A Salt Chemistry of Light Noble Gas Compounds[1a]

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Abstract: Considering the stability of $XeF^+PtF_6^-$ and the absence of isolable He and Ne compounds (clathrates excluded) we have theoretically investigated diatomic cations of these elements. *Ab initio* molecular orbital wave functions were employed throughout our study. HeF^+ and NeF^+ have bound $^1\Sigma$ states of sufficient stability to allow synthesis of their PtF_6^- and SbF_6^- salts. On the basis of our calculations, we feel XeN^+ salts are feasible. The salts of HeO^+ and NeO^+ are expected to decompose to those of O_2^+.

Although the chemistry of xenon is well documented, the synthesis of helium and neon compounds (other than clathrates) has eluded all experimental attempts. This is supported by theoretical calculations of the lower noble gases which show the neutral compounds to be unbound with regard to the separated atoms.[2] On the other hand, singly charged diatomic cations should have at least one bound state,[3] and therefore we have investigated cations of the type HeX^+ and NeX^+ (where X is one of the elements H through Ne). Because of the Madelung energy (ionic crystal coulombic stabilization) the thermodynamically unfavored HeX^+ and NeX^+ cations should be stabilized in an ionic crystal[4] and since they are anticipated to have a high electron affinity, the logical counterions are SbF_6^- and PtF_6^-. Fortunately use of Born–Haber cycles permits almost all of the relevant data to be obtained from the potential curve of the positively charged diatomics.

HeH^+ and He_2^+ (and neon analogs) are highly stable species which have been thoroughly studied in gas phase experiments and by theoretical computations. But ionic crystals formed from these cations are unlikely to be stable because of the excessive electron affinity of He_2^+ even for such nonbasic and highly electronegative anions as SbF_6^- and PtF_6^-. With this in mind, we have calculated the potential curves for most of the lower electronic states of HeF^+, HeN^+, NeF^+, and NeN^+. $HeF^+SbF_6^-$ and $NeF^+SbF_6^-$ appear to be on the fringe area of stability[5] as $^1\Sigma\pi^4$ HeF^+ is bound by 33 kcal/mol and $^1\Sigma\pi^{*4}$ NeF^+ is bound by 30 kcal/mol. HeN^+ and NeN^+ are insufficiently bound in chemically interesting states to allow synthesis of crystalline salts. However, we anticipate XeN^+ should be sufficiently stable to be isolable as a crystalline salt.

Method of Calculation

Our wave functions are *ab initio* LCAO-MO-SCF solutions computed by means of an external set of automatic digital computer programs developed in this Laboratory.[6] The atomic basis orbitals are very close to the optimum (Hartree–Fock) form. Energies of these atoms are given in Table I. All of the two-electron multicenter molecular integrals were evaluated using the appropriate closed form and asymptotic expressions. An open shell procedure was used following Roothaan's method[7] to calculate the energy of the individual MO's, the energy components, and the total energy. The electronic states were determined by specifying the proper symmetry orbitals and open shell coefficients.

Table I. Atomic Data[a]

Species	State	Energy, hartrees
He	^1S	−2.8609
He^+	^2S	−2.0000
N	$^4Sp^3$	−54.3823
N	$^2Dp^3$	−54.2832
N	$^2Pp^3$	−54.2122
N	$^2Pp^5$	−53.2024
N^+	$^3Pp^2$	−53.8223
N^+	$^1Dp^2$	−53.7514
N^+	$^1Sp^2$	−53.6449
N^+	$^3Pp^4$	−52.8084
N^+	$^1Dp^4$	−52.7375
N^+	$^1Sp^4$	−52.6311
O	$^1Sp^4$	−74.5911
F	$^2Pp^5$	−99.3862
F^+	$^3Pp^4$	−98.7073
F^+	$^1Dp^4$	−98.6157
F^+	$^1Sp^4$	−98.4783
Ne	$^1Sp^6$	−128.5158
Ne^+	$^2Pp^5$	−127.6716

[a] Out calculated data are usually within a few hundredths of a hartree from Clementi's (E. Clementi, *IBM J. Res. Develop.*, **9**, 2 (1965), and supplement). Some of these states have hitherto not been calculated or measured. Although these numbers are considerably higher than experimental values, the order of the states and relative energies are preserved, thus giving us confidence in the adequacy of the results. In all tables but Table II, energies are given in hartrees, distances in bohrs.

It is well known that HF theory often predicts the wrong dissociation limit for a diatomic; however, because of symmetry constraints most of the open-shell molecules which have been considered here separate as one would predict from the Wigner–Wittmer rules.[8]

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(2) L. C. Allen, A. M. Lesk, and R. M. Erdahl, *J. Amer. Chem. Soc.*, **88**, 615 (1966).

(3) A plausible but not rigorous reasoning is as follows. At large R, the separated species have an attractive potential that goes as $1/R^4$ (ion–induced dipole). At small R, the nuclear repulsion dominates and introduces a $1/R$ potential. Thus since the potential is continuous, it must cross $E = 0$ to connect the two parts, therefore providing a potential well. London dispersion forces are not considered in the molecular orbital method which we used as our principal computational tool.

(4) This appears to be a general property for all otherwise thermodynamically unfavored ions.

(5) N. Bartlett, in a private communication, indicated this and cited that the Xe–F and Kr–F bond strengths in the difluorides were much weaker than in XeF^+ and KrF^+.

(6) See P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **51**, 3286 (1969), for example.

(7) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).

(8) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1950.

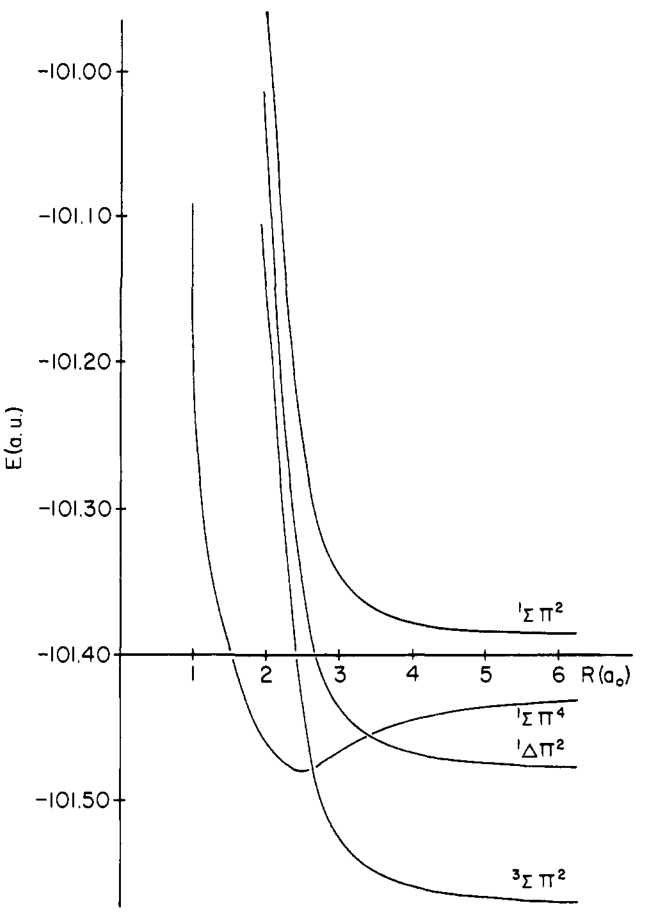

Figure 1. The potential curves for HeF$^+$ in the $^1\Sigma\pi^4$, $^1\Sigma\pi^2$, $^1\Delta\pi^2$, and $^3\Sigma\pi^2$ states.

The absence of instantaneous electron–electron correlation effects in the Hartree–Fock approximation leads to molecular binding energies that are markedly too low but this error is less pronounced for positive ions. This situation is advantageous for the present work because it provides a built in conservative bias on the extent of binding predicted. It is also important to be certain that the Hartree–Fock solution leads to a repulsive potential curve when this is appropriate chemically. For our cases we have computationally confirmed the correct behavior by essentially reproducing high-accuracy valence-bond-generated repulsive potential surfaces for HeO and NeO, which are known to dissociate properly (see Figure 1 of ref 1).

Results

Since we are concerned with low-Z rare gas ions for salts, the electronic states of greatest interest are those which are bound. Table II contains a summary of the theoretical data on the separation behavior, equilibrium bond distance, and dissociation energy of the bound states.

Table II. Summary of Data on Bound States

Compound	State	Separation behavior[a]	r_e, Å[b]	D_e, kcal[b,c]
HeF$^+$	$^1\Sigma\pi^4$	(He(^{1}S) + F$^+$(^{1}S)) + (He$^+$(^{2}S) + F(^{2}P)) + (He(^{1}S) + F$^+$(^{1}D))	1.33^B	33^B
NeF$^+$	$^1\Sigma\pi^{*4}$	(Ne(^{1}S) + F$^+$ (^{1}S)) + (Ne$^+$(^{2}P) + F(^{2}P)) + (Ne(^{1}S) + F$^+$(^{1}D))	1.65^B	30^B
HeN$^+$	$^1\Sigma\pi^4$	(He(^{1}S) + N$^+$(^{1}Sp^4)) + (He(^{1}S) + N$^+$(^{1}Dp^4))	1.06	127
HeN$^+$	$^1\Sigma\pi^2$	(He(^{1}S) + N$^+$(^{1}Sp^2)) + (He(^{1}S) + N$^+$(^{1}Dp^2))	2.12	~1
HeN$^+$	$^1\Delta\pi^2$	(He(^{1}S) + N$^+$(^{1}Dp^2))	2.12	~1
HeN$^+$	$^3\Sigma\pi^2$	(He(^{1}S) $^+$ N$^+$(^{3}Pp^2))	2.12	~1
NeN$^+$	$^1\Sigma\pi^{*4}$	(He(^{1}S) + N$^+$(^{1}Dp^4))	1.59	66

[a] When more than one state is given, this means $E(r_{\max})$ is bounded by the energies of the states. In all cases, the Wigner–Wittmer rules are obeyed. The states are given in descending order of energy. In subsequent tables $E(r = \infty)$ is given for that symmetry-allowed state of energy closest to $E(r_{\max})$ and the separated species are given in a footnote along with other possible separated species. The absence of correlation energy would help both to define the exact separated energy and also probably help the binding energy. The qualitative conclusions are probably valid although precise curve crossings are not attainable at this level of theory. As spin–orbit coupling does not connect $^1\Sigma$ and $^1\Delta$ (or $^3\Sigma$) states, salts of HeF$^+$ and NeF$^+$, the compounds of greatest synthetic interest, are still predicted to be isolable. [b] The r_e and D_e marked by B were determined by fitting three neighboring points to a parabola. The other cases had r_e chosen as that value of R such that $E(R)$ was minimum of those R's determined. [c] $D_e = E(r_{\max}) - E(r_e)$. This definition is used rather than $D_e = E(r = \infty) - E(r_e)$ because of the occasional absence of a unique state on separation.

Before discussing the detailed nature of the states of the positive ions, it is useful to recognize two phenomena characteristic of these diatomics. First, the HeN$^+$ and the NeN$^+$ species decompose into the appropriate ^{1}S rare gas and N$^+$ manifolds. However HeF$^+$ and NeF$^+$ bound states and the unbound $^1\Sigma\pi^2$ HeF$^+$ form F and He$^+$, or Ne$^+$. This could have been anticipated because the ionization potential of He or Ne is commensurate with F to form ^{1}S, but much higher than is needed to form the ground state ^{3}P F$^+$. Second, there is the rather subtle difference in the charge distribution for $^1\Sigma\pi^4$ HF and HeF$^+$. In a qualitative valence bond sense

$$\psi_{\mathrm{HF}} = c_1\psi_{\mathrm{H^+F^-}} + c_2\psi_{\mathrm{HF}} + c_3\psi_{\mathrm{H^-F^+}}$$

$$\psi_{\mathrm{HeF^+}} = d_1\psi_{\mathrm{He^{2+}F^-}} + d_2\psi_{\mathrm{He^+F}} + d_3\psi_{\mathrm{HeF^+}}$$

Whereas for HF, c_1 and c_2 are large but c_3 is almost 0, in HeF$^+$ d_2 and d_3 are large but d_1 almost vanishes; thus these two isoelectronic systems have opposite polarity.

Furthermore, the separation He$^+$ (or Ne$^+$) + F seems to violate expectations from electronegativity. The Pauling electronegativity of F is 4, and by using the Mulliken definition, that of He is about 5, and that of Ne about 4. (A more general definition of electronegativity is described in the Appendix.)

Let us consider the detailed behavior of the ions HeF$^+$, NeF$^+$, HeN$^+$, and NeN$^+$. In HeF$^+$ only the $^1\Sigma\pi^4$ state is bound, having an equilibrium separation of 1.33 Å. As shown numerically in Table III, and graphically in Figure 1, the other states constructible from the same basis set, the $^1\Sigma\pi^2$, $^1\Delta\pi^2$, and $^3\Sigma\pi^2$, are all unbound and separate correctly. As these states have no potential minimum, there is no chemistry directly from these states. States of the same spin and symmetry are not permitted to cross in diatomics and the $^1\Sigma\pi^4$ and $^1\Sigma\pi^2$ curves do not intersect. The $^1\Delta\pi^2$ curve intersects the $^1\Sigma\pi^4$ curve at about 1.8 Å, but at the minimum of the latter, the former state is about 13 kcal higher. $^1\Delta\pi^2$ is always higher than the minimum of $^1\Sigma\pi^4$ in spite of the fact that at $r = \infty$ (^{1}S He + ^{1}Dp^4 F$^+$), the energy difference is only about 6 kcal. Even if there were sufficient spin–orbit coupling to facilitate

Table III. The HeF^+ and NeF^+ Manifolds

R/E	HeF^+ $^1\Sigma\pi^4$	$^1\Sigma\pi^2$	$^1\Delta\pi^2$	$^3\Sigma\pi^2$	NeF^+ $^1\Sigma\pi^{*4}$
1	−101.1215	−97.3282	−97.4198	−97.5115	
2	−101.4620	−100.9646	−101.0562	−101.1478	−226.7227
2.5	−101.4840[b]	−101.2572	−101.3489	−101.4405	
3	−101.4660	−101.3478	−101.4394	−101.5311	−227.1337[g]
4	−101.4386	−101.3820	−101.4736	−101.5652	−227.1072
5					−227.0909
6	−101.4308	−101.3849	−101.4766	−101.5682	−227.0868
∞[a]	−101.3862[c]	−101.3862[c,d]	−101.4766[e]	−101.5682[f]	−227.0578[h]

[a] Although diatomics in the Hartree–Fock model often separate in the wrong way, it is still meaningful to consider the energy of the $r = \infty$ state as the sum of the energies of the appropriate monatomic species. The energy given is either for the single infinite separation state or for that state whose energy is the closest. In either case appropriate separation data are given in the footnotes. [b] The energy minimum was found at 2.52 a_0 with a total energy of −101.48405 au by doing a least-squares fit to a parabola. [c] It is logical that these two states should have the same energy. The energy given here, −101.3862 au, corresponds to $He^+(^2S) + F(^2P)$, while $He(^1S) + F^+(^1S)$ has a total energy of −101.3392 au and $He(^1S) + F^+(^1D)$ has an energy of −101.4766 au. Based on the VB results on HeO and NeO, it is not surprising that some of the latter state is mixed in to the wave function. [d] This corresponds to the correct and *a posteriori* reasonable $He^+(^2S) + F(^2P)$. [e] The separated species are $He(^1S) + F^+(^1D)$. [f] The separated species are $He(^1S) + F^+(^3P)$. [g] The fitted potential minimum is $r_e = 3.12\ a_0$, $E(r_e) = -227.1349$. [h] This corresponds to separation to $Ne^+(^2P) + F(^2P)$. Separation to $Ne(^1S) + F^+(^1D) = -227.1315$ au.

$^1\Sigma \rightarrow {}^1\Delta$ and predissociate the diatomic, there should still be sufficient vibrational states from the $^1\Sigma$ to characterize it and stabilize the crystal. The crossing of the $^3\Sigma\pi^2$ and $^1\Sigma\pi^4$ occurs very slightly beyond the minimum of the latter. As $^3\Sigma \leftrightarrow {}^1\Sigma$ transitions are forbidden for light atoms, again there is no decomposition. Since the counterion contains the heavy atom Sb or Pt, there exists the very slight possibility of $^1HeF^+MF_6^- \rightarrow {}^3HeF^+MF_6^-$ by long-range spin–orbit coupling. An alternative path for dissociation is electron transfer, $^1HeF^+MF_6^- \rightarrow {}^2HeF + MF_6$, as HeF is unbound. This, too, is unlikely at low temperatures. The spin-flipping processes corresponding to $^1\Sigma HeF^+ \rightarrow {}^1\Delta HeF^+$ and to $^3\Sigma HeF^+$ are increasingly facile with increase in Z for the rare gases. However, by examination of ionization potentials, this decomposition will not occur spontaneously as the total energy for ^1S Ar, Kr, Xe + ^3P F^+ is higher than for ^2P Ar^+, Kr^+, Xe^+ + ^2P F. It is thus logical to surmise that the corresponding $^1\Sigma\pi^{*4}$ state is lower in energy than the $^3\Sigma\pi^{*2}$ state.

In Table III, there are also the data on the bound $^1\Sigma\pi^{*4}$ state of NeF^+. The equilibrium bond distance is 1.65 Å and the dissociation energy is 30 kcal/mol. Comparison of NeF^+ with F_2 and HeF^+ with HF is improper as noted. A check (Table IV) shows that HeO and NeO are unbound in at least the $^1\Sigma$ configuration. (See also Figure 2 for the potential curves of the closed shell oxides and fluorides.) Therefore, it is not obvious why HeF^+ should be more stable than NeF^+. A partial explanation is lone-pair repulsion or equivalently the presence of filled π^* orbitals in NeF^+, as shown by the appropriate molecular orbitals for the two systems.

Table IV. The HeO and NeO Manifolds

R/E	HeO $^1\Sigma\pi^4$	NeO $^1\Sigma\pi^{*4}$
1	−75.9945	
2	−77.4204	−202.6191
3	−77.5232	−203.1446
4	−77.5320	−203.1854
5		−203.1877
6	−77.5328	−203.1878
∞	−77.4520[a]	−203.1878[b]

[a] This corresponds to separation to $He(^1S) + O(p^4\ ^1S)$. [b] This corresponds to separation to $Ne(^1S) - O(p^4\ ^1S)$.

$$HeF^+\ 1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 1\pi_x^2\ 1\pi_y^2$$

$$NeF^+\ 1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 5\sigma^2\ 1\pi_x^2\ 1\pi_y^2\ 1\pi_x^{*2}\ 1\pi_y^{*2}$$

All of these considerations lead to the study of HeN^+ and NeN^+ where the number of π (or π^*) electrons is reduced by two, and the internuclear repulsion is also diminished. The fact that V_{nn} is larger for NeF^+ than

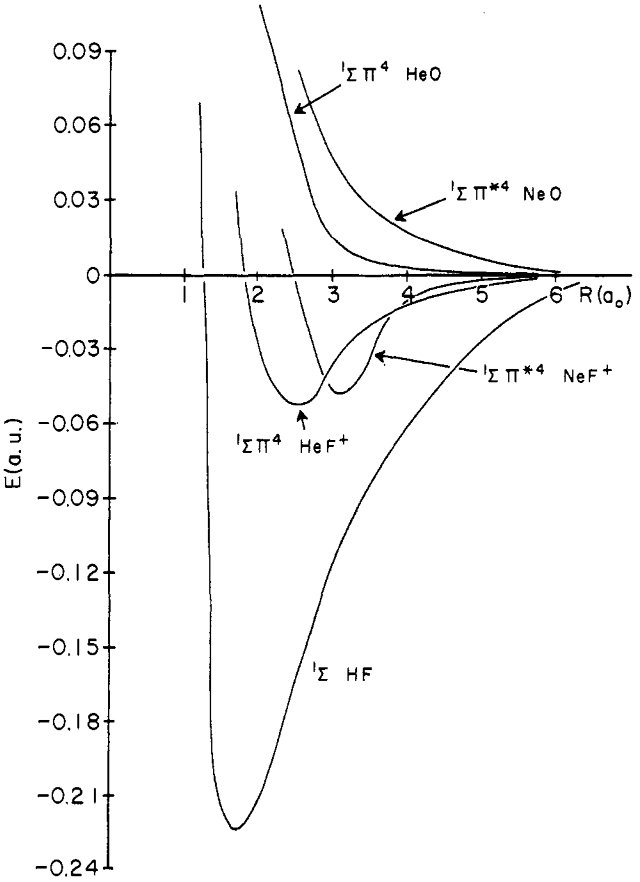

Figure 2. The potential curves for the closed-shell oxides and fluorides: $^1\Sigma\pi^4$ HeF^+, $^1\Sigma\pi^4$ HeO, $^1\Sigma\pi^{*4}$ NeF^+, $^1\Sigma^{*4}$ NeO, and $^1\Sigma$ HF. The $^1\Sigma$ HF results were the experimental ones taken from D. Steele, E. R. Lippincott, and J. T. Vanderslice, *Rev. Mod. Phys.*, **34**, 239 (1962).

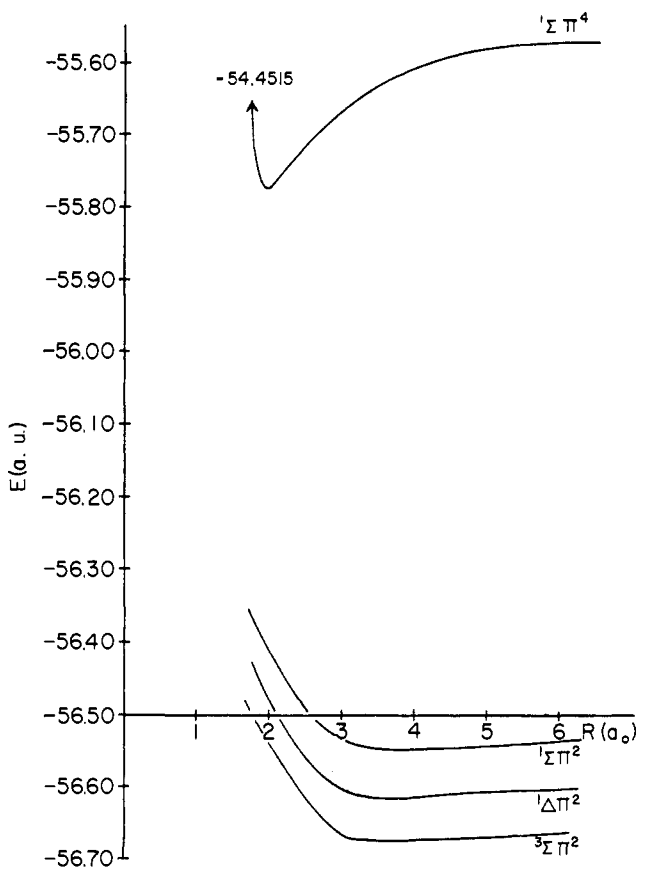

Figure 3. The potential curves for HeN^+ in the $^1\Sigma\pi^4$, $^1\Sigma\pi^2$, $^1\Delta\pi^2$, and $^3\Sigma\pi^2$ states.

for HeF^+ offers another partial explanation for the larger dissociation energy of the latter. Another motivation for investigating the nitrides is the lower electronegativity of N than F which will lower the electron affinity of the diatomic. The approximate VB wave function of HF *vs.* HeF^+ indicates that a less electronegative atom on He or Ne would reduce d_1 and d_2 and thus stabilize the compound by reducing the charge on the rare gas. This is in opposition to neutral rare gas compounds when it is desirable to have a highly electronegative group attached to stabilize ionic resonance contributors.

Four states can be constructed for HeN^+: $^1\Sigma\pi^4$, $^1\Sigma\pi^2$, $^1\Delta\pi^2$, and $^3\Sigma\pi^2$. All can be related to the corresponding states for HeF^+ by removing two electrons from the highest occupied σ orbital and lowering the nuclear charge by two (see Table V and Figure 3).

Table V. The HeN^+ Manifold

R/E	$^1\Sigma\pi^4$	$^1\Sigma\pi^2$	$^1\Delta\pi^2$	$^3\Sigma\pi^2$
1	−54.4515	−54.7313	−54.8022	−54.8732
2	−55.7759	−56.4103	−56.4813	−56.5572
3	−55.6675	−56.5381	−56.6090	−56.6800
4	−55.5999	−56.5425	−56.6134	−56.6844
5	−55.5787	−56.5415	−56.6125	−56.6834
6	−55.5730	−56.5413	−56.6123	−56.6832
∞	−55.5984[a]	−56.5058[b]	−56.6123[c]	−56.6832[d]

[a] This corresponds to separation to He(^1S) + N^+($^1Dp^4$). Separation to He(^1S) + N^+($^1Sp^4$) gives a separated atom energy of −55.4920 au. [b] This corresponds to separation to He(^1S) + N^+($^1Sp^2$). Separation to He(^1S) + N^+($^1Dp^2$) gives a separated atom energy of −56.6123 au. [c] This corresponds to separation to He(^1S) + N^+($^1Dp^2$). [d] This corresponds to separation to He(^1S) + N^+($^3Pp^2$).

The first state is highly bound with an r_e = 1.06 Å and D_e = 127 kcal. As it separates to a p^4 N^+ state, it is not unexpected that the total energy will greatly exceed those of the states which separate to a p^2 N^+ state. Radiative and radiationless transitions to the lower $^1\Sigma\pi^2$ state preclude any salt chemistry for this state. The remaining three states are very slightly bound (r_e = 2.12 Å and D_e = 1 kcal)—certainly insufficient for crystalline binding. As is to be expected, $^2\Pi\pi^3$ HeN, $^1\Delta\pi^2$ HeN^-, and $^3\Sigma\pi^2$ HeN^- are all unbound (see Table VI).

Table VI. The HeN, HeN^- Manifolds

	HeN	HeN^-	
R/E	$^2\Pi\pi^3$	$^3\Sigma\pi^2$	$^1\Delta\pi^2$
1	−55.4143	−52.4895	−52.4186
2	−56.9504	−56.3301	−56.2592
3	−57.0840	−56.9207	−56.8498
4	−57.1065	−57.0223	−56.9514
5	−57.1084		
6	−57.1086		
∞	−57.0731[a]		

[a] This corresponds to separation to He(^1S) + N($^2Pp^3$) while He(^1S) + N($^2Dp^3$) gives a total energy of −57.1441.

Preliminary calculations on NeN^+ show the $^1\Sigma\pi^{*4}$ state to be highly bound and the $^1\Sigma\pi^{*0}$ state to be unbound (see Table VII). As with the $^1\Sigma\pi^4$ HeN^+, the total energy of the $^1\Sigma\pi^{*4}$ is too high to allow salt formation. The open shell $^1\Sigma\pi^{*2}$, $^3\Sigma\pi^{*2}$, and $^1\Delta\pi^{*2}$ states are being investigated, and are expected to be bound in analogy to the isoelectronic states of O_2.

Table VII. The NeN^+ Manifold

R/E	$^1\Sigma(\pi^{*4})$	$^1\Sigma(\pi^{*0})$
2	−181.0764	−180.7743
3	−181.3585	−182.0436
4	−181.2882	−182.2097
5	−181.2550	−182.2296
6	No convergence	−182.2317
∞	−181.2533[a]	−182.2672[b]

[a] This corresponds to Ne(^1S) + N^+($^1Dp^4$). Ne(^1S) + N^+($^1Sp^4$) gives a separated atom energy of −181.1469 au. [b] This corresponds to separation to Ne(^1S) + N^+($^1Dp^2$). Ne(^1S) + N^+($^1Sp^2$) gives a separated atom energy of −182.1607 au.

Syntheses and Stability of Rare Gas Cations and Salts

We are interested in isolable salts of He- and Ne-containing cations. The logical counterions are SbF_6^- and PtF_6^- as they have ionization potentials greater than 6 eV. Although this is much higher than probably any other anion, it is not high enough to prevent $He_2^+SbF_6^- \rightarrow 2He + {}^1/_2F_2 + SbF_5$ from occurring spontaneously. This also applies to salts of $HeNe^+$ and Ne_2^+ and with the anion PtF_6^-. Similarly NeH^+ is easy to prepare and might also appear as an obvious candidate for the formation of salts. However, extrapolation of the acidities of NH_4^+, H_3O^+, H_2F^+ to NeH^+ leads to Ne + $HSbF_6$ as being more stable than $NeH^+SbF_6^-$. (HeH^+ is expected to be an even stronger acid.)

It is important to note the pertinent experimental data which currently exist. HeF^+ has been synthesized in an arc discharge and monitored in a mass spectrometer from an He–F_2, –BF_3, or –RuF_5 gas mixture.[9] Since HeF_2 is unbound with regard to the separated atoms,[2] the experimental observation[9] of HeF_2^+ and HeF_2^{2+} is of interest.[10] Analogous gaseous ion–molecule reactions yield ArN^+ from Ar and N_2.[11] Neither reaction is immediately amenable for the synthesis of crystalline salts.

On the basis of our calculations and the above experimental data, we believe the following syntheses to be viable. HeF^+ and NeF^+ should be accessible by the high-temperature, high-pressure reaction of He (or Ne), F_2, and either SbF_5 or PtF_6. This reaction is suggested by the synthesis of NF_4^+,[12] since NF_3, like He and Ne, is a very weak base with a high ionization potential.

We have not as yet mentioned salts of HeO^+ or NeO^+, although we feel these cations will be bound. There are, however, two synthetic problems.

There is no chemical source of O^+ since O_2^+ is a highly stable species which is usually formed instead of other oxygen cations. For example

$$O_2F_2 + SbF_5 \longrightarrow O_2^+SbF_6^- + {}^1/_2F_2$$

instead of O_2F^+ or O_2^{2+}, but[13a]

$$N_2F_2 + SbF_5 \longrightarrow N_2F^+SbF_6^-$$

The above synthesis of O_2^+ is a reduction reaction. It can also be prepared oxidatively

$$O_2 + PtF_6 \longrightarrow O_2^+ + PtF_6^-$$

but[13b]

$$Xe + PtF_6 \longrightarrow XeF^+PtF_6^-,\ Pt_2F_{11}^-$$

The above mitigates against syntheses such as $2He + O_2F_2 + 2SbF_5 \rightarrow 2HeO^+SbF_6^-$. On the other hand, we do not expect this problem with N- or F-containing salts since the ionization potential of O_2 is less than N_2 or F_2, but the ionization potential of O is higher than that of N.[14]

As HeO^+ is an open shell molecule (but the ground state of HeF^+ is $^1\Sigma\pi^4$), the following reaction is facilitated

$$2HeO^+SbF_6^- \longrightarrow 2He + O_2^+Sb_2F_{11}^- + {}^1/_2F_2$$

(likewise with NeO^+ and with PtF_6^-), since open-shell molecules should have a greater cross section for reactive scattering. For closed-shell molecules like HeF^+, $^1\Sigma\pi^4$, there should be a lower efficiency of reaction because of inherent closed-shell repulsion.

It is well known that Hartree–Fock calculations usually give approximately 50% of the total molecular binding energy, although over 99% of the total energy. The open-shell diatomics separate into the proper open-shell species. The energies of the closed-shell diatomics at large R are always between those of the possible separated states. These facts give us confidence that the states are ordered correctly and that the total binding is underestimated here. As shown by our calculations, it is unlikely that $^1\Sigma\pi^2$ HeF^+ falls beneath $^1\Sigma\pi^4$ in energy at any distance (likewise probably for NeF^+). As $^1\Sigma \rightarrow {}^1\Delta$ and $^1\Sigma \rightarrow {}^3\Sigma$ conversions are forbidden by spin-orbit coupling ($|\Delta S| = |\Delta L|$), the $^1\Sigma\pi^4$ HeF^+ ion should have a comparatively long lifetime. Other properties such as bond distance are usually computable to sufficiently high accuracy that we feel our calculations describe the molecules adequately.

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Appendix

There is a more general definition of electronegativity which seems almost implicit in Mulliken's original article.[15] Rather than electronegativity by $X = 0.5(I + A) = 0.5[\Delta E(\text{neutral} \rightarrow \text{most stable cation}) + \Delta E(\text{neutral} \rightarrow \text{most stable anion})]$, define $X(*;\ i, j, k) = 0.5 \cdot [\Delta E(\text{neutral in state } i \rightarrow \text{cation in state } j) + \Delta E(\text{neutral in state } i \rightarrow \text{anion in state } k)]$. Using this definition, $X(\text{F};\ {}^2P,\ {}^1S,\ {}^1S) \sim X(\text{He};\ {}^1S,\ {}^2S,\ \text{continuum}) > X(\text{F};\ {}^2P,\ {}^3P,\ {}^1S)$. Note here that we are using an extension of the Mulliken definition scaled to the normal Pauling values.

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(10) Salts of highly charged ions have been suggested to us by Dr. J. Musher ($HeF^{3+}AlF_6^{3-}$). We feel this to be far less promising than our proposals because the electron affinity of the cation is excessive. Dr. C. K. Jørgensen suggested the use of BF_4^-, BeF_4^{2-}, SiF_6^{2-}, AlF_6^{3-} to gain additional Madelung stabilization although the gaseous state ionization potential of these ions is lower than the above mentioned anions.

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