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ARTICLE *in* CHEMICAL PHYSICS · JANUARY 2001

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Ab initio study of the ground-state potential of XH^- anions ($X = \text{He, Ne, Ar}$)

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Received 7 September 2000

Abstract

The ground-state energy curves of HeH^- , NeH^- and ArH^- have been computed at coupled-cluster level using large basis sets. These dimers are weakly bound systems, due to the interaction between the negative ion H^- and the (polarised) rare-gas atom. The Schrödinger equation for the nuclei has been solved, and the energy levels have been computed. The effect of replacing the innermost electrons with pseudopotentials has also been investigated on the heaviest system ArH^- . © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

On both theoretical and experimental sides, the interest of chemists and physicists in small ionic clusters involving rare-gas (Rg) atoms increases. In particular, experimental findings on the corresponding neutral clusters are usually hard to gather without resorting to ionisation. It is therefore very important to understand how the interaction with ions modifies the structure of the original neutral clusters. Experimental studies of charged systems have been performed by injecting atomic or molecular ions into the Rg at very low temperature. In recent theoretical investigations, Gianturco and coworkers studied the structure of protonated clusters of helium and argon, founding a marked difference between the two species in the

case of very small clusters [1,2]. Much less attention has been devoted to negative clusters containing the H^- ion. Because of the closed shell character of H^- and the absence of short-range bonds between the Rg atoms and the ion, a more regular behaviour can be expected among the different Rg species. The RgH^- dimers are worth to be studied, both theoretically and experimentally, as isolated species. Several experimental studies focused on collision processes involving H^- or D^- and Rg atoms [3–5]. Moreover, the knowledge of an accurate potential-energy curve for the dimers is a necessary preliminary step towards the theoretical study of larger clusters.

In the present work, ab initio calculations on HeH^- , NeH^- and ArH^- are presented. These dimers are weakly bound van der Waals systems, whose potential well is mainly due to the dipole-moment on the Rg atom, induced by the H^- ion, interacting with the ion itself. This (charge-induced dipole) interaction has an R^{-4} long-range behaviour (R being the inter-nuclear distance), which is

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the same as in the Rg-proton systems. The long-distance interaction is similar for negative and positive systems, and goes to zero much more slowly than the usual dispersion forces, that vanishes as R^{-6} . At short distances, on the other hand, negative and positive dimers are deeply different. In the case of an H^- ion, the closed-shell character of both the neutral atom and the H^- ion prevents the two atoms to approach in regions where the overlap between the two electronic distributions becomes significant. This prevents the formation of a true chemical bond, as it happens in the positive ions. In fact, in the case of the negative dimers, the equilibrium distance is the result of the opposite effect of the attractive charge–dipole force and the repulsive effect generated by the electronic overlap. Due to the weakness of the attractive force, the equilibrium distances are extremely large, and the dissociation energies of these dimers are very small.

Because of the smallness of the interaction, a very accurate value of the asymptotic limit of the potential energy curve is extremely important. In this context, we can rule out truncated configuration–interaction (CI) methods, as they suffer from the well known size-consistency problem. On the other hand, since RgH^- dimer is a closed-shell system that dissociates into two closed-shell systems, a single determinant gives a qualitatively correct description of the dimer at any distance, and single-reference coupled cluster (CC) methods can be used even in the dissociation region. In a previous work on HeH^- [6], we had shown that coupled cluster involving single and double excitations (CCSD) gives a dissociation energy that is more than 10% off the corresponding full-CI result obtained with the same basis set. Therefore, CCSD alone is not sufficiently accurate to treat these systems. However, if the effect of triple excitations is taken into account in a perturbative way, the error goes down to a fraction of a percent only [7]. In particular, the CCSD-[T] method [8], where the effect of the triples is considered in a perturbative way, while single excitations are neglected, was found to give the most accurate values compared to the full-CI results [7]. We chose this approach for the present investigation without any further comparative calculations.

Once the potential surfaces of the ions are found, the Schrödinger equations for the nuclear motion are solved, and the vibrational levels for the three systems are obtained. Because of the flatness of the potential curves, the levels are strongly anharmonic. The effect is particularly spectacular in the case of HeH^- , where a single vibrational level was found at a fraction of a wave number below the dissociation limit: the zero-point energy predicted for this system on the basis of the harmonic frequency value is actually larger than the whole dissociation energy.

2. Details of calculations

We performed ab initio calculations on the RgH^- systems using large basis sets of uncontracted gaussian orbitals. The exponents of the ANO orbitals optimised by Widmark et al. were chosen [9], leaving all the gaussians uncontracted. In order to treat correctly the external tails of the charge distributions, we added a set of diffuse functions on each center. This is a very sensitive point. In fact, the lack of diffuse functions can lead to underestimate the size of the charge distributions, and of their repulsive effect and consequently, results in a serious overestimate of the well depth. Since the negative ion H^- is very diffuse, particular care must be employed to its description. We added a large set of diffuse orbitals of (6s6p4d) type centered on the hydrogen atom for the weakest bound system HeH^- but restricted ourselves to smaller set of diffuse functions 4s4p2d on the two other complexes. While the original basis sets for neon and argon already contain diffuse functions, we had to enrich the description of helium and thus added extra diffuse functions of (2s2p2d) type. As far as functions with higher angular momentum are concerned, our previous study on HeH^- [6] has shown that, although these orbitals give a substantial contribution to the total energy of the system, they have little or no influence on the shape of the potential curve and the dissociation energy. We therefore added no extra diffuse exponents of f- or g-type. The hydrogen electronic affinity, computed with the present basis set, is 0.74586 eV, against an

experimental result of 0.754209 eV [10]. The difference between the two values (mainly due to the absence of high angular-momentum orbitals) is negligible, since we are not interested in electron detachment processes. The value of the gaussian exponents are available upon request.

In this way, basis sets containing 133, 143 and 167 orbitals were obtained for the HeH^- , NeH^- and ArH^- systems, respectively. The corresponding CCSD calculations involve 28 798, 271 518 and 787 537 symmetry adapted Slater determinants. CCSD calculations have been carried out using the **MOLPRO** package [11,12]. The effect of triple excitations was taken into account at a perturbative level, using the CCSD[T] formalism [8], without contributions of single excitations. Different perturbative approaches (like the one proposed in Ref. [13]) give essentially the same results.

All the electrons were correlated in the three systems. We also evaluated the influence of the core correlation on argon and neon, by comparing these results with the ones obtained when the core electrons were frozen. In practice, we froze the 1s electrons in neon and the 1s, 2s and 2p electrons in argon, letting the valence shells correlated. When one goes to heavier atoms, a significant reduction of computational efforts can be achieved by using the relativistic effective core potentials (RECP or pseudopotentials), which mimic the core electrons. In the present study, we investigated this approach on ArH^- , using a small core energy-adjusted pseudopotential (EAPP) [14] with its optimised corresponding basis sets, supplemented with the most diffuse functions of s and p type of the all-electron (AE) basis set. This [7s 7p 3d 1f] basis set is indicated as B_0 . Nevertheless, as it was already mentioned before, the position and the depth of the potential well is directly related to the long-range attractive part of the potential, proportional to the polarisability. In that sense, Nicklass et al. [14] have shown that an accurate value of the atomic polarisability cannot be obtained unless the basis set is augmented with extra diffuse functions of s and p type and df polarisation functions. The resulting basis set [8s 8p 6d 6f] will be referred as B_1 . We used the finite-field method to calculate the atomic polarisabilities at the CCSD[T] level and discuss in the following section how large their

influence on the potential curve of ArH^- is. Besides, knowing that argon is the most polarisable atom in the series, we expected core-valence correlation effects to be important and considered them by means of a core polarisation potential (CPP). To complete our comparison of methods, we also used the shape-consistent-type pseudopotential (SCPP) available for the argon atom as extracted by Teichteil et al. [15] with its corresponding optimised basis set, extended with the same set of diffuse exponents as previously. For all cases, we evaluated the effect of basis set superposition errors (BSSE) following the Boys–Bernardi procedure [16,17].

As we aim at extracting the most accurate ground state energy curve, we also evaluate the influence of spin–orbit effects. Because we assume second-order spin–orbit effects to be of minor influence in the case of light atoms, we restricted the computation of spin–orbit effects to the ArH^- system. These calculations were carried out using the spin–orbit code-EPCISO [18] interfaced with Molcas-package [19] at the AE level and obtained the molecular orbital from an SCF-calculation on the ground state. The CIPSI CI-code [20] provided us with a CI-vector built on the ground state configuration and a set of excited determinants selected according to their contribution to the second-order in energy. The atomic mean-field spin–orbit integrals were calculated with the AMFI-code [21]. The spin–orbit calculations were performed on a model space which contained the latter determinants and the singly excited configuration which have a significant contribution for second-order spin–orbit effects. Furthermore, we defined an effective Hamiltonian that corrects for the missing correlation effects on the model space. Further details on the method can be found in Ref. [18]. We evaluated the lowering in energy due to second-order spin–orbit effects at the equilibrium distance and at infinity.

The Schrödinger equation for the nuclei was solved using a Numerov-type algorithm [22], following the matrix the implementation proposed by Lindberg [23]. The algorithm [24] has been used successfully to compute the vibrational structure of weakly-bound diatomic molecules [6,25].

3. Results and discussion

In Fig. 1, we show the ground-state potential energy for the three systems, the energy zero of each curve being given by the appropriate dissociation limit. At short distance the three curves are strongly repulsive but show little difference, with argon being the most repulsive one, followed by neon and then by helium. This is simply due to the growing size of the Rg atoms as a function of the atomic size number. At a distance of about 5 bohr, the three curves are very close to each other, and only a few mhartree above the asymptotic limit. It is in this region that the effect of the long-range interaction starts to become important. This interaction, due to the polarisation of the Rg atom induced by the H^- ion, is directly proportional to the Rg atomic polarisability. It is relatively large for Ar ($11.08a_0^3$), smaller for Ne ($2.669a_0^3$), and even smaller for He ($1.38a_0^3$) as indicated by the experimental values [26]. The latter variation directly explains why the equilibrium distance is the largest in helium complex and then decreases when going to the heavier Rg-atoms. The same trend was pointed out by Naumkin and McCourt [27] on the comparable RgCl^- system. A detailed picture of the curves in the well region is shown in Fig. 2.

Table 1 summarises the main features of the potential curves of the three ions. The collision diameter R_{cd} is the distance at which the energy is

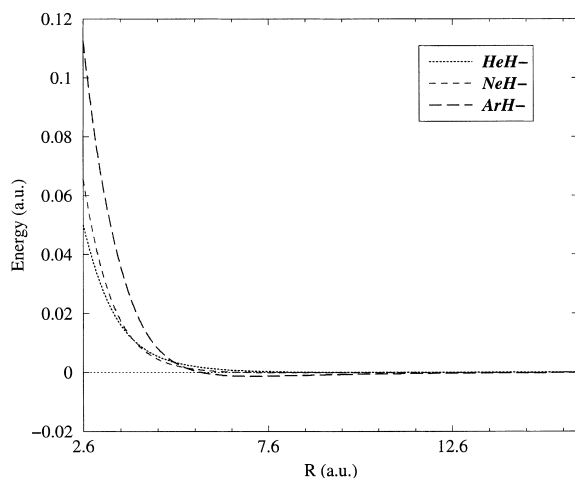


Fig. 1. Potential curves of HeH^- , NeH^- and ArH^- .

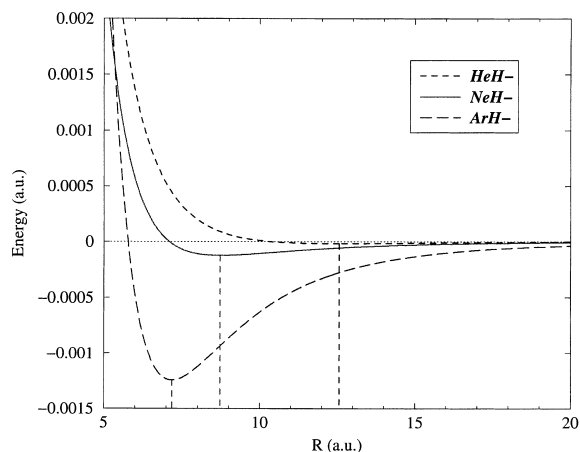


Fig. 2. Potential curves of HeH^- , NeH^- and ArH^- near the equilibrium distance.

Table 1

Spectroscopic constants calculated at the AE level with CCSD[T] method

| | R_{cd} | R_e | ω_e | D_e |
|----------------|-----------------|--------|------------|---------|
| HeH^- | 10.357 | 12.571 | 9.047 | 3.732 |
| NeH^- | 7.092 | 8.725 | 31.537 | 26.895 |
| ArH^- | 5.779 | 7.184 | 120.918 | 272.817 |

R_{cd} is the collision diameter; R_e the equilibrium distance (both in bohr); ω_e is the harmonic frequency in cm^{-1} ; D_e is the dissociation energy in cm^{-1} .

equal to the dissociation-limit energy, i.e. the distance at which the attractive and repulsive effects cancel out. The table shows that R_{cd} strongly decreases in going from helium to argon. The equilibrium distance R_e , that is about two bohr larger than R_{cd} , has a similar behaviour. At the same time the well depth increases by almost two orders of magnitude, and the harmonic constant by one. All these facts support the analysis given in the previous paragraph.

In Table 2, we reported the position of the minimum R_e and the dissociation energy D_e obtained from AE and RECP calculations at the CCSD[T] level. These values have been obtained with a quadratic interpolation on the computed points. The AE calculations at the CCSD[T] level corrected for BSSE stand for the reference to which all other results will be compared. Indeed, a previous study showed how well this approach agrees with full-CI calculations on HeH^- [7].

Table 2
AE and RECP results on ArH^-

| | Method | R_e | D_e |
|----------------------|-------------------------|-------|--------|
| AE | CCSD[T] | 7.184 | 272.81 |
| | CCSD[T] _{BSSE} | 7.230 | 261.93 |
| AE (1s 2s 2p frozen) | CCSD[T] | 7.210 | 266.13 |
| | CCSD[T] _{BSSE} | 7.231 | 261.13 |
| EAPP B_0 | CCSD[T] | 7.304 | 244.50 |
| | CCSD[T] _{BSSE} | 7.354 | 235.23 |
| | CCSD[T] _{CPP} | 7.306 | 244.48 |
| EAPP B_1 | CCSD[T] | 7.202 | 273.74 |
| | CCSD[T] _{BSSE} | 7.220 | 261.82 |
| SCPP | CCSD[T] | 7.371 | 236.34 |
| 0-electron ECP | CCSD[T] | 6.95 | 313.00 |

R_e is the optimised equilibrium distance, in bohr. D_e is the dissociation energy in cm^{-1} . The EAPP calculations have been carried out with the two following uncontracted basis sets on argon: B_0 (7s 7p 3d 1f) and B_1 (8s 8p 6d 6f).

The weakness of the Ar-H^- bond is revealed by the long equilibrium distance 7.23 Å and the small dissociation energy value 261.93 cm^{-1} . Freezing the 1s, 2s and 2p core shells does not affect the depth of the potential well, as the computed atomic polarisabilities with and without frozen core electrons are identical (c.f. Table 3) and match the experimental value ($11.08a_0^3$) within an excellent accuracy. Moreover, replacing the core by a pseudopotential leads systematically, though only slightly, different results from the AE ones.

Table 3
Atomic dipole polarisabilities (in a_0^3) of the Rg-atom from AE level or RECP (EAPP or SCPP) calculations at the CCSD[T] level, and experimental values

| Atom | Method | α_D | Experimental |
|------|----------------------|------------|--------------|
| He | AE | 1.384 | 1.38 |
| Ne | AE | 2.595 | 2.669 |
| | AE (1s frozen) | 2.600 | |
| Ar | AE | 11.147 | 11.08 |
| | AE (1s 2s 2p frozen) | 11.158 | |
| | EAPP B_0 | 10.823 | |
| | EAPP B_1 | 11.065 | |
| | SCPP | 10.771 | |

When BSSE corrections are included, the equilibrium distance is found to be 0.14 hartree longer and the dissociation energy underestimated by 20 cm^{-1} . The inclusion of core-polarisation effects by means of a CPP has no effect. As the position of the potential well is related to the charge-induced dipole long-range interaction, the discrepancy might be related to how well the polarisability of the Rg atom is calculated. Indeed, when the smallest basis set B_0 is used, the polarisability derived amounts to 95% of the corresponding reference value, leading to a deviation of 5% from the AE dissociation energy. This error can be canceled out if as larger basis set B_1 is used as it was demonstrated by Nicklass et al. [14] as the computed value ($11.06a_0^3$) reaches now the experimental value. This results in a significant lengthening of the equilibrium distance by 0.1 Å and a simultaneous increase of the dissociation energy of 30 cm^{-1} . After accounting for BSSE corrections, the RECP results are in excellent agreement with the AEs ones. As a conclusion, we may say that pseudopotentials can reach a fine accuracy when they are used with a complete basis set.

The results obtained with the shape-consistent pseudopotential differ from the AE ones by an even larger amount. An obvious reason might be the computed atomic dipole polarisability which differs by more than 5% from experiment. Such pseudopotentials are extracted with the constrain that the nodeless pseudo-orbital matches the corresponding relativistic AE orbital in the valence region. If the reference calculation used for the extraction is a single-state calculation, the derived pseudopotential contains less information than a pseudopotential of the energy-consistent type, fitted to reproduce numerous transition energies. Recently, Maron and Teichleil [28] proposed to improve the shape-consistent procedure by extracting pseudopotentials from multiconfigurational four-component calculations including core-polarisation effects. Given the excellent quality of their results on halogens atoms, their approach should lead to results with a comparable accuracy as the EAPP.

One may go one step further in the reduction of the number of valence electrons and use a zero-valence pseudopotential on argon, extracted by

Duplà and Spiegelmann [29] in view of argon-cluster calculations. It overestimates by 50 cm^{-1} the dissociation energy and leads to a fairly too short equilibrium distance. The Ar–H[−] core–core repulsion is missing and should be added to get a proper interaction.

We completed our study on ArH[−] by the evaluation of second-order spin–orbit effects. As it is a closed-shell system, we expected a fairly small influence on the absolute energy. Van Lenthe et al. [30] have studied the influence of spin–orbit coupling on properties of a series of closed-shell molecules. They observed that the equilibrium distance was not changed by more than 0.03 Å , and that the influence on the frequencies never exceeded 10%. The largest effects on dissociation energies were noticed for systems where the atomic effects dominate, as observed on I₂ by Teichteil and Péliissier [31]. In our case, since ArH[−] dissociates in two closed shell atoms, both the molecule at the equilibrium and the atoms are stabilised in the same way. Indeed, we find an absolute lowering of 19.25 cm^{-1} at the equilibrium distance and of 16.89 cm^{-1} on argon atom, neglecting the effect on H[−], resulting in a slight increase of the dissociation energy by 2.36 cm^{-1} .

The results of the calculations on NeH[−] at the AE level are summarised in Table 4. As for argon, the results are insensitive to core-correlation as the dissociation energy only increases by 0.62 cm^{-1} when freezing the 1s shell in the correlation treatment. As in the case of argon, the computed polarisabilities agree very well with the experimental data (c.f. Table 3).

We also computed the spectroscopic value of HeH[−] with the aim of improving the previous calculations [6] carried out in a large basis set containing both diffuse and high angular-momen-

tum functions, but limited to the CCSD level. The present CCSD[T] calculations here lead to a longer equilibrium distance, 12.571 a.u. compared to the previous 11.90 a.u. and simultaneously to a larger dissociation energy (3.723 cm^{-1} relative to 3.25 cm^{-1}).

The potential, being dominated at long distance by the R^{-4} tail, is strongly anharmonic. This can be seen from the structure of the vibrational levels. We did not investigate the rotational structure of the levels, that have been therefore computed for a total angular momentum $J = 0$. These levels are reported in Table 5. For each level, we report the depth with respect to dissociation, the height with respect to the well minimum, and the difference with respect to the previous level. In all cases we considered the most abundant isotope for the Rg atom (⁴He, ²⁰Ne, ⁴⁰Ar), combined with both normal hydrogen H and deuterium D. In the case of helium,

Table 5
Vibrational levels of the Rg atoms combined with hydrogen H or deuterium D

| System | n | $E_n - E_\infty$ | $E_n - V_0$ | $E_n - E_{n-1}$ |
|------------------|-----|------------------|-------------|-----------------|
| HeH [−] | 1 | −0.531 | 3.200 | – |
| HeD [−] | 1 | −0.970 | 2.762 | – |
| NeH [−] | 1 | −13.425 | 13.470 | – |
| | 2 | −1.398 | 25.497 | 12.027 |
| NeD [−] | 1 | −16.623 | 10.272 | – |
| | 2 | −4.497 | 22.398 | 12.126 |
| | 3 | −0.437 | 26.458 | 4.060 |
| ArH [−] | 1 | −215.866 | 56.950 | – |
| | 2 | −125.815 | 147.002 | 90.052 |
| | 3 | −64.191 | 208.626 | 61.624 |
| | 4 | −26.510 | 246.307 | 37.681 |
| | 5 | −7.579 | 265.238 | 18.931 |
| | 6 | −1.144 | 271.673 | 6.435 |
| ArD [−] | 1 | −231.261 | 41.555 | – |
| | 2 | −160.618 | 112.198 | 70.643 |
| | 3 | −105.256 | 167.561 | 55.363 |
| | 4 | −63.969 | 208.848 | 41.287 |
| | 5 | −34.944 | 237.873 | 29.025 |
| | 6 | −16.265 | 256.551 | 18.678 |
| | 7 | −6.060 | 266.757 | 10.206 |
| | 8 | −1.551 | 271.265 | 4.508 |
| | 9 | −0.198 | 272.619 | 1.353 |

($E_n - E_\infty$) is the depth with respect to dissociation, ($E_n - V_0$) the height with respect to the well minimum, and ($E_n - E_{n-1}$) the difference with respect to the previous level. All values are in cm^{-1} .

Table 4
AE results on NeH[−]

| | Method | R_e | D_e |
|----------------|-------------------------|-------|-------|
| AE | CCSD[T] | 8.725 | 26.80 |
| | CCSD[T] _{BSSE} | 8.766 | 26.11 |
| AE (1s frozen) | CCSD[T] | 8.716 | 27.05 |

R_e is the optimised equilibrium distance, in bohr. D_e is the dissociation energy in cm^{-1} .

a single level is predicted, both in the case of H and D. Two levels are computed for NeH^- and three for NeD^- . The only case where a rather rich vibrational structure is present is the case of argon, with six levels for ArH^- and nine for ArD^- .

4. Conclusions

The calculations carried out in the present study allow us to draw several conclusions:

- In the RgH^- systems, the bond results from opposite effects induced by the long range attractive charge–dipole interaction and the repulsive effect at short distance. When going down in the series of rare gas atoms, the polarisability gradually increases and induces a significant shortening of the Rg-H^- distance combined with an increase of the dissociation energy.
- We have compared various theoretical approaches on ArH^- and in particular tested the possible substitution of the Ar^{8+} core by a pseudopotential. It is demonstrated that, together with large basis sets including polarisation functions, this approach reproduces exactly the AE results. Core-polarisation effects prove to be negligible. Second-order spin–orbit effects, that were estimated both at the equilibrium and at dissociation, lower the whole potential curve and result in a slight increase of the dissociation energy by not more than 1%.
- Vibrational levels for a total angular momentum $J=0$ were computed for the three systems. HeH^- presents one single vibrational level, lying 0.5 cm^{-1} below dissociation. This is a sign of the strong anharmonicity of the levels. The number of levels available increases with the depth of the potential well. It also depends on changes in the nuclear masses (e.g., hydrogen replaced by deuterium).

Acknowledgements

We wish to thank Franco Gianturco (Università La Sapienza, Rome), and Fernand Spiegelmann and Christian Teichteil (Université P.

Sabatier, Toulouse) for stimulating discussions. We are also grateful to both the French Centre National de la Recherche Scientifique and the Italian Ministero dell'Università e della Ricerca Scientifica for their financial support. V. Vallet would like to thank the program of “cotutelle de Thèse” financed by the French government.

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