On the negative dipole moment derivatives of HNgX molecules

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Introduction

The HNgX (Ng = Ar, Kr; X = F, Cl) molecules were studied using the CCFDF model about a decade ago[1] because the stretching of this bond leads to a decrease of the molecular dipole moment, while for most molecules the opposite is observed. After that, substantial improvements were achieved to this partition scheme until a new model was proposed, called CCTDP[2]. Although the latter can be viewed as a rearrangement of the CCFDF terms, it provides us deeper and more accurate interpretations of IR intensities. In this work the CCTDP model will be used to analyze the dipole moment derivatives of HNgX (Ng = Ar, Kr; X = F, Cl, Br) and compare them with the derivatives for the respective HX molecules.

Theory

Both the CCFDF and CCTDP models are based on theories which express the molecular dipole moment as a sum of atomic charges and atomic electric dipoles:

$$\vec{p} = \sum_{\alpha=1}^{N} q_\alpha \vec{r_\alpha} + \sum_{\alpha=1}^{N} \vec{m_\alpha} \tag{1}$$

Since the j^{th} IR intensity is proportional to the squared dipole moment derivative, it turns that:

$$\left(\frac{\partial \vec{p}}{\partial Q_j}\right) = \left(\frac{\partial \vec{p}}{\partial Q_j}\right)_{(C)} + \left(\frac{\partial \vec{p}}{\partial Q_j}\right)_{(CF)} + \left(\frac{\partial \vec{p}}{\partial Q_j}\right)_{(DF)} \tag{2}$$

The second and third terms in this CCFDF model can be summed since most of the times they act together in the IR absorption phenomena:

$$\left(\frac{\partial \vec{p}}{\partial Q_j}\right) = \left(\frac{\partial \vec{p}}{\partial Q_j}\right)_{(C)} + \left(\frac{\partial \vec{p}}{\partial Q_j}\right)_{(CTDP)} \tag{3}$$

Within this context, the "*Charge Flux–Dipole Flux*" label was changed to "*Charge Transfer–Dipolar Polarization*" since the latter describes better the molecular electronic structure behavior during the IR absorption.

Calculations

Both the geometry optimizations and vibrational analyses were carried out using GAUSSIAN09 at the MP2(full)/aug–cc–pVTZ level of theory. The CCTDP partition was obtained using the PLACZEK program. Unlike the previous reference, which used CHelpG charges, the population analysis chosen here was QTAIM, employing the AIMALL software for the integrations.

Results and discussion

Even though the CCFDF model can be employed with any population analysis which delivers both atomic charges and atomic dipole moments, the results with these different schemes will not be necessarily equivalent. For example, the derivatives reported for the CHelpG/CCFDF analyses[1] differ considerably from the respective QTAIM/CCFDF derivatives reported here. For instance, while the charge term, C, is much lower for HCl than for HF in the QTAIM/CCFDF model, they are very similar in the CHelpG/CCFDF, against our expectation based on chemical electronegativities. Moreover, in the CHelpG/CCFDF model the charge flux (CF) derivative for the HArF and HArCl differ by a large amount while they are about equal for HKrF and HKrCl molecules. Since the same model is being used in these two pairs, similar trends would be expected. These differences are not observed for the QTAIM/CCFDF results, where nice patterns are found for all the contributions.

Table 1. Dipole moment derivatives for the H stretching (in units of $e.amu^{\frac{1}{2}}$).

	C	**CF**	**DF**	**Total**
HF	0.770	–0.308	–0.109	0.353
HCl	0.300	0.370	–0.443	0.226
HBr	0.098	0.927	–0.895	0.130
HArF	0.331	–1.415	0.131	–0.953
HArCl	0.327	–2.710	0.427	–1.955
HArBr	0.282	–3.525	0.629	–2.614
HKrF	0.134	–0.675	–0.186	–0.727
HKrCl	0.150	–1.665	0.104	–1.411
HKrBr	0.135	–2.196	0.265	–1.796

	C	**CTDP**	**Total**	*ab initio*
HF	0.770	–0.418	0.353	0.353
HCl	0.300	–0.073	0.226	0.226
HBr	0.098	0.032	0.130	0.131
HArF	0.331	–1.284	–0.953	–0.954
HArCl	0.327	–2.283	–1.955	–1.958
HArBr	0.282	–2.896	–2.614	–2.618
HKrF	0.134	–0.861	–0.727	–0.727
HKrCl	0.150	–1.561	–1.411	–1.411
HKrBr	0.135	–1.931	–1.796	–1.798

The only CCFDF contribution which does not display a singular trend along the $Ar \rightarrow Kr$ and $F \rightarrow Br$ series in HNgX is the charge term, C. This is interesting since this term exhibit a nice linear correlation with the electronegativies of the halogen atoms in the HX molecules. The invariance of the charge term in the HNgX molecules could be described in terms of a shielding character of the noble gas, which makes the charge assigned to the hydrogen atom independent of the halogen bonded to it. This is supported because both CHelpG and QTAIM charges display the same trend, though with different magnitudes for this term.

Finally, for the HX molecules all the CCFDF terms display clear trends related to the size and electronegativity character of the halogen atom. Both the CF and DF derivatives increase in magnitude when passing from fluorine to bromine, but they also tend do cancel each other more effectivelly in this series. This is summarized in the CCTDP results, for which the CTDP term is much lower (in magnitude) for HBr than for HF. For the HNgX molecules, however, the magnitude of this term increases rapidly when passing from HNgF to HNgBr. Since the CTDP term is related to the rearrangements in the electronic density while the molecule is vibrating along that normal coordinate, this is in agreement with the larger polarizability of bromine compared to chlorine and chlorine compared to fluorine.

Conclusions

The results suggest that the models employing the QTAIM density partition are better suited to the description of infrared intensities because their results follow more closely what is expected from chemical insight, in agreement with similar works in the literature[3]. While the CCFDF model configures a good choice when employed with the QTAIM density partition, it is harmed when the CHelpG charges are used instead.

The CCTDP results also display simpler patterns for their contributions, making the interpretation of the derivatives easier. The CTDP term is the main responsible for the high IR intensity of the HNgX molecules since the charge term is very small for all of them.

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