Theor Chem Acc (2000) 104:195–198
DOI 10.1007/s002140000136

Theoretical
Chemistry Accounts

Regular article

Nature and importance of three-body interactions in the $(H_2O)_2HCl$ trimer

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Received: 15 September 1999 / Accepted: 3 February 2000 / Published online: 2 May 2000

Abstract. The nature and importance of nonadditive three-body interactions in the $(H_2O)_2HCl$ cluster have been studied by the supermolecule coupled-cluster method and by symmetry-adapted perturbation theory (SAPT). The convergence of the SAPT expansion was tested by comparison with the results obtained from the supermolecule coupled-cluster calculations including single, double, and noniterative triple excitations [CCSD(T)]. It is shown that the SAPT results reproduce the converged CCSD(T) results within 3% at worst. The SAPT method has been used to analyze the three-body interactions for various geometries of the $(H_2O)_2HCl$ cluster. It is shown that the induction nonadditivity is dominant, but it is partly quenched by the first-order Heitler–London-type exchange and higher-order exchange–induction/deformation terms. This implies that the classical induction term alone is not a reliable approximation to the nonadditive energy and that it will be difficult to approximate the three-body potential for $(H_2O)_2HCl$ by a simple analytical expression. The three-body energy represents as much as 21–27% of the pair CCSD(T) intermolecular energy.

Key words: Symmetry-adapted perturbation theory – Three-body interactions – Ab initio calculations – $(H_2O)_2HCl$

1 Introduction

Molecular clusters formed by H_2O and HCl are the subject of continuing investigations in the fields of atmospheric chemistry, catalytic reactions, and surface chemistry. One route to understand the observed properties of the $(H_2O)_nHCl$ clusters is through the computations of intermolecular potentials for these clusters followed by quantum mechanical or classical simulations. In a recent article [1] we reported a theoretical study of the trimer $(H_2O)_2HCl$. Our theoretical predictions concerning the minimum energy structure and the nuclear quadrupole coupling constants of the trimer, as well as the qualitative picture of the tunneling dynamics, were in very good agreement with the high-resolution spectroscopic measurements in the microwave region [2]. However, a theoretical calculation of the spectra requires the knowledge of the full potential-energy surface, including the nonadditive three-body effects. In this article we address the question of the nature and importance of nonadditive three-body interactions in $(H_2O)_2HCl$.

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2 Methods of calculation

In the present work both symmetry-adapted perturbation theory (SAPT) and the supermolecule approach have been used. The supermolecule interaction energies were represented by the following many-body expansion,

$$E_{\rm int}^{\rm SM} = \sum_{N=2}^{3} E_{\rm int}^{\rm SM}(N,3) \ , \tag{1}$$

where $E_{\rm int}^{\rm SM}(N,M)$ denotes the N-body contribution to the supermolecule interaction energy for a cluster of M molecules and the superscript SM is a shorthand notation for the supermolecule method used in the calculations. The superscript CCSD(T) is used for the coupled-cluster single and double excitations calculations with a noniterative inclusion of the connected triple excitations. The pair and three-body interaction energies are given by the standard formulas

$$E_{\rm int}^{\rm SM}(2,3) = \frac{1}{2}\sum_{i\neq j=1}^{3}\left(E_{\rm X_iX_j}^{\rm SM} - E_{\rm X_i}^{\rm SM} - E_{\rm X_j}^{\rm SM}\right) \ , \tag{2}$$

$$E_{\rm int}^{\rm SM}(3,3) = E_{\rm X_1X_2X_3}^{\rm SM} - E_{\rm X_1X_2}^{\rm SM} - E_{\rm X_2X_3}^{\rm SM} - E_{\rm X_3X_1}^{\rm SM} + E_{\rm X_1}^{\rm SM} + E_{\rm X_2}^{\rm SM} + E_{\rm X_3}^{\rm SM} \ , \tag{3}$$

where $E_{\rm X_1\cdots X_m}^{\rm SM}$ denotes the total energy of a system composed of molecules $\rm X_1, \ldots, X_m$. The supermolecular energies were corrected

for the basis set superposition error with the counterpoise method of Boys and Bernardi [3] by performing all the calculations of the N-body interaction energies ($N = 2, 3$) in the full basis of the trimer.

In the SAPT calculations the interaction energy of the cluster is given by

$$E_{\rm int}^{\rm SAPT} = E_{\rm int}^{\rm SAPT}(2,3) + E_{\rm int}^{\rm SAPT}(3,3) \ , \tag{4}$$

where $E_{\rm int}^{\rm SAPT}(N,M)$ denotes the N-body SAPT interaction energy for a cluster of M molecules. The pair interaction energies were taken from Ref. [1], while the three-body interaction energy in SAPT was represented as

$$E_{\rm int}^{\rm SAPT}(3,3) = E_{\rm ind}^{(2)}(3,3) + E_{\rm ind}^{(3)}(3,3) + E_{\rm ind-disp}^{(3)}(3,3) + E_{\rm disp}^{(3)}(3,3) + E_{\rm exch}(3,3) \ . \tag{5}$$

The consecutive terms on the right-hand side of Eq. (5) denote the nonadditive second- and third-order induction energies, the induction–dispersion and dispersion terms, and the exchange contribution, respectively. See Ref. [4] for precise definitions of these quantities and their physical interpretation. The exchange term contains several contributions,

$$E_{\rm exch}(3,3) = E_{\rm HL}^{(1)}(3,3) + E_{\rm exch-ind}^{(2)}(3,3) + E_{\rm exch-ind}^{(3)}(3,3) + \delta E_{\rm int}^{\rm HF}(3,3) + E_{\rm exch-disp}^{(2)}(3,3) + E_{\rm exch}^{\rm MP2}(3,3) \ . \tag{6}$$

Here, $E_{\rm HL}^{(1)}(3,3)$ is the Heitler–London nonadditive energy, $E_{\rm exch-ind}^{(2)}(3,3)$ and $E_{\rm exch-ind}^{(3)}(3,3)$ denote the second- and third-order exchange–induction terms, and $E_{\rm exch-disp}^{(2)}(3,3)$ is the exchange–dispersion nonadditivity. The two additional exchange contributions, $\delta E_{\rm int}^{\rm HF}(3,3)$ and $E_{\rm exch}^{\rm MP2}(3,3)$, approximate the nonadditive exchange–deformation effects, $[\delta E_{\rm int}^{\rm HF}(3,3)]$, and the sum of the first-order exchange–correlation and exchange–induction–dispersion terms, $[E_{\rm exch}^{\rm MP2}(3,3)]$: see Ref. [5] for their precise definitions. In practice, the induction, induction–dispersion, and dispersion terms were evaluated within the random-phase approximation [4], while the exchange contributions were computed with the neglect of the intramolecular correlation effects [4]. The computational approach to nonadditive interactions in the $(H_2O)_2HCl$ trimer is the same as in our previous work on Ar_2HF and $(H_2O)_n$ [5, 6].

In the present work we investigated the lowest energy structures of the $(H_2O)_2HCl$ trimer, i.e. the minima and the saddle points on the potential-energy surface of the trimer. The geometries corresponding to these structures were taken from Ref. [1]. The CCSD(T) calculations were made with the Gaussian 94 code [7]. In all calculations we used the augmented correlation-consistent polarized valence double zeta basis set [8]. In the supermolecule CCSD(T) calculations we kept the 1s orbitals frozen. SAPT calculations of the nonadditive interaction energies were made with the program SAPT3 [9]. The SAPT three-body energies were always computed with the full basis of the trimer.

3 Numerical results and discussion

The interaction energies and their decomposition into pair and three-body contributions are reported in Table 1 for various structures of the $(H_2O)_2HCl$ trimer. A schematic representation of the geometries considered in Table 1 is given in Fig. 1. The details of the geometries can be obtained from the authors on request. An inspection of Table 1 shows that the nonadditive three-body effects are very important. The pair interaction energy represents only 73–79% of the total interaction energy of the trimer. Thus, the inclusion of the nonadditive three-body interactions is essential to obtain a correct potential-energy surface for the $(H_2O)_2HCl$ trimer.

Before we look at the physical origins of the nonadditive interactions in the $(H_2O)_2HCl$ trimer, let us first discuss the accuracy of the SAPT results. An inspection of Table 1 shows that the performance of the SAPT approach is excellent both for the pair and nonadditive interactions. Indeed, the comparison of the SAPT and CCSD(T) pair and three-body interaction energies shows that the deviations between the two sets of results are of the order of 1–2%, the largest being 3%. This level of agreement between the results from highly correlated supermolecule and perturbative calculations suggests that the SAPT method is a good tool to describe pair interactions in the clusters of H_2O and HCl. One should note, however, that the nonadditive interaction energy is dominated by the Hartree–Fock contribution. Since our three-body SAPT interaction energy fully includes the Hartree–Fock term, the observed very good convergence of the SAPT expansion for the three-body energy may be due to this fact.

The decomposition of the SAPT nonadditive energies into various physical contributions as defined by Eqs. (5) and (6) is reported in Table 2. An inspection of this table shows that the induction terms are dominant. The second-order induction contribution is by far the largest. This could be expected since it describes the interactions of permanent moments of one molecule with the moments induced on the second molecule by the electrostatic field of the third one; however, higher induction terms are not negligible. The third-order induction represents about 20% of the total three-body effect. Hence, in order to include the induction effects by iteration [10] of the induced dipole moments and the corresponding electric fields, one should proceed with this iteration beyond the first step. As in the case of the H_2O clusters [6], other long-range contributions, such as the third-order induction–dispersion energy and the Axilrod–Teller three-body dispersion energy, are very small. They represent less than 3% of the total three-body energy and cancel one another to a large extent.

Table 1. Pair, three-body, and total interaction energies (kcal/mol) for various geometries of the $(H_2O)_2HCl$ trimer

	ud	uu	$p_O u$	up_{Cl}	ub_{Cl}	bp_{Cl}
$E_{\rm int}^{\rm SAPT}(2,3)$	−9.786	−9.467	−9.512	−9.617	−9.460	−8.360
$E_{\rm int}^{\rm CCSD(T)}(2,3)$	−9.617	−9.306	−9.312	−9.323	−9.380	−8.318
$E_{\rm int}^{\rm SAPT}$ (3,3)	−2.662	−2.540	−2.507	−2.038	−2.051	−1.978
$E_{\rm int}^{\rm CCSD(T)}(3,3)$	−2.612	−2.498	−2.467	−1.999	−2.005	−1.927
$E_{\rm int}^{\rm SAPT}$	−12.448	−12.007	−12.019	−11.655	−11.511	−10.337
$E_{\rm int}^{\rm CCSD(T)}$	−12.229	−11.804	−11.779	−11.321	−11.385	−10.245

The smallness of the induction–dispersion energy is quite unexpected. As shown in Ref. [4] this term describes the pair dispersion interaction between an unperturbed molecule A and a molecule B deformed (to the first order) by the electrostatic field of molecule C. Given the relative importance of the pair dispersion interactions in the $(H_2O)_2HCl$ trimer [1] and the large dipole moments of the H_2O and HCl monomers, one would expect a large nonadditive induction–dispersion effect. In contrast, the three-body exchange effects are substantial, so one cannot restrict the treatment of the nonadditive effects in the $(H_2O)_2HCl$ trimer to the classical induction terms only. One may note that for all structures considered in the present work the nonadditive exchange effect is always attractive.

Since the nonadditive exchange effects play such an important role, it is interesting to analyze their decomposition into various contributions as defined by Eq. (6). The results reported in Table 2 show that $E_{\mathrm{exch}}(3,3)$ is not dominated by a single term. Surprisingly, for all geometries of the $(H_2O)_2HCl$ trimer considered in the present work the Heitler–London nonadditivity is not the largest contribution. In fact, the Hartree–Fock exchange–deformation contribution, $\delta E_{\mathrm{int}}^{\mathrm{HF}}(3,3)$, is the largest one and the remaining part comes from the Heitler–London term and the exchange–induction energies. The exchange–dispersion and the second-order Møller–Plesset exchange contributions are relatively less important. They are opposite in sign and cancel each other to a large extent.

4 Conclusions

In this article we reported the first analysis of the nature and importance of the three-body interactions in the

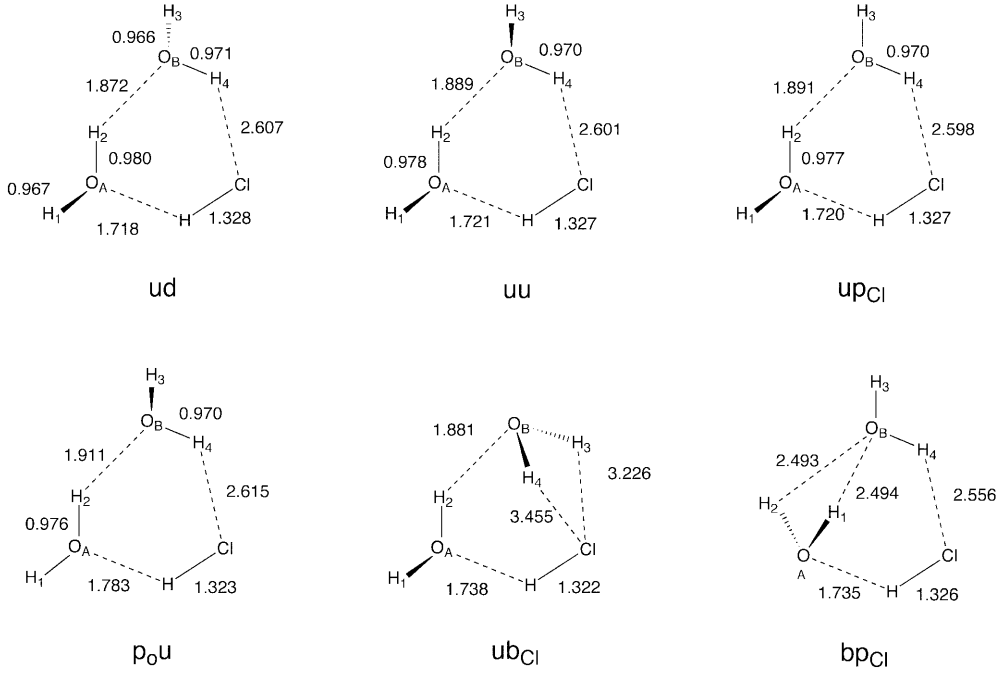

Fig. 1. Geometry of the global (*ud*) and local (*uu*) minima and of the saddle points (p_Ou, up_{Cl}, ub_{Cl}, and bp_{Cl}) on the potential-energy surface of the $(H_2O)_2HCl$ trimer. Distances in Å

Table 2. Components (kcal/mol) of the nonadditive interaction energy for various geometries of the $(H_2O)_2HCl$ trimer

	ud	uu	p_Ou	up_{Cl}	ub_{Cl}	bp_{Cl}
$E_{\mathrm{ind,resp}}^{(2)}$ (3,3)	−1.104	−1.069	−1.052	−0.992	−0.923	−0.929
$E_{\mathrm{ind,resp}}^{(3)}$ (3,3)	−0.554	−0.518	−0.492	−0.403	−0.454	−0.427
$E_{\mathrm{ind-disp,RPA}}^{(3)}$ (3,3)	−0.094	−0.073	−0.062	−0.055	−0.083	−0.076
$E_{\mathrm{disp,RPA}}^{(3)}$ (3,3)	0.064	0.061	0.060	0.050	0.057	0.060
E_{exch} (3,3)	−0.974	−0.941	−0.962	−0.638	−0.649	−0.605
$E_{\mathrm{HL}}^{(1)}$ (3,3)	−0.255	−0.236	−0.234	−0.156	−0.183	−0.186
$E_{\mathrm{exch-ind,resp}}^{(2)}$ (3,3)	−0.194	−0.188	−0.197	−0.133	−0.123	−0.116
$E_{\mathrm{exch-ind}}^{(3)}$ (3,3)	0.107	0.063	0.031	0.012	0.130	0.096
$\delta E_{\mathrm{int}}^{\mathrm{HF}}$ (3,3)	−0.652	−0.603	−0.587	−0.392	−0.508	−0.438
$E_{\mathrm{exch-disp}}^{(2)}$ (3,3)	0.111	0.104	0.102	0.081	0.093	0.088
$E_{\mathrm{exch}}^{\mathrm{MP2}}$ (3,3)	−0.090	−0.081	−0.077	−0.050	−0.058	−0.049
$E_{\mathrm{int}}^{\mathrm{SAPT}}$ (3,3)	−2.662	−2.540	−2.507	−2.038	−2.051	−1.978
$E_{\mathrm{int}}^{\mathrm{CCSD(T)}}$(3,3)	−2.612	−2.498	−2.467	−1.999	−2.005	−1.927

$(H_2O)_2HCl$ trimer. Our theoretical analysis was based on the SAPT decomposition as well as on results obtained from supermolecule coupled-cluster calculations. The results obtained can be summarized as follows:

1. The assumption of the pairwise additivity of the interaction in the $(H_2O)_2HCl$ trimer is not correct. The nonadditive three-body contribution is very large and represents as much as 21–27% of the pair interaction energy.
2. The convergence of the symmetry-adapted perturbation expansion for the pair and the three-body interactions in the $(H_2O)_2HCl$ trimer is very good. For both two- and three-body interaction energies the SAPT results reproduce the reference CCSD(T) values with errors smaller than 3%.
3. The three-body potential for $(H_2O)_2HCl$ is dominated by the second-order induction nonadditivity; however, the third-order induction is nonnegligible and represents about 20% of the total three-body effect. The three-body exchange term is a substantial stabilizing contribution to the total three-body potential. All this information is important for the development of a realistic model of the three-body interactions that can be applied in the theoretical modeling of HCl absorption on the surface of ice.

Acknowledgements. The calculations were performed in Grenoble, in Warsaw, and at the Centre IDRIS (project 991219) of CNRS (Orsay, France). CNRS, the University Joseph Fourier of Grenoble, and the University of Warsaw are acknowledged for providing the computer facilities. The travel expenses of A.M. and R.M. were supported by the French Ministère des Affaires Etrangères and by the Polish Scientific Research Council KBN (projet concerté de coopération scientifique et technique entre la France et la Pologne, project no. 7137).

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