

# Rovibrational energies and spectroscopic constants for H<sub>2</sub>O–Ng complexes

William F. da Cunha · Rhuiago Mendes de Oliveira ·  
Luiz F. Roncaratti · João B. L. Martins ·  
Geraldo M. e Silva · Ricardo Gargano

Received: 31 March 2014 / Accepted: 13 October 2014 / Published online: 26 November 2014  
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**Abstract** In this work, rovibrational energies and spectroscopic constants for the water–Ng complexes (Ng = He, Ne, Ar, Kr and Xe) were calculated through two different approaches (by solving the Nuclear Schrödinger equation and by applying the Dunham's method) and using two different potential energy curves (PEC). These PEC were determined using potential parameters obtained through molecular beam scattering experiments and accurate theoretical calculation, respectively. It was found that the theoretical rovibrational energies are in a good agreement (only for the lowest numbers of vibrational states) with those obtained through experimental PEC. Another important conclusion was regarding the calculated first two rovibrational energies for the H<sub>2</sub>O–Ar system, that are in a good agreement with the experimental data.

**Keywords** Water · Noble gas · DVR · Dunham's Method · Rovibrational energies · Spectroscopic constants

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This paper belongs to Topical Collection Brazilian Symposium of Theoretical Chemistry (SBQT2013)

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W. F. da Cunha · R. M. de Oliveira · L. F. Roncaratti ·  
G. M. e Silva · R. Gargano (✉)  
Institute of Physics, University of Brasilia, CP 4455, Brasilia,  
70919-970, Brazil  
e-mail: gargano@unb.br

J. B. L. Martins  
Institute of Chemistry, University of Brasilia, CP 4478, Brasilia,  
70904-970, Brazil

R. Gargano  
Departments of Chemistry and Physics, Quantum Theory Project,  
University of Florida, Gainesville, FL 32611, USA

## Introduction

Water and other closed shell species complexed by non-covalent hydrophobic and hydrophilic interactions [1] are of importance in gaseous and condensed phases. Among such non-covalent interactions the most characteristic is the hydrogen-bond (HB), and due to its outstanding relevance for water properties description, H-bond has been steadily the target of experimental and theoretical investigations [2, 3]. Indeed, a comprehensive picture of the HB nature and characteristics would require accounting for the critical balancing of electrostatic, charge transfer, induction, dispersion and exchange (or size) repulsion components of this interaction. Therefore, this subject continues today to present many open questions [4–6]. There are well-established energy and charge decomposition methods from quantum chemistry [7–11] that may be usefully brought to study this problem. However, in the case of very weak interactions, where the energy terms involved are remarkably small (only a fraction of kJ/mol), there may be elusive to both calculations and experiments. It must be pointed that weakly interacting complexes of water in the gas phase yield collisional complexes, either stable or metastable, that can play important roles in atmospheric problems [12]. In particular, complexes concerning water and air components have been suggested as possible contributors to the absorption of solar radiation [13, 14], thus disturbing the Earth atmosphere energy balance. Detailed description of dynamical and optical properties of such weakly interacting systems is still unsatisfactory [15]. Then, it requires the knowledge of more precise potential energy surfaces (PES). Therefore, modeling the whole set of components of this non-covalent interaction is a task of great interest [16]. Closed shell molecules interacting with other non-polar closed shell particles generally bound by the well known van-der-Waals

interaction, to which a small induction effect is included. In this paper we focus on the simplest water aggregates, those with the five noble gases (Ng). In such systems the contributions to the interaction from the electrostatic component are missing, thus making possible to model the remaining terms. Recent experimental and theoretical studies were mostly focused on H<sub>2</sub>O and He system [17–23] and H<sub>2</sub>O and Ar system [23–28]. In particular, Cohen and Saykally [23] have calculated a very accurate PES for H<sub>2</sub>O and Ar analyzing the absorption measurements. Information on the molecular structure of the H<sub>2</sub>O and Kr and H<sub>2</sub>O and Xe complexes were also determined from microwave spectroscopy [29, 30]. A systematic and internally consistent study of the strength of the interaction involved and of its variation along the entire Ng series was given by Roncaratti et al. [31] by means of molecular beam scattering experiments and the use of a suitable potential energy function [32]. It is well known that, while the dispersion and induction attractions show a low dependence on the molecular orientation, the polarizability of the involved molecules having a nearly isotropic behavior. Thus, at intermediate or long range, a water–Ng complex can be treated as a diatomic system whose the interaction energy is given by an effective radial potential  $V(R)$ . This fact has been supported by accurate theoretical studies [31], which showed that when the water interacts with a Ng atom (for example Ar atom), its geometries are practically unaffected, i.e. the O–H distances and H–O–H angle change less than 0.001 Å and 0.2°, respectively. The same observation was found for the interaction energy [31]. It is important to mention that the values of the potential parameters were obtained from molecular beam scattering experiments. Therefore, the interaction potentials used in this work are effective. This means that they represent the interaction of rotationally hot molecules with noble gas atoms. In this situation one could expect the vanishing of the short range anisotropic behavior.

In general, an *ab initio* non-covalent interaction description is not a easy task [33, 34] because weak intermolecular interactions require the use of theoretical methods that describe electronic correlation accurately and large basis sets. In this work, we determined the rovibrational energies and spectroscopic constants considering both experimental and *ab initio* water–Ng energy curves  $V(R)$  [31]. The theoretical potential parameters were determined using an angular averaging (coplanar configurations) of both equilibrium distance and the interaction energy using the BSSE-corrected CCSD(T)/aug-cc-pV5Z levels [31]. We used of the Discrete Variable Representation (DVR) to solve the nuclear Schrödinger equation, subjected to the corresponding  $V(R)$ , to obtain the spectroscopic constants. For the sake of comparison, we have also obtained the spectroscopic constants by applying the Dunham's methodology of using the perturbation theory and finding an expression for the

rovibrational energies of each water–Ng complexes in terms of the energy curve derivatives. It is important to note that both methods yielded spectroscopic constants in a good agreement, thus, indicating that our methodology is suited to treat this kind of system.

## Methods

The Improved Lennard-Jones model (ILJ) [32], found to be suitable to formulate  $V(R)$  for several systems of different nature and at increasing complexity [31, 32, 35–38], stands out as an interesting model that eliminates most of the original LJ model inadequacies, particularly those from short and long range. This is accomplished in an elegant fashion through the consideration of a single extra parameter. The ILJ potential functions is

$$V(R) = \varepsilon \left[ \frac{6}{n(R) - 6} \left( \frac{R_e}{R} \right)^{n(R)} - \frac{n(R)}{n(R) - 6} \left( \frac{R_e}{R} \right)^6 \right], \quad (1)$$

where

$$n(R) = \beta + 4 \left( \frac{R}{R_e} \right)^2. \quad (2)$$

In the above equations, the parameter  $\varepsilon$  is the depth of the potential well,  $R_e$  the equilibrium distance and  $\beta$ , associated to the hardness of the involved chemical species, determines the shape of the potential in the region of the well.  $\beta$  is expected to be nearly constant for homologous systems and for the water–Ng family we use  $\beta = 9$ , a value typical of weak intermolecular interactions between neutral species [32]. These parameters can be predicted from correlation formulae given in terms of polarizabilities of the interacting partners. One could expect small changes on the  $\beta$  value due to different polarizability along the noble gases species (0.2 to 4 Å<sup>3</sup>). Therefore, a constant value of  $\beta$  value is acceptable. One big change on this parameters happens when atoms or molecules with large polarizabilities are involved (e.g. alkali metals). The experimental and theoretical potential parameters for each water–Ng system [31] are given in Table 1. As mentioned, the theoretical equilibrium distance and the

**Table 1** Experimental and theoretical (in parentheses) Potential parameters for each water–Ng system

System	$\varepsilon$ (meV)	$R_e$ (Å)
H <sub>2</sub> O–He	22.1800(25.7289)	3.45(3.32)
H <sub>2</sub> O–Ne	45.9732(50.4092)	3.50(3.33)
H <sub>2</sub> O–Ar	116.1429(119.3691)	3.63(3.58)
H <sub>2</sub> O–Kr	137.9197(144.5334)	3.75(3.71)
H <sub>2</sub> O–Xe	162.9226(171.4472)	3.93(3.89)

interaction energy values were determined using the BSSE-corrected CCSD(T) methods and aug-cc-pV5Z basis sets [31]. From Table 1, one can observe that the theoretical depth of the potential well (for all systems) is large than experimental one. This feature suggests that the H<sub>2</sub>O–Ng complexes are more strongly bound when the theoretical potential parameters are used.

The smallest difference found between the theoretical and experimental potential well was for the H<sub>2</sub>O–Ar system (about 3.2cm<sup>-1</sup>). On the other hand, the theoretical equilibrium distances for all systems are less than experimental equilibrium distances. The smallest difference was found for the H<sub>2</sub>O–Kr and H<sub>2</sub>O–Xe systems (about 0.04Å). All these observations are very important to analyze the rovibrational energies and spectroscopic constants.

The spectroscopic rovibrational constants are then evaluated through two different approaches. The first one is the Discrete Variable Representation (DVR), which is an approximation based on the expansion of the wave function in an orthogonal basis set and subsequent use of quadrature rules to solve the resulting integrals [39–42]. Thus, the matrix elements of potential energy (evaluated only on the Gaussian quadratures) becomes diagonalized and the matrices elements of the kinetic energy operator can be analytically calculated. In this way, the rovibrational energies  $E_{v,J}$  of Eq. 3, where  $v$  and  $J$  represent the vibrational and the rotational quantum numbers respectively, arise after solving the nuclear Schrödinger equation [43].

$$E_{v,J} = \left(v + \frac{1}{2}\right)\omega_e - \left(v + \frac{1}{2}\right)^2\omega_e x_e + \left(v + \frac{1}{2}\right)^3\omega_e y_e + \dots + \left[B_e - \alpha_e\left(v + \frac{1}{2}\right) + \gamma_e\left(v + \frac{1}{2}\right)^2 + \dots\right]J(J+1) + \dots \quad (3)$$

In this expression,  $B_e = \frac{h}{8\pi^2c\mu R_e^2}$  is the rotational equilibrium constant,  $h$  the Planck's constant,  $c$  the speed of light, and  $\mu$  the reduced mass of the system.

If one substitutes the values of the rovibrational energies  $E_{(v,J)}$  obtained by means of solving the nuclear Schrödinger equation an system of equations can be built for the spectroscopic rovibrational constants as follows [44]:

$$\omega_e = \{141[E(1, 0) - E(0, 0)] - 93[E(2, 0) - E(0, 0)] + 23[E(3, 0) - E(1, 0)]\} / 24$$

$$\omega_e x_e = \{13[E(1, 0) - E(0, 0)] - 11[E(2, 0) - E(0, 0)] + 3[E(3, 0) - E(1, 0)]\} / 4$$

$$\omega_e y_e = \{3[E(1, 0) - E(0, 0)] - 3[E(2, 0) - E(0, 0)] + [E(3, 0) - E(1, 0)]\} / 6 \quad (4)$$

$$\alpha_e = \{-12[E(1, 1) - E(0, 1)] + 4[E(2, 1) - E(0, 1)] + 4\omega_e - 23\omega_e y_e\} / 8$$

Solving these equations self consistently yields the desired rovibrational constants within the DVR methodology. The second approach used to obtain spectroscopic constants was the application of the Dunham's method [45].

### Results and discussion

In order to better present and compare our results, the analyzed systems are presented in order of increasing reduced mass, i.e., H<sub>2</sub>O–He < H<sub>2</sub>O–Ne < H<sub>2</sub>O–Ar < H<sub>2</sub>O–Kr < H<sub>2</sub>O–Xe. We start our analysis by discussing the results for the energy levels, together with the potential energy curve for each complex. Table 2 presents the vibrational energies accessible within the two first rotational states J=0 and J=1. The available data consist in the vibrational energies smaller than the dissociation value for each system.

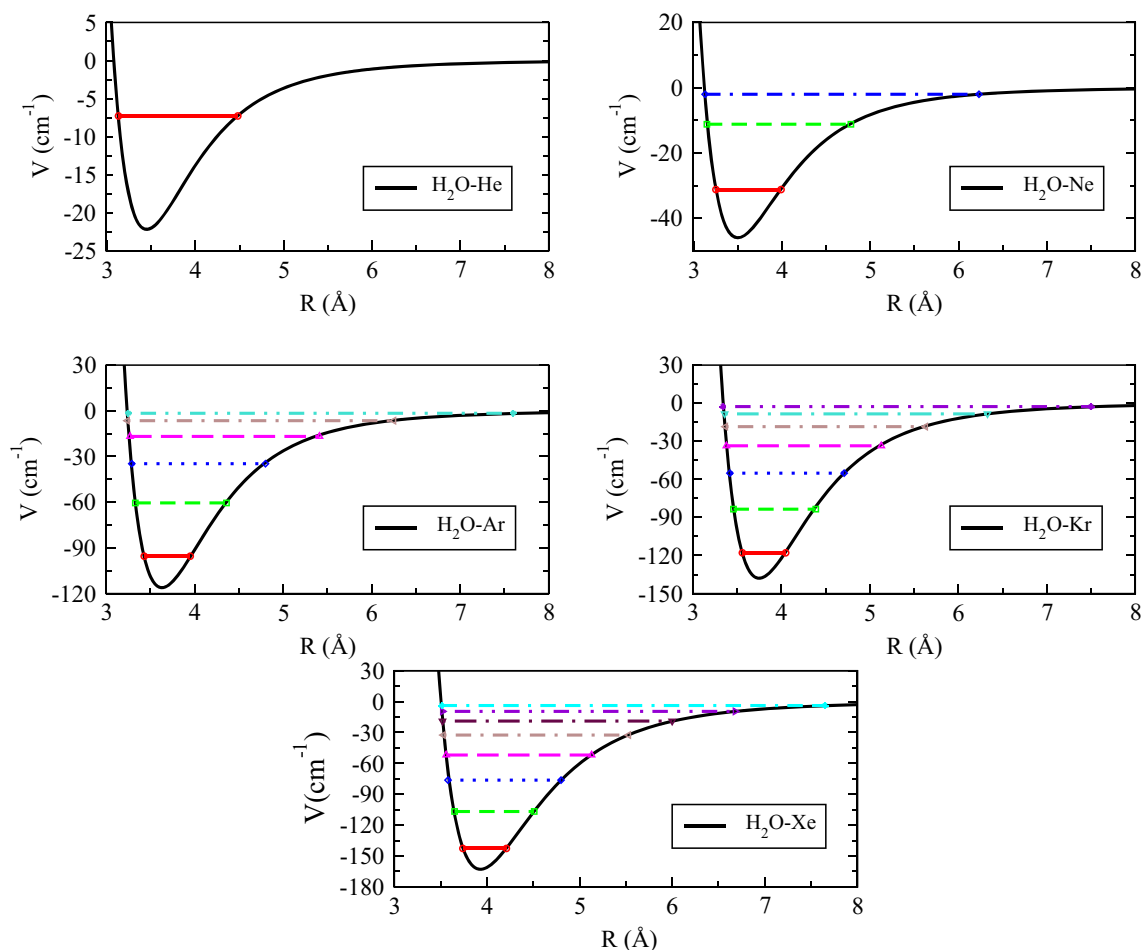
The first feature worthy to be mentioned is the closeness between the vibrational states energies for the fundamental and first excited rotational states. These facts happen for all H<sub>2</sub>O–Ng experimental and theoretical potential energy curves. This property can be observed by carrying out a direct comparison between the corresponding values of  $v$  for the two considered rotational states. One can see that the highest difference between any two corresponding levels for J=0 and J=1 is in the order of 10<sup>-3</sup>cm<sup>-1</sup>, which takes place for the fundamental vibrational state of the H<sub>2</sub>O–He complex. This extremely low value shows that, in this range, the rotational influence is negligible, for its value is very low. It can be also noted that the higher the reduced mass of the system, the lower is the rotational contribution. This is in accordance to the rigid rotor model for the complexes and explains why the rotation, although still very small, is slightly more important for H<sub>2</sub>O–He than for H<sub>2</sub>O–Ne, and so forth.

The vibrational energy levels, for each complex, considering both the experimental and *ab initio* PEC are presented in Fig. 1. The number of vibrational levels inside the well — consistent to the data available in Table 2 — as well as their spreading are clearly shown in the figure. It is important to note that, for the complexes with several vibrational levels inside the well, the spreading of these energy levels decreases for increasing values of  $v$ . This is an usual feature observed in complexes due to the anharmonicity of their PEC. This fact is also in agreement to expected trend of approaching continuous states for unbound systems.

As higher dissociation energies yield corresponding higher number of vibrational levels inside the well, we can trace a comparison between the number of levels and the

**Table 2** H<sub>2</sub>O–Ag rovibrational energies  $E_{(v,J)}$  (in  $\text{cm}^{-1}$ ) obtained using experimental and theoretical (in parentheses) potential parameters

$v$	$J$	H <sub>2</sub> O–He	H <sub>2</sub> O–Ne	H <sub>2</sub> O–Ar	H <sub>2</sub> O–Kr	H <sub>2</sub> O–Xe
0		14.9389(16.7889)	14.6849(16.0356)	20.7871(21.0814)	19.9974(20.6986)	20.2404(21.0630)
1	–	–	34.7038(37.9807)	55.5150(56.3506)	54.7118(56.6947)	56.2456(58.6443)
2	–	–	43.9437(48.1504)	81.5120(82.8416)	82.6352(85.7419)	86.4634(90.3338)
3	–	–	–	99.2319(101.1451)	104.0604(108.1429)	111.0009(116.1456)
4	0	–	–	109.7375(112.2380)	119.4304(124.3458)	130.0599(136.2424)
5	–	–	–	114.9411(118.0760)	129.4248(135.0226)	144.0118(151.0041)
6	–	–	–	–	135.1108(141.2331)	153.4317(161.0343)
7	–	–	–	–	–	159.1610(167.1729)
0		14.9390(16.7890)	14.6850(16.0356)	20.7872(21.0814)	19.9974(20.6986)	20.2404(21.0630)
1	–	–	34.7039(37.9807)	55.5150(56.3507)	54.7118(56.6948)	56.2456(58.6443)
2	–	–	43.9437(48.1504)	81.5120(82.8416)	82.6352(85.7419)	86.4635(90.3338)
3	–	–	–	99.2319(101.1451)	104.0604(108.1429)	111.0009(116.1456)
4	1	–	–	109.7319(112.2380)	119.4304(124.3458)	130.0599(136.2425)
5	–	–	–	114.9411(118.0760)	129.4248(135.0226)	144.0118(151.0041)
6	–	–	–	–	135.1108(141.2332)	153.4317(161.0343)
7	–	–	–	–	–	159.1610(167.1729)

**Fig. 1** Experimental potential energy curves for H<sub>2</sub>O–He, H<sub>2</sub>O–Ne, H<sub>2</sub>O–Kr, and H<sub>2</sub>O–Xe systems and its vibrational states

stability of the system. Naturally, a high dissociation energy is a fundamental signature of a highly stable complex. For the system to be considered stable, besides the dissociation energy be a minimum, the system must also present at least one vibrational state with energy smaller than the dissociation of the molecule [46]. If the system presents few excited vibrational states it means that small external excitation can give rise to its destabilization. In this sense, one concludes that the H<sub>2</sub>O–Xe complex is the most stable system, for it covers seven vibrational excited states. In the opposite sense, the H<sub>2</sub>O–He complex covers only the ground vibrational state. Therefore the first excited state would yield an energy higher than its dissociation and the system would collapse. One should, thus, conclude that H<sub>2</sub>O–He complex is the most unstable system analyzed. It should be noted that the trend observed in our calculations is expected since the increase of reduced mass of the system resulted in deeper potential wells and thus in a higher number of vibrational excited states.

Table 2 shows also the H<sub>2</sub>O–Ag rovibrational energies obtained using the theoretical PEC (in parentheses). One can see that the theoretical PEC rovibrational energies are in a good agreement with the experimental PEC rovibrational energies mainly for smaller number of vibrational excited states. In all cases analyzed, the theoretical PEC rovibrational energies are higher than experimental PEC results. The smallest difference found between these rovibrational energies were for the H<sub>2</sub>O–Ar system. This feature can be explained taking into account the smallest difference between the H<sub>2</sub>O–Ar theoretical and experimental potential well (about 3.2cm<sup>-1</sup>). Furthermore, the calculated first two H<sub>2</sub>O–Ar rovibrational energies using both experimental (20.7871cm<sup>-1</sup> and 55.5150cm<sup>-1</sup>) and *ab initio* (21.0814cm<sup>-1</sup> and 56.3506cm<sup>-1</sup>) PEC are in a good agreement with the experimental data obtained using a multipass infrared absorption spectrometer with a quantum cascade

laser (about 20cm<sup>-1</sup> and 45cm<sup>-1</sup>) [47]. These experimental data were estimated from Figure 7 of the reference [47].

Taking into account the rovibrational levels and energies accurately described, we can carry out the calculations for the spectroscopic constants using both experimental and theoretical PEC. In order to do this, we followed two different approaches, namely the DVR solution for the nuclear Schrödinger equation and the application of Dunham's methodology. A drawback in the DVR approach is that it is incapable of performing the calculation for the H<sub>2</sub>O–Ne and H<sub>2</sub>O–He complexes. This is a consequence of the small number of vibrational bound excited states present for these systems. One can see in Fig. 1 that they present less than four excited states (more precisely, 1 and 3 respectively). As we make use of the Equation set (4), the small number of available energies would yield an undetermined system, since there are four unknown spectroscopic constant. An interesting way to circumvent this difficulty of the DVR methodology is to apply the Dunham method. Through this procedure, all the spectroscopic constants can be obtained in an approximation as precise desired.

The results from DVR and Dunham methodologies for both PEC are presented together in Table 3 for means of better comparison. Two feature deserves special attention. First we can see that the good accordance between DVR and Dunham's methodology for the harmonic part of the well is a strong indication of the quality of our results, as well as the suitability of both approaches to the treated systems. For instance, the accordance between the  $\omega_e$  constant for the two methodologies is greater than 98% for all the complexes.  $\omega_e x_e$  values for DVR and Dunham are also achieved in a reasonable accordance, particularly for more massive complexes. Actually we can see that the greater the reduced mass, the better is the agreement. This fact is related to the greater contribution of harmonic part of the potential for more massive systems. Finally, one can also

**Table 3** Spectroscopic constants (cm<sup>-1</sup>) for each complex through both DVR and Dunham approaches

Systems	Methods	$\omega_e$	$\omega_e x_e$	$\omega_e y_e$	$\alpha_e$
H <sub>2</sub> O–He	DVR	–	–	–	–
	Dunham	38.68(43.29)	18.99(20.51)	–	0.16(0.17)
H <sub>2</sub> O–Ne	DVR	–	–	–	–
	Dunham	32.20(35.44)	6.35(7.01)	–	0.02(0.02)
H <sub>2</sub> O–Ar	DVR	43.89(44.61)	4.70(4.83)	0.07(0.09)	2.03x10 <sup>-06</sup>
	Dunham	43.20(44.41)	4.52(4.65)	–	0.008(0.008)
H <sub>2</sub> O–Kr	DVR	41.78(43.23)	3.61(3.70)	0.04(0.05)	6.70x10 <sup>-07</sup>
	Dunham	41.70(43.15)	3.55(3.62)	–	0.005(0.005)
H <sub>2</sub> O–Xe	DVR	41.89(43.48)	2.97(2.95)	0.01(0.002)	4.19x10 <sup>-07</sup>
	Dunham	41.84(43.37)	3.02(3.08)	–	0.005(0.003)

The values in parentheses were obtained using theoretical potential parameters



see from Table 3 that the rovibrational spectroscopic constants obtained from both experimental and theoretical PEC are in a good agreement, being the H<sub>2</sub>O–Ar system with the smallest difference. This fact is expected because the theoretical depth of the potential well and equilibrium distance are in a better agreement with those determined through the molecular beam scattering experiment.

## Conclusions

In this work we presented the rovibrational energies and the spectroscopic constants calculations for the complexes formed between the water molecule and several noble gases. Our calculations were based on potential energy curves obtained through both molecular beam scattering experiments and accurate theoretical calculations. It was observed that the distribution of the vibrational energy levels followed the pattern qualitatively expected for the nature of each system. The spectroscopic constants calculated with DVR and Dunham methodologies are in excellent agreement. This is a strong indication of the suitability of our methodology to describe water–Ng complexes. Although the H<sub>2</sub>O–He experimental and theoretical PEC have a small depth of the potential well, it was observed that these PEC present one vibrational state. This result suggests that the H<sub>2</sub>O–He system can remain bonded even with small dissociation energy. It was found, for all studied systems, that the rovibrational energies obtained through theoretical PEC are higher than those obtained via experimental PEC. The rovibrational energies obtained through the two PEC are in a good agreement, but only for first numbers of vibrational states. Another important fact that should be mentioned is that the H<sub>2</sub>O–Ar first two rovibrational energies are in a good agreement with the experimental data obtained using a multipass infrared absorption spectrometer with a quantum cascade laser. This study can help on understanding of the hydration of gas noble atoms and it can be helpful on understanding of complicated interactions between water and biological molecules.

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