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Ab Initio Studies of $MgNe_n^+$ Complexes with $n = 1-4$

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$MgNe_n^+$ complexes, with $n = 1-4$, are investigated by performing ab initio calculations, using the MP2-(full)/6-311+G(3df) method, as implemented by the Gaussian 98 computer program. The complexes are found to be stable and the agreement with the experimental data available for $n = 1$ is good. Accordingly, the predicted geometries of larger clusters should be reliable.

Introduction

Atom−atom or ion−atom interactions in clusters have formed the subject of numerous experimental and theoretical studies. The forces that keep the clusters together range from weak van der Waals interactions to much stronger metallic, covalent, or ionic bonds. Clusters bridge the gap between the behavior of gas-phase single molecules or atoms and that of condensed matter.[1] This transition makes cluster research of fundamental importance since it helps to elucidate the understanding of problems such as nucleation phenomena and phase transitions, as well as solvation and cluster specific reactions.[1] Solvation of positive atomic ions is extremely important in many areas of inorganic chemistry and biochemistry. Many studies, both theoretical and experimental have investigated cation solvation, starting with a simple interaction between the ion and a molecule of solvent, increasing the number of solvent molecules to 2−4 and more, and eventually treating the solvent as a continuum with a cavity in which the cation is placed.

The simplest of solvents are inert gas atoms, due to their filled outer shell.

Several theoretical and experimental papers have investigated the interaction between metal cations and inert gas atoms.[2,3] Among these, Reddic and Duncan[4] have performed experiments on the $MgNe^+$ system, using ion-photodissociation measurements. This system has also been investigated by Leung et al.[5] with ab initio calculations using the Dunning[6] augmented correlation consistent polarized basis set of the quality aug-cc-pVQZ

In this work, we have performed ab initio calculations on the $MgNe_n^+$ systems with $n = 1-4$.

Methods

The Gaussian 98 computer program[7] was used to perform ab initio (Hartree−Fock and post-Hartree−Fock) calculations on $MgNe_n^+$ complexes. The basis set used is the augmented 6-311+G(3df) basis set, which includes diffuse functions, as well as polarization functions on the non-hydrogen atoms. This basis is flexible enough to describe electron correlation effects while being small enough to be applicable to all the systems up to $MgNe_4^+$. Larger basis set calculations were performed on $MgNe^+$ for calibration purposes. Electron correlation effects were included by means of second order perturbation theory. Geometry optimizations were carried out at the MP2 level (1) using only the valence electrons and (2) including all electrons. The latter calculations are referred to as MP2(full). Calibrations were performed for $MgNe^+$ at the CCSD(T,full) level.

All geometry optimizations were performed with “tight” convergence criteria. This is particularly important for systems with small force constants, to ensure adequate convergence and reliability of frequencies.

Table 1 shows the optimized parameters of the complexes at different theoretical levels. Table 2 lists the corresponding vibrational frequencies. Table 3 shows the binding energies, including the zero-point corrections.

TABLE 1: Optimized Geometrical Parameters (Bond Lengths in Å and Angles in Degrees)

complex	parameter	HF	MP2	MP2(full)	CCSD(T,full)
$MgNe^+$	Mg−Ne	3.490	3.160	3.091	3.038
$MgNe_2$+	Mg−Ne	3.489	3.159	3.093	
	Ne−Ne	3.305	3.047	3.020	
	Ne−Mg−Ne	56.5	57.7	58.4	
$MgNe_3^+$ (C_{3v})	Mg−Ne	3.479	3.156	3.093	
	Ne−Ne	3.346	3.037	3.006	
	Ne−Mg−Ne	57.5	57.5	58.2	
$MgNe_4^+$ (C_{2v})	Mg−Ne1	3.467	3.154	3.095	
	Mg−Ne3	3.496	3.187	3.130	
	Ne1−Ne2	3.506	3.058	3.021	
	Ne1−Ne3	3.363	3.028	2.996	
	Ne1−Mg−Ne2	60.8	58.0	58.4	
	Ne1−Mg−Ne3	57.8	57.0	57.5	

TABLE 2: Frequencies of the Complexes (cm^{-1})

	frequencies		
complex	HF	MP2	MP2(full)
$MgNe^+$	37 (σ_g)	49 (σ_g)	51 (σ_g)
$MgNe_2^+$	18 (a1), 32 (b2)	29 (a1), 43 (b2)	32 (a1), 45 (b2)
	42 (a1)	55 (a1)	58 (a1)
$MgNe_3^+$	14 (e), 18 (a1)	26 (e), 34 (a1)	28 (e), 37 (a1)
	33 (e), 46 (a1)	44 (e), 61 (a1)	46 (e), 63 (a1)
$MgNe_4^+$	7 (a1), 11 (b1)	19 (a1), 20 (b1)	21 (a1), 22 (b1)
	14 (a1), 17 (a2)	32 (a2), 33 (a1)	35 (a2), 36 (a1)
	17 (b2), 28 (a1)	35 (b2), 38 (a1)	39 (b2), 40 (a1)
	35 (b1), 39 (b2)	45(b1), 51 (b2)	47 (b1), 54 (b2)
	48 (a1)	64 (a1)	66 (a1)

TABLE 3: Binding Energies (kcal/mol)

reaction	HF	MP2	MP2(full)	CCSD(T,full)
$Mg^+ + Ne = MgNe^+$	0.35	0.72	0.85	0.94
$Mg^+ + 2Ne = MgNe_2+$	0.73	1.53	1.53	
$Mg^+ + 3Ne = MgNe_3+$	1.16	2.47	2.88	
$Mg^+ + 4Ne = MgNe_4+$	1.61	3.40	3.95	

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Discussion

Burns et al.[2b] have investigated a large number of ion−rare gas systems, both theoretically and experimentally. They suggest as the best values for the $MgNe^+$ complex a distance of 3.16 Å (as determined by Reddic and Duncan), a vibrational frequency of 46 cm^{-1}, and a dissociation energy of 216 ± 40 cm^{-1} (0.62 ± 0.1 kcal/mol). These values represent experimental data estimated by Burns et al. [2b] using thermochemical data for D_e and the results of Reddic and Duncan.[4] As seen in Tables 1−3, the values obtained by using the MP2, MP2(full), and the CCSD(T,full) methods provide values quite close to these results. The closest is the MP2 value of 3.16 Å. The Hartree−Fock predicted value is substantially longer. The values of the frequency as determined by the MP2 and MP2(full) methods, 49 and 51 cm^{-1}, respectively, are close to the experimental value while the Hartree−Fock value of 37 cm^{-1} is too small. The dissociation energies are similar to the "best" value, especially the MP2 value of 250 cm^{-1} (0.72 kcal/mol). The MP2(full) and the CCSD(T,full) values appear to be somewhat high. This might be due to the basis set superposition error, indicating the need for larger basis sets. The simplest counterpoise correction overcorrects significantly and is unreliable.

These results are in better agreement with the "best" results than the results obtained by Leung et al.,[5] which predict a dissociation energy of 179 cm^{-1}, a frequency of 39 cm^{-1} and a bond length of 3.25 Å.

To explore the convergence with basis set size, the $MgNe^+$ complex was also investigated using a much larger basis set (6s 5p 4d 3f 2g on Ne and 7s 6p 4d 3f 2g on Mg). The resulting bond length (3.296 Å), at the MP2(FC) level, is in worse agreement with the "best value". It seems that increasing the basis set size and increasing the correlation effects act in opposite direction. Indeed, the tables show that for the 6-311+G-(3df) basis set, the frequencies and the dissociation energies become larger (too large) on going from MP2 to MP2(full) to CCSD(T), while the Mg−Ne distance becomes too short. Using a larger basis set, as shown above, works in the opposite direction. To verify this hypothesis, the large basis set was used to perform Mp2(full) and CCSD(T)(fc) calculations. The energy versus bond length curve is very flat and the minima obtained are 3.134 Å for the MP2(full) calculation and 3.207 Å for the CCSD(T)(fc) calculation. These values are close to the 3.16 Å value, but still the MP2(fc)/6-311G(3df) method affords a value for the bond length closest to the experimental one. In any case, calculations involving very large basis sets at high correlation levels are not computationally feasible for the larger clusters. However, the errors cancel at the MP2/6-311+G(3df) level, providing results in good agreement with the "best" results.

The complexes containing several neon atoms were all optimized using the "tight" convergence criteria, as mentioned before.

The complexes featuring two and three neon atoms are symmetric, with the neon atoms equivalent. The complex containing four neon atoms shows two of them to be equivalent to each other, while the other two are also equivalent to each other but different from the first two. The pyramidal structure of the $MgNe_3^+$ and $MgNe_4^+$ complexes as opposed to a planar one for the former and a tetrahedral one for the latter is probably due to the Ne−Ne interactions. Indeed, calculations performed on the planar-trigonal conformation of the $MgNe_3^+$ complex exhibits an energy higher by 0.47 kcal/mol than the pyramidal conformation, at the MP2(fc)/6-311+G(3df) calculational level. In the case of the complex featuring four neons, the tetrahedral structure, also at the MP2(fc)/6-311+G(3df) calculational level, exhibits an energy higher by 0.79 kcal/mol than the pyramidal structure. These conformations are local minima.

The calculation of net atomic charges on the atoms of the complexes, using the Mulliken population analysis shows the transfer of a very small positive charge (∼0.03 eu) from the Mg^+ to the neons, a fact that should contribute to the lack of electrostatic repulsion between the neon atoms. If the structure of the $MgNe_4^+$ complex is compared to the one of the $NaNe_4^+$ complex, which is tetrahedral,[8] and in which the neon atoms feature a larger positive charge (0.05 eu), one can explain the difference by two effects: the difference in the charge on the neons and the presence of an additional electron on the magnesium as compared to sodium. The electron pushes the Mg−Ne bonds together, in the same way as a lone pair on nitrogen, for example, makes ammonia pyramidal and not planar. A calculation on Ne_4, where the neon atoms are set in square, shows a binding energy of 0.93 kcal/mol, as compared to four separate neon atoms (at MP2(fc)/6-311+G(3df) level). This fact shows that the neon atoms exhibit a binding energy. However, this value should be considered an upper limit since the neon atoms are neutral, while, as shown before, in the complex they exhibit a small positive charge, which should lead to a certain amount of repulsion.

One notices that the number of neon atoms in the complex does not significantly modify either the bond lengths or the Ne−Mg−Ne angles. This might be explained by the fact that additional neon atoms increase the Ne−Ne attraction, compensating thus for the crowding.

In conclusion, investigating the $MgNe_n^+$ complexes with the MP2(fc)/6-311+G(3df) method provides satisfactory results for the $n = 1$ complex, and this fact might be extrapolated to complexes with $n > 1$. Using higher correlation terms and much larger basis sets does not seem to improve the agreement with the experiments. The complexes appear to be stable at all calculational levels and would benefit from experimental studies for higher n.

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