Theor Chim Acta (1992) 82: 165–187

Theoretica
Chimica Acta

Analysis of the interaction energy in the Cu^+-H_2O and Cl^--H_2O systems, with CP corrections to the BSSE of the separate terms, and MC simulations of the aqueous systems with and without CP corrections

M. Natália D. S. Cordeiro[1], **Roberto Cammi**[2], **José A. N. F. Gomes**[1], **and Jacopo Tomasi**[3]

[1] Departamento de Química, Faculdade de Ciências do Porto, 4000 Porto, Portugal

[2] Istituto di Chimica Fisica, Università di Parma, Viale delle Scienze 7, I-43100 Parma, Italia

[3] Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italia

Received October 31, 1990/Accepted May 24, 1991

Abstract. The interaction energy ΔE of the systems Cu^+-H_2O and Cl^--H_2O has been computed over a wide range of distances and orientations with the MINI-1 basis set in the SCF approximation. The interaction energy has been decomposed according to the Kitaura–Morokuma scheme, with and without counterpoise (CP) corrections to the basis set superposition error. The importance of this correction is analysed by its effect upon Monte Carlo calculations of the Cu^+-water and Cl^--water systems, using two-body potentials without and with CP corrections. The effect of CP corrections on the ΔE analysis is similar to that found in other systems of analogous composition (of the general type ion plus neutral ligands), but with significant differences in the details. The effect of the CP corrections to the interaction potential, and then on the results of the Monte Carlo simulations, is small for the Cu^+ ion, but remarkable for the Cl^- ion.

Key words: Bimolecular interactions – Basis set superposition error – Counterpoise corrections – Monte Carlo simulations – Cu^+-H_2O – Cl^--H_2O

1 Introduction

The numerous theoretical determinations of bimolecular interaction energies available in the literature may be roughly divided into two classes, differing in the scope, and to some extent, in the strategy of the investigation. One class is aimed at obtaining interaction potentials to be used in computer simulations. There is an almost standard procedure, consisting in a balanced sampling of the nuclear configuration space (often reduced to a six dimensional space, keeping fixed the internal geometry of the partners) giving as output a number of interaction energy values sufficient to secure a reliable analytical expression of the potential. The interpretation of the interaction is not the primary goal and it is rarely performed.

The second class of computations is directed to the study of chemical interactions. Attention is focused on the most reactive interactions, giving rise to stable non-covalent complexes, or to real chemical interactions. Here a balanced sampling of the whole configuration space is not strictly necessary (and seldom done). More important is a closer scrutiny of the interaction act, in which the dissection of the interaction energy into physically meaningful components plays an important role.

In both classes the correction of the non-covalent interaction energies via the counterpoise procedure (CP) has been considered. In a well known paper, Kolos [1] showed how it is possible to get reliable interaction potentials to be used in computer simulations, using calculations with small basis sets, when the basis set superposition error (BSSE) present in these calculations is corrected with the CP procedure of Boys and Bernardi [2]. This approach has been adopted in several subsequent determinations of analytical expressions of the interaction potential.

In the detailed study of the reactive interaction the analysis of the reaction act has been accompanied in the last few years by the inclusion of CP corrections to the separate components of ΔE. There are now several approaches available, to be used with variational procedures [3, 4] or with perturbation theory approaches [5, 6]. The Pisa's group has applied its own version of decomposition analysis with CP corrections [4] to a systematic survey of non-covalent interactions giving rise to stable complexes; complexes of different chemical nature were studied with a fairly large number of basis sets. The main contributions regard hydrogen-bonded complexes (with neutral partners), cation-neutral complexes, and anion-neutral complexes; some of these papers will be quoted in the following text when necessary. Complexes of other types have also been examined, albeit in a less systematic way, but with one exception [4], only attractive portions of the configuration space have been considered. Analogous studies performed by other groups also neglect the repulsive portions of the configuration space.

We consider it convenient, however, to extend the analysis of intramolecular interactions to repulsive situations. A better understanding of the mechanism of these repulsions could be of some help in elaborating the form of the analytical potential that is to be fitted to the numerical data.

In a molecular system there is always a balance between attractions and repulsions. When the chemical groups are assumed as basic entities in the theoretical analysis at the molecular and supramolecular level, it is necessary to know and understand the attractive and the repulsive components at the same level of accuracy. The analysis of attractive molecular interactions has made important contributions to understanding intramolecular effects. Limiting our consideration to the work performed by the Pisa's group, the results coming from this approach have been amply documented (see e.g. [7]). Analogous contributions have been done by other groups (a selection of the pertinent literature, and a general discussion is reported in [7]). A similar analysis of repulsive interactions is presumed to give additional contributions to our understanding of molecular systems.

A first attempt in this direction is reported in the present paper. We have selected examples coming from a very simple class of two-body systems, composed of water and a second partner of atomic nature.

The combination of these basic indications, and the scientific interests of the persons involved in the present investigation, prompted us to select the system Cu^+-H_2O for which separate investigations [8] have been published. The analysis of this system is accompanied by the analysis of a second system Cl^--H_2O, which in some sense is complementary to the preceding one.

2 Method

The interaction energy of the two-body system A-B is computed at the SCF level and accompanied by corrections performed with the CP procedure. The resulting interaction energies, ΔE_{AB} and $\Delta E_{AB}{}^{CP}$ are decomposed according to the Kitaura–Morokuma (KM) scheme [9] or the CP corrected KM scheme proposed by Cammi et al. [4]. Descriptions and justifications of the decomposition scheme and of the corresponding CP corrections have been repeated in many papers. For the reader's commodity, it will suffice to rewrite here only the formal expressions used later on.

The interaction energy of an A-B complex at distance $\boldsymbol{R}$, without the CP corrections,

$$\Delta E_{AB}(\boldsymbol{R}) = E_{AB}(\boldsymbol{R}) - (E_A + E_B) \tag{1}$$

is decomposed as:

$$\Delta E_{AB}(\boldsymbol{R}) = ES(\boldsymbol{R}) + PL(\boldsymbol{R}) + EX(\boldsymbol{R}) + CT(\boldsymbol{R}) + MIX(\boldsymbol{R}) \tag{2}$$

where ES, PL, EX, CT and MIX are the electrostatic, polarization, exchange-repulsion, charge-transfer and coupling components, respectively.

The corresponding energy after the CP corrections:

$$\Delta E_{AB}{}^{CP}(\boldsymbol{R}) = E_{AB}(\boldsymbol{R}) - (E_A{}^{CP} + E_B{}^{CP}) \tag{3}$$

when decomposed has the general form:

$$\Delta E_{AB}{}^{CP}(\boldsymbol{R}) = ES(\boldsymbol{R}) + PL(\boldsymbol{R}) + EX^{CP}(\boldsymbol{R}) + CT^{CP}(\boldsymbol{R}) + MIX^{CP}(\boldsymbol{R}) \tag{4}$$

The difference between corrected and uncorrected interaction energies as well as their energetic components are given by:

$$\Delta^{TOT}(\boldsymbol{R}) = \Delta E_{AB}{}^{CP}(\boldsymbol{R}) - \Delta E_{AB}(\boldsymbol{R}) = \Delta^{EX}(\boldsymbol{R}) + \Delta^{CT}(\boldsymbol{R}) + \Delta^{MIX}(\boldsymbol{R}) \tag{5}$$

and each component of the CP corrections can be further divided into the following monomeric contributions:

$$\Delta^{X}(\boldsymbol{R}) = \Delta_A{}^{X}(\boldsymbol{R}) + \Delta_B{}^{X}(\boldsymbol{R}) \quad X = TOT, EX, CT, MIX \tag{6}$$

In this paper we have kept water at a fixed internal geometry, so we have not introduced in the previous expressions a term (denoted by DEF or REL according to the case) that takes into account energy contributions not amenable to the simple computational scheme summarized in Eq. (1). The $\mathfrak{R}$ space is thus limited to the configurational space of the dimer.

We note that there are other decomposition schemes, other definitions of the CP corrections, and other decompositions of these CP corrections. An exhaustive examination of all these variants is not considered here.

3 Computational details

Given a fixed geometry for the water molecule, the position of this molecule relative to the ionic centre is described by three coordinates. In the present work, we have limited the scope of these variables to the contemporary variation of the distance R between the ionic centre and the oxygen atom, and one of the two angles that describe the orientation of the water molecule. The angles are defined with reference to the starting conformation reported in Fig. 1.

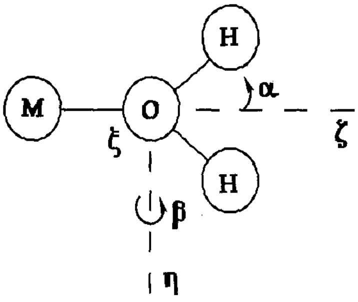

Fig. 1. Reference position of water molecule. The water molecule is assumed coplanar with the ion and has the rotation axis colinear with the ion-oxygen direction. The local axes ξ, η, ζ are defined as shown, with the ξ-axis perpendicular to the plane of the figure drawing. The conformations used in this study are obtained from this original one by rotating one angle, either the angle α around the ξ-axis or the angle β around the η-axis

Instead of the Eulerian rotations we use rotations around three fixed axes, as is common practice in the study of molecular interactions. A *configuration* in the $\mathfrak{R}$ space is defined by the values of the three parameters R, α, β and a *conformation* by the value of the two angles. A rotation around the ξ axis (angle α) maintains the molecule in the plane and a rotation around the η axis (angle β) takes the H atoms out of the reference plane, keeping the symmetry plane of the complex. Unless otherwise specified, the indication of a single angle means that the other one is kept equal to its original zero-value.

In all calculations the MINI-1 basis set [10] (with Tatewaki and Huzinaga [11] scale factors for the hydrogen atoms) was used. The *d* orbitals are described by a set of 6 functions. The MINI-1 basis set has been employed in several previous calculations on analogous systems, and its relatively good performance was originally signalled by Sauer and Hobza [12].

The experimental geometry of the water molecule was used, i.e., $r_{OH} = 0.9572$ Å and $< \mathrm{HOH} = 104.5°$ [13].

The calculations were performed on the GOULD 32/8705 and GOULD NP1 computers (Pisa) using a modified version of Monstergauss [14], supplemented by the necessary subroutines to perform the decompositions and CP corrections.

4 The Cu^+–H_2O system

4.1 The effect of the CP *correction on the interaction energy*

The total CP correction to the interaction energy, i.e., Δ^{TOT} defined in Eq. (5), depends on the distance between partners, as well as on their relative orientation. Starting from vanishingly small angles and large distances, the correction attains, for the equilibrium configuration ($\alpha, \beta = 0°$ and $R \approx 2$ Å), some 20% of the interaction energy and much larger values for shorter, repulsive, distances. This is clear from Fig. 2 where the dependence of the interaction energy on R is depicted for an attractive and a repulsive configuration. The CP correction has the effect of making the stability well shallower and shifting the equilibrium position outwards.

The angular dependence (in α or β) of the CP correction may be seen more clearly in the plots of Fig. 3, where that dependence is displayed for two particular R distances. This correction, however complex, does not appear to change the major qualitative features of the rotational potentials. The 2-d potential well around the equilibrium configuration (α, $\beta = 0°$) is made shallower and narrower by the correction.

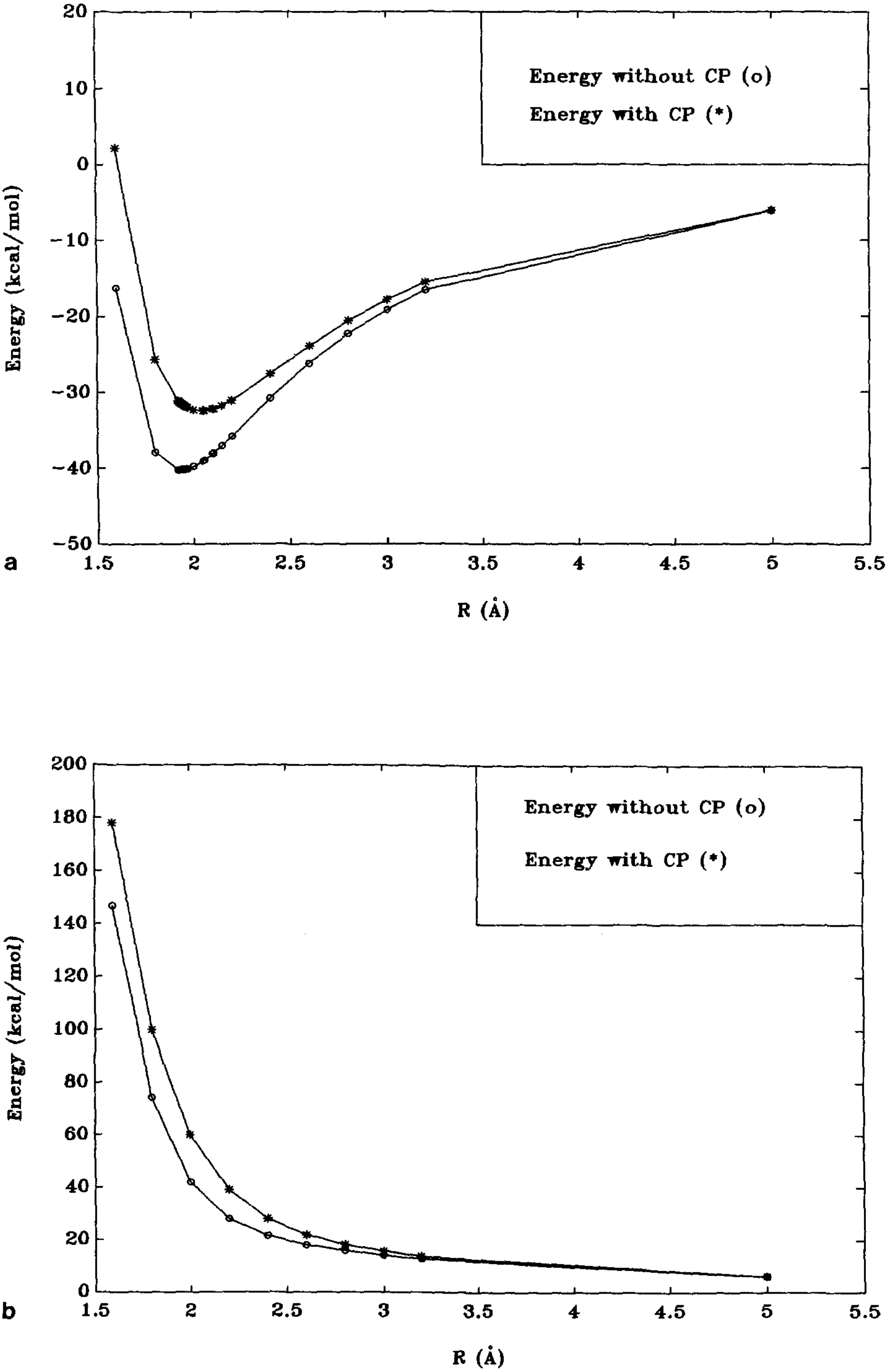

Fig. 2a,b. Interaction energies of the Cu^+–H_2O system as a function of the distance R, without and with CP corrections: **a** The attractive Cu^+–H_2O interaction with $\alpha = 0°$; **b** The repulsive Cu^+–H_2O interaction with $\alpha = 180°$

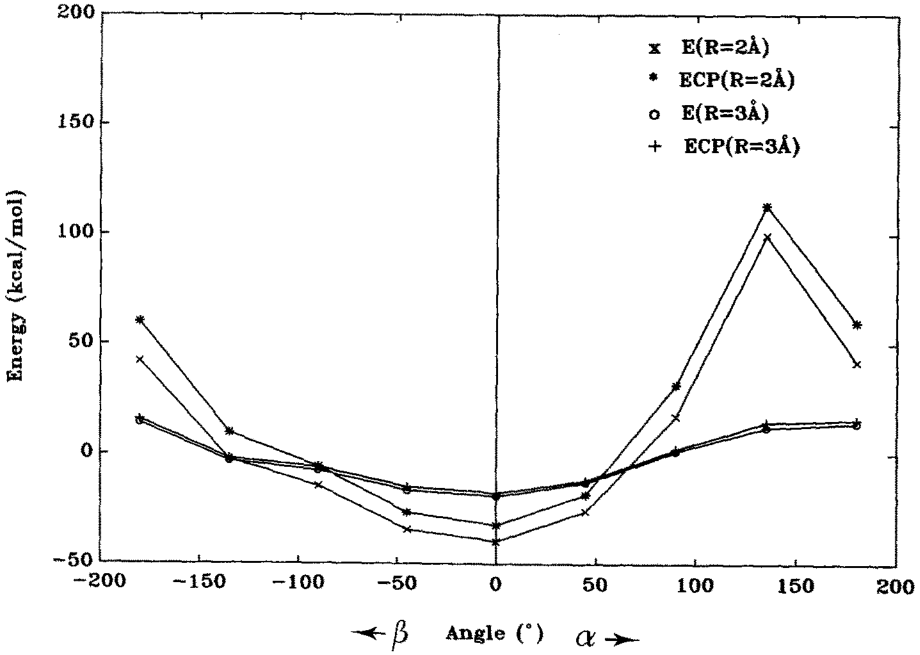

Fig. 3. Dependence of the Cu^+-H_2O interaction energy on angle α (right side) or angle β (left side). The uncorrected (E) and the CP corrected (ECP) energy values correspond to R distances of 2 Å and 3 Å

4.2 The effect of the CP *correction on the hydration of the* Cu^+ *ion*

To analyse the effects of the CP corrections on a practical application of bimolecular interactions, we report here the study of a dilute aqueous solution of Cu^+ ion using Monte Carlo (MC) techniques [15]. This study uses interaction pair-potentials derived from the quantum energies (computed without and with the CP corrections) of the dimer Cu^+-H_2O, in the configurations already referred to, together with some additional configurations involving another angle (see [8] for the definition of this new angle γ). A total of 119 and 116 points were calculated for the uncorrected and CP corrected interaction energies, respectively. These energies were fitted to an analytical function that is a linear combination of r^{-n} terms with a special weight for energy points with energy below -3.14 kcal/mol (for details on the fit see [8]). Table 1 shows the parameters of this function obtained by fitting the uncorrected and CP corrected interaction energies. The water-water interaction energies were evaluated with the MCY function of Matsuoka et al. [16], which is based on fairly large *ab initio* calculations and was shown to give a reliable description of water in condensed state [17].

All MC simulations were carried out in the (*NVT*) ensemble using the Metropolis algorithm [18]. The dilute aqueous solution was simulated by a system of one Cu^+ ion and 100 water molecules confined within a cubic volume of length 14.46 Å, at 25°C. Periodic boundary conditions using the minimum image convention were used. Statistical equilibration was carried out over 1×10^6 configurations and averaging was performed on the next 1×10^6 configurations. In this way no problems of lack of convergence were detected. In fact, the extremely

Table 1. Parameters of the fitted analytical potential[a] determined for the uncorrected and CP corrected Cu^+–H_2O pair-interaction

Type of parameter	Uncorrected value[b]	CP corrected value[c]
C_1	$+0.5988631310$	$+0.5441825835$
C_2	$-0.1742548585 \times 10^2$	$+0.7069062622 \times 10^1$
C_3	$-0.7089716121 \times 10^5$	$-0.3637607192 \times 10^5$
C_4	$+0.1850474183 \times 10^4$	$+0.2235077956 \times 10^4$
C_5	$-0.1941816522 \times 10^4$	$-0.7087048429 \times 10^3$
C_6	$+0.1733480939 \times 10^3$	$+0.1702257844 \times 10^3$
C_7	$+0.7209045748$	-0.3167382688
C_8	$+0.207910789 \times 10^3$	$-0.1919202549 \times 10^2$
C_9	$-0.1866832021 \times 10^2$	$-0.1402644171 \times 10^2$
C_{10}	$-0.1082334543 \times 10^4$	$-0.1949381954 \times 10^3$
C_{11}	$+0.1149459809 \times 10^3$	$+0.1032820486 \times 10^3$

[a] The same analytical function was adopted as Eq. (2) of [8]. Energies in E_h when distances are in a_0

[b] Mean square deviation of the fit is 1.93 kcal/mol

[c] Mean square deviation of the fit is 1.55 kcal/mol

low values of 0.0016 kcal and 0.0015 kcal (per mol of water) are obtained for the standard deviations of the energy simulated with the uncorrected and CP corrected pair-potential. (This standard deviation is calculated for the average energy in each sequence of steps [15] with respect to the energy mean value.)

The end results of the simulations are summarized in table 2. It is clear how the weakening of the Cu^+–H_2O interaction introduced by the CP correction increases the average total energy, especially through its ion-water component which increases from −277.25 kcal/mol to −249.35 kcal/mol; this is reflected directly in a decrease of the orientation parameter of the water molecules (defined by the average cosine of the angle of the water rotation axis to the local radial direction). The oxygen atoms in the first coordination sphere are also moved outwards by some 5%; this expansion does not show up in the position of the hydrogens but may be associated with the higher freedom of motion of this type of atoms in their external sphere.

In Fig. 4 the effect of the CP correction on the ion-oxygen radial distribution function (RDF) is shown, the shift outwards of the first coordination shell being

Table 2. Effect of the counterpoise correction on simulated first coordination sphere of the Cu^+–$(H_2O)_{100}$ at 25°C

	Total energy (kcal/mol)	Orientation parameter	Oxygen[a] position (Å)	Hydrogen[a] position (Å)	Hydration[b] number
Without CP	−1106.60	0.290	2.05	2.75	6.0
With CP	−1064.25	0.253	2.15	2.75	6.0

[a] Position of the maximum of the first peak of the ion-oxygen and ion-hydrogen radial distribution functions

[b] Calculated by integrating the ion-oxygen radial distribution function up to its first minimum

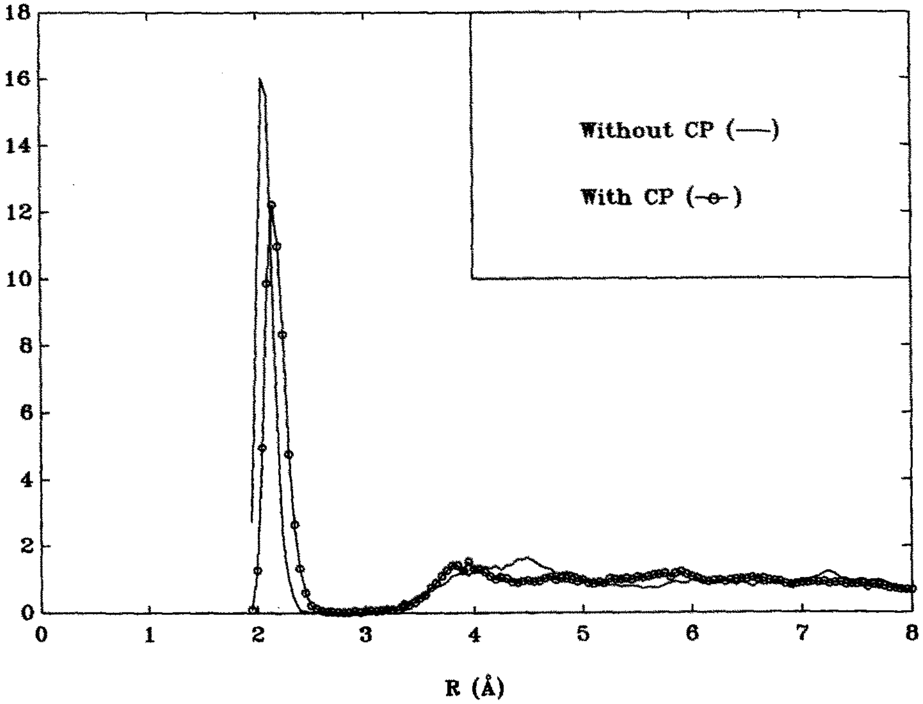

Fig. 4. Ion-oxygen radial distribution functions from the simulation of a dilute aqueous solution of the Cu^+ ion at 25°C, using the Cu^+–H_2O pair-potential without and with the CP corrections

clear. The slight loosening of the coordinated structures already apparent in the broadening of the RDF peak in Fig. 4 is made clearer in Fig. 5, where the water orientation parameter distribution is shifted outwards and its features broadened. However important the effects on the structure of the first hydration shell may be though, the coordination number of six is rigorously unchanged. Fig. 4 and especially Fig. 5 show that a second hydration shell may be clearly identified and that the CP correction has the effect of shifting it slightly and loosening its structure in a way similar to that observed for the first shell.

4.3 The decomposition of the interaction energy, before and after the CP *corrections*

The cation-ligand interactions along the minimum energy approach path have been analysed on several occasions. The general trend of the different components of ΔE along this path is well known, and sufficient to put in evidence second order effects related to the peculiarities of the cation and, especially, of the ligand (see, e.g., Cimiraglia et al. [19]).

On the other hand, information regarding other configurations is quite scarce.

a The electrostatic component, ES. A CP correction does not exist for the *ES* calculation [see Eq. (4)]. However, the relative importance of *ES* with respect to the other components does change when CP corrections are included. For the

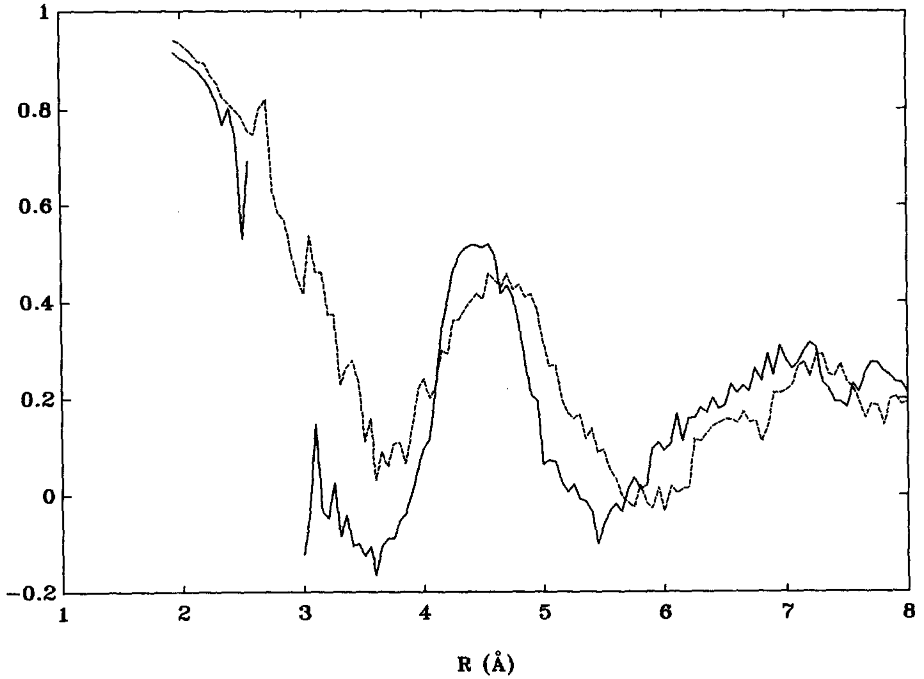

Fig. 5. Orientation parameter distribution of the water molecules using the uncorrected (solid line) and CP corrected (dashed line) Cu^+–H_2O interaction potential. The hiatus in the first distribution is due to the fact that the simulation predicts a zero oxygen density in that region

energetically favoured approach $[(\alpha, \beta) = (0, 0)]$ the Cu^+ complex has $ES/\Delta E^{CP}$ ratios similar to those found for other M^+–H_2O systems, with values lying between those found for Li^+–H_2O and Na^+–H_2O [20].

A variation of β in the range 0°–90° or of α in the range 0°–60° does not modify the $ES/\Delta E^{CP}$ ratios markedly; the ES contribution gives a fair description of the angular properties of the associative interaction. This is a feature already recognized and exploited for noncovalent interactions among neutral partners (see, e.g., Legon and Miller [21]). On the repulsive part of the potential energy surface the $ES/\Delta E^{CP}(R)$ function has a different trend (starting from negative values at the shortest distances and increasing as the R_{CuO} distance increases up to ca. 3 Å).

At very short distances the values of ES are in apparent contrast with the intuitive electrostatic description of the interaction. Intuitive or semiquantitative descriptions of the electrostatic interaction depict the cation as a point charge and the water molecule as a dipole; in this approximation the interaction at $\alpha = 180°$ is repulsive over the whole set of distances, and the repulsion increases when R decreases. This description is too simple, even when the ligand has a simple structure, as it is the case for water [20, 22]. A better description is given by the complete electrostatic potential of H_2O, $V_{\mathrm{H_2O}}$, coupled with a single point charge mimicking the charge distribution of Cu^+. The approximate expression:

$$ES(R) \approx q \cdot V_{\mathrm{H_2O}}(R) \qquad (7)$$

$(q = +1e)$ actually gives a good description of ES over a large portion of the $\mathfrak{R}$

space. The analysis done for $\alpha = 0°$ in a set of related M^{n+}–H_2O and M^{n+}–NH_3 systems is confirmed here: for distances $R > R_{eq}$ the ratio $(q \cdot V_{H_2O} - ES)/ES$ is always smaller than 0.1. The enlargement of the basis set does not alter this trend. At shorter distances there are deviations however. These deviations are usually called "penetration effects" [23], although they are not related to a physical effect and simply measure the error given by the use of multipole expansion in the evaluation of ES:

$$ES = ES(mult) + E_{es}(pen) \tag{8}$$

Equation (7) corresponds to an intermediate multipole expansion, because the electrostatic potential of the ligand is described exactly by V_{H_2O} without resorting to a multipole expansion, while the charge distribution of the cation is represented by the first term of its (one centre) multipolar expansion. The $q \cdot V_{H_2O}(R)$ expression is thus affected by the "penetration effect". This error is sizeable at small values of R for the (0, 0) conformations: at $R = 1.6$ Å it amounts to 52% of ES. Even more evident is the error at the other conformations: at shorter distances for the (0, 180) conformations it produces a reversal of the sign. At $R = 1.8$ Å the electrostatic potential estimates a positive value for ES (41.2 kcal/mol), and the penetration effect amounts to −48.9 kcal/mol. In these regions of $\mathfrak{R}$ space the ES contribution is negative, in contrast with the simple models, and not well represented by $q \cdot V_{H_2O}(R)$. Table 3 reports some numerical results that show the decrease of the penetration effect when the distance increases.

b The polarization component, PL. As was the case for ES the PL component also does not have a CP correction [see Eq. (4)]. There is a function, $P_{H_2O}(R)$, akin to $V_{H_2O}(R)$, which may be used as a molecular index to probe the polarization energy [24, 25]. The considerations expressed for the use of $V_{H_2O}(R)$ in describing ES also hold in the present case. By using the expression

$$PL(R) \approx q^2 \cdot P_{H_2O}(R) \tag{9}$$

one adopts a one-centre multipolar approximation of the rigid cation charge distribution coupled to an unexpanded expression of the ligand polarized potential [26]. The approximate relation of Eq. (9) must thus be corrected by adding a "penetration" term.

Table 3. Comparison between ES and $q \cdot V_{H_2O}$ for some (α, β) conformations of the Cu^+–H_2O system. MINI-1 basis set results, in kcal/mol, Å and °

(α, β)	(0, 180)		(0, 90)		(0, 0)	
R	ES	$q \cdot V_{H_2O}$	ES	$q \cdot V_{H_2O}$	ES	$q \cdot V_{H_2O}$
1.8	−7.72	41.17	−40.10	−19.24	−59.23	−41.84
2.0	16.78	34.52	−20.22	−14.53	−39.15	−34.49
2.2	23.23	29.36	−12.57	−11.19	−29.99	−28.88
2.4	23.20	25.22	−9.08	−8.77	−24.76	−24.52
2.6	21.22	21.86	−7.06	−7.00	−21.13	−21.08
2.8	18.90	19.09	−5.68	−5.67	−18.32	−18.32
3.0	16.74	16.79	−4.65	−4.66	−16.06	−16.06
3.2	14.87	14.87	−3.86	−3.87	−14.19	−14.20
5.0	6.27	6.27	−1.02	−1.04	−5.96	−5.99

$PL(R)$ and $P_{H_2O}(R)$ are, however, smoother functions than $ES(R)$ and $V_{H_2O}(R)$ and the penetration effects are less important in the polarization contribution (the percentage contribution of the penetration term to PL may be of the same order as to ES, because the absolute value of PL is always smaller than the absolute value of ES). The analysis performed in [20] for the most favoured approach of cation and ligand (i.e., for the (0, 0) conformations) is also confirmed in the present case: the ratio $(q^2 \cdot P_{H_2O} - PL)/PL$ is smaller than 0.1 for $R > R_{eq}$ and increases a little for shorter distances. The penetration effect is more remarkable for repulsive conformations, but the absolute value remains modest until very short distances are attained. There is, on the whole, a fair parallel between $PL(R)$ and $P_{H_2O}(R)$ over the entire configuration space $\mathfrak{R}$. The polarization is not isotropic and there is clear evidence of a higher polarization when Cu^+ is colinear with a OH bond.

The limited size of the basis set has of course a noticeable influence on the $PL(R)$ values and on the anisotropy of this function. Calculations performed with larger basis sets indicate that the trend of $PL(R)$ for the (0, 0) conformation is fairly well represented by MINI-1 calculations (see [20] and table 4). The deficiencies of the minimal basis set are more evident for other conformations; for example for the (0, 90) conformations PL and P_{H_2O} are extremely small because there are no empty basis functions of π type. Also, the difference in the polarization of the OH bonds and the O lone pairs is exaggerated by the limitations of the basis set.

To show the anisotropy effects we report in table 4 a sample of PL values at fixed values of R. These results are accompanied by the corresponding P_{H_2O} values, and by an additional set of P_{H_2O} values obtained with a more reliable basis set [27]. While PL and P_{H_2O} strongly depend on the basis set, the penetration corrections are less basis set dependent, and so the last set of values may give a fair assessment of the real polarization contribution to the interaction energy between Cu^+ and H_2O.

c The exchange-repulsion component, EX. The CP correction to EX, Δ^{EX} in our terminology, has been the object of many discussions, arising from the objection

Table 4. Values of PL and P_{H_2O} for the Cu^+–H_2O system, computed at fixed distances R for a set of angular conformations (α, β). Values in kcal/mol, Å and °

		(α, β)								
	R	(0, 180)	(0, 135)	(0, 90)	(0, 45)	(0, 0)	(45, 0)	(90, 0)	(135, 0)	(180, 0)
PL[a]	2.0	−5.095	−1.177	−0.475	−2.014	−3.035	−3.423	−16.509	−97.008	−5.095
	2.6	−1.116	−0.322	−0.101	−0.682	−1.056	−1.197	−3.233	−7.103	−1.116
	3.2	−0.493	−0.163	−0.028	−0.294	−0.472	−0.557	−1.288	−1.898	−0.493
P_{H_2O}[a]	2.0	−2.348	−0.583	−0.320	−1.730	−2.645	−2.995	−7.987	−20.243	−2.348
	2.6	−1.031	−0.293	−0.076	−0.643	−1.010	−1.164	−2.953	−5.247	−1.031
	3.2	−0.486	−0.159	−0.024	−0.287	−0.463	−0.551	−1.277	−1.846	−0.486
P_{H_2O}[b]	2.0	−14.653	−14.586	−14.286	−12.549	−11.946	−11.385	−15.325	−36.540	−14.653
	2.6	−4.981	−9.513	−4.747	−4.256	−4.066	−3.881	−5.110	−9.158	−4.981
	3.2	−2.045	−9.829	−1.848	−1.770	−1.710	−1.648	−2.114	−3.113	−2.045

[a] Basis set MINI-1
[b] Basis set 6-31G** + $VP^S(2d)^S$

that the occupied orbitals cannot be used for the expansion of the basis set of the partner in the evaluation of CP corrections: [28, 29] are representative of the two opposing opinions on this subject. We have recently shown that in calculations with a relatively good basis set, and then with a small Δ^{TOT}, Δ^{EX} is practically equal to zero [30]; the relative importance of Δ^{EX} could be used as an indirect index of the deficiencies of the basis set, and in this sense MINI-1 behaves better than other larger basis sets.

The $EX(R)$ values are positive everywhere, rapidly rising at short distances. The inclusion of Δ^{EX} corrections has little effect on the shape of this function. For the (0, 0) conformation a comparison with other cation-water complexes is possible: the values of EX and Δ^{EX} for Cu^+ are larger than those found for Li^+ and Na^+ and similar to those found for Mg^{2+} [20].

d The remaining terms, CT and MIX components. We have pointed out in earlier papers that the CT contribution has in many cases a characteristic dependence on the distance R. In the cation-ligand systems thus far examined [20, 31–33] there is a local minimum, followed at shorter distances by a local maximum. This trend has not been found in the Cu^+–H_2O complex. The $CT(R)$ curve for the (0, 0) conformation is monotonic and decreases in going to shorter distances. The Δ^{CT} correction is also monotonic, in agreement with what is found for the other cation-ligand systems, and in contrast with what is found for neutral hydrogen bonded dimers for which the correction has a non-monotonic behaviour for all the basis sets we have examined [33].

The relative importance of CT^{CP} with respect to ΔE^{CP} at R_{eq} amounts to 13% (similar to that for Zn^{2+} ion and larger than that for other alkaline and alkaline-earth metals [20]). At R_{eq}, the Δ^{CT} term represents the 27% of the total CP correction. It should be noted, however, that the relative value of the correction, Δ^{CT}/Δ^{TOT}, for Cu^+ is similar to that for Zn^{2+} and smaller than that for the other metals considered [20].

The residual MIX contribution represents, at the equilibrium distance R_{eq}, 24% and the 26% of the total interaction energy, without and with CP corrections, respectively. These values are larger than those found for other cation-water dimers [20]. At R_{eq}, the Δ^{MIX} correction corresponds to the 18% of Δ^{TOT} The decrease of MIX^{CP} and of Δ^{MIX} when R increases is quite rapid. The rate of decrease is similar to that found for the EX term. At large distances the MIX^{CP} values are all positive (the shape of the $MIX(R)$ function is more complex), going to zero for $R \to \infty$.

5 The Cl^-–H_2O system

5.1 The effect of the CP *correction on the interaction energy*

The anisotropy and the dependence on R of the total CP correction, Δ^{TOT}, is illustrated in Figs. 6 and 7, which have a format equivalent to that of Figs. 2 and 3. The equilibrium geometry is slightly influenced by the inclusion of the CP correction. The CP correction to the stabilization energy amounts to 17% of ΔE.

Similar results have been found by Sauer and Hobza [12] who limited their investigations on the CP correction to the equilibrium distance in the linear conformation of the complexes. Sauer and Hobza also report a set of results for the X^-–H_2O complexes ($X = F$, Cl, Br) with modifications to the MINI-1 basis

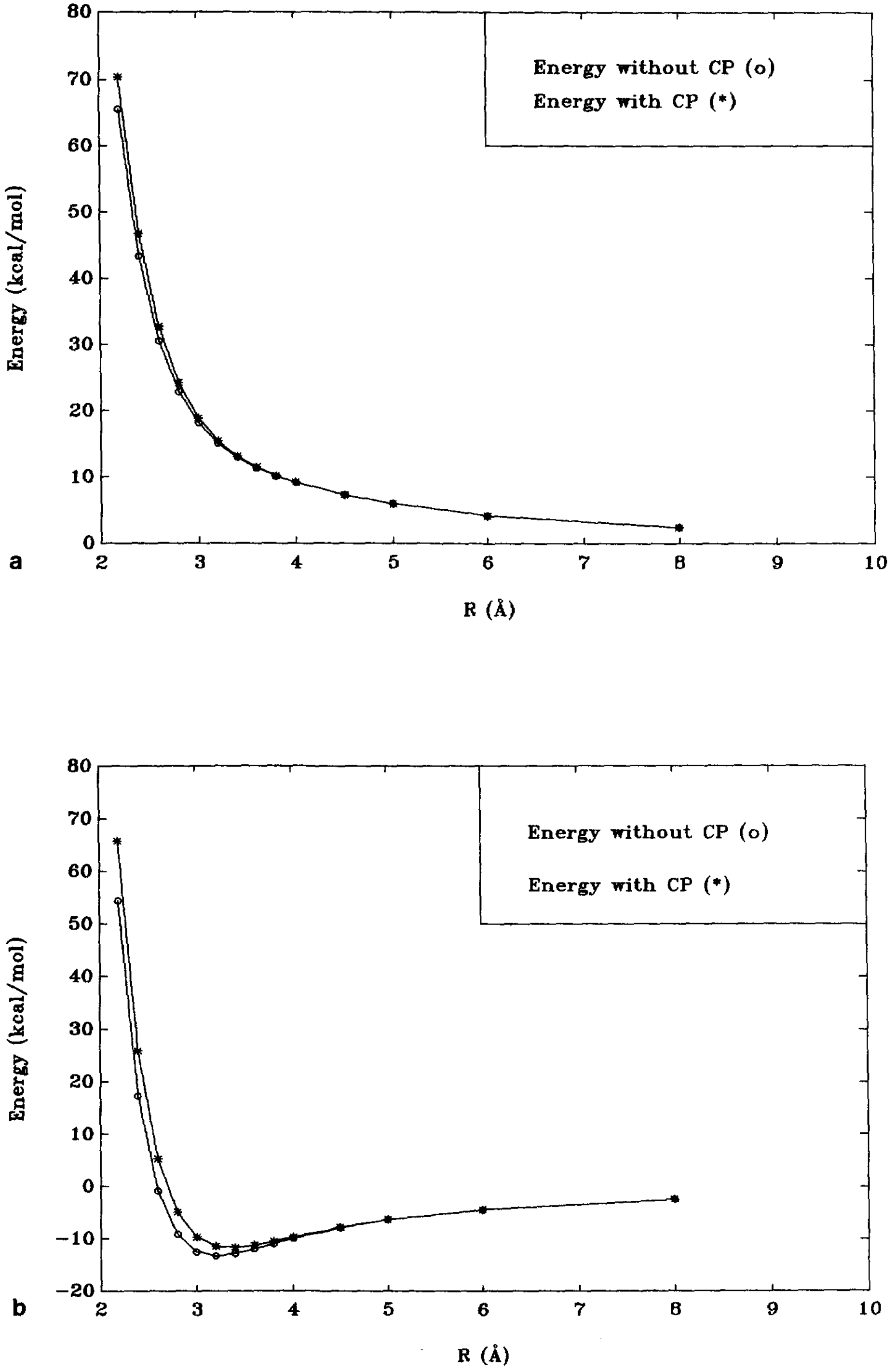

Fig. 6a,b. Interaction energies of the Cl^-–H_2O system as a function of the distance R, without and with CP corrections: **a** The repulsive Cl^-–H_2O interaction with $\alpha = 0°$; **b** The attractive Cl^-–H_2O interaction with $\alpha = 180°$

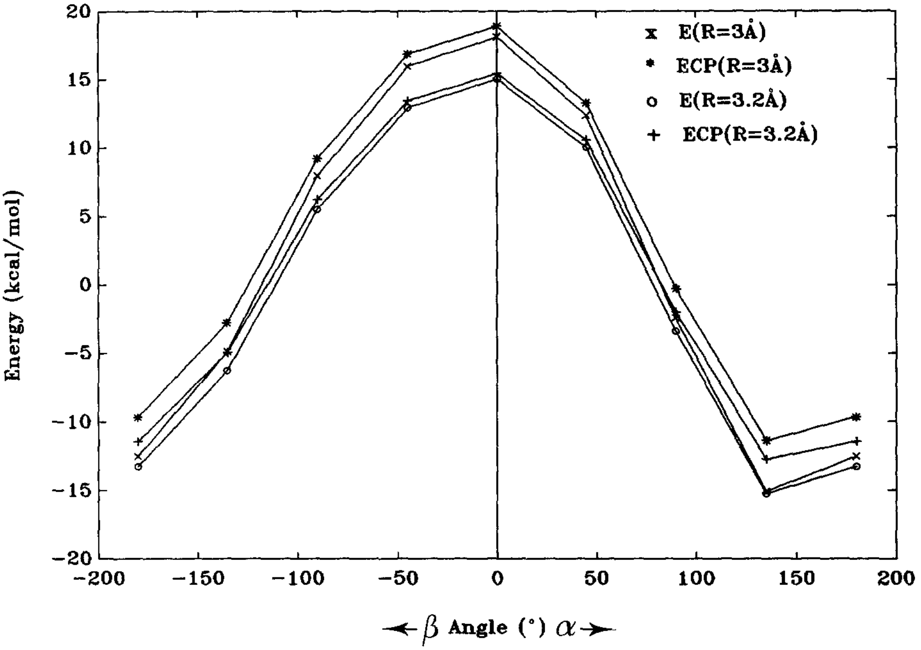

Fig. 7. Dependence of the $Cl^- -H_2O$ interaction energy on angle α (right side) or angle β (left side). The uncorrected (E) and the CP corrected (ECP) energy values correspond to R distances of 3 Å and 3.2 Å

set for the anion. Their comparisons of the energies are, however, limited to linear conformations of the complexes. A good performance of the MINI-1 basis set supplemented by diffuse functions in the description of anion-water complexes has been demonstrated by Alagona and Ghio in a recent study [34] based on the analysis of the CP correction to the interaction energy components. The analysis in [34] is limited to a couple of fixed conformations. We have found remarkable differences in the most favoured conformation of $Cl^- -H_2O$ when diffuse functions of different characteristics are added to the MINI-1 basis set. So we decided to report here only results related to the original MINI-1 basis set, deferring to a future report a more detailed analysis of the effect of the basis set on the complexes involving anions like Cl^- and Br^-.

The shallow 2-d potential well around the minimum energy conformation is not changed significantly by the introduction of CP corrections at the MINI-1 level.

5.2 The effect of the CP *correction on the hydration of the* Cl^- *ion*

By analogy with the strategy described in Sect. 4.2 for the cation, the hydration of the anion was simulated by the MC method using the same MCY potential for the water-water interactions; the $Cl^- -H_2O$ interactions are described by an analytical function similar to that used for the cation (see Sect. 4.2 and [8]). To fit this analytical function, 122 points (and 121 points) were computed by the quantum mechanical method without the CP correction (and with the CP correction), supplementing the α, β conformations (see Fig. 1) used for the cation-water system by intermediate α angles between 135° and 180°.

A weight system somewhat similar to that described in Sect. 4.2 was used, but choosing a weight ratio of 50 : 1 for points below and above 15 kcal/mol so that a relative standard deviation is obtained similar to that of the cation fit. The fitted parameters are shown in table 5.

The same type of MC calculation was used as that described in Sect. 4.2 and the standard deviation of the energy was even smaller than that found for the cation solution.

The results of the Cl^- simulations showed a CP energy effect analogous to that observed for the Cu^+ simulations, i.e. an increase in the total energy of the system $[Cl^-(H_2O)_{100}]$ which is essentially due to the increase in the energy of its ion-water component (from −998.09 kcal/mol to −981.64 kcal/mol for the total energy and, from −164.05 kcal/mol to −145.62 kcal/mol for the Cl^-–H_2O energy). The trends in the CP corrected Cl^- results for the distribution of the ion-oxygen radial distribution function (RDF) (Fig. 8) are also similar to the Cu^+ distributions reported in Sect. 4.2 (see Fig. 4).

The weakening of the Cl^-–H_2O interaction by the introduction of the CP correction has the predictable effect of shifting and broadening the peaks of these distributions. On the other hand, in the Cl^- case, the Cl–H RDF is also displaced to larger R, and this is even more pronounced than the one observed for the Cl–O RDF. This is not surprising, since the freedom of motion of the

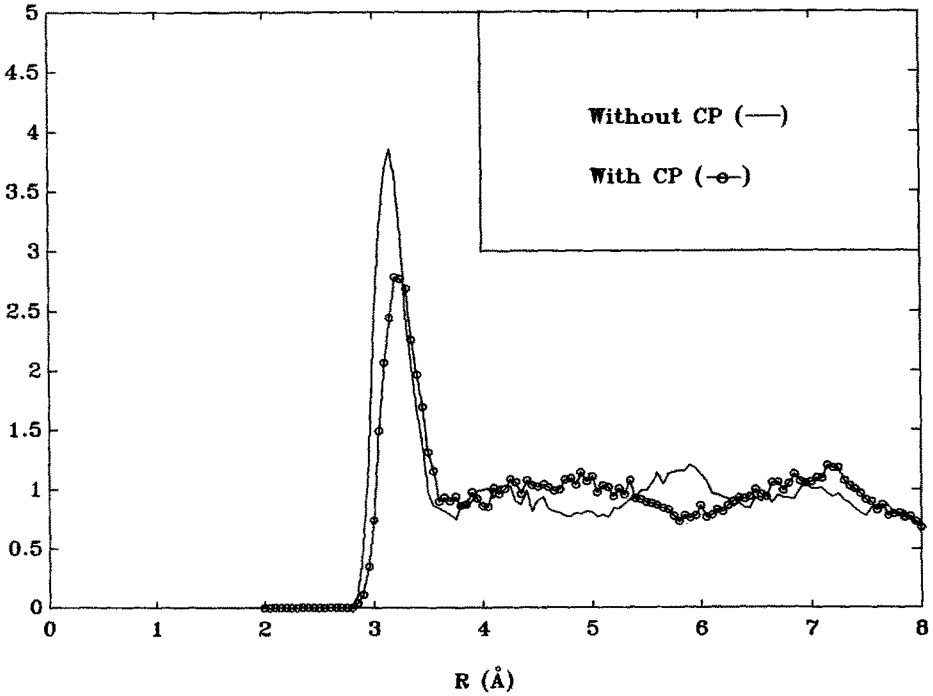

Fig. 8. Ion-oxygen radial distribution functions from the simulation of a dilute aqueous solution of the Cl^- ion at 25°C, using the Cl^-–H_2O pair-potential without and with the CP corrections

Table 5. Parameters of the fitted analytical potential determined for the uncorrected and CP corrected Cl^-–H_2O pair-interaction[a]

Type of parameter	Uncorrected value[b]	CP corrected value[c]
C_1	-0.6672532950	-0.6840041150
C_2	$-0.2886695540 \times 10^2$	$-0.1590523882 \times 10^2$
C_3	$-0.5343210607 \times 10^7$	$-0.5014456503 \times 10^7$
C_4	$-0.5817108364 \times 10^4$	$-0.5135576623 \times 10^4$
C_5	$-0.1138681229 \times 10^5$	$-0.9481915606 \times 10^4$
C_6	$-0.3742465639 \times 10^3$	$-0.3549035439 \times 10^3$
C_7	$+0.4229186057$	$+0.8840426434 \times 10^{-1}$
C_8	$+0.5125284635 \times 10^3$	$+0.3309130526 \times 10^3$
C_9	$-0.4076274739 \times 10^4$	$-0.3076117204 \times 10^4$
C_{10}	$-0.2058776022 \times 10^3$	$-0.2029093742 \times 10^3$
C_{11}	$+0.1149459809 \times 10^3$	$+0.1032820486 \times 10^3$

[a] Same analytical function and entities as those of table 1. For additional details see text

[b] Mean square deviation of the fit is 1.18 kcal/mol

[c] Mean square deviation of the fit is 1.20 kcal/mol

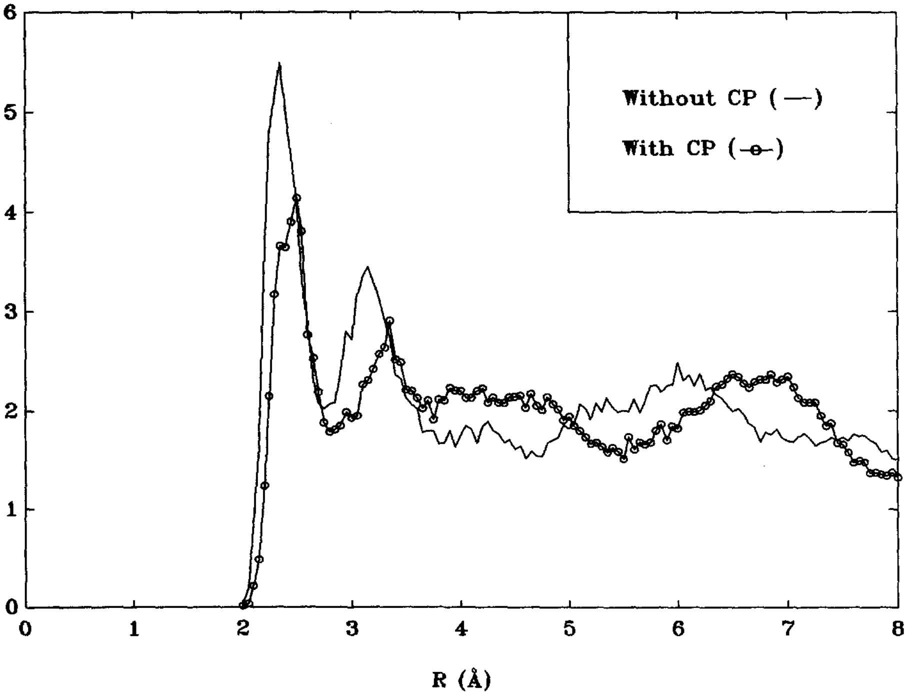

Fig. 9. Ion-hydrogen radial distribution functions from the simulation of a dilute aqueous solution of the Cl^- ion at 25°C, using the Cl^-–H_2O pair-potential without and with the CP corrections

hydrogen atoms in the Cl^- solution should be much smaller than those on the Cu^+ solution. In fact, both Cl^- RDF functions (Figs. 8 and 9) show that there is one H atom of the first-shell of water molecules closer to the anion than the oxygen atom. The second bands present on the two Cl–H RDF functions (see Fig. 9) could be attributed to the far hydrogen atoms of the first-shell of water molecules. The trends followed by both Cl–H RDF functions probably reflect a preferential linear H-bonding for the Cl^- hydration. However, as the first peaks of both Cl–O RDF functions do not drop to zero, this is not so clear and, some exchange between the water molecules of the first and second shell of the Cl^- anion is to be expected.

In table 6, four characteristic values of the RDF functions for the Cl^- simulations – the O–Cl–H angle, the positions of the first maxima in the Cl–O and Cl–H RDF functions and the hydration number – are compared with a selection of experimental and theoretical results. It should be said that no particular new features which have not been noted by other experimental or theoretical work emerge from the present results. There is a general agreement between the calculated and experimental results, although some small differences can be detected. Some Cl distances of the MD studies of Heinzinger et al. [38c] are too short, while, our CP corrected Cl–H distance as well as that of the MC work of Clementi et al. [37a] (which also uses the MCY pair potential) are a bit large. The results from the Integral equations [39] seem to give Cl–H distances that are too short and Cl–O distances that are too high. Overall, the calculated hydration numbers appear to be higher than those observed experimentally. However, it is very satisfactory to notice that, although our uncorrected value is also high (8), the CP corrected value (6) is very close to those found by the accurate neutron-diffraction studies [37]. Here, it should be emphasized that the

Table 6. Structural results for the first solvation shell of Cl^-

Method		First solvation shell				Ref.
		O–Cl–H[a] angle (°)	R_{Cl-O}[b] (Å)	R_{Cl-H}[b] (Å)	Hydration number	
Without CP		11	3.15	2.35	7.7[c]	this work
With CP		13	3.20	2.50	5.7[c]	this work
Exp.	X-ray	—	3.06–3.35	—	5–11	[35]
	Neutron diffraction	0–11	3.20–3.35	2.23–2.29	4–6	[36]
Theor.	MC	0–6	3.21–3.55	2.25–2.55	6–8	[37]
	MD	4–12	2.70–3.30	1.70–2.35	6–8	[38]
	Integral equations	0	3.45–3.46	2.00	9–12	[39]

[a] Calculated with the corresponding RDF results, and assuming $R_{O-H} = 0.957$ Å

[b] Position of the maximum of the first peak of the anion-oxygen and anion-hydrogen radial distribution functions

[c] Calculated by integrating the anion-oxygen radial distribution function up to its first peak minimum

experimental studies [37] suggest that the hydration of the Cl^- anion is not particularly influenced by the concentration of the sample solution and by the counter-ion present on it.

Finally, it is interesting to note that the CP correction does have a clear effect on the anion hydration, as the hydration number of the Cl^- ion is decreased (from 8 to 6). This is in marked contrast with the results of the cation solution, where the CP correction rigorously did not affect the Cu^+ hydration number (it remains fixed at 6).

5.3 The decomposition of the interaction energy, before and after the CP *corrections*

The decompositions of the anion-ligand interaction energies are not abundant in the literature and are often limited to a single geometry. The most abundant and coherent set of results we know, derives from the Pisa's laboratory and it is limited to the interaction with water of three oxygenated anions, $HCOO^-$, CH_3COO^-, $H_2PO_4^-$ and of the F^- anion [30, 34, 40]. In these papers the analysis of ΔE is refined by the introduction of CP corrections to the energy components, using the same technique employed here, and performed over a representative number of basis sets, of increasing complexity and reaching basis sets practically without BSSE [34]. In the following, we shall use data derived from these investigations, which have, however, been limited to a scan over the distance R for a couple of favoured conformations, corresponding to a linear or to a bifurcated arrangement of the stable form of the complex. To the best of our knowledge, an examination of the ΔE decomposition over the whole configuration space $\Re$ has not yet been done.

a The electrostatic component, ES. The ratio $ES/\Delta E$ at the equilibrium geometry is 1.18 before CP correction and 1.23 after CP correction; the two values are computed at the R_{eq} obtained without and with CP correction. The corresponding ratios for the F^-–H_2O system are 0.77 and 1.25 [30] (MINI-1 values). For better basis sets the ratios for the F^-–H_2O system are in the range, 1.02–1.50 before CP and 1.47–1.51 after CP correction. Also for oxyanions the spread in the ratio due to the basis set is remarkably reduced by the CP correction. The number of worked examples is not yet sufficient for anion-ligand dimers to establish correlations between ES and ΔE values similar to those found for neutral H-bonded dimers [33].

The penetration term, evidenced by the difference between ES and $q \cdot V_{H_2O}$ ($q = -1e$), is of comparable importance in the Cl^- and Cu^+ cases at the equilibrium distances. For the equilibrium configuration we found $(q \cdot V_{H_2O} - ES)/ES = -0.115$ while the corresponding value for the Cu^+ complex was -0.099. At the same geometry the penetration term is larger for the Cl^- complex. In table 7 we report a comparison of ES and $q \cdot V_{H_2O}$ values analogous to that reported in table 3 for the Cu^+ case.

b The polarization component, PL. The molecular index P_{H_2O} accounts for the polarization of the ligand through Eq. (9), but not for the polarization of the anion. The minimal basis sets are unable to describe the anion polarization, and this is the most prominent weakness of all the minimal basis sets in describing anion-neutral bonding; such a defect is partly removed by the addition of diffuse functions, which are more efficient for this component of ΔE than polarization functions.

Table 7. Comparison between *ES* and $q \cdot V_{H_2O}$ for some (α, β) conformations of the Cl^-–H_2O system. MINI-1 basis set results, in kcal/mol, Å and °

(α, β)	(0, 180)		(0, 90)		(0, 0)	
R	ES	$q \cdot V_{H_2O}$	ES	$q \cdot V_{H_2O}$	ES	$q \cdot V_{H_2O}$
2.2	−67.62	−29.36	−14.41	11.18	5.51	28.87
2.4	−44.62	−25.22	−3.59	8.77	13.76	24.52
2.6	−31.08	−21.86	1.34	7.00	16.20	21.08
2.8	−23.51	−19.02	3.14	5.67	16.15	18.31
3.0	−18.87	−16.79	3.55	4.66	15.13	16.06
3.2	−15.82	−14.87	3.41	3.87	13.81	14.20
3.4	−13.67	−13.25	3.06	3.25	12.48	12.64
3.6	−12.06	−11.87	2.68	2.75	11.26	11.32
3.8	−10.77	−10.70	2.32	2.35	10.18	10.20
4.0	−9.72	−9.68	2.01	2.02	9.23	9.24
5.0	−6.25	−6.25	1.01	1.04	5.99	5.99
6.0	−4.35	−4.35	0.61	0.61	4.19	4.19
8.0	−2.45	−2.45	0.26	0.26	2.38	2.38

The defects in the description of *PL* produced by using a minimal basis set are rather disturbing for describing the process of reaction, but are probably less important in deriving an analytical expression for simulations of liquid systems. At each distance and orientation, *PL* represents only a minor contribution to ΔE. At large distances the decay of *PL* is ruled by a r^{-4} term, making the polarization contribution relatively more important than *EX*, *CT*, and *MIX*; however the ratio *ES*/*PL* increases with the distance and *ES* remains the only significant contribution.

At short and intermediate distances the deficiencies of the minimal basis sets in describing the two monomeric contributions to *PL*(*R*) reinforce each other. Table 8 lists a set of *PL* values, compared, as in table 7, with the corresponding P_{H_2O} values obtained with the MINI-1 and the 6-31G** + $VP^S(2d)^S$ basis set. Note that the $P_{H_2O}(R)$ function to be used with a negative point charge differs slightly from the analogous function to be used with a positive charge. In the language of perturbation theory, the difference derives from considering perturbation orders higher than second in deriving this function.

c The exchange-repulsion component, EX. The *EX* and EX^{CP} values are positive everywhere, rapidly rising at short distances. Including the Δ^{EX} correction has little effect on the shape of this function. The inclusion of the Δ^{EX} correction in the MINI-1 values of the F^-–H_2O system makes the shape of EX^{CP} quite similar to that found with large basis sets, and better than that found with the conventional 4-31G and 6-31G** basis sets [30]. Making allowance for the different ionic radius of the two anions, the similarity of the trends in $EX^{CP}(R)$ for the F^-–H_2O and Cl^-–H_2O complexes makes it reasonable to suppose that this function also gives a fairly good description of the actual interaction energy component in the present case.

d The remaining terms, CT and MIX components. In the F^-–H_2O system, as well as in the $RCOO^-$–H_2O and $H_2PO_4{}^-$–H_2O systems, we have found for *CT* at the MINI-1 level a non-monotonic behaviour, with a minimum in the vicinity of R_{eq}.

Table 8. Values of PL and P_{H_2O} for the Cl^-–H_2O system, computed at fixed distances R for a set of angular conformations (α, β). Values in kcal/mol, Å and °

		(α, β)								
	R	(0, 180)	(0, 135)	(0, 90)	(0, 45)	(0, 0)	(45, 0)	(90, 0)	(135, 0)	(180, 0)
PL[a]	2.8	−0.586	−0.195	−0.052	−0.482	−0.770	−0.896	−1.625	−1.451	−0.586
	3.4	−0.364	−0.125	−0.017	−0.230	−0.378	−0.458	−0.952	−1.163	−0.364
	4.0	−0.204	−0.075	−0.007	−0.121	−0.202	−0.252	−0.515	−0.605	−0.204
P_{H_2O}[a]	2.8	−0.761	−0.232	−0.035	−0.508	−0.799	−0.947	−2.149	−3.311	−0.761
	3.4	−0.377	−0.128	−0.009	−0.230	−0.381	−0.460	−1.242	−1.306	−0.377
	4.0	−0.205	−0.075	−0.007	−0.121	−0.202	−0.252	−0.517	−0.614	−0.205
P_{H_2O}[b]	2.8	−3.312	−3.048	−2.952	−2.819	−2.737	−2.641	−3.455	−5.028	−3.312
	3.4	−1.502	−1.390	−1.344	−1.302	−1.273	−1.237	−1.575	−2.082	−1.502
	4.0	−0.772	−0.718	−0.694	−0.680	−0.670	−0.655	−0.815	−1.012	−0.772

[a] Basis set MINI-1

[b] Basis set 6-31G** + $VP^S(2d)^S$

This minimum is still present in the CT^{CP} functions of those systems, even if noticeably reduced by Δ^{CT}. The functions CT and CT^{CP} obtained with larger basis sets have a regular trend, without local minima [30, 34, 40]. In the present case we found a regular trend at all the angles, with values consistently decreasing from $R = 8.0$ to 2.0 Å.

The relative importance of CT^{CP} with respect to ΔE^{CP} at $R_{eq}{}^{CP}$ amounts to 30%. The data derived from preceding calculations show that a minimal basis set exaggerates the relative importance of the CT contribution (this feature of the minimal basis sets is, however, noticeably reduced in the MINI-1 one). This overestimation is not completely corrected by the split-valence basis sets.

In the Cl^-–H_2O complex, this spurious effect is surely present but it has a less dramatic effect on the decomposition of ΔE. In the present case, as in the preceding ones, the CP correction has a beneficial effect, reducing this unjustified emphasis put on the CT contribution.

The MIX component is responsible for the 6% and 4% of ΔE at the equilibrium distance, before and after CP correction; here again the two ratios are computed at the R_{eq} obtained without and with CP correction. At $R_{eq}{}^{CP}$, Δ^{MIX} is the 40% of the total correction Δ^{TOT}. MIX and MIX^{CP} rapidly decrease for $R > R_{eq}$. MIX is everywhere negative with a regular trend with respect to R; MIX^{CP} is less regular, having negative values at small distances, and positive values, with maximum in the range $R = 3.0$–3.4 Å, according to the angle.

6 Conclusions

In this paper, we have enlarged a number of bimolecular systems subjected to detailed analysis of the interaction energy components, with the inclusion of CP corrections to the interaction energy terms, by considering the Cu^+–H_2O and Cl^-–H_2O systems. Novel features with respect to preceding papers are:

(1) the extension of the configuration space under examination to three dimensions, the mutual distance and the two angles defining the mutual orientation of the partners, and

(2) the study of the effect of the CP corrections on the energy upon Monte Carlo simulations of the aqueous solutions of Cu^+ and Cl^-.

In both systems the CP corrections do not modify the three dimensional shape of the potential drastically. The modifications are, however, sufficient to lower the number of water molecules in the first coordination shell of Cl^- from 8 to 6. No appreciable changes have been found in the Cu^+-water system.

The detailed analysis of the ΔE components has been also compared with previous results concerning other cation-ligand and anion-ligand systems. The general trends of the ΔE terms, and their corresponding corrections, are similar to those found for other systems. However, some peculiarities are found in certain cases; this fact suggests that generalizations from a restricted number of cases may be misleading, even for systems with a simple material composition.

Acknowledgements. Financial support from INIC (Lisbon), CRN (Pisa) and the European Commission (Contract No. SC1-0037-c) is acknowledged.

References

1. Kolos W (1979) Theor Chim Acta 151:219
2. Boys SF, Bernardi F (1970) Mol Phys 19:553
3. Sokalski WA, Roszak S, Hariharan C, Kaufman JJ (1983) Int J Quant Chem 23:847
4. Cammi R, Bonaccorsi R, Tomasi J (1985) Theor Chim Acta 68:271
5. Hayes IC, Stone AJ (1984) Mol Phys 53:83
6. Gutowski M, Duijneveldt FB van, Chalasinski G, Piela L (1987) Mol Phys 61:233
7. Tomasi J, Alagona G, Bonaccorsi R, Ghio C, Cammi R. In: Maksic Z (ed) Theoretical Models of Chemical Bonding. Part 3, Springer, Berlin, Heidelberg, New York, 1990
8. Cordeiro MNDS, Gomes JANF, Gonzàlez-Lafont A, Lluch JM, Oliva A, Bertrán J (1988) J Chem Soc Faraday Trans 2 84:693
9. Kitaura K, Morokuma K (1976) Int J Quant Chem 10:325
10. Andzelm J, Huzinaga S, Klobukowsky M, Radzio-Andzelm E, Sakay Y, Tatewaki KI. In: Huzinaga S (ed) Gaussian Basis Set For Molecular Calculations, Elsevier, Amsterdam 1984
11. Tatewaki KI, Huzinaga S (1980) J Comp Chem 1:202
12. Sauer J, Hobza P (1984) Theor Chim Acta 65:291
13. Benedict WS, Gailar N, Plyler EK (1956) J Chem Phys 24:1139
14. Peterson MR, Poirier RA, Monstergauss, Department of Chemistry, University of Toronto, Ontario, Canada,
15. Valleau JP, Wittington SG. In: Berne BJ (ed) Statistical Mechanics, vol. A, chap. 4 and chap. 5, Plenum Press, New York, 1977; Wood WW, In: Temperley HNV, Rowlinson JS, Rushbrooke GS, Physics of Simple Liquids, chap. 5 (eds). North-Holland, Amsterdam, 1968
16. Matsuoka O, Clementi E, Yoshimine M (1976) J Chem Phys 64:1351
17. Clementi E, Corongiu G (1983) Int J Quant Chem Biol Symp 10:31; Wojcik M, Clementi E (1986) J Chem Phys 84:5970; Wojcik M, Clementi E (1986) J Chem Phys 85:3544; Wojcik M, Clementi E (1986) J Chem Phys 85:6085
18. Metropolis N, Rosenbluth AW, Rosenbluth MN, Teller AH, Teller E (1953) J Chem Phys 21:1087
19. Cimiraglia R, Tomasi J, Cammi R, Hofmann H-J (1989) Chem Phys 136:399
20. Cammi R, Hofmann H-J, Tomasi J (1989) Theor Chim Acta 76:297
21. Legon AC, Miller DJ (1987) Chem Soc Rev 16:467
22. Dacre PD (1987) J Chem Phys 80:5677
23. Jeziorski B, Kolos W. In: Ratajczak H, Orville-Thomas WJ (eds) Molecular Interactions. vol. 3, Wiley, Chichester, 1982
24. Bonaccorsi R, Scrocco E, Tomasi J (1976) Theor Chim Acta 43:63
25. Miller Francl M (1985) J Phys Chem 89:428
26. Kaplan IG, Theory of Molecular Interactions. Elsevier, Amsterdam, 1986
27. Latajka Z, Scheiner S (1987) J Comp Chem 8:663
28. Lenthe JH van, Duijneveldt-van de Rijdt JCM van, Duijneveldt FB van (1987) Adv Chem Phys 69:521
29. Tolosa S, Esperilla JJ, Espinosa J, Olivares del Valle FJ (1988) Chem Phys 127:65; Olivares del Valle FJ, Tolosa S, Ojalvo EA, Espinosa J (1988) Chem Phys 127:343
30. Alagona G, Ghio C, Latajka Z, Tomasi J (1990) J Phys Chem 94:2267
31. Alagona G, Bonaccorsi R, Ghio C, Tomasi J (1986) J Mol Struct (Theochem) 135:39
32. Hofmann H-J, Hobza P, Cammi R, Tomasi J, Zahradník R (1989) J Mol Struct (Theochem) 201:339
33. Alagona G, Ghio C, Cammi R, Tomasi J. In: Maruani J (ed) Molecules in Physics, Chemistry, and Biology, vol. II, p. 507, Reidel, Dordrecht, 1988; Alagona G, Ghio C, Cammi R, Tomasi J (1987) Int J Quant Chem 32:227
34. Alagona G, Ghio C (1990) J Comp Chem 11:930
35. a Neilson GW, Enderby JE (1979) Annu Rep Prog Chem Sect. C 76:185; Enderby JE, Neilson GW. In: Franks F (ed) Water. A Comprehensive Treatise, vol. 6, chap. 1, Plenum Press, New York, 1979. b Magini M (1981) J Chem Phys 74:2523. c Pálinkas G, Radnai T, Dietz W, Szász GyI, Heinzinger K (1982) Z Naturforsch. A 37A:1049; Probst MM, Radnai T, Heinzinger K, Bopp P, Rode M (1985) J Phys Chem 89:753

36. Enderby JE, Neilson GW (1981) Rep Progr Phys 44:594; Enderby JE (1985) Pure Appl Chem 57:1025
37. a Kistenmacher HP, Clementi E (1974) J Chem Phys 61:799; Clementi E, Barsotti R, Fromm J, Watts RO (1976) Theor Chim Acta 43:101; Clementi E, Barsotti R (1989) Chem Phys Lett 59:21. b Mezei M, Beveridge DL (1981) J Chem Phys 74:6902. c Chandrasekhar J, Spellmeyer DC, Jorgensen WL (1984) J Am Chem Soc 106:903. d Lybrand TP, Kollman PA (1985) J Chem Phys 83:2923
38. a Impey RW, Madden PA, McDonald IR (1983) J Phys Chem 87:5071. b Bounds DG (1985) Mol Phys 54:1335. c Heinzinger K, Vogel PG (1976) Z Naturforsch 29a:463; Palinkas G, Riede WO, Heinzinger K (1977) Z Naturforsch 32a:1137; Szász GyI, Heinzinger K (1979) Z Naturforsch 34a:840; Bopp P, Dietz W, Heinzinger K (1979) Z Naturforsch 34a:1424; Szász GyI, Dietz W, Heinzinger K, Pálinkas G, Radnai T (1982) Chem Phys Lett 92:388; Probst MM, Radnai T, Heinzinger K, Bopp P, Rode M (1985) J Phys Chem 89:753; Heinzinger K (1985) Pure Appl Chem 57:1031; Spohr E, Pálinkas G, Heinzinger K, Bopp P, Probst MM (1988) J Phys Chem 92:6754
39. Pettitt BM, Rossky PJ (1986) J Chem Phys 84:5836; Brooks III CL (1987) J Chem Phys 86:5156
40. Alagona G, Ghio C, Tomasi J (1989) J Phys Chem 93:5401