Theoret. chim. Acta (Berl.) 13, 262—263 (1969)

A CNDO and INDO Calculation of Nuclear Spin-Spin Coupling Constants in HF, HF_2^- and $H_2F_3^-$

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Received February 21, 1969

Two semiempirically SCF methods are used to calculate nuclear spin-spin coupling constants in hydrogen bonded systems. Hydrogen bonding is found to influence strongly the spin-spin coupling constants and this can give valuable informations about changes in electron densities with hydrogen bonding.

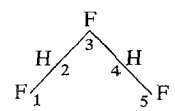
The all electrons semiempirical SCF methods [1] render the study of changes in the electron configuration with hydrogen bonding relative easily. The purpose of this work is to show that the nuclear spin-spin coupling constants give valuable information on the changes of electron configuration upon hydrogen bond formation. They were calculated by the Pople and Santry molecular orbital approach [2] with the Fermi contact term [3] being the perturbation. Recently Kato and Saika [4] have shown that the contribution of the other terms is not negligible. We assume that those contributions are of the same order of magnitude as in HF [4] and thus do not change the calculated values too much.

Nuclear spin-spin coupling constants were calculated from the expression [2]

$$K_{AB} = -\left(\frac{256}{9}\pi^2\right)\beta^2 (S_A|\delta(r_A)|S_A)\, S_B\,|\,\delta(r_B)S_B) \sum_{i}^{\text{occ.}} \sum_{j}^{\text{unocc.}} ({}^3\Delta E_{ij})^{-1} C_{is_A} C_{js_A} C_{js_B} C_{is_B},$$

$(S_A|\delta(r_A)|S_A)$ and $(S_B|\delta(r_B)|S_B)$ being taken from [5]. The wave function and the transition energies were determined from semiempirical methods. To this end we used CNDO/2 and INDO methods [1]. Semiempirical parameters were taken from the paper by Sichel and Whitehead [6]. We used their M2 parametrization (Ref. [6], Table 2) and one-center exchange integrals from [1]. The results are given in the Table.

Table. *Coupling constants K_{HF} in units 10^{20} cm^{-3}*

	CNDO	INDO
HF	−34.02	−29.29
HF_2^-	− 8.66	− 7.33
$H_2F_3^-$		$K_{12} = 1.96$ $K_{23} = -1.59$ $K_{14} = -0.289$ $K_{24} = -0.723$

From there it is evident that the influence of the exchange integrals is of considerable degree. The calculated value K_{HF} in HF reproduces the sign [1] and even approaches the observed value 46.1×10^{20} cm^{-1}.

The sign of the coupling constant remains the same in HF_2^- although the value dropps remarkably. Still lower values were calculated for $H_2F_3^-$ and the calculation predicts even a positive and negative sign for K_{HF}.

The nuclear spin-spin coupling constants appear to be very sensitive to changes introduced by the formation of the hydrogen bond. Unfortunately only one measured constant is available for comparison with the calculated values so that further experimental data seem to be very desirable.

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[1] Discussion about sign see Ref. [2].