Evidence is being presented that \( \text{F}_2 \) has a different type of electronic structure than those of \( \text{Cl}_2 \), \( \text{Br}_2 \), \( \text{I}_2 \), as suggested by the quanticule theory. The internuclear distance, the vibrational force constant and their changes on excitation for \( \text{F}_2 \) do not agree with those expected for the structures \( 3\text{Z}_2 \) \( \text{X}^+ \text{Z}_2 \text{X}^- \) and \( 3\text{Y}_2 \text{E}^+ \text{Y}^+ \), which fit the 3 other halogen and interhalogen molecules respectively.

### 1. INTRODUCTION

It is a well known peculiarity of \( \text{F}_2 \) 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 \( \Delta H \) 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 \( \text{F}_2 \) 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 \( \text{F}_2 \) and those of the other halogen molecules \( \text{X}_2 \) and \( \text{XY} \). We finally wish to suggest that the ideas of the quanticule theory may point to the essence of these differences.

### Table 1

<table>
<thead>
<tr>
<th>Various measures of binding strength</th>
<th>( \text{F}_2 )</th>
<th>( \text{Cl}_2 )</th>
<th>( \text{Br}_2 )</th>
<th>( \text{I}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (-\Delta H ) (kcal/mol)</td>
<td>37.5</td>
<td>57.2</td>
<td>45.4</td>
<td>35.5</td>
</tr>
<tr>
<td>2 (-I ) (kcal/mol)</td>
<td>803.4</td>
<td>600.0</td>
<td>546.0</td>
<td>482.0</td>
</tr>
<tr>
<td>3 (1/\text{r}_e ) a. Å(^{-1})</td>
<td>0.7081</td>
<td>0.5030</td>
<td>0.4379</td>
<td>0.3750</td>
</tr>
<tr>
<td></td>
<td>1.888</td>
<td>1.3413</td>
<td>1.1677</td>
<td>1.0000</td>
</tr>
<tr>
<td>4 (\text{r}_e ) a. md/Å</td>
<td>4.752</td>
<td>3.2865</td>
<td>2.4578</td>
<td>1.7206</td>
</tr>
<tr>
<td></td>
<td>2.762</td>
<td>1.9100</td>
<td>1.4284</td>
<td>1.0900</td>
</tr>
<tr>
<td>5 (4\text{b}/3\text{b} )</td>
<td>1.463</td>
<td>1.4240</td>
<td>1.2232</td>
<td>1.0000</td>
</tr>
<tr>
<td>6 (\text{r}_e ) (Å)</td>
<td>1.411</td>
<td>1.988</td>
<td>2.2836</td>
<td>2.6666</td>
</tr>
</tbody>
</table>

\( a \) The data for \( \omega_0 \), from which \( \text{k}_e \) is calculated, as well as of \( \text{r}_e \) are, if not differently stated, from Herzberg's \( b \) The data for \( \text{r}_e \) and \( \omega_0 \) of \( \text{F}_2 \) are estimated in ref. [3] on the basis of \( \text{r}_0 \) and \( \omega_0 \) 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 (III) (see section 4), the ΔUI 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)]

\[ X \rightarrow X^+ + e^- \]  
(1)

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

\[ X_2 \rightarrow 2X^+ + 2e^- \]  
(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 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 \( r_e (\text{Å}) \)

The \( r \) values are known for the following \( XY \) molecules:

- FCl 1.6281; FBr 1.7556; FI 1.9089;
- CIBr 2.138; CII 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 \( \Delta \), e.g. I-Cl, for molecules containing one common atom. It results in Å:

\[ F-I 0.2808, CII-CI 0.333, I_2-CII 0.3459, \]

leading to the average 0.317 ± 0.027. For the 5 other \( \Delta \), 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 \( \Delta \)'s involving \( F_2 \) with the corresponding ones in column 5, 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 FCI, FBr, FI. Since the \( r \) of the latter three molecules shows approximate additivity when combined with the values of CIBr, CII, 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 \( F \),

\[ k(\text{XY}) = [k(X_2)k(Y_2)]^{1/2} \]  
(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 CIBr, CII, BrI, the average being 0.982. Contrary to this the values in line 4 for FCI, FBr, FI are dis-

\[ \dagger \] Here and in the following text the symbols \( r \) and \( k \) mean \( r_e \) and \( k_e \). The same applies to \( \omega \).

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

<table>
<thead>
<tr>
<th>No.</th>
<th>Aver.</th>
<th>Δ</th>
<th>Not involving F_2</th>
<th>Involving F_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Cl-F</td>
<td>2</td>
<td>0.371</td>
<td>0.011</td>
<td>Fcl-F_2</td>
</tr>
<tr>
<td>Br-F</td>
<td>2</td>
<td>0.519</td>
<td>0.009</td>
<td>FBr-F_2</td>
</tr>
<tr>
<td>I-F</td>
<td>2</td>
<td>0.775</td>
<td>0.025</td>
<td>FI-F_2</td>
</tr>
<tr>
<td>Br-Cl</td>
<td>2</td>
<td>0.141</td>
<td>0.009</td>
<td></td>
</tr>
<tr>
<td>I-Cl</td>
<td>2</td>
<td>0.317</td>
<td>0.027</td>
<td></td>
</tr>
<tr>
<td>I-Br</td>
<td>2</td>
<td>0.168</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>2</td>
<td>±0.016</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Testing of eq. (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 XY FCl FBr F1 ClBr ClI BrI</td>
</tr>
<tr>
<td>2 (k(XY)) 4.562 4.071 3.600 2.674 2.383 2.064</td>
</tr>
<tr>
<td>3 (k(X)_2 k(Y)_2)^1/2 3.952 3.418 2.859 2.842 2.378 2.057</td>
</tr>
<tr>
<td>4 2/3 1.154 1.190 1.269 0.941 1.602 1.003</td>
</tr>
</tbody>
</table>

The changes of properties of F_2 on excitation are quite different from those just described for the other molecules. While the ground state and a C state are \(1\Sigma^+\), a B state is \(1\pi\). 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 \(\omega\). They both show an increase of BS, contrary to the decrease on excitation of the other 7 molecules. The excitation of F_2 to the C state causes the much smaller increase of \(\omega\) to 977.4.

4. THE PROBABLE QUANTICULE STRUCTURE OF F_2

The evidence presented above is in agreement with the assumption, arrived at on the basis of the quanticule theory, that F_2 has a different electronic structure from Cl_2, Br_2, I_2. While Lewis represented all 4 molecules by formula (I) and the molecular orbital theory uses [8] for them (II), the quanticule theory

\[
\begin{align*}
\text{(I)} & : X^2Y^2Z^2(\text{or} X^2Y^2Z^2) \\
\text{(II)} & : X^2Y^2Z^2(\text{or} X^2Y^2Z^2) \\
\text{(III)} & : X^2Y^2Z^2(\text{or} X^2Y^2Z^2) \\
\text{(IV)} & : X^2Y^2Z^2(\text{or} X^2Y^2Z^2) \\
\text{(V)} & : X^2Y^2Z^2(\text{or} X^2Y^2Z^2) \\
\text{(VI)} & : X^2Y^2Z^2(\text{or} X^2Y^2Z^2)
\end{align*}
\]

makes the following distinction: the 3 heavier molecules are represented by (III) which expres-
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 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 quanticule $\tilde{\varepsilon}_{10}$ 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$_2$ (23.84), 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 $\tilde{\varepsilon}_{10}$ quanticule, namely NF, O$_2^-$, NO, NO$^+$, N$_3^-$, 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 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


† Other consequences of the $\tilde{\varepsilon}_{10}$ quanticule are discussed in ref. [11].