isolated $XeF_2$ molecule in its $^1\Sigma_g$ ground state (B3LYP-TD results). The transition energy, *E*, and oscillator strength, *f*, are shown, along with the predominant orbital contribution to the transition. All transitions to triplet states are spin-forbidden (provided that heavy-atom effects are neglected), and many transitions to singlet states are symmetry-forbidden. HOMO and HOMO−1 of $XeF_2$ are $\pi_u$, HOMO−2 is $\sigma_g$, while HOMO−3 and HOMO−4 are $\pi_g$; LUMO is $\sigma_u$.

| *E*/eV | *f*/1 | Excited state | Orbitals contributing | *E*/eV | *f*/1 | Excited state | Orbitals contributing |
|---|---|---|---|---|---|---|---|
| 4.33 | 0 | $^1\Pi_g$ | $\pi_u \rightarrow \sigma_u^*$ | 3.56 | 0 | $^3\Pi_g$ | $\pi_u \rightarrow \sigma_u^*$ |
| 5.64 | 0.006 | $^1\Pi_u$ | $\pi_g \rightarrow \sigma_u^*$ | 3.78 | 0 | $^3\Sigma_u$ | $\sigma_g \rightarrow \sigma_u^*$ |
| 7.28 | 0 | $^1\Pi_g$ | $\pi_u \rightarrow \sigma_u^*$ | 5.00 | 0 | $^3\Pi_u$ | $\pi_g \rightarrow \sigma_u^*$ |
| 7.73 | 0.786 | $^1\Sigma_u$ | $\sigma_g \rightarrow \sigma_u^*$ | 6.40 | 0 | $^3\Pi_g$ | [a] |

[a] Deeper occupier $\pi_u$ orbitals are involved.

## 2.6 Still more new bonds as it gets colder

You want to play even more exotic bond creation games? Then you must first freeze your building blocks well enough. For a low temperature is often a prerequisite for success... This simple indication has been long used by this part of the chemical community, which prefers ultracold noble gas matrices over flasks, and laser photolysis over a smelly synthetic kitchen. Additional advantages of matrix synthesis are that it only seldom leads to many side-products, and that product molecules may be isolated from one another; but even if several different products are simultaneously formed, they may still be identified quite easily by *in-situ* IR spectroscopy supplemented by quantum mechanical calculations. The major disadvantage of matrix synthesis is, however, that it is more difficult to utilize the newly-formed product for subsequent reactions, so a big part of the fun is lost.

Despite this disadvantage, matrix synthesis has several times outdistanced 'bulk synthesis' in the race for new Ng–element bonds.[41] In 1995, in their pioneering work, a Finnish group reported the formation of HXeX (X = Cl, Br, I, H) and of HKrCl.[42] Impressive as these Ng-containing molecules are, they only hinted at what was yet to come. During the next decade several known bonds (Xe–O, Xe–N, Xe–C, Xe–Cl, Kr–F, Kr–O) were achieved in many new small molecules, and a total of nine new bonds were formed, including Xe–H, Xe–Br, Xe–I, Xe–S, Kr–H, Kr–Cl, Kr–C.[43] Even Ar was forced into two new types of connections (Ar–H and Ar–F) in the unique FArH molecule.[44] With this discovery another noble gas has been conquered at the dusk of the old millenium.[45]

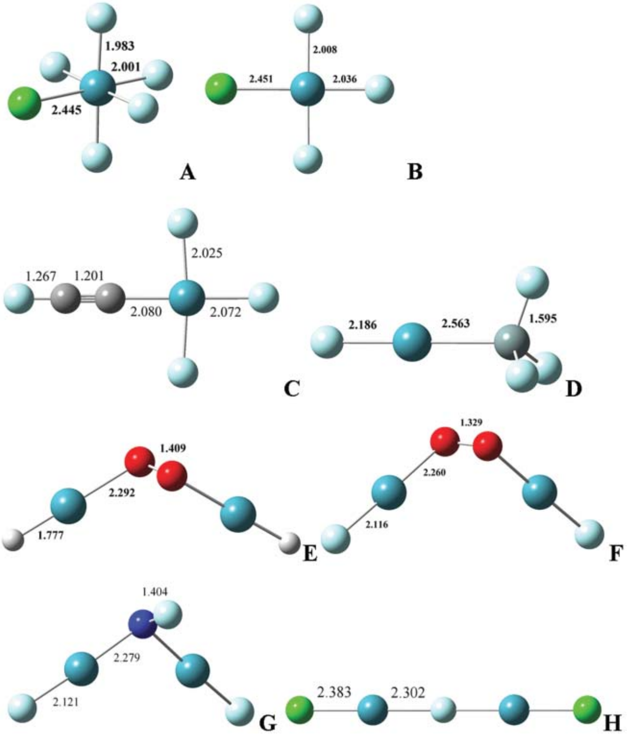


**Fig. 5** The calculated structures of: (A) $Xe^{VI}F_5Cl$ in $C_{4v}$ symmetry; (B) $Xe^{IV}F_3Cl$ in $C_{2v}$ symmetry; (C) $Xe^{IV}F_3(C_2F)$ in $C_{2v}$ symmetry; (D) $FXe^{II}SiF_3$ in $C_{3v}$ symmetry; (E) $HXe^{II}OOXe^{II}H$ in $C_2$ symmetry; (F) $FXe^{II}OOXe^{II}F$ in $C_2$ symmetry; note, the O–O bond is shorter than for $HXe^{II}OOXe^{II}H$; (G) $FXe^{II}(NF)Xe^{II}F$ in $C_s$ symmetry; (H) $ClXe^{II}FXe^{II}Cl^+$ in $D_{\infty h}$ symmetry.[146] Most of these compounds (A–G) are predicted to be unstable thermodynamically with respect to the substrates (eqn (12)–(17), but they are genuine minima on the PES's. Calculated bond lengths are given in Å.

This surfeit of completely new chemical connections has completely overturned our traditional view of Group 18 elements; it might have overwhelmed the public, which has seen people striving for 30 years to develop classical chemistry of Xe and Kr. New bonds also required more detailed understanding; insight into their nature was gained in numerous theoretical studies.[46]

Some of new molecules may be considered as products of insertion of Ng atoms into common single bonds of quite stable molecules; for example, HXeOH[47] may be viewed as a product of Xe's insertion in the O–H bond of water, HXe–C≡CH[48] into the C–H bond of acetylene, HXe–Br into the H–Br bond of hydrogen bromide *etc.* By analogy, $FXeC_6F_5$[49] *might* constitute the product of a smart photochemical reaction between Xe and $C_6F_6$, but as far as we know, a similar reaction has never been attempted.

As the noble gas saga continues, even more unstable bonds (Xe–Se, Xe–Te, Xe–P, Xe–As, Xe–Si,[50] Xe–Ge, Xe–B, Kr–Br, Kr–Si, Kr–S, Ar–Cl *etc.*), if preparable, still await discovery. But, we think that there are still more challenges then just formation of the new bonds. We have here in mind the following specific reactions:

$$Xe^0 + H\text{–}CF_3 \rightarrow H\text{–}Xe^{II}\text{–}CF_3 \tag{12}$$

$$Xe^0 + F_3C\text{–}CF_3 \rightarrow F_3C\text{–}Xe^{II}\text{–}CF_3 \tag{13}$$

$$FXe^{II}F + C_2F_2 \rightarrow Xe^{IV}F_3(C_2F) \tag{14}$$

$$Xe^{IV}F_4 + FCl \rightarrow Xe^{VI}F_5Cl \tag{15}$$

$$FXe^{II}Cl + F_2 \rightarrow Xe^{IV}F_3Cl \tag{16a}$$

$$FXe^{II}F + FCl \rightarrow Xe^{IV}F_3Cl \tag{16b}$$

$$Xe^0 + H_2O_2 \rightarrow H\text{–}Xe^{II}\text{–}OO\text{–}Xe^{II}H \tag{17a}$$

$$Xe^0 + F_2 + {}^1O_2 \rightarrow F\text{–}Xe^{II}\text{–}OO\text{–}Xe^{II}F \tag{17b}$$

The first two reactions would lead to unprecedented alkyl and dialkyl derivatives of $Xe^{II}$. The next one would yield the first alkynyl $Xe^{IV}$ compound (Fig. 5(c)). Eqn (15) and (16) in turn describe formation of the tetravalent and hexavalent Xe embedded in a mixed fluoride/non-fluoride environment (Fig. 5(a),(b)),[51] while eqn (17) proposes the creation of the first binuclear peroxide derivatives of Xe (Fig. 5(e),(f)).[52] Obviously, eqn (12)–(17) might be infinitely modified and extended to derivatives of C, N, S, Cl *etc.* Notably, studies of the thermal stability of the reaction products (on warming of the matrix) would show how realistic is the prospect of obtaining these and related species in larger quantities 'in the flask'.

## 2.7 A Xe atom is just a Lewis base

So far we have discussed compounds of Xe and Kr in their positive oxidation states, predominantly those of divalent Ng elements. In all these connections Ng was bound to nonmetal(s). But could a (formally neutral) atom of a Ng element form a strong chemical bond?

A naked Xe$^0$ atom is isoelectronic to I$^-$, Te$^{2-}$ and Bi$^{3-}$; these anions are well known from a variety of inorganic connections. All have octet electronic structure (5s$^2$5p$^6$) and may formally act as Lewis bases. But there are two important quantitative differences which makes Xe$^0$ qualitatively apart from the other ligands: (i) Xe atom carries no negative charge, so that most of the electrostatic stabilization on interaction with cations is lost, and (ii) its lone pairs are firmly contracted and lie very low in the energy scale (*i.e.* the ionization potential is high), which makes interactions with many cations very weak. So, telluride and iodide anions are very polarizable, easily ionizable and *very soft*, and they may be oxidized easily, while the Xe atom is *harder*, and it gets oxidized only by aggressive F$^{0\bullet}$ (from photochemical splitting of F$_2$).

The first hints that Xe *can*, however, bind to strong Lewis acids (positively charged metal centers) were obtained in 1992, and then in 1994, when XeM(CO)$_5$ (M = Cr, Mo, W) and XeBe$^{II}$O were observed.[53] The case of XeBe$^{II}$O is pretty straightforward: a coordinatively unsaturated Be$^{II}$ cation exposes its empty (sp) hybrid, and it is ready to bind whatever Lewis base you provide.[54] So it will bind a Xe atom, too, and the binding energy is surprisingly high, over 0.3 eV. Many still say it is just an anomalous large dispersive interaction but it is probably fair to describe it as a weak chemical bond.[55]

So matters rested till early 2000 when further confirmation was obtained that Ng atoms may bind firmly to Lewis acids at sufficiently low temperatures. In a series of landmark papers,[56] following their accidental discovery of ArAgCl, researchers from Vancouver showed that in supersonic jets of argon, Ng binds to isolated MX molecules (where M = Cu, Ag and Au, X = F, Cl, Br), and the binding energy was estimated to be as large as 0.25 eV for the Ar···AgF derivative.[57,58] The work started from the most inert element (Ar) of the Ar···Kr···Xe set, and Kr and Xe were conquered in the following steps (2000–2004). To date, most of the molecules in the NgMX series (where M = Cu, Ag and Au, X = F, Cl, and Br, Ng = Ar, Kr, Xe) have been synthesized, and their fundamental properties measured and calculated.[59] The XeAuF molecule, synthesized only recently[60] (recollect: the inherently unstable Au$^I$F wasn't synthesized until as late as 1994[61]), has proved to be most strongly bound of all the complexes, and the Xe–Au$^I$ bond energy was estimated to exceed 1 eV.[62] No doubts may exist any longer on the genuine 'chemical bond' nature of this twin-noble connection.[63]

But this was not the end of miracles, since the year 2000 was an excellent for Ng chemistry, as 1999 was for red wine. In the autumn of 2000—unexpectedly to the entire noble gas and fluorine community—the first isolable compound containing an Xe–metal bond entered the stage. It is black, its solutions in HF are deep red–black, and it has the most weird formula [Au$^{II}$Xe$_4$](Sb$_2$F$_{11}$)$_2$.[64] This species contains two rarities: a genuine divalent gold (which is very susceptible to disproportionation, and elsewhere known in less then ten complex fluorides) and Xe atoms acting as Lewis bases. Not just one but four Xe atoms coordinate the Jahn–Teller Au$^{II}$ d$^9$ center in a more-or-less square-planar fashion (Fig. 6)! This—admittedly accidental—discovery opened the door to further developments. At the moment there are seven compounds of this kind known, and all but one of them contain gold (in the oxidation states I, II or III), the seventh containing mercury instead. These are: *cis*- and *trans*-[Au$^{II}$Xe$_2$](Sb$_2$F$_{11}$)$_2$, [(Au$^{II}$Xe)$_2$F](SbF$_6$)$_3$, [Au$^{III}$FXe$_2$](Sb$_2$F$_{11}$)(SbF$_6$) and [(F$_3$As)Au$^I$Xe](Sb$_2$F$_{11}$).[65] They were synthesized in superacidic conditions (anhydrous HF/SbF$_5$) and they decompose with loss of gaseous Xe either below or only slightly above room temperature. The only compound of Hg has formula [Hg$^{II}$Xe](Sb$_2$F$_{11}$)(SbF$_6$), and it has been achieved *via* a direct solid state/gas reaction in a glass ampoule at 60 °C. In this compound Xe is so weakly bonded to Hg$^{II}$ that when [Hg$^{II}$Xe](Sb$_2$F$_{11}$)(SbF$_6$) is immersed in anhydrous HF (and this 'superacidic' solvent is a poor base, indeed!), HF easily substitutes Xe as a ligand.[66]

Crystal structures reveal the presence of regular Au–Xe bonds with lengths of 2.61 Å (for Au$^I$), 2.65–2.78 Å (for Au$^{II}$) and down to 2.59–2.62 Å (for smaller Au$^{III}$). These values are slightly larger than the one of 2.54 Å seen in the XeAuF molecule in the supersonic jets, but still well below the sum of the van der Waals radius of Xe$^0$ and cationic radius of Au$^I$ (2.95 Å). The single Hg–Xe contact is at 2.77 Å. In all these compounds Xe is attached to Au or Hg as a *terminal* ligand.

The reader will find other examples confirming strong affinity of Xe to Au and Hg in Sections 3.3, 3.6 and 3.10.

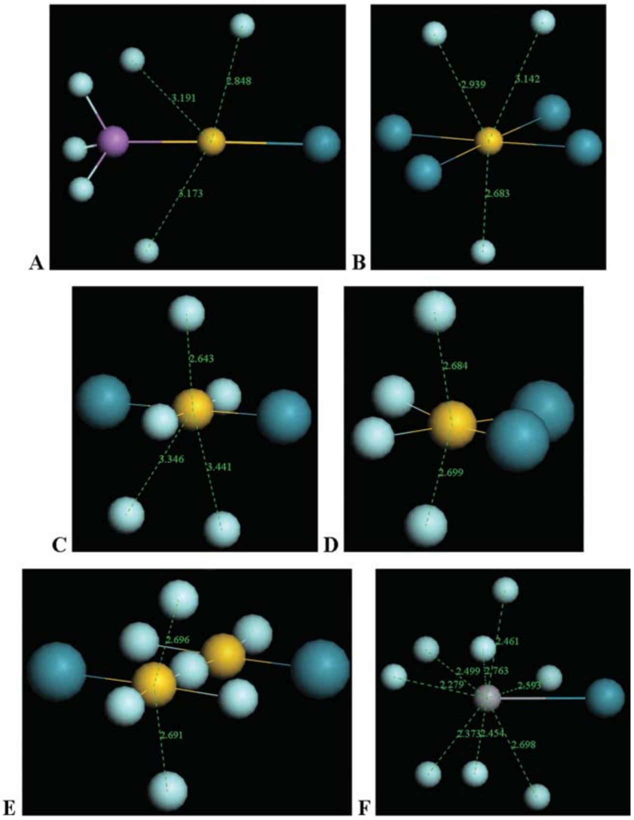


**Fig. 6** The local coordination of Au and of Hg in three different compounds with the Xe ligand: (A) (F$_3$As–Au)(Sb$_2$F$_{11}$); (B) the triclinic form of (AuXe$_4$)(Sb$_2$F$_{11}$)$_2$; (C) *trans*-(AuXe$_2$)(SbF$_6$)$_2$; (D) *cis*-(AuXe$_2$)(Sb$_2$F$_{11}$)$_2$; (E) [(AuXe)$_2$F](SbF$_6$)$_3$; (E) (HgXe)(Sb$_3$F$_{17}$); Selected secondary contacts are shown (values in Å).

### 2.8 Why does Xe bind so strongly to selected cations

Noble gases gave us the ‘octet rule’, and its violations (‘hypervalence’), and it is clear that Seppelt’s compounds do not bend the octet rule (at least if one considers the number of electrons surrounding the Xe atom). Nothing is also weird about $Xe^0$–$Au^+$–$F^-$ and XeAuOH[67] for they are isoelectronic with the known $I^-$–$Hg^{2+}$–$F^-$,[68] $I^-$–$Tl^{3+}$–$O^{-2}$,[69] and with hypothetical $I^-$–$Pb^{3+}$–$N^{-3}$ or $Te^{-2}$–$Tl^{3+}$–$F^-$. In all these compounds the negative charge on $I^-$ or $Te^{2-}$ ligand is reduced by interaction with cations, and similar depopulation happens to Xe in its connections; Xe attains partial positive charge *via* a σ bonding to the empty orbitals of a metal center. What is different here, however, is that a Xe atom can easily turn fully neutral, forget coulombic forces, and escape from the coordination sphere of a metal. All this happens without any *major* rearrangement of the electronic density, *i.e.* formally speaking, no redox reaction occurs. Evolution of Xe is additionally stimulated by the beneficial translational entropy term for gaseous Xe, which is pretty large at 298 K, over 0.5 eV atom$^{-1}$.

So, can one easily calculate the strength of the Xe–metal bond in a quantum mechanical calculation? Is this just a plain acid–base interaction, where a high acidic strength of the cationic center (often inversely proportional to the cation’s size) is crucial for strong interaction? The variety of molecules synthesized so far in matrices (where the Xe–Au$^I$ bond proves to be the strongest, and the Xe–Cu$^I$ one is much weaker), and the difficulties of getting isolable compounds beyond the scarce connections of heavy metals (Au, Hg), tell us that there must be more to it than that.

The sparkling advances in Ng–metal chemistry have stimulated theoretical chemists to examine Xe–metal bonding. And a relatively simple picture has been obtained. Even *prior* to the discovery of $[Au^{II}Xe_4](Sb_2F_{11})_2$ and of XeAuF, Pyykkö *et al.* argued that $Xe^0$ may form very strong bonds to $Au^I$ (in $AuXe^+$, $AuXe_2^+$ and other species), with Au$^I$–Xe bond energies being as large as 0.9–1.3 eV![70] And at least 50% of the binding energy is provided by relativistic effects: contraction of an empty 6s orbital, and the better exposure of a more diffuse 5d valence set.[71] The presence of the relativistic 6s orbital of Au is essential for the appreciable acid–base interaction between Au cations and neutral Xe to take place. Note that the first ionization potentials of $Xe^0$ and of $Au^0$ are not far from each other (12.14 and 9.23 eV, respectively). Provisionally adopting the Koopmans theorem, we might argue that the energies of the half-filled 6s orbital of Au and of the filled 6p orbital of Xe are close to each other. The match must be even better if the empty s orbital belongs to the positively charged (cationic) Au center; recollect, the most stable Au–Xe compounds are seen for divalent gold, Au$^{II}$. Thus, to a reasonable degree of approximation, the Au$^I$–Xe interaction is guided by old good criterion of the sufficient match of energy and of spatial extent of interacting orbitals (provided these are *relativistically* determined orbitals in one’s calculations).

So it seems that in the rich world of chemical misalliances similarities continue to attract: hard $Xe^{2+}$ still prefers hard $F^-$, soft $Xe^0$ adores softer $Au^{2+}$, while noble sticks to noble… And we sense that we will soon see more ‘cold’ Ng-containing molecules, like ones similar to NgAuF (for example NgM$^{II}$O or NgM$^{II}$O$_2$, where M = Hg, Pd, Pt (Fig. 7); $NgMF_3$, NgMN or $NgMO^+$, where M = Tl, Rh, Ir, Au, Ac), $NgMOF_2$, $Ng_2MO_2$ and $NgMO(O_2^{2-})$ (M = Pb, Hf, Th), $NgMF_5$ and $NgMO_2F$ (M = Bi, Ta, Pa), $NgMO_3$ (M = Te, W, U), $NgMO_3^+$ (M = I, Re, Pu), pretty exotic ones as Xe–Au$^I$–($O_2^{2-}$)–Au$^I$–Xe (Fig. 7), and more. A range of new compounds ‘in the flask’ will also be obtained, the number of cations expanded, and maybe even an isolable coordination compound of Kr ligand will be synthesized by solvent-free techniques—despite all difficulties which await experimental chemists on the way.

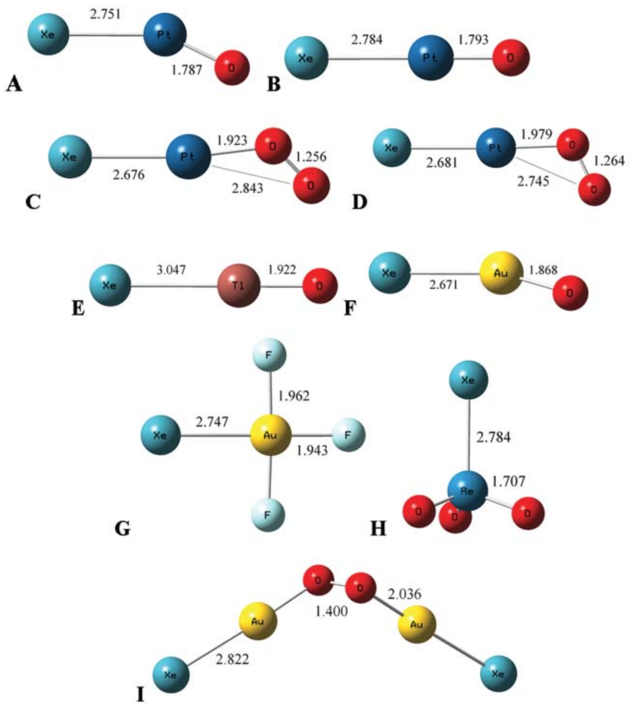


**Fig. 7** The calculated molecular structures of novel hypothetical species: (A) $^1$XePt$^{II}$O in $C_s$ symmetry; the metal–Xe stretching mode, $\nu$, is at 113 cm$^{-1}$; (B) $^3$XePt$^{II}$O ($C_{\infty v}$), $\nu$ = 105 cm$^{-1}$; (C) $^1$XePt$^{II}$O$_2$, $\nu$ = 124 cm$^{-1}$; (D) $^3$XePt$^{II}$O$_2$, $\nu$ = 123 cm$^{-1}$; (E) XeTl$^{III}$O$^+$ ($C_{\infty v}$), $\nu$ = 92 cm$^{-1}$; (F) XeAu$^{III}$O$^+$ ($C_{\infty v}$), $\nu$ = 147 cm$^{-1}$; (G) XeAu$^{III}$F$_3$ ($C_{2v}$), $\nu$ = 120 cm$^{-1}$; (H) XeRe$^{VII}$O$_3^+$ ($C_{3v}$), $\nu$ = 136 cm$^{-1}$; (I) XeAu$^I$($O_2^{2-}$)Au$^I$Xe ($C_2$), $\nu$ = 87 and 90 cm$^{-1}$.[147] Calculated bond lengths in Å are shown. All these compounds are bound (*i.e.* local minima) in the DFT/relativistic pseudopotential calculations, but most likely the M–Xe interaction is slightly underestimated. Correct assessment of their thermodynamic and kinetic stability requires use of more advanced methods explicitly including electronic correlation and relativistic effects.

### 2.9 XeF$_2$ as a ligand to naked metal cations

Any lone pair is good for interaction with an empty orbital, the problem is just how strong the interaction may be. A nearly naked $F^-$ ion, though itself a rarity (as in $NMe_4F$), is a pretty strong base. When $F^-$ anion is coordinated to a powerful Lewis acid, say to $BF_3$ in $BF_4^-$, its potential for the secondary acid–base interactions is of course diminished ($BF_4^-$ is considered a ‘weakly coordinating anion’). But when fluoride anions are firmly bound to the enormously electron-deficient

$Xe^{II}$ in a neutral $XeF_2$ molecule, this secondary basicity is even more drastically reduced: the fluoride lone pairs become very contracted and lie deep down in the energy scale. Their basicity is then weak, and an appropriate strong Lewis acid is needed for a substantial interaction.[72]

The coincidental formation of $Ag(XeF_2)_2(AsF_6)$[73] first achieved in 1991 (in the course of systematic attempts to oxidize Xe with $Ag^{II}$), has corroborated this general idea. The cationic $Ag^I$ center is nearly 'naked' in $Ag(AsF_6)$, as $AsF_5$ is a potent superacid—this makes the $Ag^I$ cation here far and away a stronger acid than in $Ag^IF$. $Ag(XeF_2)_2(AsF_6)$ is a colourless solid, where the $Ag^I$ center is eight-fold coordinated by F atoms: four of these (at 2.466 Å) come from $XeF_2$, four others (at 2.732 Å) from $AsF_6^-$ (Fig. 8).[74] The $Ag^I\cdots FXeF$ interaction cannot be very strong, as (i) the Xe–F bond lengths (1.979 Å) resemble those found in the $XeF_2$ crystal (2.00 Å),[75] and (ii) crystals decompose in vacuum at a room temperature, losing $XeF_2$. Thus, $Ag(XeF_2)_2(AsF_6)$ might well be called an 'adduct' by some.[76]

$Ag(XeF_2)_2(AsF_6)$ has been harbinger of a whole family of salts, including homologic $Ag(XeF_2)_2(PF_6)$, made over a decade later; it can be prepared in anhydrous HF directly from its components:[77]

$$AgPF_6 + 2\ XeF_2 \rightarrow Ag(XeF_2)_2(PF_6). \qquad (18)$$

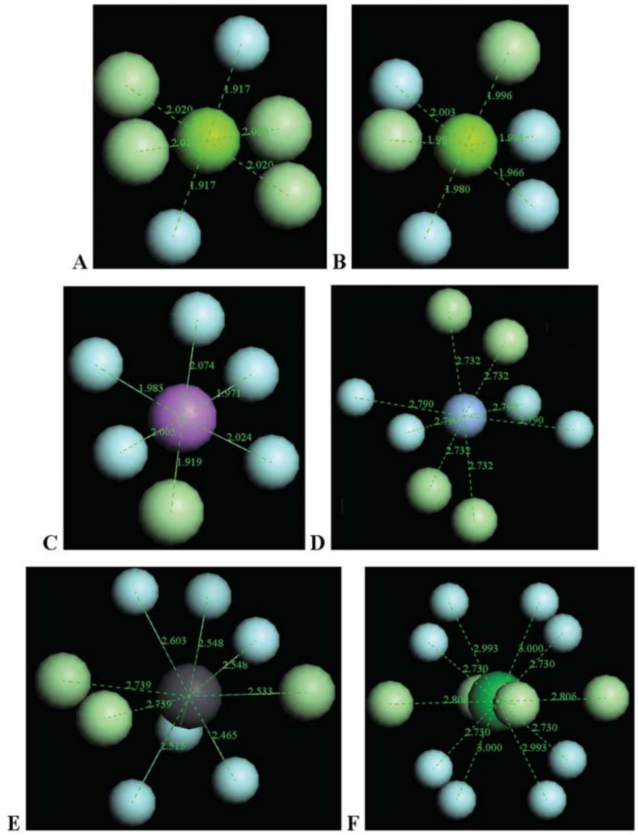


**Fig. 8** The local coordination of metal centers in six different compounds with the $XeF_2$ ligand: (A) $Mg(XeF_2)_2(AsF_6)_2$; (B) $Mg(XeF_2)_4(AsF_6)_2$; (C) $Li(XeF_2)_3(AsF_6)$; (D) $Ag(XeF_2)_2(AsF_6)$; (E) $Pb(XeF_2)_3(AsF_6)_2$; (F) $Ba(XeF_2)_5(SbF_6)_2$. F atoms coming from $MF_6^-$ counterion are light green, those coming from $XeF_2$ are in light blue.

Here, $XeF_2$ ligand coordinates $Ag^I$ in a similar fashion as in $Ag(XeF_2)_2(AsF_6)$, but now Xe is forced into more asymmetric hypervalent bonding (Xe–F bond lengths are 1.983 and 2.040 Å). As the $Ag\cdots FPF_5^-$ distance is now 2.859 Å, F atoms of $XeF_2$'s may coordinate $Ag^I$ even more strongly than for the fluoroarsenate salt, with four $Ag\cdots FXeF$ contacts at 2.405 Å. This compound is more stable thermally, and it may be melted at 144 °C without a preceding loss of $XeF_2$! Interestingly, synthesis has failed of analogous $MF_6^-$ derivatives where M = Sb, Nb and Ta, proving that balance of the ligands' basicities is subtle.

In 1991, Bartlett's $Ag(XeF_2)_2(AsF_6)$ set the stage, but for the next nine years it seemed like it would be a lone stranger. This prompted Žemva and co-workers to systematically investigate connections between $XeF_2$ and various salts of Group 2, Group 12, lanthanide elements and Group 1 (2000–2006).[78] Soon it turned out that number of $XeF_2$ molecules entering the adduct's formula may be as large as 3 (for example in $M(XeF_2)_3(AsF_6)_2$, where M = Pb, Sr, in $Ln(XeF_2)_3(AsF_6)_3$, where Ln = La, Nd, Sm, Eu, Gd, Dy, Ho, in $Ln(XeF_2)_3(BiF_6)_3$, where Ln = La, Nd), 3 (for example in $Ba(XeF_2)_4(AsF_6)_2{\cdot}XeF_2$),[79] 4.5 (in $Ca_2(XeF_2)_9(AsF_6)_4$) or even 5 (in $Cd(XeF_2)_5(SbF_6)_2$).[80] For some of these compounds the thermal stability exceeds that noted for the parent $Ag(XeF_2)_2(AsF_6)$. These and related compounds (Table 4) are yet another testimony to the true 'renaissance in Ng chemistry' occurring right now.[81]

As mentioned above, an unusual thing about these compounds is that number of ligands per metal cation is quite large (recollect, both $XeF_2$ and $MF_6^-$ may still act as bridging ligands to more then one metal center!). The total number of ligands may be as large as 3 per $Ag^I$, $Li^I$ or $Cd^{II}$ cation, 4 per $Mg^{II}$, 4½ per $Ca^{II}$, 5 per $Pb^{II}$ and $Sr^{II}$, 5½ or 6 per $Ln^{III}$, 6 per $Mg^{II}$, 6½ per $Ca^{II}$, and 7 per $Cd^{II}$! In some cases this leads to rare coordination numbers for a given metal cation: 8 for $Ag^I$, 9 for $Ca^{II}$ or for the small $Ho^{3+}$ cation, 12 for $Ba^{II}$. These CN's are larger than those typically seen in pure binary fluorides (6 for $Ag^I$, 8 for $Ca^{II}$, $Ho^{3+}$ and $Ba^{II}$).

The metal–ligand polyhedra (resulting from coordination of $XeF_2$ and $MF_6^-$ ligands to metal centers) only exceptionally are isolated from one another (like for $Mg(XeF_2)_4(AsF_6)_2$). Typically they interconnect into larger ensembles, using as linkers either $XeF_2$ alone ($Ca(XeF_2)_4(AsF_6)_2$), or $MF_6^-$ alone ($Mg(XeF_2)_2(AsF_6)_2$), or simultaneously both $XeF_2$ and $MF_6^-$ ligands ($Pb(XeF_2)_3(AsF_6)_2$). The (formal) dimensionality of the network may be 1D (chains, for $Cd(XeF_2)_4(AsF_6)_2$ or

**Table 4** List of compounds with $XeF_2$ as a ligand, for which the crystal structure has been determined. The coordination number (CN) of central metal cation is listed

| Compound | CN | Compound | CN |
|---|---|---|---|
| $Mg(XeF_2)_2(AsF_6)_2$ | 6 | $Mg(XeF_2)_4(AsF_6)_2$ | 6 |
| $Li(XeF_2)_3(AsF_6)$ | 6 | $Cd_2(XeF_2)_{10}(SbF_6)_4$ | 7, 8 |
| $Ag(XeF_2)_2(PF_6)$ | 8 | $Ag(XeF_2)_2(AsF_6)$ | 8 |
| $Cd(XeF_2)_4(AsF_6)_2$ | 8 | $Ca(XeF_2)_4(AsF_6)_2$ | 8 |
| $Cd(XeF_2)_1(BF_4)_2$ | 8 | $Nd(XeF_2)_{2.5}(AsF_6)_3$ | 9 |
| $Sr(XeF_2)_3(AsF_6)_2$ | 9 | $Pb(XeF_2)_3(AsF_6)_2$ | 9 |
| $Ca(XeF_2)_{2.5}(AsF_6)_2$ | 9 | $Ca_2(XeF_2)_9(AsF_6)_4$ | 8, 9 |
| $Ln(XeF_2)_3(BiF_6)_3$ (Ln = La, Nd) | 9 ? | $Ba(XeF_2)_4(AsF_6)_2{\cdot}XeF_2$ | 12 |

double-chains, for $Nd(XeF_2)_{2.5}(AsF_6)_3$), 2D (for $Ca(XeF_2)_4(AsF_6)_2$) or 3D (for $Ba(XeF_2)_4(AsF_6)_2 \cdot XeF_2$). A great variety of structures is delivered by these seemingly uninteresting and usually colourless compounds.

$XeF_2$ is not the only Ng fluoride which forms adducts with metal fluorides. There is experimental evidence that $KrF_2$ may also serve as a ligand in various fluoroarsenate connections. Also, very recently, the very first adduct with $XeF_4$ (a very poor Lewis base), $Mg(XeF_4)(AsF_6)_2$, has been isolated.[80] $XeF_6$, however, has problems in forming similar adducts, due to its significant Lewis basicity. Specifically, $XeF_6$ most frequently detaches a fluoride anion and forms $XeF_5^+$ or $Xe_2F_{11}^+$ salts. Use of large cations, such as $Cs^+$, $Rb^+$ or $Tl^+$ (provided no $Tl^{3+}$ forms) might help to solve this problem, but it has never been tested.[82]

### 2.10 Brief stop for a summary: preferences of Xe for the chemical bond formation

The preferences of Xe for chemical bond formation are summarized using the Grand Periodic Table of Chemical Elements (Fig. 9(A)). Other known connections of Xe (not described here in detail), such as $Xe_2^+$,[83] $(OUC)Xe_4$,[84] $FXeBF_2$,[85] $OScXe_5^+$,[86] PtNg, $PtNg_2$ and $PdNg_2$,[87] XeM(CO) (M = Ni, Co), and $XeM(N_2)$ (M = Ni),[88] NgMO (M = Cr···Ni, Ng = Ar···Xe),[89] organometallic complexes of Re and Xe,[90] and $XeTi_2$,[91] have also been considered in this figure. Affinity of $XeF_2$ to act as a ligand towards 'naked' metal cations has been summarized in Fig. 9(B). $(Cr^{IV}F_4)(XeF_2)$—known since 1992[92]—and $(Cr^{IV}F_4)_2(XeF_2)$[93] have also been taken into account.

For compounds of $Xe^{II}$ the importance of the classical 'diagonal line' within the p-block of the Periodic Table, is prevalent in Fig. 9(A). Any nonmetallic element which has its first ionization potential smaller than that of Xe (1070 kJ $mol^{-1}$, like I, S, P, Si, B *etc.*) meets problems when forming bonds to $Xe^{II}$; such compounds are unstable at ambient temperature conditions due to the ease of redox reactions, but often achievable in matrices. For connections of $Xe^0$ with metals, importance of the relativistic stabilization is evident (Fig. 9(A)).

Fig. 10 gives a timeline for the synthesis of compounds containing new Ng–element bonds.

The list of people primarily responsible for these fascinating developments is very long. Taking the risk of omitting someone, we would like to specifically mention the laboratories of Hermann J. Frohn (Duisburg-Essen, Germany), Dieter Naumann (Cologne, Germany), Gary J. Schrobilgen (McMaster, Canada), Konrad Seppelt (Berlin, Germany),

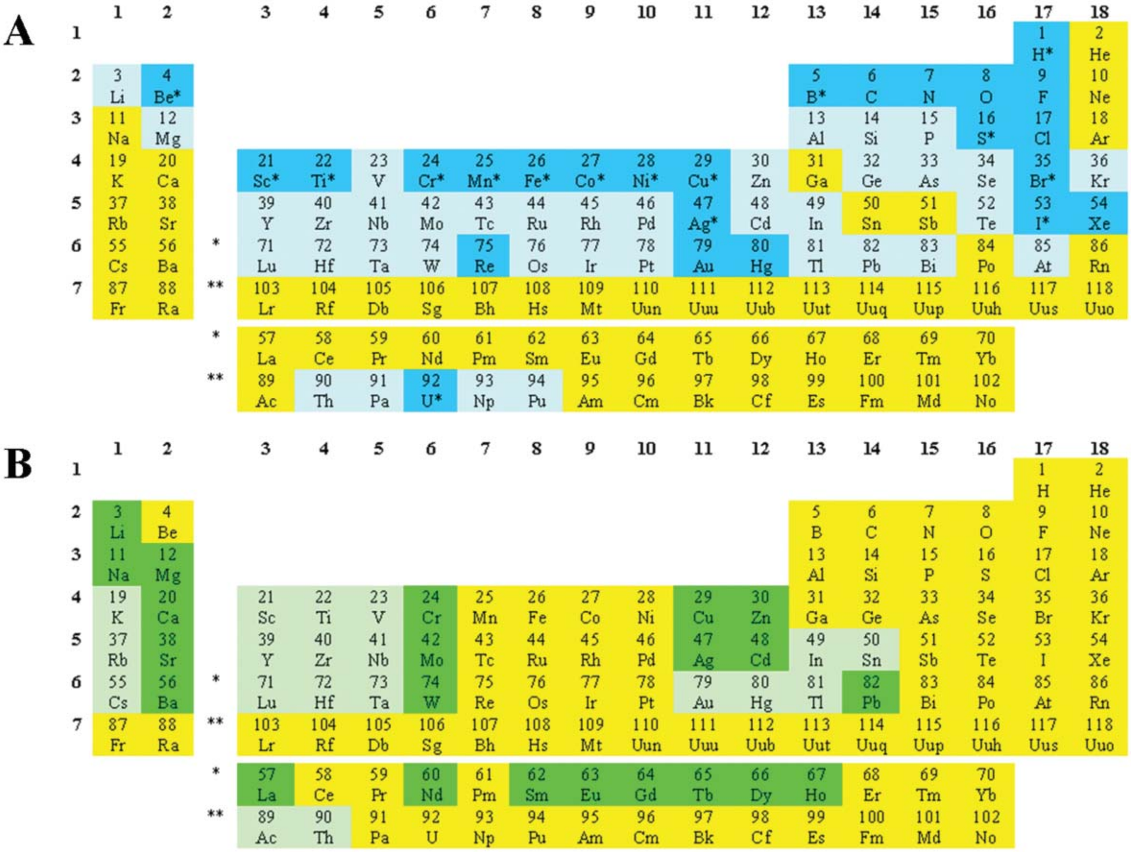


**Fig. 9** (A) Preferences of Xe for chemical bond formation are shown in blue; element–Xe bonds detected only at low temperatures in the noble gas matrices or in supersonic jets, are marked with an asterisk at the element symbol. Light blue areas indicate regions were the Xe–element bonding could possibly be extended in the near future. (B) In green are shown elements whose 'naked' cations show affinity to the $XeF_2$ ligand. Light green fields marks elements where the $XeF_2$–element interactions could possibly be detected in the coming years.

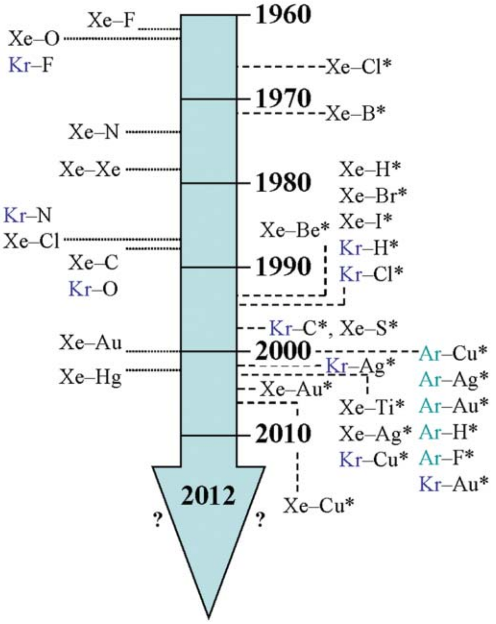


**Fig. 10** The year of discovery of every new Ng–element bond (Ng = Xe, Kr, Ar) is shown along a time arrow; bonds detected only at low temperatures in noble gas matrices or in the supersonic Ng jets are marked with an asterisk. In 2012 the semicentential will be celebrated for the discovery of the very first Ng compound.

Michael C. L. Gerry (Vancouver, Canada), Markku Räsänen (Helsinki, Finland) and Lester Andrews (Virginia, USA) (Fig. 11). Particular credit should also be given to Boris Žemva (Slovenia, Ljubljana), who has greatly advanced chemistry of $XeF_2$ as a ligand to naked metal cations in anhydrous HF, also studied by Neil Bartlett (Berkeley, USA), and John H. Holloway (Leicester, UK).[94] We pay special tribute to two theoreticians: Pekka Pyykkö (Helsinki, Findland), who predicted the existence of the strongly bound Au–Xe species, and to Benny J. Gerber (Irvine, US) who pointed out the stability of HArF, *before* these species were actually synthesized in the laboratories. Many young researchers, MSc students, PhD students and postdocs, have advanced this research field, working under guidance of their older colleagues.

Chemistry might have had its highs and lows during the last 200 years, but it seems that a relatively young noble gas chemistry has got only the highs. Much, so much has happened in the Ng chemistry during the last five decades; what else still awaits us around the corner…?

## 3 The bonds to come

### 3.1 Going in new directions: prediction of novel species

The advent of the ‘new chemistry’ of Ng’s has inspired many to search for even more unusual interatomic connections. Of course, this is easiest done *in silico*, as monetary costs are then relatively low, risk of explosion of inherently unstable molecules is eliminated,[95] and technical obstacles to unleashing one’s imagination virtually disappear. But there are also several interesting experimental reports on new species.

**Fig. 11** Leaders of the laboratories predominantly responsible for the emerging Ng chemistry. (A) Hermann J. Frohn; (B) Dieter Naumann; (C) Gary J. Schrobilgen; (D) Konrad Seppelt; (E) Michael C. L. Gerry; (F) Markku Räsänen; (G) Boris Žemva; (H) Neil Bartlett; (I) Lester Andrews; (J) John H. Holloway; (K) Pekka Pyykkö; (L) Benny J. Gerber.

Theoretical and experimental research now goes in the following exciting directions:

(i) ability of the lightest Ng’s (He, Ne) for kinetically stable bonding has been estimated, and the results are encouraging; aside from the predicted $OBHe^+$, $SBHe^+$ and $Al^{3+}\cdots He$ cations,[96,54*b*] a range of neutral species like HHeF,[97] SBeHe,[54*b*] XN = BeNg where X = F, OH, Ng = He···Ar,[98] and $(H_3B)OBeHe$[99] have been hypothesized; none of these species, except for He-solvated $Al^{3+}$, has been observed so far in experiment;

(ii) triple bonds between Ar and N (in $NgN^{3+}$) and between heavier Ng’s (Ar, Kr, Xe, Rn) and N (in $O_3NgN^{3+}$), have been theorized;[100]

(iii) obvious extensions of the chemistry of Ar and Kr have been analyzed, as exemplified by HArCl,[46*e*] $FNgSiF_3$ where Ng = Ar, Kr,[50*d,e*] and many more;

(iv) properties of linear $Xe^{II}{}_2H_3{}^+$ (analogous to the well known fluoride derivative, which is bent on central F),[101] $XeH_2$,[102] and of many organoxenon derivatives[103] have been calculated;

(v) Xe–$C_n$ where $n = 2, 3, 5, 7, 9$,[104,105] have been discovered, and the issue of stability of a hypothetical 1D polymer (–Xe–$C_2$–),[106] was immediately addressed;[107]

(vi) using the isoelectronic analogy between $C_2$ and BN, as the yet unknown and quite strongly bound species Xe–BN, Xe–NB, HXeNBH and HXeBNH[108] have been considered;

(vii) the suggestion that Xe might form an alloy with Fe or Pt has not been supported by theoretical calculations and experiments up to 150 GPa;[109] also, the ability of Xe to substitute Si in high-pressure modifications of quartz has been tested experimentally;[110]

(viii) significant involvement of Xe's empty d orbitals in bonding at high pressures has been postulated;[111] this might open new avenues for Xe's interaction with selected transition metals under megabar pressures.

We are by no means less courageous than other researchers, and we would like to propose here a selection of novel molecular and extended compounds of Xe. Several such attempts, based on a blend of chemically reasonable Lewis structures, chemical intuition and DFT calculations, will be discussed in the forthcoming sections.

### 3.2 Perchlorates, permanganates, nitrates

We begin our exploration with as yet unsynthesized connections of $Xe^{II}$, namely its nitrate, perchlorate and permanganate salts.

In Fig. 12 we show the DFT–optimized structures of $Xe^{II}(NO_3)_2$ ($C_2$), $Xe^{II}(ClO_4)_2$ ($C_1$) and $Xe^{II}(MnO_4)_2$ ($C_2$). All three molecules are local minima on the potential energy surfaces, as indicated by the absence of imaginary vibrational modes.[112] The $Xe^{II}$–O separation is in the 2.21–2.29 Å range, which may be compared with the value calculated for $HXe^{II}OH$ (2.238 Å).

The $Xe^{II}L_2$ compounds where $L = NO_3^-$, $ClO_4^-$, $MnO_4^-$, are 'classical' in the sense that Xe is bound to O atom, in a similar fashion as it does in $HXe^{II}OH$. Other hypothetical compositions of this type include $FXe^{II}L$ where $L = NO_3^-$, $VO_3^-$, $PaO_3^-$, $ClO_4^-$, $BrO_4^-$, $MnO_4^-$, *etc.* These molecules are simply salts of the $XeF^+$ cation with the anions of strong acids, similar to the known $FXeOSO_2F$. Supposedly, the complexity of these molecules excludes their facile formation in the noble gas matrixes; it remains an open question if these molecules could form in condensed phases, and form at low temperatures *via* methathetic ligand-exchange reactions utilizing the known compounds of $Xe^{II}$.

### 3.3 What about peroxides?

The peroxide dianion ($O_2^{2-}$), a derivative of hydrogen peroxide $H_2O_2$, is frequently found in chemical compounds. $O_2^{2-}$ may be considered as an oxidized form of oxide (2 $O_2^-$) or as a reduced form of oxygen ($O_2$). Indeed, stability of peroxide connections of various metals may be limited by two[113] processes, as outlined in eqn (19) for a peroxide of a divalent metal, $M^{II}$:

$$M^{II} + O_2^{2-} \rightarrow M^{IV}(O^{2-})_2, \qquad (19a)$$

$$M^{II} + O_2^{2-} \rightarrow M^0 + O_2\uparrow. \qquad (19b)$$

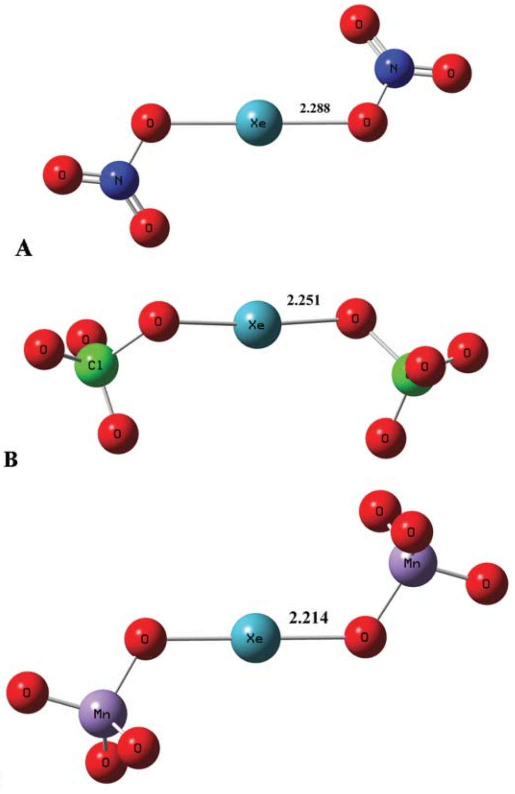


**Fig. 12** The DFT–optimized structures of: (A) $Xe^{II}(NO_3)_2$, with the softest torsional vibration at 7 $cm^{-1}$, (B) $Xe^{II}(ClO_4)_2$, 20 $cm^{-1}$ and (C) $Xe^{II}(MnO_4)_2$, 13 $cm^{-1}$.

If M = Ba, the tetravalent core $Ba^{IV}$ state is of course unaccessible, and the stability of $BaO_2$ is limited only be evolution of gaseous $O_2$ (eqn (19b)). But if M = Pb, intermolecular charge transfer readily occurs for a hypothetical $Pb^{II}(O_2)$ thus leading to well known $Pb^{IV}O_2$ (eqn (19a)). For other metals, one or both processes may be operative.

Due to its valence structure (in particular due to the unfavourable spatial arrangement of two lone pairs on adjacent O atoms), the peroxide anion often meets difficulties in serving as a bidentate ligand at *one* cationic center; more frequently O's are unequally engaged in bonding (in molecular species), or each of them coordinates only one metal center in a polymeric extended structure (*i.e.* each $O_2^{2-}$ is bridging two metal centers). Because of that, and of the more positive oxidation state of O for $O_2^{2-}$ than for $O^{2-}$, the basicity of the lone pair of O atom in $O_2^{2-}$ is smaller than that of $O^{2-}$. Therefore, metal centers coordinated by $O_2^{2-}$ (for example $Be^{II}$) should be much more exposed to auxiliary ligands than for analogous oxide species, and the former should form shorter and stronger bonding to $Xe^0$ than the latter. Unfortunately, to the best of our knowledge, no connections of Ng's containing peroxide anion have been observed so far.[114]

The potential of peroxide dianion for serving as a counterion in molecular complexes of Xe is illustrated in Fig. 13. Here, we have explored a series of neutral XeBeL complexes, where $L = CH_2^{2-}$, $NH^{2-}$, $O^{2-}$, and $O_2^{2-}$. Note that the Xe–$Be^{II}$ separation slightly decreases as the basicity of the counterligand decreases in the order: $H_2C^{2-} > HN^{2-} \sim O^{2-} > O_2^{2-}$.

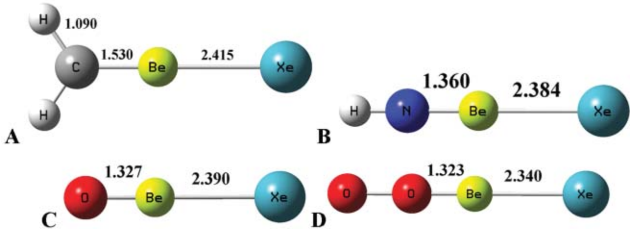


**Fig. 13** The potential of the peroxide ion for stabilizing various connections of Xe with metal cations is illustrated, as exemplified by four $Be^{II}$ species: (A) $(H_2C^{2-})Be\cdots Xe$, the force constant for the Be–Xe stretching mode, *f*, is 0.194 [mDyn $Å^{-1}$]; (B) $(HN^{2-})Be\cdots Xe$, $f = 0.307$; (C) $(O^{2-})Be\cdots Xe$, $f = 0.460$; (D) $(O_2^{2-})Be\cdots Xe$, $f = 0.456$.

A similar trend is seen when comparing oxide and peroxide connections of $Pt^{II}$ (Fig. 6(A)–(D)) and for other model systems (not shown). $O_2^{2-}$ might possibly link two $XeAu^I$ units (as in Fig. 6(I)), and hopefully even bridge two $XeF^+$ or $XeH^+$ cations (Fig. 7(E) and (F)).

Although $O_2^{2-}$ is more basic than two $F^-$ counteranions, we think that chemistry of isolable solids containing Xe connected to transition metal cations (so far limited to fluoride-only environment) might be extended, with some effort, also to molecular peroxides with coordinatively unsaturated metal centers.

### 3.4 Unusual topological isomers

A chemist asked to assign oxidation states in a XeAuF molecule is likely to formulate it as: $Xe^0 \rightarrow Au^I–F^{-1}$. But imagine another valence isomer, $Au^{-1}\rightarrow Xe^{II}\leftarrow F^{-1}$: here gold would formally serve as a monovalent *auride anion* (pseudo-halide isostructural to $I^-$!)—as found for the $Cs^+Au^-$ *semiconductor*. This idea may seem crazy at first; some might suppose that $Au^{-1}–Xe^{II}–F^{-1}$ should not survive even as an isolated 'cold' molecule, as it contains very strong oxidant ($Xe^{II}$) linked to very strong reducing agent ($Au^{-1}$). In other words, that $Au^{-1}–Xe^{II}–F^{-1}$ might too easily undergo an intramolecular redox reaction with the liberation of $Xe^IF$ and $Au^0$, by analogy to $I^{-1}–Xe^{II}–H^{-1}$ (for IXeH the ionic/neutral curve crossing happens at very short Xe···I distance, and excitation of several vibrational modes suffices to dissociate this molecule). However, the chemistry of Au is often surprising, and often more similar to that of H than that of I.[115] This auride/hydride analogy gives more hope for existence of $Au^{-1}–Xe^{II}–F^{-1}$.

Indeed, our DFT calculations (Fig. 14(D)) allowed for the detection of a linear AuXeF as a genuine minimum on the potential energy surface for this triatomic system. Remarkably, the computed Au–Xe bond length is slightly shorter (by ~0.02 Å) than one predicted for the 'common' XeAuF isomer. A qualitatively similar result is obtained in MP2/SDD calculations for these species; here the bond length difference exceeds 0.03 Å. This result is interesting, but it requires confirmation in fully relativistic calculations. Fortunately, such calculations have actually been done, and they are described below.[116]

As predicted by Benkova and Sadlej,[117] linear $Au^{-1}–Xe^{II}–F^{-1}$ is a local minimum, indeed. The equilibrium geometry reveals the surprisingly short Au–Xe bond length of 2.556 Å and the Xe–F bond length of 2.136 Å. The Au–Xe separation is again slightly shorter than that calculated by these authors for the XeAuF isomer (2.564 Å). As the predicted Ng–Au bond length (for NgAuF, Ng = Ar, Kr) is consistently shorter (by ∼0.007 Å) than the actual experimental values, one may suppose that the AuXeF isomer will indeed deliver the shortest Au–Xe bond ever observed.

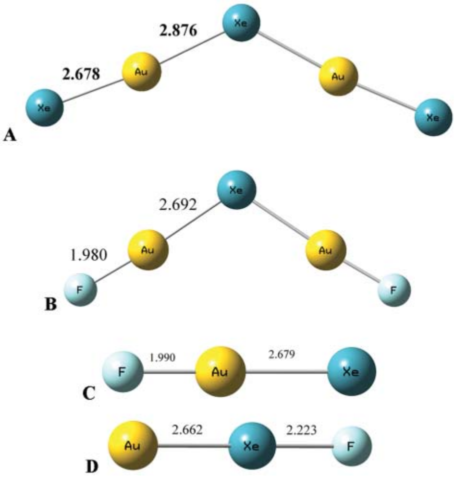


**Fig. 14** Illustration of the relative weakness of the bonds formed by a bridging Xe ligand in two hypothetical species with the $Au^I\cdots Xe^0\cdots Au^I$ moiety: (A) $[XeAu^I\cdots Xe^0\cdots Au^IXe]^{2+}$; (B) $FAu^I\cdots Xe^0\cdots Au^IF$, as compared to (C) the classical $FAu^I\cdots Xe^0$ with one terminal Xe ligand. Note, the $Xe_{bridge}\cdots Au$ contact is 2.88 Å for (A), as compared to 2.68 Å for the terminal Au–Xe bond. (A) and (B) are also interesting in context of possible weak aurophilic interactions. (D) The AuXeF isomer—see section 3.4; note, the Au–Xe bond length is slightly shorter for (D) than for (C).

Benkova and Sadlej also predict that AuXeF will be thermodynamically stable towards decomposition to Au, Xe and F radical (by +1.15 eV at the MP2 level) but unstable with respect to AuF and Xe (by −1.67 eV). Anyway, it should exhibit significant kinetic stability, as the calculated harmonic frequencies for the Xe–Au stretching and for the molecule's bending are ∼30% larger then their counterparts calculated for the XeAuF isomer.

The remarkable stability of the isolated AuXeF molecule will certainly be violated when other similar molecules are in its vicinity, thus opening new intermolecular channels for decomposition (dimerization *via* electric dipole/dipole interactions *etc.*). But it might be dramatically enhanced again if external pressure is applied, thus preventing such decomposition. This will be discussed again in section 3.10.

### 3.5 $Xe^0$ as a *bridging* ligand between two metal centers

In all known compounds of $Xe^0$ with transition metals, be these molecules or extended solids, the Xe is attached to a metal cation as a *terminal ligand*. So far Xe has never been seen to bridge two metal centers, and there are sound reasons for it: the M···ligand···M bridging bonds are always longer, less covalent and weaker than M···ligand terminal bonds; they are simply more fragile, and less likely to appear even in Xe-poor systems. All bridging bonds behave this way. The other obstacle, usually not experienced by typical negatively charged ligands, is that zerovalent Xe shares some electron density with neighbouring cations, and itself becomes *positively* charged. Thus, the $M^{\delta+}\cdots Xe^{\sigma+}\cdots M^{\delta+}$ configuration is not favoured from a purely electrostatics point of view.

Thus, even some ligand-hungry systems, like polymeric $MF_5$ (M = Bi, Sb, Nb, Ta, U, Ru *etc.*) and other oxofluoride derivatives with five ligands to a metal cation, like $UOF_4$, $ReO_2F_3$ *etc.*, might form adducts with neutral Xe to create the hexacoordinated metal centers with Xe as a *terminal* ligand. An analogous situation is likely to persist for other strong Lewis acids like $AuF_3$: a hypothetical $Au^{III}F_3Xe$ will form isolated $AuF_4^-$-like units (if the redox reaction leading to $Xe^{II}$ and $Au^{I}$ does not intrude) without the Au···Xe···Au bridges. The same type of reaction product will presumably appear for Xe attached at very low temperatures to $IF_3$, or to $BF_3$.

Could, despite these problems, new molecular or extended compounds be crafted which contain M···Xe···M bridges? Simplistic calculations show that careful approach to the Xe-poor systems might help to bring Xe bridges to life in the matrices[118] or in molecular jets, as exemplified by $FAu^{I}\cdots Xe\cdots Au^{I}F$ (Fig. 14(B)), but there is still the risk of isomerization to [FAu···FAu···Xe]. The Xe–rich systems, like $[XeAu^{I}\cdots Xe\cdots Au^{I}Xe]^{2+}$, come up less strongly bound in calculations (Fig. 14(A)), and should be searched for in the gas phase for they must be very sensitive to (even inherently weak) Lewis bases.

Utilization of external pressure brings better prospect for both terminal (M···Xe) and the M···Xe···M bridging bonds. this will be outlined in sections 3.6–3.10.

### 3.6 Pressure as an independent variable

'Ours is a material(s) world, but remarkably, we are still unable to predict the chemical composition, the crystal structure and the physical properties of most known, and all emerging new materials'.[119] It must be honestly admitted that we have very limited knowledge of phase diagrams even for binary connections of chemical elements, as far as the very broad range of achievable temperatures and pressures is considered. The range of attainable pressures now extends to well over 3 Mbar (3 million atmospheres), laser heating can simultaneously provide temperatures above 5000 K. The behaviour of matter at such harsh conditions is usually drastically different from that known to us from the ambient world.[120]

The simplest binary fluorides of Xe, $XeF_2$, $XeF_4$ and $XeF_6$ have never been exposed to large pressures, largely due to technical problems with strong oxidants inside the diamond anvil cell. What might happen at one or two million atmospheres to, say, $XeF_4$? Let us now see what is delivered by a squeezing-in-computer experiment.[121]

Unit cells of $XeF_4$ at $\sim$1 atm (experimental) and at 200 GPa = 2 million atm (computed) are compared in Fig. 15. At ambient pressure $Xe^{IV}$ adopts square planar geometry, and is reluctant to secondary bonding. The coordination number of Xe equals 4, with nearly identical Xe–F bond lengths of 1.900–1.914 Å. The electronic bandgap is *ca.* 3.5 eV, and $XeF_4$ is colourless. At 200 GPa the Xe–F bonds get shrunk to 1.894 Å, and *eight* new short contacts at 2.297 Å appear. The Xe–F bonds of $XeF_4$ prove to be extremely incompressible; this may be traced back to the protective effect of lone pairs on F and on the Xe center, which prevent molecules from being squeezed one into another.[122]

The shortest F···F distance at 200 GPa is less then 2 Å; the coordination environment of Xe is then 4 + 8. The direct electronic band gap is now as small as 1.7 eV, therefore $XeF_4$ should be green at this pressure.

But how much would the chemistry of $XeF_4$ change under high pressure? Consider for example the following reactions:

$$2\ XeF_4 \rightarrow (Xe^{IV}F_3^{+})(Xe^{IV}F_5^{-}) \tag{20a}$$

$$XeF_4 \rightarrow Xe^{II}F_2 + F_2 \tag{20b}$$

$$2\ XeF_4 \rightarrow Xe^{II}F_2 + Xe^{VI}F_6 \tag{20c}$$

The first process (autodissociation, eqn (20a)) is forbidden by *ca.* 7.0 eV in the gas phase (value for a non-interacting $Xe^{IV}F_5^-$ anion/$Xe^{IV}F_3^+$ cation system; electrostatic stabilization will obviously decrease this value for a solid); the second process is not permitted by 0.7 eV; the third reaction is inhibited by a mere 0.2 eV at ambient pressure.[123] Albeit these reactions are thermodynamically forbidden at ambient pressure, they might occur at sufficiently large pressures. For example, reaction (20a) is analogous to autodissociation of $CO_2$ (into $CO^{2+}$ and $CO_3^{2-}$), which has been observed experimentally at elevated pressure; an analogous process might happen for a compressed $XeF_2/XeF_6$ mixture, leading to $XeF^+$ and $XeF_7^-$; eqn (20b) resembles a pressure-activated decomposition of thermodynamically unstable CuH, while an analogue of eqn (20c) has been detected for $N^{I}_2O$ (*i.e.* disproportionation to $N_2^0$ and $(N^{III}O^+)(N^{V}O_3^-)$). The outcome of squeezing $XeF_4$ is as yet unknown...

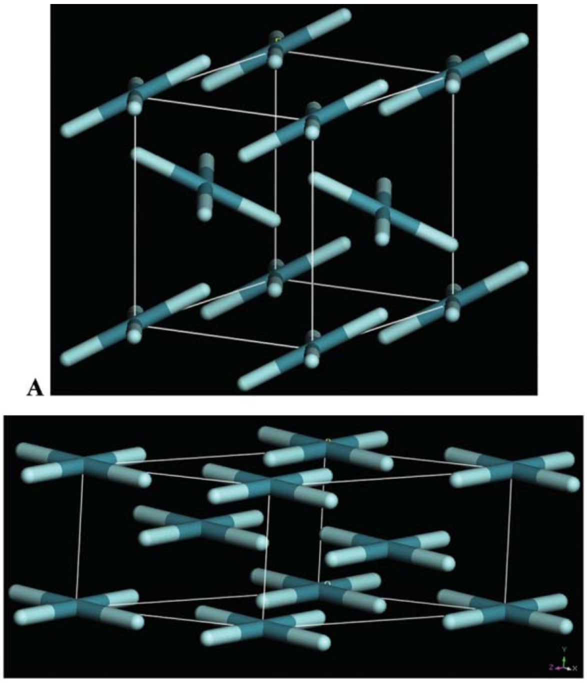


**Fig. 15** Comparison of unit cells of $XeF_4$ (A) at $\sim$1 atm (experimental) and (B) at 200 GPa (computed). (A) *a* = 5.05 Å, *b* = 5.92 Å, *c* = 5.77 Å, $\beta$ = 99.6°; (B) *a* = 4.53 Å, *b* = 3.39 Å, *c* = 6.42 Å, $\beta$ = 134.9°.

Application of high pressures may be profitable not only for the well known compounds of Xe. As we will see in the forthcoming sections, it also offers an exciting chance for the extension of the Ng–nonmetal and Ng–transition metal chemistry to entirely new elements or structures. Importantly, some of these compounds might form metastable polymorphs upon decompression, not achievable through other routes.

### 3.7 Metallic alloys of Xe

As Xe is squeezed, it undergoes martensitic transformation from the fcc to the hcp structure and becomes metallic at *ca.* 132–150 GPa. A natural question arises if at these conditions Xe might form alloys with other metallic elements (very few *are not* metallic at 2 Mbar) or compounds. Elements close to Xe in the periodic table with similar energies of valence orbitals, like Te or I, are obvious elements of choice. Due to the strong Pt–Xe, Au–Xe and Hg–Xe interactions discussed in the previous sections, platinum, gold and mercury are interesting options, as well. The $XeAu_2$ and XePt are two particularly reasonable stoichiometries, which contain $Au^{-1}$ and isoelectronic $Pt^{-2}$, as far as ionic formulation is enforced.[124] Such stoichiometries (i) favour natural $Xe^{\delta+}TM^{\sigma-}$ polarization and (ii) utilize the enhanced electron-accepting abilities of the relativistic 6s orbitals of Au and Pt.

As far as simple compounds are concerned, the ability of CsI or BaTe (in which both anions and cations are isoelectronic with "$Xe_2$", and are metallizable at, respectively, 115 GPa[125] and 200 GPa),[126] and of CsAu (isostructural to CsI) to form alloys with Xe, are worth theoretical analysis. Xe might also merge into more complex (ternary and higher) systems, as exemplified by eqn (21):

$$\mathrm{Xe} + 2\,\mathrm{Au} + \mathrm{CsAu} \rightarrow \mathrm{Cs^{I}Xe^{II}Au_3}, \qquad (21a)$$

$$\mathrm{Xe} + \mathrm{MTe} \rightarrow \mathrm{MTeXe}\ (\mathrm{M} = \mathrm{Be, Pb}, \textit{etc.}) \qquad (21b)$$

Let us concentrate on the Hg–Xe system. A Hg atom in a sense resembles the Xe atom to the largest extent among all TM atoms; both elements have a closed or quasi-closed shell (at an even-electron configuration), a pretty large HOMO–LUMO gap (*i.e.* they are less polarizable than the neighbouring elements in the same period), and they only weakly interact with other atoms of the same kind (recollect an anomalous property of Hg—it is *liquid* at normal conditions, while all its elemental neighbours are solids).

Above 45 GPa Hg adopts the hcp structure;[127] Xe does too, over the whole broad pressure range beyond 70 GPa.[128] Therefore, the chance exists that these elements might form an hcp alloy at pressures close to or exceeding 70 GPa. Actually, preliminary DFT calculations for HgXe[129] (Fig. 16) point to something qualitatively different: the novel HgXe binary compound should indeed form at similar pressure of 75 GPa, but the HgXe product prefers the CsCl structure over ordered variants of the hcp arrangement. The HgXe lattice is modestly

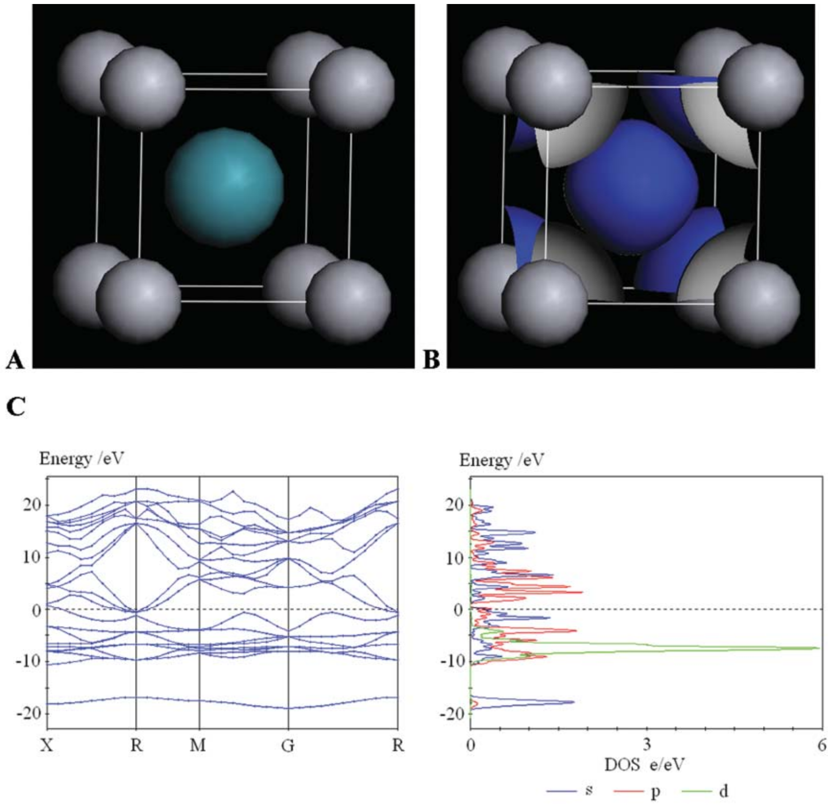


**Fig. 16** (A) Unit cell of HgXe at 50 GPa from DFT calculations (the CsCl structure, $a = b = c = 3.49$ Å); Hg – gray, Xe – blue balls. (B) electron density integrated over band No. 10, one of the bands which cross the Fermi level; density isovalue 0.03 e Å$^{-3}$; (C) electronic band structure and density of states of HgXe at 50 GPa.

polarized, with a partial positive charge residing on Xe, and a negative one on Hg. Despite its slightly ionic character, HgXe is metallic even when decompressed to 50 GPa. Electron density at the Fermi level comes mainly from s and p states, and Xe sublattice participates in metallic bonding on a nearly equal footing with Hg (Fig. 16).

Concluding this section we would like to emphasize that Xe is predicted to form a *metallic amalgam* with mercury at pressures as moderate as three fourths of a megabar, although Xe alone is not yet metallic at this pressure. The HgXe compound might be forerunner for a whole family of analogous alloys. It would be interesting to check if the alloy formation of Xe could be extended to the AuTl and PtPb compositions, both isoelectronic to "$Hg_2$".

### 3.8 Reversing of the redox reactions

$KrF_2$, $XeF_2$ and other binary fluorides of Xe are relatively unstable; they decompose thermally with the liberation of $F_2$ and Ng (or in some cases of a lower fluoride). $NgX_2$ compounds, where Ng = Xe or Kr, and X = Cl, Br, I, have never been isolated. Obviously, in this family of compounds, $XeCl_2$ would be the least and $KrI_2$ the most thermodynamically unstable one. But it is a common experience for an inorganic chemist that many species may be oxidized more easily when the pressure of the oxidant is increased. Therefore we think that the synthesis of selected $NgX_2$ compounds might be targeted at elevated pressure; they could be accessed directly from Ng and elemental halogens, or reactive halogen precursors.

To test the viability of this approach, we have performed DFT calculations for bromine in the *Immm* structure (adopted >80 GPa, with dissociated $Br_2$ molecules), Xe in the hcp structure (also preferred in this pressure range over fcc), and hypothetical $XeBr_2$ in its presumed $XeF_2$ structure (as illustrated in Fig. 17). The $XeF_2$ structure type might favour formation of $XeBr_2$; here pressure allows for compression of the (otherwise unstable) Xe–Br bonds and may prevent the $Br^-$–to–$Xe^{II}$ electron transfer and the concomitant defragmentation of the molecule. In other words, in full analogy to an ambient pressure reaction involving $F_2$, also $Br_2$ might oxidize $Xe^0$ to $Xe^{II}$ if the external pressure is sufficiently large.

Indeed, our DFT calculations indicate that at 80 GPa $XeBr_2$ has enthalpy of formation (from hcp Xe and the elemental phase of Br) of *ca.* $-0.4$ eV molecule$^{-1}$. This suggests that $XeBr_2$ might be formed directly from the elements at pressures lower than 80 GPa, *i.e.* from ccp Xe and $Br_2$ in its molecular phases.[130]

Describing the crystal structure of $XeBr_2$ (relaxed back from 80 to 50 GPa) as one analogous to that of molecular $XeF_2$ would, however, be misleading; it is more fair to say that $XeBr_2$ is in fact a $MoSi_2$-type polymer (Fig. 15) with each Xe surrounded by 8 equidistant Br atoms (at 2.933 Å); the $XeBr_8$ unit propagates in the ***a*** and ***c*** crystallographic directions; each Xe forms two more short Xe–Br contacts (at 3.032 Å) along the ***c*** axis. The $XeBr_2$ compound is still a narrow-gap semiconductor at 50 GPa, indicating a modest inter-cell orbital overlap.

The anticipated formation pressure of semiconducting (ionic) $XeCl_2$ should of course be much lower than for $XeBr_2$ (*i.e.* of the order of $\sim$10 GPa), because $Cl_2$ is a much stronger oxidant than $Br_2$, and since $Xe^{II}$–Cl bonds are known even from the 1 atm world. And maybe even $KrCl_2$ and $XeAu_2$ (with its partial $Xe^{II}(Au^-)_2$ character) might be achieved when the pressure is large enough?

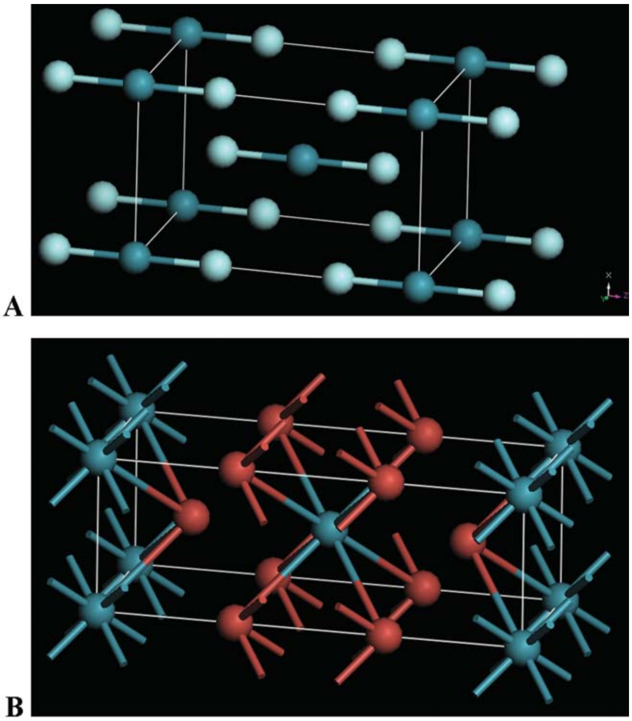


**Fig. 17** (A) Unit cell of $XeF_2$ at ~1 atm (experimental), $a = b =$ 5.05 Å, $c$ = 5.77 Å; (B) unit cell of $XeBr_2$ at 50 GPa (computed), $a = b =$ 3.44 Å, $c$ = 9.34 Å. Xe – dark blue, F – light blue, Br – red-brown balls. Structure of $XeBr_2$ (closer to $MoSi_2$-type) may be derived from that of $XeF_2$ by slightly moving halogen atoms along the crystallographic ***c*** axis (symmetry is preserved).

It is an interesting issue whether the novel high-pressure $NgX_2$ phases would be quenchable, *i.e.* if they could be decompressed to the ambient pressure while remaining metastable. Unfortunately, the $XeF_2$-type structure of $XeBr_2$ doesn't seem to support metastability to a great extent: a simple symmetry-preserving Br···Br pairing distortion within the bromine sublattice may easily result in the electron transfer between the potential energy surfaces of the reactants and of the products, and in the subsequent appearance of the $Xe^0$ and $Br_2{}^0$ sublattices.

These promising theoretical results now await being confirmed—or refuted—in experimental studies.

### 3.9. Forget solvents, just put the squeeze on

As emphasized in section 2.7, all reactions leading to complexes of Au with Xe ligands were realized in anhydrous HF. As HF is still a stronger Lewis base than Kr, attempts to prepare analogous complexes of Kr have failed. Notably, as Au–Xe complexes are on the verge of thermodynamic stability, Seppelt *et al.* have observed that the thermal stability of selected metal–Xe complexes in the $HF/SbF_5$ solvent may be significantly increased by applying a very modest pressure of gaseous Xe (10 atm). Obviously, this is an excellent prognostic for synthesizing a very rich spectrum of new Xe compounds at pressures exceeding 1 GPa (=1 tonne $cm^{-2}$ = 10 thousand atm), even in systems where metal cations are not as 'naked' as in, say, $Au(Sb_2F_{11})_2$.

Complete elimination of the anhydrous HF solvent in the high–pressure solid state synthesis opens an exciting possibility to synthesize the first metal–Kr and possibly even metal–Ar bonds. Recollect, the Xe → Kr substitution costs less than 0.5 eV per metal–Ng bond. Enthalpic effects of this size are usually overcome in the pressure range of 50–100 GPa, which is 3–4 times less than the actual record of static pressures achieved in the laboratory. In such preparative techniques (which up to 50 GPa works even for substantial volumes of reagents, $\sim 1\ cm^3$), the only Lewis bases which could still compete with Ng come from the counteranions of the parent compounds. It is therefore possible that polymerization (leading to new more compact polymorphs of, for example, $Au(Sb_2F_{11})_2$) will still constitute an obstacle for the attachment of the light Ng atoms (Kr, Ar). An additional difficulty here is that the formation of Ng complexes at room temperature or at lower temperatures may be very slow and difficult to detect in the timescale of experiment. When reagents are firmly compressed, and solvent is not present, one typically pays a price of increased kinetic barriers to reactions. Applying the standard method of laser heating may not help, as it works *against* the formation of the thermally unstable Ng complexes. Therefore, there might be only a very narrow niche of the $(p,T)$ conditions which favours formation of this fascinating class of solids.

No mater how difficult it would be to detect this $(p,T)$ regime, it is certainly worth trying, as a beautiful extension of Xe chemistry to its lighter homologues might be achieved this way.

### 3.10 Keep electron count, decrease dimensionality

Increasing the oxidation state of an element in binary connections is often connected to the decrease of dimensionality of its compounds. Take for example fluorides of Ru: $RuF_3$ is a 3D solid, $RuF_4$ forms puckered sheets and is quasi-2D, $RuF_5$ is quasi-1D (it is a molecular tetramer *i.e.* finite polymer; the related $SbF_5$ polymerizes into an infinite 1D chain), while $RuF_6$ is 0D (isolated molecules forming a molecular crystal). The idea arises to use Xe (a formally zerovalent ligand) to decrease the electronic dimensionality of various solids, while preserving the oxidation state of a metallic element. Deliberate manipulation of electronic dimensionality of an extended network, while preserving the electron count, might be indispensable for achieving desired electric and/or magnetic properties of a solid.

This concept will be illustrated using $Hg^{II}F_2$ as an example. Binary $HgF_2$ adopts the cubic $CaF_2$ structure, with eight-cordinated $Hg^{II}$ forming an isotropic three-dimensional fcc network (Fig. 18(A)). Upon attachment of a large Xe ligand $Hg^{II}$ is expected go six-coordinate, forming $HgF_2Xe$ in the tetragonally-distorted $RuO_3$ structure (Fig. 18(D)).[131] This compound is two-dimensional, as far as the Hg–F sublattice is considered. The progressive attachment of another Xe ligand might allow hypothetical $HgF_2Xe_2$ (Fig. 18(F)) to retain two-dimensionality, by forming a variant of the $PbF_4$-type structure (note, this structure type is typical for a *tetravalent*, and not a *divalent* element in the fluoride environment!). Therefore, the entire transformation:

$$HgF_2\ (3D) \rightarrow HgF_2Xe\ (2D) \rightarrow HgF_2Xe_2\ (2D) \qquad (22)$$

might hopefully be realized at a sufficiently large pressure.

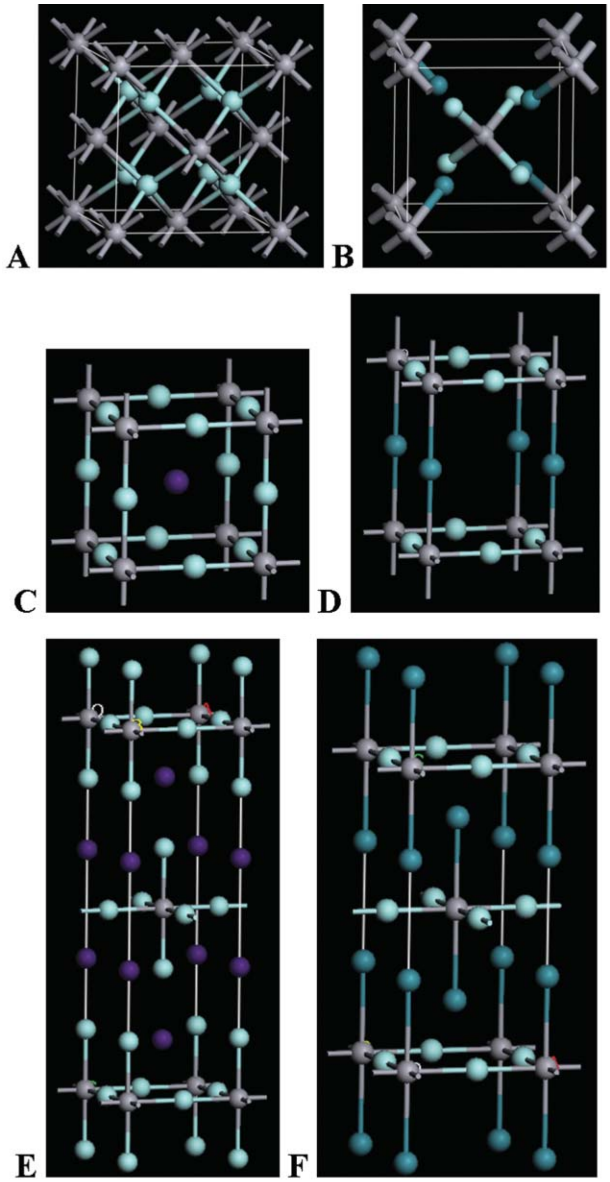


**Fig. 18** Unit cells of several known and hypothetical (*) fluorides of Hg at 10 GPa: (A) cubic $Hg^{II}F_2$, $a = b = c = 5.55$ Å; (B) $Hg^{II}F_2Xe_2$* in an ordered variant of the $Hg_4Pt$ structure, $a = b = c = 6.36$ Å; (C) $CsHg^{II}F_3$ perovskite, $a = b = c = 4.50$ Å; (D) $Hg^{II}F_2Xe$*, $a = b = 4.27$ Å, $c = 5.87$ Å; (E) $Cs_2Hg^{II}F_4$ in the $K_2NiF_4$ structure, $a = b = 4.45$ Å, $c = 14.10$ Å; (F) $Hg^{II}F_2Xe_2$* in the $PbF_4$ structure, $a = b = 4.70$ Å, $c = 9.87$ Å;. Hg – gray, F – light blue, Xe – blue, Cs – violet balls. Known compounds were optimized in their experimental structures for $p$ = 10 GPa. Note that electronic dimensionality of the Hg–F network has been reduced from three (for $HgF_2$) to two (for compounds containing Hg–Xe bonds) and that structures (C) and (E) are analogous to, respectively, (B) and (D), with vacancies at the Cs sites.

Some might argue that an identical transformation might be easily achieved by use of the weak CsF base; indeed, $CsHgF_3$ and $Cs_2HgF_4$ are known, and they adopt a perovskite[132] and a $K_2NiF_4$ structure,[133] respectively. However, the bonding nature in these solids is different than one of the $HgF_2Xe_n$ compounds: $CsHgF_3$ is clearly a 3D material, but $\square_1HgF_2Xe$ (where, $\square$ stands for a vacancy) is 2D, as apical $Xe^0$ forms much weaker bonding to $Hg^{II}$ than does $F^-$. $HgF_2Xe_2$ is a layered compound, as well, with $[HgF_2]$ sheets sandwiched between puckered $[Xe_2]$ layers.

The as yet unexplored Hg–F–Xe ternary system may offer still more surprises; $HgF_2Xe_2$ might also adopt an ordered variant of the distorted $Hg_4Pt$ structure (Fig. 18(B)). This compound is best written as $(HgXe_4^{2+})(HgF_4^{2-})$ and is electronically zero-dimensional, with its isolated $HgXe_4^{2+}$ cations and $HgF_4^{2-}$ anions.

As our calculations show, the attachment of two Xe atoms to $HgF_2$ with the simultaneous formation of any of the structures considered, is not favoured thermodynamically at pressures up to 10 GPa. However, the molar volume of the $K_2NiF_4$-like product is smaller (by nearly 6%) than for the $HgF_2$ and 2 Xe reactants together. This means that formation of the ternary phase should be favoured at elevated pressure (linear tangent method gives estimated value of $\sim$15 GPa). As decreasing the molar volume is a major advantage in achieving a better enthalpic score at elevated pressure, other structure types (with even better packing) may pop out at pressures even smaller than 15 GPa.

A compound with the $HgF_2Xe_2$ stoichiometry might open a series of novel ternary Xe–containing solids; alternatively, the $Xe/HgI_2$ phases may be considered as the size of $Xe^0$ is similar to that of $I^-$ (the $HgI_2Xe_n$ phases would then adopt the compact structure types). Use of metals other than Hg should also be taken into account.

We feel that these theoretical results are very encouraging, and they show hopeful prospects for the high-pressure synthesis of novel compounds with metal–Ng bonds, even those containing Kr and Ar.[134]

### 3.11 Xe as a mediator of formation reactions of novel chemical compounds

Xenon's ability to form adducts with chemical compounds, described in the sections above, might be utilized for the synthesis of new connections between the elements (*i.e.* such stoichiometries as have not yet been synthesized and are unknown at ambient conditions). Consider a direct reaction of formation of the AB compound from the A and B elements. If AB is kinetically unstable at $p$ = 1 atm, and various side reactions may occur, the direct synthesis may be very difficult. In an alternative path, Xe might be used to form an intermediate phase [AXe]B upon compression of reagents. The intermediate phase might subsequently decompose to Xe and the desired AB product upon careful decompression:

$$\begin{gathered}\mathrm{A + B + Xe\ (compression)} \rightarrow \\ \mathrm{[AXe]B\ (decompression)} \rightarrow \mathrm{AB + Xe}\end{gathered} \tag{23}$$

We will now illustrate this exciting prospect utilizing the classical case of a binary gold monofluoride, AuF.[135]

Scarce molecules of $Au^IF$ in the gas phase were first synthesized in 1994 and unequivocally characterized as late as in 2000.[136] However, binary $Au^IF$ in the solid state is still unknown.[137] The main reason for this striking lack of stability is in the propensity of $Au^IF$ towards disproportionation into the very stable $Au^{III}F_3$ and elemental Au. Our preliminary calculations show that this behaviour might be reversed under high pressure. The synthesis of $Au^IF$ (in the CsCl structure, preferred above 12 GPa over various infinite chain structures, Fig. 19):

$$1/3\ AuF_3 + 2/3\ Au \rightarrow Au^IF\ (>46\ GPa) \tag{24}$$

might indeed take place at pressures larger than 46 GPa. However, if 'inert' Xe is added to the reaction mixture, a novel adduct $(Au^IXe)F$ forms:

$$1/3\ AuF_3 + 2/3\ Au + Xe \rightarrow (Au^IXe)F\ (>26\ GPa) \tag{25}$$

at a much smaller pressure of 26 GPa. The $(Au^IXe)F$ compound is predicted to adopt the InOBr structure (Fig. 17), with the infinite chains of AuF stoichiometry, reminiscent of the hypothesised structure of pure $Au^IF$ at 1 atm. Upon subsequent decompression to 15 GPa, this intermediate might decompose to $Au^IF$ (CsCl type, Fig. 19), while releasing Xe:

$$(Au^IXe)F \rightarrow Au^IF + Xe\ (15\ GPa > p > 12\ GPa) \tag{26}$$

Reduction by nearly 45% of the pressure necessary for the formation of AuF may seem spectacular; recollect, however, that the Au–Xe interaction has proved very strong in Pyykkö's calculations and in the synthesized Seppelt's compounds.

Summarizing this section, extended phases might be obtained which are simply unknown at ambient pressure. Thus, Xe might act here as an ***indispensable mediator*** in forming compositions, which cannot be obtained on other paths.

### 3.12 Unprecedented polymorphs: cage structures, sponges and other 'negative pressure' forms

The ability of Xe to form moderately-bound connections with various compounds at high pressure, might be utilized for synthesis of as yet unknown high-energy polymorphs of these compounds. Let us assume that (i) a compound AB forms

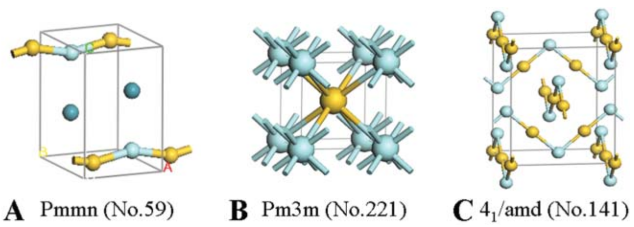

**A** Pmmn (No.59) **B** Pm3m (No.221) **C** $4_1$/amd (No.141)

**Fig. 19** Illustration of the idea of using Xe for the formation of solid $Au^IF$ (in the AuCl structure) compound *via* synthesis of (A) an $[Au^IXe]F$ intermediate at 26 GPa, its decomposition to (B) $Au^IF$ (in the CsCl structure) upon decompression to 15 GPa, and the formation of the final product (C) at pressures below 12 GPa. Au – yellow, F – light blue, Xe – dark blue balls.

$ABXe_n$ under pressure, (ii) the bonding pattern of the AB subsystem in $ABXe_n$ is different from that in pure AB, and (iii) the new phase is *not* quenchable, *i.e.* it would decompose upon decompression. If decomposition can be realized by smooth extraction of Xe and without definitive collapse of the AB network, a novel polymorph (AB)′ will result from decomposition, possibly with an unprecedented bonding topology.

The idea presented above may now be applied to porous structures, ***P***, and with the pore size of several Å's (Fig. 20). Of course, such structures are not frequently met at high pressure, as they usually tend to turn into their higher-density siblings, ***S***. However, ***P*** might be greatly stabilized (as compared to ***S***) if Xe could be allowed to interact with ***P*** at high pressure, forming bridges between various metal atoms in ***P***, or simply filling in the cages. In such cases, the atomic framework of ***P*** would be firmly supported. Upon slow decompression, Xe would slowly leave the network, yielding a novel metastable sponge polymorph (unattainable on other routes), and without its transformation to ***S***. Preparation of such polymorphs might enrich the set of cage structures such as Prussian Blue type structures, or metal–organic frameworks (MOFs). In this way novel important ultra-lightweight materials (such as the cage Al/Be alloys) might be obtained, their densities being significantly smaller than those of their classical (bulk) counterparts.

The idea described above is nicely exemplified by the known water–xenon clathrate. It will now be illustrated using two more exotic examples, which come from the fields of inorganic and organic chemistry.

The first example is provided by $Ag_3N$. This compound is extremely explosive at ambient pressure,[138] due to its susceptibility to decompose to the constituent elements. However, our GGA/PBE calculations show that hypothetical $Ag_3N$ might be stabilized by addition of atomic Xe with the concomitant formation of $[Ag_3Xe]N$ under elevated pressure. This compound would adopt the cubic perovskite $CaTiO_3$ (*Pm*3*m*) cage structure (Fig. 20(A)), which—upon decompression—would yield Xe and a cage form of $Ag_3N$ ($Cu_3N$-type) rather than the compact layered $[(AgN)(Ag_2)]$ type (with an fcc Ag sublattice, *Pm*3*m*, Fig. 20(B)).

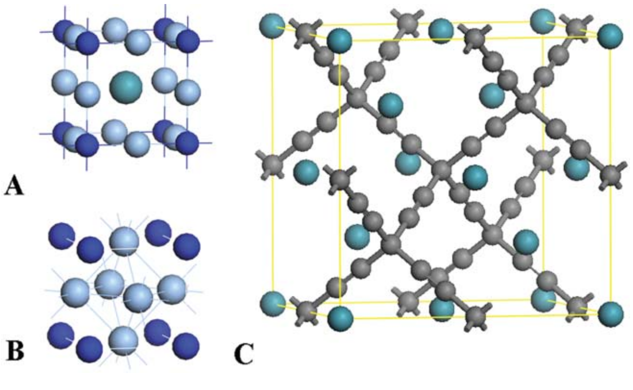


**Fig. 20** Two examples of utilizing Xe for the formation of novel cage polymorphs of various elements and compounds. (A) Perovskite structure of $[Ag_3Xe]N$, formed under elevated pressure; this compound is likely to yield the cage $AuCu_3$-type structure of $Ag_3N$ upon careful decompression, instead of the compact layered polymorph, (B). Ag – grey, Xe – light blue, N – dark blue balls. (C) Diamond-type sponge polymorph of elemental carbon with empty volumes filled with Xe, with the formula of $C_{10}Xe_2$. C – dark grey, Xe – light blue balls.

A hypothetical sponge polymorph of carbon is another interesting case (Fig. 20(C)). Here, the cubic diamond structure is inflated through the insertion between every C–C bond of a –C≡C– linker. The overall formula may be written as $\{C(C_2)_2\}$ and two such $C_5$ units enter a primitive cell of this hypothetical solid. Expansion of the diamond lattice results in a remarkable decrease of the density; our DFT calculations predict the specific gravity of this moderate-bandgap (4.5 eV) colourless insulating polymorph of carbon of about 0.88 g $cm^{-3}$, thus this material would float over water.

Synthesis of the above-mentioned 'negative pressure' sponge form of carbon has not been successful *via* a classical organic chemistry approach. It would certainly be difficult; our calculations predict that the sponge allotrope is unstable by 1.15 eV per carbon atom with respect to the classical 'collapsed' material (graphite).[139] However, the situation may change dramatically under very high pressure, but only if Xe is present as a stabilizer. Under such conditions, the $C_{10}Xe_2$ adduct (Fig. 18(C)) might form. Careful and slow decompression of $C_{10}Xe_2$ might result in the formation of the sponge polymorph, $C_{10}$. Analogous clathrates, containing iodine-filled Si sponges, have been synthesized at elevated pressure.[140]

We summarize this section with the statement that the 'inert' Xe reagent might be a remedy to the inherent instability of various fragile cage polymorphs of elements and compounds.

### 3.13 Prospect for new compounds—summary

As the process of the discovery of new elements is nearly finished by now,[141] chemistry is the art of crafting new compounds, of synthesizing entirely novel connections between the known atomic building blocks. There is nothing more essential to our enterprise than making new kinds of bonds, and new compounds which contain a cornucopia of the known bonds—but in previously unknown patterns.

In this work we have summarized recent achievements of Ng chemistry. We have also discussed the emerging directions in this field. In addition we have analyzed perspectives for the synthesis of entirely novel systems with particular emphasis on high-pressure techniques. Our most preliminary, simplistic calculations and chemical intuition have yielded several hypotheses. Specifically, we have predicted the existence of:

- the first alkyl derivatives of $Xe^{II}$, alkynyl compounds of $Xe^{IV}$, and mixed fluoride/chloride complexes of $Xe^{VI}$;
- molecular and extended compounds with terminal or bridging peroxide anions in metal-free and metal-containing connections, such as *e.g.* $FXe^{II}O_2Xe^{II}F$, $Xe\cdots Pt^{II}(O_2)$ or $XeAu^{I}O_2Au^{I}Xe$;
- complexes of $XeF_6$ as a ligand with fluoride salts containing large monovalent cations ($Cs^+$, $Rb^+$);
- molecules and solids containing $Xe^0$ atoms as ligands bridging two or more cations;
- the first metallic alloy of Xe, namely HgXe, achievable at pressures lower than 1 Mbar; the difficulty is in achieving this amalgam at a temperature low enough to prevent its decomposition, yet high enough to overcome kinetic barriers to the reaction;

- a range of $NgX_2$ solids, where Ng = Xe, Kr and X = Cl, Br, I, attainable at elevated pressures;

- novel compounds containing a neutral Xe ligand, notably $HgF_2Xe_2$, $AuFXe^0$ and its unusual $AuXe^{II}F$ isomer;

- metastable sponge polymorphs of chemical elements and compounds, such as $Ag_3N$ and C, stabilized at high pressure in the form of their adducts with Xe (filled sponges).

It would be fascinating if confirmation of these simplistic predictions were achieved in more advanced calculations, and particularly in experiments.

## 4 Methodology of calculations

The DFT and MP2 calculations using relativistic pseudopotentials have been employed in the past to rationalize[64,84,142] and predict[115b] properties of the Xe–containing species. However, they are not meant to predict with enormous accuracy certain absolute molecular properties (geometry, energetics)[143] but rather (i) illustrate the general concept, (ii) *highlight important trends* across a series of related systems (such as $O_2^{2-}$ *vs.* $O^{2-}$, XeAuF *vs.* AuXeF *etc.*), (iii) allow for fast screening of a large set of species, (iv) point out exciting new areas for future higher level (fully relativistic) calculations and (v) provide guidance and encouragement to experimentalists. Note that the trends of molecular properties are often much better reproduced than their absolute values, even with fast, low level calculations, because the origin of largest differences between the elements sits in the periodicity of properties of chemical elements (as expressed by Mendeleyev's Table) and many errors cancel when comparing same-level calculations for two chemically related species. It is therefore important to realize that all (previously unpublished) calculations presented in this contribution have a preliminary character.

The density functional theory in its present implementation in commercial packages has the well-known deficiency of predicting too small (and even 'negative') bandgaps; in other words, real systems show larger Pearson's hardness than the calculated ones; therefore, the values of pressure at which phase transitions, metallization or decomposition reactions should occur (as derived from the calculations for extended solids), must also be treated as an approximation only.

In most calculations for solids we have used the moderate cutoff of 300 eV, the convergence criterion of $10^{-6}$ eV per atom, the *k*-point mesh corresponding to 0.04 $Å^{-1}$, and the ultrasoft Vanderbilt pseudopotentials. We have used the Generalized Gradient Approximation (GGA) and the exchange–correlation functional of Perdew–Burke–Ernzerhof (PBE).

The more specific computational details allowing one to repeat the calculations, are given in the endnotes.[39, 66, 100, 117, 121, 129, 139, 149, 150]

## Note added in proof

When this paper was in proof, the author became aware of two important theoretical papers, where the properties of the first chemically bound *anionic* species containing helium, such as for example $FHeO^-$, have been predicted.[151] The author would like to thank Dr Mazej for attracting his attention to these important works.

## Acknowledgements

I would like to gratefully acknowledge Prof. Naumann and Prof. Frohn for providing hardcopies of their selected publications, and Prof. Boris Žemva for sharing unpublished results related to $Li(XeF_2)_3(AsF_6)$ and $Cd(XeF_2)_5(SbF_6)_2$. I also wish to thank Boris, Gary Schrobilgen, Pekka Pyykkö and Mike Gerry for the fast exchange of information. Prof. Andrzej J. Sadlej (Nicolaus Copernicus University, Toruń, Poland) has made available a large set of unpublished computational results for Au–Ng–F molecules. I am greatly indebted to Danny Fredrickson (Stockholm, Sweden), Boris Žemva (Ljubljana, Slovenia), Mike Gerry (Vancouver, Canada), Ji Feng (Cornell, USA), and Lucjan Piela (Warsaw, Poland) for their kind and thoughtful comments on this work.

The continuing support of ICM and of the Department of Chemistry (The Warsaw University) is gratefully appreciated. Calculations have been performed on the machines of the ICM supercomputer center using the Gaussian'98 and Castep packages. Many thanks to Jacek Piechota for providing access to his license of CASTEP.

This contribution has been supported *via* the national KBN grant No. N204 167 32/4321.

## References

1 P. Pyykkö, *Science*, 2000, **290**, 64.
2 The reaction of Mendeleyev to this discovery was strange; at first he claimed that Rayleigh and Ramsay were wrong, and that such elements cannot exist as there is no room for them in the Periodic Table. Later on, when the discovery was unequivocally confirmed, Mendeleyev started a propaganda campaign insisting that, in fact, existence of Group VIIIA elements *confirms* his proposal of a Periodic Table.
3 (*a*) W. Kossel, *Ann. Phys.*, 1916, **49**, 229; (*b*) G. N. Lewis, *J. Am. Chem. Soc.*, 1916, **38**, 762.
4 (*a*) A. Antropoff, *Z. Angew. Chem.*, 1924, **37**, 217; (*b*) A. Antropoff, *Z. Angew. Chem.*, 1924, **37**, 695; (*c*) L. L. Pauling, *J. Am. Chem. Soc.*, 1932, **54**, 3570.
5 (*a*) N. Bartlett, *Proc. Chem. Soc. (London)*, 1962, 218. $XeF_4$ and $XeF_6$ were isolated months later: (*b*) H. H. Claassen, H. Selig and J. G. Malm, *J. Am. Chem. Soc.*, 1962, **84**, 3593; (*c*) J. Slivnik, B. Brčič, B. Volavšek, J. Marsel, V. Vrščaj, A. Šmalc, B. Frlec and Z. Zemljič, *Croat. Chem. Acta*, 1962, **34**, 253.
6 For historical background and contribution of R. Hoppe please see: P. Laszlo and G. J. Schrobilgen, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 479.
7 (*a*) K. A. Goettel, J. H. Eggert, I. F. Silvera and W. C. Moss, *Phys. Rev. Lett.*, 1989, **62**, 665; (*b*) R. Reichlin, K. E. Brister, A. K. McMahan, M. Ross, S. Martin, Y. K. Vohra and A. L. Ruoff, *Phys. Rev. Lett.*, 1989, **62**, 669.
8 (*a*) B. Žemva, personal communication. Xe is an excellent anaesthetic, and may even be used as a chemical probe of the surface minority sites; (*b*) H. Guo and F. Zaera, *Nat. Mater.*, 2006, **5**, 489.
9 I. H. Krouse, C. Hao, C. E. Check, K. C. Lobring, L. S. Sunderlin and P. G. Wenthold, *J. Am. Chem. Soc.*, 2007, **129**, 845.
10 J. F. Lehmann, H. P. A. Mercier and G. J. Schrobilgen, *Coord. Chem. Rev.*, 2002, **233**, 1.
11 J. H. Holloway and E. G. Hope, *Adv. Inorg. Chem.*, 1999, **46**, 51.
12 M. Tramšek and B. Žemva, *Acta Chim. Slov.*, 2006, **53**, 105.
13 B. E. Pointner, R. J. Suontamo and G. J. Schrobilgen, *Inorg. Chem.*, 2006, **45**, 1517.

14 (*a*) G. A. Schumacher and G. J. Schrobilgen, *Inorg. Chem.*, 1983, **22**, 2178; (*b*) A. A. A. Emara and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 1987, 1644; (*c*) A. A. A. Emara and G. J. Schrobilgen, *Inorg. Chem.*, 1992, **31**, 1323; (*d*) G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 1988, 1506.

15 Y. L. Yagupolskii, W. Tyrra, R. Gnann, N. Maggiarosa and D. Naumann, *J. Fluorine Chem.*, 2002, **113**, 143.

16 G. L. Smith, H. P. A. Mercier and G. J. Schrobilgen, *Inorg. Chem.*, 2007, **46**, 1369.

17 J. M. Whalen and G. J. Schrobilgen, *J. Fluorine Chem.*, 1995, **71**, 225.

18 A. Schulz and T. M. Klapotke, *Inorg. Chem.*, 1997, **36**, 1929.

19 M. Gerken and G. J. Schrobilgen, *Coord. Chem. Rev.*, 2000, **197**, 335.

20 G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 1988, 863.

21 J. C. P. Sanders and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 1989, 1576.

22 (*a*) Results presented during the 12th International Symposium on Fluorine Chemistry, Santa Cruz, 1988, by two groups independently, and later published as; (*b*) D. Naumann and W. Tyrra, *J. Chem. Soc., Chem. Commun.*, 1989, 47; H. J. Frohn and S. Jakobs, *J. Chem. Soc., Chem. Commun.*, 1989, 625.

23 H. J. Frohn and V. V. Bardin, *Chem. Commun.*, 1999, 919.

24 (*a*) V. V. Zhdankin, P. J. Stang and N. S. Zefirov, *J. Chem. Soc., Chem. Commun.*, 1992, 578; (*b*) H. J. Frohn and V. V. Bardin, *Chem. Commun.*, 2003, 2352; (*c*) H. J. Frohn and V. V. Bardin, *Eur. J. Inorg. Chem.*, 2006, 3948.

25 (*a*) H. J. Frohn, S. Jakobs and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1506. More of those are known now: (*b*) H. J. Frohn, T. Schroer and G. Henkel, *Z. Naturforsch., B: Chem. Sci.*, 1995, **50**, 1799; (*c*) Y. L. Yagupolskii, W. Tyrra, R. Gnann, N. Maggiarosa and D. Naumann, *J. Fluorine Chem.*, 2002, **113**, 143.

26 A nice review is available covering organoxenon chemistry up to 2001: (*a*) H. J. Frohn and V. V. Bardin, *Organometallics*, 2001, **20**, 4750. See also: (*b*) H. Butler, D. Naumann and W. Tyrra, *Eur. J. Solid State Inorg. Chem.*, 1992, **29**, 739; (*c*) D. Naumann, H. Butler, R. Gnann and W. Tyrra, *Inorg. Chem.*, 1993, **32**, 861; (*d*) D. Naumann, W. Tyrra and D. Pfolk, *Z. Anorg. Allg. Chem.*, 1994, **620**, 987.

27 (*a*) N. Maggiarosa, D. Naumann and W. Tyrra, *Angew. Chem., Int. Ed.*, 2000, **39**, 4588; (*b*) H. J. Frohn and M. Theissen, *Angew. Chem., Int. Ed.*, 2000, **39**, 4591.

28 D. Naumann, R. Gnann, N. Ignatev and S. Datsenko, *Z. Anorg. Allg. Chem.*, 1995, **621**, 851.

29 (*a*) H. J. Frohn, N. LeBlond, K. Lutar and B. Žemva, *Angew. Chem., Int. Ed.*, 2000, **39**, 391; (*b*) N. Maggiarosa, PhD thesis, University of Cologne, 1999.

30 (*a*) H. J. Frohn and T. Schroer, 15th International Symposium on Fluorine Chemistry, Vancouver, Canada, 1997; (*b*) H. J. Frohn, T. Schroer and G. Henkel, *Angew. Chem., Int. Ed.*, 1999, **38**, 2554.

31 S. Seidel and K. Seppelt, *Angew. Chem., Int. Ed.*, 2001, **40**, 4225.

32 H. Bock, D. Hinz-Hubner, U. Ruschewitz and D. Naumann, *Angew. Chem., Int. Ed.*, 2002, **41**, 448.

33 J. Emsley, *New Sci.*, 1989, **124**, 20.

34 Compare: (*a*) H. A. Bent, *Chem. Rev.*, 1968, **68**, 587; (*b*) H. B. Bürgi, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1998, **54**, 873.

35 As a referee correctly reminds us, term 'hypervalence' refers to finger counting of electrons assuming covalent formulation. In fact, ionic resonance plays an important role in the Ng species and there are simply not more than eight electrons around the Ng atom—actually less. The reader is referred to; R. J. Gillespie and B. Silvi, *Coord. Chem. Rev.*, 2002, **233**, 53. Nevertheless, we think that hypervalence is useful to classify compounds based on a small integer.

36 (*a*) G. A. Landrum and R. Hoffmann, *Angew. Chem., Int. Ed.*, 1998, **37**, 1887; (*b*) G. A. Landrum, N. Goldberg and R. Hoffmann, *J. Chem. Soc., Dalton Trans.*, 1997, 3605. This behaviour also resembles one frequently found for Jahn–Teller active species: (*c*) J. GaŽo, *Pure Appl. Chem.*, 1974, **38**, 279; (*d*) J. GaŽo, I. B. Bersuker, J. Garaj, M. Kabesova, J. Kohout, H. Langfelderova, M. Melnik, M. Serator and F. Valach, *Coord. Chem. Rev.*, 1976, **19**, 253.

37 W. Grochala and P. P. Edwards, *Chem. Rev.*, 2004, **104**, 1283.

38 B. Fir, J. M. Whalen, H. P. A. Mercier, D. A. Dixon and G. J. Schrobilgen, *Inorg. Chem.*, 2006, **45**, 1978.

39 The energies of these transitions are overestimated by the B3LYP/TD calculations They yield the first weakly allowed electronic transition in the UV, at 5.21 eV ($^1\Pi_u$), with the lowest triplet state ($^3\Sigma_u$) at 2.89 eV; the major orbital contributions to both transitions are analogous to those computed for $XeF_2$; W. Grochala, unpublished DFT results (SDDAll Stuttgart pseudopotential for Xe and Kr with the concomitant $2\zeta$ function basis set, 6–311++G** basis for F; the basis set for Xe contains an extensive set of functions: four sets of s, four sets of p, three sets of d, and one set of f functions).

40 As long as the stability problem rests in the bending of the hypervalent element–Xe–element moiety, it might be avoided by functionalizing the elements in question with bulky substituents. For example, $FXeSiF_3$ might be difficult to isolate, but $Xe(SiR_3)_2$ where R is a bulky, preferably saturated perfluorinated organic substituent should be easier to get. This approach, however, cannot be extended to all elements, because at some point the stability will be related to Xe–element bond stretching. An analogous situation may occur for $KrF_2$ (ref. 35) and other connections of $Kr^{II}$. But even softening of the bond–stretching may sometimes be suppressed, as indicated by recent theoretical results: (*a*) A. Lignell, L. Khriachtchev, M. Räsänen and M. Pettersson, *Chem. Phys. Lett.*, 2004, **390**, 256. Decomposition of quasi-linear $Ng^{II}$ molecules is in fact a complex process where both coordinates matter: (*b*) G. M. Chaban, J. Lundell and R. B. Gerber, *Chem. Phys. Lett.*, 2002, **364**, 628; (*c*) C. Z. Ai, R. A. Sun and J. Yan, *Chin. J. Struct. Chem.*, 2005, **24**, 1445.

41 It is even easier to get new bonds in cationic species in the gas phase or in the conditions of a mass spectrometer; many Xe–element bonds were seen in such experiments.

42 (*a*) M. Pettersson, J. Lundell and M. Räsänen, *J. Chem. Phys.*, 1995, **102**, 6423; (*b*) M. Pettersson, J. Lundell and M. Räsänen, *J. Chem. Phys.*, 1995, **103**, 205. Note that there was earlier evidence for $Xe^{II}$–$H^{-1}$ bonding in charged $XeH^+$ species in the gas phase: (*c*) S. A. Rogers, C. R. Brazier and P. F. Bernath, *J. Chem. Phys.*, 1987, **87**, 159. A range of other Ng–element bonds were seen in the gas phase, preceding their discovery in neutral species in noble gas matrices.

43 (*a*) M. Pettersson, J. Nieminen, L. Khriachtchev and M. Räsänen, *J. Chem. Phys.*, 1997, **107**, 8423; (*b*) M. Pettersson, J. Lundell, L. Khriachtchev and M. Räsänen, *J. Chem. Phys.*, 1998, **109**, 618; (*c*) M. Pettersson, J. Lundell, L. Khriachtchev, E. Isoniemi and M. Räsänen, *J. Am. Chem. Soc.*, 1998, **120**, 7979; (*d*) M. Pettersson, J. Lundell and M. Räsänen, *Eur. J. Inorg. Chem.*, 1999, 729; (*e*) M. Pettersson, L. Khriachtchev, J. Lundell and M. Räsänen, *J. Am. Chem. Soc.*, 1999, **121**, 11904; (*f*) M. Lorenz, M. Räsänen and V. E. Bondybey, *J. Phys. Chem. A*, 2000, **104**, 3770; (*g*) J. Lundell, L. Khriachtchev, M. Pettersson and M. Räsänen, *Low Temp. Phys.*, 2000, **26**, 680; (*h*) M. Pettersson, L. Khriachtchev, A. Lignell, M. Räsänen, Z. Bihary and R. B. Gerber, *J. Chem. Phys.*, 2002, **116**, 2508; (*i*) L. Khriachtchev, H. Tanskanen, J. Lundell, M. Pettersson, H. Kiljunen and M. Räsänen, *J. Am. Chem. Soc.*, 2003, **125**, 4696; (*j*) L. Khriachtchev, H. Tanskanen, A. Cohen, R. B. Gerber, J. Lundell, M. Pettersson, H. Kiljunen and M. Räsänen, *J. Am. Chem. Soc.*, 2003, **125**, 6876; (*k*) H. Tanskanen, L. Khriachtchev, J. Lundell, H. Kiljunen and M. Räsänen, *J. Am. Chem. Soc.*, 2003, **125**, 16361; (*l*) V. I. Feldman, F. F. Sukhov, A. Y. Orlov and I. V. Tyulpina, *J. Am. Chem. Soc.*, 2003, **125**, 4698; (*m*) V. I. Feldman, F. F. Sukhov and A. Y. Orlov, *Chem. Phys. Lett.*, 1997, **280**, 507. The $HXeC_2$ radical and the HNgCCCN species (Ng = Kr, Xe) were synthesized while this paper was in preparation: (*n*) L. Khriachtchev, H. Tanskanen and M. Räsänen, *J. Chem. Phys.*, 2006, **124**, Art. No 181101; (*o*) L. Khriachtchev, A. Lignell, H. Tanskanen, J. Lundell, H. Kiljunen and M. Räsänen, *J. Phys. Chem. A*, 2006, **110**, 11876.

44 L. Khriachtchev, M. Pettersson, N. Runeberg, J. Lundell and M. Räsänen, *Nature*, 2000, **406**, 874. Remarkably, FArF has not been isolated so far.

45 G. Frenking, *Nature*, 2000, **406**, 836.

46 It is beyond the scope of this essay to present the details of the electronic structure of various Ng molecules; the reader is

therefore referred to more specialized reviews and papers on this topic: (*a*) D. C. Grills and M. W. George, *Adv. Inorg. Chem.*, 2001, **52**, 113; (*b*) R. B. Gerber, *Annu. Rev. Phys. Chem.*, 2004, **55**, 55; (*c*) S. Berski, Z. Latajka and B. Silvi, *J. Lundell, J. Chem. Phys.*, 2001, **114**, 4349; (*d*) N. Runeberg, M. Pettersson, L. Khriachtchev, J. Lundell and M. Räsänen, *J. Chem. Phys.*, 2001, **114**, 836; (*e*) S. A. C. McDowell, *J. Chem. Phys.*, 2001, **114**, 8395; (*f*) N. Runeberg, M. Seth and P. Pyykkö, *Chem. Phys. Lett.*, 1995, **246**, 239; (*g*) A. Lignell, L. Khriachtchev, J. Lundell, H. Tanskanen and M. Räsänen, *J. Chem. Phys.*, 2006, **125**, Art. No 184514. It is especially interesting that Ng–H bonding is reasonably stable, and the hydride–fluoride analogy seems to work well in these compounds: see ref. 194 in our Ref. 34.

47 H. G. Yu and J. T. Muckerman, *J. Theor. Comput. Chem.*, 2003, **2**, 573.

48 (*a*) S. A. C. McDowell, *J. Chem. Phys.*, 2004, **120**, 9077. See also: (*b*) L. Sheng, A. Cohen and R. B. Gerber, *J. Am. Chem. Soc.*, 2006, **128**, 7156; (*c*) L. Sheng and R. B. Gerber, *J. Chem. Phys.*, 2006, **124**, 231103–1; (*d*) L. Sheng and R. B. Gerber, *J. Chem. Phys.*, 2006, **125**, 201101–1; (*e*) L. Sheng and R. B. Gerber, *J. Chem. Phys.*, 2007, **126**, 021108–1; (*f*) T. Ansbacher and R. B. Gerber, *Phys. Chem. Chem. Phys.*, 2006, **8**, 4175; (*g*) H. Tanskanen, L. Khriachtchev, J. Lundell and M. Räsänen, *J. Chem. Phys.*, 2006, **125**, 074501–1; (*h*) L. Khriachtchev, A. Lignell, H. Tanskanen, J. Lundell, H. Kiljunen and M. Räsänen, *J. Phys. Chem. A*, 2006, **110**, 11876.

49 J. Baker, P. W. Fowler, A. Soncini and M. Lillington, *J. Chem. Phys.*, 2005, **123**, 174309.

50 Xe–Si bonds form easily in cationic species in the gas phase: (*a*) R. Cipollini and F. Grandinetti, *J. Chem. Soc., Chem. Commun.*, 1995, 773; (*b*) A. Cunje, V. I. Baranov, Y. Ling, A. C. Hopkinson and D. K. Bohme, *Eur. J. Inorg. Chem.*, 2001, **105**, 11073. FXeSiF was predicted to be a kinetically stable compound: (*c*) J. Lundell, J. Panek and Z. Latajka, *Chem. Phys. Lett.*, 2001, **348**, 147. No data is available for $FXeSiF_3$, but since its Kr and Ar analogues were predicted to be local minima, $FXeSiF_3$ should be achievable, too: (*d*) A. Cohen, J. Lundell and R. B. Gerber, *J. Chem. Phys.*, 2003, **119**, 6415; (*e*) S. Yockel, A. Garg and A. K. Wilson, *Chem. Phys. Lett.*, 2005, **411**, 91.

51 Compare reports on $XeCl_2$ and $XeCl_4$: (*a*) L. Y. Nelson and G. C. Pimentel, *Inorg. Chem.*, 1967, **6**, 1758; (*b*) G. J. Perlow and M. R. Perlow, *J. Chem. Phys.*, 1964, **41**, 1157. The only report on the $Xe^{VI}$–Cl bonding may be misleading, as the postulated terminal Xe–Cl bond length is not shorter than the bridging Xe–Cl bond lengths; (*c*) R. D. Willett, S. W. Peterson and B. A. Coyle, *J. Am. Chem. Soc.*, 1977, **99**, 8202.

52 The HXeO radical, which may formally be regarded as $H^{-1}Xe^{II}O^{-1\bullet}$, has already been observed: (*a*) L. Khriachtchev, M. Pettersson, J. Lundell, H. Tanskanen, T. Kiviniemi, N. Runeberg and M. Räsänen, *J. Am. Chem. Soc.*, 2003, **125**, 1454; (*b*) T. Kiviniemi, M. Pettersson, L. Khriachtchev, M. Räsänen and N. Runeberg, *J. Chem. Phys.*, 2004, **121**, 1839. It is puzzling that chemically bound dimers of $H^{-1}Xe^{II}O^{-1\bullet}$ have not yet been generated.

53 (*a*) C. A. Thompson and L. Andrews, *J. Am. Chem. Soc.*, 1994, **116**, 423; J. R. Wells and E. Weitz, *J. Am. Chem. Soc.*, 1992, **114**, 2783.

54 No wonder Xe has recently been predicted to be bound to an even stronger Lewis acid, $B^{III}$, in a novel as yet unknown molecule, $FXeB^{III}O$: (*a*) T. Y. Lin, J. B. Hsu and W. P. Hu, *Chem. Phys. Lett.*, 2005, **402**, 514. Binding of Xe to the BeS analogue has also been predicted theoretically: (*b*) S. Borocci, N. Bronzolino and F. Grandinetti, *Chem. Phys. Lett.*, 2004, **384**, 25.

55 Lighter Ng's were found to bind to the BeO molecule much more weakly, and yet we are tempted to say that linear $Ar\cdots Be^{II}O$ is a powerfully perturbed, distant isoelectronic sibling of $BeF_2$. Even weaker bonding energies, typical of vdW complexes, are seen for Ne and He: (*a*) P. Pyykkö and Y.-F. Zhao, *J. Phys. Chem.*, 1990, **94**, 7753; (*b*) P. Pyykkö, *Chem. Phys. Lett.*, 1989, **162**, 349; (*c*) P. Pyykkö and Y.-F. Zhao, *Mol. Phys.*, 1990, **70**, 701.

56 (*a*) C. J. Evans and M. C. L. Gerry, *J. Chem. Phys.*, 2000, **112**, 1321; (*b*) C. J. Evans and M. C. L. Gerry, *J. Chem. Phys.*, 2000, **112**, 9363; (*c*) C. J. Evans, A. Lesarri and M. C. L. Gerry, *J. Am. Chem. Soc.*, 2000, **122**, 6100; (*d*) C. J. Evans, D. S. Rubinoff and M. C. L. Gerry, *Phys. Chem. Chem. Phys.*, 2000, **2**, 3943.

57 This family of species nicely spans between weak interactions (as in ArAgCl) up to quite strong bonding (as in XeAuF).

58 Prof. Gerry so wrote to me about this discovery (Mar 2006): "I agree that the work was done in my group, and I have put in a lot of thought and effort, especially in trying to assess the nature of the Ng–metal bonding. However, many people have worked on the complexes, and the work was not easy. In particular, the complexes were discovered accidentally by my post-doc Corey Evans, who found the first spectrum while he was looking for something else. After some painstaking and careful work he identified the cause as ArAgCl, and it was clear from the outset that the complex is rigid and the ArAg bond is very short. Interestingly this is one of the most weakly bonded of the NgMX complexes we have found. This was a textbook example of how a brilliant researcher reasons through an unexpected observation and comes to a really interesting discovery. He deserves full credit for this, for without it none of this would have happened, and I hope you will indicate this in your article. Once he had found this we realized the full implication and pushed the project to greater things, as you have seen. The most recent published work, on XeAuF, the most strongly bound of all the complexes (but which was unexpectedly tricky to find), was carried out by a more recent post-doc, Stephen Cooke".

59 (*a*) L. M. Reynard, C. J. Evans and M. C. L. Gerry, *J. Mol. Spectrosc.*, 2001, **206**, 33; (*b*) N. R. Walker, L. M. Reynard and M. C. L. Gerry, *J. Mol. Struct.*, 2002, **612**, 109; (*c*) J. M. Thomas, N. R. Walker, S. A. Cooke and M. C. L. Gerry, *J. Am. Chem. Soc.*, 2004, **126**, 1235; (*d*) M. Michaud, S. A. Cooke and M. C. L. Gerry, *Inorg. Chem.*, 2004, **43**, 3871; (*e*) S. A. Cooke and M. C. L. Gerry, *Phys. Chem. Chem. Phys.*, 2004, **6**, 3248. KrCuBr, XeAgBr, XeAuCl, XeAuBr and XeCuBr have not yet been the subjects of research. Data for XeCuF and XeCuCl were published when this paper was in preparation: (*f*) J. M. Michaud and M. C. L. Gerry, *J. Am. Chem. Soc.*, 2006, **128**, 7613, and (unpublished) the rotational spectrum of KrAuBr has also been assigned: (*g*) M. C. L. Gerry, personal communication.

60 S. A. Cooke and M. C. L. Gerry, *J. Am. Chem. Soc.*, 2004, **126**, 17000.

61 D. Schröder, J. Hrušak, I. C. Tornieporth–Oelting, T. M. Klapötke and H. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 212.

62 (*a*) C. C. Lovallo and M. Kłobukowski, *Chem. Phys. Lett.*, 2003, **368**, 589. $Pt(0)Xe_2$, isoelectronic with $AuCl_2^-$, is bound by ~0.72 eV per Xe atom and, remarkably, the second Xe atom has even larger binding energy than the first one: (*b*) Y. Ono, T. Taketsugu and T. Noro, *J. Chem. Phys.*, 2005, **123**, 204321.

63 Obviously, it is much easier to get $Xe^0$ involved in chemical bonding in positively charged species than in neutral ones. This is exemplified by $Ng_2^{+\bullet}$ radical cations (even $He_2^{+\bullet}$ is a strongly bound species) and by $Ng–H^+–Ng$ cations (isoelectronic to the well-known $HF^{2-}$) isolated in cold matrices: (*a*) H. Kunttu, J. Seetula, M. Räsänen and V. A. Apkarian, *J. Chem. Phys.*, 1992, **96**, 5630; (*b*) L. Khriachtchev, A. Lignell and M. Räsänen, *J. Chem. Phys.*, 2005, **123**, 064507; (*c*) J. Lundell, M. Pettersson and M. Räsänen, *Phys. Chem. Chem. Phys.*, 1999, **1**, 4151.

64 S. Seidel and K. Seppelt, *Science*, 2000, **290**, 117.

65 (*a*) K. Seppelt, *Z. Anorg. Allg. Chem.*, 2003, **629**, 2427; (*b*) I. C. Hwang and K. Seppelt, *Z. Anorg. Allg. Chem.*, 2002, **628**, 765; (*c*) T. Drews, S. Seidel and K. Seppelt, *Angew. Chem., Int. Ed.*, 2002, **41**, 454; (*d*) I. C. Hwang, S. Seidel and K. Seppelt, *Angew. Chem., Int. Ed.*, 2003, **42**, 4392.

66 The ligand field strength of Xe and Kr may be estimated using a $Pt^{II}$ ($d^8$) probe *via* evaluation of the energy difference between its low-spin and high-spin configurations. Our DFT results for $Pt^{II}L_4$ species (where L = Kr, Xe, HF, HCl) indicate that the ligand field strength increases in the order: Kr < FH < Xe < ClH (A. Sokołowski, W. Grochala, B3LYP, 6-311++G** for F and H, SDDAll for Pt, Pd, Xe and Kr). For direct comparison, all complexes were consistently frozen in $D_{4h}$ symmetry despite appearance of soft imaginary bending modes which coupled HF or HCl molecules to one another).

67 (*a*) T. K. Ghanty, *J. Chem. Phys.*, 2005, **123**, 074323; (*b*) T. K. Ghanty, *J. Chem. Phys.*, 2006, **124**, 124304-1.

68 This molecule has been investigated in matrices: A. Givan and A. Loewenschuss, *J. Chem. Phys.*, 1980, **72**, 3809.

69 The structure of solid TlOF is known: A. W. Sleight, J. L. Gillson and B. L. Chamberlain, *Mater. Res. Bull.*, 1970, **5**, 807.

70 (*a*) P. Pyykkö, *J. Am. Chem. Soc.*, 1995, **117**, 2067; (*b*) D. Schroder, H. Schwarz, J. Hrusak and P. Pyykkö, *Inorg. Chem.*, 1998, **37**, 624. The properties of other species, like $Pt^0Xe$, $Ni^0Xe$, or $PtXe_2$, were predicted later by this and other groups: (*c*) J. V. Burda, N. Runeberg and P. Pyykkö, *Chem. Phys. Lett.*, 1998, **288**, 635. See also: (*d*) W. P. Hu and C. H. Huang, *J. Am. Chem. Soc.*, 2001, **123**, 2340.

71 See, for example, the beautiful review: P. Pyykkö, *Angew. Chem., Int. Ed.*, 2004, **43**, 4412.

72 Of course, the basicity of the sp hybrid on $F^-$ is still larger than that of the lone pair of a bare Xe atom, and the formation of $XeF_2$ adducts should be easier than achieving Seppelt's rare complexes.

73 R. Hagiwara, F. Hollander, C. Maines and N. Bartlett, *Eur. J. Solid State Inorg. Chem.*, 1991, **28**, 855.

74 Judging from Ag–F distances only, the neutral $XeF_2$ is a better Lewis base than the anionic hexafluoroarsenate ion.

75 D. H. Templeton, A. Zalkin, J. D. Forrester and S. M. Williamson, *J. Am. Chem. Soc.*, 1963, **85**, 241. Notably, engagement of a terminal F atom's lone pairs in secondary bonding helps to partially remove electron density from the four-electron–three-center bond, and this slightly strengthens the intramolecular Xe–F bond.

76 The formation of [metal···FXeF] bridges was in fact observed as early as 1979 for the coordinatively unsaturated $MOF_4$ derivatives (M = Mo, W), but the adducts could not be isolated: J. H. Holloway and G. J. Schrobilgen, *Inorg. Chem.*, 1980, **19**, 2632.

77 K. Matsumoto, R. Hagiwara, Y. Ito and O. Tamada, *Solid State Sci.*, 2002, **4**, 1465.

78 (*a*) M. Tramšek, P. Benkič and B. Žemva, *Solid State Sci.*, 2002, **4**, 9; (*b*) M. Tramšek, P. Benkič, A. Turičnik, G. Tavčar and B. Žemva, *J. Fluorine Chem.*, 2002, **114**, 143; (*c*) A. Turičnik, P. Benkič and B. Žemva, *Inorg. Chem.*, 2002, **41**, 5521; (*d*) P. Benkič, M. Tramšek and B. Žemva, *Solid State Sci.*, 2002, **4**, 1425; (*e*) M. Tramšek, P. Benkič and B. Žemva, *Inorg. Chem.*, 2004, **43**, 699; (*f*) G. Tavčar, P. Benkič and B. Žemva, *Inorg. Chem.*, 2004, **43**, 1452; (*g*) G. Tavčar, M. Tramšek, T. Bunič, P. Benkič and B. Žemva, *J. Fluorine Chem.*, 2004, **125**, 1579; (*h*) B. Žemva, M. Tramšek, A. Turienik, P. Benkič and G. Tavčar, *Abstr. Pap. Am. Chem. Soc.*, 2003, 225U144 767-INOR Part 2; (*i*) M. Tramšek and B. Žemva, *J. Fluorine Chem.*, 2006, **127**, 1275; (*j*) G. Tavčar, E. Goreshnik and Z. Mazej, *J. Fluorine Chem.*, 2006, **127**, 1368; (*k*) G. Tavčar and B. Žemva, 17th International Symposium on Fluorine Chemistry, Shanghai, China, July 2005; (*l*) "There was an indication that in the case of Na the compound $Na(XeF_2)_n(AsF_6)$ is present in a solution; it was never isolated."; "We already have compounds of Zn and Cu and their structures were not published yet; in both cases these are homoleptic compounds $M(XeF_2)_6(SbF_6)_2$"—personal communications of B. Žemva to the author.

79 B. Žemva wrote to me in January 2007: "We isolated three coordination compounds of the type $Ba(XeF_2)_4(MF_6)_2{\cdot}XeF_2$ with M = Sb, As and Ru. All three compounds are isostructural but only the compound with M = Sb was published till now. The other two will be published together with their NMR data".

80 G. Tavčar and B. Žemva, personal communication.

81 K. O. Christe, *Angew. Chem., Int. Ed.*, 2001, **40**, 1419.

82 When I wrote in Feb 2006 to Prof. Žemva suggesting the possible formation of the $XeF_6$ adducts with $Cs^+$ salts, he admitted: "We did not try that one yet. It is in our plans".

83 (*a*) L. Stein, J. R. Norris, A. J. Downs and A. R. Minihan, *J. Chem. Soc., Chem. Commun.*, 1978, 502; (*b*) T. Drews and K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 273. The $Xe_2^+$ species is analogous to the $He_2^+$ cation (well-known from the gas phase) and the bonding resembles that of the isoelectronic XeI molecule. Yet the stability of $Xe_2^+$ is surprising; it has a weird electron count of 15 valence electrons per atom pair, which is different from 14 (as for stable $I_2$) and from 16 (as for two Xe atoms). A tendency of $Xe_2^+$ to disproportionate into ½ $Xe^{2+}$ and Xe has not been discussed in the literature.

84 (*a*) J. Li, B. E. Bursten, B. Y. Liang and L. Andrews, *Science*, 2002, **295**, 2242; (*b*) L. Andrews, B. Y. Liang, J. Li and B. E. Bursten, *J. Am. Chem. Soc.*, 2003, **125**, 3126; (*c*) L. Andrews, B. Y. Liang, J. Li and B. E. Bursten, *J. Am. Chem. Soc.*, 2003, **125**, 3126.

85 (*a*) C. T. Goetsche and K. R. Loos, *J. Am. Chem. Soc.*, 1972, **94**, 3018. If the authors' interpretation is correct, this would formally be a compound of rare monovalent boron, $(F^-Xe^+)^-B^+F_2^-$. Note, there is a suggestion in the literature that the analogous $(Li^+)^-B^IH_2$ phase might be an intermediate in the thermal decomposition of $LiB^{III}H_4$. Compare also; (*b*) T. Jayasekharan and T. K. Ghanty, *J. Chem. Phys.*, 2006, **125**, 234106-1 where a larger set of species is studied, including Ng–Al connections.

86 Y. Y. Zhao, G. J. Wang, M. H. Chen and M. F. Zhou, *Eur. J. Inorg. Chem.*, 2005, **109**, 6621.

87 (*a*) Y. Ono, T. Taketsugu and T. Noro, *J. Chem. Phys.*, 2005, **123**, 204321–1; (*b*) Y. Taketsugu, T. Taketsugu and T. Noro, *J. Chem. Phys.*, 2006, **125**, 154308-1.

88 (*a*) Y. Ono and T. Taketsugu, *Monatsh. Chem.*, 2005, **136**, 1087; (*b*) Y. Ono and T. Taketsugu, *J. Chem. Phys.*, 2004, **120**, 6035.

89 Y. Y. Zhao, Y. Gong and M. F. Zhou, *J. Phys. Chem. A*, 2006, **110**, 10777.

90 G. E. Ball, T. A. Darwish, S. Geftakis, M. W. George, D. J. Lawes, P. Portius and J. P. Rourke, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 1853.

91 Xe binds easily to $Ti_2$ molecule: H. J. Himmel and A. Bihlmeier, *Chem.–Eur. J.*, 2004, **10**, 627.

92 K. Lutar, I. Leban, T. Ogrin and B. Žemva, *Eur. J. Solid State Inorg. Chem.*, 1992, **29**, 713.

93 K. Lutar, H. Borrmann and B. Žemva, *Inorg. Chem.*, 1998, **37**, 3002. Note that a range of compounds has been isolated: $MnF_4(XeF_2)_n$ ($n$ = 1, 0.5); $TiF_4(XeF_2)_n$ ($n$ = 1.5, 1, 0.5); $PdF_4(XeF_2)_n$ ($n$ = 4, 3, 2, 1, 0.5), $SnF_4(XeF_2)_n$ ($n$ = 0.75, 0.5), $VF_5(XeF_2)$ and even $VF_5(KrF_2)$. Unfortunately, the crystal structures of these species have not been refined, and many of them may be ionic compounds where $XeF^+$ cations can be distinguished; B. Žemva, personal communication.

94 These leading experts in fluorine chemistry have devoted a big part of their professional research to beautiful basic studies, for which a very limited number of sponsors can usually be found. In addition, fluorine chemistry in anhydrous HF can be dangerous, and Teflon vessel explosions may occasionally happen.

95 Danny Fredrickson, a theoretician, so commented on that: "Actually, my worst science-related injury occurred in the Hoffmann group offices. A large, heavy, antique balance fell off of one of the bookshelves and landed on my head, sending me to the hospital.".

96 (*a*) S. Borocci, N. Bronzolino and F. Grandinetti, *Chem. Phys. Lett.*, 2004, **398**, 357; (*b*) T. G. Wright, E. P.F. Lee, M. Hotokka and P. Pyykkö, *Chem. Phys. Lett.*, 2004, **392**, 281; (*c*) D. J. D. Wilson and E. I. von Nagy-Felsobuki, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3399; (*d*) See also the review on He–containing species: F. Grandinetti, *Int. J. Mass Spectrom.*, 2004, **237**, 243.

97 (*a*) M. W. Wong, *J. Am. Chem. Soc.*, 2000, **122**, 6289; (*b*) T. Takayanagi and A. Wada, *Chem. Phys. Lett.*, 2002, **352**, 91; (*c*) A. Lignell, L. Khriachtchev, M. Räsänen and M. Pettersson, *Chem. Phys. Lett.*, 2004, **390**, 256.

98 P. Antoniotti, N. Bronzolino and F. Grandinetti, *Eur. J. Inorg. Chem.*, 2003, **107**, 2974.

99 S. Borocci, N. Bronzolino and F. Grandinetti, *Chem. Phys. Lett.*, 2005, **406**, 179.

100 (*a*) P. Pyykkö, *Chem.–Eur. J.*, 2000, **6**, 2145; (*b*) P. Pyykkö, S. Riedel and M. Patzschke, *Chem.–Eur. J.*, 2005, **11**, 3511; (*c*) It should be relatively easy to bind many He atoms to very strong Lewis acids such as small multiply charged cations ($Al^{3+}$, $Sc^{3+}$, $Be^{2+}$). Our unpublished B3LYP/6-311++G** calculations show that $MHe_6^{3+}$ (M = Al, Sc) and $BeHe_4^{2+}$ are local minima, indeed.

101 J. Lundell, S. Berski and Z. Latajka, *Chem. Phys.*, 1999, **247**, 215.

102 A. Lignell, L. Khriachtchev, J. Lundell, H. Tanskanen and M. Räsänen, *J. Chem. Phys.*, 2006, **125**, 184514.

103 C. C. Lovallo and M. Kłobukowski, *Int. J. Quantum Chem.*, 2002, **90**, 1099.

104 H. Y. Wang, J. Szczepanski and M. Vala, *Phys. Chem. Chem. Phys.*, 2004, **6**, 4090.

105 M. Frankowski, A. M. Smith-Gicklhorn and V. E. Bondybey, *Can. J. Chem.*, 2004, **82**, 837.

106 E. C. Brown, A. Cohen and R. B. Gerber, *J. Chem. Phys.*, 2005, **122**, 171101.

107 Note that $XeO_2TeF_4$ is likely to be polymeric material: L. Turowsky and K. Seppelt, *Inorg. Chem.*, 1990, **29**, 3226.

108 A. M. Smith-Gicklhorn, M. Frankowski and V. E. Bondybey, *Mol. Phys.*, 2005, **103**, 11.

109 (*a*) W. A. Caldwell, J. H. Nguyen, B. G. Pfrommer, F. Mauri, S. G. Louie and R. Jeanloz, *Science*, 1997, **277**, 930. However, Xe may chance to co-alloy with Fe at the level of 1 mol%; (*b*) K. K. M. Lee and G. Steinle–Neumann, *J. Geophys. Res.*, 2006, **111**, B02202.

110 (*a*) C. Sanloup, B. C. Schmidt, E. M. C. Perez, A. Jambon, E. Gregoryanz and M. Mezouar, *Science*, 2005, **310**, 1174; (*b*) P. F. McMillan, *Science*, 2005, **310**, 1125.

111 (*a*) M. Ross, R. Boehler and P. Soderlind, *Phys. Rev. Lett.*, 2005, **95**, 257801. Compare also: (*b*) R. Boehler, M. Ross, P. Soderlind and D. B. Boercker, *Phys. Rev. Lett.*, 2001, **86**, 5731.

112 W. Grochala, DFT results (B3LYP/6-311++G** basis for light elements, LANL2DZ pseudopotential for Mn).

113 Seldomly, peroxide may be involved in one-electron oxidation.

114 Note, $\{Xe\cdots O_2\}^+$ was observed this year, but the O–O bond length testifies to it being $Xe^0\cdots(O_2^+)$ rather than the much less probable $Xe^I\cdots(O_2)$ or $Xe^{III}\cdots(O_2^{2-})$ valence structures of this species: M. Zhou, Y. Zhao, Y. Gong and J. Li, *J. Am. Chem. Soc.*, 2006, **128**, 2504.

115 (*a*) J. W. Lauher and K. Wald, *J. Am. Chem. Soc.*, 1981, **103**, 7648; (*b*) A. Avramopoulos, M. G. Papadopoulos and A. J. Sadlej, *Chem. Phys. Lett.*, 2003, **370**, 765.

116 When I talked to Prof. Saldej in Feb 2006, it turned out that he, also, has been thinking (since 2000) of the AuXeF isomer, *i.e.* preceding the discovery of XeAuF, and that his PhD student Zuzanna Benkova has calculated some properties of this and related molecules. Results of their calculations have never been published, and A. J. S. has kindly made this data available to me. We note that the AuXeF isomer was very recently predicted independently by Ghanty (ref. 63).

117 Z. Benkova, A. J. Sadlej, unpublished relativistic MP2 calculations for the AuNgF, HNgF and Ng-AuF species where Ng = Ar, Kr, Xe (the Douglas–Kroll approximation was employed and the Pol_dk basis sets were used for all elements).

118 Here, Xe must be treated as a reagent and therefore it should not constitute the matrix (Ar might be used for this purpose).

119 Citation from P. P. Edwards' *et al.* application to the Leverhulme Trust.

120 W. Grochala, R. Hoffmann, J. Feng and N. Ashcroft, *Angew. Chem., Int. Ed.*, 2007, **45**, 3620.

121 W. Grochala, DFT results (GGA/PBE calculation, cutoff of 300 eV, *k*-point grid of 4 × 3 × 4).

122 This unusual behaviour of the $XeF_4$ crystal violates the usual notion of 'hardness' and 'compressibility'. It turns out that firmly squeezed molecular crystals may be very hard and incompressible, provided they are composed of very electron-rich molecules. The repulsive lone pair/lone pair interaction prohibits polymerization and yet provides the efficient response of the crystal to external pressure.

123 W. Grochala, B3LYP results (SDD pseudopotential and concomitant 2ζ basis set for Xe, and the 6-311++G** basis set for F). The ZPE correction was applied.

124 A. Karpov, J. Nuss, U. Wedig and M. Jansen, *Angew. Chem., Int. Ed.*, 2003, **42**, 4818.

125 M. I. Eremets, K. Shimizu, T. C. Kobayashi and K. Amaya, *Science*, 1998, **281**, 1333. The metallization of CsI and of Xe was predicted by theory well before it was actually observed.

126 T. A. Grzybowski and A. L. Ruoff, *Phys. Rev. Lett.*, 1984, **53**, 489.

127 O. Schulte and W. B. Holzapfel, *Phys. Rev. B: Condens. Matter*, 1996, **53**, 569.

128 E. Kim, M. Nicol, H. Cynn and C. S. Yoo, *Phys. Rev. Lett.*, 2006, **96**, 035504.

129 W. Grochala, DFT results (GGA/PBE calculation, cutoff of 300 eV, k-point grid of 8 × 8 × 8). At 75 GPa, the formation of the HgXe alloy is beneficial by −0.33 eV in enthalpy, at the volume change of ~ −2 Å$^3$ per HgXe unit. At 100 GPa the reaction enthalpy amounts already to −0.85 eV. The presence of other phases, like $Hg_2Xe$ or $HgXe_2$, cannot be completely ruled out.

130 Even at this pressure the difference in enthalpy of the ccp and hcp phases of Xe, is not large, as typical for martensitic transformations. This is similar to the behaviors of Xe at 1 atm; see: *Rare Gas Solids*, ed. M. L. Klein and J. A. Venables, Academic Press, London, 1976, vol. 1 p. 574. (b) As usual in high-pressure synthesis, laser heating should be used to overcome kinetic barriers, followed by cooling of the reaction product.

131 This compound might also show two distinct $Hg^{II}$ cations in different homoleptic coordination environments, occurring as $(HgXe_2^{2+})(HgF_4^{2-})$.

132 R. Hoppe and R. Homann, *Z. Anorg. Allg. Chem.*, 1969, **369**, 212.

133 F. Schrotter and B. G. Müller, *Z. Anorg. Allg. Chem.*, 1992, **618**, 53.

134 When I showed an early draft of this paper (Mar 2006) to Ji Feng (Cornell), he came up with the exciting idea of preparing solids which contain extended 2D $(AuNg_2^{2+})$ networks. Importantly, the $(AuNg_2^{2+})$ unit is isoelectronic with $(CuO_2^{2-})$; the latter is a fundamental building block of the oxocuprate superconductors. This concept can probably be verified for the $(AuXe_2^{2+})(F^{1-})_2$ stoichiometry.

135 These results will be described in detail in a separate contribution: D. Kurzydłowski, W. Grochala, manuscript in preparation.

136 C. J. Evans and M. C. L. Gerry, *J. Am. Chem. Soc.*, 2000, **122**, 1560.

137 At 1 atm, AuF might adopt the infinite-chain structure taken by AuCl: T. Sohnel, H. Hermann and P. Schwerdtfeger, *J. Phys. Chem. B*, 2005, **109**, 526.

138 E. S. Shanley and J. L. Ennis, *Ind. Eng. Chem. Res.*, 1991, **30**, 2503.

139 Our preliminary GGA/PBE calculations show that the hypothetical xenon acetylenide $Xe^{II}(C_2^{2-})$ and xenon carbide $(Xe^{II})_2(C^{4-})$ are unlikely to form at pressures even as high as 200 GPa, and despite similar values of the first ionization potentials of Xe (12.13 eV) and C (11.26 eV).

140 E. Reny, S. Yamanaka, C. Cros and M. Pouchard, *Chem. Commun.*, 2000, 2505.

141 Only element 117 still awaits discovery. Element 118 (the heaviest 'noble' gas) has been discovered in 2006: Y. T. Oganessian *et al.*, *Phys. Rev. C*, 2006, **74**, 044602-1.

142 S. Berski, J. Lundell and Z. Latarka, *J. Mol. Struct.*, 2000, **552**, 223.

143 J. A. Panek, Z. Latajka and J. Lundell, *Phys. Chem. Chem. Phys.*, 2002, **4**, 2504.

144 W. Grochala and R. Hoffmann, *Angew. Chem., Int. Ed.*, 2001, **40**, 2743.

145 W. Grochala, *Nat. Mater.*, 2006, **5**, 513.

146 Ł Maj and W. Grochala, *Adv. Funct. Mater.*, 2006, **16**, 2061.

147 W. Grochala, R. G. Egdell, P. P. Edwards, Z. Mazej and B. Žemva, *ChemPhysChem*, 2003, **9**, 997.

148 M. S. Liao and Q. E. Zhang, *Eur. J. Inorg. Chem.*, 1998, **102**, 10647.

149 W. Grochala, B3LYP and MP2 results (SDD pseudopotential and concomitant 2ζ basis set for Xe, and the 6-311++G** basis set for Cl and F). The bond lengths and harmonic frequencies are listed according to DFT. Note, these are preliminary calculations, and bond lengths are not predicted here with great accuracy. They show bond stability trends rather then absolute values.

150 W. Grochala, B3LYP results (SDD pseudopotential and concomitant 2ζ basis set for heavy elements, 6-311++G** basis set for light elements). For XePtO, the ground state is predicted to be a triplet.

151 (*a*) T.-H. Li, C.-H. Mou, H.-R. Chen and W.-P. Hu, *J. Am. Chem. Soc.*, 2005, **127**, 9241; (*b*) Y.-L. Liu, L.-H. Chang, T.-H. Li, H.-R. Chen and W.-P. Hu, *Chem. Phys. Lett.*, 2007, **439**, 14.