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Nature of the guest-host interactions for dibromine in the T, P, and H clathrate cages

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The guest-host intermolecular potentials for the ground states of Br₂ in the tetrakaidecahedral (T), pentakaidecahedral (P), and hexakaidecahedral clathrate (H) cages have been calculated using *ab initio* local correlation methods. Applying the local correlation energy partitioning analysis together with first-order symmetry adapted perturbation theory, we obtain a detailed understanding of the nature of the interactions. In particular, the debated question concerning the possible presence of halogen bonding (XB) is carefully analyzed. In the case of the T cage, given its smaller size, the Br–O distance is too short leading to a larger exchange-repulsion for XB orientations which therefore do not represent minima. For the other two cages, the Br–O distance is too large leading to little orbital overlap effects and thus weaker donor-acceptor interactions; however, these orientations coincide with the global minima. *Published by AIP Publishing.* <https://doi.org/10.1063/1.4993465>

INTRODUCTION

The structural, spectroscopic, and dynamical properties of halogen clathrates have been the subject of extensive and recent experimental studies.^{1–7} As a result, many interesting questions have been raised concerning the nature of the guest-host interactions. From the structural point of view, whether halogen bonding (XB) can be of relevance is still debated.^{7,8} In a recent theoretical study,⁹ we found evidence that halogen bonding is present for chlorine in the small dodecahedral cage but absent in the case of bromine inside the tetrakaidecahedral cage (T). We used a combination of analysis of the components of the interaction energy in the ground state but also looked at the interaction in the valence excited states which is expected to be repulsive in the case of XB in the excited states since the electronic transition involved places an electron in the region of the sigma hole characteristic of XB.^{10–13}

The nature of the halogen bond and its relevance in a variety of supramolecular structures has been the subject of intense research in the recent past.^{14–19} It is interesting to point out two pioneer studies in the field of van der Waals complexes which were precursors to the definition of halogen bonding. In 1976, the first high-resolution spectrum of the HF–ClF dimer was obtained²⁰ with the surprising result that instead of the expected hydrogen bonded isomer the most stable species had a bond between F and Cl suggesting the donation of a fluorine free electron pair into the σ^* acceptor orbital at the end of ClF.²¹ From the theoretical side in 1993, a detailed analysis of the intermolecular forces for the Ar–ClF complex using

intermolecular Moller-Plesset perturbation theory²² showed that the global minimum was linear, with an unusually short Ar–Cl distance and polarization playing a significant role. Furthermore the authors pointed out an indentation in the charge distribution around Cl which allowed the close approach of Ar.

In this work, we analyze the guest-host interactions for dibromine in the T(5¹²6²), pentakaidecahedral P(5¹²6³), and hexakaidecahedral H(5¹²6⁴) clathrate cages. We use local correlation methods^{23–27} and their associated energy partitioning analysis.²⁸ Combined with an Symmetry Adapted Perturbation Theory (SAPT) decomposition²⁹ for the HF energy, it provides a complete picture of the main factors determining the dependence of the intermolecular potential on the dihalogen orientation including the possible appearance of halogen bonding interactions.

METHODOLOGY

Geometry and inclusion energy

The geometry of the water in each cage was fixed according to their experimental values^{6,7,30,31} in the TS-I and CS-II structures as has been done in all of our previous studies.^{9,12,13} The oxygen positions were obtained in X-ray experiments and the hydrogen atoms are arranged as to yield cages with low values of the dipole moment.³² The halogen molecule was positioned in the center of the cage and its intramolecular distance was fixed to the optimal value in the isolated diatomic as provided by the DF-LMP2/AVTZ level of theory (2.29 Å). As our main purpose is to model the guest-host interaction as present in the crystal, the water molecules are fixed and no geometry optimization is performed. Test calculations indicate

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that indeed the optimal position of the dihalogen in the cages is very close to the cage center with a displacement of only 0.10 Å.

We use spherical coordinates to rotate the bromine molecule inside the cages: ϕ is the azimuthal angle and θ is the polar angle. The Z axis in the T clathrate cage was located in the direction that joins the centers of the respective hexagonal faces, in the P clathrate cage was along the straight line connecting the most distant oxygens, and in the H clathrate cage was in the direction that joins the centers of the edges that unite two hexagonal faces each on opposing sides of the cage. Notice that due to the different distribution of hydrogen atoms among the oxygen atoms (vertices), the symmetry of the cages is lower than expected for regular polyhedra.

Regarding the basis sets, we use in the case of Br the AVTZ³³ basis and for the H₂O molecules the AVDZ³⁴ set as done in our previous studies.

The angular dependence of the intermolecular potential for the inclusion of Br₂ inside the T, P, and H cages was calculated as

$$E_{Int} = E_{Br_2@T,P,H} - E_{Br_2} - E_{T,P,H}. \quad (1)$$

Although the local methods make an important reduction^{12,13,28} of the basis set superposition error (BSSE), the presence of several water molecules led to a non-negligible BSSE, and for this reason, we have applied the usual counterpoise procedure.^{35,36}

We report total inclusion energies at the DF-LCC2 level of theory.

Local energy partitioning

The methods based on local correlation are able to decompose the inclusion energy for Br₂ inside the water cages. This is achieved by identifying each of the double excitations that are generated in the correlation process.²⁸ Some of them can be associated with different components of the SAPT methodology.²⁹ The SAPT methodology is based on a double many-body perturbation theory where the zeroth-order Hamiltonian corresponds to the non-interacting fragments, and perturbative corrections are made to include correlation in each fragment and of course their interaction. The association between the components obtained by SAPT and those obtained by local correlation has been given in the original work of the local partitioning technique;²⁸ here we only give a brief summary. In the case where double excitations occur in the same fragment, either in bromine molecule or in the water cage, it defines the intramolecular component (E_{Intra}).²⁸ This component is approximately equal to the sum of second-order intramonomer correlation correction to the electrostatic, repulsive exchange, and induction, according to the SAPT theory.²⁸ In the case that simple excitations occur simultaneously in each fragment, it defines the dispersion component (E_{Disp}). This dispersive component is less attractive than the same obtained according to SAPT theory since in the local methodology, the wave function used is completely antisymmetric. On the other hand, in the SAPT methodology, the wave function for each fragment is separated, so the exchange-dispersion component is completely isolated from pure dispersion. If the excitations are single, simultaneous, and crossover of one fragment to the

virtual space of the other one, it will be defined as an exchange-dispersion component ($E_{Exch-Disp}$). This component is very small because the wavefunction used is already antisymmetric. There is another component in the local correlation energy partitioning that is due to a single excitation within one fragment and simultaneously another single excitation of the other fragment to the virtual space of the first. This latter component is called the ionic component (E_{Ionic}) and does not have a direct equivalent in the SAPT methodology. The E_{Ionic} component has been found to be as important as E_{Disp} in hydrogen bonds²⁸ and metallophilic interactions,^{37,38} although it depends more sensitively on the size of the basis set.²⁸ The remaining possible combinations of double excitations are not included since they mainly contribute to the BSSE and this is the way in which local methods approximately eliminate this problem.

Using this scheme of correlation energy excitations, we propose for the inclusion energy of a bromine molecule into the water cages the following equation:

$$E_{Inc}^{Br_2@T,P,H} = {}_{HF}E_{Inc}^{Br_2@T,P,H} + E_{Intra}^{Int} + E_{Exch-Disp} + E_{Disp} + E_{Ionic}, \quad (2)$$

where ${}_{HF}E_{Inc}^{Br_2@T,P,H}$ is the inclusion energy calculated at the HF level of theory and E_{Intra}^{Int} is the difference between E_{Intra} and the correlation energy of both fragments.

In order to evaluate the importance of electrostatic and exchange-repulsion components, we use SAPT to obtain the first-order terms.³⁹ Although the first-order terms include correlation effects, the most important contribution comes from the HF level and therefore they mainly reflect the behavior of the HF components.

To further characterize the possible presence of halogen bonding, we use the natural bonding orbital (NBO) donor-acceptor analysis⁴⁰ as a qualitative tool. We also analyze the electronic shifts for excitation to the lowest valence states, particularly at the attractive or repulsive nature of the interaction in the excited states as has been done in our previous studies.^{9,12,13}

All calculations have been performed with the Molpro 2012 package.⁴¹

RESULTS AND DISCUSSION

Br₂@5¹²6² system

Optimized geometries and energy partitioning analysis

We start by reminding the coordinate system: the Z axis is aligned in the direction that joins the centers of opposing hexagonal faces. In Fig. 1, we show the minimum energy orientation of the dihalogen within the cage. It clearly indicates that canonical XB interactions are not present since the Br–Br–O angle is 146° as opposed to the expected value of 180° and the Br–O distance is 3.15 Å which is slightly shorter than that expected from van der Waals radius estimates of 3.37 Å.¹⁰ The bromine molecule is pointing to a pentagonal face in one direction and near the center of a hydrogen bond on the edge joining two pentagonal faces in the other. This orientation is consistent with recent studies of X-ray diffraction in clathrates⁷ as has been pointed out in a previous study.⁹

FIG. 1. Minimum energy orientation for $\text{Br}_2@5^{12}6^2$ system calculated at DF-LCC2($\text{Br}_2/\text{AVTZ-H}_2\text{O}/\text{AVDZ}$) level of theory. Hydrogen atoms were omitted for clarity.

In Fig. 2, we present the interaction potential energy surfaces of bromine inside the $5^{12}6^2$ cage. The angular potential energy at the HF level [Fig. 2(a)] is repulsive for all

FIG. 2. Contour maps of the angular inclusion energy at (a) DF-HF ($\text{Br}_2/\text{AVTZ-H}_2\text{O}/\text{AVDZ}$) and (b) DF-LCC2($\text{Br}_2/\text{AVTZ-H}_2\text{O}/\text{AVDZ}$) for the ground state of $\text{Br}_2@5^{12}6^2$ system. θ coordinate represent the angle between the Br-Br and Z axes, whereas ϕ is the polar angle in perpendicular plane to Z axis. Z axis is in the direction of the center of the two hexagonal faces.

orientations clearly indicating that the electrostatic component is not sufficient to stabilize the system. Notice the regions of equivalent minima due to the symmetry associated with the homonuclear guest. The energy barrier required to go through from one minimum to another is small and it is roughly $2.5 \text{ kcal mol}^{-1}$ so that at typical temperatures for bromine clathrates (around 0°C), the dibromine can rotate between both configurations. In Fig. 2(b), we present the interaction potential including correlation at the LCC2 level of theory. It is remarkable that the overall angular dependence is quite similar to that obtained without correlation; however, the barrier between equivalent minima is reduced to $1.5 \text{ kcal mol}^{-1}$. The minima in these surfaces are located where the diameter of the cage is larger presumably minimizing the exchange-repulsion component.

In order to analyze in greater detail the relative importance of the exchange-repulsion and electrostatic components, we performed calculations using SAPT as explained in the section titled Methodology and the results are summarized in Fig. 3. First, the exchange-repulsion component [Fig. 3(a)] dominates the electrostatic component [Fig. 3(b)] in all orientations, as expected from the HF results. Two remarkable results can be observed: (a) The overall angular dependence of the

FIG. 3. Contour maps at the SAPT first-order level of theory (a) Exchange component and (b) Electrostatic component for the $\text{Br}_2@5^{12}6^2$ system.

exchange-repulsion term determines the final shape of the interaction potential both at uncorrelated and correlated levels of theory. (b) The angular dependence of the exchange-repulsion and electrostatic terms is completely opposite with the maxima of the former being the minima of the latter. Both observations confirm the fact that the fit of dibromine in the smallest $5^{12}6^2$ cage is quite tight and the stability of the system is dictated by minimizing repulsion.

To further characterize the nature of the interactions, we analyze the correlated part of the interaction using the local energy partitioning analysis and the results are presented in Fig. 4. The intramolecular component [Fig. 4(a)] is repulsive and very anisotropic. Comparing the intramolecular component with the electrostatic component obtained by the SAPT methodology [Fig. 3(b)], we can see that where the first is maximum, the second is minimum and vice versa. This is still true, as will be seen below, for the remaining cages. It is reasonable to assume that this coincidence is due to the well-known HF overestimation of the water dipole moment. This overestimation is corrected at the correlated level by the intramolecular component, since it includes the double excitations in each fragment separately.

Another important correlation is seen between the ionic component [Fig. 4(b)] and both the intramolecular and electrostatic components, specifically the minima of the ionic and electrostatic components coincide. At these geometries, the bromine molecule is nearly collinear with oxygen atoms possessing free electron pairs on opposing sides of the cage favoring the bromine quadrupole to local water dipole interaction at a short Br–O distance of 2.78 Å. Furthermore the ionic component is associated with charge-transfer interactions, and in fact at this geometries, we observe a polarization in the halogen and a considerable charge transfer from oxygen to Br₂ molecule (charges: Br₁ −0.0240 and Br₂ −0.2203), all of this pointing to the presence of halogen bonding interactions at this orientation. This same conclusion had been drawn in a recent study,³ where additionally the donor-acceptor NBO analysis was performed but is now more clearly seen through a more complete understanding of the main components of the intermolecular interactions. The connection between attractive regions for the ionic component and geometries that can favor halogen bonding will be reaffirmed when discussing the other cages. Notice that although halogen bonding orientations may exist in a given cage, the optimal conditions may not be satisfied as is the case in the $5^{12}6^2$ cage where the too short Br–O distance leads to higher interaction energies compared with that of the global minimum where repulsion is minimized.

As pointed out before, the HF inclusion energy is positive and as could be expected the main attractive component at the local correlated level is given by dispersive forces shown in Fig. 4(c). Compared with all other components, it is much more isotropic and we can conclude that for this cage, the overall stability is largely determined by dispersive van der Waals forces. In this context, it is interesting to mention that useful approximate representations of the intermolecular forces could be based on a Hartree-Fock plus dispersion approach. In fact, recent molecular dynamics studies of bromine clathrates^{8,42} have used force fields specifically designed to represent the

FIG. 4. Ground state local correlation energy partitioning of Br₂@ $5^{12}6^2$ system. (a) Intramolecular component, (b) Ionic component, and (c) Dispersion component.

main components of the interaction energy. A challenge in such methods is the proper inclusion of halogen bonding effects which depend on explicit orbital interactions.

Br₂@ $5^{12}6^3$ system

Optimized geometries and inclusion energy

In Fig. 5, we show the orientation of the global energy minimum for the dihalogen inside this cage. The orientation of

FIG. 5. Minimum energy orientation for $\text{Br}_2@5^{12}_6{}^3$ system calculated at DF-LCC2($\text{Br}_2/\text{AVTZ-H}_2\text{O}/\text{AVDZ}$) level of theory. Hydrogen atoms were omitted for clarity.

bromine molecule lies in the straight line between the opposite farthest oxygen atoms which coincides with the Z axis in the chosen coordinate frame.

FIG. 6. Contour maps of the angular inclusion energy at (a) DF-HF ($\text{Br}_2/\text{AVTZ-H}_2\text{O}/\text{AVDZ}$) and (b) DF-LCC2($\text{Br}_2/\text{AVTZ-H}_2\text{O}/\text{AVDZ}$) for the ground state of $\text{Br}_2@5^{12}_6{}^3$ system. θ coordinate represent the angle between the Br-Br and Z axes, whereas ϕ is the polar angle in perpendicular plane to Z axis. Z axis is in the direction connecting two farthest oxygen in the cage.

The general topology of the HF angular potential energy surface is presented in Fig. 6(a). At this level of theory, the surface is completely repulsive with energies in the range between 4 and 8 kcal mol⁻¹. There are two local minima in addition to the global minimum of Fig. 5, and due to the homonuclear symmetry of the diatomic, corresponding equivalent structures appear on the angular inclusion potential for this cage. The non-equivalent local minima are connected by a path with an energy barrier of roughly 2.5 kcal mol⁻¹ indicating the possibility of hindered rotation inside the cage. The total angular surface obtained at the DF-LCC2 level of theory is shown in Fig. 6(b). We again observe that the overall shape is captured at the HF level including the two local minima. The barrier for interconversion between the local minima is 3.3 kcal mol⁻¹ increasing from the HF value but is still small enough to guarantee hindered rotational motion. The difference in stabilization energies between the global and lowest local minimum is only 0.1 kcal mol⁻¹ so that for practical purposes they are isoenergetic.

We now proceed with the analysis of intermolecular energy components starting with the SAPT decomposition for the HF energy as shown in Fig. 7. As was the case for the smaller T cage, the exchange-repulsion term dominates over the electrostatic yielding a purely repulsive interaction at the

FIG. 7. Contour maps at the SAPT first-order level of theory (a) Exchange component and (b) Electrostatic component for the $\text{Br}_2@5^{12}_6{}^3$ system.

HF level; however, some important differences with that case are evident. First, the exchange-repulsion term is significantly less anisotropic as could be expected from the much larger effective diameter (ED) of the P cage: $ED(5^{12}6^3) = 7.0$ Å, $ED(5^{12}6^2) = 5.86$ Å. Second, for this cage, the electrostatic component is crucial in determining the geometries of the local minima as opposed to the case of the T cage where the

electrostatic component was most attractive at geometries which correspond to maxima.

In the case of the local correlation partition components, we notice patterns that have been suggested in the T cage. First, looking at the intramolecular component in Fig. 8(a), there is a clear correspondence between its maxima and the minima of the electrostatic component as expected from the overestimation of the dipole moment of water by HF and the subsequent correction at the correlated level. Also notice that this component is slightly attractive for $(\theta = 0^\circ, \phi)$ and this ends up favoring the global minimum geometry over the lowest local minimum. Second, analyzing the angular dependence of the ionic component in Fig. 8(b), we again observe a correlation between its most attractive regions and those of the electrostatic component [Fig. 7(b)]. At the minimum of the ionic component, the dibromine is oriented collinearly with oxygen atoms on opposite sides that possess free electron pairs suggesting the possibility of halogen bonding. The shortest Br–O distance is 3.22 Å which is only slightly shorter than the estimate from van der Waals radii (3.37 Å), still we decided to perform an NBO donor-acceptor analysis which we used in a previous study⁴ of halogen clathrate cages to characterize halogen bonding. The donor-acceptor stabilization is only 0.6 kcal mol⁻¹ as opposed to 1.7 kcal mol⁻¹ found in the case of Cl₂@5¹² and 2.9 kcal mol⁻¹ in the optimal case of the Br₂–H₂O complex. In that study, we also used the electronic shifts for transition to the lowest excited states ³Π, ¹Π as indicative of halogen bonding in the case of strong blue-shifts. As has been discussed in detail before,¹ the blue-shift reflects the repulsive nature of the interaction in the excited state due to promotion of an electron to the sigma antibonding orbital of the dihalogen acting as an acceptor of electron density from an oxygen lone pair. We calculated the excited states for Br₂@5¹²6³ and find that in all cases the interaction in the excited state is attractive. We conclude that for this cage there are no halogen bonding interactions.

Finally we comment on the dispersion interaction shown in Fig. 8(c). As was the case for the smaller T cage, dispersion represents the largest attractive contribution and is mainly responsible for the overall stability of the system. However notice that in this case it is very nearly isotropic which again points to the possibility of building approximate models for the interaction based on HF + dispersion. As has been discussed in detail above to obtain a highly accurate representation of the guest-host interactions, other correlated terms such as the ionic

FIG. 8. Ground state local correlation energy partitioning of Br₂@5¹²6³ system. (a) Intramolecular component, (b) Ionic component, and (c) Dispersion component.

FIG. 9. Minimum energy orientation for Br₂@5¹²6⁴ system calculated at DF-LCC2(Br₂/AVTZ-H₂O/AVDZ) level of theory. Hydrogen atoms were omitted for clarity.

component associated with polarization and charge transfer should be included.

Br₂@5¹²6⁴ system

Optimized geometries and inclusion energy

In Fig. 9, we show the orientation of global energy minimum for the dihalogen inside this cage. The Z axis is in the direction that joins the centers of two opposing hexagonal faces.

At the DF-HF level of theory, there are two equivalent minima in this cage, as shown in Fig. 10(a). This level of theory, as was the case for the other cages, is not sufficient to predict the stability of the system. However notice that the positive inclusion energies are much smaller than for the previous cases. There is a barrier of 2 kcal mol⁻¹ for interconversion between equivalent minima. The topology of the interaction energy at the DF-LCC2 level of theory is shown in Fig. 10(b). The minimum energy orientation of the halogen molecule is similar to that obtained at an uncorrelated level of theory (DF-HF minimum, $\phi = 146^\circ$ and $\theta = 93^\circ$, DF-LCC2

minimum, $\phi = 146^\circ$ and $\theta = 93^\circ$); however, notice the appearance of two nearby local minima at the correlated level. The barrier of interconversion between the equivalent minima is 1.5 kcal mol⁻¹, indicating a facile interconversion movement. Although 5¹²6³ cage is larger than the 5¹²6⁴ cage, in terms of effective diameter [DE(5¹²6³) = 7.0 Å and DE(5¹²6⁴) = 6.6 Å], the second is closer to spherical symmetry so that in the 5¹²6⁴ cage, the Br₂ molecule has greater freedom in its rotational movement.

SAPT analysis reveals that the exchange-repulsion component [Fig. 11(a)] is more isotropic than the other cages, as expected due to the structure of this cage. In addition, although this component still dominates over the electrostatic component [Fig. 11(b)], its absolute values are significantly smaller than for the previous cages. Therefore for this cage, the electrostatic component, which is much more anisotropic, is more important in determining the overall shape and in fact the minimum geometries coincide with those of the HF surface.

The intramolecular component [Fig. 12(a)] has a repulsive behavior in the region where the electrostatic [Fig. 11(b)] and ionic [Fig. 12(b)] components are most attractive, as expected from the previous analysis and analogous to the behavior found

FIG. 10. Contour maps of the angular inclusion energy at (a) DF-HF (Br₂/AVTZ-H₂O/AVDZ) and (b) DF-LCC2(Br₂/AVTZ-H₂O/AVDZ) for the ground state of Br₂@5¹²6⁴ system. θ coordinate represent the angle between the Br-Br and Z axes, whereas ϕ is the polar angle in perpendicular plane to Z axis. Z axis is in the direction that joins the centers of two opposing hexagonal faces.

FIG. 11. Contour maps at the SAPT first-order level of theory (a) Exchange component and (b) Electrostatic component for the Br₂@5¹²6⁴ system.

FIG. 12. Ground state local correlation energy partitioning of $\text{Br}_2@5^{12}_6{}^4$ system. (a) Intramolecular component, (b) Ionic component, and (c) Dispersion component.

in the other cages. Also the minima of both electrostatic and ionic component are close to the DF-LCC2 minimum so it is natural to again enquire on the possible presence of halogen bonding. As expected the dihalogen is pointing towards opposing oxygen atoms with one free lone pair but again the shortest Br–O distance is too large for optimal halogen bonding: 3.53 Å, longer than the sum of van der Waals radii. The donor-acceptor NBO analysis confirms a weak interaction of

0.35 kcal mol^{-1} smaller than for the P cage. Finally a calculation of the valence excited states for that geometry confirms that the interaction is attractive so all these facts point to not having a halogen bonding interaction.

The dispersion component again is crucial to stabilize the system and as could be expected is highly isotropic [Fig. 12(c)].

SUMMARY AND CONCLUSIONS

We have presented a detailed analysis of the intermolecular interactions for dibromine in the T, P, and H clathrate cages. Our most important findings are as follows:

- The electrostatic plus exchange repulsion components, already included at the HF level, largely determine the overall angular dependence of the interaction. However, the inclusion energy is positive for all orientations. This is in contrast to the case of dihalogens interacting with water clusters where HF yields attractive binding energies mainly determined by halogen bonding interactions.^{11,12}
- For a quantitative treatment of the interactions, it is necessary to include dispersion which is mainly responsible for the stabilization of these systems. Polarization and charge transfer also play a role in determining with precision the structure and energetics of local minima as reflected in the ionic component of the local correlation partitioning.
- Regarding halogen bonding, we find that the electrostatic and ionic components can be used as markers of its presence. However, further analysis such as donor-acceptor interaction strength or topological studies of the electron density should be performed to confirm its presence.
- In all the cages, we find orientations where XB could be present as indicated by electrostatic and ionic components. For the T cage, the orientation does not coincide with minima; in fact, it is a maximum due to the very short Br–O distance and therefore dominance of repulsion. For the P and H cages, there are minima which coincide with markers for halogen bonding; however, in these cases, the Br–O distance is longer than optimum leading to only weak donor-acceptor interaction.
- We conclude that HF plus dispersion models should yield a reasonable description of these systems' interactions though a highly accurate representation should include polarization and charge transfer as represented by the ionic component of the local correlation partitioning scheme. Along the same line, one can consider density functional theory (DFT) studies with careful inclusion of exchange and dispersion.

¹G. Kerenskaya, I. U. Goldschleger, V. A. Apkarian, and K. C. Janda, *J. Phys. Chem. A* **110**, 13792–13798 (2006).

²G. Kerenskaya, I. U. Goldschleger, V. A. Apkarian, E. Fleischer and K. C. Janda, *J. Phys. Chem. A* **111**, 10969–10976 (2007).

³I. U. Goldschleger, G. Kerenskaya, V. Senekerimyan, K. C. Janda, and V. A. Apkarian, *Phys. Chem. Chem. Phys.* **10**(48), 7226–7232 (2008).

⁴I. U. Goldschleger, G. Kerenskaya, K. C. Janda, and V. A. Apkarian, *J. Phys. Chem. A* **112**, 787–789 (2008).

- ⁵M. I. Bernal Uruchurtu, G. Kerenskaya, and K. C. Janda, *Int. Rev. Phys. Chem.* **28**, 223–265 (2009).
- ⁶K. A. Udachin, G. D. Enright, C. I. Ratcliffe, and J. A. Ripmeester, *J. Am. Chem. Soc.* **119**(47), 11481–11486 (1997).
- ⁷K. A. Udachin, S. Alavi, and J. A. Ripmeester, *J. Phys. Chem. C* **117**(27), 14176–14182 (2013).
- ⁸H. Dureckova, T. K. Woo, S. Alavi, and J. A. Ripmeester, *Can. J. Chem.* **93**, 864 (2015).
- ⁹D. Ochoa-Resendiz, F. Batista-Romero, and R. Hernandez-Lamonedá, *J. Chem. Phys.* **145**, 161104 (2016).
- ¹⁰R. Hernández-Lamonedá, V. H. Uc Rosas, M. I. Bernal Uruchurtu, N. Halberstadt, and K. C. Janda, *J. Phys. Chem. A* **112**, 89–96 (2008).
- ¹¹M. I. Bernal Uruchurtu, R. Hernández-Lamonedá, and K. C. Janda, *J. Phys. Chem. A* **113**, 5496–5505 (2009).
- ¹²F. Batista-Romero, P. Pajón-Suárez, M. I. Bernal-Uruchurtu, and R. Hernández-Lamonedá, *J. Chem. Phys.* **143**, 094305 (2015).
- ¹³F. Batista-Romero, A. Gamboa-Suárez, R. Hernández-Lamonedá, and K. C. Janda, *J. Chem. Phys.* **146**, 144311 (2017).
- ¹⁴M. A. Ibrahim, *J. Comput. Chem.* **32**(12), 2564–2574 (2011).
- ¹⁵W. L. Jørgensen and P. Schyman, *J. Chem. Theory Comput.* **8**(10), 3895–3901 (2012).
- ¹⁶M. Kolář and P. Hobza, *J. Chem. Theory Comput.* **8**(4), 1325–1333 (2012).
- ¹⁷K. E. Riley and P. Hobza, *J. Chem. Theory Comput.* **4**, 232–242 (2008).
- ¹⁸T. Clark, M. Hennemann, J. S. Murray, and P. Politzer, *J. Mol. Model.* **13**, 291 (2007).
- ¹⁹S. Kozuch and J. M. L. Martin, *J. Chem. Theory Comput.* **9**, 1918–1931 (2013).
- ²⁰K. C. Janda, W. Klemperer, and S. E. Nowick, *J. Chem. Phys.* **64**, 2698 (1976).
- ²¹S. E. Nowick, K. C. Janda, and W. Klemperer, *J. Chem. Phys.* **65**, 5115 (1976).
- ²²J. Sadlej, G. Chałasiński, and M. M. Szczyński, *J. Chem. Phys.* **99**, 3700 (1993).
- ²³M. Schütz, G. Hetzer, and H.-J. Werner, *J. Chem. Phys.* **111**(13), 5691 (1999).
- ²⁴G. Hetzer, M. Schütz, H. Stoll, and H. J. Werner, *J. Chem. Phys.* **113**, 9443 (2000).
- ²⁵M. Schutz, H. J. Werner, R. Lindh, and F. R. Manby, *J. Chem. Phys.* **121**(2), 737–750 (2004).
- ²⁶H. J. Werner and M. Schütz, *J. Chem. Phys.* **135**(14), 144116 (2011).
- ²⁷D. Kats, T. Korona, and M. Schütz, *J. Chem. Phys.* **125**(10), 104106 (2006).
- ²⁸M. Schütz, G. Rauhut, and H. J. Werner, *J. Phys. Chem. A* **102**, 5997–6003 (1998).
- ²⁹B. Jeziorski, R. Moszynski, and K. Szalewicz, *Chem. Rev.* **94**, 1887–1930 (1994).
- ³⁰S. Alavi, J. A. Ripmeester, and D. D. Klug, *J. Chem. Phys.* **123**, 024507 (2005).
- ³¹D. P. Schofield and K. J. Jordan, *J. Phys. Chem. A* **113**, 7431–7438 (2009).
- ³²V. Buch, P. Sandler, and J. Sadlej, *J. Phys. Chem. B* **102**, 8641–8653 (1998).
- ³³A. K. Wilson, D. E. Woon, K. E. Peterson, and T. H. Dunning, *J. Chem. Phys.* **110**, 7667 (1999).
- ³⁴R. A. Kendall, T. H. Dunning, and R. J. Harrison, *J. Chem. Phys.* **96**(9), 6796 (1992).
- ³⁵S. F. Boys and F. Bernardi, *Mol. Phys.* **19**, 553–566 (1970).
- ³⁶F. B. van Duijneveldt, J. G. C. M. van Duijneveldt-van de Rijdt, and J. H. van Lenthe, *Chem. Rev.* **94**, 1873–1885 (1994).
- ³⁷N. Runeberg, M. Schütz, and H.-J. Werner, *J. Chem. Phys.* **110**(15), 7210 (1999).
- ³⁸L. Magnko, M. Schweizer, G. Rauhut, M. Schütz, H. Stoll, and H.-J. Werner, *Phys. Chem. Chem. Phys.* **4**(6), 1006–1013 (2002).
- ³⁹G. Jansen and A. Heßelmann, *J. Phys. Chem. A* **105**, 11156 (2001).
- ⁴⁰A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.* **88**, 899–926 (1988).
- ⁴¹H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz *et al.*, MOLPRO, version 2012.1, a package of *ab initio* programs, 2012, see <http://www.molpro.net>.
- ⁴²H. Dureckova, T. K. Woo, and S. Alavi, *J. Chem. Phys.* **144**, 044501 (2016).