A theoretical study of the global and local electrophilicity, nucleophilicity, polarizability and QTAIM theory for calix[4]arene-gas interaction

B. Gassoumi a,c,*, H. Ghallab b, R. Ben. Chaabane a,**

a Laboratory of Advanced Materials and Interfaces (LIMA), University of Monastir, Faculty of Science of Monastir, Avenue of Environment, 5000, Monastir, Tunisia
b University of Monastir, Quantum and Statistical Physics Laboratory, Faculty of Science, Monastir, 5079, Tunisia
c Institute of Light and Matter, UMR5306 University of Lyon 1-CNRS, University of Lyon, 69622, Villeurbanne Cedex, France

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ABSTRACT

The calix[4]arene molecule, abbreviated as CX[4], is known by the four phenolic groups and a hydrophobic cavity able to enclose small molecules. The interactions between CX[4] and NO3, NO2, CO2, and N2 gas molecules have been studied. These guest species are placed inside and outside the cavity of the host molecule CX[4]. The formation of H-bonding has been deeply discussed based on the infrared spectrum and the polarizability analysis. Global and local indices have been calculated for a series of gas (NO3, NO2, CO2, and N2) in interaction with the CX[4] molecule to explain the electrophilic or nucleophilic activations in endo-vs. exo-cavity interaction zone. As expected, there is a correlation between the proposed global electrophilicity and global nucleophilicity together for an explanation of the chemo-selectivity region. Finally, the topological parameter analyses of the host-guests interactions have been estimated by using DFT calculations.

1. Introduction

The selectivity of the anionic or cationic guests in microscopic or macroscopic systems facilitates the recognition of the magnetic and electrostatic properties of the several guests’ complexes [1, 2, 3, 4, 5]. The CX[4] exhibit a hydrophobic cavity form [6] and a specific chemical composition. Moreover, the CX[4] is characterized by a specific height and a diameter, these two parameters facilitate the complexation with small molecules [7, 8, 9]. The specific cavity of the CX[4] has attracted the experimenters and may be used in the medical [10, 11, 12] or micro-biological field [13, 14]. In the literature, there are several works which discuss the interaction of CX[4] with small molecule (CH4) and gas molecules (NH3 and C2H2) [5, 15, 16, 17]. Herein, we have studied the physical and chemical properties of the CX[4]-NO3, CX[4]-NO2, CX[4]-N2 and CX[4]-CO2 complexes (The specific gas in the endo or exo-cavity position). We have discussed the interactions between the CX[4] molecule and NO3, NO2, CO2 and N2 gases inside or outside the cavity. The encapsulation of these gases may be a good subject for pollution. The NO3, NO2, CO2 and N2 gases have been chosen in our study because they can form a dipole-dipole or CH…π hydrogen-bonding interactions with CX[4].

By using DFT calculations, we have described the dynamic stabilities of the endo-vs. exo-cavity of the CX[4]-gas complexes. The electrophilicities and electrophilicities distribution sites of these host-guests complexes have been performed. The vibrational properties of the CX[4]-gas complexes have been studied. The polarizability study of the stable host-guests has explained the transfer of the charge to the π-electron of the phenol ring. The recognition of the weak or the strong and the nature of the interactions of such guest with a cage molecule have been analyzed by the AIM topological parameters.

2. Computational details

The optimization of CX[4] and CX[4]-gas have been performed by the Density Functional Theory (DFT) method by using the global hybrid generalized gradient approximation B3LYP [15, 18, 19, 20] coupled to the D3BJ (empirical Becke and Johnson damping dispersion corrections) in combination with the 6-31+G(d) basis set, as implemented in a Gaussian 09 package [21] and the GaussView [22] as a visual program. The binding energies have been calculated taking into account the Basis Set Superposition Error (BSSE) counterpoise correction (CP) according to the formalism of Boys and Bernardi [23].

The binding energies (Eb) are given by the following formula:

* Corresponding author.
** Corresponding author.
E-mail addresses: gassoumibouzid2016@gmail.com (B. Gassoumi), rafik.benchaabane@fsm.rnu.tn (R. Ben. Chaabane).
\[ \Delta E_{\text{CX4-gas}} = E_{\text{CX4-gas}} - E_{\text{CX4}} - E_{\text{gas}} + \text{BSSE} \]  

(1)

where \( E_{\text{CX4-gas}} \), \( E_{\text{CX4}} \) and \( E_{\text{gas}} \) are the total energies of the host-guest and host or guest molecules. The reactivity parameters based on the Fukui function have been calculated in the same framework. The infrared spectrum and the polarizability of these studied compounds have been analyzed by the DFT/B3LYP-D3BJ method. The different topological parameters have been calculated using the Bader's atoms in molecules (AIM) theory by the AIM2000 program [24,25].

3. Results and discussions

The CX [4]-gas complexes have been optimized at B3LYP-D3BJ/6-31+G(d) level of theory, and shown in Figures 1 and 2. The NO3, NO2, CO2 and N2 gases have been studied in the endo and exo-cavity positions. The highest binding energy value (21.33 kcal/mol) has been obtained for CX[4]-CO2 complex.

The binding energy values are listed in Table 1. Obviously, the CX[4]-CO2(endo) complex is more stable than CX[4]-CO2(exo). Based on the dipole-dipole interactions between the CX[4] and the CO2 gas, the CX[4]-CO2(endo) complex has the larger stability. The NO2 gas may be placed in the exo or endo-cavity positions. In this context, we have shown that the interaction of the NO2 gas outside the cavity is very weak (There is a divergence).

Moreover, we have calculated tow complexes of the CX[4]-NO3, NO3 perpendicular to the 4-fold axis of CX[4] and the NO3 gas parallel to the 4-fold axis. The CX[4]-NO3(//) is characterized by a very weak energy in comparison with the CX[4]-NO3(\perp). The \( E_b \) energy of the CX[4]-NO3(//) is equal to 22.56 kcal/mol. The CX[4]-NO3(\perp) have a larger binding energy than CX[4]-N2(endo) and CX[4]-CO2(endo) complexes. In the CX[4]-NO3(//) complex, we have noted a C4 symmetry. In addition, the formation of the low dipole moment between the CX[4] and the NO3(//) gas imposed a larger stability for this host-guest. The orientation of the O⋯H groups does not change during the interaction of the CX[4] with the NO3 gas. For the CX[4]-N2 complex, we have optimized two geometries based on the position of the N2 in order to show the stable host-guest. First, the N2 gas is located outside of the cavity. Second, this gas located perpendicular to the 4-fold axis of CX[4].

From Table 1, we conclude that the binding energy \( E_b \) calculated for CX[4]-N2(endo) is stronger than that of CX[4]-N2(endo). Also, we note that the more stable complex is characterized by a binding energy value equal to 18.90 kcal/mol. However, we show a single O⋯H stretching band position in the infrared spectrum of the CX[4]-N2(N2 in parallel position). For CX[4]-NO2, we show that the NO2 is placed in the area of the O-H link of the phenolic groups in the two CX[4]-NO2(endo) complexes. The CX[4]-NO2(endo) is specified by the energy binding equal to 20.54 kcal/mol. The CX[4]-NO2(endo) has the highest \( E_b \) value in comparison to CX[4]-CO2(endo/endo). This stability may be explained by the lowest dipole moment. The IR spectrum shows that this complex has a single O-H stretching band. The same results are obtained from CX[4]-N2(endo) and CX[4]-CO2(endo).

Finally, we demonstrate that the stabilization of these complexes is explained by the formation of the dipole-dipole interactions between the host and the guest. We have used the NO3, NO2, CO2 and N2 gas to be encapsulated by the CX[4] molecules [26, 27, 28, 29, 30]. We have carried out several gas capture tests inside and outside the cavity. Moreover, we conclude that the host-guests complexes given in Figure 2 are the most stable. The specific gas studied in the endo-vs. exo-cavity region will be very important to explain several electronic properties. Moreover, it is useful for the chemist to understand the photo-physical proprieties of these new gases.
endo-vs. exo-CX[4] complexation. There is a very recent work that has used a TFSI^- molecule as a guest for the β-cyclodextrin molecule [21]. In the same context, we try to test the interaction of these gases with the CX[4]. We note that these complexes can be a solution for new applications in the future.

The local and global reactivity parameters have been stimulated by the Fukui function theory [32], such as these parameters can be calculated by two methods; Frontier molecular orbital (FMO) or charge distribution for $q = ±1, q = 0$ and $q = -1$ using the equations of Fukui:

$$f_+ = q(N+1) - q(N)$$  \hspace{1cm} (2)

$$f_- = q(N) - q(N-1)$$  \hspace{1cm} (3)

$$f_1^A = \frac{1}{2} (q(N+1) - q(N-1))$$  \hspace{1cm} (4)

In this context, first, we attempt to find out the reactive sites for electrophilic and nucleophilic attacks of CX[4]-gas by means of Fukui function. The approximate form of Fukui function based on atomic charge distribution will be used here. Commonly, there is no evident qualitative difference between the dual descriptor evaluated based on charge electron density of the three states (N+1, N, N-1) and the one based on the charge spin density of the two states (N+1, N-1). We have calculated the electronic parameters Softness ($S^0$, $S^-$ and $S^+$), hardness ($h^0$, $h^-$ and $h^+$) by using the Fukui functions ($f^0$, $f^-$ and $f^+$) by the orbital aspect. In addition, we have investigated the QTAIM topological parameter of the endo-vs. exo-CX[4]-gas complexes to understand the nature of the interactions of these supra-molecular complexes in detail and the nature of bonds, particularly the cooperativity of hydrogen bonding of each system.

The study of the infrared spectrum and the linear polarizability ($\alpha_0$) [5, 33] explained the frequency shifting phenomena for CX[4]-CO$_2$, CX[4]-N$_2$, CX[4]-NO$_2$ and CX[4]-NO$_3$ complexes (Figure 3 and Table 2). These organic compounds can be used in optical switching, optical logic

![Figure 2. Optimized geometries of the stable CX[4]-gas (CX[4]-CO$_2$ (a), CX[4]-N$_2$ (b), CX[4]-NO$_2$ (c), and CX[4]-NO$_3$ (d)) structures using B3LYP-D3BJ/6-31+G(d) method (Top view).](image)

| Complexes | $E_b$ (in kcal/mol) | BSSE | $E_b$ (with BSSE) |
|-----------|---------------------|------|------------------|
| CX[4]-NO$_3$ (//) | 24.62 | 6.17 | 30.79 |
| CX[4]-NO$_3$ (+) | 16.51 | 6.05 | 22.56 |
| CX[4]-N$_2$(endo) | 16.89 | 1.70 | 18.59 |
| CX[4]-N$_2$(exo) | 16.90 | 1.80 | 18.70 |
| CX[4]-NO$_2$(exo)* | 18.17 | 1.82 | 19.99 |
| CX[4]-NO$_2$(endo)* | 18.11 | 1.80 | 19.91 |
| CX[4]-NO$_2$(endo) | 17.83 | 2.71 | 20.54 |
| CX[4]-CO$_2$(endo) | 18.62 | 2.71 | 21.33 |
| CX[4]-CO$_2$(endo) | 18.10 | 2.71 | 20.81 |
and optical interconnections for developing new technologies. The harmonic frequencies have been calculated for different complexes in order to show the effect of the encapsulation of host gases in the CX[4] cavities. The red-shifted of the O–H stretching vibrations found in (CX[4]-NO3, CX[4]-NO2, CX[4]-CO2, and CX[4]-N2) are compared to the free CX[4] one. In Figure 3, we have plotted the infrared spectra of the four stable host-guest complexes. In the literature, Furel et al. [35, 36] have been studied the experimental infrared spectrum of the free CX[4] molecule. The experimental spectrum shows O–H stretching vibration in the region varying from 2900 to 3500 cm⁻¹. This region is characterized by five stretching vibrational bands around 3254 (νO-H), 3168 (νO-H), 2951 (υC-H) and 2916 cm⁻¹ (υC-H sym), respectively.

To take into account the anharmonic effect, we have scaled our calculated frequencies by 0.956. The region between 3250 and 3400 cm⁻¹ is characterized by the O–H stretching vibration. However, the CX[4]-N2 complex have two peaks around 3177 cm⁻¹ and 3181 cm⁻¹, respectively. These bands may be assigned to the O–N stretching vibrations. The same result for the CX[4]-CO2 complex. Furthermore, the band located at 3160 cm⁻¹ is due to the degenerate of the H-bonding vibration of the phenolic O–H groups. The H-bonding between the phenol groups in the CX[4]-CO2(endo) and CX[4]-N2(endo) complexes are affected by the incorporation of CO2 and N2 gases. This fact is explained by the red-shift of the O–H stretching band in each compound. Contrarily, the CX[4]-NO2 complex have a peak located at 3170 cm⁻¹ corresponding to the vibration of the O–N asymmetric band. One may observe another peak in the region of 3193 cm⁻¹ (O–N sym. stretching vibration). In addition, the CX[4]-NO2 complex is characterized by several C–H stretch bands located less than 1800 cm⁻¹. From Figure 3, we show that the interactions of the NO2 gas with the CX[4] lead to a split of the O–H peak to four peaks. These later are located in the vicinity of 2928, 3100, 3204 and 3298 cm⁻¹, respectively. Also, we show that the CX[4]-NO2 complex have a very red-shifted O–H band in comparison to the others complexes. Finally, we note that the region between 600 and 1800 cm⁻¹ is specified by the C=C-H, C=C-H and C–C stretching vibrations in the CX[4]-NO2 and CX[4]-CO2 complexes.

Likewise, we demonstrated that a region appears in the CX[4]-N1 complex less than 1800 cm⁻¹ is characterized by several peaks corresponding to the C=C-H and C=C-H stretching vibrations. We have noted that the red-shifted values between the CX[4]-gas complexes are around to 44 (CX[4]-NO3), 24 (CX[4]-NO2), and 9 cm⁻¹ (CX[4]-CO2), respectively. In conclusion, the red-shift of the O–H stretching bands explain the sensibility of the gas to encapsulate in the inside cavity of the CX[4] molecule. From Table 2, we may deduce that the polarization values of the CX[4]-CO2, CX[4]-N2 and CX[4]-NO2 are approximately between 50 × 10⁻²⁴ and 58 × 10⁻²⁴ esu. In addition, these values are almost 10 times higher than the value of the prototype molecule (The α0 of urea is equal to 5 × 10⁻²⁴ esu).

Also, it is very clear that the CX[4]-NO3 complex may be a good candidate of nonlinear optical applications, this complex is characterized by a polarizability almost to 60 × 10⁻²⁴ esu. The value of the polarizability (α0) of the CX[4]-NO2 explained the red-shifting of the H-binding stretching vibration. The greater polarizability of the three host-guests relative to the urea may be explained by the charge transfer between the gases to the π-electron of the phenol ring.

Understanding the relative affinity of each stable host-guest complexes is very important to known the specific properties of atoms. For this idea, we have calculated the local and global softness or hardness, recently proposed by Franco-Pérez et al. [37]. These reactive parameters have been used to take into account the distribution of electrophilic and nucleophilic active sites. All these reactive parameters are calculated in the same framework. The studied systems have been chosen to test the new index of the Softness/hardness parameters in these specific regions. Indeed, regarding the MEP graphs (Figure 4), it is the zone with V(r) < 0 that we are interested in. For both CX[4]-gas interactions, with V(r) > 0 where an electrophilic zone and V(r) < 0 is a nucleophilic zone. The results are illustrated in Table 3. To better understand the sites to interpret (See Figure 2 and Table 3). For the explanation of the reactive interactions of the CX[4]-gas complexes using the atomic charge distribution, we have taken into account the Fukui function in each site. From Table 3, we can deduce that, the O2 atom has the strongest nucleophilic sites in the CX[4]-CO2 complex with the highest S⁻ value connect to the H1. However, S⁻ values for H3 is the biggest than the S⁺ of H1.

This zone is characterized by the strongest attraction of electrons (electrophilic region). The S⁺/S⁻ values of the specific atoms are more descriptive for this gas. Concerning the orbital interaction in the CX[4]-N2 gas, the oxygen atom O1 has the strongest nucleophile with the least value S⁺/S⁻ ratio in comparison with N2 atoms (see Table 3). As expected, this atom seems decreasing the nucleophilicity to the center of the cavity.

In addition, the O3 atom includes the maximum nucleophilic sites with the highest value of S⁻/S⁺ ratio in comparison with other specific atoms (see Figure 2 and Table 3). For the CX[4]-NO3 complex, we find that the O4 atom exhibits a large nucleophilic site characterized by the highest values of S⁻/S⁺. The minimum of the repulsive electron has been surrounded by the O4 atom. This information explained that the maximum of nucleophilic region co-exists in the center of the cavity. The NO2 gas is the hardest guest with a local/hardness value equal to 0.7871 and 0.0499 respectively. This guest is characterized by the h⁺/h⁻ values equal to 15.6504. The nucleophilic minimum sites exist in the CX[4]-NO3 complex, such as the O4 atom that has a h⁺/h⁻ ratio values equal to -1506.609. Looking again Table 3, O4 in the center of the cavity of the CX[4]-NO3 complex explains well the strong electrostatic interaction of NO2 gas with the CX[4] molecule. In the CX[4]-NO3 complex, the most electrophilic zone (H3) is described by the strongest H-binding interaction. The CX[4]-NO3 complex exhibits the most dramatic change (RSD = 85.3%). It means that the local hyper-softness (LHS) should be a much better candidate for the correlations with the experimental catalytic activity. The explanations of the relative nucleophilicity (S⁻/S⁺ ratio), electrophilic and nucleophilic hardness/softness check that, the CX[4]-NO2 and CX[4]-NO3 complexes are very iso-electronic in comparison with the other host-guests.

The nature and the strength of the interactions between CX[4] and the specific gases have been determined by the AIM and NCI-3D analysis. For all Bond Critical Points (BCPs) caused by the encapsulation of the host gases in CX[4], we have calculated the chief topological parameters; the electron density (ρ) and it’s laplacian (κ(ρ)) by the Atom In Molecule (AIM) theory. Other topological parameters are also extracted, such as the kinetic energy density (G), the Hamiltonian kinetic energy (H), the interaction energy (E₉), and the ellipticity (ε). The AIM molecular graphs have been shown in Figure 5 the different BCPs in the CX[4]-gas complexes.

The topological parameters calculated at selected BCPs are listed in the Table 4. One may see that for the CX[4]-CO2, the electron density
values are found between 0.0021 to 0.0064 a. u. and the Laplacian is negative. The BCP2 of this complex has a highest electron density value. The interaction energy (E_{BCP2}) is equal to -5.614 kJ/mol. Also, we note that the ellipticity is equal to 1.67 a. u. which indicates that the C59⋯O56 is an unstable interaction. Moreover, the CX[4]-N2 complex is characterized by the existence of four BCPs. The electron density values in these BCPs of this complex are around to 0.0020 a. u. The Laplacian values are positive. We show that the interactions between the CX[4] and the N2 gas are weak, which is proved by the N58⋯O26 and N58⋯O27 interactions. The H-bonding energy in these BCPs is equal to -1.296 kJ/mol. We have noted that the CX[4]-NO2 complex is characterized by weak intermolecular interactions.

The value of the interaction energy in the BCP3 is worth to 1.82 kJ/mol. In this BCP, we can deduce the height stability of the interaction between O58 and C26 atoms by the low value of the ellipticity ε = 1.43. The AIM topological parameters for the CX[4]-NO3 complex demonstrated that this complex has the highest interactions at the level of the BCP5 and BCP6. Moreover, the electron density values in these interactions are equal to 0.0375 and 0.0194 a. u., respectively. The ellipticity value is equal to 3 in these BCPs. This result has explained that the interaction between O60 and C9 is less stable in comparison with other inter-atomic interactions. On the other side, we notice that the H-bonding interaction O58⋯H51 has a weak value of ellipticity equal to 0.06. In addition, this result confirm that this H-bonding interaction is very stable than others. This idea proves that the interaction between the host and the guest is related to the stability of the inter-atomic interactions. The NCI-RDG analysis shows that the CX[4]-NO3 complex is characterized by the existence of weak Van der Waals interaction (green color) between O60⋯C12, O60⋯C9, O58⋯C20 and O58⋯C25 (Figure 6).

We found that this complex shows the existence of the H-bonding type interaction between the O58 atom and H53 atom (blue color). We have noted that the CX[4]-NO3 complex shows that the O58⋯C26 interaction (NCI graphs) reflect the larger stability of this host-guest. This result is well confirmed by the AIM theory. The AIM and the NCI-RDG analyses have demonstrated that the presence of attractive and repulsive interactions between the gas and the CX[4] molecule is very necessary for the stability of the encapsulated complexes inside of its cavity.

### Table 2. Polarizability (α₀) and first order hyperpolarizability (β₀) values of the CX[4]-gas complexes calculated at B3LYP-D3BJ/6-31+G(d) level of theory.

| CX[4]-gas      | CX[4]-CO₂ | CX[4]-N₂ | CX[4]-NO₂ | CX[4]-NO₃ |
|----------------|----------|----------|-----------|-----------|
| α₀ (10⁻²⁴ esu) | 50.12    | 52.55    | 56.41     | 58.28     |
| β₀ (10⁻³³ esu) | 2521.41  | 2543.54  | 2574.83   | 2586.62   |

Polarizability (α₀): 1 a. u. = 0.1482 × 10⁻²⁴ esu, for hyperpolarizability (β₀): 1 a. u. = 8.6393 × 10⁻³³ esu.

Figure 4. MEP analysis of the stable CX[4]-gas (CX[4]-CO₂ (a), CX[4]-N₂ (b), CX[4]-NO₂ (c) and CX[4]-NO₃ (d)) complexes calculated by B3LYP-D3BJ/6-31+G(d) level.
### Table 3. Condensed to atom: Fukui function, local softness, local hardness and relatives softness and relatives hardness values of reactive atom of CX[4]-gas complexes.

|       | $f$   | $f^+$ | $f^-$ | $S$  | $S^+$ | $S^-/S^+$ | $h$   | $h^+$ | $h^+/h^+$ |
|-------|-------|-------|-------|------|-------|-----------|-------|-------|------------|
| **CX [4]-CO$_2$** O1 | 0.0308 | -0.0028 | 0.0139 | 0.0039 | -0.0004 | -9.7500 | 0.4941 | -0.0287 | -17.2160  |
|       | O2    | 0.00001 | -0.0001 | -0.00008 | 0.000002 | -0.00002 | -0.1000 | 0.0015 | -0.0014 | -1.1232  |
|       | O3    | 0.00004 | -0.00008 | -0.00001 | 0.000006 | -0.00001 | -0.6000 | 0.0014 | -0.0007 | -1.9985  |
|       | H1    | -0.00005 | 0.0014 | 0.00069 | -0.000008 | 0.00019 | -0.0421 | -0.0118 | 0.0115 | -1.0260  |
|       | H2    | 0.00005 | 0.0026 | 0.00135 | 0.000007 | 0.00034 | 0.0205 | -0.0192 | 0.0211 | -0.9099  |
|       | C1    | -0.0002 | 0.0014 | 0.00059 | -0.00025 | 0.00018 | -0.1389 | -0.0133 | 0.0110 | -1.2090  |
| **CX [4]-N$_2$** O1 | 0.0455 | -0.0029 | 0.0213 | 0.0059 | -0.00038 | -15.5261 | 0.7194 | -0.0333 | -21.6036 |
|       | H1    | 0.0003 | 0.0013 | 0.00078 | 0.000029 | 0.00017 | 0.1705 | -0.0068 | 0.0106 | -0.6409  |
|       | N1    | 0.0000 | 0.000005 | 0.000002 | 0.00000 | 0.000001 | 0.0000 | -0.000003 | 0.00003 | -0.1000  |
|       | N2    | 0.000004 | 0.000007 | 0.000005 | 0.00000 | 0.00000 | 1.0000 | 0.000013 | 0.00005 | 0.2600   |
| **CX [4]-NO$_2$** O1 | 0.000001 | 0.2096 | 0.1305 | 0.0000 | 0.0392 | 0.0000 | -1.9727 | 1.5044 | -1.3111  |
|       | O2    | -0.0003 | 0.2605 | 0.1302 | -0.00004 | 0.0391 | -0.000102 | 1.9696 | 1.5017 | -1.3116  |
|       | O3    | 0.0551 | 0.00099 | 0.0277 | 0.0083 | 0.000015 | 553.3333 | 0.7817 | 0.0499 | 15.6504  |
|       | H1    | 0.0004 | -0.0004 | 0.00015 | 0.00052 | -0.000006 | -8.6666 | 0.0054 | 0.00007 | 77.0000  |
|       | N1    | 0.00006 | 0.4674 | 0.2337 | 0.00008 | 0.0702 | 0.00011 | -3.5322 | 2.6943 | -1.31103 |
| **CX [4]-NO$_3$** O1 | -0.00007 | 0.0004 | 0.00017 | 0.0000 | -0.00009 | -0.6000 | -0.0039 | 0.0029 | -1.33525 |
|       | 02    | 0.0003 | -0.0028 | -0.0013 | 0.00032 | -0.000027 | -0.0864 | 0.0244 | -0.0206 | -1.1850  |
|       | 03    | -0.0006 | -0.0054 | -0.0029 | 0.000069 | -0.000072 | 0.0958 | 0.0326 | -0.0401 | -0.8121  |
|       | 04    | 0.1103 | -0.0004 | 0.0549 | 0.0147 | -0.000052 | -282.6923 | 1.6572 | -0.0111 | -1506.6  |
|       | N1    | 0.0002 | 0.0010 | 0.0042 | -0.000026 | 0.00014 | -0.1857 | -0.0106 | 0.0077 | -1.3903  |
|       | H1    | 0.0016 | 0.00017 | 0.00089 | 0.00022 | 0.000022 | 10.0000 | 0.0231 | 0.0013 | 18.4880  |

**Figure 5.** AIM molecular graphs showing the different BCPs in CX[4]-CO$_2$ (a), CX[4]-N$_2$ (b), CX[4]-NO$_2$ (c) and CX[4]-NO$_3$ (d) calculated at B3LYP-D3BJ/6-31+G(d) level of theory.
**Table 4.** Topological parameters: electron density $\rho(r)$, Laplacian of electron density $\nabla^2 \rho(r)$, electronic kinetic energy density $G(r)$, total electron energy density $H(r)$, the eigenvalues $\lambda_1, \lambda_2, \lambda_3$, ellipticity of electron density $\varepsilon$ and interaction energy $E_{X \cdot Y}(\text{kJ/mol})$.

| BCPS          | $\rho$ (a.u) | $\Delta \rho$ (a.u) | $G$ (a.u) | $H$ (a.u) | $E_{X \cdot Y}$ (kJ/mol) | $\lambda_1$ (a.u) | $\lambda_2$ (a.u) | $\lambda_3$ (a.u) | $\lambda_1/\lambda_3$ | $\varepsilon$ |
|---------------|--------------|----------------------|-----------|-----------|--------------------------|-------------------|-------------------|-------------------|---------------------|-------------|
| **CX [4]-CO$_2$** |              |                      |           |           |                          |                   |                   |                   |                     |             |
| BCP1         | 0.0029       | -0.0029              | 0.0022    | 0.0007    | -1.968                   | -0.0022           | -0.0021          | 0.0160            | 0.1375              | 0.05         |
| BCP2         | 0.0064       | -0.0070              | 0.0057    | 0.0014    | -5.614                   | -0.0056           | -0.0021          | 0.0358            | 0.1564              | 1.67         |
| BCP3         | 0.0021       | -0.0022              | 0.0016    | 0.0006    | -1.337                   | -0.0016           | -0.0011          | 0.0115            | 0.1391              | 0.45         |
| **CX [4]-N$_2$** |              |                      |           |           |                          |                   |                   |                   |                     |             |
| BCP1         | 0.0021       | -0.0017              | 0.0014    | 0.0004    | -1.296                   | -0.0012           | -0.0004          | 0.0086            | 0.1395              | 2.00         |
| BCP2         | 0.0020       | -0.0017              | 0.0013    | 0.0004    | -1.296                   | -0.0012           | -0.0004          | 0.0085            | 0.1412              | 2.00         |
| BCP3         | 0.0020       | -0.0017              | 0.0013    | 0.0004    | -1.288                   | -0.0012           | -0.0004          | 0.0085            | 0.1412              | 2.00         |
| BCP4         | 0.0020       | -0.0017              | 0.0013    | 0.0004    | -1.271                   | -0.0012           | -0.0004          | 0.0084            | 0.1429              | 2.00         |
| **CX [4]-NO$_2$** |             |                      |           |           |                          |                   |                   |                   |                     |             |
| BCP1         | 0.0021       | -0.0019              | 0.0016    | 0.0004    | -1.576                   | -0.0014           | -0.0007          | 0.0097            | 0.1443              | 1.00         |
| BCP2         | 0.0024       | -0.0018              | 0.0015    | 0.0003    | -1.500                   | -0.0013           | -0.0006          | 0.0093            | 0.1398              | 1.17         |
| BCP3         | 0.0026       | -0.0023              | 0.0019    | 0.0005    | -1.816                   | -0.0017           | -0.0007          | 0.0117            | 0.1453              | 1.43         |
| BCP4         | 0.0026       | -0.0023              | 0.0018    | 0.0005    | -1.775                   | -0.0017           | -0.0007          | 0.0115            | 0.1478              | 1.43         |
| BCP5         | 0.0019       | -0.0019              | 0.0015    | 0.0004    | -1.386                   | -0.0012           | -0.0004          | 0.0093            | 0.1290              | 2.00         |
| BCP6         | 0.0019       | -0.0019              | 0.0014    | 0.0004    | -1.319                   | -0.0011           | -0.0004          | 0.0090            | 0.1222              | 1.75         |
| **CX [4]-NO$_3$** |             |                      |           |           |                          |                   |                   |                   |                     |             |
| BCP1         | 0.0016       | -0.0015              | 0.0012    | 0.0004    | -1.019                   | -0.0007           | -0.0002          | 0.0071            | 0.0986              | 2.50         |
| BCP2         | 0.0023       | -0.0021              | 0.0016    | 0.0004    | -1.538                   | -0.0012           | -0.0003          | 0.0097            | 0.1237              | 3.00         |
| BCP3         | 0.0064       | -0.0048              | 0.0040    | 0.0008    | -4.280                   | -0.0047           | -0.0018          | 0.0256            | 0.1836              | 1.61         |
| BCP4         | 0.0072       | -0.0057              | 0.0050    | 0.0007    | -5.578                   | -0.0054           | -0.0018          | 0.0300            | 0.1800              | 2.00         |
| BCP5         | 0.0375       | -0.0302              | 0.0309    | -0.0006   | -41.348                  | -0.0612           | -0.0579          | 0.2400            | 0.2550              | 0.06         |
| BCP6         | 0.0194       | -0.0154              | 0.0141    | 0.0014    | -16.671                  | -0.0175           | -0.0128          | 0.0920            | 0.1902              | 0.37         |
| BCP7         | 0.0079       | -0.0063              | 0.0056    | 0.0007    | -6.428                   | -0.0053           | -0.0029          | 0.0334            | 0.1587              | 0.83         |

**Figure 6.** NCI-RDG plots of the electron density and its reduced gradient of the inclusion complexes for CX[4]-gas (CX[4]-CO$_2$(a), CX[4]-N$_2$(b), CX[4]-NO$_2$(c) and CX [4]-NO$_3$(d)). The iso-surfaces were constructed with RGD = 0.5 a. u and the colors scaling from -0.01 to -0.01 a. u.
4. Conclusion

The encapsulation of NO3, NO2, CO2 and N2 gases in the CX[4] cavities have been investigated by using DFT calculations. The optimization of the studied complexes has shown that the position of the gas inside the cavity is very stable than that outside of the cavity. This fact is clearly explained by the distribution of electrophilic and nucleophilic active sites. The infrared spectrum and the polarizability study have explained the role of the NO3 gas in the red shifted of the O H band in comparison with the other gases. The local softness and hardness parameters of the various inclusion complexes specified the high rigidity and conductivity of CX[4]-NO3 in comparison with the other complexes. The AIM analysis has shown clearly the strong interactions of the gas NO3 and NO2 with the endo-cavity environment of the CX[4].

Declarations

Author contribution statement

B. Gassoumi, H. Ghalla, R. Ben. Chaabane: Conceived and designed the analysis; Analyzed and interpreted the data; Contributed analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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