the same order, even including the order of the proton affinities of the three xylenes.

Acknowledgment. This work was sponsored by Project SQUID which is supported by the Office of Naval Research, Department of the Navy, under Contract N0014-67-A0226-0005, NR-098-038. Reproduction in full or in part is permitted for any use of the U. S. Government.

Electronic Structure and Properties of Krypton Difluoride

Paul S. Bagus,*[1a] Bowen Liu,[1a] and Henry F. Schaefer III[1b]

Contribution from IBM Research Laboratory, San Jose, California 95114, and the Department of Chemistry, University of California, Berkeley, California 94720.

Received January 19, 1972

Abstract: *Ab initio* calculations have been performed on the linear symmetric configuration of KrF_2, using a 993-configuration "first-order" wave function and an extended basis set of Slater functions. These calculations yield a bound potential curve with respect to three infinitely separated atoms; the Kr–F bond distance is 1.907 Å and the dissociation energy is 0.39 eV, as compared to the experimental values of 1.889 ± 0.01 Å and 1.013 eV, respectively. A potential maximum is found at Kr–F distance 2.42 Å, lying 0.22 eV above the dissociation limit. The electric field gradient at the Kr nucleus, near the potential minimum, is very near the self-consistent field (SCF) value for an isolated Kr^+ ion but drops rapidly to zero near the potential maximum. These results show that the Kr–F bond is ionic in nature near the equilibrium separation and becomes covalent at larger separations, as proposed by Coulson. In contrast to the "first-order" wave function results, one configuration SCF calculations yield an attractive potential curve with a minimum at 1.813 Å and 2.98 eV *above* the SCF energy of three separated atoms. This behavior is permitted because the one-configuration SCF wave function does not dissociate to neutral separated atoms. However, two-configuration SCF calculations which allow proper dissociation to neutral separated atoms yield a repulsive potential curve with an *inflection point* near 1.85 Å. CI calculations using the two-configuration SCF occupied orbitals and including all eight valence shell configurations yield results quantitatively similar to the two-configuration SCF results. In addition, a series of SCF calculations has been carried out to study the importance of polarization functions. The results indicate that 4d functions centered on Kr are much less important than suggested by minimum basis set calculations. Finally, Koopmans' theorem ionization potentials are compared with the experimental photoelectron spectrum.

The chemistry of krypton centers about KrF_2,[2a] since most of the interesting xenon compounds (*e.g.*, XeF_4, XeF_6, and XeO_4) appear to have no stable krypton analogs.[2b] We have previously[3] studied KrF[4] and KrF^+ [5] by *ab initio* theoretical methods; the only other well-characterized krypton-containing molecule is the ionic $[KrF^+][Sb_2F_{11}]$ recently synthesized and characterized (by its Raman spectrum) by McKee and Bartlett.[6]

The only previous nonempirical quantum mechanical treatment of KrF_2 is that of Collins, Cruickshank, and Breeze,[7] who carried out a self-consistent field (SCF) calculation using a minimum basis set. The stated purpose of this calculation[7] was to investigate the importance of 4d basis functions in the electronic structure of KrF_2. However, recent work with extended basis sets[8] on the second-row hydrides SiH_4, PH_3, and H_2S showed that minimum basis set studies[9] greatly overestimated the importance of 3d functions in these molecules. We have used an extended basis set to study the effects of different types of "polarization" functions[10] within the SCF approximation.

Electron correlation[11,12] has been investigated using "first-order" wave functions, which have proven quite effective[13] in predicting the dissociation energies and geometries of simple molecules. KrF_2 provides an important test for any theoretical approach which attempts to properly treat electron correlation, since the molecule lies on the fringe of stability. A number of molecular properties are reported. These properties are obtained using the "first-order" wave functions and also wave functions of lesser accuracy.

The "first-order" wave function as we use the term here does not include all of the configurations which would appear in the first-order Schroedinger perturbation theory wave function. The sense of our use of the term has been described elsewhere.[13] Later in the

---

(1) (a) IBM Research Laboratory; (b) University of California; supported by grants from the Petroleum Research Fund and the Research Corporation.

(2) (a) F. Schreiner, J. G. Malm, and J. C, Hindman, *J. Amer. Chem. Soc.*, **87**, 25 (1965); J. J. Turner and G. C. Pimentel, *Science*, **140**, 974 (1963); (b) N. Bartlett and F. O. Sladky, "The Chemistry of Krypton, Xenon, and Radon," University of California Radiation Laboratory Report 19658, June 1970.

(3) B. Liu and H. F. Schaefer, *J. Chem. Phys.*, **55**, 2369 (1971).

(4) W. E. Falconer, J. R. Morton, and A. G. Streng, *ibid.*, **41**, 902 (1964).

(5) J. Berkowitz and W. A. Chupka, *Chem. Phys. Lett.*, **7**, 447 (1970).

(6) H. Selig and R. D. Peacock, *J. Amer. Chem. Soc.*, **86**, 3895 (1964); D. McKee and N. Bartlett, unpublished.

(7) G. A, D. Collins, D. W. J. Cruickshank, and A. Breeze, *Chem. Commun.*, 884 (1970).

(8) S. Rothenberg, R. H. Young, and H. F. Schaefer, *J. Amer. Chem. Soc.*, **92**, 3243 (1970).

(9) D. B. Boyd and W. N. Lipscomb, *J. Chem. Phys.*, **46**, 910 (1967); F. P. Boer and W. N. Lipscomb, *ibid.*, **50**, 989 (1969).

(10) R. K. Nesbet, *Advan. Quantum. Chem.*, **3**, 1 (1965).

(11) P. O. Lowdin, *Advan. Chem. Phys.*, **2**, 207 (1959).

(12) E. Clementi, *J. Chem. Phys.*, **38**, 2248 (1963).

(13) H. F. Schaefer, *ibid.*, **54**, 2207 (1971); **55**, 176 (1971); H. F. Schaefer and C. F. Bender, *ibid.*, **55**, 1720 (1971).

Table I. Basis Set and Self-Consistent Field Wave Function for Linear KrF_2 at 3.5 Bohrs KrF Separation. Basis Functions Are of the Form $r^{n-1}e^{-\zeta r}$

Orbital	$1\sigma_g$	$2\sigma_g$	$3\sigma_g$	$4\sigma_g$	$5\sigma_g$	$6\sigma_g$	$7\sigma_g$	$8\sigma_g$
ϵ	−520.3516	−70.0784	−26.2860	−11.0232	−4.0122	−1.5791	−1.2412	−0.5406
Basis functions								
1s (ζ = 37.85)	0.713139	0.027940	0.000068	0.006223	−0.000017	−0.003513	0.009623	0.001609
1s (28.94)	0.300969	−0.471571	−0.000098	−0.182071	−0.000720	0.023116	−0.066071	−0.018299
2s (18.86)	−0.035995	−0.271496	0.000350	−0.374273	−0.002095	0.027174	−0.082243	−0.033315
2s (15.55)	0.025434	1.384445	−0.000407	0.975337	0.004837	−0.089060	0.264111	0.093108
3s (8.370)	−0.006176	0.063106	0.000650	−0.425996	−0.002536	0.001596	−0.003239	−0.010280
3s (6.506)	0.004807	−0.033851	−0.000829	−0.721608	−0.004041	0.171852	−0.495306	−0.132248
4s (4.406)	−0.001084	0.005531	0.000491	−0.025724	0.005713	−0.147115	0.462744	0.163336
4s (2.435)	0.000452	−0.001965	−0.000816	0.002428	−0.004261	−0.208050	0.682749	0.315397
3d (12.47)	−0.000006	0.000170	0.000032	−0.000116	0.170666	0.005151	0.001810	0.015295
3d (6.942)	0.000016	−0.000082	−0.000145	−0.000100	0.602450	0.011807	0.002236	0.033137
3d (4.060)	−0.000013	0.000026	−0.000227	−0.003132	0.331367	0.016910	0.009030	0.053278
4d (3.200)	−0.000018	0.000143	−0.000170	0.001152	−0.006930	−0.024087	−0.019794	−0.103371
4d (1.600)	0.000161	−0.000669	−0.000341	0.000714	0.001481	−0.023896	−0.001383	−0.113532
1s + 1s (11.01)	0.000064	−0.000183	0.167823	0.000120	−0.000070	−0.018052	−0.005273	0.000265
1s + 1s (7.917)	−0.000083	0.000254	0.544098	−0.000176	−0.000497	0.199102	0.083550	−0.005439
2s + 2s (3.096)	0.000134	−0.000503	0.000448	0.000541	0.000381	−0.421441	−0.179897	0.020516
2s + 2s (1.946)	−0.000229	0.000901	0.001207	−0.001114	0.002194	−0.258316	−0.165233	0.016148
2p − 2p (6.165)	−0.000022	0.000075	0.000721	−0.000075	0.000245	−0.002150	0.005527	−0.052242
2p − 2p (3.176)	0.000075	−0.000272	−0.000535	0.000225	0.000428	−0.022390	0.064764	−0.277077
2p − 2p (1.612)	−0.000132	0.000501	0.000570	−0.000708	0.002650	−0.028036	0.028257	−0.419482
3d + 3d (4.000)	0.000005	−0.000009	−0.000149	−0.000002	−0.000046	0.000444	0.002133	0.002290
3d + 3d (2.000)	−0.000028	0.000083	0.000195	−0.000147	0.001219	−0.010164	0.002956	−0.032911
4f − 4f (3.000)	0.000006	−0.000035	0.000063	0.000018	0.000322	−0.003616	0.002383	−0.007684

Orbital	$1\sigma_u$	$2\sigma_u$	$3\sigma_u$	$4\sigma_u$	$5\sigma_u$
ϵ	−63.1862	−26.2860	−8.5120	−1.5599	−0.7662
Basis functions					
2p (ζ = 29.22)	−0.051278	−0.000010	0.010853	−0.000446	0.001723
2p (15.46)	−0.934922	0.000026	0.421101	−0.019360	0.072896
3p (8.131)	−0.074667	−0.000251	−0.445062	0.022762	−0.084202
3p (6.057)	0.039775	0.000396	−0.638880	0.034631	−0.134681
4p (3.218)	−0.008778	−0.000574	−0.042618	−0.075002	0.349933
4p (1.809)	0.007401	0.002066	0.024985	−0.061459	0.229208
4f (3.200)	−0.000937	−0.000144	−0.004165	−0.003618	0.008265
4f (1.600)	0.002467	0.000782	0.008243	−0.022308	0.023336
1s − 1s (11.01)	−0.000643	0.167664	−0.001087	0.019464	0.002602
1s − 1s (7.917)	0.000934	0.544343	0.001852	−0.212085	−0.045696
2s − 2s (3.096)	−0.001868	−0.000125	−0.004969	0.449863	0.111539
2s − 2s (1.946)	0.004354	0.002425	0.013034	0.269686	0.114875
2p + 2p (6.165)	−0.000045	0.000773	−0.000088	0.001799	−0.038185
2p + 2p (3.176)	−0.000207	−0.000785	−0.000365	0.016736	−0.222114
2p + 2p (1.612)	0.001257	0.001127	0.003401	0.023780	−0.290637
3d − 3d (4.000)	0.000302	−0.000163	0.000883	−0.000586	0.001422
3d − 3d (2.000)	−0.000419	0.000296	−0.001591	0.009033	−0.035136
4f + 4f (3.000)	−0.000346	0.000065	−0.001006	0.002783	−0.007740

Orbital	$1\pi_u$	$2\pi_u$	$3\pi_u$	$4\pi_u$
ϵ	−63.1819	−8.4974	−0.7115	−0.5672
Basis functions				
2p (ζ = 29.22)	0.051244	0.010893	−0.001817	0.001867
2p (15.46)	0.935298	0.422236	−0.085196	0.089452
3p (8.131)	0.072413	−0.448072	0.103956	−0.110132
3p (6.057)	−0.037133	−0.638772	0.146205	−0.151440
4p (3.218)	0.006105	−0.033698	−0.424090	0.459439
4p (1.809)	−0.003003	0.011720	−0.347028	0.388867
4f (3.200)	0.000340	−0.002232	−0.004916	0.000371
4f (1.600)	−0.000954	0.003806	−0.015266	−0.029542
2p + 2p (6.165)	0.000287	−0.000695	−0.032960	−0.041329
20 + 2p (3.176)	−0.000825	0.002450	−0.215779	−0.235146
2p + 2p (1.612)	0.001130	−0.003834	−0.244653	−0.315237
3d − 3d (4.000)	−0.000171	0.000444	−0.001421	−0.000096
3d − 3d (2.000)	0.000434	−0.001322	−0.012614	−0.004590
4f + 4f (3.000)	−0.000020	0.000123	−0.004358	−0.001141

Orbital	$1\pi_g$	$2\pi_g$
ϵ	−4.0034	−0.6484
Basic functions		
3d (ζ = 12.47)	−0.170584	0.005393
3d (6.942)	−0.603050	0.012314
3d (4.060)	−0.330364	0.017504
4d (3.200)	0.005887	−0.031587
4d (1.600)	−0.002069	−0.048606
2p − 2p (6.165)	0.000002	0.052171
2p − 2p (3.176)	0.000193	0.310962
2p − 2p (1.612)	0.000086	0.393501
3d + 3d (4.000)	−0.000084	−0.000072
3d + 3d (2.000)	0.000539	0.017805
4f − 4f (3.000)	0.000290	0.005155

Orbital	$1\delta_g$
ϵ	−3.9837
Basic functions	
3d (ζ = 12.47)	0.170565
3d (6.942)	0.605081
3d (4.060)	0.326872
4d (3.200)	−0.003901
4d (1.600)	0.002749
3d + 3d (4.000)	0.000038
3d + 3d (2.000)	−0.000096
4f − 4f (3.000)	0.000036

Table II. Effect of Polarization Functions on the KrF_2 SCF Energy and Quadrupole Moment at 3.5 Bohrs Bond Distance. Energies Are in Hartrees (1 hartree = 27.21 eV) and Quadrupole Moments in Atomic Units (1 atomic unit = 1.3449×10^{-26} esu cm^2)

Basis set	Description	Energy	Lowering	Quadrupole moment
(8s 6p 3d)/(4s 3p)	Atomic functions	−2950.6347		−15.64
Add two 3d, one 4f on F	Fluorine polarization	−2950.6905	0.0558	−14.23
Add two 4d on Kr	Krypton d polarization	−2950.6921	0.0574	−14.61
Add two 4d, two 4f on Kr	Krypton polarization	−2950.7104	0.0757	−14.35
Add two 4d on Kr; two 3d on F	d polarization	−2950.7219	0.0872	−13.64
Add two 4f on Kr; one 4f on F	f polarization	−2950.6561	0.0214	
(8s 6p 5d 2f)/(4s 3p 2d 1f)	Full polarization	−2950.7341	0.0994	−13.66

paper we will explicitly define the configurations included in our KrF_2 "first-order" wave functions.

The work reported here was made possible by a recently developed series of computer programs, called ALCHEMY,[14] for the computation of multiconfiguration wave functions for linear molecules.

Basis Set and SCF Wave Function near Equilibrium

The basis set of Slater functions used here is essentially the same (the fluorine 3d exponents have been slightly lowered) as that used in previous calculations[3] on KrF and KrF^+. The basis includes eight s, six p, five d, and two f functions on Kr. The krypton basis is thus designated (8s 6p 5d 2f). Similarly, our fluorine basis is (4s 3p 2d 1f). The atomic SCF energies obtained with this basis are −2752.0311 and −99.4081 hartrees, as opposed to the true Hartree–Fock energies −2752.054[15] and −99.4093[16] for Kr and F. We carried out calculations[8] on KrF and KrF^+ using this basis and a much larger (near Hartree–Fock) set and found the SCF potential curves to be parallel to within 0.17 eV. Further, the molecular properties for SCF wave functions of KrF^+ calculated with the present basis are very close to those obtained with the larger set.[3] For example, the dipole and quadrupole moments were 0.103 and 2.47 atomic units, as opposed to 0.106 and 2.37 with the near Hartree–Fock basis. Therefore, it seems reasonable to suppose that the present KrF_2 results would not be significantly changed if the calculations were performed using a larger, more complete basis set. The basis of Slater-type orbitals and the resulting SCF wave function for KrF_2 at 3.5 bohrs bond length are given in Table I. The orbital energies ϵ are also given in this table.

Importance of "Higher" Orbitals

The degree of importance of "higher" orbitals for the description of the electronic structure of molecules containing noble gas atoms is the subject of considerable controversy.[2b,7,17–20] For KrF_2, the "higher" orbitals or polarization functions[10] expected to be most important are the 4d and 4f functions on krypton.

To test the importance of polarization functions, a series of SCF calculations has been carried out for KrF_2 at 3.5 bohrs separation. The calculations, summarized in Table II, show rather clearly the energy effects of the different functions. The most surprising result is that 3d and 4f functions on *fluorine* are nearly as important as the krypton polarization functions. Since the promotion energy from ground-state F atom to the lowest configuration involving a 3d orbital is 15.9 eV,[21] one would probably not argue that 3d orbitals are "physically accessible" for a particular hybridization scheme. Table II shows that Kr 4d and F 3d functions are about four times more important than 4f functions on both atoms. Another point worth making is that the effects of polarization functions on Kr and F are not additive; the sum of the two effects lowers the energy by 0.1315 hartrees, while the lowering obtained using all the functions simultaneously is only 0.0994 hartree.

Our results are in striking contrast to the results of Collins, Cruickshank, and Breeze,[7] who obtained an energy lowering of 0.306 hartree for a single 4d function. They concluded[7] "that krypton 4d orbitals must be included to give an adequate description of the bonding." Table II shows that with two 4d functions we find a lowering of only 0.0574 hartree. We conclude, as was the case in SiH_4, PH_3, and H_2S,[8] that SCF calculations with minimum basis sets falsely overestimate the importance of polarization functions in KrF_2. The addition of almost any type of function will significantly lower the molecular SCF energy of a minimum basis set calculation. Table II also shows the molecular quadrupole moment as a function of the different types of polarization.

Treatment of Electron Correlation

The SCF configuration for linear symmetric KrF_2 is (excluding the inner 38 electrons)

$$5\sigma_u{}^2 3\pi_u{}^4 2\pi_g{}^4 8\sigma_g{}^2 4\pi_u{}^4$$

1

In order for the KrF_2 wave function to dissociate to wave functions for neutral separated Kr and F atoms, a second configuration with $8\sigma_g{}^2$ replaced by $6\sigma_u{}^4$

$$5\sigma_u{}^2 3\pi_u{}^4 2\pi_g{}^4 6\sigma_u{}^2 4\pi_u{}^4$$

2

must be mixed with **1**. In the weak interaction limit (*i.e.*, large Kr–F separation), the orbitals in **1** and **2** can all be associated with Kr4p and F2p orbitals, as follows.

---

[14] A system of programs developed by B. Liu, M. Yoshimine, P. S. Bagus, and A. D. McLean. For a description see (a) A. D. McLean, "Potential Energy Surfaces from *Ab Initio* Computations: Current and Projected Capabilities of the ALCHEMY Computer Program," Proceedings of the Conference on Potential Energy Surfaces in Chemistry, RA18, IBM Research Laboratory, San Jose, Calif., 1971; (b) P. S. Bagus in "Selected Topics in Molecular Physics," Verlag Chemie, Weinheim/Bergstr., Germany, 1972.

[15] E. Clementi, *J. Chem. Phys.*, **41**, 303 (1964).

[16] P. S, Bagus, T. L. Gilbert, and C. C. J. Roothaan, *J. Chem. Phys.*, **56**, 5195 (1972).

[17] L. C. Allen and W. D. Horrocks, *J. Amer. Chem. Soc.*, **84**, 4344 (1962).

[18] C. A. Coulson, *J. Chem. Soc.*, 1442 (1964).

[19] J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, *Chem. Rev.*, **65**, 199 (1965).

[20] K. A. R. Mitchell, *J. Chem. Soc. A*, 1637 (1968); R. C. Catton and K. A. R. Mitchell, *Chem. Commun.*, 457 (1970).

[21] C. E. Moore, *Nat. Bur. Stand.* (*U. S.*), *Circ.*, **1**, 467 (1949).

Table III. Total Energies (in hartrees) for KrF_2

R, bohrs	SCF	Two-configuration SCF	Eight configurations	993 configurations
3.0	−2950.6686	−2950.6857	−2950.6888	−2950.7640
3.25	−2950.7283	−2950.7541	−2950.7583	−2950.8412
3.50	−2950.7341	−2950.7749	−2950.7796	−2950.8655
3.75	−2950.7120	−2950.7800	−2950.7833	−2950.8647
4.0	−2950.6771	−2950.7902	−2950.7913	−2950.8554
4.5		−2950.8202	−2950.8203	−2950.8450
5.0		−2950.8375	−2950.8375	−2950.8477
5.5		−2950.8448	−2950.8448	−2950.8509
6.0		−2950.8476	−2950.8476	−2950.8524
7.0		−2950.8488	−2950.8488	−2950.8531
10.0		−2950.8489	−2950.8489	−2950.8531
∞	−2950.8473[a]			

[a] This is the sum of the SCF energy of atomic Kr and twice the SCF energy of atomic F.

Table IV. Mixing Coefficients for the Two-Configuration SCF and Eight-Configuration CI Wave Functions. The Numbering of the Configurations Corresponds to That Given in the Text

R,	Two-configuration SCF		Eight-configuration CI							
bohrs	C_1	C_2	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
3.0	0.994	−0.111	0.994	−0.106	−0.035	0.001	0.015	0.010	0.008	0.005
3.25	0.987	−0.161	0.987	−0.152	−0.050	0.001	0.017	0.010	0.009	0.005
3.50	0.970	−0.242	0.972	−0.226	−0.061	−0.002	0.017	0.010	0.009	0.003
3.75	0.929	−0.369	0.934	−0.352	−0.057	−0.008	0.015	0.008	0.009	−0.002
4.0	0.860	−0.510	0.864	−0.502	−0.033	−0.005	0.008	0.007	0.006	−0.004
4.5	0.764	−0.646	0.764	−0.645	−0.009	−0.001	0.002	0.004	0.003	−0.002
5.0	0.729	−0.684	0.729	−0.684	−0.003	0.000	0.001	0.001	0.001	−0.001
6.0	0.711	−0.704	0.711	−0.704	−0.001	0.000	0.000	0.000	0.001	0.000
10.0	0.707	−0.707	0.707	−0.707	0.000	0.000	0.000	0.000	0.000	0.000

$$5\sigma_u \longrightarrow \mathrm{Kr4p}$$
$$3\pi_u \longrightarrow \mathrm{F2p} + \mathrm{F'2p}$$
$$2\pi_g \longrightarrow \mathrm{F2p} - \mathrm{F'2p}$$
$$8\sigma_g \longrightarrow \mathrm{F2p} - \mathrm{F2p}$$
$$6\sigma_u \longrightarrow \mathrm{F2p} + \mathrm{F2p}$$
$$4\pi_u \longrightarrow \mathrm{Kr4p}$$

However, near the equilibrium Kr–F bond distance this association is not valid.

In addition to single configuration SCF calculations on **1**, we carried out two-configuration SCF (TCSCF) calculations including both **1** and **2**. In the TCSCF calculations, we have solved variational equations for the orbitals in **1** and **2** (including the core orbitals not explicitly shown) and *simultaneously* for the mixing coefficients of the two configurations.[22] The TCSCF wave function is the simplest functional form which dissociates correctly. Thus, it is the simplest form for which we expect that the remaining correlation energy may be a slowly varying function of internuclear separation.

Six other orbital occupancies (yielding six $^1\Sigma_g^+$ symmetry eigenfunctions) may also be constructed from the KrF_2 valence orbitals.

$$3\pi_u{}^4 2\pi_g{}^4 8\sigma_g{}^2 4\pi_u{}^4 6\sigma_u{}^2 \quad \mathbf{3}$$
$$5\sigma_u 3\pi_u{}^4 2\pi_g{}^4 6\sigma_u{}^2 4\pi_u{}^4 6\sigma_u \quad \mathbf{4}$$
$$5\sigma_u{}^2 3\pi_u{}^4 2\pi_g{}^4 8\sigma_g{}^2 4\pi_u{}^2 6\sigma_u{}^2 \quad \mathbf{5}$$
$$5\sigma_u{}^2 3\pi_u{}^2 2\pi_g{}^4 8\sigma_g{}^2 4\pi_u{}^4 6\sigma_u{}^2 \quad \mathbf{6}$$
$$5\sigma_u{}^2 3\pi_u{}^4 2\pi_g{}^2 8\sigma_g{}^2 4\pi_u{}^4 6\sigma_u{}^2 \quad \mathbf{7}$$
$$5\sigma_u{}^2 3\pi_u{}^3 2\pi_g{}^4 8\sigma_g{}^2 4\pi_u{}^3 6\sigma_u{}^2 \quad \mathbf{8}$$

Configurations **1–8** thus comprise the full-valence configuration interaction (CI) for KrF_2. From a valence bond standpoint, configurations **1–8** have the variational flexibility in a multiconfiguration Hartree–Fock calculation to include all structures involving Kr, Kr^+, Kr^{2+}, F, and F^-. Thus, the ability or inability of this eight-configuration wave function to properly describe KrF_2 is of theoretical importance. Eight-configuration CI calculations showed configuration **2** to be far more important energetically than any of **3–8**. For this reason, we have concluded that the molecular orbitals of KrF_2 determined by a TCSCF calculation would not be significantly changed by an eight-configuration multiconfiguration SCF calculation. Therefore, a straightforward CI calculation using the TCSCF orbitals was used to defermine the eight-configuration wave function.

The most extensive calculations were of the first-order variety.[13] The general restriction placed on first-order wave functions is that only those configurations are included in which no more than a single electron occupies an orbital beyond the valence shall (*i.e.*, beyond $6\sigma_u$). Further restrictions invoked here are (a) 38 electrons are constrained to occupy the innermost TCSCF orbitals in all configurations, and (b) no δ or ϕ orbitals (except the fully occupied $1\delta_g$ TCSCF orbital) are employed in the calculation. With these restrictions, the first-order wave function for KrF_2 includes 993 configurations.

Potential Curves

For linear symmetric KrF_2, calculations were carried out at eleven different Kr–F bond distances. The resulting energies are given in Table III. The mixing coefficients for the two- and eight-configuration wave functions are given in Table IV. The one-, two-, and

---

(22) The TCSCF approach is a special case of the multiconfiguration Hartree–Fock method which has recently been applied by several workers to atomic and molecular problems; see, for example, for molecules: A. C. Wahl and G. Das, *Advan. Quantum Chem.*, **5**, 261 (1970); and for atoms: P. S. Bagus and C. M. Moser, *J. Phys. B*, **2**, 1214 (1969).

993-configuration potential curves are shown in Figure 1. Table III shows that the two-configuration and eight-configuration energies would be difficult to distinguish between in such a figure. The main conclusion to be drawn from Figure 1 is that the three calculations yield remarkably *dissimilar* results.

The SCF or one-configuration potential curve has its minimum at 1.813 Å, in reasonable agreement with the experimental values,[23,24] 1.875 and 1.889 Å. However, the minimum of the SCF potential curve lies 0.1095 hartree above the comparable SCF energies for Kr + F + F. That is, the SCF calculation predicts KrF_2 to be unbound by 2.98 eV.

The two-configuration potential curve dissociates properly but is repulsive, although it contains an interesting inflection point. Thus, the correlation effects which lead to binding in KrF_2 are much more subtle than those found by Das and Wahl[25] for F_2, where the analogous two-configuration treatment yields an attractive potential curve. As mentioned above, the shape of the eight-configuration potential curve is essentially the same as the TCSCF curve.

The eight-configuration calculation is relevant to models for bonding in KrF_2, proposed by Coulson[26] and Nesbet.[27] Coulson[26] proposed an ionic–covalent resonance model for the binding of KrF_2. The binding is described as due to a resonance between

$$\widehat{\text{F Kr F}} \text{ and } \text{F–Kr}^{+}\text{F}^{-} \text{ and } \text{F}^{-}\text{Kr}^{+}\text{–F}$$

Coulson did not attempt to quantitatively predict the binding energy of KrF_2 but used his model to describe the qualitative features of the potential curve of linear symmetric KrF_2. Nesbet's[27] theory is expressed in terms of localized orthogonal transforms of Hartree–Fock molecular orbitals. In terms of these orbitals binding is ascribed to the interaction among the structures FKrF, F^-KrF^+, and $F^-Kr^{2+}F^-$.

As noted above, our eight-configuration wave function has the variational flexibility to include both of these sets of structures. Since the eight-configuration potential curve is repulsive and quite dissimilar from Coulson's[26] Figure 1, we conclude that more complicated correlation effects than those described by Coulson are required to describe binding in KrF_2. However, as we shall discuss below, very important aspects of binding in KrF_2 are correctly described in Coulson's model.

Nesbet[27] predicts that KrF_2 at a KrF distance of 1.75 Å (3.31 bohrs) will be unstable relative to Kr + F_2 (BE(F_2) = 1.68 eV[27]) by either 0.80 or 0.00 eV, depending on the value used for an interaction integral. The result of our eight-configuration CI calculation is that KrF_2 at a KrF distance of 3.25 bohrs is unstable by 4.15 eV. Nesbet[27] has also made predictions of the stability of other rare gas difluorides, in particular, XeF_2 and RnF_2. It would be interesting to compare results from eight-configuration calculations in these systems.

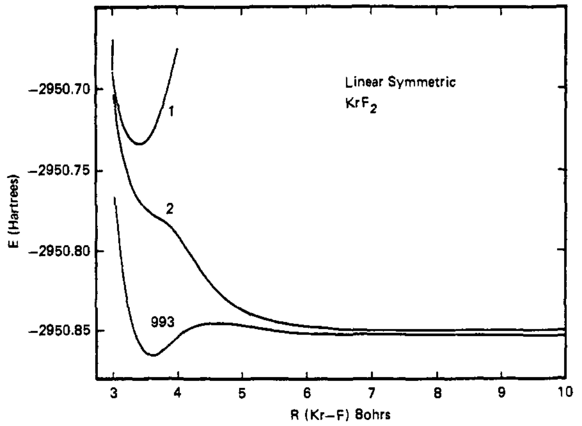

Figure 1. Potential curves for the symmetric dissociation of KrF_2. 1 refers to the conventional SCF calculation, 2 to the two-configuration SCF, and 993 to the approximate first-order wave function.

A technical point should be raised concerning the dissociation limit for the KrF_2 TCSCF calculation. On the face of it, one would expect the TCSCF calculation to yield at infinite separation an energy of −2950.8473 hartrees, the restricted SCF energy of Kr + F + F. However, at 10 bohrs separation, the calculated TCSCF energy is −2950.8489 hartrees, or 0.04 eV lower than the expected dissociation limit. This difference is due to the fact that the TCSCF calculation does not describe two F atoms with electron configuration

$$1s^2 2s^2 2p^5$$

but rather with

$$1\sigma^2 2\sigma^2 3\sigma 1\pi^4$$

That is, in the TCSCF calculation, the fluorine $2p\sigma$ and $2p\pi$ orbitals are not forced to be identical. Thus, the TCSCF dissociation limit is slightly lower than expected from the atomic calculations, in which all five 2p spin orbitals are required to be equivalent.

Only the 993-configuration calculation yields a physically reasonable potential curve. The computed bond distance is 1.907 Å, 0.018 Å greater than one of the two experimental values. The calculated dissociation energy, the difference between the energy at R_e and that at infinite separation, is 0.39 eV, only about 40% of the experimental value of 1.01 eV.[2b] However, calculations on KrF^+ with a much larger basis set[3] indicate that the KrF_2 basis may be about 0.35 eV better for the separated atoms than for the molecule near R_e. The additional fact that δ and ϕ orbitals were not included in the CI makes it difficult to determine the degree to which the small absolute error in the dissociation energy is due to the model adopted, the first-order wave function. The most important point in this regard is that the molecule *is* predicted to be bound.

A very interesting feature of the first-order potential curve is the existence of a potential maximum at 2.42 Å, lying 0.22 eV above the dissociation limit. Since a potential maximum has never been established or computed[28] for the ground state of any neutral molecule, this prediction for KrF_2 appears to be unique.

---

(23) W. Harshbarger, R. K. Bohn, and S. H. Bauer, *J. Amer. Chem. Soc.*, **89**, 6466 (1967).

(24) C. Murchison, S. Reichman, D. Anderson, J. Overend, and F. Schreiner, *ibid.*, **90**, 5690 (1968).

(25) G. Das and A. C. Wahl, *J. Chem. Phys.*, **44**, 876 (1966).

(26) C. A. Coulson, *ibid.*, **44**, 468 (1966).

(27) R. K. Nesbet, *ibid.*, **38**, 1783 (1963).

(28) We have recently learned of a calculation on BeH by T. H. Dunning, Caltech, which predicts a ground-state potential maximum of 0.075 eV at 5.7 bohrs separation. Further, S. Hagstrom, Indiana, has recently predicted a potential maximum for the symmetric dissociation of ground-state BeH_2.

This maximum is in harmony with Coulson's[26] ionic-covalent resonance model for the structure of KrF_2. This model suggests that there may be an avoided crossing between the repulsive covalent structure and the two equivalent attractive ionic structures, as is clearly indicated in Coulson's Figure 1. Such an avoided crossing would clearly account for our predicted maximum in the potential curve.

We have computed natural orbitals,[11] NO's, for the 993-configuration first-order wave function although we have not made an extensive analysis of these orbitals. At a Kr–F bond distance of $R = 3.5$ bohrs, there are $11\sigma_g$, $8\sigma_u$, $4\pi_g$, and $5\pi_u$ NO's with occupation numbers less than 10^{-5}. At the same bond distance, there are, including the orbitals occupied in the TCSCF wave function, $10\sigma_g$, $7\sigma_u$, $4\pi_g$, and $7\pi_u$ NO's with occupation numbers larger than 5×10^{-4}. Clearly the NO's with small occupation numbers could be deleted from the calculation without significantly changing the results. Most likely the NO's with occupation numbers larger than 5×10^{-4} would have to be retained.

Thus the number of configurations in the first-order wave function could be considerably reduced but would still remain moderately large. The point is that the 993 configuration does not yield physically reasonable results because it contains 993 configurations but rather because it includes physically important correlation effects not contained in the one-, two-, or eight-configuration calculations. A careful analysis using the NO's should provide more detailed insight into these important effects.

Photoelectron Spectrum

According to Koopmans' theorem, orbital energies from SCF calculations may be associated with ionization potentials.[29] However, the ionization potentials thus obtained correspond to calculations on the positive ion states using the neutral molecule SCF orbitals. Thus, the Koopmans' theorem ionization potentials do not include the effects of orbital relaxation in the ions. Further, neither these values nor values obtained by direct SCF calculations on the ions take proper account of the changes of electron correlation between the parent and ion. Nevertheless, Koopmans' theorem ionization potentials are frequently useful as a *qualitative* guide to the photoelectron spectra of molecules.

Very recently, Brundle and Jones[30] have reported the valence level photoelectron spectrum of KrF_2. Their experimental results are compared with the present orbital energies in Table V. The most obvious trend observed in Table V is that the Koopmans' theorem ionization potentials are too large. This indicates, as discussed in the above paragraph, that the states of the KrF_2^+ ion are not treated as well as the ground state of the neutral molecule. However, except for the $8\sigma_g - 4\pi_u$ error, the ordering of the positive ion levels agrees with the assignments of Brundle and Jones.[30] On the basis of the theoretical results, one might be tempted to question the experimental assignments of the $8\sigma_g$ and $4\pi_u$ orbitals. However, the two $4\pi_u$ IP's at 13.34 and 13.47 eV comprise a spin-orbit doublet, which would not be possible for the $8\sigma_g$ level.

Table V. Comparison between Koopmans' Theorem Ionization Potentials and the Experimental Photoelectron Spectrum of KrF_2

Orbital removed	Koopmans' theorem	Experiment[a]
$8\sigma_g$	14.71	13.90
$4\pi_u$	15.43	13.34, 13.47
$2\pi_g$	17.64	14.37
$3\pi_u$	19.36	16.92
$5\sigma_u$	20.85	17.7
$7\sigma_g$	33.77	23.0

[a] Reference 33.

Molecular Properties

In Table VI are reported calculated molecular quadrupole moments and electric-field gradients as a function of internuclear separation. For these properties near the equilibrium geometry, the SCF and CI results are qualitatively similar. The largest difference reported is for the Kr field gradient, which is 30% larger in the SCF than in the 993-configuration calculation. The two-configuration SCF and 993-configuration results display the same general behavior as a function of internuclear separation. Therefore, the discussion below involves only the 993-configuration results.

The molecular quadrupole moment plotted as a function of Kr–F distance is very reminiscent of a potential energy curve. In fact, the minimum value of the quadrupole moment, ~ -12.7 atomic units, occurs very close to the equilibrium bond distance, 3.61 bohrs. If one assumed Coulson's model, $F^{-0.5}Kr^{+1.0}F^{-0.5}$, electrostatics yield a molecular quadrupole moment of -12.74 atomic units. The agreement between the two values is remarkable.

The electric-field gradient at krypton decreases monotonically from 16.3 atomic units to zero as R increases from 3.0 bohrs to ∞. On the contrary, the fluorine field gradient *increases* monotonically over the same range. For comparison, the Hartree–Fock field gradient of an isolated fluorine atom is 3.02 atomic units.[31]

The most interesting feature seen in Table VI concerns the abrupt change in all three reported properties between $R = 3.75$ bohrs and $R = 5.0$ bohrs. The field gradient at Kr changes particularly abruptly. At this point, it is useful to observe that the maximum in the potential energy curve (Figure 1) occurs at 4.57 bohrs Kr–F separation. Thus, in Coulson's picture,[26] KrF_2 might be labeled "ionic" ($Kr^+ + F + F^-$) for $R < 4.57$ bohrs and "covalent" ($Kr + F + F$) for $R > 4.57$ bohrs. The strongest verification of this model is given by the theoretical Kr field gradients. Near R_e, the field gradient at Kr is not far from 6.77, the SCF value[31] for the isolated Kr^+ ion. However, near the potential maximum, the field gradient at Kr drops precipitously, corresponding to the change from ionic (Kr^+) to covalent (Kr) character.

Conclusion

The results reported above give a clear demonstration of the usefulness of *ab initio* calculations as a tool for gaining understanding and insight into noble gas chemistry. Here, we briefly review these results. (1) The Kr–F bond in KrF_2 is essentially ionic in nature.

---

(29) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955).

(30) C. R. Brundle and G. R. Jones, *Chem. Commun.*, 1198 (1970).

(31) G. Malli and S. Fraga, *Theor. Chim. Acta*, **6**, 54 (1966).

Table VI. *Ab Initio* Electric-Field Gradients and Molecular Quadrupole Moments, in Atomic Units, for KrF_2. The Kr–F Bond Distances are in Bohr Radii. SCF, TCSCF, and 993 Refer to the Calculations Involving 1, 2, and 993 Configurations

R	Quadrupole moment			Field gradient at Kr			Field gradient at F		
(Kr–F)	SCF	TCSCF	993	SCF	TCSCF	993	SCF	TCSCF	993
3.00	−12.21	−12.10	−11.87	9.217	8.658	8.134	1.055	1.085	1.060
3.25		−12.67	−12.39		8.401	7.934		1.363	1.304
3.50	−13.66	−12.84	−12.70	9.431	7.275	7.243	1.515	1.713	1.570
3.75		−12.28	−12.76		4.959	6.040		2.132	1.841
4.50		−10.01	−11.08		0.345	1.595		2.725	2.550
5.00		−9.72	−10.14		0.074	0.461		2.794	2.743
5.50		−9.62	−9.78		0.046	0.167		2.822	2.806
6.00		−9.58	−9.64		0.043	0.084		2.835	2.828
7.00		−9.54	−9.55		0.030	0.035		2.844	2.841
10.00		−9.52	−9.52		0.005	0.005		2.846	2.844

(2) A maximum exists in the linear symmetric KrF_2 potential curve, which results from an avoided crossing of an attractive ionic curve and a repulsive covalent curve. (3) The single configuration model fails to give a stable KrF_2 molecule but does give fairly good approximations to such molecular properties as electric quadrupole moment and electric-field gradient at the nuclei. (4) Two-configuration SCF and valence excited CI calculations give repulsive potential curves with a point of inflection. However, they also give reasonably good approximations for quadrupole moment and field gradient. Finally (5) the details of binding in KrF_2 depend on complicated electron-correlation effects which must be treated with sophisticated forms of wave functions. These effects are not included in the relatively simple SCF, TCSCF, or valence-shell configuration interaction models.

Acknowedgments. We thank Dr. N. Bartlett, Dr. A. D. McLean, and Dr. R. K. Nesbet for helpful discussions.

Sign of the Dipole Moment and Other Properties of Methylsilane

Dean H. Liskow and Henry F. Schaefer III*

Contribution from the Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720. Received March 14, 1972

Abstract: Nonempirical electronic structure calculations have been carried out on CH_3SiH_3 in its staggered form. A flexible basis set of contracted Gaussian functions was used. The present self-consistent-field calculations predict the electric dipole moment to be 0.58 D, +C Si−. This result is in good agreement with the experimental magnitude, 0.73 D, but disagrees with simple electronegativity arguments concerning the polarity of carbon–silicon bonds. However, Shoemaker and Flygare have recently argued on the basis of molecular Zeeman experiments that the sign of the dipole moment should be +C Si−. The predicted sign of the molecular quadrupole moment agrees with experiment, but the quantitative agreement in magnitude is poor. The *ab initio* sign of the dipole moment is not consistent with atomic charges obtained from a Mulliken population analysis of the wave function. The electronic structure of CH_3SiH_3 is discussed and several other molecular properties are reported.

Methylsilane is one of the simplest stable molecules containing a carbon–silicon bond. The absolute value of the dipole moment of CH_3SiH_3 has been known for some time to be 0.73 D.[1–3] Since carbon is usually considered to be more electronegative than silicon (2.5 for C as opposed to 1.8 for Si on Pauling's scale[4]), it might appear reasonable to assume that the electric dipole moment of methylsilane points toward the carbon, that is, −C Si+. However, recent molecular Zeeman effect measurements by Shoemaker and Flygare[5] have challenged this assumption. If the dipole moment is −C Si+, Shoemaker and Flygare find the molecular quadrupole moment along the C–Si axis to be $+(11.74 \pm 0.46) \times 10^{-26}$ esu cm^2. However, if the dipole is oriented +C Si−, the quadrupole moment is $-(6.31 \pm 0.46) \times 10^{-26}$ esu cm^2. Citing several arguments, Shoemaker and Flygare conclude that $-(6.31 \pm 0.46)$ is the correct value of the quadrupole moment and hence that the dipole moment of CH_3SiH_3 points toward silicon, *i.e.*, +C Si−. Shoemaker and Flygare close their communication[5] with "the large difference between the two choices (of the quadrupole moment) should make an *ab initio* calculation useful in the differentiation."

The only previous *ab initio* calculations on CH_3SiH_3 of which we are aware are those of Veillard.[6] Veil-

---

(1) D. R. Lide and D. K. Cole, *Phys. Rev.*, **80**, 911 (1950).

(2) R. W. Kilb and L. Pierce, *J. Chem. Phys.*, **27**, 108 (1957).

(3) J. S. Muenter and V. W. Laurie, *ibid.*, **45**, 855 (1966).

(4) L. Pauling, "General Chemistry," W. H. Freeman, San Francisco, Calif., 1970.

(5) R. L. Shoemaker and W. H. Flygare, *J. Amer. Chem. Soc.*, **94**, 684 (1972).

(6) A. Veillard, *Chem. Phys. Lett.*, **3**, 128 (1969).