

Noblesse Oblige

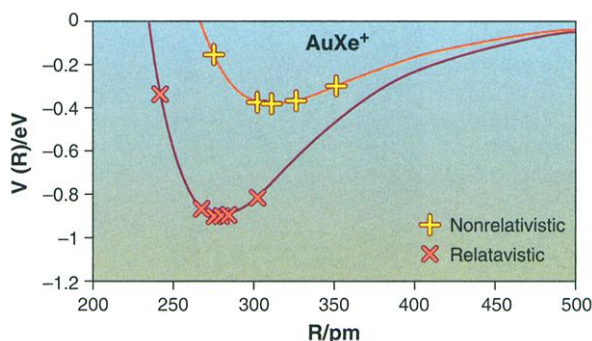
Pekka Pyykkö

The stable elements helium, neon, argon, krypton, and xenon were believed to be “noble gases” that eschewed all bonds until Bartlett (1) synthesized the first xenon compound in 1962. Noble gases are unreactive because they have completely filled outer electron shells, but Bartlett believed that it should not be not impossible to oxidize them. The ionization potential of xenon—the energy required to strip an electron from the element—is high but comparable with that of molecular oxygen. Hence, Bartlett argued, if the strong oxidant platinum hexafluoride could oxidize O_2 into the known compound $(O_2)^+(PtF_6)^-$, it should also be able to oxidize xenon. Indeed it did, and thus was the first noble gas compound made.

Since then, numerous noble gas compounds have been synthesized. Generally, gas-phase cations are easier to make than neutral species, and neutral species dispersed in noble gas matrices (cold environments containing excess noble gas) are easier to make than bulk compounds. Neutral species containing covalent bonds to light noble gases, such as argon, have until recently remained elusive. Khriachtchev *et al.* (2) have now synthesized the first neutral, covalently bonded argon compound, proving that such a bond is possible. And on page 117 of this issue, Seidel and Seppelt (3) report the first bulk compound containing a noble-gas–noble-metal bond, thus overcoming a double challenge as both noble gases and noble metals are considered unreactive.

The heavier noble gases xenon and krypton have a more varied chemistry than the lighter noble gases. Neutral compounds with Xe-H, Xe-S, Xe-Br, Xe-I, Kr-H, Kr-C, and Kr-Cl bonds have recently been made, mostly in noble gas matrices (4). It is important to note that these are covalent molecules, not weak van der Waals complexes. The total energy of such a molecule can be as high as that of the isolated atoms. Nevertheless, in sufficiently cold, frozen matrices, these exotic molecules are long-lived, trapped behind a barrier to dissociation.

In contrast to xenon and krypton, compounds containing argon—the noble gas that forms 0.93% by volume of the atmosphere—have been elusive. Its ionization



The role of relativity. In the diatomic $AuXe^+$, roughly half of the Au-Xe bond strength arises from relativistic effects. V , bonding energy; R , interatomic distance. Data from (7).

potential is very high, calling for a really electron-hungry oxidant. No bulk compounds of argon exist yet. A matrix species, $ArBeO$, was produced (5) following a theoretical proposal (6) that the strong electric field outside the small, highly charged Be^{2+} cation of BeO could bind rare-gas atoms through their electric polarizability. But the calculated Ar-Be bond energy is only 0.3 eV, and the bond can only be considered weakly covalent. In contrast, the matrix compound $HArF$ recently synthesized by Khriachtchev *et al.* (2) has a strongly covalent $(ArH)^+$ bond. The argon atom sits in the middle of the linear H-Ar-F structure. The $HArF$ molecules decompose if they come into contact with each other or are warmed up and can therefore not be isolated from the matrix.

Seidel and Seppelt (3) take noble gas bonds a step further, reporting a bulk compound held together by covalent bonds between gold and xenon. If gold were a truly noble metal and xenon a truly noble gas, such an Au-Xe bond would be impossible. In actual fact, noble metals such as platinum and gold have a rich chemistry. It has been theoretically predicted (7) that $XeAuXe^+$, which has the same number of valence electrons in similar molecular orbitals as the $ClAuCl^-$ anion, should possess short, strong covalent bonds between xenon and gold. The lighter rare gases were predicted to form similar, but more weakly bound systems. The simpler diatomic species, such as $AuXe^+$, were also predicted to have similar bonds.

Two of the predicted species, $AuXe^+$ and $XeAuXe^+$, have recently been observed experimentally by mass spectroscopy (8). Improved calculations gave a bond energy of 1.30 eV and a bond length

of 257.4 pm for $AuXe^+$. Seidel and Seppelt (3) have now produced the bulk compound $[AuXe_4^{2+}][Sb_2F_{11}^-]_2$. The crystallized compound is stable up to $-40^\circ C$, a remarkably high temperature for such an exotic species. In solution, the dark red

$AuXe_4^{2+}$ even remains stable up to room temperature if kept under a xenon pressure of about 10 bars. The crystal structure contains the planar, square cation $AuXe_4^{2+}$, with an average Au-Xe distance of 274 pm. This clearly is a bulk compound with covalent Au-Xe bonds. The calculated average Au-Xe bond energy is as much as 2.2 eV per bond, and this may be a lower limit (9).

Relativity plays a large role in stabilizing these Au-Xe compounds; about half of the Au-Xe bonding energy comes from relativistic effects (see the figure). The high nuclear charge of gold accelerates the 6s valence electrons to high speeds when they dive near the nucleus. In a simple picture, the consequent relativistic mass increase compresses and stabilizes the valence 6s shell. In addition, the interaction with the underlying $5d^{10}$ shell causes a local “gold maximum” of relativistic effects (10). This relativistic stabilization of the 6s shell makes covalent bonds to gold anomalously strong and short.

In addition to the gold-xenon species detected by mass spectroscopy (8) and in crystal and solution phase (3), a third class of noble-gas–noble-metal molecules was recently observed with microwave spectroscopy on molecular beams (11). These spectroscopically well-characterized neutral three-atom species contained the noble gases Ar or Kr, the metals (M) Cu, Ag, or Au, and the halogens (X) F, Cl, or Br. The calculated argon-metal bond energy was 0.49 eV for $ArCuF$ and $ArAuCl$. The molecular properties all point to a partial covalent bonding character of the noble-gas–noble-metal bond, but as in the case of the BeO moiety described above, the metal-halogen unit remains relatively unperturbed.

The bond length between two atoms in a compound gives an indication of the covalent character of the bond. The covalent radius of argon can be deduced from the strong covalent bonds of the two gas-phase ions ArH^+ and ArF^+ (12), which both give a lower limit of 98 pm. The H-Ar distance calculated for $HArF$, 133 pm (2), corresponds to an argon radius of 103 pm, near the suggested Ar covalent radius of 98 pm, with covalent radii for Be(II), Cu(I), Au(I),

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and the halogens as listed in (13); the effective Ar radius is 120 pm in ArMX and 126 pm in ArBeO. These values are clearly above the suggested Ar covalent radius, but far below the van der Waals radius of argon, 188 pm (14). Given their longer effective argon radii, the triatomic argon molecules reported in (6, 11) can only be weakly covalent.

More weakly bound, neutral complexes between xenon and transition metals have been made previously. For example, XeM(CO)₅ has a Xe-M dissociation energy of 0.36 eV for the three metals Cr, Mo, and W (15). Gas-phase cations with noble-gas-transition-metal bonds are also known but generally require a large positive charge of +2 or +3 on the metal. The doubly or triply charged helides such as VHe³⁺ or HePtHe²⁺ found by Müller, Tsong, and co-workers (16) in the debris of field-ion

microscope tips after a strong laser pulse are a striking example of this type of species.

The compounds reported in (2) and (3) show that noble gas chemistry is much richer than most chemists would expect. Hydridoargon fluoride, HARF, is the first neutral argon compound with a covalent chemical bond to argon, the abundant "rare" gas of the atmosphere. The Seidel-Seppelt compound is the first bulk compound with a covalent noble-gas-noble-metal bond. New chemical bonds between strange bedfellows, like noble metals and noble gases, can still be found.

References and Notes

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PERSPECTIVES: ATMOSPHERIC SCIENCE

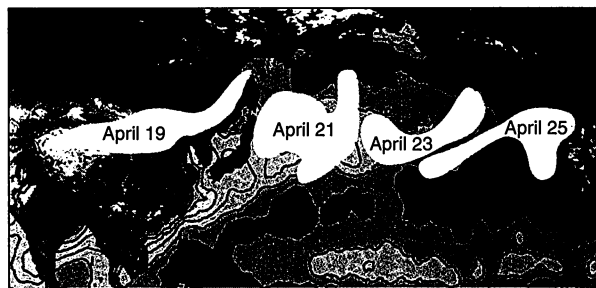
Trans-Pacific Air Pollution

Kenneth E. Wilkening, Leonard A. Barrie, Marilyn Engle

The once-pristine air above the North Pacific Ocean is polluted. Pollutants are transported on mid-latitude westerly winds from Eurasia to the Pacific Ocean basin and across to North America. The expected economic expansion around the Pacific Rim and in the rest of the world will deliver even more pollution unless preventative measures are taken. The risk of adverse effects to wildlife, ecosystems, climate, and human health throughout the Pacific region will increase. Even remote areas such as Arctic and alpine environments are threatened. Ocean productivity and the atmospheric energy budget over the North Pacific Ocean could be altered.

Earlier research exists (1), but two recent events have been particularly important in focusing researchers' attention on trans-Pacific pollutant transfer. In 1997, rapid transport of pollutants from Asia to the Olympic Peninsula of Washington State was observed (2). And in April 1998, satellite remote sensing showed aerosols being whisked across the Pacific to North America from a massive dust storm in

western China (see the figure) (3). Observational data, computer simulations, and research on pollutant concentrations in various media such as snow, fish, or eagles



Pollution from afar. Satellite remote sensing images of trans-Pacific transport of aerosols in April 1998 originating from a massive dust storm in China.

have since provided additional evidence of a potential pan-Pacific air quality problem. In July 2000, over 100 experts gathered in Seattle, Washington, to synthesize and evaluate the existing knowledge about trans-Pacific pollutant transport and identify research needs (4).

Pollutant transport across the Pacific is one of many intercontinental and trans-oceanic pathways of pollutant transport. Numerous routes exist within the Pacific region, but transport on the mid-latitude westerly winds is dominant. The pollutants may be particles or gases and include coal combustion aerosols, ozone, persistent organic pollutants (POPs), and heavy metals such as mercury. Unfortunately, there are insuffi-

cient observational data to provide more than a sketchy picture of transport routes and concentrations. The Pacific Exploratory Mission (PEM)-West campaigns, conducted in 1991 and 1994, were among the first large-scale programs to investigate long-range transport of pollutants in the Pacific (5). Soil dust transported from Asia has been observed at Mauna Loa Observatory in Hawaii for over 30 years; high concentra-

tions of anthropogenic pollutants (including sulfur, black carbon, and enriched trace metals) have also been measured (6). Pollutant outflow from the Asian continent into the air masses above the Pacific is found to be highest in the winter and spring seasons (5). Transit times across the Pacific during this period usually range from 5 to 10 days depending on altitude and weather patterns.

Pollution flowing off the Asian continent reaches North America episodically. At Cheeka Peak Observatory on the coast of Washington State, Jaffe and co-workers (7) have observed five springtime Asian pollution events since 1997. At Tagish in the Canadian Rocky Mountains, Bailey *et al.* (8) detected elevated levels of pesticides (lindane, chlordane, and DDT) during winter and spring and attributed them to pollution transported from continental Asia. Both studies used computer analysis to trace the origin of the polluted air masses.

Computer simulations of trans-Pacific air pollution transport are numerous. According to one study, between three and five important pollution events associated with

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