Possible Argon Compounds

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Summary Theoretical investigation of the $^1\Sigma\sigma^2\pi^4\pi^{*4}$ state of ArF^+ and ArO has shown ArF^+ to be sufficiently stable to allow the probable isolation of $ArF^+ PtF_6^-$.

THE experimental bound-state chemistry of xenon and krypton is well characterized, but there are essentially no rigorous calculations on these systems. However, there are *ab initio* calculations on bound-state helium and neon compounds,[1] but no experimental verification. We have investigated ArF^+ and ArO by an LC(H–F)AO–MO–SCF procedure[2] with programmes developed in this laboratory.[3]

The $^1\Sigma\sigma^2\pi^4\pi^{*4}$ state of ArF^+ is calculated to be highly bound with $r_e = 1·8$ Å and D_e at least 70 kcal./mole; $D_e = E(R_{\max}) - E(r_e)$ [not E_∞)] as Hartree–Fock calculations often separate into mixture of states and/or do not converge at all for large internuclear distances. There appears to be clean separation to the allowed ^1S Ar + ^1D F^+. Open-shell states have not been studied and thus we cannot preclude level-crossing with the $^1\Sigma\sigma^2\sigma^{*2}\pi^4\pi^{*2}$ state or separation to ^2P Ar^+ + ^2P F. The Table contains the requisite R/E data for both $^1\Sigma\sigma^2\pi^4\pi^{*4}$ ArF^+ and ArO. As experimentally observed with Xe and probably with Kr,[4] and predicted for He and Ne,[1] the most logical compound to consider is $ArF^+ PtF_6^-$. Synthesis from Ar + F_2 + PtF_6 seems the simplest experimental route.

The $^1\Sigma\sigma^2\pi^4\pi^{*4}$ state of ArO was found to have a repulsive potential surface. This does not militate against the possibility of an open shell state with a potential minimum. The experimental data on ArO shows the species to be short lived but is insufficient to appraise whether the $^1\Sigma\sigma^2\pi^4\pi^{*4}$ or $^1\Sigma\sigma^2\sigma^{*2}\pi^4\pi^{*2}$ state was observed.[5]

R	$^1\Sigma\sigma^2\pi^4\pi^{*4}$ ArF^+	$^1\Sigma\sigma^2\pi^4\pi^{*4}$ ArO
2	−624·3423	−600·0240
3	−625·5038	−601·3177
3·5	−625·5399	
4	−625·5166	−601·4583
5	−625·4592	−601·4705
6	−625·4291	−601·4715
∞	−625·4153	

Internuclear distances in Bohrs; energies in Hartrees.

We are beginning an investigation of ArF_2 by VB to complement the theoretical data on the unbound HeF_2 and NeF_2 and the experimental data on the bound KrF_2 and XeF_2. If $ArF^+ PtF_6^-$ is stable, low temperature reaction with KF in an inert solvent should provide a viable synthetic route to ArF_2.

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[1] J. F. Liebman and L. C. Allen, submitted to *J. Amer. Chem. Soc.*

[2] The Ar wavefunctions were taken from S. Huzinaga, *J. Chem. Phys.*, 1969, **50**, 1371; the *s* functions of F were the *s* Gaussian lobes calculated by J. Whitten, *ibid.*, 1966, **44**, 359; 1965, **42**, 1293.

[3] See P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, in the press, for a description of the programme and method of calculation.

[4] Dr. N. Bartlett, personal communication.

[5] J. R. Wilt, Ph.D. Thesis, University of California, Los Angeles.