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DECOMPOSING MOLECULAR NONLINEAR OPTICAL PROPERTIES

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ABSTRACT

Great attention has been paid to materials that are characterized by a large nonlinear optical response, as they being commonly used in new technologies such as optical communication technology, optical rectification. The nonlinear optical properties of the materials strongly depend on the intermolecular interactions. For that reason, the understanding of different intermolecular interactions on nonlinear optical properties is so important, since it can allow a better knowledge of these properties and so, facilitate the design of new types of materials with large NLOP. In this work, it is investigated the role of the different contributions to the NLOP of a set of dimers, all of them with a HCN molecule as a monomer. Whereas for the dipole moment and polarizability of the studied dimers the main contribution is the electronic, the nonlinear optical properties (first and second hyperpolarizability) are governed by vibrational contribution.

The NLOP properties will be partitioned in two different ways, all based on methodologies used to decompose the molecular energy. The first one, is a variational-perturbational energy decomposition scheme (VP-EDS), which split the NLOP into different interaction energy contributions like electrostatic or repulsion exchange. The second one is a real-space partition of the NLOP that splits the property in to an origin-independent atomic contributions.

The decompositions with VP-EDS have shown, in general, some tendency on its terms (i.e. always increase or always decrease while increasing the atomic number of the atom bonded to the halogen). The comparison with other kind of interactions, such as hydrogen bonds, showed that the tendencies are quite similar between the two types of interactions. For instance, for $\Delta\mu^{\text{el}}$ the predominant term is electrostatic and the second one is delocalization, decreasing while increasing the volume of the atom(s) bonded to the halogen/hydrogen.

Unexpectedly, the real space origin-independent methodology showed that, instead of distributing the excess of the property due to the interaction into the two monomers, all excess property is concentrated in the HCN monomer.

RESUM

Durant els últims anys els materials amb propietats òptiques no lineals (NLOP) grans han cridat molt l'atenció, degut a que són utilitzats molt sovint en noves tecnologies com per exemple tecnologies de comunicació òptica o rectificació òptica. Les propietats òptiques no lineals dels materials tenen molta dependència de les interaccions intermoleculares. Per aquesta raó, entendre l'efecte de les diferents interaccions intermoleculares en les propietats òptiques no lineals ha esdevingut molt important, ja que permet conèixer millor les propietats, i gràcies a això, dissenyar nous tipus de materials que estiguin caracteritzats per grans NLOP. En aquest treball, s'investigarà el paper de les diferents contribucions pel que fa a les NLOP d'un conjunt de dímers, tots ells amb la molècula d'HCN com a monòmer. Mentre que la major contribució pel moment dipolar i la polaritzabilitat dels dímers estudiats és l'electrònica, per les propietats òptiques no lineals (primera i segona hiperpolaritzabilitat) la que predomina és la contribució vibracional.

La partició de les NLOP s'ha portat a terme de dues maneres diferents, totes dues basades en metodologies utilitzades en la descomposició de l'energia molecular. La primera que s'aplicarà, és un esquema de descomposició de l'energia basada en la teoria *variational-perturbational* (VP-EDS), la qual separa les NLOP en diferents contribucions de l'energia d'interacció com *electrostàtica* i la *repulsió de intercanvi*. La segona es una partició de les NLOP en l'espai real que separa la propietat en contribucions atòmiques independents de l'origen.

Les descomposicions amb el mètode VP-EDS mostren, en general, una tendència en els seus termes, és a dir, sempre creix o sempre disminueix quan augmenta el nombre atòmic de l'àtom enllaçat a l'halogen. La comparació amb altres tipus d'interacció, com per exemple els ponts d'hidrogen, demostren que les tendències són bastant similars. Un exemple és el $\Delta\mu^{\text{el}}$, pel qual el terme electrostàtic és el predominant, essent el segon la deslocalització. A més, aquests dos termes disminueixen quan augment el volum de l'àtom(s) enllaçats al halogen/hidrogen.

La metodologia de la partició en l'espai real independent de l'origen, mostra que sorprenentment, en comptes de que l'excés es distribueixi en els dos monòmers que formen el dímer, tot es diposita en el monòmer HCN.

RESUMEN

Durante estos últimos años, los materiales con propiedades ópticas no lineales (NLOP) grandes han sido de gran atención debido a que se utilizan en nuevas tecnologías como por ejemplo la comunicación óptica o la rectificación óptica. Las propiedades ópticas no lineales de los materiales dependen mucho de las interacciones intermoleculares. Por ésta razón, la comprensión de las interacciones intermoleculares con respecto a las propiedades ópticas no lineales se ha convertido en un estudio muy importante, ya que permite conocer mayor éstas propiedades y debido a eso, diseñar nuevos tipos de materiales que requieran grandes NLOP. En este trabajo se estudiará el papel de las diferentes contribuciones en referencia a las NLOP de un conjunto de dímeros, todos ellos con una molécula de HCN como monómero. Mientras que para el momento dipolar y la polarizabilidad la contribución electrónica es la predominante, para las propiedades ópticas no lineales (primera y segunda hiperpolarizabilidad) la mayor es la vibracional.

La partición de las NLOP se ha llevado a cabo de dos formas distintas, las dos basadas en metodologías utilizadas en la descomposición de la energía molecular. La primera que se investigará es un esquema de la descomposición de la energía basada en la teoría *variational-perturbational* (VP-EDS) la cual separa las NLOP en diferentes contribuciones de la energía de interacción, como por ejemplo la *electrostática* y la repulsión de intercambio. La segunda es una partición de las NLOP en el espacio real que separa la propiedad en contribuciones atómicas independientes del origen.

Las descomposiciones con el método VP-EDS demuestran que, generalmente, hay cierta tendencia en los términos que componen la propiedad, es decir, siempre incrementa o disminuye cuando aumenta el número atómico del átomo enlazado al halógeno. La comparación con otro tipo de interacciones, como el puente de hidrógeno, ha demostrado que las tendencias son bastante similares entre ellos. Por ejemplo, para $\Delta\mu^{\text{el}}$ la contribución electrostática es la predominante mientras que la deslocalización es la segunda más relevante. Además, cuándo incrementa el volumen del átomo(s) enlazados al halógeno/hidrógeno, éstas dos contribuciones disminuyen.

Para la metodología de la partición en el espacio real independiente del origen se ha obtenido que, en lugar de distribuir la propiedad de exceso entre los dos monómeros del dímero, sorprendentemente todo el exceso se atribuye al monómero de HCN.

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1. INTRODUCTION

1.1 LINEAR AND NONLINEAR OPTICS

Optics is the branch of physics concerned with the study of light, represented as an electromagnetic wave, and its behavior when it interacts with matter.^[1] This interaction is produced between the two fields present in an electromagnetic wave, electric and magnetic, and the charged particles that constitute the molecules, nuclei and electrons. Since the effect of the electric field of the electromagnetic wave is much more noticeable when the interaction with matter is produced, magnetic field is often ignored.

Optics can be conveniently divided into two types of phenomena: linear and nonlinear. When the interaction of the light with matter doesn't modify its wave properties, like wavelength and frequency, is known as linear optical phenomena, and it is originated when the intensity of the electromagnetic wave is low, as it is the case of most ordinary light sources. It means that in nature we only can observe linear optics phenomena. In linear optics, the electromagnetic wave induces a charge separation or polarization due to the electric field interaction with nuclei and electrons, which move in the same/opposite direction as the field, depending on their charge. This polarization is directly proportional to the electric field intensity.^[2]

It wasn't until 1961 that the study of nonlinear optical properties (NLOP) began due to the discovery of second-harmonic generation by Franken *et al.* (1961), one year after the demonstration of the first working laser by Maiman in 1960. With that discovery, different nonlinear phenomena were observed. Peter Franken *et al.* irradiated a quartz crystal with a laser and observed the generation of a wave with doubled frequency with respect the incident wave.^[3] This and other frequency-mixing processes occur when the irradiation comes from a light source with intensity enough to generate an electrical field of comparable strength to the internal electric field of the molecules. These sources are mainly lasers. In these cases, the dependence between the polarization and the electric field is not linear.

To study the polarization of systems irradiated with high intensity light sources, we can expand the dipole moment (μ) as a Taylor expansion in the strength of electric field (F):

$$\mu = \mu_0 + \alpha \cdot F + \frac{1}{2!} \cdot \beta \cdot F^2 + \frac{1}{3!} \cdot \gamma \cdot F^3 + \dots \quad [1]$$

where μ_0 is the dipole moment without an applied electric field, α is the linear polarizability, β is the first hyperpolarizability and γ is the second hyperpolarizability. The latter two terms are the electrical properties related to the nonlinear optical effects of the first and second order, respectively.

These properties can be calculated as the derivatives of the dipole moment respect to the electric field. But knowing that the dipole moment can be written as the minus first derivative of the energy with respect to an applied electric field, these properties can also be written as derivatives of the energy, as we can see in Eq. 2.

$$E = E_0 - \mu \cdot F - \frac{1}{2!} \cdot \alpha \cdot F^2 - \frac{1}{3!} \cdot \beta \cdot F^3 - \frac{1}{4!} \cdot \gamma \cdot F^4 \quad [2]$$

Great attention has been paid to the materials with large nonlinear optical response as they are commonly used in optical rectification, modern waveguides and optical communication technology.

Because of all these different applications of NLO, a great effort has been put on the development of NLO materials. Computationally, the main problem for designing them is the viability of wavefunction-based calculations, which have a high computational cost for large conjugated polymers and other NLO materials. The alternative to these methods is Density Functional Theory (DFT), which calculates energy very accurately, but still commits large errors in the evaluation of NLO.^[4] Because of this, NLO are one of the biggest challenges of DFT.

The interaction-induced (excess) (non)linear optical properties are defined for any system as the difference between a property of the system and the sum of the properties of the noninteracting subsystems.^[5] In a previous work, Robert Zalesny *et al.* (2018) performed the decomposition of linear and nonlinear optical properties of dimers containing HCN and hydrogen bonds.^[6] Therefore, a possible next step to improve the understanding of the contribution of the intermolecular interactions to the NLO is studying other kind of intermolecular interactions, like for instance π - π interaction (π stacking), π -hydrogen interaction and halogen bonds. Using small dimers based on HCN monomer is not possible to optimize the structures of the dimers based on π - π and π -hydrogen interactions. Therefore, the main goal of this work was focus on studying the NLO of molecular dimers with halogen bonds.

1.2 HALOGEN BOND

The first systematic theoretical explanation for this apparently counterintuitive phenomena was that, in covalently-bonded halogens, their electrostatic potential is anisotropic, possessing positive regions at the tip of X (X = Cl, Br, I) of Fig. 1, which was later named as σ -hole. Therefore, halogen bonds were described as an electrostatically-driven noncovalent interaction between that positive σ -hole and a nucleophile B. The electrostatic potential characteristics elegantly explain the main features and directional preferences of the interactions with halogen atoms: side-on interactions are observed with electrophiles whereas head-on interactions correspond to halogen bonds with nucleophiles (Fig. 1).

It must be pointed out that, if X is less polarizable and very electron-attracting, the σ -hole might be neutralized or even absent. Therefore, typically, the halogen bond strength increases from chlorine to iodine, whereas fluorine is not usually considered a halogen bond donor.^[7]

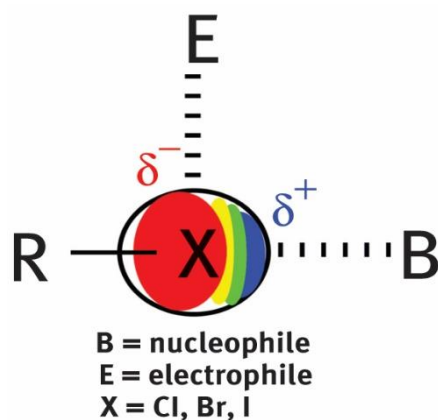


Figure 1. Representation of halogen bond with the anisotropic distribution of charge around atom X

It is difficult to establish exactly when the term halogen bond was first proposed for interactions formed by electrophilic halogens and even more difficult to give an exact date for when the concept was developed and accepted. The concept began to emerge in the middle of the 20th century when it began to be identified as the cause of a well-defined and relatively homogeneous set of phenomena. In 1961, R. Zingaro and M. Hedges,^[8] while describing the complexes formed in solution by halogens and interhalogens with phosphine oxides and sulfides, were probably the first to use the term halogen bond to describe interactions where halogens act as electrophilic species, in analogy to the behavior of hydrogen in the HB. In 1976 D. E. Martire *et al.* used the term to describe adducts formed in the gas phase by haloforms with ethers and amines.^[9]

However, it was the review of J.-M. Dumas, M. Gomel, and M. Guerin in 1983^[10] that first separated results obtained by using several experimental techniques in the gas, liquid, and solid phases from other domains (e.g., other electron donor–acceptor interactions) and organized them under the term halogen bond.^[11] Although this interaction has been investigated for a few decades, there are not works analyzing the effect of this interaction on the NLO, which could be important to design new NLO materials for future applications.

1.3 ELECTRICAL (HYPER)POLARIZABILITES DECOMPOSITION

The decomposition of the total value of the properties into different contributions is interesting because the complexity of the system is reduced in the partitioning. The result of the partitioning gives parts that are easier to analyze. Within the Born-Oppenheimer approximation, the total

properties studied here, P , may be defined as the sum of electronic, P^{el} , nuclear relaxation, P^{nr} , and curvature, P^{curv} , contributions:

$$P = P^{el} + P^{nr} + P^{curv} \quad [3]$$

where P^{nr} and P^{curv} arise from the change of electronic and vibrational energies caused by the field-induced relaxation of the equilibrium geometry, respectively. The nuclear relaxation contributions contain the anharmonic corrections of the lowest order while higher order are included in curvature contributions.^[5]

For this study, two different decomposition schemes will be used. Firstly, variational-perturbational interaction-energy decomposition scheme (VP-EDS), which is based on the partitioning of the supermolecular interaction energy in different physic contributions (e.g. electrostatic, dispersion...). Secondly, in a previous work of Montilla et al.^[12] a real space origin-independent partition was achieved, and it was demonstrated that doing the partition of the property into functional group contributions, good transferability of the polarizability values can be obtained. So, this origin-independent real-space decomposition of nonlinear optical properties, using two different methodologies (Topological Fuzzy Voronoi Cells (TFVC) and Becke) for the partition of the real-space into atomic domains will be used.

In other words, in this work the NLOP of systems that contain halogen bonds will be decomposed in two different ways. The first one, using VP-EDS, with which different contributions will be computed. The other decomposition will be in the real space (e.g. atoms, functional groups).

1.4 SUSTAINABILITY

Doing this work some ethics and sustainability procedures has been done. It is known, that investigation in computational science is more sustainable, due to the non-use of any kind of chemical compound, like metals, solvents, water... So, for this part my work complies with good sustainability. Also, all papers or materials extracted from internet hasn't been printed, all has been sent by email and so avoiding wasting paper. Regarding ethics, all works referenced here are publics or has been left to me. None of the results have been manipulated or hided, and they are showed in this work. Also, I thanked in acknowledgments Dr. Robert Zaleśny for sharing me some results, such as hydrogen bond decomposition and the decomposition of iodine halogen bonds.

2. OBJECTIVES

The main objective of this work is to decompose the linear and nonlinear optical properties of HCN dimers formed by different kinds of intermolecular interactions, in different ways that can help us to understand the physical origin of the total optical properties of these dimers.

First, the total electric properties (μ , α , β and γ) of the dimers will be computed to see how large they are. For this task, finite-field method will be used to obtain the electrical properties numerically, and these will be compared with the analytical results. Romberg's mathematical method will be used in this work, which iteratively removes the numerical errors due to higher-order derivatives. Then the decomposition of the properties will be done. Using the variational-perturbational decomposition scheme, the different contributions to the property (e.g. electrostatic, exchange repulsion) will be obtained. Again, finite-field method and Romberg's methodology will be used in this section.

For these results, it will be interesting to compare them with the ones given in Robert Zaleśny *et al.* study, which is about hydrogen bonds, to see if there is any similarity between the NLOP decomposition of H-bonded systems and halogen bonded ones. In this comparison, we will search for some kind of trend in the different contributions obtained in the decomposition.

Finally, the polarizability of the same systems will be computed, using a real space origin-independent methodology. In a previous work, Marc Montilla *et al.* developed an approach to perform the decomposition of polarizability in the real space.^[12]

Another goal of this project is to investigate if halogen bond systems can be decomposed in the real space showing some transferability in polarizability values, so that the values of the property for a molecule of this kind can be predicted without the necessity of doing calculations.

3. METHODOLOGY

3.1 FINITE-FIELD METHOD

The finite field (FF) method is a quick and easy-to-implement tool for the prediction of molecular electrical (hyper)polarizabilities that uses a rational function to fit a molecule's energy with respect to an electric field. This method was used to compute dipole moment (μ), static polarizability (α), first hyperpolarizability (β) and second hyperpolarizability (γ) for all dimers studied in this work.^[13]

3.1.1 Dipole moment

The dipole moment can be defined as the minus derivative of the energy with respect to an external electric field:

$$\mu = -\frac{\partial E(F)}{\partial F} \quad [4]$$

Using the finite-field method we can obtain the Eq. 5, which allows us to calculate dipole moment numerically.

$$\mu_i = -\frac{1}{2} \left(\frac{E(F_i) - E(-F_i)}{F_i} \right) \quad [5]$$

where i is the direction x, y or z and $E(F_i)$ is the energy of the system with an electric field with intensity F applied in direction i .

3.1.2 Polarizability

The polarizability can be defined as the derivative of dipole moment but, as we said before, we can write the dipole moment as the minus derivative of the energy with respect to an external electric field (Eq. 4). So we can write the polarizability as the minus second derivative of the energy with respect to an external field:

$$\alpha_{ii} = -\left(\frac{E(F_i) + E(-F_i) - 2E(0)}{F_i^2} \right) \quad [6]$$

where $E(0)$ is the energy without an electric field applied.

3.1.3 First hyperpolarizability

So, continuing the previous section we can say that the first hyperpolarizability can be defined as the minus third derivative of the energy with respect to an external field:

$$\beta_{iii} = -\left(\frac{E(2F_i) - 2E(F_i) + 2E(-F_i) - E(-2F_i)}{F_i^3} \right) \quad [7]$$

3.1.4 Second hyperpolarizability

Finally, the second hyperpolarizability can be defined as the minus fourth derivative of the energy with respect to an external field:

$$\gamma_{iiii} = -\left(\frac{E(2F_i) - 4E(F_i) + 6E(0) - 2E(-F_i) + E(-2F_i)}{F_i^4} \right) \quad [8]$$

The halogen bond systems, ones of the dimers studied in this work, are linear. We were interested in computing only the linear contribution to the dipole moment and (hyper)polarizabilities for these systems, which is by far the largest contribution. Therefore, the field was placed along the molecular axis (z axis), so i in the Eqs. 5, 6, 7 and 8 is substituted for z.

When calculating derivatives numerically, there is always a certain error because of the higher order derivatives. For this reason, Romberg's mathematical method has been used in this work,

which corrects the derivative calculated with a certain field iteratively, using the derivative calculated with higher fields. A more detailed explanation of Romberg's method is given in the 3.2 section.

3.2 ROMBERG'S METHOD FOR THE NUMERICAL DERIVATIVES CORRECTION

With finite-field method, one can use more points of the function (with different specific coefficients for each derivative) to obtain different orders of accuracy. But using more points of the function requires computing energies at higher fields. For example, the result of improving the accuracy of Eq. 7 is the next equation:

$$\beta_{iii} = - \left(\frac{E(3F_i) - 8E(2F_i) + 13E(F_i) - 13E(-F_i) + 8E(-2F_i) - E(-3F_i)}{F_i^3} \right) \quad [9]$$

An alternative approach to obtain more accurate derivatives is the Romberg's method. Romberg's method improves the accuracy of the numerical derivatives by using the derivatives calculated with the large field $n+1$ to correct the derivative calculated with the small field n . In other words, Romberg's method improves the accuracy correcting the derivative obtained with field n using the derivative obtained with the field $n+1$. The results obtained after the first iteration of the Romberg method can be refined with a second Romberg iteration, which can be used for the calculation of third iteration and so on. Therefore, Romberg's approach allows computing and correcting the numerical derivatives in an iterative manner. This overall process is described by the following equation.

$$x_n^k = \left(\frac{4^k \cdot x_n^{k-1} - x_{n+1}^{k-1}}{4^k - 1} \right) \quad [10]$$

Where x is the property (e.g. α), x_n^k are the approximations to the numerical derivative, k indicates the value of the Romberg iteration, and n indicates the field used to calculate the original x value. In this work, the properties were calculated with a field intensity progression of 2 (with the initial field being $2 \cdot 10^{-4}$ a.u., and the next field having twice the intensity). This means that field can be expressed as:

$$F = 2^n \cdot 10^{-4} \text{ a.u.} \quad [11]$$

The $k = 0$ values (i.e. before applying Romberg) are obtained according to Eq. 4, and the equivalent ones for the other properties. Looking at Eq. 10, it becomes clear that there can be $n-1$ iterations, because the initial iteration (before Romberg) has n values, and each iteration has $n-k$ values. The most accurate numerical derivative out of all the possible values given by this method is chosen by calculating how two consecutive values (n and $n+1$, i.e. values calculated for two consecutive fields) converge. In other words, the smaller difference between

two consecutive values of the same iteration the better accuracy.

3.3 VARIATIONAL-PERTURBATIONAL DECOMPOSITION SCHEME

VP-EDS or variational-perturbational decomposition scheme is used as an energy partition scheme and, specifically, it is used for the partitioning of supermolecular interaction energy. With this scheme the total interaction energy of a dimer is partitioned into Hartree-Fock (HF) and the electron correlation interaction energy components. This partitions are calculated by a supermolecular approach in the dimer-centered basis set (DCBS), using the second-order Møller-Plesset perturbation theory (MP2). So, using VP-EDS the total MP2 energy can be described as:

$$\Delta E_{int}^{MP2} = \Delta E_{int}^{HF} + \Delta E_{corr}^{MP2} \quad [12]$$

But both terms, the HF (ΔE_{int}^{HF}) and the second-order electron correlation (ΔE_{corr}^{MP2}) can be further partitioned. The first one can be partitioned in electrostatic interactions, $\varepsilon_{el}^{(10)}$, exchange repulsion, ΔE_{ex}^{HL} , which is due to the Pauli repulsion principle, and charge delocalization, ΔE_{del}^{HL} . Then, Hartree-Fock term can be described as:

$$\Delta E_{int}^{HF} = \varepsilon_{el}^{(10)} + \Delta E_{ex}^{HL} + \Delta E_{del}^{HL} \quad [13]$$

On the other hand, the second-order electron correlation can be partitioned in the second order dispersion interaction, $\varepsilon_{disp}^{(20)}$, electron correlation correction to the first order electrostatic interaction, $\varepsilon_{el,r}^{(12)}$, and the remaining electron correlation effects, $\Delta E_{ex}^{(2)}$. ΔE_{corr}^{MP2} accounts mainly for the uncorrelated exchange-dispersion and electron correlation corrections to the Hartree-Fock exchange repulsion. The indices in parentheses denote perturbation orders in the intermolecular interaction operator and intramonomer correlation operator, respectively.^[5]

So, as for HF term, the second-order electron correlation can be described as:

$$\Delta E_{corr}^{MP2} = \varepsilon_{disp}^{(20)} + \varepsilon_{el,r}^{(12)} + \Delta E_{ex}^{(2)} \quad [14]$$

Finally, if Eqs 12, 13 and 14 are put together:

$$\Delta E_{int}^{MP2} = \varepsilon_{el}^{(10)} + \Delta E_{ex}^{HL} + \Delta E_{del}^{HL} + \varepsilon_{disp}^{(20)} + \varepsilon_{el,r}^{(12)} + \Delta E_{ex}^{(2)} \quad [15]$$

Eq. 15 describes the partitioning of interaction energy that will be done in this work.

So, in order to calculate the (non)linear optical properties the derivative of energy with respect to the external electric field must be done, and maintaining the latter equation for each NLOP and also its excess produced by the interaction.

3.4 FINITE-FIELD CALCULATION OF THE NUCLAR RELAXATION (HYPER)POLARIZABILITIES.

Referring to section 1.3, the main problem of the P^{curv} is that it is computationally expensive. Furthermore, usually P^{curv} is far smaller than P^{nr} . Then, the curvature contributions will not be computed in this work. The electronic contribution to the (hyper)polarizabilities are obtained using always the field-free optimized geometries in the finite field approach. On the contrary, the calculation of the nuclear relaxation contribution requires the optimization of the field-dependent equilibrium geometries. But one requirement to use this formalism is needed: the field-dependent optimization must be performed maintaining the Eckart conditions which simplify the nuclear motion (rovibrational) Schrödinger equation that arises in the second step of the Born–Oppenheimer approximation. The Eckart conditions allow the separation of the external (rotation and translation) motions from the internal (vibration) motions. Although the rotational and vibrational motions of the nuclei in a molecule cannot be fully separated, the Eckart conditions minimize the coupling between these two nuclear movements.

The field-dependent optimization fulfilling the Eckart conditions are feasible thanks to a procedure developed by Luis et al, which can be used to obtain the nuclear relaxation contribution to the NLOP. Once the field-dependent equilibrium geometries are obtained, VP-EDS should be applied to decompose the sum of the electronic and nuclear relaxation contributions.

One can obtain the nuclear relaxation values by subtracting the latter results minus their electronic counterparts (where the geometries were frozen) which are calculated previously.

3.5 REAL SPACE ORIGIN-INDEPENDENT PARTITION AND MOLECULAR ENERGY DECOMPOSITION

In this work, the real-space partition scheme that will be used defines the atoms as fuzzy regions around their nuclei, allowing the different regions to overlap, giving them the name of fuzzy atoms. Therefore, each point of the space does not belong to only one single atom, but to various atoms. To do the calculations properly, a positive weight function must be defined to describe, for each position of the real space, which fraction belongs to each atom. This function has, for a given atom A, values very close to 1 in the area near the nucleus of atom A, but it decreases inversely proportional to the distance to the nucleus asymptotically reaching the zero value. So, because of that definition, the sum of all values of the function in any point of the space must be 1. This function can be described in many ways, but in this work we will use Topological Fuzzy Voronoi Cells (TFVC)^[13] and Becke's method.

The TFVC method considers an intermediate point between all pairs of neighboring atoms, and then describes the weight function for each atom. At the nucleus, the weight function value is 1 and it decays to 0 when it gets closer to the neighboring atoms, (with a given value at the intermediate point). This intermediate point is placed in the minimum of the electron density between two atoms.

For Becke's method the definition of weight functions are very similar as TFVC. Both of them define an intermediate point between these pairs of neighboring atoms but Becke's places this intermediate point based on parameters, as atomic radii, that are chosen from empirical values.

Once it is decided the methodology of the real-space partition it must be decided a molecular energy decomposition scheme. In this work it is used a methodology based on the calculation of two kinds of energy components, intra-atomic contributions and inter-atomic contributions. The first one can be written as E_{AA} and it refers to the interaction between nucleus and electrons of the atom A, the interactions among its electrons, and the kinetic energies of all these particles. The inter-atomic contributions can be written as E_{AB} and reflect the favorable or unfavorable interactions between the particles of each pair of atoms A and B. The total energy decomposition can be expressed as:

$$E = \sum_A E_{AA} + \sum_{A,B>A} E_{AB} \quad [16]$$

The energies used in Eq. 16 are calculated taking into account the weight functions of each atom involved in the calculations.

Also, for each atom A, an "effective" atomic energy can be described, which is defined as the contribution to the total energy that corresponds to that atom. The expression for that atomic energy can be written as:

$$\varepsilon_A = E_{AA} + \frac{1}{2} \sum_{B \neq A} E_{AB} \quad [17]$$

The atomic energy (ε_A) is the intra-atomic contribution of that atom plus half the inter-atomic contributions of atom A with the other atoms. This decomposition fulfills that the sum of all atomic energies, ε_A , are equal to the total energy of the molecule, E. This approach is implemented in the APOST3D program.^[12]

The atomic partition is not the unique possible 3D partition. These Eqs. 16, 17, can refer not only to atoms but also to fragments of the molecule, making it possible to study functional groups (or monomers) contributions.

Using this molecular energy decomposition scheme and knowing that polarizability is the minus second derivative of the energy with respect to an external electric field, the expression of Eq. 18 can be obtained:

$$\alpha_A = \frac{\partial^2 \varepsilon_A(F)}{\partial F^2} \quad [18]$$

This relation can be done thanks to the decomposition of the atomic or fragment energy contributions in a way that the total energy is the sum of all energy contributions. For that reason, the total polarizability of the molecule can be described as the sum of all atomic polarizabilities:

$$\alpha = \sum_A \alpha_A \quad [19]$$

3.6 SOFTWARE AND COMPUTATIONAL DETAILS

For VP-EDS all geometry optimizations and single point calculations have been performed using GAUSSIAN 16, using the MP2 method and aug-cc-pVTZ basis set for H, C, N, Cl and F atoms and aug-cc-pVTZ-PP and its corresponding pseudopotential for Br and I. From now on, we will label this basis as BASE1. The VP-EDS decompositions of the energy were carried out using GAMESS (US) program.

All α have been calculated analytically using GAUSSIAN16 keyword polar, as a reference for our finite-field method application results. For the finite-field calculations, several fields have been computed. For Eq. 11, fields ranging from $n=1$ to $n=8$ have been used (i.e. fields of 0.0002, 0.0004, 0.0008, 0.0016, 0.0032, 0.0064, 0.0128 and 0.0256 a.u.), only for positive and negative z direction (i.e. the axis of the dimers). This task has been done with the keyword `field=z[sign][magnitude]` where [sign] is + or - and [magnitude] is the intensity of the field. `NoSymm` keyword has been also used to ensure that there is not any rotations of molecule and thus ensure that all calculations are done with the same orientation of the molecule.

For the VP-EDS decomposition, a set of set of very useful scripts from Dr. Robert Zaleśny have been used, and for the nuclear relaxation optimizations ECKART program from Dr. Josep Maria Luis has been used. For real-space partition all geometry optimizations and single point calculations have been performed using GAUSSIAN 16, using LC-wPBE functional and aug-cc-pVTZ for H, C, N, F, Cl, Br and the Sadlej pVTZ for I. From now on, we will label this basis as BASE2. The energy decomposition has been performed using APOST 3D program indicating in the input which method is used to define the atomic regions (TFVC or Becke).

4. RESULTS AND DISCUSSION

4.1 NONLINEAR OPTICAL PROPERTIES

As we said previously, different types of interactions will be studied. In this section the analysis of the (non)linear properties will be done, comparing electronic and vibrational contributions to NLO properties to find out which contribution is larger and so governs the property. There is the list of all the possible chemical systems that we plan to study in this work: HCN...BrH, HCN...BrF, HCN...BrCl, HCN...BrBr, HCN...IH, HCN...IF, HCN...ICl, HCN...IBr, HCN...II, HCN...HNC, HCN...HCl, HCN...HCCH, HCN...HCCF and others systems which have π - π interaction or π -H interaction.

For hydrogen bond systems, only the real-space partition with the origin-independent molecular energy decomposition has been performed, because all the results and analysis of their partition in contributions with different physical origin (VP-EDS) are already described in the paper by Robert *et al.*^[6]

The first step to do analyze the NLO of these dimers is to optimize their geometries. During this task, we had to put aside the systems that have π - π interaction and π -H interaction because of the results of the geometry optimization: the geometries displaying this kind of interaction do not present minima in the potential energy surface, so we decided to focus on halogen bond systems, which had stable equilibrium geometries.

4.1.1 Electronic (non)linear optical properties

After optimization of all halogen bond systems, the nonlinear optical properties were computed and calculated with finite-field and Romberg method. The results obtained at MP2/BASE1 using the methods previously mentioned are shown in Table 1.

Table 1. Electronic dipole moment, polarizability, first hyperpolarizability and second polarizability of the HCN...XR systems in a.u. obtained with GAMESS (US) program at MP2/BASE1 level.

	μ^{el}	α^{el}	β^{el}	γ^{el}
HCN...BrH	-1.064	52.68	-56.4	1.03E+04
HCN...BrF	-2.567	68.04	-15.5	1.88E+04
HCN...BrCl	-2.058	91.22	-245.2	3.46E+04
HCN...BrBr	-1.822	102.03	-356.8	4.41E+04
HCN...IH	-1.309	67.30	-74.0	1.74E+04
HCN...IF	-2.901	80.76	190.5	2.92E+04
HCN...ICl	-2.553	110.37	-92.8	4.24E+04
HCN...IBr	-2.327	123.87	-262.5	5.33E+04
HCN...II	-2.007	143.89	-450.6	7.20E+04

In this Table 1 we can see electronic contributions to the electrical properties for each system studied. One thing to comment is that for α^{el} and γ^{el} the value always increases from hydrogen to fluorine, and then from fluoride going down in the periodic table. For μ^{el} the decrease of the property can be noticed, with the exception of the HCN...BrH which is larger than the others and doesn't follow the pattern. For β^{el} it seems to increase, like for α^{el} and γ^{el} , with the exception of HCN...BrF and HCN...IF, which have in common the fluorine bonded to the halogen.

One way to check if the results of GAMESS (US) are correct is comparing these values to the results obtained Gaussian16 (using the energy obtained from the keyword polar and applying finite-field). Both values resulted to be very similar, and knowing that for higher order derivatives the error is larger, the difference between Gaussian16 and GAMESS (US) is larger for β and γ but still being a small average difference. So we can say that the results obtained with both programs are very similar, and then, that GAMESS (US) values are correct.

4.1.2 Vibrational (non)linear optical properties

After the calculations of the electronic electrical properties, which are obtained as derivatives of the electronic energy at the frozen field-free equilibrium geometry, the calculation of the vibrational contribution to the NLOP were performed. To do this task, we had to use ECKART program developed by Josep M. Luis *et al.*, which allows the relaxation of the geometries for each field applied. So, the main difference between the calculation of the vibrational and electronic contributions is that for electronic ones the geometry doesn't change with the field applied while for vibrational contributions it does. In Table 2 we present the nuclear relaxation contribution to the electrical properties for the dimers studied in this work.

Table 2. Vibrational dipole moment, polarizability, first hyperpolarizability and second polarizability of the HCN...BrX systems in a.u. obtained with GAMESS (US) program at MP2/BASE1 level.

	α^{nr}	β^{nr}	γ^{nr}
HCN...BrH	2.59	-192.4	1.21E+04
HCN...BrF	97.69	-2158.4	8.16E+04
HCN...BrCl	25.36	-3251.5	3.65E+05
HCN...BrBr	24.05	-3245.2	4.07E+05
HCN...IH	4.77	-384.5	2.45E+04
HCN...IF	26.36	-1473.3	-7.05E+03
HCN...ICl	39.10	-4083.2	1.84E+05
HCN...IBr	39.22	-4771.0	3.49E+05
HCN...II	35.58	-5038.7	5.99E+05

The first comment on the results is that the nuclear relaxation contribution to the dipole moment μ^{nr} by definition has to be zero (because we are working with field-dependent equilibrium geometries and then applying the stationary point condition, which implies that the first derivative of the energy respect to the nuclear displacement is zero). For that reason the μ^{nr} is not presented in the table. Another thing we can see is that compared with electronic results in Table 1, α is smaller for vibrational contributions (except for HCN...BrF) while β and γ are higher than their electronic counterparts.

Analyzing both electronic and vibrational properties is interesting, but it is also important to see which relation exist between them and which one is the most relevant. In order to do so, the electronic/vibrational ratio has been calculated and shown in Table 3.

Table 3. Ratio between electronic and nuclear electrical properties of the HCN...BrR systems.

	α^{el}/α^{nr}	β^{el}/β^{nr}	γ^{el}/γ^{nr}
HCN...BrH	20.34	0.29	0.85
HCN...BrF	0.70	0.01	0.23
HCN...BrCl	3.60	0.08	0.09
HCN...BrBr	4.24	0.11	0.11
HCN...IH	14.10	0.19	0.71
HCN...IF	3.06	-0.13	-4.14
HCN...ICl	2.82	0.02	0.23
HCN...IBr	3.16	0.06	0.15
HCN...II	4.04	0.09	0.12

Looking at Table 3 we can see that the column of dipole moment doesn't appear, and this is because we know that all dipole moment property will be attributed to electronic contribution, due to the 0 value for nuclear relaxation.

On one hand, the polarizability ratio gives us the information that the main contribution to that property comes from electronic polarizability because the ratio is higher than 1 with the exception of HCN...BrF. On the other hand, for first hyperpolarizability and second hyperpolarizability we can note that the vibrational contribution will be higher than the electronic, being these two properties ruled by the first. For HCN...BrH γ we can consider that both contributions (electronic and vibrational) must be important when analyzing the partition and for HCN...IF it seems that electronic contribution is predominant. Also, we can see that HCN...BrH has always the bigger ratio and this fact can be attributed to the relative low vibrational contribution to the properties. One more thing to comment is that, similar to what happened for β^{el} , the HCN...BrF dimer has an unexpected α^{nr} compared with the others. Also, in

Table 3 we can notice that for the a couple of dimers ($\text{HCN}\cdots\text{BrCl}$ and $\text{HCN}\cdots\text{BrBr}$) the properties do not change too much, which initially, one could think that the properties will increase while increasing the atomic number of the atom bonded to the bromine. The same thing occurs with the analogous $\text{HCN}\cdots\text{ICl}$ and $\text{HCN}\cdots\text{IBr}$.

4.2 INTERACTION-INDUCED NONLINEAR OPTICAL PROPERTIES

Before analyzing the electrical properties, it is also interesting to investigate decomposition of the interaction energy for the set of dimers studied in this work.

4.2.1 Interaction energy partition

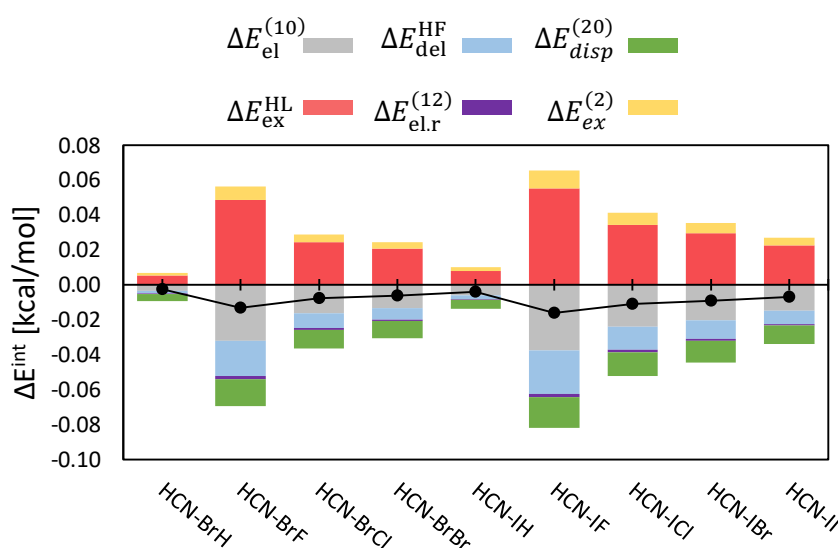


Figure 2. Interaction energy partition for $\text{HCN}\cdots\text{XA}$ systems

Fig. 2 show the VP-EDS partition of the interaction energy for each dimer. We can observe that for those dimers which have a halogen-hydrogen monomer (i.e. $\text{HCN}\cdots\text{BrH}$, $\text{HCN}\cdots\text{IH}$), the interaction energy is smaller than -0.0038 kcal/mol.

For the dimers which have a halogen-halogen monomer (e.g. $\text{HCN}\cdots\text{BrF}$, $\text{HCN}\cdots\text{BrCl}$), we can see that the value of interaction energy decreases with the increase of the atomic number of the atom bonded covalently to the halogen. So, for those dimers which have $\text{HCN}\cdots\text{XF}$ the interaction energy is bigger than for the others. Nevertheless, the actual value of the interaction energy for this type of dimers is very small (i.e. smaller than -0.0161 kcal/mol).

The largest interaction energy, which is -0.0161 kcal/mol, belongs to $\text{HCN}\cdots\text{IF}$. This value, is so small compared with the interaction energy of a H-bond for this type of dimers (i.e. approximately, a 0.32% of the H-bond interaction energy). It is logical that the interaction energy of halogen bond is lower than hydrogen's, as we know that hydrogen bonds are far stronger than halogen bonds.

If we analyze the interaction energy by contributions, we can see that all contributions decrease with the increase of the atomic number of the atom bonded covalently to the halogen, except those that have a hydrogen, which don't follow this tendency. The HF exchange contribution (ΔE_{ex}^{HL}) is predominant over the others, and added to exchange delocalization term ($\Delta E_{ex}^{(2)}$) are the only which are positive, unlike the total interaction energy value. Also, the sum of electrostatic ($\Delta E_{el}^{(10)}$) and delocalization (ΔE_{del}^{HF}) terms (which are the second largest), has a similar value to the exchange contribution, but with opposite sign.

If we compare these results with the ones of the paper of Robert *et al.*, which was a study of hydrogen bond systems, we can conclude that both are very similar, with a few key differences. These differences are the magnitude of the values, as for halogen bond the largest value is -0.0161 kcal/mol, while for hydrogen bond the smallest is approximately -2.5 kcal/mol. Another difference is that, for hydrogen-bonded systems, electrostatic contributions have the same magnitude as exchange ones, but the halogen-bonded dimers the exchange contribution is bigger. The other remaining difference is that for some dimers of the paper of Robert *et al.* (such as HCN...HCCH or HCN...HCCF) the correlation correction ($\Delta E_{el,r}^{(12)}$) is positive, although its contribution is very small.

4.2.2 Interaction induced electronic and vibrational nonlinear optical properties

Once we have analyzed the interaction energy, we can continue to analyze the interaction-induced electronic nonlinear optical properties. The results of the VP-EDS partition are shown in Table 4. These results are the excess of the properties due to the interaction, calculated just as the same way as the properties (i.e. the derivatives of the interaction energy with respect to an external electrical field).

Table 4. Interaction induced electronic (non)linear optical properties.

	$\Delta\mu^{el}$	$\Delta\alpha^{el}$	$\Delta\beta^{el}$	$\Delta\gamma^{el}$
HCN...BrH	-0.194	5.75	-49.4	4.79E+03
HCN...BrF	-0.797	17.04	-73.4	1.48E+04
HCN...BrCl	-0.661	17.94	-288.5	2.52E+04
HCN...BrBr	-0.636	18.65	-370.2	3.18E+04
HCN...IH	-0.301	8.25	-78.4	8.41E+03
HCN...IF	-0.939	19.63	61.5	2.32E+04
HCN...ICl	-0.907	22.20	-204	2.97E+04
HCN...IBr	-0.888	23.45	-333.3	3.54E+04
HCN...II	-0.823	23.57	-476.1	4.50E+04

First of all, if we focus on the electronic excess dipole moment ($\Delta\mu^{\text{el}}$) and we separate the two different type of systems ($\text{HCN}\cdots\text{BrA}$ and $\text{HCN}\cdots\text{IA}$) we observe that the property decreases when going down in the periodic table (i.e. heavier halogen A in the Br-A or I-A monomer), with the exception of those systems that have a hydrogen bonded to the halogen, which do not follow this tendency. This tendency for $\Delta\mu^{\text{el}}$ can be seen in Fig. 3, where the black dots are the total electronic excess property. Another fact of these numbers is that they are larger than their counterpart for the hydrogen bond values, which have a maximum value of about -0.45 a.u.

For the electronic excess polarizability ($\Delta\alpha^{\text{el}}$) there is a subtle increase going down in the periodic table, and again as we observed for the dipole moment, the $\text{HCN}\cdots\text{XH}$ ($X=\text{Br},\text{I}$) dimers don't follow this tendency. In this case, they are lower than expected if they would have followed the pattern. For this property, when comparing with the hydrogen bond systems, there is a clear trend: the excess property is much bigger for halogen bond systems (between 17 and 24 a.u.), than for hydrogen bond systems (between 3 and 7 a.u.), with the exception of $\text{HCN}\cdots\text{XH}$, where the property has a similar magnitude to those observed for the hydrogen bond systems.

The electronic excess first hyperpolarizability ($\Delta\beta^{\text{el}}$) shows a very clear tendency increasing the value while increasing the atomic number of the atom bonded to the halogen. In this case, the exceptions are $\text{HCN}\cdots\text{XF}$, in other words, those which have fluorine. For $\text{HCN}\cdots\text{BrF}$ the increment is far lower than the expected to fulfill the tendency. For $\text{HCN}\cdots\text{IF}$, the value is positive, being very different from the others. Again, compared with hydrogen bond systems, the values of this $\Delta\beta^{\text{el}}$ for halogen bond dimers are bigger in the majority of the cases.

Table 5. Interaction induced nuclear relaxation NLOP computed at MP2/BASE1 level.

	$\Delta\alpha^{\text{nr}}$	$\Delta\beta^{\text{nr}}$	$\Delta\gamma^{\text{nr}}$
HCN\cdotsBrH	1.79	-173.9	9.76E+03
HCN\cdotsBrF	33.91	-3641.4	2.76E+05
HCN\cdotsBrCl	25.62	-4272.2	6.97E+05
HCN\cdotsBrBr	21.78	-3811	7.30E+05
HCN\cdotsIH	4.26	-378.5	2.33E+04
HCN\cdotsIF	31.06	-2265.6	3.36E+04
HCN\cdotsICl	42.51	-6020.2	6.37E+05
HCN\cdotsIBr	39.08	-6889.2	8.62E+05
HCN\cdotsII	32.43	-5538.1	9.80E+05

The last one, $\Delta\gamma^{\text{el}}$, show a perfect tendency, without any odd value. It is obvious that the value increases from the top of the periodic table to the bottom (separating the two different type of

systems), as we can see in the upper panel of Fig. 6. One more thing can be extracted from these results, and this is that even though interaction energy for halogen bond is smaller than for hydrogen bond, the NLOP properties are much bigger.

The next step is to analyze interaction-induced vibrational (or nuclear relaxation, *nr*) NLOP, which are presented in Table 5. The nuclear relaxation excess dipole moment ($\Delta\mu^{nr}$) does not appear in the latter table because, as it was said before in section 4.1.2, by definition, the μ^{nr} is 0, so the interaction-induced nuclear relaxation dipole moment. The nuclear relaxation excess polarizability ($\Delta\alpha^{nr}$) of HCN \cdots XA dimers increases with atomic value of A from H to Cl, but for A = Br and I the trend change and the value of $\Delta\alpha^{nr}$ decrease when going down in the periodic table, as we can see in Fig. 4. Comparing these halogen bond systems, with hydrogen bond systems, the $\Delta\alpha^{nr}$ values for the latter are smaller than for the former.

For the nuclear relaxation excess first hyperpolarizability ($\Delta\beta^{nr}$) the results are again quite similar for both types of different dimers, rounding -4000 a.u. for HCN \cdots BrA and -6000 a.u. for HCN \cdots IA, with the exceptions of HCN \cdots XH, which have an absolute value of $\Delta\beta^{nr}$ much lower than the others. In this case, the absolute value of $\Delta\beta^{nr}$ HCN \cdots IF is also far smaller than the ones that follow it in the table. For this property, the $|\Delta\beta^{nr}|$ values for halogen bond systems are much larger than for hydrogen bond ones, like we saw for the previously discussed NLOP properties.

Finally, the nuclear relaxation excess second hyperpolarizability ($\Delta\gamma^{nr}$) shows some tendency to increase, with values for HCN \cdots BrH, HCN \cdots IH and HCN \cdots IF far smaller than the other dimers.

Like we did in section 4.1.2, looking at the ratio between electronic and nuclear will be interesting to determine which one is more relevant. To do so, Table 6 has been elaborated.

Table 6. Ratio between interaction-induced electronic properties and interaction-induced nuclear relaxation properties of the HCN \cdots XA systems.

	$\Delta\alpha^{el}/\Delta\alpha^{nr}$	$\Delta\beta^{el}/\Delta\beta^{nr}$	$\Delta\gamma^{el}/\Delta\gamma^{nr}$
HCN\cdotsBrH	3.21	0.28	0.49
HCN\cdotsBrF	0.50	0.02	0.05
HCN\cdotsBrCl	0.70	0.07	0.04
HCN\cdotsBrBr	0.86	0.10	0.04
HCN\cdotsIH	1.94	0.21	0.36
HCN\cdotsIF	0.63	-0.03	0.69
HCN\cdotsICl	0.52	0.03	0.05
HCN\cdotsIBr	0.60	0.05	0.04
HCN\cdotsII	0.73	0.09	0.05

For the excess polarizability, it can be seen that the ratio is smaller than 1 (except HCN...BrH and HCN...IH, i.e. those with a halogen-hydrogen monomer), meaning that the vibrational contribution is larger than electronic. This is the opposite from what we observed for the ratio of the electronic and vibrational contributions to the total property (α^{el}/α^{nr} , Table 4), where the main contribution was electronic.

Similarly, for interaction-induced first hyperpolarizability the ratio is always smaller than 1, so we can say that nuclear relaxation governs this property. One fact to comment is that we can see a negative value, given by the positive unexpected valor of HCN...IF of Table 5. Another fact to comment is that the ratio is very small, so we can confirm that not only nuclear relaxation governs the property, but also it contributes the majority of the property. The same thing happens with the interaction-induced second hyperpolarizability. In this case, all ratios are very small, so we can say that vibrational contribution contributes the majority of the property too.

To sum up, for excess dipole moment the main contribution is the electronic one, while for the other excess properties, nuclear relaxation contribution is the main one.

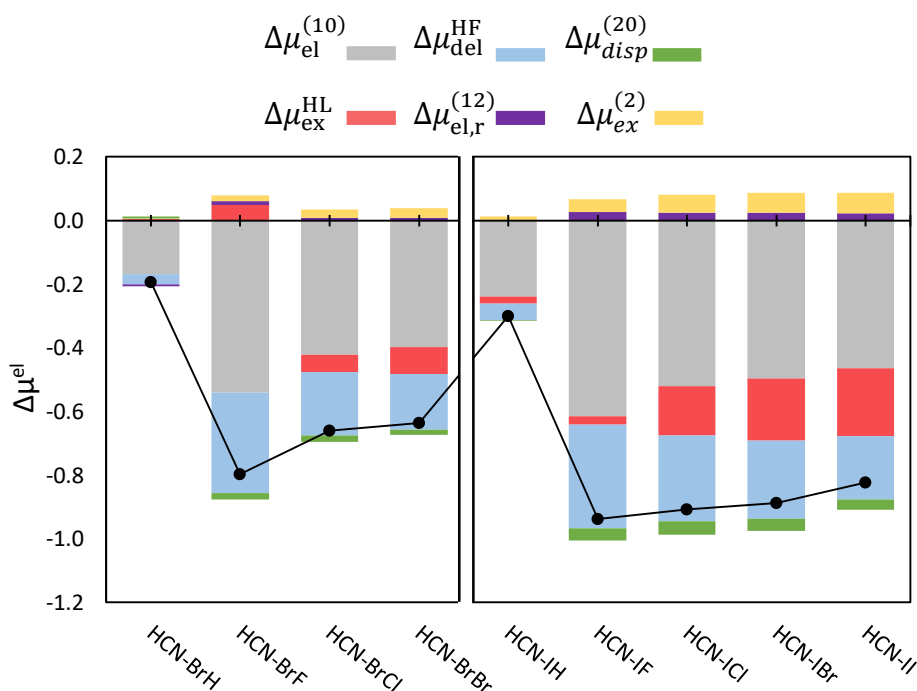


Figure 3. Interaction-induced electronic dipole moment contributions obtained with variational-perturbational decomposition.

4.2.3 Interaction induced electronic and vibrational NLOP decomposition

Once the excess properties are analyzed, we can proceed to analyze their partition. The decomposition of the interaction-induced electronic dipole moment shown in Fig. 3 reveals that

this property is strongly dominated by the electrostatic contribution ($\Delta\mu_{el}^{(10)}$) but the delocalization term ($\Delta\mu_{del}^{HF}$) also contributes noticeably to the excess dipole moment.

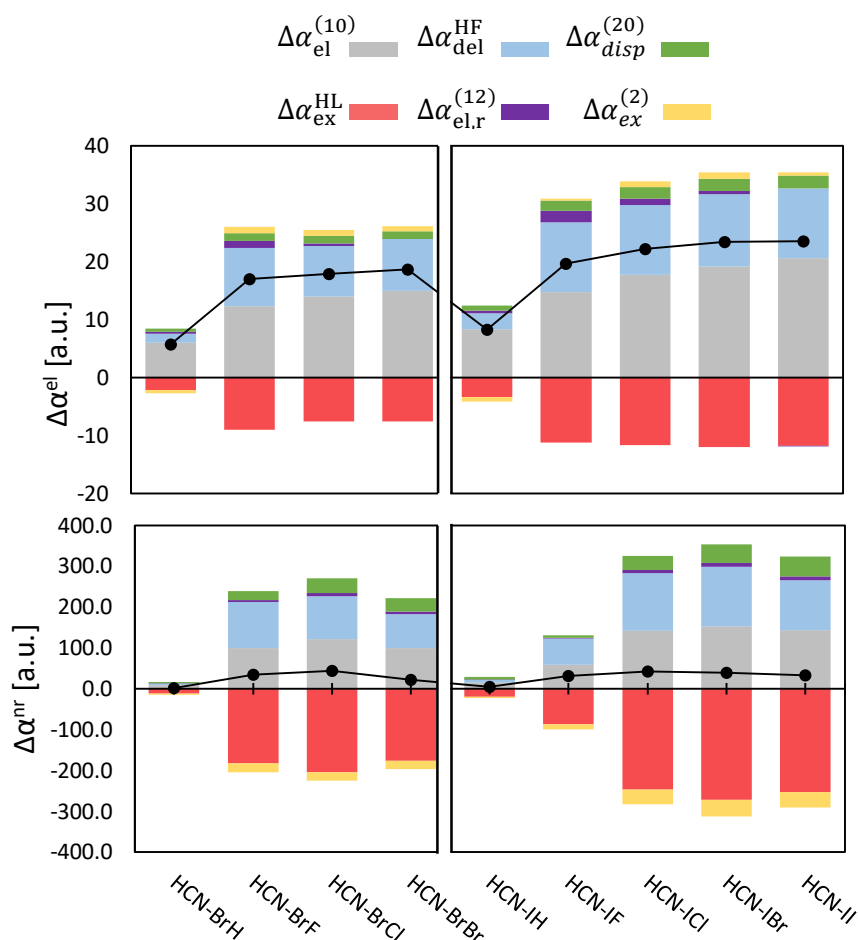


Figure 4. Interaction-induced electronic and vibrational polarizability partition contributions obtained with variational-perturbational decomposition.

These two contributions are negative, as the total value of the excess property. The exchange repulsion contribution ($\Delta\mu_{ex}^{HL}$) of iodine halogen bonds is bigger than that of bromine halogen bonds, and it is always the opposite sign in comparison with the total value. In addition, $\Delta\mu_{ex}^{HL}$ increases with the increase of the atomic number of the halogen bonded to the halogen that forms the bond. The other contributions do not play an important role to this property.

In comparison with hydrogen-bonded systems, the halogen-bonded systems seem to follow a similar pattern, where the most important contribution comes from electrostatic contribution, and the delocalization term contributes noticeably. The biggest difference between both types of systems is the exchange term, which is more relevant in halogen bonded systems than in hydrogen ones. So, to sum up, as the nuclear relaxation contribution of dipole moment is zero, we can conclude that the interaction-induced dipole moment is ruled by electrostatic and delocalization terms.

Next, the excess polarizability can be analyzed. From now on, the figures will have four panels. The upper ones will describe electronic contribution, while the ones below will refer to vibrational contribution. Those on the left will be the ones referred to HCN \cdots BrA dimers, while the right ones will be referred to HCN \cdots IA dimers.

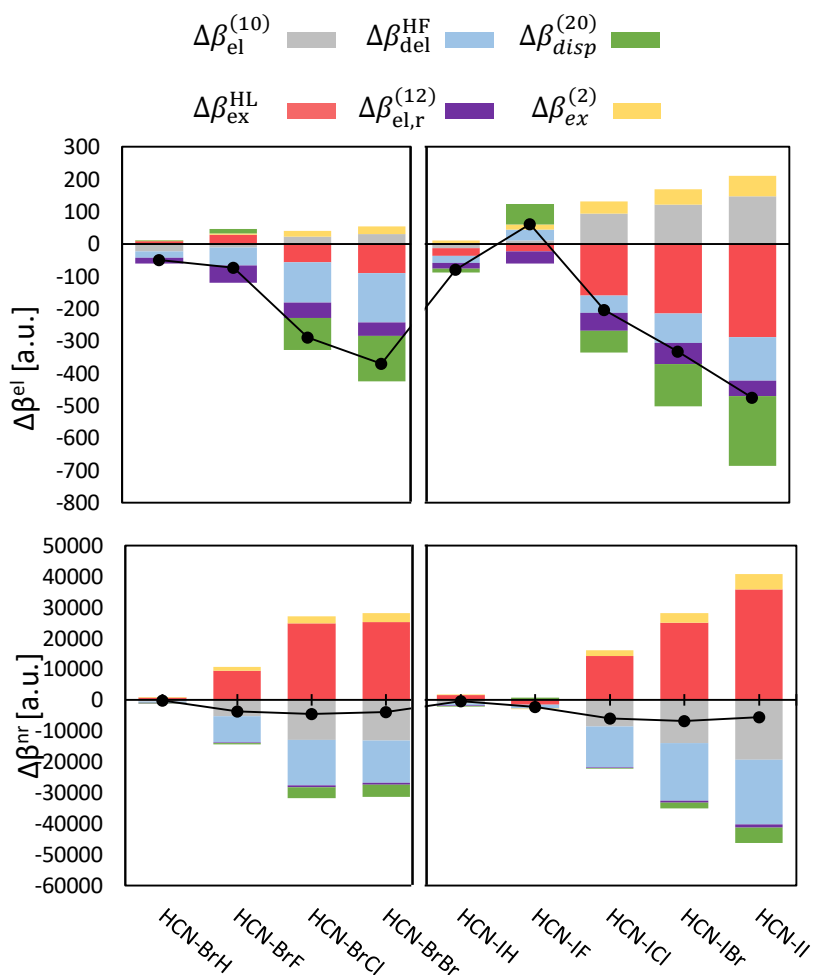


Fig. 5. Interaction-induced electronic and vibrational first hyperpolarizability partition contributions obtained with variational-perturbational decomposition.

The electronic decomposition of the interaction-induced electronic polarizability shown in Fig. 4 reveals a similar pattern to the one observed for interaction-induced electronic dipole moment. For the electronic part, the electrostatic contribution ($\Delta\alpha_{el}^{(10)}$) is the largest one, which in this case increases when the atomic number of the atom bound to the halogen increases (unlike the electrostatic dipole moment contribution, which decreased). It is followed by delocalization ($\Delta\alpha_{del}^{HF}$) and exchange ($\Delta\alpha_{ex}^{HL}$) contributions. With the exception of the dimers with a XH monomer, the exchange contribution has a similar magnitude for the dimers of the same type (again different from the behavior that the dipole moment exchange contribution had, which increased with the atomic number of the halogen). It is important to notice that exchange terms

have the opposite sign than the electrostatic and delocalization terms, and that exchange and delocalization terms have similar value. Another fact is that exchange is the only one with negative sign (with some exceptions), with the other terms having a higher combined value. For that reason the total excess electronic polarizability is positive. In comparison with hydrogen-bonded systems, the relative weigh of the different contributions is similar, being electrostatic term the larger, followed by exchange and delocalization terms.

Regarding the nuclear relaxation, we can note that exchange-delocalization term ($\Delta\alpha_{ex}^{(2)}$) has the same sign as HF exchange contribution, having both the opposite sign compared to the other contributions. However, the relative importance of exchange contribution is larger than for $\Delta\alpha^{el}$ and on the contrary, electrostatic contribution has a minor weigh for nuclear relaxation. This changes the most relevant contribution, which was electrostatic for $\Delta\alpha^{el}$ and is exchange for $\Delta\alpha^{nr}$. In the nuclear relaxation case, as was the case for electronic as well, the sum of all terms is positive, and this means that even though exchange is the most relevant contribution, it is not the determinant. To sum up, for electronic excess polarizability, electrostatic is the most relevant term, while for vibrational it is exchange. For both cases, exchange contribution is negative, and even though it is a large contribution, the total excess property is positive.

The decomposition of the interaction-induced electronic first hyperpolarizability shown in Fig. 5 reveals that it is difficult to point out any general trends for all the studied systems.

First, for both electronic and vibrational contributions the HCN...IF dimer is the one with far more differences compared with the other ones. The majority of the terms have the opposite sign compared to the other dimers. If we ignore this dimer, we can note that, for electronic contribution, when bromine acts in the halogen bond, the largest contribution is the delocalization ($\Delta\beta_{del}^{HF}$), while for iodines the exchange contribution ($\Delta\beta_{ex}^{HL}$) is the largest. However, the exchange contribution and the dispersion term ($\Delta\beta_{disp}^{(20)}$) always increase with the atomic number, and they are a significant contribution to the total value. Another fact is that in almost all the systems, the electrostatic contribution ($\Delta\beta_{el}^{(10)}$) increases with the atomic number and has the opposite sign of the total value (and also opposite sign compared to exchange and dispersion). All contributions increase with the atomic number of the atom bonded to the halogen. If it is difficult to see a pattern in electronic first hyperpolarizability of halogen bonded systems, it is far more difficult to compare these systems with hydrogen bonded ones, which have a difficult pattern too. Nevertheless, we remark here that exchange and exchange delocalization ($\Delta\beta_{ex}^{(2)}$) contributions in hydrogen bond systems are both positive, while for

halogen bond dimers, exchange contribution is negative and exchange delocalization term is positive, with their sum being negative (the opposite of the hydrogen ones).

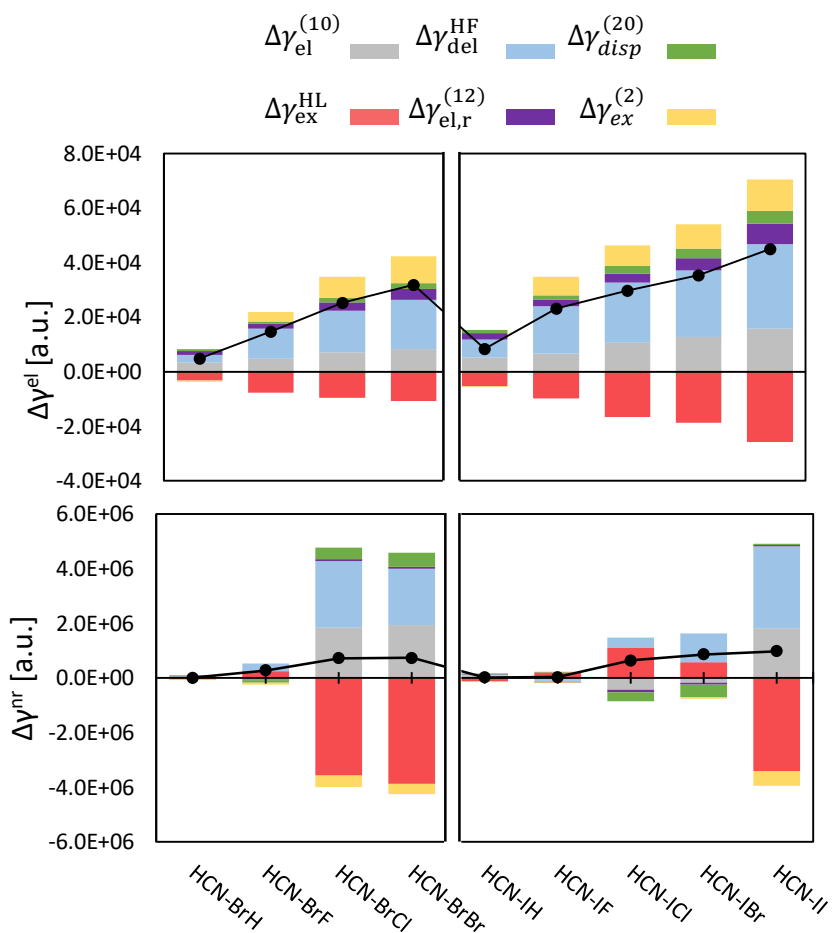


Fig. 6. Interaction-induced electronic and vibrational second hyperpolarizability partition contributions obtained with variational-perturbational decomposition

Related to nuclear relaxation, which is represented in the lower panels of Fig. 5 we can see that the interplay of the interaction types is much more regular than electronic. In addition, all contributions seem to have the opposite sign than $\Delta\alpha^{nr}$ values but with quite similar pattern. It is clear that electrostatic and delocalization contribution have the opposite sign than exchange one. The three of them increases when the atomic number of the atom bonded to halogen increases. For $\Delta\beta^{nr}$, exchange and exchange-delocalization terms have the same sign, unlike their electronic counterparts, which had opposite sign. However, even though they have the same sign and their sum leads to considerable contribution, the total $\Delta\beta^{nr}$ has the opposite sign. The comparison the relative weight of the hydrogen bond systems and halogen bond systems contributions show that they present a similar trend; i.e. the contributions have the same sign and relative weigh for both type of systems. In summary, for $\Delta\beta^{el}$, the largest contribution for bromine dimers is the delocalization term while for iodines it is the exchange contribution. As

for $\Delta\beta^{nr}$, there is a noticeable pattern where the exchange term is the largest.

Finally, the decomposition of the interaction-induced electronic second hyperpolarizability shown in Fig. 6 reveals a systematic pattern. We can note that the sign of each contribution is always the same and they always increase with the atomic number of the atom bonded to the halogen.

The electrostatic contributions ($\Delta\gamma_{el}^{(10)}$) are similar to the exchange ($\Delta\gamma_{ex}^{HL}$) counterparts. The largest contribution is always the delocalization term ($\Delta\gamma_{del}^{HF}$). For $\Delta\gamma^{el}$, the electron-correlation ($\Delta\gamma_{el,r}^{(12)}$), dispersion ($\Delta\gamma_{disp}^{(20)}$) and exchange-delocalization ($\Delta\gamma_{ex}^{(2)}$) terms are important, even though they often had very small values for the lower-order excess properties. Then, the most important contributions are delocalization and electrostatic terms, and also exchange (with opposite sign). The signs of the contributions for $\Delta\gamma^{el}$ are the same as for hydrogen-bonded systems, (except for exchange-delocalization term). In addition, the relative weight of contributions is similar. The main difference is the delocalization contribution, which is much larger in halogen bond systems.

$\Delta\gamma^{nr}$ partition it is hard to analyze due to the messiness of the results. For HCN...BrCl, HCN...BrBr and HCN...I all terms are quite similar between them and they follow the $\Delta\alpha^{nr}$ pattern. Delocalization term is the only contribution which has always the same sign, which is positive, like the total value. In comparison with hydrogen bond systems, the latter has a very clear tendency while the halogen bond systems do not.

The delocalization term is positive in both types of systems but the oddity of the halogen bond results make the comparison not easy.

Then, we can conclude that for $\Delta\gamma^e$ there is a clear tendency where all the terms increase while increasing the atomic number of the atom bonded to the halogen, with delocalization term being the largest for all the dimers. On the contrary, for $\Delta\gamma^{nr}$ contribution a summary is difficult to do because of the complexity of the results.

4.3 REAL SPACE PARTITION

The results from this section are fundamentally different from the ones we have just discussed for VP-EDS. We still decompose nonlinear optical properties (although here we focus exclusively on alpha) and for the same systems, but rather than decomposing the total property into contributions with different physical meaning, we decompose it into contributions of each atom (or, by combining them, contribution of each dimer in the monomer). In this 3D partition, the

contribution to the electrical properties due to the interaction between the two monomers (i.e. the excess property) is included to the contributions of the monomers.

When applying this methodology, we could expect different possibilities:

- (1) The first one, which a priori is the most likely option, is that the excess property is distributed between the two monomers, so each one must have their contribution to the property plus some fraction of the excess contribution.
- (2) The other hypothesis is that one monomer takes all the excess produced by the interaction and the other monomer just has its contribution to the property.

In this section not only the halogen bond with bromine has been studied, but also halogen bond with iodine, as well as some hydrogen bonded systems (of Robert Zalesny *et al.* paper)⁷, which offered a nice opportunity to compare the results for different kinds of intermolecular interactions.

In the table 7 the α^{el} calculated with different methods is presented. The polarizabilities of each system are quite similar for both methodologies, LC-wPBE and MP2. The differences between them can be attributed to different factors, but the main one is that the property has been computed with different methods and that for the compounds that contain I different basis set have been used.

Table 7. Electronic polarizabilities obtained at LC-wPBE/BASE2 functional using the TFVC partition and APOST3D code, and with Gaussian16 program at LC-wPBE/BASE2 level and at MP2/BASE1 level in a.u.

	α^{el} (TFVC - LC-wPBE)	α^{el} (Gaussian16 - LC-wPBE)	α^{el} (Gaussian16 - MP2)
HCN...BrH	51.20	53.29	52.66
HCN...BrF	65.72	68.41	67.59
HCN...BrCl	86.67	91.74	90.40
HCN...BrBr	97.00	103.54	101.14
HCN...IH	69.54	68.815	67.338
HCN...IF	68.68	68.466	80.896
HCN...ICI	102.83	101.746	109.917
HCN...IBr	138.35	137.037	123.205
HCN...II	155.33	140.474	143.069

While to analyze the VP-EDS partition we have used the MP2 method and BASE1 and its corresponding pseudopotential for Br, for real space partition we have used the LC-wPBE functional and BASE2. This was necessary because the MP2 and pseudopotentials are not implemented in while working with APOST3D program yet. Then, we had to perform our real

space analysis with one of the DFT functionals implemented in APOST3D, which are B3LYP, BLYP, HSE06, LC-wHPBE, M06, MN15, BHandHLYP, CAM-B3LYP, LC-BLYP, LC-wPBE, M062X, PBE0 and wB97X. In Table 7 we present the comparison between LC-wPBE values and MP2 done with Gaussian16 program. The results show that LC-wPBE functional gives one of the values more similar to MP2 one. Taking into account that this functional is also reliable to compute the first and second hyperpolarizability, it was chosen to perform APOST3D analysis.

Another source of the difference between the results obtained with the different methods and codes is the numerical errors of the calculation of the derivatives and the numerical error of the numerical integration required in APOST3D to compute the field-dependent energies.

Once we selected the functional, we can compare the results of TFVC with the Gaussian16 which have the same functional (LC-wPBE). As we can see, there are small differences between the results obtained with both methods fruit of the numerical errors, so we can confirm that TFVC method lead to the correct values for the total polarizabilities. The values of the total and excess properties computed with APOST3D are presented in table 8.

Table 8. TFVC method results for the polarizability and its excess for all the systems.

	α (TFVC)	$\Delta\alpha$ (TFVC)
HCN...BrH	51.20	4.41
HCN...BrF	65.72	15.29
HCN...BrCl	86.67	14.72
HCN...BrBr	97.00	14.58
HCN...IH	69.54	7.26
HCN...IF	68.68	11.22
HCN...ICI	102.83	17.04
HCN...IBr	138.35	24.86
HCN...II	155.33	38.53
HCN...HNC	52.24	6.17
HCN...HCl	47.48	6.52
HCN...HCCH	57.16	3.23
HCN...HCCF	60.99	4.73

But, before the analysis of the results, it is important to mention that I also computed the real space contributions using Becke approach for the partitioning the energy in the real space. The results showed that the results obtained with both methods (i.e. TFVC and Becke) are very similar. So we can assume the TFVC results are correct.

The second column of Table 8 gives us the excess of the property ($\Delta\alpha$) due to the interaction. Similarly to what we have observed for the total polarizability, the excess polarizability increases

when the atomic number bonded to the halogen/hydrogen increases, as one could expect because there is a relationship between alpha, and electronic volume of an atom, so bigger halogens will have higher values for alpha.

To analyze the results, we will look at them group by group (i.e. bromine halogen bond, iodide halogen bond, hydrogen bond). Starting with the HCN...BrA dimers, all four dimers seem to have a similar excess of property, with the exception of HCN...BrH (which we also observed in the previous section that have a different VP-EDS partition). These result could point that the excess polarizability for these type of dimers with this type of halogen bond is around 15 a.u, regardless of the atom A in the dimer, which would be very useful for prediction of properties for other dimers (since the total property of the dimer is equal to the properties of the isolated monomers plus 15 a.u.).

On the contrary, if we now observe the HCN...IA dimers it is immediately observable that the excess is always increasing with the atomic number of the atom bonded to the iodine. Unlike the bromine case, it would be a difficult task to attempt to predict these properties without doing all the calculations.

Table 9. Polarizability of the HCN monomer in dimer and isolated, and the excess of the dimer distributed to the HCN monomer.

Dimer	HCN α (in dimer)	HCN α (monomer)	DIFFERENCE ($\Delta\alpha_{\text{HCN}}$)
HCN ... BrH	25.20	22.10	3.10
HCN ... BrF	39.17	22.04	17.13
HCN ... BrCl	40.62	22.08	18.54
HCN ... BrBr	40.17	22.09	18.09
HCN ... IH	32.24	22.42	9.82
HCN ... IF	36.24	22.35	13.89
HCN ... ICl	45.26	22.35	22.91
HCN ... IBr	63.19	22.35	40.83
HCN ... II	52.59	22.35	30.23
HCN ... HNC	26.69	22.74	3.95
HCN ... HCl	28.46	22.75	5.72
HCN ... HCCH	25.11	22.77	2.33
HCN ... HCCF	25.24	22.78	2.47

Finally, related to HCN...HR dimers, the excess does not follow any pattern, as expected because of the variety of the dimer. Still, the excess for all the dimers seems to be around the same value (approximately 5 a.u.).

Now that we have seen the total excess, it is interesting to see how this excess is distributed within the dimer. The answer to this can be found in Table 9, where the polarizability of the HCN

monomers in the dimer and isolated are shown, with the difference between them.

Here we can see that all the polarizability values in the second column (polarizability of the monomer for the different geometries it has in the different dimers) are always similar, with the small differences being attributed to the difference in the geometry. Then, the last column of Table 10 gives us some important information that has to be analyzed. We can see that all the values are larger than 0, so at least some part of the excess property is distributed to the HCN monomer. But, if we look to the excess property in Table 9 we can see that the excess of this monomer is, in general, larger than the one in the dimer (with a few exceptions). To check it, Table 10 has been elaborated to see the excess property of the second monomer in each dimer. Looking to the polarizability of the monomers we can see that for halogen bond (with the exceptions of HCN...BrH and HCN...I) the monomer has a larger value isolated than in the dimer. For this reason, the difference (in other words, the excess property that belongs to this monomer) is negative. However, most values for this excess (whether negative or positive) are quite small.

Table 10. Polarizability of the non HCN monomers, in dimer and isolated, and the excess of the dimer distributed to the XR monomers.

	α IN DIMER	α IN MONOMER	DIFFERENCE ($\Delta\alpha_{XR}$)
BrH	26.00	24.69	1.31
BrF	26.55	28.39	-1.84
BrCl	46.05	49.87	-3.82
BrBr	56.82	60.33	-3.51
IH	37.296	39.85	-2.56
IF	32.442	35.11	-2.67
ICl	57.566	63.43	-5.87
IBr	75.168	91.13	-15.97
II	102.74	94.45	8.30
HNC	25.55	23.33	2.22
HCl	19.018	18.22	0.80
HCCH	32.06	31.16	0.89
HCCF	35.75	33.48	2.26

There are two specific values that are big enough, which are HCN...IBr and HCN...II. These two dimers show a different behavior:

- for HCN...II, it seems that the excess of polarizability induced by the interaction is distributed into both monomers (both HCN and II have positive excess property).
- for HCN...IBr, it seems that the IBr monomer gives polarizability to HCN when the interaction is produced.

Nevertheless, for the majority of the systems, unexpectedly it can be seen that the excess of the property is distributed entirely to HCN, meaning that the property of the monomers in the dimers for HCN is given by its own polarizability plus the excess polarizability.

5. CONCLUSIONS

In this work, we have studied a set of dimers involving halogen bonds, performing decompositions of the linear and nonlinear optical properties, in order to see how different interactions influence the values of the NLOP. For each of the molecules, we have calculated the electronic and vibrational contributions to their (non)linear optical properties. Our results show that, for the systems studied, the main contribution to the μ and α is the electronic term, while for the β and γ the main contribution is the vibrational term. However, for excess properties, it happens that electronic contribution only governs the $\Delta\mu$, while for the other excess properties vibrational does. The interaction-induced contribution to the studied properties have been decomposed using two different methodologies. For the first one, VP-EDS has been used to decompose the energy of the systems and then, using the finite-field method, the corresponding (non)linear optical properties have been obtained.

These results have been also compared with the work of Robert *et al.*, where they performed a similar study, but for systems with hydrogen bonds. The comparison of both systems show that the magnitude of halogen bond interaction energy is much smaller than the hydrogen bond one. This is expectable because it is well-known that hydrogen bond is much stronger than halogen bond. On the contrary, the magnitude of the properties are always larger for halogen bonds than for hydrogen bonds. Regarding the decomposition of the different electronic and nuclear relaxation to properties, generally there is a clear tendency in their decomposition and there are a few terms that are more relevant than the others. In general, these trends are similar to the hydrogen bonds dimers. Therefore, we can conclude that even though the interactions are different and the properties have values of different magnitudes, the relative weight of the different contribution present general similar trends. This is especially true for the cases of the electronic contributions to $\Delta\mu$ and $\Delta\alpha$, and the nuclear relaxation for $\Delta\beta$ and $\Delta\gamma$. For instance for $\Delta\alpha$, the electrostatic term of the electronic contribution prevails over the other and all the terms have the same sign, and the relative weights of the different terms remain similar for both halogen and hydrogen bond systems.

Finally, the polarizability has been decomposed using a real space origin-independent methodology. With this decomposition, we have been able to analyze how the excess of the polarizability induced by the different interactions is distributed into the monomers. The results

showed that the excess property, instead of being distributed into the two monomers as it could be expected a priori, has been entirely assigned to the HCN monomer. This conclusion is valid for both the hydrogen-bonded and halogen-bonded systems.

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