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Application of the FAKE molecular-orbital method to diatomic molecules XY (X, Y = H, F, Cl, Br, I)

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The FAKE (fast, accurate kinetic energy) method of semiempirical molecular orbital calculation is applied to diatomic molecules XY (X, Y = H, F, Cl, Br, I). The method differs from the extended Hückel theories in that it applies simple approximations only to the potential energy integrals, while including accurately calculated kinetic energy effects. This more appropriate treatment of the kinetic energy renders unnecessary the adjustment factors ordinarily introduced in Wolfsberg-Helmholz and Cusachs approximations to obtain a reasonable description of chemical bonding and leads to iterative procedures with greatly improved convergence characteristics. From our present application of FAKE calculations to diatomic molecules we found that the method mimics "real" selfconsistent-field studies to a considerable accuracy; however, the method is primarily designed for our work on large molecules and polymers, for which only the most rapid of semiempirical methods are practical.

Key words: Semiempirical molecular orbital method—diatomic interhalogen molecules—equilibrium distances—dipole and quadrupole moments—force constants—electric field gradients—ionisation potentials

1. Introduction

The FAKE (fast, accurate kinetic energy) method is a logical descendent of the various extended Hückel procedures [1, 2], and shares with them the ability to handle large systems with very modest computational effort. It differs, however, from the Hückel theories in that it applies simple approximations only to the potential energy integrals [3, 4]. Before applying the method to large systems we wanted to study a series of smaller molecules; thus in the present contribution we describe results obtained for representative diatomic molecules of H, F, Cl, Br, and I. Our calculated quantities, which we compare with experimental data as well as with values obtained by more sophisticated methods such as Hartree-Fock (HF) [5] and SCC-X_α [6] procedures, include interatomic distances, force constants, orbital energies, atomic charges, molecular dipole and quadrupole moments, and electric field gradients at the nuclear positions of Cl, Br, and I.

2. Method

FAKE calculations are based on an effective one-electron Hamiltonian, the diagonal matrix elements H_{ii} of which consist of the following terms:

(i) A kinetic energy, T_{ii}, actually calculated for the single Slater-type orbital (STO) representing orbital *i*.

(ii) A one-center potential energy, $-\alpha_i - T_{ii}$, given as an empirically based expression depending on the type of atom and orbital involved and on the net charge of that atom. As in the ω-technique [7] we assume the following dependence of α_i on the net atomic charge q:

$$\alpha_i = \alpha_i^0 + q\alpha_i' + q^2\alpha_i''. \tag{1}$$

The quantities α_i' and α_i'' were fixed at values consistent with atomic data [8]. The α_i^0 (and the ζ_i) were adjusted to optimize the correspondence between FAKE, *ab initio* and experimental orbital energies and equilibrium distances.

(iii) An interaction energy between orbital *i* on atom *A* and the core and electron charges of each other atom *B*, calculated by a formula of the Mataga-Nishimoto [9] or Ohno-Klopman [10] type:

$$-\sum_{B\neq A} (q_B + n_{BA})[ii|B] + \sum_{B\neq A} n_{BA}[ii|e_B], \tag{2}$$

with overlap-charges $n_{BA} = \sum_{i \text{ on } A,\, j \text{ on } B} P_{ij}S_{ij}$ (P_{ij} and S_{ij} representing first-order density and overlap matrix elements), and point-charge formulae

$[ii|B] = [R_{AB} + 1/\gamma_B]^{-1}$ and $[ii|e_B] = [R_{AB} + 1/\gamma_{eB}]^{-1}$. The empirical parameters γ_B and γ_{eB} were adjusted to optimize orbital energies and equilibrium distances. A specific feature of our parametrization is that γ_B takes very large values ($\triangleq \infty$ for all elements used here).

Thus the diagonal matrix elements H_{ii} take the following form:

$$H_{ii} = -\alpha_i - \sum_{B\neq A} (q_B - n_{BA})[ii|B] + \sum_{B\neq A} n_{BA}[ii|e_B]. \tag{3}$$

Off-diagonal matrix elements H_{ij} are determined as follows:

(i) Matrix elements between orbitals i and j on different atoms consist of the actually computed kinetic energy matrix element T_{ij}, plus a two-center potential energy matrix element computed from the overlap integral S_{ij} by the Mulliken formula [1]:

$$H_{ij} = T_{ij} + 1/2[(H_{ii} - T_{ii}) + (H_{jj} - T_{jj})]S_{ij}. \tag{4}$$

We have also investigated the influence of a so-called screening factor, $f = \exp(-C[(\zeta_i + \zeta_j)R_{AB}/(n_i + n_j)]^2)$, upon the two-center potential energy matrix elements; however, we found that $f = 1$ (corresponding to $C = 0$) yields more realistic results than any other choice for this factor.

(ii) One-center off-diagonal matrix elements H_{ij} are evaluated according to Eq. (4). We deviate here from our former approximation [3, 4], where we have calculated H_{ij} from the first-order density matrix using Slater-Condon parameters, because this approximation under certain circumstances might include artefacts such as self-repulsion [11].

The atomic orbital (AO) parameters which we have used in the present study are summarized in Table 1. We want to emphasize that α' and α'' are taken from atomic data [8]. Parameter optimization for α^0, ζ, γ_B and γ_{eB} was achieved in the following way: We started our inspection of orbital energies of homonuclear diatomic molecules with α^0 taken from atomic data [8] and with ζ obtained from the relation $\langle r \rangle_{\mathrm{STO}} = \langle r \rangle_{HF}$, where $\langle r \rangle_{HF}$ has been derived from HF atomic orbitals of neutral atoms [12]. In the next step the parameters γ_B and γ_{eB} were used to optimize equilibrium distances of homonuclear molecules; during this procedure slight changes of α^0 and ζ were necessary to keep the differences between calculated orbital energies and experimental ionization potentials small. The final

Table 1. AO parameters

Element	AO	ζ (a.u.)	α^0 (eV)	α' (eV)	α'' (eV)	γ_{eB} (eV)
H	1*s*	1.5[a]	9	14	3	10
F	2*s*	2.35	30	17	1.7	0
	2*p*	2.35	10	15	1.7	0
Cl	3*s*	2.25	27	10	1.65	10
	3*p*	2.25	10	6	1.65	10
Br	4*s*	2.65	24	9	1.7	5
	4*p*	2.65	9	6	1.7	5
I	5*s*	2.6	23	9	1.7	2
	5*p*	2.6	7	6	1.7	2

[a] Compare the relatively large ζ (H1*s*)-value of 1.5 with ζ-values derived by A. D. McLean and M. Ioshimine (in Tables of linear molecule wave functions, IBM J. Res. Developm., Nov. 1967) from *ab initio* calculations for FH and ClH: 1.37, 2.46 and 1.50, 2.56

Table 2. Equilibrium distances (Å)

Molecule	R^{exp} [a]	R^{calc} [b]	R^{calc} [c]
H_2	0.7416	0.7351	0.72
HF	0.9171	0.898	0.98
F_2	1.417	1.3375	1.41
HCl	1.2746	1.251	1.30
FCl	1.62813	1.5854	1.71
Cl_2	1.988	1.9907	2.06
HBr	1.413	1.4063	1.45
FBr	1.7555	1.7192	1.74
ClBr	2.138	2.1373	2.18
Br_2	2.283	2.29	2.20
HI	1.604	1.61	1.70
FI	1.908[d]	1.86	1.73
ClI	2.32069	2.33	2.35
BrI	2.47	2.40	2.38
I_2	2.666	2.59	2.57

[a] Lucken, E. A.: in Nuclear quadrupole coupling constants. London, New York: Academic Press 1969

[b] Straub, P. A., McLean, A. D., Ref. [5]

[c] This work; values obtained from a parabolic potential energy curve, which was fitted to four equidistant points (steps 0.2 a.u.)

[d] Friedt, J. M., private communication

Table 3. Force constants (10^5 dyn cm^{-1})

Molecule	k^{exp} [a]	k^{calc} [b]	k^{calc} [c]
H_2	5.2	5.4	5.5
HF	8.8	9.6	10.2
F_2	4.5	6.1	9.5
HCl	4.8	5.9	5.2
FCl	5.0	5.8	5.9
Cl_2	3.2	3.4	5.7
HBr	3.8	4.0	6.8
FBr	4.4	5.1	6.6
ClBr	2.9	3.2	5.1
Br_2	2.4	2.7	4.4
HI	2.9	3.1	3.7
FI	—	4.7	3.3
ClI	2.6	2.8	2.7
BrI	2.6	3.3	2.7
I_2	1.7	2.3	1.7

[a] Lucken, E. A.: in Nuclear quadrupole coupling constants. London, New York: Academic Press 1969; Barrow, G. M.: in Introduction to molecular spectroscopy. New York: McGraw-Hill 1962

[b] See (b) of Table 2

[c] See (c) of Table 2

α^0, ζ, γ_B ($=\infty$) and γ_{eB} were obtained by optimizing orbital energies of XY- and equilibrium distances of HX-molecules (X, Y = H, F, Cl, Br, I).

3. Results and discussion

For each diatomic molecule XY we have calculated the total energy E_{tot} in dependence of the interatomic distance R_{AB}. We have then fitted our results assuming a parabolic behavior for this dependence. From this procedure we derived the equilibrium distances R and force constants k, which are summarized in Table 2 and Table 3, respectively, together with experimental and *ab initio* results. From the corresponding diagrams of these results it is directly obvious that the FAKE method with its present parameter set is better in reproducing equilibrium distances (Fig. 1) than vibrational frequencies (Fig. 2). This is not a surprising result if one keeps in mind that we partially (for X_2 and HX) have used the empirical parameters γ_{eB} to adjust the minimum of the calculated total energy curve to the actual equilibrium distance R^{exp}. All calculated frequencies turn out to be larger than the corresponding spectroscopic vibrational frequencies, indicating that the true curvature of the total energy curve must be flatter at the equilibrium position. This behavior of a diatomic molecule is typical for a single configuration calculation at large separations R_{AB}, where the wavefunctions have considerable ionic character, as was already pointed out by Bowman et al. [13] and Straub et al. [5].

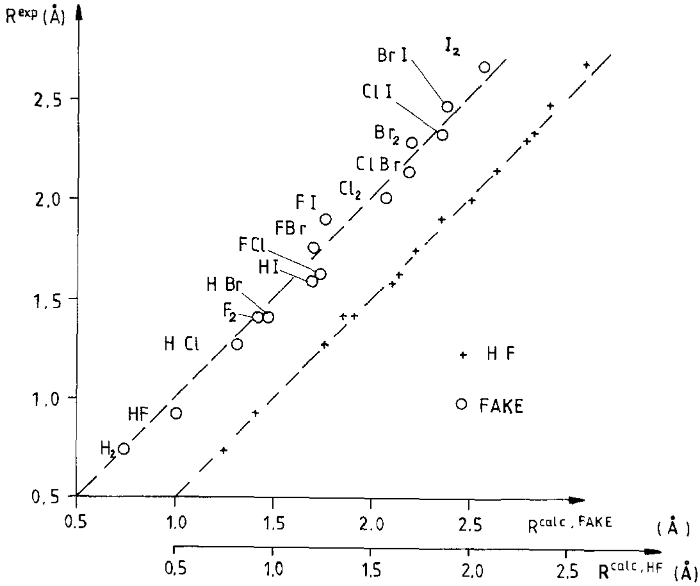

Fig. 1. Equilibrium distances, R^{exp}, from Table 2 as function of the internuclear distance of the FAKE calculations, $R^{\text{calc,FAKE}}$, and of the Hartree-Fock (*HF*) calculations (Straub et al. [5]), $R^{\text{calc},HF}$, at minimum total energy

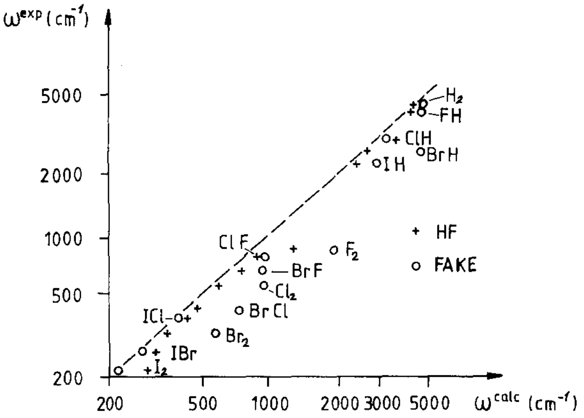

Fig. 2. Vibrational frequencies, ω^{exp}, as a function of the calculated frequencies, ω^{calc}, obtained from the FAKE potential energy curve and from the HF potential energy curve (Straub et al. [5]). Vibrational frequencies ω and force constants k (from Table 3) are related by $\omega = 2\pi\sqrt{k/\mu_{\mathrm{eff}}}$, with $\mu_{\mathrm{eff}} = m_A m_B/(m_A + m_B)$

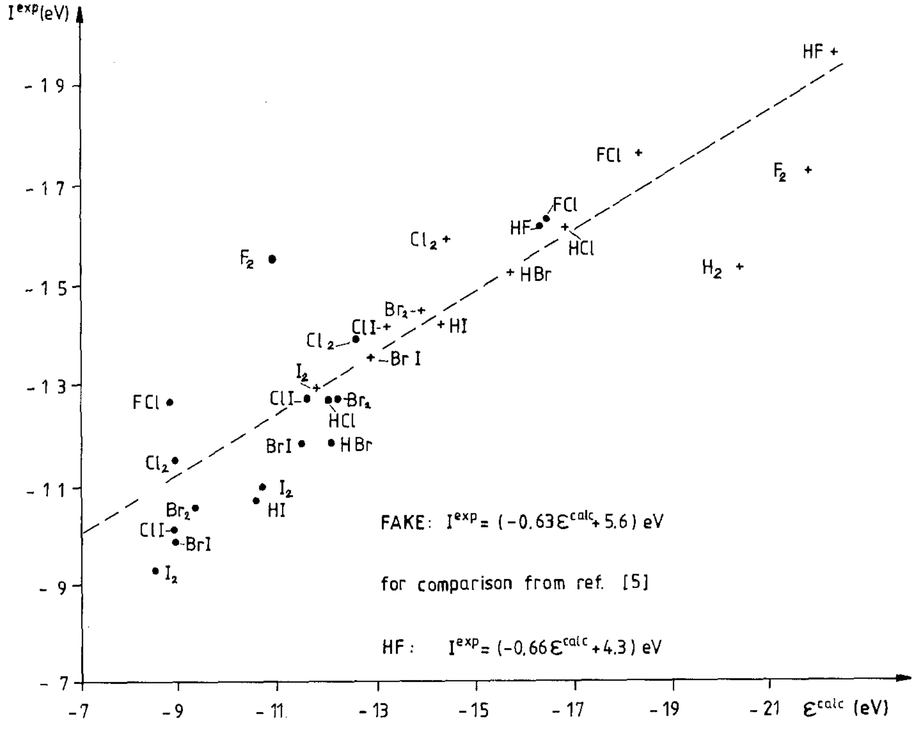

Fig. 3. Averaged vertical ionization potentials, I^{exp}, as function of the calculated FAKE orbital energies, $\varepsilon^{\mathrm{calc}}$, of the highest occupied molecular orbitals; + represents σ-orbitals; • represents π-orbitals. The orbital energies $\varepsilon^{\mathrm{calc}}$ correspond to a FAKE-MO calculation at the minimum of the total energy curve. Experimental values are taken from Refs. [14, 15]

In Fig. 3 we have drawn experimental ionization potentials, I^{exp}, against the FAKE orbital energies, $\varepsilon^{\mathrm{calc}}$. The "experimental" values in Fig. 3 are averaged ionization potentials, identical to the arithmetic mean of the two experimental vertical ionization potentials $I_{1/2}$ and $I_{3/2}$ as obtained from UPS measurements [14, 15]. The regression line through our $I^{\mathrm{exp}}-\varepsilon^{\mathrm{calc}}$-plot has a gradient of 0.63 and intersects the I^{exp}-axis at a positive value (5.6 eV). Using Koopmans' theorem [16] the ionization potentials of the diatomic molecules XY should be equal to the negative FAKE orbital energies. According to the obtained regression line, Koopmans' theorem happens to be correct for orbital energies of about 15 eV only. Similar behavior of the theoretical Koopmans' theorem was observed in other semiempirical calculations [17] as well as in *HF* calculations [5] (see Fig. 3). Contrary to this behavior SCC-Hückel [18] and SCC-X_α [6] calculations yield energy plots with gradient close to one and intersecting the I^{exp}-axis at zero, because "orbital energies" of these theories are normally parametrized by using ionization potentials.

The FAKE molecular wavefunctions were used to calculate effective atomic charges, electric field gradients at the nuclear positions of Cl, Br, and I, and molecular dipole and quadrupole moments of the molecules XY using the appropriate one-electron operator. The resulting expectation values are sensitive measures of the MO charge distribution and will be compared here with corresponding experimental data.

In Table 4 calculated effective atomic charges are tabulated. We have derived these charges from a centroid projection method [19] by apportioning the overlap charges among the atoms involved in a fashion, which preserves the projection

Table 4. Effective atomic charges

Molecule XY	q_X[a]	q_X[b]	q_X[c]	q_X[d]
HF	0.171	0.355	0.337	0.681
HCl	0.090	0.248	0.207	0.798
FCl	−0.177	−0.171	−0.178	−0.358
HBr	0.102	0.269	0.178	0.790
FBr	−0.167	−0.127	−0.158	−0.377
ClBr	0.011	−0.019	−0.083	−0.037
HI	0.031	0.260	0.142	0.873
FI	−0.215	−0.176	−0.18	−0.505
ClI	−0.102	−0.091	−0.058	−0.260
BrI	−0.098	−0.081	−0.011	−0.071

[a] This work; derived from a centroid projection method [19]

[b] This work; derived from a Mulliken population analysis using the STO's of Table 1

[c] This work; derived from a Mulliken population analysis using $\zeta(\mathrm{H}1s)=1.50$ a.u. and Clementi-wavefunctions for neutral halides [12]

[d] HF-results taken from Straub et al. [5]; derived from a Mulliken population analysis

of the charge centroid on the intercenter line; this causes the atomic charges to be approximately consistent with computed dipole moments and to reflect the actual MO charge distribution better than an equal division of overlap charge would do (Mulliken population analysis, which for comparison is also given in Table 4). The FAKE data in contrast to the *HF* results seem to indicate that the charge polarity of the molecules XY studied here is only minor. This, however, is not conclusive because effective atomic charges cannot directly be compared with experimental data. In this respect much better measures for the MO charge distribution than effective atomic charges are the molecular dipole and quadrupole moments and the electric field gradient (efg) at the nuclear positions of Cl, Br, and I within the diatomic molecules XY. The corresponding molecular expectation values we have calculated from

$$\langle\hat{o}\rangle^{\mathrm{MO}} = \sum_{i,j} P_{ij}\langle\phi_i|\hat{o}|\phi_j\rangle. \tag{5}$$

The first-order density matrix elements P_{ij} were taken from the FAKE MO calculations, while the atomic expectation values $\langle\phi_i|\hat{o}|\phi_j\rangle$ have been derived using Clementi-wavefunctions for neutral atoms X and Y [12], the radial part of the two-center efg contribution by numerical integration otherwise analytically. Calculating $\langle\hat{o}\rangle^{\mathrm{MO}}$ with this procedure we are along the lines of our MO interpretation of Mössbauer-parameters of various iron and halogen containing compounds [20, 21]. In Figs. 4–6 we compare molecular dipole and quadrupole moments and efg's as derived from FAKE and HF [5] calculations with corresponding experimental data. From this comparison it is obvious that in the present study of diatomic molecules the FAKE MO charge distribution reaches a similar level of agreement with experimental data as the HF charge distribution does. In the case of efg calculations (Fig. 6) the agreement of FAKE results with experimental values seems even to be better than that of the HF results. The partial disagreement of HF and experimental efg data is due to the fact that Straub et al. [5] in their HF work have used:

(i) nuclear quadrupole moments Q for the isotopes ^{35}Cl, ^{79}Br, and ^{127}I (i.e. -0.079 barn, 0.31 barn, and -0.79 barn) – in order to derive efg's from experimental nuclear quadrupole coupling constants – which somewhat differ from the Q-values which we have found to be more reliable (i.e. -0.065 barn, 0.25 barn, and -0.59 barn [21]), and

(ii) an AO basis set which is not the same throughout all MO calculations (reduced basis set for Br_2, BrI, and I_2, and double zeta basis set for the other diatomic molecules).

In addition to the rather uniformly satisfactory representation of the orbital energy patterns we found the FAKE MO charge distribution to yield expectation values of single-electron operators which agree well with corresponding experimental observables (i.e. molecular dipole and quadrupole moments and efg). From both the results presented here and those presented previously [3, 4], we conclude that FAKE calculations have promise in situations where more detailed studies are impossible or too costly. We particularly expect that applications to

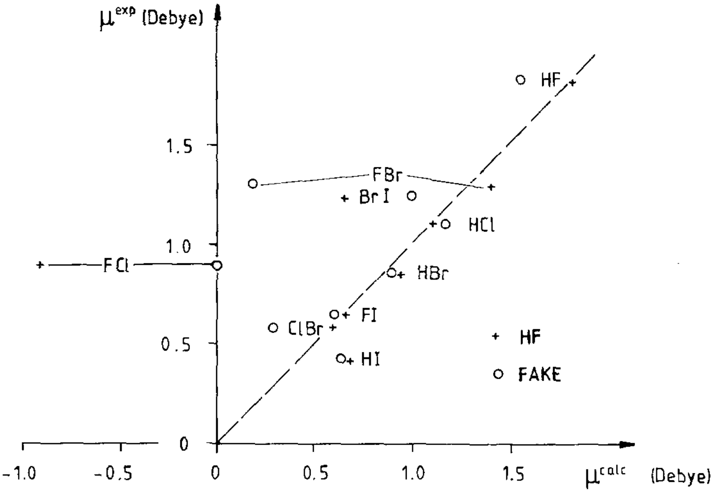

Fig. 4. Experimental molecular dipole moments, μ^{exp}, as function of the calculated dipole moments, μ^{calc}, obtained from the FAKE method and from *HF* calculations (Straub et al. [5]. Experimental data are summarized in Table 2 of Ref. [21]. The plus-sign for μ^{exp} of FCl has been reported by Ewing, J. J.: J. Chem. Phys. **56**, 1957 (1972)

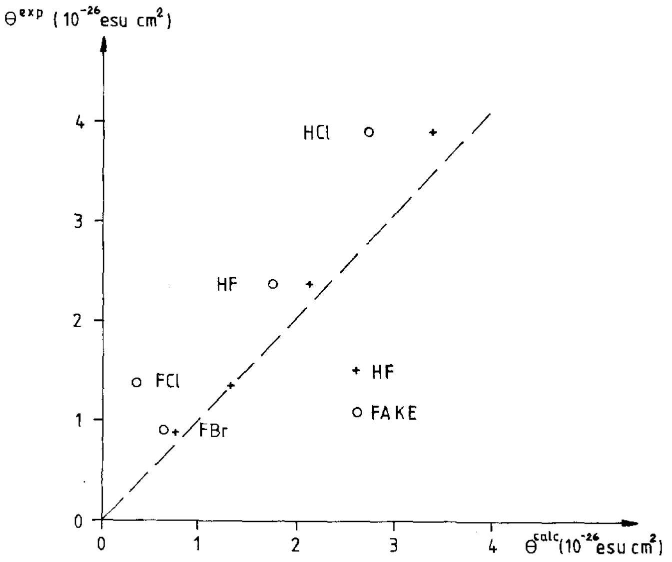

Fig. 5. Experimental molecular quadrupole moments, Θ^{calc}, obtained from the FAKE method and from *HF* calculations (Straub et al. [5]). Experimental data are taken from Leeuw, F. A.: 26th. Symp. on Molecular Structure and Spectroscopy. Ohio, USA 1971 and from Ewing, J. J.: J. Chem. Phys. **56**, 1957 (1972)

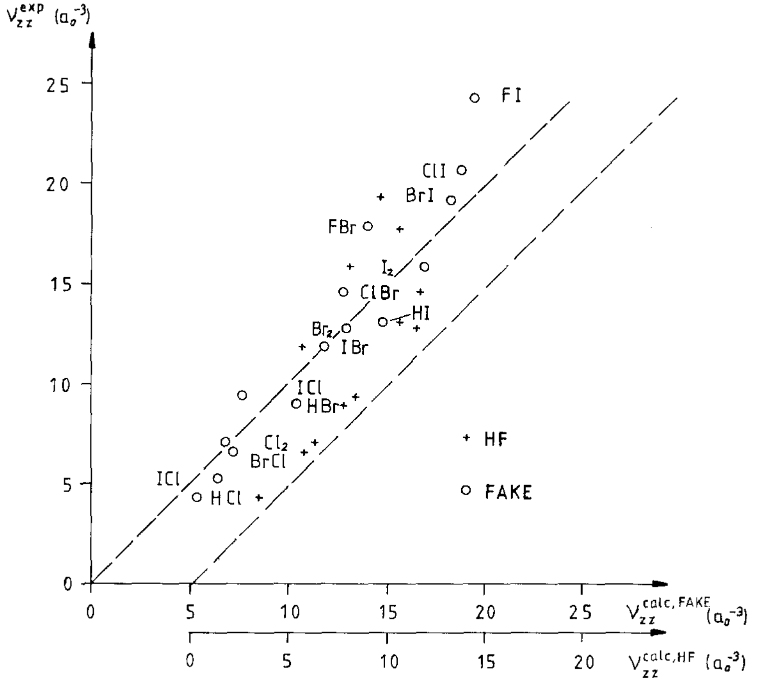

Fig. 6. Experimental electric field gradients, V_{zz}^{exp}, of Y within the diatomic molecule XY plotted against calculated values, V_{zz}^{calc}, obtained from the FAKE method and from *HF* calculations (Straub et al. [5]). V_{zz}^{exp} data have been derived from experimental nuclear quadrupole coupling constants summarized in Refs. [5, 21] using nuclear quadrupole moments for the isotopes ^{35}Cl, ^{79}Br, and ^{127}I as −0.065 barn, 0.25 barn, and −0.59 barn [21]

large molecules or clusters are valuable for the interpretation of electronic groundstate properties of such systems.

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