ESTUDO DE ESPECTROSCOPIA DE CLUSTER $\text{MCl}_2(\text{H}_2\text{O})_n$ USANDO CÁLCULOS
AB INITIO

SPECTROSCOPY STUDY OF $\text{MCl}_2(\text{H}_2\text{O})_n$ CLUSTER USING AB INITIO CALCULATIONS

AB INITIO دراسة طيفية لمعقدات $\text{MCl}_2(\text{H}_2\text{O})_n$ باستخدام حسابات

SADOON, Ahmed M.^{1*}; SHEEJ AHMAD, Omar^{1,2}

¹ Department of Chemistry, College of Education for Pure Sciences, University of Mosul, Mosul, Iraq

² Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, United Kingdom

* Corresponding author

e-mail: ams95@uomosul.edu.iq

Received 13 August 2020; received in revised form 27 September 2020; accepted 15 October 2020

RESUMO

A espectroscopia de infravermelho (IV) de complexos de sal de haleto alcalino-terroso (MX_2) com poucos números de moléculas de água foi investigada pela primeira vez neste trabalho. BeCl_2 e MgCl_2 são sais divalentes e foram incorporados com água como solvente polar para formar complexos do tipo $\text{MX}_2(\text{H}_2\text{O})_n$. O efeito do tamanho do íon desempenha uma regra crítica nas interações entre solvente e soluto. Portanto, os sais de berílio e magnésio com cloreto foram escolhidos para explorar essa diferença. A importância do BeCl_2 e do MgCl_2 vem de suas diversas aplicações na indústria e farmácia. Por exemplo, BeCl_2 é amplamente utilizado na indústria como catálise de reações de Friedel-Craft, enquanto a principal aplicação de MgCl_2 em farmácia é como fluidos de hemodiálise e diálise peritoneal. Três complexos de cada BeCl_2 e MgCl_2 com água, $\text{MX}_2(\text{H}_2\text{O})_n$ ($n = 1-3$) foram estudados e as estruturas químicas desses complexos foram realizadas usando cálculos ab initio. Cálculos ab initio foram usados para prever estruturas possíveis, isômeros e seus espectros de IV correspondentes usando a teoria de perturbação de Møller-Plesset de segunda ordem (MP2) com 6-311 ++ G como conjuntos de base. As avaliações de geometria, buscas de energia, cálculos de frequência vibracional e a energia de ligação de cada complexo também foram extraídos teoricamente. As energias mínimas das estruturas complexas foram calculadas e diferentes isômeros foram registrados. As ligações iônicas de hidrogênio (IHBs) entre o OH em cada molécula de água e o íon cloreto no MCl_2 foram propostas como sendo a principal contribuição prevalente para a ligação entre o sal e a água. O comprimento da ligação entre o metal alcalino e o cloro mostrou um aumento significativo com o aumento da molécula de água ligada como resultado da formação do IHB. Além disso, as bandas vibracionais infravermelhas da região de alongamento OH foram registradas para as estruturas mínimas e redshift dramático foi executado. A formação de estruturas de pares de íons de contato nas quais cada molécula de solvente forma uma ligação de hidrogênio iônica (IHB) ao par de íons de sal ($\text{X-M} + \text{X-}$) foi confirmada pelos espectros infravermelhos previstos.

Palavras-chave: Espectroscopia, cálculos Ab initio, Complexos metal alcalino-terrosos-água.

ABSTRACT

The Infrared (IR) spectroscopy of alkali earth halide salt (MX_2) complexes with few numbers of water molecules have been investigated for the first time in this work. BeCl_2 and MgCl_2 are divalent salts and have been incorporated with water as a polar solvent to form complexes of type $\text{MX}_2(\text{H}_2\text{O})_n$. The effect of ion size plays a critical rule in the interactions between solvent and solute. Therefore, Beryllium and Magnesium salts with chloride were chosen to explore this difference. The importance of BeCl_2 and MgCl_2 comes from their several applications in the industry and pharmacy. For instance, BeCl_2 is widely used in the industry as a catalysis of Friede-Craft reactions, while the main application of MgCl_2 in pharmacy is as hemodialysis and peritoneal dialysis fluids. Three complexes of each BeCl_2 and MgCl_2 with water, $\text{MX}_2(\text{H}_2\text{O})_n$ ($n=1-3$), were studied, and the chemical structures of these complexes have been performed using *ab initio* calculations. *Ab initio* calculations were used to predict possible structures, isomers, and their corresponding IR spectra using Second-order Møller-Plesset perturbation theory (MP2) with 6-311++G as a basis sets. The Geometry evaluations, energy searches, vibrational frequency calculations, and the binding energy of each complex were also extracted theoretically. The minimum energy of complexes structures was calculated, and different isomers have been recorded. Ionic hydrogen bonds (IHBs) between the OH in each water molecule and the chloride ion in the MCl_2 was proposed to be the main prevalent contribution to the binding between the salt and water. The bond length between the alkaline metal and chlorine

showed a significant increase with increasing the attached water molecule as a result of forming the IHB. Also, the infrared vibrational bands of the OH stretching region were recorded for the minimum structures, and dramatic redshift was performed. The formation of contact-ion pair structures in which each solvent molecule forms an ionic hydrogen bond (IHB) to the salt ion-pair ($X^+M^+X^-$) has been confirmed by the predicted infrared spectra.

Keywords: Spectroscopy, Ab initio calculations, Alkaline earth metal-water complexes.

المخلص

تمت دراسة وتسجيل طيف الأشعة تحت الحمراء (IR) لمعقدات تتكون من أملاح الهاليدات القلوية (MX_2) مع الماء لأول مرة في هذا البحث. تعتبر أملاح كلوريد البريليوم وكلوريد المغنيسيوم من الأملاح الرئيسية والمعروفة والتي تم استخدامها مع الماء كمذيب قطبي لتكوين معقدات من النوع $MX_2(H_2O)_n$. إن تأثير حجم الأيونات يلعب دوراً رئيسياً في التداخلات بين المذيب والمذاب. لذلك تم اختيار أملاح البريليوم والمغنيسيوم مع الكلوريد لاستكشاف هذا الاختلاف. إن أهمية أملاح كلوريد البريليوم والمغنيسيوم تأتي من التطبيقات العديدة لهذه الأملاح في الصناعة والتطبيقات الصيدلانية. على سبيل المثال، يستخدم ملح كلوريد في الصناعة لحفاز في تفاعل فيدل كرافت بينما يستخدم كلوريد المغنيسيوم في الصناعات الصيدلانية في محاليل غسيل الكلى. كل هذه التطبيقات تجعل هذه الدراسة ذات فائدة وأهمية كبيرة. تمت دراسة ثلاثة معقدات من كل من $BeCl_2$ و $MgCl_2$ مع الماء تحمل الصيغة العامة التالية، $MX_2(H_2O)_n$ ($n=1-3$)، وتم إجراء حساب التراكيب الكيميائية لهذه المعقدات باستخدام حسابات *ab initio*. تم استخدام هذه الحسابات لاستكشاف التراكيب الممكنة والأيزومرات وأطياف الأشعة تحت الحمراء المقابلة لها باستخدام نظرية اضطراب Møller-Plesset من الدرجة الثانية (MP2) مع 311-6 $G++$ كمجموعات أساسية. كما تم استخلاص الحسابات التركيبية الهندسية، الطاقة الاوطأ، وحسابات التردد الاهتزازي وطاقة الارتباط لكل معقد نظرياً في هذه الدراسة.

تم حساب الحد الأدنى من الطاقة لتراكيب المعقدات المدروسة وتم تسجيل أيزومرات مختلفة. أوضحت النتائج أن الارتباط بين الملح والماء من يأتي من خلال روابط الهيدروجين الأيونية (IHBS) بين مجموعة الهيدروكسيل في كل جزيء ماء وأيون الكلوريد في جزيئة الملح MCl_2 . يظهر طول الاصرة بين الفلز القلوي والكلور زيادة كبيرة مع كل إضافة لجزيء الماء نتيجة لتكوين الاواصر الهيدروجينية. أيضاً، تم تسجيل طيف الأشعة تحت الحمراء للحزم الاهتزازية لمجموعة الهيدروكسيل للمعقدات ذات للحد الأدنى من الطاقة وتم ملاحظة انزياح أحمر كبير لهذه الحزم. تتوافق الأطياف المسجلة مع تكوين الأزواج الأيونية المترابطة حيث يشكل كل جزيء مذيب رابطة هيدروجين أيونية مع الزوج الأيوني $X^+M^+X^-$.

الكلمات المفتاحية: دراسة طيفية، حسابات *Ab initio*، معقدات الماء- فلزات الارترية القلوية

1. INTRODUCTION:

Over many decades, the behavior of ions in solutions has been in the spotlight of many studies (Burgess, 1999; Conway; Weller, 1988). Understanding the behavior of the ion in solution became necessary as a result of their critical role in the chemical solutions, in addition to their applications in specific areas such as environmental chemistry and electrochemistry (Grossfield, Ren, and Ponder, 2003).

kosmotropic or *chaotropic* ions behavior is usually used to express the salt and water interaction as a solvent. Kosmotropic ions have a relatively high charge density, which increases the stability of the hydrogen bonding grid and then increases the water-water interactions, and, for this aspect, it is called (order-makers). However, chaotropic ions (disorder-makers) reduce the stability of the hydrogen bonding grid and thus destabilize the structures of water clusters due to their large size with low charge density that disrupts the water-water structure. (Marcus, 2010; Moelbert, Normand, and De Los Rios, 2004).

It is well known that alkaline earth halides behave as divalent salts. These salts are dissolved in water after distributing the crystalline structure of the solid salt by water to form separated ions in dilute solutions. The size and charge density of the cation and anion are

expected to be the main factor that gives the ability of a single alkaline earth halide molecule to dissolve in a small number of water molecules. $BeCl_2$ and $MgCl_2$ were chosen for this study as an example of salt with a positively charged ion coupled with Cl^- as an anion.

The importance of $BeCl_2$ and $MgCl_2$ comes from their applications in industry and pharmacy. The primary usage of $BeCl_2$ in the industry is a raw material for the electrolysis of beryllium, and as catalysis of Friedel-Craft reactions (Lide, 2004; Raiz, Noor, Rasheed, and Mohammad, 2017). On the other hand, Magnesium chloride is used in several medical applications, especially related to skin. Also, $MgCl_2$ is widely used in pharmaceutical requirements as hemodialysis and peritoneal dialysis fluids (Coşofre and Buck, 1993; Luzzi and Palmieri, 1984).

The comparison between the Alkaline halide (MX) and Alkaline earth halide (MX_2) complexes with water looks useful because of the close behavior between these two kinds of salts in the aqueous solution. Several early researches (Li *et al.*, 2013; Mizoguchi, Ohshima, and Endo, 2003, 2011; Sadoon *et al.*, 2016; Tandy *et al.*, 2016) were concentrated on studying the structure and behavior of Alkaline halide (MX) complexes with water focusing on their geometry structures by recording the infrared (IR) and Mass spectrum using Helium nanodroplet apparatus. These

studies proved that the ionic hydrogen bonds (IHBs) perform a critical role in the formed structures.

Few recent pieces of research deal with MX_2 water complexes. Keshri and Tembe (2017) focused on studying the dynamical and structural properties of MCl_2 in the bulk solution using Molecular dynamics (MD) simulations. The binding energies of $\text{M}^{+2}(\text{H}_2\text{O})_n$ ($n=4,6$) complexes were performed by Ariyaratna and Miliordos (Ariyaratna and Miliordos, 2019). The electronic structures of these complexes are studied using quantum chemical calculations. Naleem *et al.* proposed the force field simulation of alkaline earth halide salts in an aqueous solution (Naleem, Benteritis, and Smith, 2018).

The structures, energetics of alkaline earth metal anion-water clusters $\text{M}-(\text{H}_2\text{O})_n$ ($n=3-6$) were performed by Bajaj and *et al.*, (Bajaj *et al.*, 2019) using Molecular dynamics MD simulations and vibrational spectroscopy calculations. This study suggested the formation of three hydrogen-bond in the metal-ligand clusters for the $\text{M}-(\text{H}_2\text{O})_3$ cluster and this number of ionic hydrogen bonds (IHBs) were increased with increasing the number of attached waters. Another *ab initio* calculations study (Glendening and Feller, 1996) was performed in the gas phase and reported the structures, enthalpies, and binding energies for alkaline earth cation M^{+2} clusters with water $\text{M}^{+2}(\text{H}_2\text{O})_n$ ($n=1-6$). The formation of Contact ion pair structures has been suggested in this study by attaching water molecules to MCl_2 via IHBs between the water H atom and the chloride ion. These structures are similar to the salt-water structures mentioned in the previous researches (Sadoon *et al.*, 2016; Tandy *et al.*, 2016) for Alkaline halide salt (NaCl) complexes with water and methanol.

The theoretical calculation of chemical reactions has been widely used in many recent studies (Mattje, Pinheiro, and Pereira, 2019; Rodrigues, Assis, and Bruni, 2019). The formation of salt-water complexes are usually prepared and studied in bulk solutions (Nancollas, 1970; Turq, Barthel, and Chemla, 2012). Even in the diluted solutions, the separation of $\text{MX}_2(\text{H}_2\text{O})_n$ complexes, where n has a small value, is difficult because of the strong ionic hydrogen network (Meot-Ner, 2012). Unfortunately, an accurate simulation of the properties is still tricky to record even in simple electrolytic solutions (Eisenberg, 2013). Considering this limited experimental evidence, the *ab initio* calculations study of these complexes looks useful and provides a unique tool to explore the chemistry of these complexes.

Therefore, this work aimed to study the interaction of Alkaline earth halides (MX_2) with water in the gas phase theoretically using *ab initio* calculations.

2. MATERIALS AND METHODS:

2.1. $\text{MX}_2(\text{H}_2\text{O})_n$ complexes

The complexes of (MCl_2) salts in the existence of a small number of water molecules ($\text{H}_2\text{O})_n$ where $n=1-3$ were drawn using Chemcraft software package (Zhurko and Zhurko, 2016). Several premier structures were generated with different places and randomly rotating of MCl_2 and water molecules to explore a wide range of potential geometries and possible isomers of $\text{MCl}_2(\text{H}_2\text{O})_n$ complexes. The matrix of geometry was then utilized to find the minima structures of each complex using *ab initio* calculations.

2.2. *Ab initio* calculations

Ab initio calculations were performed using Second-order Møller-Plesset perturbation theory (MP2) (Møller and Plesset, 1934) within the gaussian 03 software package (Frisch, Trucks, and Schlegel, 2009). The basis set (6-311++G) obtained from the EMSL basis set exchange library (Schuchardt *et al.*, 2007) was then used to extract the isomer's geometry, energy, and the infrared (IR) spectra, (vibrational frequency values). To reduce the calculation time, Hartree-Fock (HF) level of theory was first used with (6-311++G) bases set to evaluate the optimized structures. The optimized structures at the HF level were then re-optimized using MP2 level of theory at the same bases set. The vibrational frequencies of the final optimized structures were scaled by 0.950 to gain the correct final values of vibrational frequencies. This scaling factor is suggested by the National Institute of Standards and Technology (NIST) for MP2 level of theory (Johnson III, 2005).

2.3. Geometry and structure data

The final results of the infrared (IR) spectra, frequencies of the OH stretching bands, the minimum energy of isomers, bond length, angles, and the Binding Energy (BE) were extracted later using Chemcraft software.

3. RESULTS AND DISCUSSION:

3.1. Predicted structures of $\text{MCl}_2(\text{H}_2\text{O})_n$

3.1.1 $\text{BeCl}_2(\text{H}_2\text{O})_n$ structures

Two structures of $\text{BeCl}_2(\text{H}_2\text{O})$ were found in the MP2 calculations, shown in Figure 1, for the $\text{BeCl}_2(\text{H}_2\text{O})$ complex corresponding to distinct minima. The global minimum structure shows that the BeCl_2 ions take the position so that the chloride ion can form an IHB with the Hydrogen atom of water. Another IHB is formed between the other chloride of BeCl_2 with the other water molecule. Additional stabilization comes from the Be^{+2} ion to the O^- atom. The next energy minimum structure has an energy 105.64 kJ/mol higher than the global minimum.

As shown in Figure 2, three minima structures were noticed for $\text{BeCl}_2(\text{CH}_2\text{O})_2$. The global minimum structure is similar to the $n = 1$ complex but now has four IHBs bonding the chloride ion and the H atoms of water. The next minimum structure has 20.4 kJ/mol higher than the global minimum structure and has only two IHB. One with water attached to the BeCl_2 via an IHB. The other water molecule in this structure takes the position to allow partial interaction with the other water molecule and another interaction with the chloride atom by IHB. The bond length of these two structures was 1.93 and 1.8 Å, respectively. The last minimum structure was raised in energy above the global minimum structure in about 58.28 kJ/mol. The two water molecules in this structure inserted between the Be^+ ion and one of the Cl^- ions forming two IHBs and increase the bond length between these two atoms to 3.423 Å compared with 1.838 Å for the other Be-Cl bond length.

For $n = 3$, Five minima structures were found (Figure 3). The global minimum for $\text{BeCl}_2(\text{H}_2\text{O})_3$ is different from those found for $\text{BeCl}_2(\text{H}_2\text{O})$ and $\text{BeCl}_2(\text{H}_2\text{O})_2$. Two water molecules were bonded by IHB and then interacted with BeCl_2 with one IHB. The other water molecule is oriented far from the two water molecules and interact with BeCl_2 separately by IHB. However, other minima structures have higher energy from the global minimum structure in about 12.04, 21.004, 24.47, 26.255 kJ/mol, respectively. These structures have different water positions and interact with BeCl_2 via IHBs (Figure 3).

3.1.2 $\text{MgCl}_2(\text{H}_2\text{O})_n$ structures

The predicted calculations for $\text{MgCl}_2(\text{H}_2\text{O})_n$ ($n=1-3$) were found and seen in Figures 4, 5, and 6, respectively. No significant changes were observed in these structures for $\text{MgCl}_2(\text{H}_2\text{O})$ and $\text{MgCl}_2(\text{H}_2\text{O})_2$ compared with the $\text{BeCl}_2(\text{H}_2\text{O})_n$ ($n=1$ and 2) predicted structures. For $n=3$, The minimum structure is different from

$\text{BeCl}_2(\text{H}_2\text{O})_3$ and similar to the minimum structures for $\text{MgCl}_2(\text{H}_2\text{O})$ and $\text{MgCl}_2(\text{H}_2\text{O})_2$ were three water molecules bonded to chloride atom by IHBs. The other minima structures for $\text{MgCl}_2(\text{H}_2\text{O})_n$ complexes illustrated different isomers with higher energy than the minimum structure (Figures 4, 5 and 6).

3.2. IR Spectra Analysis in OH Stretching Region for $\text{MCl}_2(\text{H}_2\text{O})_n$ Complexes

The assignment of IR spectra of $\text{BeCl}_2(\text{H}_2\text{O})_n$ $n=1-3$ were recorded theoretically using MP2 level of theory concentrating on the OH stretching region to evaluate the effect of IHBs on the OH bands frequencies. The global minimum structures of $\text{BeCl}_2(\text{H}_2\text{O})_n$, $n=1-3$ were chosen for this IR analysis, and the OH stretching frequencies are summarized in Table 1. The prediction of MP2 calculations shows a significant decrease in the OH frequency from 3651 cm^{-1} in the $\text{BeCl}_2(\text{H}_2\text{O})$ complex to 3625 cm^{-1} and 3575 cm^{-1} for the $\text{BeCl}_2(\text{H}_2\text{O})_2$ and $\text{BeCl}_2(\text{H}_2\text{O})_3$, respectively. This redshift can be assigned to the OH band which bonded to the chloride ion via ionic hydrogen bond (IHB). Relative to the free OH frequency band, the predictive OH stretching frequency is strongly red-shifted in about 146 cm^{-1} compared to the OH frequency of $\text{BeCl}_2(\text{H}_2\text{O})$ complex. This redshift can be assigned to the IHB that weakens the OH bond and so the OH stretching frequency. This trend of OH stretching redshift has been recorded previously in several studies (Cabarcos, Weinheimer, Martínez, and Lisy, 1999; Tandy *et al.*, 2016).

The OH stretching frequency for the minimum structures of $\text{MgCl}_2(\text{H}_2\text{O})_n$ complexes are seen in Table 2. Similar behavior of OH stretching bands was seen in $\text{MgCl}_2(\text{H}_2\text{O})$ and $\text{MgCl}_2(\text{H}_2\text{O})_2$ complexes compared to $\text{BeCl}_2(\text{H}_2\text{O})_n$ $n=1-2$ complexes. Redshifts for OH stretching bands are also seen in these complexes due to the IHBs effect compared to the free OH frequency band. For $\text{MgCl}_2(\text{H}_2\text{O})_3$, only two bands at 3671 and 3790 cm^{-1} were observed and assigned to the OH stretching, which bonded to the chloride atom via IHBs.

3.3. Binding energy calculations for $\text{MCl}_2(\text{H}_2\text{O})_n$ ($n = 1-3$) complexes

The Binding energy (BE) of the global minimum complexes was extracted from the MP2 calculations and summarized in Table 3 for $\text{BeCl}_2(\text{H}_2\text{O})_n$ and in Table 4 for $\text{MgCl}_2(\text{H}_2\text{O})_n$ complexes. The BE were calculated using the following equation:

$$BE = \Delta E = E(\text{BeCl}_2(\text{H}_2\text{O})_n) - (E(\text{BeCl}_2) + E(\text{H}_2\text{O})_n)$$

In both $\text{MCl}_2(\text{H}_2\text{O})_n$ ($n=1-3$) complexes, a gradual increase was seen in the value of BE with increasing n value. The high values of BE in $\text{MCl}_2(\text{H}_2\text{O})$ complex come from the IHB and the proximity of M^+ ion to O atom. The addition of water molecule in the $\text{BeCl}_2(\text{H}_2\text{O})_n$ $n=1-2$ complexes raised the BE in about 176 and 149 kJ/mol, respectively. For $\text{MgCl}_2(\text{H}_2\text{O})_n$ complexes, BE were increased in about 189 kJ/mol for $\text{MgCl}_2(\text{H}_2\text{O})_2$ and 163 kJ/mol for $\text{MgCl}_2(\text{H}_2\text{O})_3$. As can be seen, there is a pronounced reduction in the BE value with adding water molecule to form $\text{M}^{+2}\text{Cl}_2(\text{H}_2\text{O})_3$ complexes compared with adding Water molecule in $\text{M}^{+2}\text{Cl}_2(\text{H}_2\text{O})$ to form $\text{M}^{+2}\text{Cl}_2(\text{H}_2\text{O})_2$. This decrease in the BE value with increasing (n) value may result from dividing the Be^+ ion charge between the water molecules. Furthermore, the increase of IHBs number will weaken the chloride ion charge and reduce the BE value.

4. CONCLUSIONS:

Infrared spectra (IR), structure parameters, Binding Energy of $\text{M}^{+2}\text{Cl}_2(\text{H}_2\text{O})_n$, $n=1-3$ complexes have been performed in this work theoretically for the first time. The results were performed using *Ab initio* calculations. Vibrational bands in OH stretching regions for the minimum structures and other isomers were recorded for the complexes. A Redshift in the positions of the OH stretching bands was seen and this consistent with the formation of the IHBs between the chloride ions and the H atom of each water molecule. Also, a significant increase in the Binding energy (BE) was seen with increasing n value of water. This increase indicated that the IHB and the proximity of M^+ ion to O atom play an essential role in $\text{MX}_2(\text{H}_2\text{O})_n$ complexes. A significant observation was seen for $\text{MCl}_2(\text{H}_2\text{O})_3$ complexes that show a dramatic increase in the M-Cl bond length, which increased by 30% compared with $\text{MCl}_2(\text{H}_2\text{O})$ complex. This increment comes from the effect of water molecules that insert between M and Cl atoms.

5. ACKNOWLEDGMENTS:

This work was supported and funded by the University of Mosul and the Chemistry department at the College of Education for pure sciences. The authors thank the University of Leicester for access to its High-Performance Computer facility.

6. REFERENCES:

1. Ariyaratna, I. R., and Miliordos, E. (2019). Superatomic nature of alkaline earth metal–water complexes: the cases of Be (H_2O)_{0,+4} and Mg (H_2O)_{0,+6}. *Physical Chemistry Chemical Physics*, 21(28), 15861-15870.
2. Bajaj, P., Riera, M., Lin, J. K., Mendoza Montijo, Y. E., Gazca, J., and Paesani, F. (2019). Halide Ion Microhydration: Structure, Energetics, and Spectroscopy of Small Halide–Water Clusters. *The Journal of Physical Chemistry A*, 123(13), 2843-2852.
3. Burgess, J. (1999). *Ions in solution: basic principles of chemical interactions*: Elsevier.
4. Cabarcos, O. M., Weinheimer, C. J., Martínez, T. J., and Lisy, J. M. (1999). The solvation of chloride by methanol—surface versus interior cluster ion states. *The Journal of chemical physics*, 110(19), 9516-9526.
5. Conway, B. Ionic hydration in chemistry and biophysics. 1981. *Studies in Physical and Theoretical Chemistry*, 12.
6. Coşofre, V. V., and Buck, R. P. (1993). Recent advances in pharmaceutical analysis with potentiometric membrane sensors. *Critical Reviews in Analytical Chemistry*, 24(1), 1-58.
7. Eisenberg, B. (2013). Ionic interactions are everywhere. *Physiology*, 28(1), 28-38.
8. Frisch, M., Trucks, G., and Schlegel, H. (2009). Gaussian 03 package software, Gaussian Inc. Wallington CT USA.
9. Glendening, E. D., and Feller, D. (1996). Dication– Water Interactions: $\text{M}^{2+}(\text{H}_2\text{O})_n$ Clusters for Alkaline Earth Metals $\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}, \text{and Ra}$. *The Journal of Physical Chemistry*, 100(12), 4790-4797.
10. Grossfield, A., Ren, P., and Ponder, J. W. (2003). Ion solvation thermodynamics from simulation with a polarizable force field. *Journal of the American Chemical Society*, 125(50), 15671-15682.
11. Johnson III, R. D. (2005). NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101, Release 15b. 2011. *cccbdb.nist.gov*.
12. Keshri, S., and Tembe, B. (2017). Structural and Dynamical Properties of Alkaline Earth Metal Halides in Supercritical Water: Effect of Ion Size and Concentration. *The Journal of Physical Chemistry B*, 121(46), 10543-10555.

13. Li, R.-Z., Liu, C.-W., Gao, Y. Q., Jiang, H., Xu, H.-G., and Zheng, W.-J. (2013). Microsolvation of LiI and CsI in water: Anion photoelectron spectroscopy and ab initio calculations. *Journal of the American Chemical Society*, 135(13), 5190-5199.
14. Lide, D. R. (2004). *CRC handbook of chemistry and physics* (Vol. 85): CRC press.
15. Luzzi, L., and Palmieri, A. (1984). An overview of pharmaceutical applications. In *Biomedical Applications of Microencapsulation* (pp. 1-18): CRC Press Boca Raton, FL.
16. Marcus, Y. (2010). Effect of ions on the structure of water. *Pure and Applied Chemistry*, 82(10), 1889-1899.
17. Mattje, V. M., Pinheiro, A. R., and Pereira, D. H. (2019). Theoretical study of structural geometry and electronic properties of magnesium diboreth (MgB₂). *Periodico tche quimica*, 16(31), 301-307.
18. Meot-Ner, M. (2012). Update 1 of: Strong Ionic Hydrogen Bonds. *Chemical reviews*, 112(10), PR22-PR103. doi:10.1021/cr200430n
19. Mizoguchi, A., Ohshima, Y., and Endo, Y. (2003). Microscopic hydration of the sodium chloride ion pair. *Journal of the American Chemical Society*, 125(7), 1716-1717.
20. Mizoguchi, A., Ohshima, Y., and Endo, Y. (2011). The study for the incipient solvation process of NaCl in water: The observation of the NaCl-(H₂O)_n (n= 1, 2, and 3) complexes using Fourier-transform microwave spectroscopy. *The Journal of chemical physics*, 135(6), 064307.
21. Moelbert, S., Normand, B., and De Los Rios, P. (2004). Kosmotropes and chaotropes: modelling preferential exclusion, binding and aggregate stability. *Biophysical chemistry*, 112(1), 45-57.
22. Møller, C., and Plesset, M. S. (1934). Note on an approximation treatment for many-electron systems. *Physical Review*, 46(7), 618.
23. Naleem, N., Benteinitis, N., and Smith, P. E. (2018). A Kirkwood-Buff derived force field for alkaline earth halide salts. *The Journal of chemical physics*, 148(22), 222828.
24. Nancollas, G. H. (1970). The thermodynamics of metal-complex and ion-pair formation. *Coordination Chemistry Reviews*, 5(4), 379-415.
25. Raiz, S., Noor, S. H., Rasheed, N., and Mohammad, A. S. (2017). Conceptual Importance of Electrolytic Replenishers: A Review. *Asian Journal of Research in Pharmaceutical Science*, 7(2), 77-80.
26. Rodrigues, C. H. P., Assis, V. O., and Bruni, A. T. (2019). y theoretical spectroscopy in the infrared region: a didactic approach. *Periodico tche quimica*, 16(31), 398-407.
27. Sadoon, A. M., Sarma, G., Cunningham, E. M., Tandy, J., Hanson-Heine, M. W., Besley, N. A., . . . Ellis, A. M. (2016). Infrared spectroscopy of NaCl (CH₃OH)_n complexes in helium nanodroplets. *The Journal of Physical Chemistry A*, 120(41), 8085-8092.
28. Schuchardt, K. L., Didier, B. T., Elsethagen, T., Sun, L., Gurumoorthi, V., Chase, J., Windus, T. L. (2007). Basis set exchange: a community database for computational sciences. *Journal of chemical information and modeling*, 47(3), 1045-1052.
29. Tandy, J., Feng, C., Boatwright, A., Sarma, G., Sadoon, A. M., Shirley, A., Ellis, A. M. (2016). Communication: Infrared spectroscopy of salt-water complexes. In: AIP Publishing LLC.
30. Turq, P., Barthel, J. M., and Chemla, M. (2012). *Transport, relaxation, and kinetic processes in electrolyte solutions* (Vol. 57): Springer Science and Business Media.
31. Weller, K. (1988). *Ion Solvation*: Y. Marcus. Wiley, Chichester, New York, Brisbane, Toronto, Singapore, 1985, ISBN 0-471-90756-1, viii+ 306 pp., £ 42.00. In: Elsevier.
32. Zhurko, G., and Zhurko, D. (2016). Chemcraft-graphical software for visualization of quantum chemistry computations. In.

Figure 1. The calculated structures for $\text{BeCl}_2(\text{H}_2\text{O})$ with their energies in kJ/mol

Figure 2. The calculated structures for $\text{BeCl}_2(\text{H}_2\text{O})_2$ with their energies in kJ/mol

Figure 3. The calculated structures for $\text{BeCl}_2(\text{H}_2\text{O})_3$

Figure 4. The calculated structures for $\text{MgCl}_2(\text{H}_2\text{O})$ with their energies in kJ/mol

Figure 5. The calculated structures for $\text{MgCl}_2(\text{H}_2\text{O})_2$ with their energies in kJ/mol

0.0 kJ/mol

+13.91515 kJ/mol

+30.166997 kJ/mol

Figure 6. The calculated structures for $\text{MgCl}_2(\text{H}_2\text{O})_3$ with their energies in kJ/mol

Table 1. The OH Stretching frequencies for the minimum structures of $\text{BeCl}_2(\text{H}_2\text{O})_n$ ($n=1-3$) Complexes at MP2 Level of Theory

OH Band position cm^{-1}	Assigned Complex
3651	$\text{BeCl}_2(\text{H}_2\text{O})$
3625 3727	$\text{BeCl}_2(\text{H}_2\text{O})_2$
3575 3625 3701	$\text{BeCl}_2(\text{H}_2\text{O})_3$

Table 2. The OH Stretching frequencies for the minimum structures of $\text{MgCl}_2(\text{H}_2\text{O})_n$ ($n= 1-3$) Complexes at MP2 Level of Theory

OH Band position cm^{-1}	Assigned Complex
3792	$\text{MgCl}_2(\text{H}_2\text{O})$
3669 3775	$\text{MgCl}_2(\text{H}_2\text{O})_2$
3671 3790	$\text{MgCl}_2(\text{H}_2\text{O})_3$

Table 3. The Binding Energy (BE) for $\text{BeCl}_2(\text{H}_2\text{O})_n$ ($n = 1-3$) Complexes at MP2 Level of Theory

BE kJ/mol	Assigned Complex
194.287	$\text{BeCl}_2(\text{H}_2\text{O})$
370.196	$\text{BeCl}_2(\text{H}_2\text{O})_2$
519.849	$\text{BeCl}_2(\text{H}_2\text{O})_3$

Table 4. The Binding Energy (BE) for $\text{MgCl}_2(\text{H}_2\text{O})_n$ for $n = 1-3$ Complexes at MP2 Level of Theory

BE kJ/mol	Assigned Complex
199.538	$\text{MgCl}_2(\text{H}_2\text{O})$
388.574	$\text{MgCl}_2(\text{H}_2\text{O})_2$
551.355	$\text{MgCl}_2(\text{H}_2\text{O})_3$