The influence of cations on the dipole moments of neighboring polar molecules

Imre Bakó¹ | Dániel Csókás¹ | István Mayer¹ | Szilvia Pothoczki² | László Pusztai²,³

¹Institute of Organic Chemistry, Research Centre for Natural Sciences, Budapest, Hungary
²Wigner Research Centre for Physics, Budapest, Hungary
³International Research Organization for Advanced Science and Technology (IROAST) Kumamoto University, Kumamoto, Japan

Correspondence
Imre Bakó, Institute of Organic Chemistry, Research Centre for Natural Sciences, H-1519 Budapest, P.O.Box 286, Hungary.
Email: bako.imre@ttk.hu

Funding information
János Bolyai Research Scholarship of the Hungarian Academy of Sciences.; National Research, Development and Innovation Office (NRDIO NKFIH, Hungary), Grant/Award Numbers: 124885, 128136, KH 130425

Abstract
In this review/perspective article we show how the dipole moment of a single molecule in a cluster can be calculated and used for describing the polarization effect. Additionally, we review the accuracy of the calculation of the dipole moment of several simple protic and aprotic molecules. It is shown that the dipole moment of polar (water, methanol, formamide, acetone and acetonitrile) molecules in the neighborhood of a cation is increased primarily by polarization from the bare electrostatic charge of the cation, although the effective value of the latter is somewhat reduced by “back donation” of electrons from neighboring polar molecules. In other words, the classical picture may be viewed as if a point charge slightly smaller than the nominal charge of the cation would be placed at the cation site. It was found that the geometrical arrangement of the polar molecules in the first solvation shell is such that their mutual polarization reduces the dipole moments of individual molecules, so that in some cases they become smaller than the dipole moment of the free protic or aprotic molecule. We conjecture, for the first time, that this behavior, namely the about 10%–20% decrease of the dipole moment of water in the first shell of cations, with the cation itself removed, is essentially a manifestation of the Le Chatelier-Braun principle. We also remark that if the cation-molecule bond order is too large then the calculated dipole moment for these complexes can be questionable, due to the questionable definition of a single molecule within the “supermolecule”-like cluster.

KEYWORDS
cation, dipole moment, dipole moment, localisation

1 | INTRODUCTION

The uneven distribution of positive or negative charges in a molecule gives rise to a dipole moment. This dipole moment is uniquely defined, independently of the choice of coordinate system, if the total charge of the molecule is zero. The dipole moment (and also, other quantities that are
sensitive to the deviation of the charge distribution from spherical symmetry) of an uncharged molecule can be calculated by defining the origin of the molecule in such way that the following equations holds true: \( \sum_{i} r_i = 0 \), where \( r_i \) is the vector point from the centre of the coordinate system to the centre of the \( i \)-th centroid. The dipole moment of a molecule as a physical quantity can be defined using the equation below,

\[
\mu = \sum_{i=1}^{n} q_i r_i + \int \rho(r) r^2 dr
\]

where the first and second terms correspond to the contributions from nuclei (\( q_i \) are nuclear charges) and the electron distribution (more precisely, first moment of electron distribution), respectively. Alternatively, the \( i \)-th component of a dipole moment \( \mu \) can be calculated using the following formula

\[
\mu_i = \frac{\partial E}{\partial q_i} \approx \frac{E(\delta_{q_i}) - E(-\delta_{q_i})}{2\delta_{q_i}}.
\]

Equation 2 describes the response of the total energy \( E \) to a constant finite electric field \( \varepsilon \). \( \varepsilon \) is the \( x, y, \) or \( z \) components of the electric field.)

This definition can be applied when the electronic densities are not available at a certain computational level (CCSD(T)).

The dipole moment is one of the simplest quantities that is related to the distribution of electronic density in a polar molecule. In the absence of the dipole moment, the induction, long-range electrostatic interactions and the information incorporated in structure of infrared and sum-frequency generation spectra are uninterpretable.

In the gas phase the molecular dipole moment (\( \mu \)) can be determined experimentally by microwave spectroscopy, molecular beam electric resonance spectroscopy, and other high-resolution spectroscopic techniques [1–6]. Experimentally measured values of \( \mu \) in the liquid phase are very scarce and most often have large errors. Several indirect routes (X-ray diffraction experiment, Compton Scattering, dielectric spectra) exist for estimating the dipole moment of water, methanol.. for example, molecules in condensed phases [3–6].

The most detailed studies on the value and variation of the dipole moment in different phases (vapor, liquid..) can be found for the water molecule. A dipole moment of 1.8546 Debye (D) in the gas phase was obtained [4]. Estimations of the experimental dipole moment in condensed phases fall between 2.6 and 2.9 D [1–3], where the lower limit (2.6 D) is related to a calculation based on the dielectric properties of hexagonal ice [3]. It should be remembered that these values are always based on some theoretical approximation. Direct determinations of the dipole moment in the liquid state exist for acetone, acetonitrile, methanol and formamide molecules [2–9]. The dipole moment is increased by approximately 10% compared to the gas phase for two non-hydrogen-bonded polar aprotic liquids (acetone and acetonitrile). On the other hand, the dipole moment of methanol in the liquid state increases significantly, from approx. 1.7–2.87 D.

It is apparent that in condensed phases the dipole moment of polar molecules increases due to the interaction with the environment (polarization, charge transfer, geometrical deformation, etc...). At present, three methodically different approaches exist in the literature for calculating dipole moments of monomers in condensed phase. In the simplest case, one considers a single molecule described quantum mechanically (QM), using some reliable method and flexible basis set, that is embedded into an environment of point charges and/or multipoles determined by different assumptions. The coordinates of particles that build up the environment can be derived from simulations (Monte Carlo or Molecular Dynamics), or from local energy minimum configurations of various cluster sizes. According to this scheme, the dipole moment of water molecules increases by about 30%–50% [7–9] in the liquid phase, while for acetone and acetonitrile the increase is estimated to be 10% to 30% (the exact values depend significantly on the exact QM approximation applied) [8,9]. These values depend on he applied QM method [7–9]. Even this scheme can account for the significant increase of the dipole moment as compared with a single monomer (in the gas phase).

The second methods rely on the determination of a clear resolution of the total electron density for a given species. One of them can be applied at any level of theory, and involves performing a three dimensional (3D) analysis based on Bader or Voronoi like decomposition scheme [10] into atomic (or, grouped together, to molecular) domains by studying the charge distribution. In this case the charge of the molecular domain can be different from 0.0, as already shown by Devereux et al. [11].

Another approach for analyzing the electronic properties of individual molecules in a super molecular system (cluster) is by using a localisation technique to the molecule (or part of a molecule) in the Hilbert space. It is known that localized orbitals are not uniquely determined but depend on the localization criterion used. In this case, if we apply it to a neutral molecule, the net charge of the molecule is 0.0. Experience gained by References [12,13] showed that it is practically irrelevant which type of localization (Boys [14], Natural Localized Orbital [15] or two different version of the Magnasco–Perico [16,17] localization scheme) is used for water clusters. These methods result in dipole moments for water in clusters that are larger than those based on the Bader-type analysis by approximately 0.4–0.5 D [12,18,19].

Recent theoretical studies indicated a significant enhancement (up to ~2.9–3.05 D) of the dipole moment of individual water, methanol and acetonitrile molecules in clusters and in condensed phases [20–27]. It is conceivable that the more than 40% increase of dipole moments of water and methanol molecules in the liquid state should be taken as a collective effect that is connected with the existence of H-bonded structures in
these liquids. This collective effect can be well reproduced by considering relatively small water clusters, therefore such an approach helps in gaining deeper insight into its nature by performing various calculations on model water clusters. It has also been shown that the dipole moment of a water molecule depends on its hydrogen bonded local environment [27].

Liquid water and methanol are highly complex systems hence their theoretical and experimental studies are continuously revealing new aspects of their structure [28–34]. The introduction of ions into bulk liquids causes a strong perturbation of the molecule structure in the close proximity of the cation. The various physical and chemical properties of ions in aqueous solutions are of evident importance in many biological, geological, and industrial processes [35–40]. Specific ionic effects are important in chemistry and biology. Such effects exhibit a recurring trend called the Hofmeister series [41–44]. In this series there are connections between effectiveness of salts in precipitating proteins and “their water ordering capacity.”

There are different views concerning the importance of various effects in forming the modified water structure around an ion. In References [45–56], it was assumed that collective effects between water molecules are the most crucial ones. However, in 1992 one of us [57] demonstrated computationally that the shortening of the distance between the first and second hydration shells around a cation is primarily caused by the direct electrostatic effect of the cation on the hydrogen bonds between water molecules: there is no need to assume any complicated collective effects to explain this experimentally (by diffraction) observed phenomenon.

Local polarization and charge transfer effects, induced by monovalent, divalent and trivalent cations in water, strongly influence structural and dynamical properties of the solvent (water). One of the manifestations of the polarization terms is the perturbation of electronic density due to the ion-water interaction: this phenomenon can be characterized by the dipole moment of water molecules. Theoretical calculations revealed a significant increase of the dipole moment of water molecules around divalent (Mg$^{2+}$: 3.4 D [45,48], Ca$^{2+}$: 3.1 D [46,48,53]) and trivalent (Al$^{3+}$: 4.1 D [52,53]) cations. However, the dipole moment of water in the first shell of monovalent cations remains nearly the same (or slightly smaller than) as it is in bulk water [47–51].

Based on ab initio molecular dynamic simulation, Faralli et al. showed, that the average dipole moment of methanol molecules in the first shell of Li$^+$ [56], Ca$^{2+}$ [54] and Mg$^{2+}$ [55] is significantly larger than in bulk liquid methanol. Also, in Na$^+$ and K$^+$ solutions the average value of dipole moment of methanol molecules in the first solvation shell is $\sim$ 0.2 D lower [56] than the average calculated for the entire volume of the solution. These ions, in both the aqueous and methanolic solutions, have a similar effect on the dipole moment of the solvate molecules that build up solvation spheres.

In our recent paper [12] we showed that the dipole moment of a large water cluster can be reproduced only if one takes into account properly that there is a significant electron delocalization along the hydrogen bonds. The dipole moments of individual molecules contain significant components originating to the “tails” of the orbitals due to this delocalization (‘quantum chemical bond formation’), which even questions the concept of a water cluster consisting of individual molecules (as opposed to the concept of the whole clusters is considered as one single molecules). In these cases the conventional Mayer bond order between the H-bonded molecules are in the range of 0.02–0.15. Building on the latter result, it was of interest to consider how the presence of a cation influences the dipole moments of the neighboring solvate (water, methanol, formamide, acetone, acetonitrile) molecules. For this reason, we have compared results of three types of calculations. First, we calculated the dipole moments of the individual solvent molecules in clusters surrounding the cation. In calculations of the second type, we kept the geometry of the clusters as obtained with ions, but replaced the latter with point-like charges of different values, then recalculated the wave functions of formamide, acetone, acetonitrile) molecules. For this reason, we have compared results of three types of calculations. First, we calculated the dipole moments of the individual solvent molecules in clusters surrounding the cation. In calculations of the second type, we kept the geometry of the clusters as obtained with ions, but replaced the latter with point-like charges of different values, then recalculated the wave functions of the resultant cluster. Next we examined how this change influences the values of the dipole moments. In the third type of calculations the ion was completely removed, but the arrangement of the molecules was kept the same as with ions. Again, the dipole moments were determined after recalculating the cluster.

2 | COMPUTATIONAL DETAILS AND MOLECULAR ORBITAL LOCALISATION METHOD

We have performed quantum chemical calculations for different cation-molecule clusters (first or first two hydration shells for water) with or without cations (Li$^+$, Na$^+$, Mg$^{2+}$, Ca$^{2+}$, Al$^{3+}$) by the Gaussian program suite Version 09 [58], using the M05-2X DFT functional [59] and the cc-pVTZ basis set. We use this basis set here since in our earlier studies [12] the dipole moment of water molecules in water cluster we applied the same set. In another work [27], we used the BLYP functional for calculating the dipole moment of water in water clusters: the conclusions were the same as when using the more sophisticated density functional method. We investigated three kinds of protic molecules, with the ability of acting as H-bond donors and acceptors (DA), methanol, formamide and water, and two aprotic polar molecules (A), acetone and acetonitrile. The coordination properties of the metal-DA molecular complexes have been investigated in several articles [40,45–56,60–62]. In the $M + 6$ DA molecule cluster ($M = Mg^{2+}$, $Ca^{2+}$, $Al^{3+}$) water, methanol and formamide molecules occupy octahedral positions around the metal ion, whereas these molecules in the inner sphere of Li$^+$ are accommodated on tetrahedral positions. Each water molecule of the inner sphere form two hydrogen bonds with outer shell water molecules as H-bond donor. In the $M + 4A$ complexes solvent molecules occupy tetrahedral position.

In the Na$^+$–DA cluster, molecules form two virtually planar cyclic trimers (bonded through typical OH..O H-bonds or CH..O type H-bonds), above and below the ion.
The structures of these clusters are shown in Figure 1A,C,D for the first shell, and in Figure 1B for both the first shell and second shells of water. Atomic coordinates of these complexes can be found in the data repository. Additionally, the metal–ligand characteristic distances and complexation energies (with and without BSSE [63] correction and at aug-cc-pVTZ/cc-pVTZ level) are presented in the Supp. Mat. Table S1. At this level of theory (m052x/cc-pVTZ) the BSSE correction is about 1%–9% (the largest corrections is obtained for the Na⁺-6methanol complex). The metal–ligand characteristic distances for Li¹⁺, Mg²⁺ and Al³⁺ are similar (the difference is less than 5%).

In order to calculate the dipole moment of a species in the clusters, the electronic density corresponding to the localized orbitals of the given monomers (five and nine in the cases of water and methanol, respectively) needs to be investigated. It has been known that these orbitals are not uniquely determined and depend somewhat on the localization criterion applied [12]. The experience gained in Reference [12] showed that it is practically irrelevant what localization scheme is used. Here, we apply the scheme based on the Magnasco–Perico [17] localization criterion (with subsequent orthogonalization), by applying the algorithm developed by our group [13]. A more detailed description of this localisation scheme can be found in the supplementary material S1.

In these localization criteria the Mulliken net population of each orbital is maximized on a given individual monomer. Here we remark that if the delocalisation tail (contributions from different monomers, covalent bond order among the monomer) is too large than the exact interpretation of the monomer molecule becomes questionable. In these cases, we must interpret the obtained dipole moment values with great care. This localisation technique has the advantage that by introducing an additional procedure for truncating the orbitals to the basis of the defined monomer studied, one obtains an orthogonal set of orbitals. After normalizing these orbitals one can easily calculate the dipole moment of the monomer studied, without the influence of delocalization effects [12]. This way, a different localization transformation of the orbitals of the whole cluster is performed for each monomer separately. We denoted this type of technique as the Magnasco–Perico truncated (Mag-Per-trunc) scheme. In their previous work, Mayer et al. [12] found that for the dipole moment of water molecules in water cluster is in good agreement with that obtained by the Bader (3D type of decomposition scheme) method (Further details are described in Reference [12,13]. In that work we studied how the dipole moments of water molecules change when the number of water molecules in the cluster increases).

For assessing the accuracy of our calculations, we have also calculated the dipole moments of the investigated monomers of the above mentioned, as well as of some other polar DA and A type molecules at the M052X/cc-pVTZ level of theory. There are several comprehensive benchmark data sets [64–68] for quantifying the accuracy of different DFT functional for calculating the dipole moment of molecules. In these works the authors mainly apply Equation (2) at the CCSD(T)/aug-cc-pVQZ level as a benchmark value for calculation. In the present work, due to the missing electronic densities at the CCSD(T) level of theory, we applied Equation (2) at the CCSD(T)/aug-cc-pVQZ and PVTZ level as a benchmark values. Additionally, we checked the accuracy of Equation (2) at the level of theory mentioned above against Equation (1) at the highest theoretical level where electronic densities are available (CCSD). It is possible to calculate the dipole moment of molecules at this level of theory since the electronic densities are available. In Equation (2) we apply a field strength of 0.001 au (note that application of field strengths of an order of magnitude higher changes the results only insignificantly, by less than 0.3%). The calculated data are presented in Table 1. These data clearly prove

FIGURE 1 Mₙ₋water investigated complexes: (A) Octahedral and tetrahedral arrangements of water molecules around the metal cation, (B) arrangement of water molecules in the second shell of metal ion in Mₙ₋water +m-water, n = 4,6 and m = 8,12 respectively. (C) Arrangement of acetone and acetonitrile around metal cation, (D) arrangement of formamide and methanol molecule around Na⁺ ion
that the accuracy of Equation (2) at the CCSD level of theory is better than 0.1%. Additionally, these data also showed that the dipole moment of the molecules under study at the m052x/cc-pvTZ level of theory deviate from the benchmark theory by less than approximately 5%. Thus the accuracy of our calculations appears sufficient to draw further conclusions.

Some of the localized orbitals belonging to water molecules near the ions are shown in Figure 2. In these molecular orbitals we can find significant contributions from atomic orbitals of the ions, as well ("back donation"). The actual charges on the metal ions, that can give us an insight into the extent of charge transfer process, were calculated using Bader [1], Mulliken and NBO [15] methods. The mixing term (contribution from different monomers in the MP scheme) or the Mayer bond order can provide information about the applicability of a given localisation scheme. If it is too large (Mayer bond order is close to 1, as a real covalent single bond) then the definition of a monomer in a supermolecule, as well as calculation of the dipole moment itself, become questionable.

### 3 RESULTS AND DISCUSSION

#### 3.1 Dipole moment of water molecules around cations

Table 2 contains data of some calculations devoted to assessing the qualitative and quantitative adequacy of the level of theory applied. For this purpose, we calculated the dipole moment for a single water molecule in the neighborhood of an ion and/or point-like charge at the position of the ion. (The geometries correspond to ions and water molecules were taken from an optimized geometry of the ion-first hydration shell complex.) Point charge models are also considered for some charge values that are smaller than the nominal ones of the cations, in order to reflect the fact that effective cation charges are expected to be smaller than nominal ones.

Results obtained at the M05-2X/cc-pVTZ DFT level of theory are also compared with those calculated at the CCSD level—the highest level of theory for which dipole moment calculations are actually feasible without applying the approximation of Equation (2). CCSD calculations were performed for cases where the cation is represented by a point charge; the calculation of the dipole moment of water molecules separately would not be possible at the CCSD level if the ions were also treated at the full quantum mechanical level. For comparison, DFT and CCSD results obtained by using the aug-cc-pVTZ basis are also shown for the point charge models.
Inspecting data in Table 2, three main conclusions can be drawn. First, practically in all cases, the M05-2X DFT results are very close to those of the CCSD ones, giving us confidence in the adequacy of the DFT scheme applied. Second, the effect of a cation on the dipole moment is essentially the electrostatic effect of its charge. Third, the use of augmented basis set should be avoided in such calculations, as they lead to unrealistically large dipole moment values. Apparently, the presence of the diffuse functions lacking true localization on water leads to an overestimated relocation of the electron density to the positive center (overestimated "back donation"). The value of dipole moment of water in M..L water complex for (Li+, Na+, Mg2+, Ca2+, Al3+) ions also agrees well with results obtained from Krekeler et al. [47–49], who used different functional and localisation scheme.

For reference, we quote some further numerical values. The experimental dipole moment of a single water molecule in vacuum is 1.855 D [4]; the dipole moment of a water molecule in bulk water is estimated (experimentally and theoretically) to be between 2.8 and 2.95 D [1–3,18–23]. Using the cc-pVTZ basis set and optimized geometry, the dipole moment of a free water molecule was obtained 1.986 D for the M05-2X DFT model and 1.908 D at the CCSD level of theory. The average value of the dipole moments of individual monomers in different clusters containing 20–30 water molecules was ca. 3.05 D at the M05-2X/cc-pVTZ level [27]. It is apparent from Table 2 that the presence of a cation (its positive charge) polarizes water molecule resulting in an increased dipole moment.

Tables 3–5 contain dipole moments of water molecules in water complexes containing the first two hydration shells around Li+, Na+, Mg2+, Ca2+, Al3+ ions. Reduced complexes, with the first hydration shell only, are also shown, along with results when the cations were replaced by point charges slightly smaller than their nominal values. These data indicate, again, that the dipole moments of water molecules

### Table 2
Dipole moments of a single water molecule in the neighborhood of an ion and/or point-like charge (charge:Ch)

| System         | Dipole moment/D | CCSD+p.c. | DFT-aug | CCSD-aug |
|----------------|-----------------|-----------|---------|----------|
| Cation         | Point charge    | R(me-O) Å | DFT+ ion | DFT+ p.c. |         |         |
| Point ch.      | 0.50            | 1.92      | 2.54    | 2.46     | 2.68    | 2.61    |
| Li+/point ch.  | 1.00            | 1.92      | 3.13    | 3.15     | 3.07    | 3.66    | 3.59    |
| Point ch.      | 0.50            | 2.38      | 2.25    | 2.26     | 2.31    | 2.24    |
| Na+/point ch.  | 1.00            | 2.38      | 2.65    | 2.58     | 2.50    | 2.87    | 2.80    |
| Point ch.      | 1.50            | 2.08      | 3.53    | 3.45     | 4.59    | 4.51    |
| Mg2+/point ch. | 2.00            | 2.08      | 4.28    | 4.11     | 4.02    | 6.06    | 6.13    |
| Point ch.      | 1.50            | 2.37      | 3.21    | 3.12     | 3.94    | 3.12    |
| Ca2+/point ch. | 2.00            | 2.37      | 3.91    | 3.26     | 3.55    | 5.22    | 5.15    |
| Point ch.      | 2.00            | 1.93      | 4.52    | 4.41     | 6.70    | 6.80    |
| Al3+/point ch. | 3.00            | 1.93      | 6.67    | 6.01     | 5.89    | 10.87   | 16.03   |

*The geometry corresponds to the cluster of Li+ with 12 water molecules.
*bThe geometry corresponds to the cluster of Li+ with 4 water molecules.
*cOnly the first hydration shell of the previous cluster conserved.
*dThe geometry corresponds to the cluster of Na+ with 18 water molecules.
*eOnly the first hydration shell of the previous cluster conserved.
*fThe geometry corresponds to the cluster of Na+ with 6 water molecules.

Inspecting data in Table 2, three main conclusions can be drawn. First, practically in all cases, the M05-2X DFT results are very close to those of the CCSD ones, giving us confidence in the adequacy of the DFT scheme applied. Second, the effect of a cation on the dipole moment is essentially the electrostatic effect of its charge. Third, the use of augmented basis set should be avoided in such calculations, as they lead to unrealistically large dipole moment values. Apparently, the presence of the diffuse functions lacking true localization on water leads to an overestimated relocation of the electron density to the positive center (overestimated “back donation”). The value of dipole moment of water in M..L water complex for (Li+, Na+, Mg2+, Ca2+) ions also agrees well with results obtained from Krekeler et al. [47–49], who used different functional and localisation scheme.

For reference, we quote some further numerical values. The experimental dipole moment of a single water molecule in vacuum is 1.855 D [4]; the dipole moment of a water molecule in bulk water is estimated (experimentally and theoretically) to be between 2.8 and 2.95 D [1–3,18–23]. Using the cc-pVTZ basis set and optimized geometry, the dipole moment of a free water molecule was obtained 1.986 D for the M05-2X DFT model and 1.908 D at the CCSD level of theory. The average value of the dipole moments of individual monomers in different clusters containing 20–30 water molecules was ca. 3.05 D at the M05-2X/cc-pVTZ level [27]. It is apparent from Table 2 that the presence of a cation (its positive charge) polarizes water molecule resulting in an increased dipole moment.

Tables 3–5 contain dipole moments of water molecules in water complexes containing the first two hydration shells around Li+, Na+, Mg2+, Ca2+, Al3+, respectively. Reduced complexes, with the first hydration shell only, are also shown, along with results when the cations were replaced by point charges slightly smaller than their nominal values. These data indicate, again, that the dipole moments of water molecules...
TABLE 4  Dipole moments of water molecules in the neighborhood of an ion and/or point-like charge calculated at the M05-2X/cc-pVTZ level for Mg$^{2+}$ and Ca$^{2+}$ complexes

|                   | Dipole moment (D) |                  |                  |                  |                  |
|-------------------|-------------------|------------------|------------------|------------------|------------------|
|                   | Point charge      | 1st shell        | 2nd shell        | 1st shell        | 2nd shell        |
|                   |                   | with cation      | with cation      | with point ch.   | with point ch.   |
| Point ch. with 18 H$_2$O$^a$ | 1.75              |                  |                  | 3.24–3.40        | 2.69–2.80        |
| Mg$^{2+}$/point ch. with 18 H$_2$O$^a$ | 2.0               | 3.25–3.42        | 2.71–2.82        | 3.45–3.58        | 2.72–2.86        |
| Point charge with 6 H$_2$O$^b$ | 1.75              |                  |                  | 3.15–3.17        |                  |
| Mg$^{2+}$/point ch. with 6H$_2$O$^c$ | 2.0               | 3.18–3.18        |                  | 3.39–3.41        |                  |
| Point ch. with 18 H$_2$O$^d$ | 1.75              |                  |                  | 3.13–3.35        | 2.71–2.84        |
| Ca$^{2+}$/point ch. with 18 H$_2$O$^d$ | 2.0               | 3.19–3.40        | 2.73–2.90        | 3.33–3.49        | 2.73–2.89        |
| Point charge with 6 H$_2$O$^e$ | 1.75              |                  |                  | 3.02–3.05        |                  |
| Ca$^{2+}$/point ch. with 6 H$_2$O$^f$ | 2.0               | 3.12–3.12        |                  | 3.22–3.24        |                  |

$^a$The geometry corresponds to the cluster of Mg$^{2+}$ with 18 water molecules.
$^b$The geometry corresponds to the cluster of Mg$^{2+}$ with 6 water molecules.
$^c$Only the first hydration shell of the previous cluster conserved.
$^d$The geometry corresponds to the cluster of Ca$^{2+}$ with 18 water molecules.
$^e$Only the first hydration shell of the previous cluster conserved.
$^f$The geometry corresponds to the cluster of Ca$^{2+}$ with 6 water molecules.

TABLE 5  Dipole moments of water molecules in the neighborhood of an ion and/or point-like charge calculated at the M05-2X/cc-pVTZ level for Al$^{3+}$ complexes

|                   | Dipole moment (D) |                  |                  |                  |                  |
|-------------------|-------------------|------------------|------------------|------------------|------------------|
|                   | Point charge      | 1st shell        | 2nd shell        | 1st shell        | 2nd shell        |
|                   |                   | with cation      | with cation      | with point ch.   | with point ch.   |
| Point charge with 18 H$_2$O$^a$ | 2.5               |                  |                  | 3.97–4.21        | 2.83–2.96        |
| Al$^{3+}$/point ch. with 18 H$_2$O$^a$ | 3.0               | 4.09–4.26        | 2.99–3.12        | 4.61–4.84        | 2.98–3.12        |
| Point charge with 6 H$_2$O$^b$ | 2.5               |                  |                  | 4.06–4.09        |                  |
| Al$^{3+}$/point Ch. with 6H$_2$O$^c$ | 3.0               | 4.14–4.14        |                  | 4.74–4.76        |                  |

$^a$The geometry corresponds to the cluster of Al$^{3+}$ with 18 water molecules.
$^b$The geometry corresponds to the cluster of Al$^{3+}$ with 6 water molecules.
$^c$Only the first hydration shell of the previous cluster conserved.

TABLE 6  The calculated charge on metal ion the M-(Wa)$_n$ cluster

|                | Bader  | Mulliken | NBO    | Mixing term |
|----------------|--------|----------|--------|-------------|
| Li$^+$ + 4H$_2$O | 0.912  | 0.191    | 0.720  | 0.065       |
| Li$^+$ + 4H$_2$O + 8H$_2$O | 0.901  | 0.010    | 0.690  | 0.010       |
| Na$^+$ + 6H$_2$O | 0.913  | 0.353    | 0.760  | 0.250       |
| Na$^+$ + 6H$_2$O + 12H$_2$O | 0.904  | 0.263    | 0.680  | 0.097       |
| Mg$^{2+}$ + 6H$_2$O | 1.790  | 0.822    | 1.381  | 0.732       |
| Mg$^{2+}$ + 6H$_2$O + 12H$_2$O | 1.781  | 0.681    | 1.342  | 0.625       |
| Ca$^{2+}$ + 6H$_2$O | 1.732  | 1.032    | 1.441  | 0.961       |
| Ca$^{2+}$ + 6H$_2$O + 12H$_2$O | 1.713  | 0.781    | 1.334  | 0.718       |
| Al$^{3+}$ + 6H$_2$O | 2.642  | 0.471    | 1.981  | 0.348       |
| Al$^{3+}$ + 6H$_2$O + 12H$_2$O | 2.631  | 0.323    | 1.974  | 0.174       |
are basically determined by the electrostatic charge of the cations. Values obtained for the cations are slightly lower than those obtained with the point charges equaling the formal charge of the cations, indicating that cations should be simulated using effective charges somewhat smaller than their nominal charges. This is in accordance with the common assumption that the presence of a bare positive charge induces some “back donation” of electrons from water molecules in the bulk. Note also that our results for dipole moments for water in the first shell of cations are in line with earlier studies, including more realistic sampling of the environment in a liquid phase (ab initio MD) [45–52].
Calculated charges on the metal atom in the clusters are shown in Table 6. Apparently, the calculated charges depend on the applied method (Bader, Mulliken, NBO, our method, i.e., mixing term in the Magnasco–Perico scheme), but all methods suggest some kind of a charge transfer process. Our calculation based on the mixing of cation and water atomic orbitals give a well defined correlation (appr. 0.99) with the Mulliken charge. This is not very suprising, as the localisation technique applied is based on the maximalization of the net Mulliken population. It is clear also that the influence of second shell water molecules to the cation’s charges is not too large, but significant. This is not surprising since all of the second shell water molecules are H-bond acceptors. The effective charges, calculated using interpolation to recover the "true" dipole moment of water in the first shell of metals, are about 0.90 and 1.81 for mono and divalent cations, and about 2.72 for Al$^{3+}$. These data support the application of scaled charges for cations in molecular dynamics studies of aqueous solution [68–71].

Dipole moments of water molecules in the first hydration shell are, as expected, sensitive to the charge of the cation while, interestingly enough, the dipole moments in the second hydration shell are more-or-less the same for all complexes—although significantly larger than that of a free water molecule. This is not suprising since there are strong H-bonds between the first and second shells. The dipole moment of water in the water dimer is about 2.1–2.2 D, which is significantly smaller than the corresponding values in the second hydration shells. For ions with formal charges +2 and +3, the dipole moments of water molecules in the first hydration shell are significantly smaller than those observed for a single water molecule in the vicinity of a cation (Table 1). At the same time, the presence of the second hydration shell increases the dipole moments in the first shell, as may be observed by comparing results obtained for whole complexes with those in which only the first hydration shell is conserved. This fact is arising to the polarization effect of the water in the second shell.

**FIGURE 3**  The calculated dipole moment in the presence of charge/cation (cross) for the investigated cluster ([A] methanol, formamide, water; [B] acetone, acetonitrile)
The significant changes of dipole moments of water molecules in the vicinity of a cation with the increase of their number has already been indicated in References [47–49]. This effect may be studied in some detail by considering our data in Table 7. These results indicate that—besides the electrostatic effect of the cation—cooperative effects of the water molecules play an important role in determining the value of the individual dipole moments. It is uncertain whether this effect is arising from the water molecules themselves in the octahedral (tetrahedral) arrangement (water–water interactions), or the polarized water molecules in the same position.

In order to obtain a better understanding of these collective effects, we have also performed calculations in which water molecules were considered in the molecular arrangement they have around a cation in the first hydration shell—but with the cations being removed. Results shown in Table 8 indicate that the geometrical arrangement of water molecules in the first hydration shell is such that their mutual polarization reduces the molecular dipole moments—in all cases, except the Na+ complex, not only as compared to the bulk value but even below that of the free monomer. In the Na+ complex the first hydration shell has a very specific hydrogen bonded network; this leads to some increase of the dipole moments due to the delocalizations along the hydrogen bonds among the water molecule. This counteracting behavior is essentially a manifestation of the Le Chatelier–Braun principle: the physico-chemical system reacts to the external perturbation in a manner so that to reduce the effect of the perturbation. In this case the perturbation to the dipole moment of water molecules is caused by the cation electrostatically, quantum chemically), and water molecules occupy special positions around cations for reducing their dipole moment.

### 3.2 Dipole moment of aprotic and protic molecules around a cation

Calculated dipole moments of these molecules around cations are presented in Table 8. It is clear from the table that the dipole moments of all molecules are increased significantly, similarly to water complexes considered in more detail. We can detect the smallest/largest effects (ca. 30%–50%/250%–350%) for the cases of Na+/Al3+ for all solvent molecules, respectively. Here we would like to remark that the overlap term for Al3+-solvent molecule complexes, and additionally, the Al3+-O or N bond order is too large, so the calculated dipole moment for these complexes, using the MP procedure without truncation, can be questionable (Table 9 and Supp. Mat. Table S2.)

These molecular dipole moments obtained for the cations are lower than those obtained with the point charges equal to the nominal charge of the cations, similarly to what we have already demonstrated for the cases of M-water complexes. Results are presented in Figure 3.

Our data suggest that cations in water should be simulated with an effective charge that is somewhat smaller (approx. 80% of the nominal charge) than the nominal charge. Here we would like to remark that the charges of ions in liquid water, applied in the scaled particle model, is also about 75%–80% of the nominal charge [68–71]. On the other hand, there are some other works in the literature that suggest the usage of the nominal charge of monovalent cations for simulating ionic liquids and electrolyte solutions [72,73].

We also showed that for the solvation of Li+, Mg2+ and Al3+ ions, where the obtained energy minimum configurations give similar metal-ligand distances (see Supp. Mat Table S1a), the dipole moment of solvent molecules is approximately linearly proportional to the charge placed into the location of the ion (Figure 3).

Distorting the geometry of solvent molecules does not cause a significant (greater than 2%) change in terms of their dipole moments, as presented in Supp. Mat Figure S1. In these cases it was also observed that the dipole moment of the solvent molecules, without ions or charges in the centre of the complex, is significantly less than the value obtained for the optimal geometry. This finding is in good agreement with results obtained for ion-water complexes (Table 8).

### 4 CONCLUSIONS

Based on our calculations it can be concluded that the dipole moment of polar molecules in the neighborhood of a cation is primarily influenced by polarization from the bare electrostatic charge of the cation. The effective value of the ionic charge is somewhat reduced by “back donation” of electrons from water molecules. The effect of distorting molecular geometry on the dipole moment of solvent molecules is very small. A further important factor is the collective effect of water molecules: their mutual arrangement and polarization counteracts the polarizing effect of the cation, resulting in less increased values of the dipole moments, in comparison with the 1 ion–1 solvent molecule setup. This behavior is essentially a manifestation of the Le Chatelier–Braun principle. In addition it can be remarked that if the cation-molecule bond order is too large then the calculated dipole moment in these complexes, can be questionable, due to the improper definition of single molecules in a “supermolecule.”

### ACKNOWLEDGMENTS

The authors acknowledge financial support from the National Research, Development and Innovation Office (NRDIO [NKFIH], Hungary), via grants Nos 124885, 128136 and KH 130425. Computational resources from NIIF supercomputer center are also acknowledged. Sz. Pothoczki acknowledges that this project was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences.
AUTHOR CONTRIBUTIONS
Imre Bakó: Conceptualization; formal analysis; validation; visualization; writing-review & editing. István Mayer: Conceptualization; software.
Dániel Csőkás: Validation; writing-review & editing. Szilvia Pothoczki: Validation; writing-review & editing. László Pusztai: Validation; writing-review & editing.

DATA AVAILABILITY STATEMENT
Data repository: https://downloadables.ttk.hu/bako/Influence_of_cations.

ORCID
Imre Bakó https://orcid.org/0000-0002-6302-5999

REFERENCES
[1] Y. S. Badyal, M. -L. Saboungi, D. L. Price, S. D. Shastri, D. Haeffner, A. K. Soper, J. Chem. Phys. 2000, 112, 9206.
[2] C. A. D. Coulson, D. Eisenberg, Proc. R. Soc. London A 1966, 291, 445.
[3] D. H. Brookes, T. Head-Gordon, J. Phys. Chem. Lett. 2015, 6, 2938.
[4] S. A. Clough, Y. Beers, G. P. Klein, L. S. Rothman, J. Chem. Phys. 1973, 59, 2254.
[5] O. Dorosh, Z. Kisiel, Acta Phys. Pol. A 2007, 112, 5-95.
[6] A. L. McClellan, Tables of Experimental Dipole Moment, Rahara Enterprises, El Cerrito, CA 1989.
[7] R. Rivelino, B. J. Costa Cabral, K. Coutinho, S. Canuto, Chem. Phys. Lett. 2005, 407, 13.
[8] J. Carmona-Espinola, E. Nunez-Rojas, V. Garcia-Melgarejo, J. L. Gazquez, J. Leon, J. Chem. Phys. 2020, 152, 124116.
[9] S. Canuto, K. Coutinho, M. C. Zerner, J. Chem. Phys. 2000, 112, 7293.
[10] R. F. W. Bader, C. F. Matta, Int. J. Quantum Chem. 2001, 85, 592.
[11] M. Devereux, P. L. A. Popelier, J. Phys. Chem. A 2007, 111, 1536.
[12] I. Bakó, I. Mayer, J. Phys. Chem. A 2016, 120, 4408.
[13] I. Mayer, J. Phys. Chem. 1996, 100, 6249.
[14] S. F. Boys, Rev. Mod. Phys. 1960, 32, 296.
[15] A. E. Reed, F. Weinhold, J. Chem. Phys. 1985, 83, 1736.
[16] V. Magnasco, A. Perico, J. Chem. Phys. 1967, 47, 971.
[17] I. Mayer, G. Räther, S. Suhai, Chem. Phys. Lett. 1998, 293, 81.
[18] C. M. Handy, P. L. A. Popelier, Synth. React. Inorg. Met. Organ. Nano-Met. Chem. 2008, 38, 91.
[19] L. D. Site, A. Alavi, R. M. Lynden-Bell, Mol. Phys. 1999, 96, 1683.
[20] A. V. Gubskaya, P. G. Kusalik, J. Chem. Phys. 2002, 117, 5290.
[21] P. L. Silvestrelli, M. Parrassi, Phys. Rev. Lett. 1999, 82, 3308.
[22] P. J. Dyer, P. J. Cummings, Chem. Phys. 2006, 125, 14451.
[23] P. L. Silvestrelli, M. Parrassi, J. Chem. Phys. 1999, 111, 3572.
[24] R. F. Dias, C. C. da Costaa, T. M. Manhabosco, A. B. de Oliveira, J. S. Matheus Matos, J. S. Soares, R. J. C. Batista, Chem. Phys. Lett. 2019, 714, 172.
[25] N. Sieffert, M. Bürk, M. Pierre Gaigeot, C. A. Morrison, J. Chem. Theory Comput. 2013, 9, 106.
[26] J. A. Moran, K. E. Haslinger, M. E. Tuckerman, J. Phys. Chem. B 2006, 110, 3712.
[27] I. Bakó, J. Daru, S. Z. Pothoczki, L. Pusztai, K. Hermansson, J. Mol. Liq. 2019, 293, 11579.
[28] B. Bagchi, Water in Biological and Chemical Processes: From Structure and Dynamics to Function, Cambridge University Press, Cambridge 2014.
[29] M. Chaplin, Water Structure and Science, London South Bank University, Cambridge. http://www.lsbus.ac.uk/water/ (accessed 14 January, 2016).
[30] D. Eisenberg, W. Kauzmann, The Structure and Properties of Water, Oxford University Press, Oxford, UK 2005.
[31] S. J. Grabowski, Series Challenges and Advances in Computational Chemistry and Physics. in Hydrogen Bonding-New Insights (Ed: J. Leszczynski), Springer, New York, NY 2006.
[32] I. Bakó, Á. Bencsura, K. Hermansson, S. Z. Bălăint, T. Grósz, V. Chilaia, J. Olah, Phys. Chem. Chem. Phys. 2013, 15, 15163.
[33] R. Lynden-Bell, S. C. Moris, J. D. Barrow, J. L. Finney, C. L. Harper, Water and Life: The Unique Properties of H2O, CRC Press, Boca Raton, FL 2010.
[34] P. Ball, Chem. Rev. 2008, 108, 74.
[35] H. Ohtaki, T. Radnai, Chem. Rev. 1993, 92, 1157.
[36] H. J. Bakker, Chem. Rev. 2008, 108, 1456.
[37] Y. Marcus, Chem. Rev. 2009, 109, 1346.
[38] M. T. Ong, O. Verners, E. W. Draeger, A. C. T. Duin, V. Lordi, J. E. Pask, J. Phys. Chem. B 2015, 119, 1535.
[39] T. A. Pham, K. E., Kweon, A. Samanta, V. Lordi, J. E. Pask, J. Phys. Chem. C 2017, 121, 21913.
[40] R. López, N. Díaz, D. Suárez, Chem. Phys. Chem. 2020, 21, 99.
[41] L. Nostro Pierandrea, W. W. Ninquam, Chem. Rev. 2012, 112, 2286.
[42] N. Vlachy, B. Jagoda-Cwilik, R. Vácha, D. Touraud, P. Jungwirth, W. Kunz, Adv. Colloid Interface Sci. 2009, 146, 42.
[43] J. Lylema, Chem. Phys. Lett. 2009, 467, 217.
[44] Y. Zhang, P. S. Cremer, Curr. Opin. Chem. Biol. 2006, 10, 658.
[45] F. C. E. Lightstone, E. Schwager, R. Q. Hood, F. Gygi, G. Galli, Chem. Phys. Lett. 2001, 343, 549.
[46] I. Bakó, J. Hutter, G. Pálinski, J. Chem. Phys. 2002, 117, 9838.
[47] C. Krekeler, B. Hess, L. Delle Site, J. Chem. Phys. 2006, 125, 054305.
[48] C. Krekeler, L. Delle Site, J. Phys. Condens. Matter 2007, 19, 192101.
[49] C. Krekeler, L. Delle Site, J. Chem. Phys. 2008, 128, 134515.
[50] T. Ikeda, M. Boero, K. Terakura, J. Chem. Phys. 2007, 126, 034501.
[51] Y. Liu, H. Lu, Y. Wu, T. Hu, Q. Li, J. Chem. Phys. 2010, 132, 124503.
[52] P. D. Mitev, I. Bakó, A. Eriksson, K. Hermansson, Phys. Chem. Chem. Phys. 2014, 16, 9351.
[53] S. Bogatko, E. Cauet, E. Bylaska, G. Schenter, J. Fulton, J. Weare, Chem. Eur. J. 2013, 19, 3047.
[54] C. Farall, M. Pagliai, M. Cardini, V. Schettino, J. Chem. Theory Comput. 2008, 4, 156.
[55] M. Pagliai, G. Cardini, V. Schettino, J. Phys. Chem. B 2005, 109, 7475.
[56] P. D. Mitev, A. Eriksson, K. Hermansson, Phys. Chem. Chem. Phys. 2014, 16, 9351.
[57] S. Bogatko, E. Cauet, E. Bylaska, G. Schenter, J. Fulton, J. Weare, Chem. Eur. J. 2013, 19, 3047.
[58] Y. Zhao, N. E. Schultz, D. G. Truhlar, J. Chem. Theory Comput. 2006, 2, 364.
[59] S. Blazquez, I. M. Zeron, M. M. Conde, J. L. F. Abascal, C. Vega, Fluid Phase Equilib. 2020, 513, 112548.
[60] M. Předota, D. Biriukov, J. Mol. Liq. 2020, 314, 113571.
[61] M. Martínez-Jiménez, M. Serrano-Ocaña, J. Alejandre, J. Mol. Liq. 2021, 329, 115488.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: I. Bakó, D. Csókás, I. Mayer, S. Pothoczki, L. Pusztai, Int J Quantum Chem 2021, e26758. https://doi.org/10.1002/qua.26758