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단 신

HCCF의 유효전하 예측

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Prediction of Effective Charges in HCCF

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From the analysis of infrared intensities in a variety of hydrocarbons and fluorocarbons, it was observed that the effective charges of hydrogen and fluorine fell within a fairly narrow range of values[1]. However, the effective charge of hydrogen in HCCH has been known to differ substantially from the values common to other carbon-hydrogen systems[2]. The peculiar behavior in HCCH was rationalized by virtue of its rather ionically bonded proton[3]. In this respect, it will be useful to study the system of fluorinated acetylene, HCCF, in order to see more firmly the nature of anomalous behavior in HCCH.

Since the experimental data are not available at present time, we have performed ab-initio calculations for the effective charges of hydrogen and fluorine in HCCF. Using the GAUSSIAN-70 program system and the standard 6-31G Gaussian basis set[4], the dipole derivatives were estimated by the finite displacement(~0.02Å) of the atoms from their positions in the equilibrium configuration. We have chosen the molecular axis as the Cartesian X axis with the fluorine atom pointing to the positive direction.

The calculated atomic polar tensors and effective charges of the H and F atoms in HCCF are given in *Table* 1. The atomic polar tensors[1], P^{α}, are defined as the derivatives of the cartesian components of the dipole moment $\{P_x, P_y, P_z\}$ with respect to the cartesian coordinates of the considering atom. For example, in HCCF, $P_{xx}^{\alpha} \equiv (\partial P_x/\partial X_{\alpha})$ and $P_{yy}^{\alpha} = P_{zz}^{\alpha} \equiv (\partial P_y/\partial Y_{\alpha})$, where α is either H or F atom. The off-diagonal elements in HCCF are null owing to its $C_{\infty v}$ type of symmetry. The effective charges[1], χ_{α}, are defined for this particular case as

$$\chi_{\alpha} = \{[(P_{xx}^{\alpha})^2 + 2(P_{yy}^{\alpha})^2]/3\}^{\frac{1}{2}}$$

For comparison, similar calculations have been performed for HCCH, CH_4, and CH_3F.

Table 1. SCF calculated atomic polar tensors and effective charges in HCCF, HCCH, CH_4, and CH_3F (units are e's)

	P_{xx}^H	$P_{yy}^H = P_{zz}^H$	χ_H	P_{xx}^F	$P_{yy}^F = P_{zz}^F$	χ_F
HCCF	0.262	0.261	0.261	−1.022	−0.107	0.597
HCCH[a]	0.244	0.261	0.255			
CH_4[a]	−0.178	0.085	0.124			
CH_3F[b]				−0.903	−0.371	0.603

[a] C-H bond is on the X-axis. [b] C-F bond is on the X-axis.

Table 1 shows that the polar tensor as well

as the effective charge of H atom in HCCF are surprisingly close to those in HCCH. Indeed, the larger values of the effective charges and the approximately isotropic polar tensors of the hydrogen atoms in HCCF and HCCH more closely resemble those expected for a free charge in an ionic compound than the smaller values and the highly directional anisotropic polar tensors associated with the atoms in strong covalent bonds like those in CH_4[3]. On the other hand, the effective charge for fluorine was found to be in good agreement with that in other fluorocarbons[5], like that in CH_3F. Along with the substantial anisotropy of the fluorine atom polar tensor, this would suggest that the C-F bond in HCCF is strongly covalent[3].

Theoretically, the atomic polar tensor can be identified with three contributing terms[6]. The first term is the contribution of a "net charge" fixed on the nucleus, and the second is the "charge flux" contribution from the transfer of charge from one nucleus to another as the result of nuclear displacement. The third term is strictly a quantum mechanical contribution resulting from the superposition of wave functions, and has no classical analogue[7]. Three contributions to the polar tensors of H and F atoms in HCCF were also estimated. For P_{xx}^H (P_{xx}^F), the second and third terms were 2.6 (3.7) and 2.8(1.9) times larger, respectively, than the first. On the other hand, for P_{yy}^H (P_{yy}^F) the ratio of the third to the first term was 0.2(0.7) without any contribution from the second term. Perhaps the safest conclusion to be drawn from these calculations is that all three terms are significant, and no one term can really be neglected relative to the others. It may suggest that one should be careful in using classical charge models for interpreting vibrational intensities.

In addition, we have predicted the fundamental vibrational intensities of HCCF. By using the normal coordinates reported by Reichman *et al.*[8], the intensities of the $\nu_1(\Sigma)$, $\nu_2(\Sigma)$, $\nu_3(\Sigma)$, $\nu_4(\pi)$, and $\nu_5(\pi)$ modes[8] were estimated to be 98, 87, 56, 137, and 21km/mol, respectively. Although we could not evaluate the reliability of those values, fairly large vibrational intensities are expected for HCCF. Indeed, the intensities of the $\nu_4(\pi)$ and $\nu_5(\pi)$ modes in HCCF appear to be close to those in HCCD[2].

In conclusion, the SCF calculated results in this work may be summarized as follows.

(1) The effective charge for hydrogen in HCCF seems to be close to that in HCCH, suggesting that H-atom in HCCF is rather ionically bonded proton.

(2) The effective charge for fluorine in HCCF seems to be close to that in various fluorocarbons.

(3) The quantum mechanical interference term seem as significant as both the "net charge" and "charge flux" contributions in the atomic polar tensors of HCCF.

(4) The intensities of five fundamental modes in HCCF seems to be fairly strong.

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