Formation of the Dixenon Cation, Xe_2^+, in Fluoroantimonate(v) Media by Oxidation–Reduction Methods: Spectroscopic Properties of the Ion

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Summary A green species has been generated both by oxidation of gaseous xenon with a dioxygenyl salt and by reduction in antimony pentafluoride solution of the XeF^+ cation, *e.g.* with water or a suitable metal; the Raman, u.v.-visible and e.s.r. spectra of the product are all consistent with the identity Xe_2^+, representing the first homonuclear noble-gas cation to be characterized in the condensed phases.

THE dixenon cation is readily formed in gaseous xenon, *e.g.* by collisions involving excited atoms [equation (1)]. Its

$$Xe^* + Xe \longrightarrow Xe_2^+ + e^- \qquad (1)$$

existence, hitherto acknowledged only in these circumstances, has been established mass spectrometrically,[1] by photoionization,[2] and by studies of elastic scattering.[3] Our recent studies give grounds for believing that Xe_2^+ can also be generated in conditions allowing its survival in the condensed phases.

When xenon reacts at room temperature with certain dioxygenyl salts, *e.g.* $O_2^+SbF_6^-$, a bright green colour is initially imparted to the solid.[4] As the reaction proceeds further, so the green colour gives place to the pale yellow colour characteristic of the ultimate solid product, XeF^+-$Sb_2F_{11}^-$ [equation (2)]. Solutions of the green species, indefinitely stable at ambient temperatures under a pressure of xenon, can also be prepared by the action, in limited supply, of water or other reducing agents, *e.g.* a metal like lead or mercury, on solutions of $XeF^+Sb_2F_{11}^-$ in antimony pentafluoride.

$$Xe + 2O_2^+SbF_6^- \longrightarrow XeF^+Sb_2F_{11}^- + 2O_2 \qquad (2)$$

The formation of the new species can be monitored as follows.

(i) E.s.r. spectrum: Figure 1 illustrates the e.s.r. spectrum associated with the green product when frozen in a matrix of antimony pentafluoride at 4·5 K; spectrum (a) corresponds to the product derived from the natural mixture of xenon isotopes, whereas spectrum (b) corresponds to the product derived from ^{136}Xe, for which $I = 0$. Spectrum (b) affirms the presence of a xenon-containing paramagnetic centre for which axial symmetry is implied. The *g*-factors thus deduced lend themselves, with the known abundances of xenon isotopes and the known ratio of the nuclear moments of ^{129}Xe and ^{131}Xe, to attempts to simulate spectrum (a). Identifying the paramagnetic centre not with a monoxenon (*e.g.* Xe^+ or Xe^{2+}) but with a dixenon unit is then wholly consistent with the features of the observed spectrum; less likely but not incontrovertibly excluded on these grounds are species containing more than two xenon atoms. Of hyperfine interaction implicating any nucleus other than xenon, *e.g.* ^{19}F, at least with $A > ca.$ 10 G,† there is no sign.

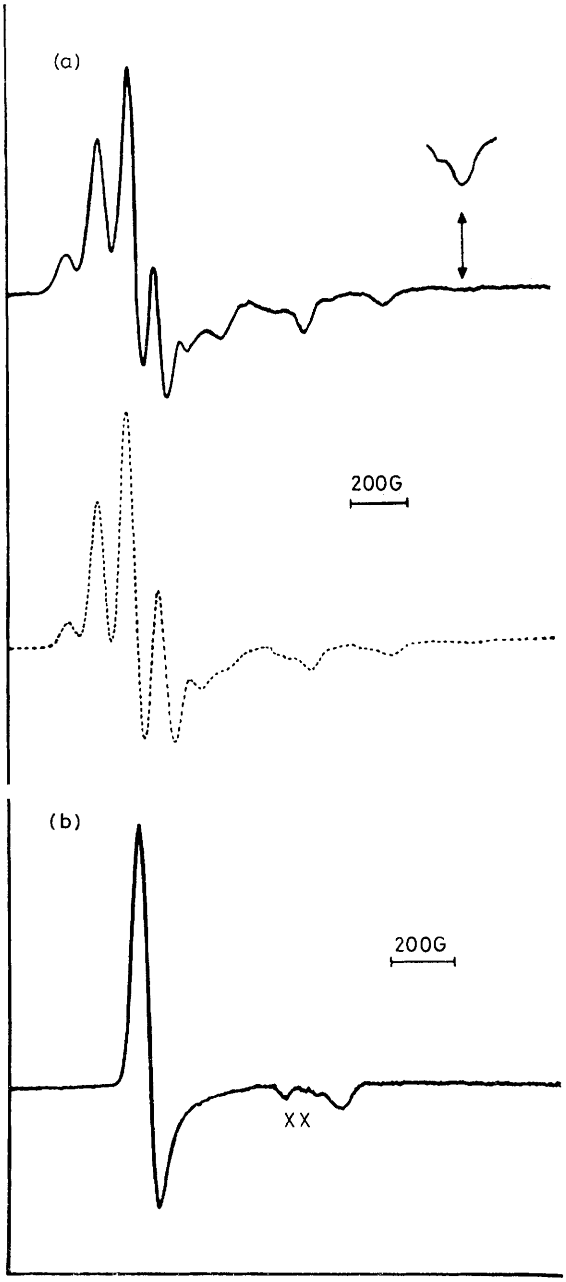

FIGURE 1. (a) E.s.r. spectrum of the green product derived from the natural mixture of xenon isotopes: ——, observed spectrum of the product frozen in a matrix of antimony pentafluoride at 4·5 K; the insert shows the weakest line at increased gain; – – – –, spectrum simulated for Xe_2^+ with $g_\perp = 2{\cdot}304$, $g_\parallel = 1{\cdot}885$, $A(^{129}Xe)_\perp = 220$ G, $A(^{129}Xe)_\parallel = 600$ G, $A(^{131}Xe)_\perp = 65{\cdot}2$ G, and $A(^{131}Xe)_\parallel = 178$ G.† (b) E.s.r. spectrum of the green product derived from ^{136}Xe frozen in a matrix of antimony pentafluoride at 4·5 K; X denotes an impurity band.

(ii) U.v.-visible spectrum: After exposure to moisture at room temperature, an antimony pentafluoride solution containing $XeF^+Sb_2F_{11}^-$ develops two prominent absorptions at 335 and 710 nm (Figure 2) as long as an overpressure of xenon is maintained.

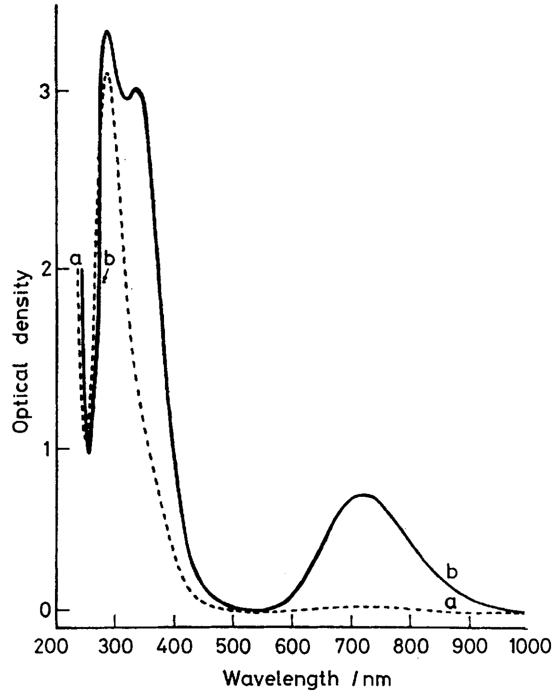

FIGURE 2. U.v.-visible spectrum (a) of a solution of $XeF^+Sb_2F_{11}^-$ in antimony pentafluoride (yellow); (b) of the same solution after exposure to humid air and with a 900 Torr over-pressure of xenon (green). The solution is held at *ca.* 300 K.

(iii) Raman spectrum: The production of the green colour, for example, by reduction of antimony pentafluoride solutions of $XeF^+Sb_2F_{11}^-$ with moisture is accompanied by the growth of a strong, polarized Raman line at 123 cm^{-1} (Figure 3). There is no other significant change, the remaining bands being attributable to vibrations of XeF^+,[5] $Sb_2F_{11}^-$, and the solvent. The new line does not shift when $H_2{}^{18}O$ supplants $H_2{}^{16}O$ as the reducing agent, and is unlikely therefore to arise from a xenon–oxygen species.

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† $1 G = 10^{-4}$ T.

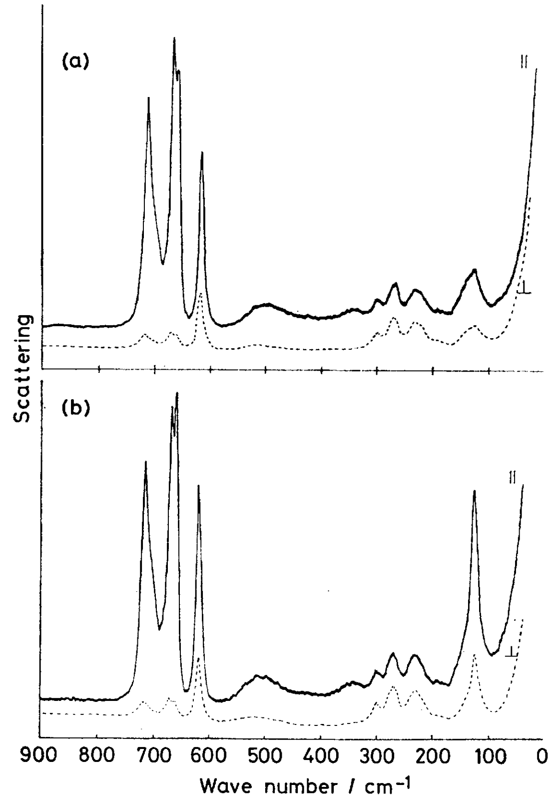

FIGURE 3. Raman spectra excited at 514·5 nm (a) of a solution of $XeF^+Sb_2F_{11}^-$ in antimony pentafluoride (yellow); (b) of the same solution after exposure to moisture and with an overpressure of xenon (green). The solution is held at *ca.* 320 K.

By contrast, replacement of the natural mixture of xenon isotopes by xenon-136 reduces the frequency of the band centre by $2{\cdot}4 \pm 0{\cdot}9$ cm^{-1} (*cf.* $2{\cdot}3$ cm^{-1} calculated for Xe_2^+). Varying the excitation wavelength from 514·5 to 676·4 nm causes a marked enhancement in the intensity of the line and the beginnings of a resonance Raman progression consistent with excitation into the absorption centred at 710 nm.

The consensus of our findings to date is that the green species is most plausibly identified with the dixenon(1+) cation Xe_2^+ formed either by oxidation of gaseous xenon or by reduction of XeF^+ [equation (3)]. The identity Xe_2^+ is

$$2\mathrm{Xe} \xrightarrow[\mathrm{O_2^+}]{-\mathrm{e}} \mathrm{Xe_2^+} \xleftarrow[\mathrm{H_2O,\ Pb,\ or\ Hg}]{+\mathrm{e}} 2\mathrm{XeF^+} \qquad (3)$$

also urged by the striking resemblance which the spectra bear to those of the isoelectronic I_2^- anion. As formed in an alkali iodide glass or in a hydroxylic solvent, I_2^- assumes a dark green colour with strong absorptions at 370—400 and 737—800 nm (*cf.* Figure 2),[6] whereas the resonance Raman spectra of matrix-isolated $M^+I_2^-$ ion-pairs (M = alkali metal) signify that $\omega_e = 114$—116 cm^{-1}.[7] Equally persuasive is the closeness with which our results are matched by *ab initio* calculations on Xe_2^+;[8,9] thus, with due allowance for spin–orbit coupling, such calculations impute to the two dipole-allowed electronic transitions highest in energy wavelengths of 375 and 775 nm and to the ground state a value of $\omega_e = 112$ cm^{-1}.[9] There have been previous allusions to transient green colourations accompanying certain reactions of XeF_2; for example, the system XeF_2–XeF_4–SbF_5 is said to afford a green paramagnetic intermediate, conceivably containing xenon(III).[10] We believe that some, possibly all, of these intermediates are identifiable with the species we judge to be Xe_2^+, the physical and chemical properties of which are now the focus of more detailed studies.

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