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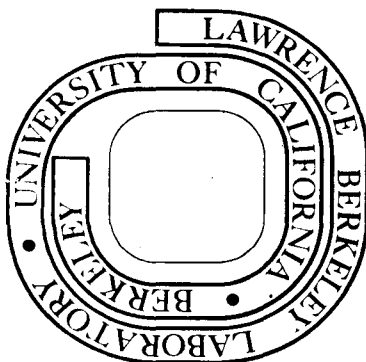
Kenneth S. Pitzer

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FLUORIDES OF RADON AND ELEMENT 118

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The formation and properties of radon fluoride have been studied by Stein¹ who found that a compound was readily formed but that its properties differed markedly from those of any xenon fluoride. Apparently radon fluoride does not vaporize as a molecular species but does decompose to the elements in a vacuum above 250°C. The writer² has considered relativistic effects in relation to chemical bonding in certain heavy elements and their compounds. Very briefly, it was found that relativistic s orbitals are suitable for bonding but that relativistic $p_{1/2}$ and $p_{3/2}$ orbitals are not. To obtain effective bonds the combination $1/3 p_{1/2} + 2/3 p_{3/2}$ must be taken which restores the angular properties of familiar non-relativistic orbitals. Relativistic differences in radial properties and in small components remain, of course.

As applied to the positive ion of a rare gas one concludes that the lowest energy state ($np_{1/2}^2 np_{3/2}^2, {}^2P_{3/2}$) is not effective in bonding. The valence state for bonding is at the energy $1/3 E({}^2P_{1/2}) + 2/3 E({}^2P_{3/2})$, i.e., higher by one third of the $p_{1/2} - p_{3/2}$ energy difference. This promotion energy is 0.44 eV for Xe, 1.42 eV for Rn, and 3.93 eV for element 118. The values for Rn and 118 come from calculations of Desclaux.³ While this promotion energy is moderate for Xe it is comparable to the energy of an electron pair bond in Rn and even larger for 118. Thus it is plausible that Rn and 118 fluorides are of an ionic rather than covalent character. While divalent ionic fluorides are possible, I consider in detail only the monovalent fluoride.

If molecular XeF_2 is stable in excess xenon as compared to an ionic crystalline Xe^+F^- , the negative enthalpy of formation of $\text{XeF}(\text{s})$ cannot be greater than about half that of XeF_2 , i.e., about 0.61 ev. If this value, $\Delta H_f = -0.61$ ev, is assumed for XeF , the ionic lattice energy is 10.76 ev, and a very approximate calculation indicates an $\text{Xe}^+ - \text{F}^-$ ionic distance of 2.34 Å. This is not unreasonable since $\text{Xe}^+ - \text{F}^-$ ionic distances range from 2.23 Å upward in various structures of solid XeF_6 and in complexes.⁴

For an estimate of the possible enthalpies of formation of ionic crystalline EF compounds of Rn and 118, we assume the above ionic lattice energy and the appropriate ionization potentials.³ Also one can assume the same bonding energy for a molecular EF_2 compound from $\text{E}^+ + \text{F}^- + \text{F}$ for radon and for 118 as for xenon, and this yields values of the enthalpy of formation of EF_2 . The results are shown on Figure 1. In the presence of excess fluorine, ionic XeF is unstable as compared XeF_2 by 0.61 ev while ionic RnF is stable by 0.37 ev and ionic 118F by 2.88 ev. These are very rough estimates, since both ionic lattice energies and bond energies will certainly change some from Xe to Rn to 118. Nevertheless, this shows that radon fluoride might be a simple Rn^+F^- ionic crystal (although an ionic RnF_2 is not necessarily excluded) and that the ionic crystal is strongly indicated for 118 fluoride.

An ionic crystalline form of RnF would be expected to be non-volatile, as observed, and to show the observed migration of Rn as a cation in electrolysis. This proposal

of ionic crystalline character for radon fluoride would appear to merit further consideration. Astatine fluoride shows a non-volatile character⁵ similar to that of radon fluoride and in contrast to other halogen fluorides. Thus an ionic crystalline state should also be considered for astatine fluoride. Although no detailed calculations have been made for that case, the same relativistic effects will occur as for radon.

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References

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Caption

Figure 1. Energies or enthalpies of various states related to rare gas fluorides; v.s. means valence state as described in the text.

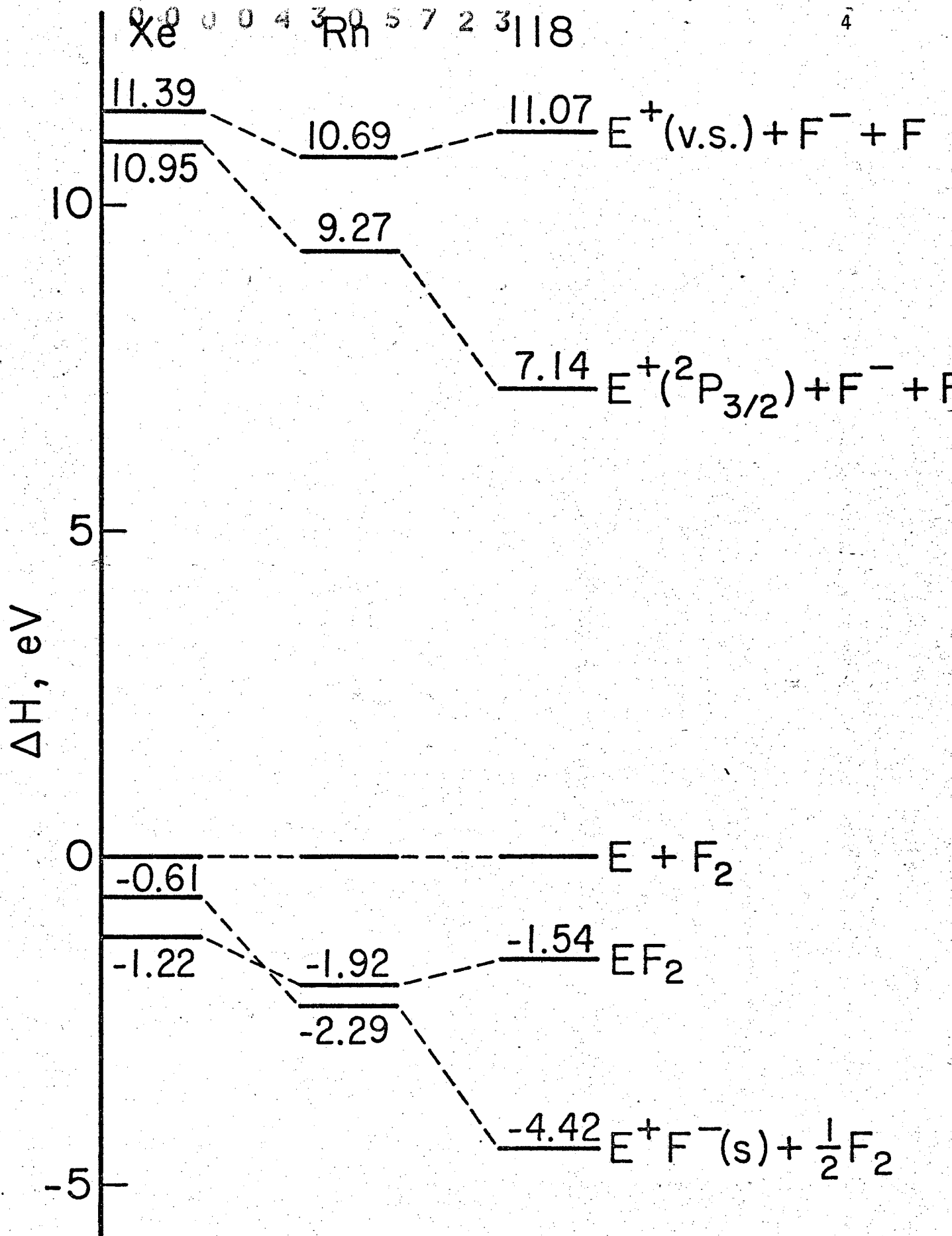


Fig. 1

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