

Effect of argon environment on small water clusters in matrix isolation

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The influence of cryogenic argon environment on small water clusters was investigated by quantum-chemical simulation of structure and vibrational spectra of water clusters consisting of different numbers of molecules. Comparison of calculation results for vacuum and argon environment shows a red shift of spectral bands in argon. Obtained IR frequencies and intensities for water clusters in argon are compared with experimentally registered FTIR spectra of water trapped in a low-temperature argon matrix.

Keywords: water clusters, argon environment, vibrational spectra.

1. Introduction

Water is intensively studied due to its essential biological, chemical and ecological properties [1–3]. The main cause of all its unique properties is the formation of hydrogen bonds between water molecules, and investigation of small water clusters is a natural starting point for an accurate description of water in its myriad forms [3–6].

The method of matrix isolation used first in 1954 by Pimentel *et al.* for investigation of unstable molecules and free radicals [7], is now a well-known technique in chemical and physical research, the main idea of which is to isolate the molecules of investigated substance in the traps (vacancies) of inert solvent. Nowadays, this method in combination with infrared absorption spectroscopy is one of the most effective methods for molecule structure investigation, and small clusters of water and other hydrogen-bonded complexes are intensively studied in such a way [8–17]. Interaction of trapped molecules with inert matrix environments is weak and usually can be neglected. However, Nemukhin in [18] admits that when a guest molecule is trapped to host solid inert matrix lattice the interaction forces are appeared between guest and host molecules, and peculiarities of such guest-host influence are studied in terms of microsolvation theory of supramolecular chemistry.

Thus, at least two types of interactions are observed in real molecular systems in matrix isolation. The first one is the interaction field created by guest molecules themselves in a matrix trap, and the second — by host matrix molecules. Therefore, when studying vibrational spectra of water molecules trapped in low-temperature matrices, it is important to estimate the solid matrix influence on them.

Cryogenic environment can affect positions and intensities of registered spectral bands, as well as their shape. Moreover, structure of isolated molecules (especially labile ones) often differs from structure of these molecules in gas phase.

Really, numerous studies of water, alcohols and many other molecules trapped in an argon matrix [19–26] show the difference between absorption bands positions in experimentally registered IR spectra and the corresponding calculated spectra of individual molecules and clusters in vacuum or in their own solvation. Even when using the most accurate calculation methods, including those that account for the anharmonicity of the vibrations and the polynomial scaling of the calculated frequencies, the difference between calculated and experimental wavenumbers cannot be reduced to less than 5–10 cm^{-1} [23]. So, one can conclude that this difference is due to the argon matrix effect on investigated molecules. Authors of [23] propose to solve the mentioned problem by calculations of vibrational spectra for model systems consisting of both the investigated molecules and the inert gas atoms, as it was successfully done for small linear molecules [27].

A model for calculation of translational vibrations of the water molecule in an Ar matrix was proposed in [28], where under the assumption about a cubic structure of a matrix the calculations were carried out for a cage formed after one argon atom deleting and substituting it by the water molecule. It is believed that due to its small size the molecule of water in an argon matrix rotates almost freely and its effective rotation constants are slightly smaller than the gas phase rotation constants [10,20,29]. In [30] the intensities of vibration–rotational transitions of an isolated water molecule in an argon matrix were calculated, and

the interaction of the water molecule with the matrix was included through the appropriate effective rotational constants.

The effects of an Ar matrix on structural and spectral properties of small water clusters $(\text{H}_2\text{O})_n$ ($n = 1-6$) were theoretically investigated by molecular dynamics simulations in [31]. Regarding the IR spectra, it was shown that the matrix environment leads to redshifts of the stretching modes and almost no shift of the bending modes.

Investigation of the gas to matrix shifts of the spectral bands can provide an interesting information about solute-solvent interactions. An isolation matrix is a dielectric medium, which redshifts the vibrational bands of species. The aim of the presented paper is investigation of an argon solvation effect on spectral bands in IR absorption spectra of water. It will be reached by comparison of the results of quantum chemical simulation of water clusters consisting of different numbers of molecules considered in two different environments — in vacuum and in argon. Such results can be used for estimation of possible band shifts in vibrational spectra of other hydrogen-bonded liquids in matrix isolation.

2. Experimental and quantum chemical calculation details

Liquid deionized and triple-distilled water was used in the experimental spectroscopic investigations. The samples for matrix isolation were prepared mixing the gaseous water obtained by natural evaporation from the liquid with argon (99.995%) in the approximate ratio 1:1000, as measured by standard manometric techniques. The obtained mixture was deposited at 10 K onto a CsI window for 1 h. The deposition rate was 5 mmol of matrix mixture per hour.

FTIR spectra of matrix samples were registered using Bruker IFS 113 FTIR spectrometer. A liquid- N_2 -cooled mercury cadmium telluride (MCT) detector was used. The stabilization of temperature was provided by a closed-cycle Leybold Heraeus RW2 He cryostat. Spectra were recorded with optical resolution 0.5 cm^{-1} . In order to increase the signal-to-noise ratio each spectrum was taken as an average of 512 scans.

Quantum chemical calculations were performed using Gaussian 03 software [32]. Adiabatic potential energy sur-

faces were obtained at normal conditions by *ab initio* method, DFT/B3LYP with *cc-pVTZ* basis set. The IR spectra were obtained for clusters consisting of n water molecules ($n = 1-6$) in two environments — in vacuum and in argon solution. The calculations were carried out in the harmonic approximation. To consider an argon environment the default Self-Consistent Reaction Field (SCRF) method with argon as a solvent was used. For the estimation of argon environment effect on thermochemical parameters of water clusters, such as thermal energy and heat capacity, the calculations in the argon solvation were performed with an additional condition for temperature, $T = 25 \text{ K}$.

3. Results and discussion

3.1. Structure parameters

Geometry of water clusters containing from 1 to 6 molecules was optimized for two different cases — in vacuum and in argon solution. Schematic pictures of the optimized structures are shown in Figs. 1, 3. It is seen that the most optimal structure of trimer, tetramer and pentamer is a closed ring consisting of 3, 4 or 5 molecules, respectively. The optimal structure for the dimer is an open one. Six water molecules occurred to be too much to form a ring, so the optimal structure of the hexamer looks like a combination of smaller clusters — joined pentamer and trimer. A similar structure of water hexamer was obtained in [33] from MP2 and CCSD(T) calculations (it was called there a “bag” conformer).

Some of the calculated parameters — intermolecular distances $\text{H}\cdots\text{O}$, intramolecular distances $\text{H}-\text{O}$, as well as angles $\text{H}\cdots\text{O}-\text{H}$ and $\text{H}-\text{O}-\text{H}$, are presented in Table 1. As is seen from Table 1, geometry of clusters in argon does not differ significantly from their geometry in vacuum. For the both media the intra-molecular distance $\text{H}-\text{O}$ increases when number of molecules in a cluster increases, while the inter-molecular distance $\text{H}\cdots\text{O}$ (the hydrogen bond) decreases with increasing number of molecules. It means that hydrogen bond strength increases with increasing number of water molecules in a cluster. One can note that the calculated geometry parameters of the hexamer deviate slightly from the general tendency. It can be explained by the fact that its structure is not a regular ring, as for smaller

Table 1. Calculated in DFT/B3LYP with *cc-pVTZ* basis set approximation geometry parameters of clusters $(\text{H}_2\text{O})_n$ ($n = 1-6$) in vacuum and in argon solution

n	$(\text{H}_2\text{O})_n$ in vacuum				$(\text{H}_2\text{O})_n$ in argon			
	$\text{H}\cdots\text{O}$, Å	$\text{H}-\text{O}$, Å	$\text{H}\cdots\text{O}-\text{H}$	$\text{H}-\text{O}-\text{H}$	$\text{H}\cdots\text{O}$, Å	$\text{H}-\text{O}$, Å	$\text{H}\cdots\text{O}-\text{H}$	$\text{H}-\text{O}-\text{H}$
1	—	0.961	—	104.53	—	0.962	—	104.45
2	1.96	0.967	136.13	104.64	1.94	0.968	134.1	104.59
3	1.88	0.977	87.53	105.68	1.88	0.977	87.53	105.68
4	1.76	0.985	101.22	105.59	1.76	0.985	101.04	105.55
5	1.72	0.987	110.59	105.48	1.73	0.987	110.41	105.48
6	1.81	0.982	101.96	105.01	1.81	0.982	101.87	104.98

Table 2. Calculated parameters of water clusters in vacuum

$(\text{H}_2\text{O})_n$ in vacuum, n	E_{total} , Hartree	E_{hb} , kcal/mol	E_{thermal} ($T = 298$ K), kcal/mol	C_v , ($T = 298$ K), cal/(mol·K)	Dipole moment, D
1	-76.460	–	15.1	6.0	1.92
2	-76.464	-2.56	31.2	12.7	3.77
3	-76.470	-6.47	50.5	23.4	1.26
4	-76.473	-8.36	68.0	31.4	0.00
5	-76.474	-8.72	85.3	40.7	1.10
6	-76.474	-8.81	102.9	49.8	2.72

Table 3. Calculated parameters of water clusters in argon environment

$(\text{H}_2\text{O})_n$ in Ar, n	E_{total} , Hartree	E_{hb} , kcal/mol	E_{thermal} , ($T = 298$ K) kcal/mol	E_{thermal} , ($T = 25$ K) kcal/mol	C_v , ($T = 298$ K) cal/(mol·K)	C_v , ($T = 25$ K) cal/(mol·K)	Dipole moment, D
1	-76.461	–	15.1	13.49	6.0	5.96	1.97
2	-76.465	-2.54	31.2	28.42	12.7	5.99	3.95
3	-76.471	-6.03	50.4	45.97	23.5	5.97	1.30
4	-76.474	-7.86	67.9	62.04	31.5	7.32	0.00
5	-76.474	-8.21	85.1	77.53	40.7	10.12	1.17
6	-76.474	-8.28	102.7	93.41	49.9	11.30	2.88

clusters. It is also interesting to note that calculated values of structural parameters of both trimers — in vacuum and in argon — are absolutely the same. This may be due to high symmetry of the trimer.

Table 2 presents some of the calculated parameters of water clusters in vacuum — total energy per mole, energy of hydrogen bond, thermal energy (for $T = 298$ K), heat capacity (for $T = 298$ K) and dipole moments. As is seen, hydrogen bond energy (per one bond) increases with cluster size increasing, as well as thermal energy and heat capacity. The results of similar calculations for the same clusters in argon environment are presented in Table 3. Here thermal energy and heat capacity were calculated also for the temperature $T = 25$ K, which is close to the temperature of an argon matrix.

3.2 Spectral region of the bending vibrations

For all optimized structures, the corresponding IR spectra were calculated at the same level of theory. The obtained spectra were scaled using standard scaling factors for this method — 0.973 for the region of the bending vibrations, 0.962 for the stretching OH vibrations [34]. The calculated spectra of water clusters containing from 1 to 6 molecules in the spectral region of the bending vibrations (ν_2) are presented in Fig. 1.

As is seen from Fig. 1, spectral bands of water clusters in argon are red-shifted by several wavenumbers in comparison with the same clusters in vacuum. The calculated frequencies and intensities of IR absorption bands for different water clusters in vacuum and argon environment as well as their deviations $\Delta\nu = \nu(\text{Ar}) - \nu(\text{vac})$; $\Delta I = I(\text{Ar}) - I(\text{vac})$ within the spectral region of the bending vibrations are presented in Table 4.

The calculated value of fundamental frequency ν_2 for water monomer in vacuum (1594.5 cm^{-1}) is very close to the known value of ν_2 for gaseous water — 1594.6 cm^{-1} [35,36]. The corresponding calculated value for water monomer in argon is 1592.6 cm^{-1} , however reported experimental IR frequencies of this vibration in argon matrices are somewhat lower — for example, 1588.7 cm^{-1} in Ref. 36 or 1589.2 cm^{-1} in Ref. 10.

In Fig. 2 the experimentally registered FTIR spectra of water trapped in an argon matrix at temperatures 15 and 25 K in the spectral region of the bending vibrations are presented. It is seen that there is an absorption band at 1590 cm^{-1} , which can be assigned to a monomer (M). An additional proof of such an assignment is that its intensity is

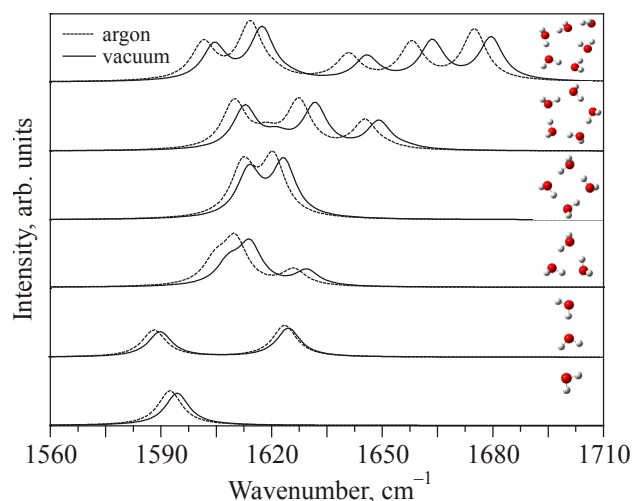


Fig. 1. (Color online) Calculated IR spectra for clusters $(\text{H}_2\text{O})_n$ ($n = 1-6$) in vacuum and in argon solution in the spectral region of ν_2 vibrations.

Table 4. Calculated by DFT/B3LYP (*cc-pVTZ*) method IR absorption frequencies and intensities for different water clusters in vacuum and in argon in the spectral region of the bending vibrations

Cluster	Vacuum		Argon		Deviations	
	ν , cm^{-1}	I , arb. units	ν , cm^{-1}	I , arb. units	$\Delta\nu$, cm^{-1}	ΔI , arb. units
Monomer	1594.5	69.5	1592.6	75.0	-1.9	5.4
Dimer	1590.1	53.1	1588.4	56.8	-1.7	3.7
	1624.9	60.7	1623.9	67.0	-1.0	6.3
Trimer	1608.2	44.2	1604.6	47.6	-3.5	3.4
	1614.0	87.2	1610.0	96.1	-4.0	9.0
	1629.5	32.8	1625.9	34.4	-3.5	1.5
Tetramer	1614.0	99.7	1612.4	110.2	-1.7	10.5
	1623.4	58.3	1620.6	62.2	-2.9	3.9
	1623.5	58.6	1620.6	62.4	-2.9	3.8
	1649.4	0.0	1645.4	0.0	-4.1	0.0
Pentamer	1612.9	89.3	1610.0	101.0	-2.9	11.6
	1621.5	23.9	1618.7	26.0	-2.8	2.0
	1631.9	93.5	1627.5	101.0	-4.4	7.5
	1649.3	58.9	1645.5	60.4	-3.8	1.5
	1656.9	3.8	1651.9	3.6	-5.0	-0.1
Hexamer	1604.6	74.7	1601.6	79.2	-3.0	4.4
	1617.6	110.1	1614.3	120.5	-3.2	10.4
	1624.9	4.7	1620.9	9.0	-4.0	4.2
	1646.0	50.5	1641.0	54.1	-5.0	3.6
	1663.7	83.3	1658.2	79.6	-5.5	-3.7
	1679.7	91.2	1675.1	108.6	-4.5	17.4

lower at 25 K than at 15 K — number of monomers in the sample decreases with temperature increasing [26,37]. According to [10], two kinds of water molecule are spectroscopically distinguishable in rare gas matrices: the rotating monomer and the non-rotating monomer. The band 1589.2 cm^{-1} was assigned there to the non-rotating

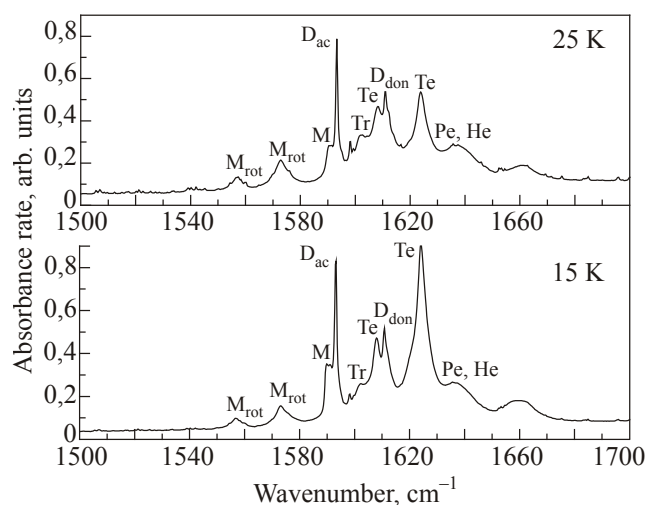


Fig. 2. FTIR spectra of water trapped in an Ar matrix at 15 and 25 K in the spectral region of bending vibrations.

monomer, while the bands 1557 and 1573 cm^{-1} were referred to the rotating monomer. These two bands are present in our spectrum too (M_{rot}). One of the most intense bands at both 15 and 25 K is that at 1593 cm^{-1} (D_{ac}). It was assigned to the proton acceptor molecules of the water dimer in [10,19], while the band at 1610 cm^{-1} (D_{don}) was assigned to the proton donor [10].

Quantum-chemical calculations for water dimers in argon give values 1588.4 cm^{-1} for the proton acceptor molecule and 1623.9 cm^{-1} for the proton donor. According to the results of calculations and Refs. 10, 38, the band at 1602 cm^{-1} is assigned to the trimer (Tr), the bands at 1608 and 1624 cm^{-1} — to the tetramer (Te). The corresponding calculated values for the trimer are 1604.6 and 1610 cm^{-1} , for the tetramer — 1612.4 and 1620.6 cm^{-1} . The broad band at about 1635 cm^{-1} corresponds to the vibrations of pentamers, hexamers and other polymers. So, it is denoted in Fig. 2 as Pe, He.

Therefore, comparing the results of quantum-chemical calculations of IR spectra of water clusters in argon environment with experimentally registered FTIR spectra of water in an argon matrix, one can see that the calculated frequencies are in average overestimated by several wavenumbers.

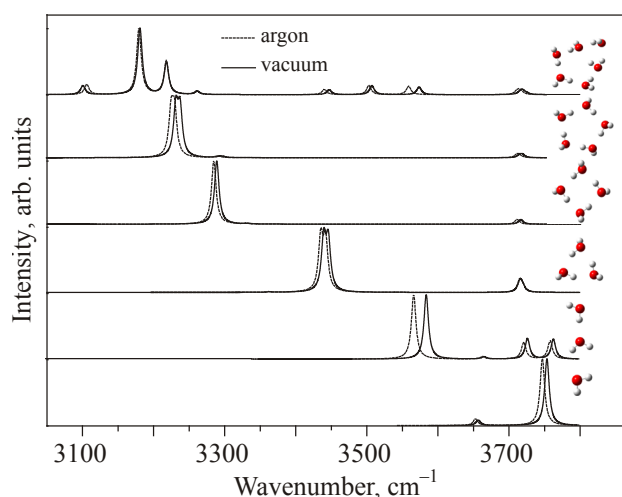


Fig. 3. (Color online) Calculated IR spectra (normalized in intensity) for clusters $(\text{H}_2\text{O})_n$ ($n = 1-6$) in vacuum and in argon solution in the spectral region of the stretching OH vibrations.

3.3. Spectral region of the stretching OH vibrations

The calculated IR spectra of water clusters containing from 1 to 6 molecules in vacuum and in argon in the spectral region of the stretching OH vibrations are presented in Fig. 3. The spectra are normalized because of the significant differences in bands intensities (from 40 arb. units for monomer to 2550 arb. units for hexamer). It is seen that all spectral bands of water clusters in argon are red-shifted by several wavenumbers in comparison with the corresponding clusters in vacuum.

The calculated frequencies and intensities of IR absorption bands for different water clusters in vacuum and argon environment as well as their differences $\Delta\nu = \nu(\text{Ar}) - \nu(\text{vac})$; $\Delta I = I(\text{Ar}) - I(\text{vac})$ within the spectral range of the stretching OH vibrations are presented in Table 5.

Table 5. Calculated by DFT/cc-pVTZ method IR absorption frequencies and intensities for different water clusters in vacuum and in argon in the spectral region of the stretching OH vibrations

Cluster	Vacuum		Argon		Deviations	
	ν , cm^{-1}	I , arb. units	ν , cm^{-1}	I , arb. units	$\Delta\nu$, cm^{-1}	ΔI , arb. units
Monomer	3658.6	3.2	3654.8	4.7	-3.9	1.5
	3755.3	40.9	3748.8	47.8	-6.5	6.9
Dimer	3585.4	225.2	3567.8	278.5	-17.6	53.3
	3666.8	7.9	3664.8	10.3	-2.0	2.4
	3727.8	71.7	3722.5	72.0	-5.3	0.3
Trimer	3764.3	69.3	3759.8	78.5	-4.5	9.2
	3363.5	5.6	3363.0	6.7	-0.4	1.1
	3439.9	591.0	3435.8	630.6	-4.1	39.6
	3446.4	561.0	3442.6	597.6	-3.8	36.7
	3715.6	83.4	3715.3	95.1	-0.3	11.7
Tetramer	3717.3	54.2	3717.1	58.0	-0.2	3.8
	3720.1	47.2	3719.9	50.3	-0.1	3.2
	3177.8	0.0	3180.9	0.0	3.1	0.0
	3288.1	1467.0	3284.0	1549.5	-4.1	82.5
	3288.3	1466.5	3284.1	1549.3	-4.2	82.8
	3331.4	29.1	3329.2	29.7	-2.2	0.6
	3715.5	84.8	3710.3	98.5	-5.1	13.8
Pentamer	3716.2	65.5	3711.2	69.9	-5.0	4.4
	3716.2	65.6	3711.2	70.0	-5.0	4.4
	3717.2	0.0	3712.4	0.0	-4.8	0.0
	3132.8	8.8	3133.7	8.7	0.9	-0.2
	3231.9	2250.1	3225.3	2372.3	-6.6	122.2
	3237.8	2159.4	3230.1	2293.3	-7.7	134.0
Hexamer	3293.2	53.0	3289.1	50.5	-4.1	-2.5
	3297.9	42.1	3293.3	42.7	-4.6	0.6
	3714.5	53.0	3710.9	59.7	-3.5	6.7

Pentamer	3716.7	60.8	3712.6	69.6	-4.2	8.8
	3718.7	41.6	3713.9	43.3	-4.8	1.7
	3718.8	43.1	3714.1	52.2	-4.7	9.0
	3720.5	55.3	3715.8	55.4	-4.7	0.1
Hexamer	3101.1	332.6	3106.6	382.0	5.5	49.4
	3181.4	2446.4	3180.0	2506.9	-1.4	60.4
	3218.6	1184.6	3218.5	1274.0	-0.1	89.4
	3261.8	123.2	3262.1	115.7	0.3	-7.5
	3447.7	180.9	3440.7	198.4	-6.9	17.6
	3507.7	334.9	3503.5	341.3	-4.3	6.5
	3574.1	278.8	3559.4	322.0	-14.8	43.2
	3715.2	54.8	3710.8	61.5	-4.4	6.7
	3718.7	51.5	3714.0	66.4	-4.7	14.9
	3719.1	86.4	3714.2	81.2	-4.9	-5.2
	3720.7	26.8	3716.2	34.2	-4.6	7.4
	3725.0	50.9	3718.9	55.6	-6.1	4.7

As one can see from Table 5, the calculated fundamental frequencies ν_1 and ν_3 at 3658.6 cm^{-1} and 3755.3 cm^{-1} , respectively, are sufficiently close to the known values of ν_1 and ν_3 in gas phase — 3657.1 cm^{-1} and 3755.8 cm^{-1} [35,36]. The corresponding calculated fundamentals in argon environment are redshifted to 3654.8 cm^{-1} and 3748.8 cm^{-1} . According to [36], experimentally registered IR absorption frequencies for water monomers in a low-temperature argon matrix are 3638.4 cm^{-1} and 3734.1 cm^{-1} .

In Fig. 4 the experimental spectra of water clusters isolated in an argon matrix at 15 and 25 K in the spectral region of OH stretching vibrations are presented. The bands assignments are made according to the calculation results and using the reported experimental data [10,19,36,39]. The intense band at 3756 cm^{-1} corresponds to the monomer fundamental ν_3 . Its intensity at 15 K is higher than at 25 K, indicating decreasing of the number of monomers in

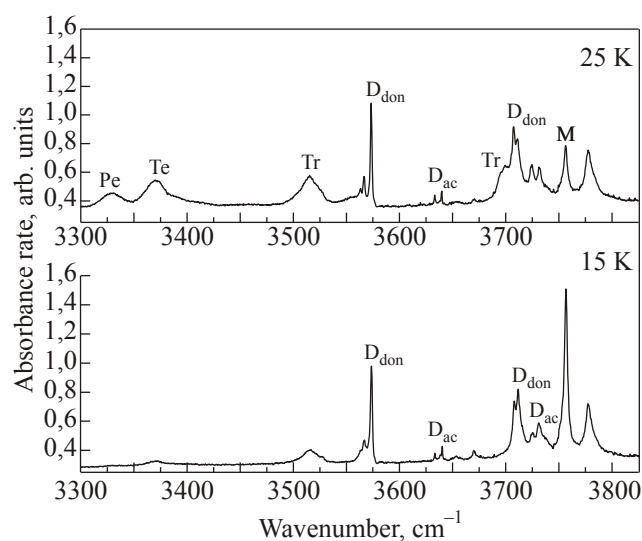


Fig. 4. FTIR spectra of water trapped in an Ar matrix at 15 and 25 K in the spectral region of the stretching OH vibrations.

the sample with temperature increasing. As was mentioned earlier, the water molecule can freely rotate in an Ar matrix, so one can observe other absorption bands, which corresponds to the monomer. One of the most intense of them is observed at 3777 cm^{-1} [10,39].

Intensive absorption bands at 3573 and 3708 cm^{-1} (D_{don}) belong to the donor molecule in a dimer. The corresponding band positions of the acceptor molecule are 3633 and 3732 cm^{-1} . Quantum-chemical calculations for the dimer in argon environment give 3567.8 and 3722.5 cm^{-1} for the proton donor and 3664.8 and 3759.8 cm^{-1} for the proton acceptor peaks. According to our calculations, trimer bands should be observed near 3440 and 3715 cm^{-1} , tetramer bands — at about 3284 and 3718 cm^{-1} , the most intense pentamer bands — near 3223 cm^{-1} and hexamer ones — near 3180 cm^{-1} . Authors of [14] registered IR absorption bands of tetramers at 3710 and 3284 cm^{-1} , pentamers — at 3230 cm^{-1} , hexamers — at 3200 cm^{-1} in an Ar matrix. The band at 3516 cm^{-1} was assigned to trimers in [10]. In our registered water spectrum in an Ar matrix at 25 K (Fig. 4) we observe absorption maxima at 3515 cm^{-1} (trimers), 3370 cm^{-1} (tetramers) and 3330 cm^{-1} (pentamers).

As is seen, the correlation between experimental and calculated spectra in the region of the stretching OH vibrations is worse than for the bending vibrations. It may be explained by the fact that the stretching OH vibrations have large amplitude and are highly anharmonic, which was not taken into account in the quantum-chemical calculations in the harmonic approximation.

Conclusions

The influence of cryogenic argon environment on water molecules and small clusters was investigated by quantum-chemical simulation of structure and vibrational spectra of different water clusters in vacuum and in argon environ-

ment. The results of simulation were compared to the experimentally registered FTIR spectra of water trapped in an Ar matrix at 15 and 25 K. The obtained redshifts of spectral bands for water in argon in comparison to water in vacuum is in a good agreement with experimental data. The calculated frequencies in the region of fundamental frequency ν_2 are in average overestimated only by several wavenumbers. Intensity behavior of spectral bands calculated for different water clusters in argon solution correlates with the behavior of experimentally registered IR spectra. An agreement between calculated vibrational frequencies and experimental data, especially in the region of the stretching OH vibrations, can be improved by carrying out more accurate calculations, for example, in the anharmonic approximation or by simulation the structure of an argon crystal with embedded water molecules.

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Вплив аргонного оточення на невеликі кластери води в матричній ізоляції

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Вплив криогенного аргонного оточення на невеликі кластери води досліджується методом квантово-хімічного моделювання структури і коливальних спектрів кластерів води, які мають змінну кількість молекул. Порівняння результатів розрахунків для вакууму та аргонного оточення показує червоне зміщення спектральних смуг в аргоні. Отримані ІК частоти та інтенсивності для кластерів води в аргоні порівнюються з експериментально зареєстрованими спектрами ІЧ поглинання води, ізолюваній в низькотемпературній аргонній матриці.

Ключові слова: кластери води, аргонне оточення, коливальні спектри.

Влияние аргонного окружения на небольшие кластеры воды в матричной изоляции

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Влияние криогенного аргонного окружения на небольшие кластеры воды исследуется методом квантово-химического моделирования структуры и колебательных спектров кластеров воды, состоящих из различного числа молекул. Сравнение результатов расчетов для вакуума и аргонного окружения показывает красное смещение спектральных полос в аргоне. Полученные ИК частоты и интенсивности для кластеров воды в аргоне сравниваются с экспериментально зарегистрированными спектрами ИК поглощения воды, изолированной в низкотемпературной аргонной матрице.

Ключевые слова: кластеры воды, аргонное окружение, колебательные спектры.