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A Theoretical Study of the Bond-Bond Interaction Force Constant in XF_2 Molecules

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A comparison of the results of a semi-empirical molecular orbital calculation for OF_2 with the empirical interaction force constants for OF_2, NF_2 and CF_2 leads to the conclusion that electron delocalization, of a type commonly identified as no bond-double bond resonance, strongly influences the magnitude of the interaction constants for these molecules. This analysis further suggests that Urey-Bradley fluorine-fluorine non-bonded interaction constants for polyfluorinated molecules may commonly be inflated by such resonance. It was expected that the MO calculation would also help clarify the origin of the unusual stability of polyfluorinated systems, but the results are largely inconclusive on this point.

Ein Vergleich der Ergebnisse einer semiempirischen MO-Rechnung für OF_2 mit den empirischen Wechselwirkungs-Kraftkonstanten für OF_2, NF_2, CF_2 führt zu dem Schluß, daß Elektronendelokalisierung unter Beteiligung ionischer Resonanzstrukturen die Größe der Wechselwirkungskonstanten dieser Moleküle stark beeinflußt. Diese Analyse führt ferner zu dem Ergebnis, daß die Urey-Bradley-Wechselwirkungskonstanten der „nicht gebundenen" Fluoratome im allgemeinen durch eine solche Resonanz stark vergrößert würde. Die MO-Berechnungen geben aber entgegen den Erwartungen keinen Beitrag zur Klärung der ungewöhnlichen Stabilität polyfluorierter Systeme.

Une comparaison de résultats de calculs semi-empiriques d'orbitales moléculaires pour OF_2 avec les constantes de force d'interaction empiriques pour OF_2, NF_2 et CF_2 conduit à conclure que la délocalisation électronique du type habituellement identifié comme résonance liaison-double liaison, a une influence sur la grandeur des constantes d'interaction de ces molécules. Cette analyse suggère en outre que les constantes d'interaction de Urey-Bradley entre atomes de fluor non liés des molécules polyfluorées peuvent être exaltées par une telle résonance. On pouvait espérer que les calculs d'orbitales moléculaires aideraient à comprendre la raison de la stabilité inhabituelle des systèmes polyfluorés, mais les résultats obtenus ne sont pas concluants.

1. Introduction

It has long been recognized that molecules with two or more fluorine atoms bonded to a common atom, when compared to singly fluorinated species, possess an added stability and significantly shortened X–F bonds. For example five kcal are evolved in the disproportionation

$$2CH_3F \rightarrow CH_2F_2 + CH_4$$

and the C – F bond is shortened ~0.03 Å [1, 2]. Such behavior has been cited as strong evidence that the usual procedure of relating large fluorine-fluorine Urey-

Bradley non-bonded interaction constants to parameters derived from a strictly repulsive Leonard-Jones two body potential is inconsistent with experimental fact [3, 4]. Two interpretations more consistent with the thermodynamic and structural data are possible. It has been suggested that perhaps the Urey-Bradley Force Field (UBFF) approximation is valid in indicating strong fluorine non-bonded interactions but that the large interaction constants might better be viewed as a rough measure of a stabilizing overlap which, in turn, is responsible for the surprising stabilities of polyfluorinated systems [4]. An alternate interpretation is that polyfluorinated molecules experience a significant delocalization of the bonding electrons of a type commonly represented qualitatively as a double bond-no bond resonance [1]. This delocalization both stabilizes the molecules and makes possible a strong bond-bond interaction which, in the UBFF model, appears as a large non-bonded interaction constant.

Because of these divergent views which chemists have developed concerning the bonding in polyfluorinated systems the research reported here was initiated to sort out the basic cause of the large fluorine-fluorine UBFF non-bonded interaction constants and to clarify, in so far as possible, the source of the unusual stability of polyfluorinated molecules. The simplest molecular system suitable for this study is OF_2 which is known to have a large bond-bond interaction constant [5, 6]. Since CF_2 and NF_2 have structural and vibrational parameters very similar to those of OF_2, we have examined these molecules as a group.

2. Experimental Quadratic Force Constants

It is generally true that the asymmetric stretching frequency, ν_3, is greater than the symmetric stretching frequency, ν_1, for symmetric triatomic molecules XY_2. For linear molecules an analysis based on a general quadratic force field shows that provided X and Y are of comparable mass this is inevitable in the absence of extremely large interaction constants [7]. Thus, no example of the inversion of this order is known for linear triatomics. The requirement of unusually large interaction constants for an inversion of this frequency order is carried over to non-linear triatomics. Thus, with the exception of the molecular series under consideration (OF_2, NF_2 and CF_2), NO_2^- is the only known case wherein $\nu_1 > \nu_3$ [4].

One must expect, therefore, that a force field analysis for these XF_2 molecules will show either a large bond-bond interaction constant, or a large non-bonded interaction constant should the UBFF approximation be applied. The latter follows since in the UBFF approach, after transformation to valence coordinates, the bond-bond interaction constant is determined by the magnitude of the non-bonded interaction. Nevertheless, it seemed necessary to examine the magnitude of these terms in a UBFF calculation for OF_2, NF_2 and CF_2 prior to any quantum chemical study of their origin.

The results for the UBFF calculations together with the pertinent experimental data appear in Table 1. The assumption was made that F', the coefficient for the term linear in the non-bonded coordinate, is zero rather than setting $F' = -0.1 F_{FF}$ as is more customary [8], but this variation has an insignificant effect on the magnitude of F_{FF}, the non-bonded constant, which is of primary interest to this study. The F_{FF} values, being of the same magnitude or larger than the principle stretching constant K, are seen to be unrealistically large.

The F_{FF} values in Table 1 are the largest non-bonded constants to be reported for any supposedly strictly sigma bonded systems, although F_{FF} values are commonly of the order of $K/2$. Since there is little reason to suspect particularly unique bonding for OF_2 it is possible that whatever is reponsible for the unacceptably large F_{FF} values in these XF_2 molecules may be at least partly responsible for the substantial F_{FF} values common to polyfluorinated systems.

Table 1. *Urey-Bradley (K, H and F) and general quadratic force constants for* XF_2 *molecules together with the relevant experimental parameters. Force constant units are all in millidyne/Å*

	CF_2	NF_2	OF_2			
					I[a]	II[b]
K	4.42	3.60	3.15	f_r	4.26	3.95
H	0.07	0.02	−0.08	f_α/r^2	0.69	0.72
F	6.01	4.51	3.14	f_{rr}	1.10	0.81
ν_1 (cm^{-1})	1222[c]	1069.6[d]	929[e]	$f_{r\alpha}/r$	0.38	0.14
ν_2	668	573.4	461			
ν_3	1102	930.7	828			
r_{xf}(Å)	1.32	1.37	1.38			
$\sphericalangle$ FXF	100°	104.2°	101.5°			

[a] Ref. [5]. — [b] Ref. [6].

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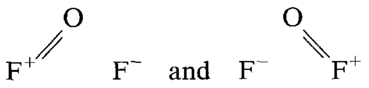
There have been several studies of OF_2 using a general valence force field model [9]. Though limited by data, Duchesne and Burnelle determined f_r, f_α and f_{rr} as a function of $f_{r\alpha}$ and then singled out the set of constants included in Table 1. A set which Pierce *et al.*, deduced more recently using centrifugal distortion data is also included. The large positive value of f_{rr} was earlier noted by Linnett and Hoare [10] who had previously found f_{rr} to be small and oftentimes negative for a large number of sigma bonded molecules. Intrigued by the size of f_{rr} for a molecule supposedly lacking significant delocalization of the bonding electrons, they identified non-bonded interaction as a likely factor.

If it is agreed that the large interaction constants are closely interrelated with the inversion of the frequency values for ν_1 and ν_3 then it becomes particularly easy to visualize the difficulty in identifying the source of these large interaction constants. Since the F–F distance oscillates with Q_1 but not Q_3, a stabilizing F–F interaction would clearly increase only ν_1 and thus also the $\nu_1 : \nu_3$ ratio. However, the same ratio would be increased, primarily by a reduction in ν_3, if double bond-no bond resonance forms



of relatively low energy contribute substantially more to the OF_2 structure in the asymmetrically distorted state than at equilibrium. In either case, the net effect is an increase in the $\nu_1 : \nu_3$ ratio and thus in the calculated value of f_{rr}.

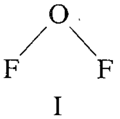
Thus, in so far as OF_2 is typical of polyfluorinated systems, this vibrational analysis only affirms the original dichotomy: either polyfluorinated molecules are stabilized by a bonding F–F interaction which also inverts the relative magnitudes of ν_1 and ν_3, or bonding in fluorinated molecules involves delocalized molecular orbitals (possibly best represented by a no bond-double bond resonance) which are responsible for both the added stability and the situation $\nu_1 > \nu_3$. Of course, some combination of these factors may in fact be operating.

3. Molecular Orbital Calculation

The unreasonably large values of F_{FF} obtained for the XF_2 molecules suggest that some significant effect other than non-bonded interaction is dominant in determining the magnitudes of the experimental interaction constants f_{rr} and F_{FF}. An apparent alternative is delocalization of the bonding electrons which, following Brockway [11] and Hine [1], we have chosen to represent by a no bond-double bond resonance. Thus to test the importance of such resonance in OF_2, particularly in asymmetrically distorted configurations, a semi-empirical molecular orbital calculation was designed with procedures chosen so as to be both feasible and, hopefully, capable of yielding a significant result.

A. *The Configuration Interaction Calculation*

The method chosen emphasized a comparison of the results for a single Slater determinant calculation based on structure I with results for a configuration interaction calculation using Slater determinants embodying structures I, II and III.



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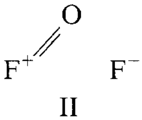

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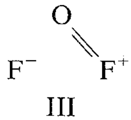

III

Molecular orbitals were constructed from Slater AO's in a manner designed to produce electron densities characteristic to each of the above structures. Eight electrons (three 2*p* electrons from each fluorine and two 2*p* electrons from oxygen) were treated explicitly while the remaining electrons were incorporated into a "non-polarizable" core. This separation into bonding and non-bonding electron sets, as well as the techniques used in integral evaluations, was based on semi-empirical methods described by Pohl *et al.* [12] which are reminiscent of the more familiar sigma-pi separability and integral evaluation techniques commonly applied to unsaturated organic systems.

The basis set of AO's is represented pictorially in Fig. 1 and symbolically, along with the localized molecular orbitals, in Table 2. These molecular orbitals have been used together with the formalism presented by Parr [13] to deduce the values of C_{II} and C_{III} in the wavefunction

$$\Psi = C_{\mathrm{I}} D_{\mathrm{I}} + C_{\mathrm{II}} D_{\mathrm{II}} + C_{\mathrm{III}} D_{\mathrm{III}} \tag{1}$$

where D_{I}, D_{II}, and D_{III} represent Slater determinants constructed from the MO's tabulated in Table 2. The reduction in electronic energy resulting from the electron delocalization associated with II and III is also obtained.

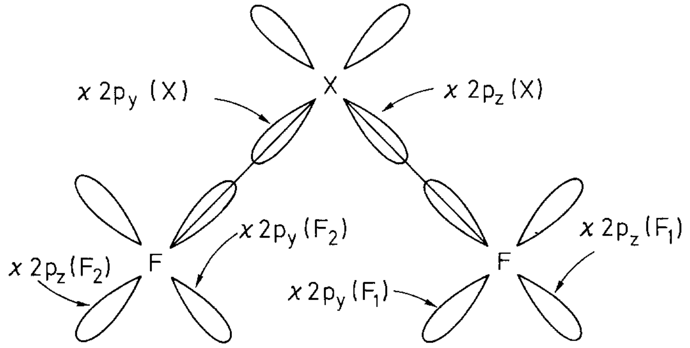

Fig. 1. Atomic orbital basis set for the CI calculations

Table 2. *Symbolic representation of the atomic and localized molecular orbitals making up the Slater determinants, D_{I}, D_{II} and D_{III}, of the configuration interaction calculation*

D_{I}	D_{II}	D_{III}
$\varphi_1 = y(\mathrm{F}_2)$	$\varphi_1 = y(\mathrm{F}_2)$	$\varphi_3 = N_2[y(\mathrm{O}) + z(\mathrm{F}_2)]$
$\varphi_2 = N_1[z(\mathrm{O}) + z(\mathrm{F}_1)]$	$\varphi_2 = N_1[z(\mathrm{O}) + z(\mathrm{F}_1)]$	$\varphi_4 = y(\mathrm{F}_1)$
$\varphi_3 = N_2[y(\mathrm{O}) + z(\mathrm{F}_2)]$	$\varphi_5 = N_3[y(\mathrm{O}) + y(\mathrm{F}_1)]$	$\varphi_7 = N_4[z(\mathrm{O}) + y(\mathrm{F}_2)]$
$\varphi_4 = y(\mathrm{F}_1)$	$\varphi_6 = z(\mathrm{F}_2)$	$\varphi_8 = z(\mathrm{F}_1)$

$y(\mathrm{A})$ is the $2p_y$ Slater AO for atom A.
$z(\mathrm{A})$ is the $2p_z$ Slater AO for atom A.

In essence, the above calculations require that the system Hamiltonian be written as

$$\mathscr{H} = -\frac{1}{2}\sum_{i=1}^{8} \nabla_i^2 + \sum_{i>j=1}^{8} 1/r_{ij} - \sum_{i=1}^{8}\sum_{\alpha=1}^{3} (Z_{\mathrm{eff}})_\alpha / r_{i\alpha} + \sum_{\alpha>\beta=1}^{3} \frac{(Z_{\mathrm{eff}})_\alpha (Z_{\mathrm{eff}})_\beta}{R_{\alpha\beta}} \tag{2}$$

where lower case subscripts run over electrons and Greek letters over core terms. The matrix elements, H_{ij}, required to formulate the secular equation have their usual form:

$$\begin{aligned} H_{ij} &= \int\limits_{\substack{\text{all}\\\text{space}}} D_i \mathscr{H} D_j \, d\tau_1 \ldots d\tau_8 \\ &= \int\limits_{\substack{\text{all}\\\text{space}}} [\lambda_1(1)\lambda_2(2)\ldots\lambda_8(8)] \mathscr{H} \left[\sum_P (-1)^P \prod_{i=1}^{8} \lambda_i(i) \right] d\tau_i \ldots d\tau_8 \end{aligned} \tag{3}$$

where the λ_i represent the spin orbitals formed from the MO's of Table 2.

The semi-empirical methods [12] employed to evaluate the integrals appearing in H_{ij} require the specification of the Slater AO exponential parameters and the effective charges, Z_{eff}, for each of the cores. The exponential parameters for the O^{+1} and F^{+2} cores were estimated from the Slater-rules while the effective core charges were obtained from Hatree-Fock potentials. That is, Z_{eff} values for the atoms were calculated from the Herman-Skillman tables of potentials [15] and were then modified for the cores by adding +1 in the case of oxygen and +2 in the case of fluorine. Three center integrals were reduced to two center integrals using Mullikens approximation and the overlap of AO's centered on the two fluorine atoms was taken as zero. The problem was further simplified by constraining the valence angle to 90° and equating the AO coefficients in the localized molecular orbitals (Table 2).

Finally, binding energies were deduced from the equation

$$E_B = P^0_O + 2P^0_F + I_{v(O)} + I_{v(O^+)} + 2I_{v(F)} + 2I_{v(F^+)} + 2I_{v(F^{+2})} + E_{\text{nuc}} + \varepsilon$$

where ε is the calculated electronic energy, P^0_x is the x atom promotion energy as given by Hinze and Jaffé [16], and $I_{v(y)}$ is the valence state ionization potential for species y [17].

B. Results of the Configuration Interaction Calculation

The procedure outlined above were used to evaluate the single configuration and three configuration energy values for the OF_2 molecule for several assumed geometries. The binding energies were determined for various phases of both the symmetric and asymmetric stretching modes with the latter results as detailed in Table 3. Variation of the symmetric stretch coordinate led to a single configuration equilibrium O–F bond length of 1.09 Å, nearly 0.3 Å shorter than observed, and an equilibrium binding energy of 4.00 eV, in excellent agreement with the accepted value of 3.9 ± 0.1 eV. The large bond length discrepancy seems to be typical of

Table 3. *Binding energy, $E_{(I)}$, for the single configuration calculation and binding energy, $E_{(II)}$, plus Slater determinant coefficients, C_{II} and C_{III}, for the configuration interaction calculation as a function of displacement in the asymmetric stretching coordinate*

R_{OF_1}(a.u.)	R_{OF_2}(a.u.)	$E_{(I)}$(eV)	$E_{(CI)}$(eV)	C_{II}	C_{III}
1.97	2.17	3.769	3.807	0.044	0.006
1.98	2.16	3.795	3.829		
1.99	2.15	3.854	3.884	0.038	0.009
2.00	2.14	3.914	3.941		
2.01	2.13	3.922	3.948	0.033	0.011
2.02	2.12	3.929	3.953		
2.03	2.11	3.936	3.959	0.029	0.014
2.04	2.10	3.976	3.998		
2.05	2.09	3.980	4.001	0.026	0.019
2.06	2.08	3.982	4.002		
2.07	2.07	3.996	4.015	0.021	0.021

such calculations [18] while the remarkable agreement of binding energies is undoubtedly fortuitous.

The presence of D_{II} and D_{III} in the calculation did not effect the calculated O–F bond length and only slightly increased the equilibrium binding energy. However, a comparison of the single configuration energy values $E_{(\mathrm{I})}$ with the three configuration energy values $E_{(\mathrm{CI})}$ (see Table 3) shows a rapid increase in the relative importance of configurations II or III as the molecule is displaced in the asymmetric stretching coordinate. Thus, the quantity $E_{(\mathrm{CI})} - E_{(\mathrm{I})}$ is doubled as the molecule is distorted by 0.05 Å in both bonds, a distance comparable to the classical turning point for this mode. This observation is consistent with a significant reduction in ν_3 as a consequence of electron delocalization.

The effect of no bond-double bond resonance in lowering ν_3, as estimated theoretically, can be expressed quantitatively in terms of a theoretically evaluated interaction constant f_d. The vibrational potential energy of OF_2 in the asymmetric mode may be expressed as

$$\Delta E = \tfrac{1}{2} f_r (\Delta r_1^2 + \Delta r_2^2) + f_{rr} \Delta r_1 \Delta r_2 \tag{4}$$

$$= f_r \Delta r^2 - f_{rr} \Delta r^2 \tag{5}$$

since $\Delta r = \Delta r_1 = -\Delta r_2$ in this coordinate. Thus, depending on the theoretical model,

$$\Delta E_{(I)} = (f'_r - f'_{rr})\, \Delta r^2 \tag{6}$$

or

$$\Delta E_{(\mathrm{CI})} = (f_r - f_{rr})\, \Delta r^2 \tag{7}$$

Combination of Eqs. (6) and (7) defines f_d as

$$f_d = f_{rr} - f'_{rr} \tag{8}$$

$$= \frac{\Delta E_{(I)} - \Delta E_{(\mathrm{CI})}}{\Delta r^2} - (f'_r - f_r)\,. \tag{9}$$

In the theoretical treatment f'_{rr} is the bond-bond interaction constant for an essentially σ bonded system with localized bonding electrons as represented by D_I only, while f_{rr} also includes contributions from the double bond-no bond resonance introduced through D_{II} and D_{III}. Of course, f'_{rr} cannot be deduced directly from the theoretical calculations but empirical results for strictly σ-bonded systems would suggest an absolute value less than 0.3 millidynes/Å. Thus f_d, if large, can be closely related to f_{rr} and, in any case, is the contribution to f_{rr} from electron delocalization and is determinate from the results in Table 3, provided the quantity $(f'_r - f_r)$ can be estimated. It is the usual view that resonance increases bond strength and thus, if significant, this quantity should be negative. This concept fixes the lower limit for f_d since then

$$f_d \geqq \frac{\Delta E_{(I)} - \Delta E_{(\mathrm{CI})}}{\Delta r^2}\,. \tag{10}$$

Table 4 shows values of f_d deduced from the above equality (i.e., assuming $f'_r = f_r$ in Eq. (9)). A value of 1.1 millidynes/Å is indicated for values of Δr comparable to the expected vibrational amplitude. Thus, the model for this calculation clearly leads to the prediction that the bond-bond interaction constant for OF_2 contains a large contribution from electron delocalization, here represented as a no bond-double bond resonance. In fact, the predicted contribution is very similar in magnitude to the experimental values of f_{rr} which appear in the Table 1.

Table 4. *Values for f_d, the theoretically determined contribution of resonance to the bond-bond interaction force constant, f_{rr}, for various displacements, Δr, in the asymmetric stretching coordinate*

Δr(Å)	f_α(millidynes/Å)
0.0212	1.17
0.0264	1.18
0.0317	1.04
0.0370	0.92
0.0423	1.00
0.0476	1.04
0.0529	1.07

However, the extent to which no bond-double bond resonance affects the binding energy for OF_2 is trivial by this calculation with the calculated stabilization per resonance structure being 0.22 kcal, an order of magnitude less than that which Hine estimates (3.2 kcal/resonance structure) for fluorocarbons [1].

4. Discussion

One of the more interesting features of this study was the acute sensitivity that the theoretical f_{rr} value displayed to variation of the wave function. Although C_{II} and C_{III} are very small, 0.02 at equilibrium, and remain less than 0.05 for a 0.05 Å distortion in the asymmetric stretching coordinate, the analysis indicates an increase of ~1.0 millidynes/Å in f_{rr} upon the inclusion of D_{II} and D_{III} in the trial wave function. This suggests that, although electron delocalization may be relatively unimportant in determining equilibrium molecular properties for such molecules, the effect on vibrational frequencies, and thus f_{rr}, may be substantial.

This study also strongly suggests that the large non-bonded fluorine-fluorine interaction constants, F_{FF}, obtained for OF_2, NF_2 and CF_2 are strongly inflated by a bond-bond interaction which has its origin in electron delocalization. It seems likely that this phenomenon occurs to some degree in most polyfluorinated molecules, and thus our results tend to support efforts to relate large interaction constants to factors other than non-bonded interactions, and the conclusion that large f_{rr} values for CF_4 and SiF_4 can be interpreted as due to non-bonded F–F repulsions seems premature [19].

For several years chemists have felt that the UBFF non-bonded interaction force constants, F_{HH}, for hydrogen are unacceptably small in comparison with values calculated for other non-bonded atoms. Since hydrogen is incapable of participating in the type of resonance embodied in our model, it seems quite possible that the F_{HH} values are, in fact, a better measure of the actual non-bonded interaction than are values obtained for other atoms.

Since our study does predict very little resonance stabilization in OF_2, the question as to the origin of the unusual stability of polyfluorinated molecules remains largely unanswered. There are at least two factors that caution against using our results as evidence of the relative insignificance of resonance stabilization in polyfluorinated molecules in general. First it is possible that the model was too constrained and, perhaps, too simple to show the complete effect of resonance [20]. Secondly, one might expect that such resonance will be enhanced by an increasing difference in the electronegativities of the fluorine and the central atom so that it is not inconceivable that the resulting resonance stabilization in CF_4 be an order of magnitude greater than for OF_2. It is certainly true that the extremely large F_{FF} value for CF_2 indicates that resonance is more extensive in CF_2 than OF_2 so that, had the molecular orbital calculation been for CF_2, we may have found a considerably greater resonance stabilization energy. Unfortunately, such a result would not have been transferable to ordinary fluorinated hydrocarbons, since, as Kaufman has pointed out for NF_2 [21], CF_2 has unoccupied carbon valence shell orbitals available for purposes of multiple bonding.

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