

Accepted Manuscript

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PII: S0009-2614(10)01643-X
DOI: [10.1016/j.cplett.2010.12.056](https://doi.org/10.1016/j.cplett.2010.12.056)
Reference: CPLETT 28901

To appear in: *Chemical Physics Letters*

Received Date: 20 September 2010
Accepted Date: 18 December 2010

Please cite this article as: A.L. Montero-Alejo, M.E. Fuentes, L.A. Montero, M.G. Vega, Coulomb and Exchange contributions to electronic excitations of benzene aggregates, *Chemical Physics Letters* (2010), doi: [10.1016/j.cplett.2010.12.056](https://doi.org/10.1016/j.cplett.2010.12.056)

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**Coulomb and Exchange contributions to electronic excitations of benzene
aggregates**

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Abstract

Coulomb and Exchange (CE) contributions to electron transition energy terms are proposed to describe the behavior of charge distributions upon electronic excitations of molecular aggregates. CE value regards the stabilizing influence of electron-electron interactions over the excitation energy obtained after the calculation of the configuration interaction of singles. The approach is used to qualitatively gauge the variations in the bounding character of excitons among different conformations of benzene dimers. The usefulness of CE is extended to address the excited state description of crystal and liquid models of benzene aggregates. Low-lying excited states of these structures were correctly described.

1. Introduction

Understanding electronic excitations of molecular aggregates, related to those of the isolated chromophores, is the key stone to model photo-induced phenomena in live and material sciences[1-5]. In fact, electron transitions that involve energy and charge-transfer processes, are the basis of operation of active components in optoelectronic devices[6,7] and many life related phenomena[8].

Considerable effort has been devoted to study clusters of small aromatic molecules as simplest models, by both experimental and theoretical procedures [9-13]. Electronic interactions, which modulate the excitation properties of these kind of systems, strongly depend on the distance and relative orientation of transition moments of monomer units. In fact, π - π stacking and, in general, non-covalent interactions that are commonly found in aromatic aggregates[14] govern their arrangement and consequently, their excitation properties.

Benzene is one of the most thoroughly experimentally and theoretically studied chromospheres in crystal[15-17], condensed[18,19] and gas phase[20] aggregates. The model motifs occurring in biomacromolecules and in complex molecular systems are found represented in the ground state of the potential energy surface (PES) calculations of the benzene dimer. Four different structures that conform an almost isoenergetic PES: T-shaped titled C_s (TT), T-shape C_{2v} (T), parallel-displacement C_{2h} (PD) and sandwich D_{6h} (S) were reported (Fig. 1), with stabilization energies following the order $TT > T \geq PD \geq S$ [21]. These results are consistent with previous *ab initio* reports, except that the TT structure has not been considered[22,23]. The singlet low-energy excited states of the S conformation of benzene dimer have also been studied in order to describe the weak molecular interactions involving them[13,24]. Assessing quantum mechanical methods for this kind of calculations to study such dimeric systems showed that the wave-function based methods perform qualitatively correctly [13].

Moreover, in order to gain insight on the nature of electronic transitions, the changes in the electronic many-body wave-function upon excitation need to be analyzed. In this sense, different approaches to address directly the differences between ground and excited state electron densities have been used to avoid the usually complex analysis of the excited state wave-function[25]. Likewise, special attention has been put on the study of the inter-chromophore electronic coupling in an excited electronic state, when

energy transfer processes are present [13, 26, 27]. This interaction is, in general, given by the values of two electron integrals, which evaluation represent a highly demanding task. However, they have been satisfactorily used in semiempirical methods for large systems as an alternative[26]. From the point of view of the exciton model, which can be formed by a photoexcitation in molecular aggregates, the electron and hole ‘quasi-particles’ are also governed by these coulomb interactions[28]. Hence, the changes in the electron-electron (e-e) interactions after excitations also need to be considered to describe the exciton bounding character. In this sense, the configuration interaction of singles (CIS) methodology have been well thought-out to get optimized transition energies, electron-hole interactions and charge redistributions due to excitons originated upon light absorption[28].

In this study, we investigate the distance and orientation dependence of the excitation energy of benzene aggregates as models of more complex systems. In order to gain insight on the nature of electronic excitations, an approach to describe the bounding character of the excited state is proposed. The CNDOL approximate quantum mechanical method [29, 30] was chosen to carry out to describe excited states for benzene aggregates, including crystal, liquid and low pressure gas models. CNDOL Hamiltonians are based on the neglect of differential overlap (NDO) of atomic orbital basis set and considering their azimuthal / quantum number. This method provided a reliable picture of the optical and in general, electronic excitations related phenomena, showing intermolecular charge transfers in large polyatomic systems [30-32].

2. Theoretical methodology

Under the CNDOL approach of the ground state wave-function of the system (Ψ_0^{CNDOL}), the electronic excitation is obtained using a CIS treatment, where the well known excited determinant wave-function basis (Ψ_ζ) is obtained by promoting one electron from an occupied to an unoccupied molecular orbital (MO):

$$|\Psi_\zeta\rangle = \sum_{r,p} a_{rp}^{(\zeta)} \hat{e}_r^+ \hat{e}_p |\Psi_0^{CNDOL}\rangle,$$

(1) holds for any electron promotion between $p \rightarrow r$ or $q \rightarrow s$, where r and s are unoccupied SCF MOs and \hat{e}^+ (\hat{e}) denotes the electron creation (annihilation) operator. Coefficients $a_{rp}^{(\zeta)}$ and excitation energies E_ζ , referred to the CNDOL ground state energy, are obtained by solving the eigenvalue problem:

$$H a = E_{\zeta} a \quad (2)$$

In order to look insight the CIS algorithm, the expression to evaluate diagonal (H_{pr}) matrix elements [33, 34] corresponding to singlet and triplet states respectively are shown as follows:

$$^1H_{pr} = (\varepsilon_r - \varepsilon_p) - [\langle pr | pr \rangle - 2\langle pr | rp \rangle], \quad (3)$$

$$^3H_{pr} = (\varepsilon_r - \varepsilon_p) - \langle pr | pr \rangle, \quad (4)$$

where the $\langle pr | pr \rangle = J_{pr}$ and $\langle pr | rp \rangle = K_{pr}$ are the two-electron repulsion integral, i.e. Coulomb (J_{pr}) and Exchange (K_{pr}) respectively, regarding MOs and ε 's are MOs eigenvalues.

Eqs. 3 and 4, as well as the general expression for matrix representation of the Hamiltonian in the space of single excited determinants[25,35], reveal that the electron interaction regarding MOs appears as a correction for the differences of their respective SCF eigenvalues. In the case of excitations that are explained just by one single excited determinant (σ), the contribution of this interaction terms, $[J_{pr} - 2K_{pr}]$ for a singlet as example, only depends on the involved donor and acceptor MOs. That is, the negative sign of this term provides the stabilization effect regarding e-e interactions between the involved MOs, p and r . However, in the same way that the electron density matrix elements of each CIS state (ζ) involve the corresponding term of each single determinant (σ) weighted by the square of CIS expansion coefficients ($a_{\sigma\zeta}^{(\zeta)}$). Next, it is possible to obtain the complete role of the electron interaction integrals to the excitation energy. Therefore, these energy contributions to each electron transition can be obtained by the following expressions:

$$^1E_{\zeta}^{CE} = -\sum_{\sigma=1}^N a_{\sigma\zeta}^2 [J_{pr} - 2K_{pr}]_{\sigma}, \quad (5)$$

$$^3E_{\zeta}^{CE} = -\sum_{\sigma=1}^N a_{\sigma\zeta}^2 [J_{pr}]_{\sigma}, \quad (6)$$

for singlet (5) and triplet (6) states, respectively, and they are named Coulomb and exchange (CE) energy.

CE values allow us, in molecular aggregates as well as in large polyatomic systems, to estimate different kinds of electron transitions in order to characterize excitations as

depending on the amount of charge reallocation upon excitation. The sum of squares of the expansion coefficients of accounted CIS provides the collective character of an excitation owing to the large number of MOs involved in each one after the variational optimization. Two electron integrals provide the energy contribution to redistribution effects of the electronic charge during the transition because of the average separation between involved functions. Therefore, in exciton models, the CE energy value could serve to predict where electrons and holes are bounded and therefore, where they act as free carriers for each configuration.

The low-lying excited state B_{2u} (π - π^*) of the most important structures of benzene dimer PES (Fig. 1) has been chosen to study the corresponding CE contributions. The starting molecular input geometries have been taken from a previous work[21], in which they were determined by all gradient-coordinate optimization based on the density functional theory including the dispersion correction (DFT-D) procedure. In order to obtain excitation energy dependence on geometry for each of these dimer conformations, their distances between monomer centers were changed along one axis (indicated by dashed arrows in Fig. 1.), and thus keeping the starting symmetry. Individual benzene geometries remain fixed in our calculations according to the starting structures. This is considered as a reliable approximation because the monomer geometry did not substantially change with the full geometry optimization at *ab initio* level of theory [24] and it isolates a single coordinate for studying dependences. Resulting one dimensional surface were explored in the range of 3.0 to 10.0 Å of inter benzene distances.

The CNDOL/1CS ground state Hamiltonian[30] has been selected in this work. A new implemented algorithm allows the selection of a convenient number of the lowest energy determinant terms (eq. 3 and 4) for building the CIS matrix. In this way, it is expected to obtain a more reliable description of the calculated electronic excitation spectrum. Perturbative doubles correction to *ab initio* CIS results (CIS(D))[36,37] of the same geometries was added to the study for the sake of reference comparison. In this case, Pople's 6-31G(d,p) basis set was used within the CIS(D) algorithm as implemented in Gaussian03 package[38].

3. Results and discussions

Fig. 2 shows CNDOL and CIS(D) results of the four expected benzene dimers. Solid colored lines are interpolations between the filled symbols and correspond to CNDOL results; CIS(D) results were added with interpolated dotted lines between the empty symbols. The inter-benzene distance that corresponds to each optimized structure has been signaled on the top axis. The CNDOL excitation energy of the first π - π^* (B_{2u}) state of all dimer appeared similar (~ 5.4 eV) when the distance between monomer centers became larger than 4 Å. CNDOL results slightly overestimate the energy of the corresponding best theoretical prediction (5.08 eV)[39] and that of experimental vapor phase absorption maximum (4.90 eV)[40]. However, the absolute deviations appear within the expected uncertainty of the method. The correspondence found between all dimer conformation excitation energies undergoes a red shift when the distance between monomers becomes smaller than their optimized value. Changes in the density of CIS states due to less stabilizing interactions between the aromatic π systems could be the explanation. Notice that T and TT dimer conformations show a major shift when the distance between the centers were artificially reduced around 1 Å. Similar tendency is observed for the S conformation, whereas PD structures present small changes.

CE contributions for each electron transition energies are shown in Fig. 3. The same as in Fig. 2 symbols were used. CE energy contributions for each electron transition show appreciable changes with respect to benzene distances, in contrast with the already shown behavior of excitation energies. There are two types of distinguishable surfaces: the S and PD dimer conformations, and the T-shape types (T and TT). In all of them, when the inter-benzene distance is larger than 8.0 Å, CE energies tend to be the same and they are maintained almost constant at larger distances. Bearing in mind the meaning of CEs, this behavior could be explained as a consequence of non interaction between benzene molecules during the excitation at this long range limit. Therefore, electron transitions should be localized within each benzene molecule. A confirmation of these results was obtained exploring the nature of these electron transitions by means of the wave function amplitude. Consequently, excitations are clearly described between MOs localized at each benzene molecule. In contrast, smaller inter benzene distance values show that CE energies undergo a general tendency to decrease. This is

possibly related to either sharing or transferring electron densities during the excitation, i.e. less bounded electron with their “holes”.

The TT conformers show similar behavior of CEs with respect to inter-benzene distances as in S and PD structures. Three differences must be highlighted: CE values are higher, the energy surface is flatter, and the minimum is found at shorter distances (4.0 - 5.0 Å). The higher CE energy contributions with respect to S and PD conformations could be interpreted as less favorable e-e interactions. A more localized character of electron density redistribution should prevail in them. Fig. 3 shows almost the same features in the case of T-shape conformers. However, the energy surface is flatter. According to above deductions, the CT character of electron transitions of T conformers are favored when benzenes come closer than their optimized distance (~ 5 Å) in the ground state.

Notice that inter-benzene distances of ground state geometries are not related with the minimum in the CE energy surface. The most stable geometries of T and TT favor electron density delocalization during the excitation. However, in the case of S and PD conformations, electron excitations that imply less bounded charges could be found at higher inter-benzene distances. That is, it is possible to interpret the bounding character of an electron transition according to the prevailing geometry in more complex systems or aggregates.

In order to get further insight into the importance of the use of CE contributions to describe excited state properties in large systems, we carried out a study on the low-lying excitations of benzene aggregates. In this case, different molecular arrangements of 14 benzene molecules were used for our modeling. Hence, two unit cells were used, either corresponding to the reported crystal structure (crystalline solid) and to an approach of this in liquid phase (herringbone liquid)[16,17], respectively. The well-known herringbone structures contain all benzene molecules in the unit cell as it was defined by Narten [16] (see Fig. 4, a). Herringbone liquid unit cell slightly differs from the solid because in the distances between the benzene ring centers [16]. Moreover, in order to obtain uncorrelated structures of liquid models, the configuration space of 14 benzene molecules was randomly explored according to the MMH procedure [41]. The ground state geometries were optimized at PM6[42] semiempirical Hamiltonian level as implemented in the MOPAC2009 package[43]. Thirteen configurations which

represent 99 % of resulting populations were chosen as the lowest energy structures of the hypersurface. Finally, a model of sufficiently separated 14 benzene molecules (~ 15 Å between the centers) was chosen for the study. This molecular arrangement has been selected for modeling the behavior of a low pressure gas.

In panel (b) of Fig. 4, unit cell models at different orientations are represented. This allows us to show that there is one predominant conformation between interacting benzenes. It is a TT like dimer conformation where the interaction occurs at both sides of the benzene plane. In contrast, in panels (c) and (d) of Fig. 4, two conformations of the optimized liquid models are shown. Figure 4 (c) represents a model compact structure with different kinds of interaction among benzenes, and Figure 4 (d) shows that some of the molecules can appear isolated or non-interacting with the aggregate.

Fig. 5 (a) shows the excitation energies of the first π - π^* (B_{2u}) state obtained for each model aggregate of benzene. Notice that the transition energy of the crystalline solid, the herringbone liquid, as well as all of those in the liquid models show smaller excitation energies than that of the low pressure gas model (all far distant molecules). These results agree with the red shift tendency (a few hundreds of cm^{-1}) observed in spectra in the transition from vapor phase to condensed phase [18,44]. Moreover, the CNDOL red shift obtained for the unit cell models (crystalline solid and herringbone liquid) are comparable to those obtained by ZINDO method with the same structures.

Low-energy electron transitions of the crystalline solid, herringbone liquid and many of the liquid model structures predicted by the method imply collective states according to their CIS expansion coefficients. However, this would not be expected for the model of the low pressure gas, in which the excitations are given between MO's that are localized in an individual molecule. In order to understand the nature of each electron transition involved in this process, Fig. 5 (b) shows the corresponding CE energies (according to 'y' axis scale) of the aggregate models under study.

In correspondence to the complexity of the liquid model structures, the distribution of points that represents CE energy (blue circles) are not expected and, effectively, does not show a regular arrangement. However, electron excitations in the regular and compact structures of crystalline solid (dark circles) and herringbone liquid (red circles) show similar CE values. Fig. 5 (b) shows that, in general, CE values corresponding to excitations in the herringbone liquid model are slightly smaller than those in solid.

Moreover, some of those uncorrelated liquid models show calculated electron transitions which present CE values as small as those in the unit cell. This fact could be interpreted as a consequence of local similarities between the spatial conformations of interacting benzenes in those aggregates and the unit cell. On the other hand, CE energy contributions to electron transitions in the low pressure gas model (green circles) are the largest. Figure 4 (d) also shows that there are some liquid models in which the electron transitions present similar CE contributions.

In general, the smallest CE values correspond to electron delocalized excitations with a collective character into the system, whereas the largest values suggest electron localized transitions in non-interacting molecules. Therefore, on the basis of our approximation, it is possible to infer that excitations in the proposed structure for the herringbone liquid, crystalline solid and other compact models of liquids, showing smaller CE values, imply less bounded excitons. Moreover, this means that CE calculations are a promising tool for determining exciton related properties in materials and other kind of either ordered or amorphous nanoscopic systems.

4. Conclusions

Results in this Letter indicate that it is expected that CE values can be used to study the nature of electronic excitations in complex molecular aggregates. While the present report is based on an approximate method, this value is proposed to qualitatively gauge variations in the bounding exciton character between different configurations that need to be taken into account to explain related phenomena. CNDOL method appropriately describes excitation energies and other corresponding properties of benzene aggregates. Consequently, it appears that both the CE value and this Hamiltonian are adequate tools to model complex systems according to the feasibility of its implementation and the usefulness of their output conclusions.

Acknowledgments

We acknowledge the Spanish Agency for International Cooperation for Development (AECID) funding. M. E. F. and the other authors are truly grateful for support from SEP-CONACYT (25380) of Mexico. JMGV is grateful for support from MEC of Spain (Grant No. CTQ 2007-63332), AECID of Spain (Grant No. D/023653/09) and CEAL-UAM.

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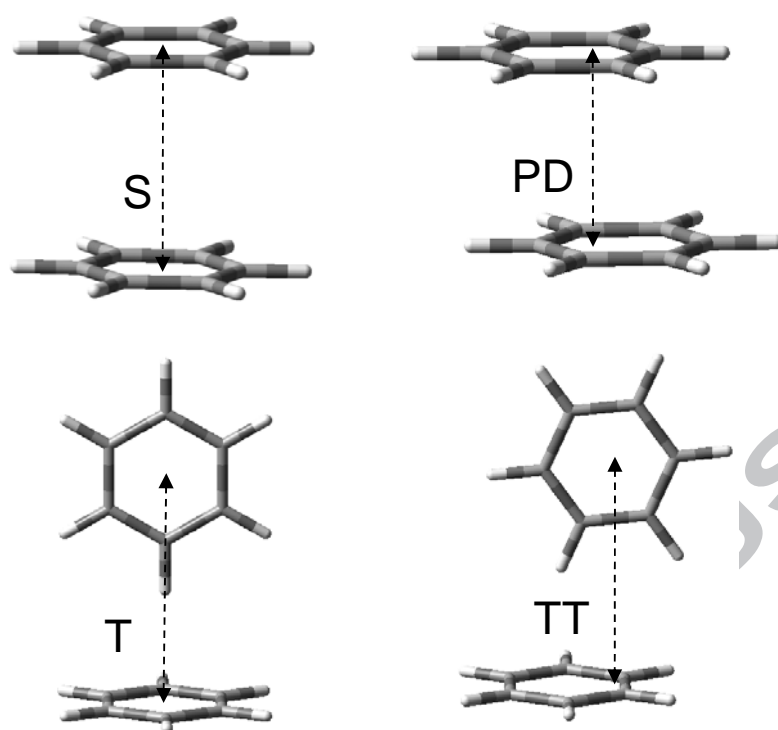


Fig. 1. Ground state structures of benzene dimers: sandwich D_{6h} (S), parallel-displacement C_{2h} (PD), T-shape C_{2v} (T) and T-shaped tilted C_s (TT). The inter benzene distances were varied along the axis indicated by dashed arrows in each representation.

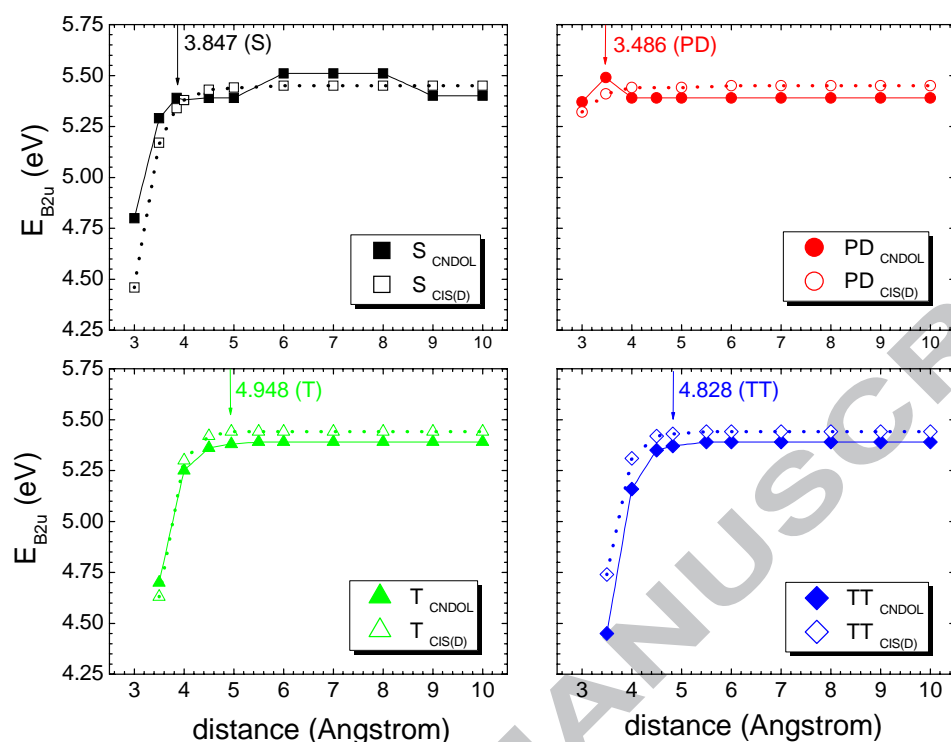


Fig. 2. Potential energy curves of the B_{2u} singlet excited state versus the inter-benzene distance of each dimer conformation (by colors). Solid colored lines (interpolations between the filled symbols) correspond to CNDOL results, whereas CIS(D) results are shown with dotted lines (interpolations between the empty symbols).

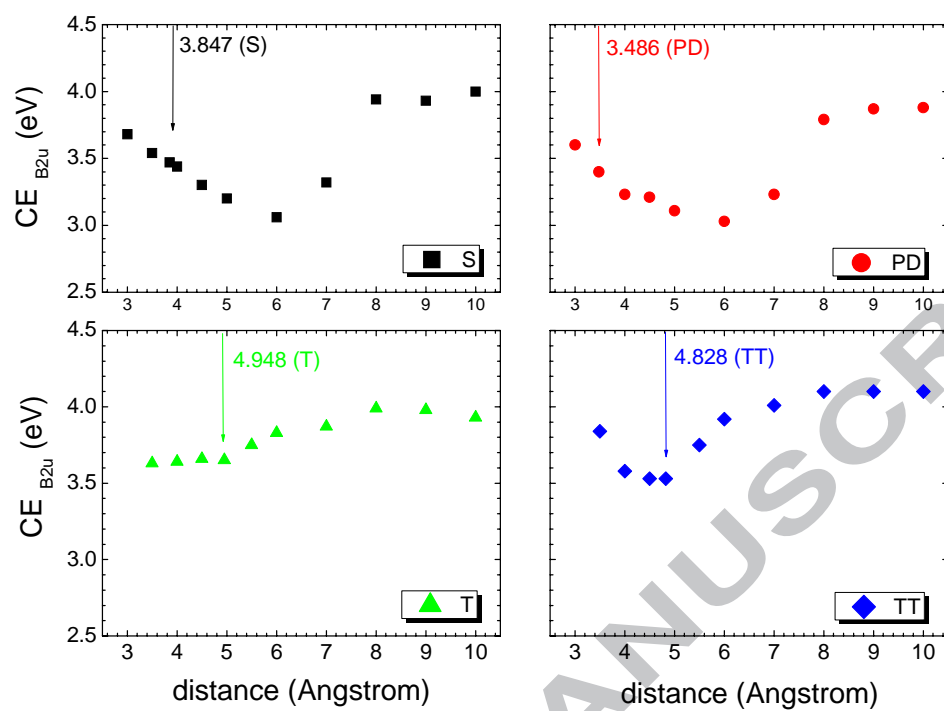


Fig. 3. CE contribution energies of the singlet excited state B_{2u} versus the interbenzene distance of each dimer conformation (in colors).

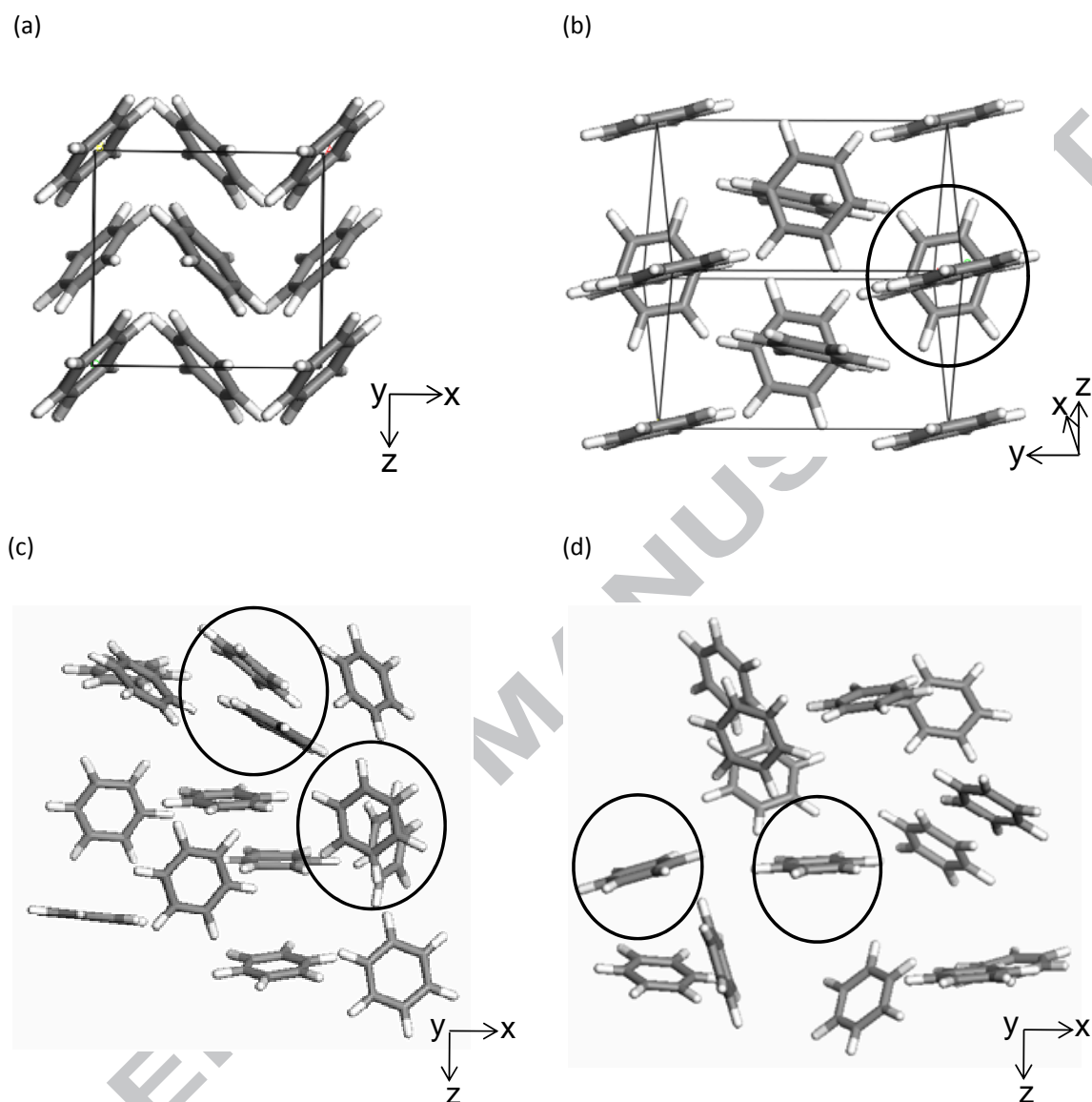


Fig. 4. Benzene aggregate models. Panels (a) and (b) show herringbone structures of the unit cell crystalline solid benzene at different orientations. Panels (c) and (d) show two typical structures of the liquid models with different conformations among all interacting benzenes and with isolated molecules into the aggregate, respectively.

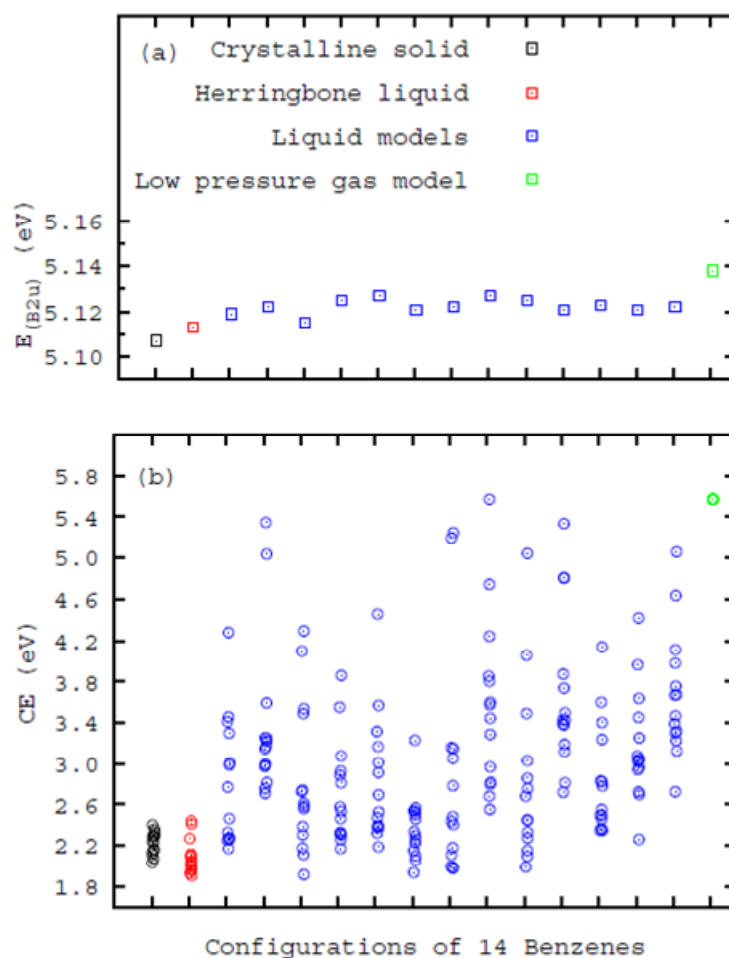
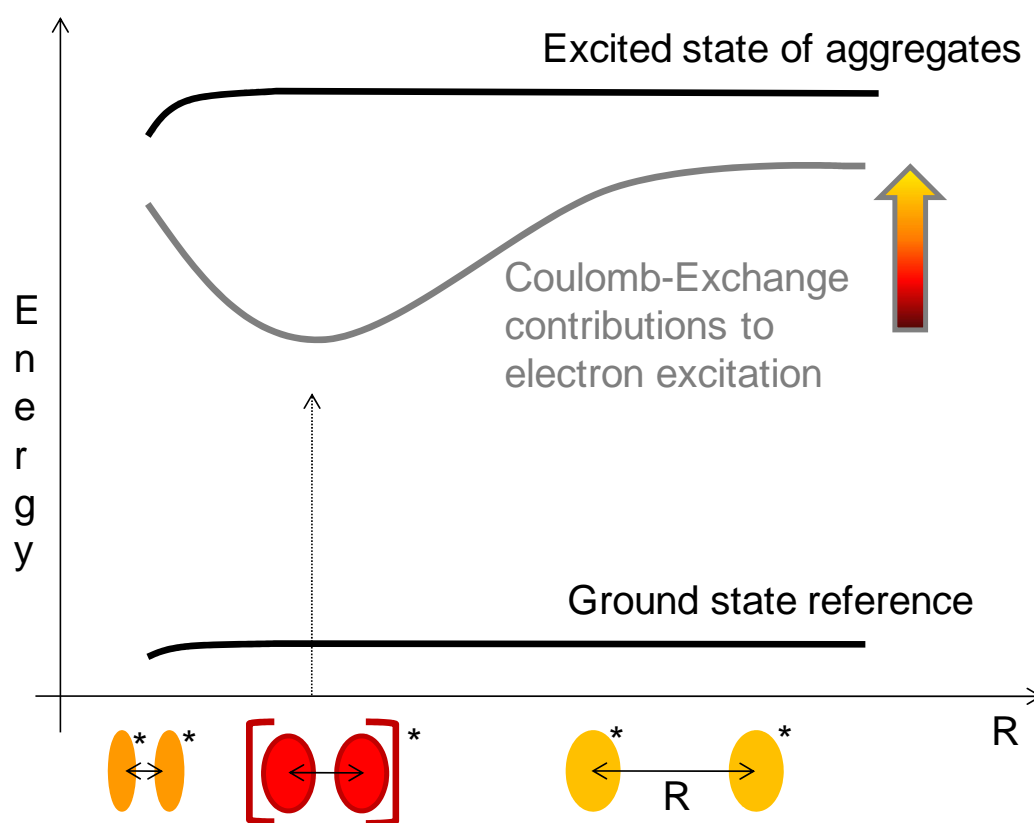


Fig. 5. Dotted squares of panel (a) correspond to the energies of the first singlet excited states of different conformations of 14 benzene molecules: crystalline solid in black, herringbone liquid in red, uncorrelated liquid models in blue and the low pressure gas model in green. Dotted circles in panel (b) show CE contributions to the corresponding low-energy excitations of each conformation (colors are in correspondence to the labels in panel (a)).

Graphical abstract



Research highlights

-Light absorption energy is not the only important feature to describe the behavior of charge distributions upon excitation of electronic systems to a different state.

-Coulomb and Exchange (CE) contributions to electron transition energy regards the stabilizing influence of electron-electron interactions over the excitation energy.

-CE value qualitatively gauge variations in the bounding character of excitons among molecular aggregates.