tion coefficients supports the molecular formula of chlorobiumquinone.

All these structural assignments were confirmed and further features established by a detailed study of chlorobiumquinone's n.m.r. spectrum in comparison with those of vitamin $K_{2(30)}$, plastoquinone and coenzyme Q_{10}, presented in Table II. Thus structure I is uniquely defined for chlorobiumquinone.

Further confirmation was found in a comparison of octadecahydrochlorobiumquinone (III) ($C_{45}H_{80}O_2$; Found, C, 82.9; H, 11.8) with hexahydrovitamin K_1 (IV).[9] In the ultraviolet, III has $\lambda_{max}^{isooctane}$ 260 mμ (ϵ 16,000) 268 (20,100), 335 (250); IV absorbs at 260 mμ

III

IV
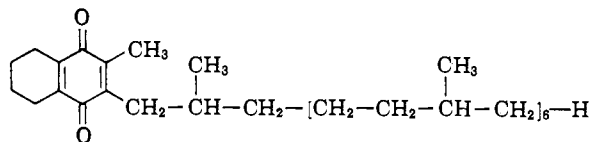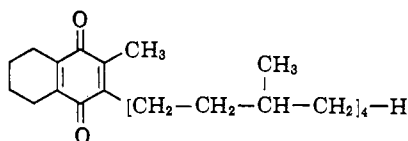
(ϵ 15,900), 268 (20,000), 335 (250). Both compounds have identical n.m.r. absorption[10] at δ 1.6 for the C_6, C_7 methylenes; δ 2.3 for the C_5, C_8 methylenes; δ 2.0 for the C_2–CH_3; δ 1.2 for the side-chain methylenes and methenes; and δ 0.8 for the side-chain methyls.

Chlorobiumquinone (I) is unique among natural vitamins K in having a double bond conjugate with the quinone[11] and one carbon less than the normal multiple-of-five carbons in the side chain. Although a vinyl naphthoquinone has not been found previously, it has been postulated as an intermediate in oxidative phosphorylation.[12]

The absence of coenzyme Q and plastoquinone in *C. thiosulfatophilum* is of interest, as is the fact that addition of a mild oxidizing agent during the extraction substantially increases the yield of chlorobiumquinone. This is not the case for the accompanying vitamin $K_{2(35)}$, and suggests that chlorobiumquinone is present mostly in a reduced form.

(9) M. Tishler, L. F. Fieser and N. L. Wendler, *J. Am. Chem. Soc.*, **62**, 2866 (1940).

(10) In deuteriochloroform with internal tetramethylsilane.

(11) A quinone recently detected spectrophotometrically in *Sarcina lutea* may be of this type [D. H. L. Bishop, K. P. Pandya and H. K. King, *Biochem. J.* **83**, 606 (1962)].

(12) I. Chmielewska, *Biochim. Biophys. Acta*, **39**, 170 (1960).

(13) Fellow of the Consejo Nacional de Investigaciones Científicas y Técnicas de la Republica Argentina, 1962.

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BOND ENERGIES AND IONIC CHARACTER OF INERT GAS HALIDES[1]

Sir:

Much interest has been aroused by the recent demonstration[2-5] that at least some of the so-called inert gases are able to form true chemical compounds. It is

(1) Acknowledgment is made to the National Science Foundation for support of this research.

(2) H. H. Claassen, H. Selig and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

(3) C. L. Chernick, *et al.*, *Science*, **138**, 136 (1962).

(4) P. R. Fields, L. Stein and M. H. Zirin, *J. Am. Chem. Soc.*, **84**, 4164 (1962).

(5) J. L. Weeks, C. L. Chernick and M. S. Matheson, *ibid.*, **84**, 4612 (1962).

very important that there be available a theoretical approach capable of treating such compounds and semi-quantitatively predicting their stabilities. We wish to report that an adaptation of the simple molecular orbital theory is applicable to the problem, and to give the results of calculations of the stabilities of some inert gas halides.

The energy of an electron in a localized two-center molecular orbital, $\psi = N(\phi_A + \lambda\phi_G)$, is given by the equation[6]

$$W = \tfrac{1}{2}(1 + x)q_A + (1 - x^2)^{1/2}\beta + \tfrac{1}{2}(1 - x)q_G \quad (1)$$

where $x = (1 - \lambda^2)/(1 + \lambda^2)$ is defined as the bond ionicity, q_A and q_G are coulomb integrals for the halogen and the central atom, respectively, and β is the exchange integral; $2W$ measures the energy of the process $1/nGA_n \rightarrow 1/nG^{n+} + A^+ + 2e^-$. From W and data available in the literature, the energy of formation of gaseous GA_n from the elements is calculated. The coulomb integrals are approximated by expressions containing the bond ionicity, the ionization potentials and the valence state preparation energy (v.s.p.e.) of the inert gas atom, the ionization potential and electron affinity of the halogen, the G–A bond distance, and a geometric factor.[6] The G–A exchange integral is approximated by the β for the appropriate interhalogen compound, using the equation of Pauling and Sherman,[7] and correcting for v.s.p.e. of the inert gas atom and van der Waals repulsion.

Xenon tetrafluoride has a square planar configuration,[8a] and XeF_2 is linear.[8b] The same geometries were assumed for other possible inert gas halides GA_4 and GA_2. The experimental values[8] of R were used for the Xe compounds. Bond lengths of the other inert gas halides were estimated from the Pauling covalent radii[9] of the halogen A and of the halogen adjacent to the inert gas in the periodic table. Other estimates were obtained from the known bond lengths[10] of the halides of elements immediately preceding the inert gas in the periodic table. Since for the tetrahalides the calculation is rather sensitive to the exact value assumed for R, calculations were made for a range of reasonable values. The valence states were assumed to be p^2ds for the tetrahalides and ps for the dihalides, and the v.s.p.e. values were estimated from spectroscopic data.[11]

Best values of the energies and ionicities are shown in Table I. The model predicts considerable stability for the known compound XeF_4, and somewhat lower stability for XeF_2. Krypton tetrafluoride is expected to exist, while KrF_2, $XeCl_4$ and ArF_4 are marginal.

The method predicts the intuitively expected increase in stability of the halides with increasing atomic number of the inert gas, and greater stability for fluorides than for the corresponding chlorides. More quantitatively, a change in the central atom from xenon to krypton or even argon is expected to entail a smaller decrease in stability than a change of ligand from fluorine to chlorine. Calculations were not made for bromides and iodides, since the trends in the calculated results strongly suggest that none of these would be stable.

A fluoride of radon has been prepared.[4] Insufficient information about the ionization potentials of radon is

(6) R. G. Pearson, S. Yamada and H. B. Gray, *Proc. 7th ICCC*, 65 (1962); R. G. Pearson and H. B. Gray, *Inorg. Chem.*, in press.

(7) L. Pauling and J. Sherman, *J. Am. Chem. Soc.*, **59**, 1450 (1937).

(8) (a) J. A. Ibers and W. C. Hamilton, *Science*, **139**, 106 (1963); (b) H. Levy and P. A. Agron, *J. Am. Chem. Soc.*, **85**, 241 (1963); we thank Dr. W. C. Hamilton for communicating these results to us prior to publication.

(9) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p. 224.

(10) "Interatomic Distances," The Chemical Society, London, 1958.

(11) C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Washington, D. C., 1949, 1952, 1958.

TABLE I

Molecule	R, Å.	Ionicity, %	Energy of formation from elements, kcal./mole G(g) + $n/2$A$_2$(g) → GA$_n$ (g)	Dissociation energy per bond, kcal./mole $1/n$GA$_n$(g) → $1/n$G(g) + A(g)
XeF$_4$	1.92	58	−123.1	49.6
KrF$_4$	1.72	49	−23.5	24.4
	1.72	55	−53.0^a	31.7^a
	1.78	47	−0.5	18.8
	1.78	52	−25.8^a	25.1^a
ArF$_4$	1.60	53	30.7	11.0
	1.64	51	53.7	5.3
NeF$_4$	1.40	33	507.1	−108.1
XeCl$_4$	2.30	45	50.9	15.8
	2.34	44	61.1	13.3
KrCl$_4$	2.11	37	137.4	−5.8
	2.11	40	132.3^a	−4.6^a
XeF$_2$	1.98	63	−11.1	24.2
KrF$_2$	1.72	63	5.3	16.1
XeCl$_2$	2.30	54	42.9	7.1

^{a} Calculated using an extrapolated value of 52.5 e.v. for the fourth ionization potential of Kr.

available to permit calculations for halides of this element. However, the trends in Table I make it fairly certain that if the data were available, calculation would predict RnF$_4$ and RnF$_2$, and perhaps RnCl$_4$ as well.

Another interesting feature is the sharp break in the sequence of predicted energies between the halides of argon and neon. While the decrease in calculated bond energy of the fluorides is slow enough from xenon to argon so that ArF$_4$ is still a possibility, the sudden drop between argon and neon virtually guarantees that neon halides cannot exist.

The present results indicate that the inert gas halides fit naturally into the sequence of halides of the non-metallic elements in their higher valence states, and that no special bonding assumptions are needed.

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THE BONDING IN THE INERT GAS–HALOGEN COMPOUNDS—THE LIKELY EXISTENCE OF HELIUM DIFLUORIDE

Sir:

In 1951, Pimentel discussed the bonding in trihalide ions in terms of a simple molecular orbital description.[1] In this widely ignored paper, the applicability of the bonding scheme to other molecular species was recognized and, in fact, the existence of inert gas–halogen compounds was predicted. *"It is to be expected that a rare gas could form complexes with halogens."*[1] At about the same time, Hach and Rundle[2] discussed bonding of trihalides in similar terms, though without any reference to possible inert gas compounds.

Since then there has appeared significant support for this molecular orbital description of the trihalides through electric quadrupole resonance studies[3,4] and infrared studies.[5] The quadrupole coupling constants in both ICl$_2$$^-$ and ICl$_4$$^-$ confirm the proposal that d orbitals do not contribute significantly to the bonding.

The recent preparation of inert gas compounds has naturally stimulated much interest in their bonding.[6–9]

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(2) R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, **73**, 4321 (1951).
(3) C. D. Cornwell and R. S. Yamasaki, *J. Chem. Phys.*, **27**, 1060 (1957).
(4) R. S. Yamasaki and C. D. Cornwell, *ibid.*, **30**, 1265 (1959).
(5) W. B. Person, G. R. Anderson and J. D. Fordemwalt, *ibid.*, **35**, 908 (1961).
(6) L. C. Allen, *Science*, **138**, 892 (1962).

Among these discussions, there has appeared a revival of the molecular orbital description proposed by Pimentel[8,9] and, we feel, the model provides a simple and sufficient basis for explaining the existence of such compounds as XeF$_2$. The ease of extension of the scheme to such compounds as ICl$_4$$^-$ and XeF$_4$ has been amply pointed out by others[4,5,8,9] and need not be reproduced here.

There is, however, one other aspect of the molecular orbital description offered by Pimentel[1] that deserves consideration. The essential similarity of the molecular orbital descriptions of HF$_2$$^-$ and I$_3$$^-$ was noted[1] and remarked upon again by Pimentel and McClellan.[10] Experimental support for this connection has also appeared[11] and we are encouraged to explore its implications in reference to inert gas chemistry. In particular, *the compound HeF$_2$ can be expected to be stable.*

The molecular orbital description of HF$_2$$^-$, based upon the halogen axial 2p orbitals and the hydrogen 1s orbital,[1] need not be repeated here and its applicability to the isoelectronic molecule HeF$_2$ is obvious. We can, however, make some comparisons between HF$_2$$^-$ and HeF$_2$ that may aid in searching for this interesting molecule. A rough estimate of the infrared spectrum of HeF$_2$ can be based upon that of HF$_2$$^-$. The vibrational frequencies and a set of force constants for HF$_2$$^-$ are shown in Table I.[12] These force constants transferred to HeF$_2$ lead to the predicted frequencies shown in the second row of Table I. We feel, however, that

TABLE I

THE VIBRATIONAL POTENTIAL FUNCTION AND FREQUENCIES OF HF$_2$$^-$ (EXPERIMENT) AND HeF$_2$ (PREDICTED)

| | Frequency, cm.$^{-1}$ | | | | Force constant^a | | |
	ν_1 (Raman active)	ν_2 (Infrared active)	ν_3 (Infrared active)	Bond length, Å	f_r	f_{rr}	f_α
HF$_2$$^-$	600	1230	1425	1.13	2.31	1.72	0.28
HeF$_2$	600	640	743	1.13	2.31	1.72	.28
HeF$_2$	585	673	1600	1.08	3.47	0.35	.28

^{a} f_r = bond stretching force constant (in millidynes/Ångstrom); f_{rr} = bond stretching interaction force constant (in millidynes/Ångstrom); f_α = angle bending force constant (in millidyne-Ångstrom/radian).

the spectrum of XeF$_2$ is relevant here. Smith has concluded[13] that the ratio f_{rr}/f_r is much smaller for XeF$_2$ than for the trihalide ions. We do not share his view that this difference vitiates the molecular orbital bonding description, for a reasonable rationale can be formulated to explain it. The molecules XeF$_2$ and ICl$_2$$^-$, though isoelectronic (in bonding electrons), involve quite different formal charge distributions. The proposed molecular orbitals tend to place somewhat less than one electron charge on the central atom and somewhat more than $1\frac{1}{2}$ electron charges on the terminal atoms. In the case of ICl$_2$$^-$, the formal charge implication is that the excess charge of the ion is distributed on the chlorine atoms and the iodine atom has a charge near zero. The case of XeF$_2$ contrasts since the central atom must have a significant positive formal charge to balance the negative charge placed on the terminal atoms. This difference can be expected to tend to strengthen the bond somewhat because of the electrostatic attractions, raising f_r.[14] At the same time, the

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