

THE ELECTRONIC STRUCTURE OF THE FLUORINE MOLECULE

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Evidence is being presented that F_2 has a different type of electronic structure than have Cl_2 , Br_2 , I_2 , as suggested by the quanticle theory. The internuclear distance, the vibrational force constant and their changes on excitation for F_2 do not agree with those expected for the structures $X^+ \bar{e}_2 X^+$ and $X^+ \bar{e}_2 Y^+$, which fit the 3 other halogen and interhalogen molecules respectively.

1. INTRODUCTION

It is a well known peculiarity of F_2 that its enthalpy of dissociation into atoms ($-\Delta H$) does not fit into the gradation valid for the other three halogen molecules, as is shown in table 1, line 1. Since ΔH is a relatively small difference of two more fundamental energies (see section 2), this irregularity in itself is not conclusive evidence for a profound difference in binding

between F_2 and the other halogens. However, it has been possible to show for a series of simpler molecules, namely of monohydrides [1] that the examination of internuclear distances and force constants allows one to distinguish for them two different types of intramolecular binding. Applying and extending this approach in the present work, we can substantiate more firmly the implication that there must exist important differences between the electronic structure of F_2 and those of the other halogen molecules X_2 and XY . We finally wish to suggest that the ideas of the quanticle theory may point to the essence of these differences.

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Table 1
Various measures of binding strength

		F_2 b)	Cl_2	Br_2	I_2
1	$-\Delta H$ (kcal/mol)	37.5	57.2	45.4	35.5
2	$-I$ (kcal/mol)	803.4	600.0	546.0	482.0
3	$1/r_e$ a. \AA^{-1}	0.7081	0.5030	0.4379	0.3750
	b. relat.	1.888	1.3413	1.1677	1.0000
4	k_e a) a. md/ \AA	4.752	3.2863 ₅	2.4578	1.7206
	b. relat.	2.762	1.9100	1.4284	1.0000
5	4b/3b	1.463	1.4240	1.2232	1.0000
6	r_e (\AA)	1.411	1.988	2.283 ₆	2.666 ₆

a) The data for ω_e , from which k_e is calculated, as well as of r_e are, if not differently stated, from Herzberg's book, ref. [2]. This applies also to the data in section 3.

b) The data for r_e and ω_e of F_2 are estimated in ref. [3] on the basis of r_0 and ω_e given in ref. [4].

2. DIFFERENT MEASURES OF BINDING STRENGTH

The binding strength (BS) within the molecules will serve here as one of the main criteria of their electronic structure. If the latter is expressed correctly by formula (II) (see section 4), the ΔH values in table 1, line 1 are not an appropriate measure of BS, because the binding involves not the neutral atoms but $2X^+$ and $2e^-$. Since the energy of ionization [eq. (1)]



is exactly known, one can derive the energy of the process in eq. (2)



and arrives at the energies of ionization, I , given in table 1, line 2. They do not show the irregularity of line 1: the energy of the dissociation of F_2 into the two positive cores and the two electrons, assumed to be binding them according to (III), is by far the largest.

In the lines 1 and 2 of table 1 the energy of the molecules is compared with that of their remote disruption products. We have two other criteria of BS which compare analogous molecules directly in their normal state. They are the reciprocal of the internuclear distance r † and the vibrational force constant k . They are given in lines 3a and 4a of table 1. Again F_2 exhibits the largest BS and does not show qualitatively the anomaly of line 1. However, a more quantitative comparison leads to the following irregularity.

In the lines 3b and 4b the relative $1/r$ and k values are given, choosing those of I_2 as 1. One sees that the corresponding values of Br_2 , Cl_2 , F_2 are larger for k than for $1/r$, e.g., for Cl_2 1.91 and 1.34 respectively. This expresses numerically the well known†† greater sensitivity of k than of r for molecules of closely analogous structure. Hence, the increase of the ratio, given in line 5, of the values in lines 4b/3b from 1.0 for I_2 to 1.42 for Cl_2 is also understandable. Contrary to this regular behavior of the heavier halogens, the ratio for F_2 (1.46) is only insignificantly larger than that for Cl_2 . This indicates more strongly than the irregularity of

† Here and in the following text the symbols r and k mean r_e and k_e . The same applies to ω .

†† According to ref. [5] k is approximately proportional to $(1/r)^2$ for Cl_2 , Br_2 , I_2 and 6XY interhalogen molecules. F_2 does not fit into the corresponding straight line in fig. 1 but no attention has been paid to this irregularity.

the energy of dissociation into atoms, that F_2 has a different type of binding than its analogues.

3. COMPARISON OF BS IN THE HALOGENS X_2 WITH INTERHALOGENS XY

The following comparison proves definitely the particularity of the binding type in F_2 .

3.1. Internuclear distances r_e (Å)

The r values are known for the following XY molecules:

FCl 1.6281; FBr 1.7556; FI 1.9089;
ClBr 2.138; ClI 2.3207.

The r values in molecules of analogous electronic structure can be expected to show approximate additivity. This is tested in table 2 forming the differences Δ , e.g. I-Cl, for molecules containing one common atom. It results in Å: FI-FCl 0.2808, ClI-Cl₂ 0.333, I₂-ClI 0.3459, leading to the average 0.317 ± 0.027 . For the 5 other Δ , not involving F_2 and given in column 3, the deviations in column 4 are even smaller and their average is ± 0.016 .

On the other hand, comparing the values in column 6 for the Δ 's involving F_2 with the corresponding ones in column 3, one sees that the difference between them, given in column 7, is on the average $0.202/0.016 = 12.6$ times larger than the average deviation in column 4. This means that $r = 1.141$ of F_2 is larger by 0.20 Å than would correspond to additivity when compared with FCl, FBr, FI. Since the r of the latter three molecules shows approximate additivity when combined with the values of ClBr, ClI, BrI, Cl₂, Br₂, I₂, one can conclude that F_2 has a different electronic structure than the other 9 molecules.

3.2. Force constants k_e

The peculiarity of F_2 can be demonstrated by the k values of the X_2 and XY halogen molecules in the following way. For the XY molecules not containing F,

$$k(XY) = [k(X_2)k(Y_2)]^{1/2} \quad (3)$$

applies closely†. This can be seen in table 3. In line 4 is given the ratio of the values at the left (line 2) over those at the right side (line 3) of eq. (3) and they are close to 1 for ClBr, ClI, BrI, the average being 0.982. Contrary to this the values in line 4 for FCl, FBr, FI are dis-

† The geometric mean applies better than simple additivity also in some other cases. See ref. [6, p. 82].

Table 2
 Δr_e (Å) between molecules with one common atom

1 Δ	Not involving F ₂			5 Δ	Involving F ₂	
	2 No.	3 Aver.	4 ±		6 A	7 3 min 6
Cl-F	2	0.371	0.011	FCl-F ₂	0.217	0.154
Br-F	2	0.519	0.009	FBr-F ₂	0.345	0.174
I-F	2	0.775	0.025	FI-F ₂	0.498	0.277
Br-Cl	2	0.141	0.009			
I-Cl	2	0.317	0.027			
I-Br	2	0.168	0.015			
Average	2		±0.016			0.202 ± 0.050

Table 3
 Testing of eq. (3)

1	XY	FCl	FBr	FI	ClBr	ClI	BrI
2	$k(XY)$	4.562	4.071	3.600	2.674	2.383	2.064
3	$[k(X)_2 k(Y)_2]^{1/2}$	3.952	3.418	2.859	2.842	2.378	2.057
4	2/3	1.154	1.190	1.259	0.941	1.002	1.003

tively larger than 1, they increase with the polarity of the molecule and the deviation from 1 can be characterized by their average 1.20 ± 0.04 .

Since in the ratio 2/3 the value of $k(F_2)$ is in the denominator, this comparison shows that the actual $k(F_2)$ is smaller than one would expect by comparison with the other molecules. This and the excessively large value of r (section 3.1) prove that the BS within F₂ is smaller than it would be if F₂ had the same electronic structure as the other X₂ and XY halogens.

3.3. Comparison of the ground with excited states

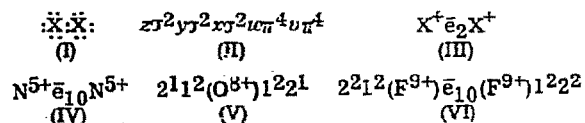
This comparison offers the simplest and most direct proof that F₂ differs from the following molecules for which the r and ω values are known for the ground (X) and the excited A states: FCl, FI, Cl₂, ClI, I₂; this is true also for FBr and Br₂ for which only ω is known†. For all these 7 molecules the X state is ¹Σ, the A state is ³π and the BS is smaller for the A state than for the X state. For instance for FI the changes on excitation are [7]: for r from 1.9089 to 2.1189 Å, for ω from 608.2 to 406.5 cm⁻¹. This unpairing and loosening is understandable if one considers the structure of the X state as X⁺e₂Y⁺, that of the A state as X⁺e⁻e⁻Y⁺. The excited electron e⁻ is farther away from the positive cores and binds them less effectively.

† These data can be found in [2, p. 512-542].

The changes of properties of F₂ on excitation are quite different from those just described for the other molecules. While the ground state and a C state are ¹Σ, a B state is ¹π. Comparable in magnitude with the other molecules are the changes from the X to the B state. These changes amount from 1.411 to 1.282 Å for r and from 921.7 to 1139.8 cm⁻¹ for ω . They both show an increase of BS, contrary to the decrease on excitation of the other 7 molecules. The excitation of F₂ to the C state causes the much smaller increase of ω to 977.4.

4. THE PROBABLE QUANTICULE STRUCTURE OF F₂

The evidence presented above is in agreement with the assumption, arrived at on the basis of the quanticule theory, that F₂ has a different electronic structure from Cl₂, Br₂, I₂. While Lewis represented all 4 molecules by formula (I) and the molecular orbital theory uses [8] for them (II), the quanticule theory



makes the following distinction: the 3 heavier molecules are represented by (III) which expres-

ses the binding forces not indicated in (I). In contrast, formula (VI) follows logically from formula (IV). The latter has been proposed in order to explain [9] the spectacular difference in the external fields of the N_2 and F_2 molecules, a fact that is not clear on the basis of their analogous representation in the molecular orbital theory [2]. Starting with formula (IV) as the structure of N_2 , it is logical to represent [10] O_2 by formula (V). The latter has the merit that the two unpaired 2^1 electrons explain at once the paramagnetism of O_2 †. One step further leads to formula (VI) as the structure of F_2 . While the binuclear quanticle \bar{e}_{10} is responsible for the very strong binding of the cores N^{5+} in N_2 , the mononuclear electrons 2^1 or 2^2 in O_2 and F_2 respectively are antibinding. This shows up in the pronounced decrease of the BS in the series N_2 (22.84), O_2 (11.78), F_2 (4.752), the numbers in parentheses representing k in md/Å.

Encouraged by the consistency of these correlations we examined the large amount of spectroscopic data involving other molecules and molecule ions which can be suspected to contain the \bar{e}_{10} quanticle, namely NF , O_2^+ , NO , NO^+ , N_2^+ , CN , CO , CO^+ , CF . The correlations found are somewhat less straightforward than those presented above for the halogen and interhalogen molecules and cannot be included in this brief

† Other consequences of the \bar{e}_{10} quanticle are discussed in ref. [11].

letter. It can only be stated here that the electronic structure of F_2 appears to be closer to that of the just mentioned molecules containing only elements of the first octave than to the other halogen molecules.

REFERENCES

- [1] K. Fajans, *J. Chem. Phys.* 40 (1964) 1773; 41 (1964) 4005; 43 (1965) 2159.
- [2] G. Herzberg, *Spectra of diatomic molecules*, 2nd Ed. (Van Nostrand, Princeton, 1950) p. 343.
- [3] G. G. Balint-Kurti and M. Karplus, *J. Chem. Phys.* 50 (1969) 478.
- [4] D. Andrychuk, *Can. J. Phys.* 29 (1951) 151.
- [5] R. P. Smith, *J. Phys. Chem.* 66 (1966) 1293.
- [6] L. Pauling, *The nature of the chemical bond*, 3rd Ed. (Cornell Univ. Press, Ithaca, 1960).
- [7] R. A. Davies, *Can. J. Phys.* 44 (1966) 337.
- [8] R. B. Helsop and P. L. Robinson, *Inorganic chemistry*, 3rd Ed. (Elsevier, Amsterdam, 1967) p. 108.
- [9] K. Fajans and T. Berlin, *Phys. Rev.* 63 (1943) 309, 399; T. H. Berlin, Thesis, University of Michigan (1944).
- [10] K. Fajans, *Chemical Binding Forces*, Lithoprinted Notes of the Graduate Seminar at the Shell Development Company, Emeryville, California (1953) p. 12.
- [11] K. Fajans, *Chimia* 13 (1959) 349; Polish transl.: *Quanticle theory of chemical binding* (State Technical Publ. House, Warsaw, 1961) p. 13; Spanish transl.: *Rev. Soc. Quim. Mex.* 7 (1963) 7; Lithoprinted English transl. at Ulrich's Book Store, Ann Arbor, Michigan.