and poly A.[7] As shown in Figure 2, the CD spectrum of this complex has a peak at 267 and troughs at 250 and 281 nm. Comparing it with the B-band region of CD spectrum of single stranded $(pA^s)_8$, which had a trough at 281 and a peak at 259 nm, one can presume that $(pA^s)_8$ in the complex also has a left-handed helix. Accordingly, the duplex $(pA^s)_8 \cdot (pU^o)_8$ may well possess a left-handed helical conformation.

This is the first case that oligonucleotides of cyclonucleosides constitute a double helical complex. Both nucleosides A^s or U^o have almost the same torsion angle of $\phi_{CN} = -122°$ [8] and the bases are rigidly fixed at the syn–anti region by the cyclo bonds. If we set these two strands in antiparallel fashion, bases in both strands situate in a position favorable for the hydrogen bonding. Since $(pA^s)_n$ could not form complexes with poly U and $(pU^o)_n$ could not form complexes with poly A, it seemed that the torsion angle of the bases have to be identical to form a double stranded complex. In the case of $(pA^s)_8 \cdot (pU^o)_8$ the direction of the helical turn would be determined by $(pA^s)_8$ which has a strong tendency toward left-handed stacking,[2] and $(pU^o)_8$ stays in a favorable position along the helix by the hydrogen bonding between A^s and U^o residues. We may suggest, therefore, that the torsion angle of bases in mononucleotides of nucleic acids is an important factor to determine the direction of the helical turn and the identity of the torsion angles in the two strands is essential for stable double helical structures.

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Probable Nonexistence of Xenon Monofluoride as a Chemically Bound Species in the Gas Phase

Sir:

The long-range interaction between Xe and F may be expressed as the sum of two terms:[1] (a) the induction energy due to the permanent quadrupole moment of the F atom and the polarizability of the Xe atom and (b) the dispersion attraction due to the polarizabilities of the two atoms. Assuming no *chemical* attraction between Xe and F, the long range terms will yield an attractive potential well similar to that found[2] for Xe–Ne, where the bond distance r_e(Xe–Ne) is 3.8 Å and the dissociation energy D_e is 0.15 kcal/mol.

However, following the discovery of XeF_2, XeF_4, and XeF_6 during the past decade, many workers have assumed[3] that XeF is a chemically bound species, with a dissociation energy of ~20 kcal/mol. This assumption is based in large part on the electron spin resonance (esr) experiments of Falconer and Morton.[4] They reported the esr spectrum of XeF in crystals of XeF_4 subjected to γ radiation at 77°K. Furthermore, kinetic studies have suggested the existence of XeF as an intermediate in water oxidation[5] and in NO and NO_2 oxidation[6] by XeF_2. Finally, it is thought[7,8] that the decomposition of both $XeF^+OsF_6^-$ and $FXeOSO_2F$ involves the XeF radical.

In the present communication we report the results of *ab initio* electronic structure calculations on the lowest $^2\Sigma^+$ and $^2\Pi$ states of XeF. This study is the logical extension of our earlier work[9,10] on the krypton fluorides. The chosen basis set of Slater-type functions centered on Xe and F is shown in Table I. The properties of the F atom basis are well understood.[9–11] For the ^1S ground state of the Xe atom, the present basis yields a self-consistent field (SCF) energy of −7232.1204 hartrees, which may be compared to the numerical Hartree–Fock results of Mann,[12] −7232.14 hartrees, and Fischer,[13] −7232.153 hartrees. In either case, it is seen that the present basis set for xenon yields an SCF total energy within 1 eV of the nonrelativistic Hartree–Fock limit.

Table I. Basis Set of Slater Functions, $r^{n-1}e^{-\zeta r}$, for Calculations of Xenon Fluorides

Atom	Type	Orbital ζ	Atom	Type	Orbital ζ
Xe	1s	55.110	Xe	3d	20.469
	1s	36.545		3d	11.964
	2s	26.283		4d	7.727
	2s	22.451		4d	5.233
	3s	14.881		4d	3.379
	3s	12.067		5d	2.0
	4s	7.620		5d	1.2
	4s	5.566		4f	3.5
	5s	3.518		4f	2.5
	5s	2.173	F	1s	11.011
	2p	30.678		1s	7.917
	2p	21.424		2s	3.096
	3p	13.721		2s	1.946
	3p	10.709		2p	6.165
	4p	7.422		2p	3.176
	4p	5.036		2p	1.612
	5p	3.516		3d	4.0
	5p	2.016		3d	2.0
				4f	3.0

The present calculations were carried out using the

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ALCHEMY program.[14] Xe plus F($P^2{}_u$) can give rise to electronic states of $^2\Sigma^+$ and $^2\Pi$ symmetry, and single-configuration SCF calculations were carried out for both states. The internuclear separations chosen ranged from 3.0 bohrs (1 bohr = 0.5292 Å) to 10.0 bohrs. In addition, a wide variety of configuration interaction (CI) calculations were carried out for the $^2\Sigma^+$ ground state. Of these CI calculations, only results from the first-order wave functions are given. Detailed descriptions of the first-order wave function have been given elsewhere.[9–11] Our wave function included all configurations in which not more than one of the 11 valence electrons occupied an orbital beyond the valence shell. The valence shell consisted of all molecular orbitals which correlated in the separated atom limit with the 2p orbital of F and the 5p orbital of Xe. For $^2\Sigma^+$ XeF using the basis set described earlier, there were 354 configurations in this first-order wave function. The additional CI calculations were performed in order to (a) test the deletion of different types of basis functions and configurations and (b) test the first-order approach by adding a large number of other configurations to the wave function. The most extensive wave function investigated contained 2142 configurations, including in addition all double excitations from the occupied valence σ orbitals. However, the qualitative result was the same as that found with the first-order wave function.

Figure 1 summarizes our results for diatomic XeF. There it is seen that both the $^2\Sigma^+$ and $^2\Pi$ states are repulsive. Note that the configuration interaction treatment of the $^2\Sigma^+$ state yields a significantly less repulsive curve. However, even in the latter case, the $^2\Sigma^+$ ground state is repulsive by ~20 kcal/mol at the experimental XeF_2 bond distance 1.977 Å = 3.737 bohrs. At a somewhat longer bond distance, 2.117 Å = 4.0 bohrs, the potential curve is repulsive by 10 kcal/mol. Thus it is clear that the present theoretical study predicts XeF to be a bound species *only* in the van der Waals sense of our first paragraph. That is, we predict no chemical bond between Xe and F. We have not explicitly calculated the van der Waals attraction, since the dispersion term is not described by the type of wave function used here.[11]

Since the experiments of Falconer and Morton[4] were carried out in the solid state, it is conceivable that there is no conflict between their work and ours. For example, the dissociative XeF radical might somehow be trapped in the XeF_4 crystal long enough to produce an esr spectrum.

It should be noted that preliminary elastic scattering molecular beam experiments by Lee[15] support our contention that XeF is not a chemically bound species. Finally, Klemperer[16] plans to determine the dipole moment of XeF using recently developed methods for studying van der Waals bound molecules. A small dipole moment (~0.1 D) would be consistent with the present theoretical results.

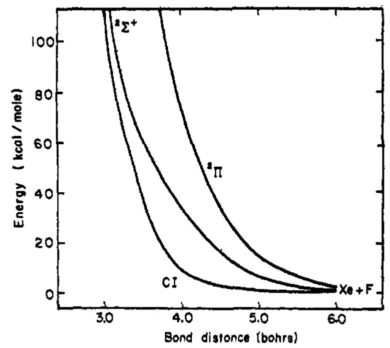

Figure 1. Potential energy curves for xenon monofluoride. The curves labeled $^2\Sigma^+$ and $^2\Pi$ are the results of single-configuration SCF calculations. The curve labeled CI refers to the 354 configuration first-order wave functions. The potential curves have been shifted to yield the same dissociation limit, Xe(^1S) + F(^2P_u).

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(17) Alfred P. Sloan Fellow.

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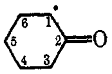
2-Alkanonyl Radicals. Allylic or Not?

Sir:

The 2-cyclohexanonyl radical (I) originally attracted our attention in connection with studies of conformational effects in free radicals containing six-membered rings.[1] However, an assessment of the role of resonance stabilization (*e.g.*, I $\underset{?}{\leftrightarrow}$ II) in 2-alkanonyl radicals



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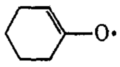

II

soon became a problem in itself, particularly in view of several conflicting data and interpretations in the literature[2–10] concerning the properties of this important class of free radicals. We now wish to report the measurement of the ^{13}C and ^{17}O hyperfine splitting constants (hfsc) of the 2-cyclohexanonyl radical by epr spectros-

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