

# Propyne-water complexes hosted in helium droplets

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Received February 10, 2019, published online April 26, 2019

A Helium Nanodroplet Isolation (HENDI) experiment was performed to explore the absorption spectrum of the propyne-water complex ( $\text{CH}_3\text{CCH}\cdots\text{H}_2\text{O}$ ). Two spectral regions were investigated, near the CH stretch  $\nu_1$  of the propyne moiety and near the asymmetric stretch  $\nu_3$  of the water moiety. *Ab-initio* calculations were performed at the MP2/aug-cc-pVTZ level to estimate the spectroscopic constants of the free complex. This provided the necessary parameters to simulate the absorption spectrum of the complex and thus facilitate the interpretation of the experiment. The observed spectrum is consistent with a structure of the complex where two H-bonds between water and propyne form a five member ring. The later was predicted by Lopes *et al.* [*J. Mol. Struct.* **834**, 258 (2007)].

Keywords: HENDI, propyne, H bonds.

## 1. Introduction

Following the IUPAC definition, the hydrogen bonding is “a form of association between an electronegative atom and a hydrogen atom attached to a second, relatively electronegative atom” [1]. Apart from fairly strong  $\text{OH}\cdots\text{O}$  bonds as in the water dimer ( $D_0 = -(15 \pm 2) \text{ kJ}\cdot\text{mol}^{-1} \approx 1254 \text{ cm}^{-1}$ ) [2] weaker H-bonds exist. Nishio distinguished four classes of H-bonds whether the H-atom donor belongs to a hard (HA) or soft (SA) acid group and the acceptor to a hard (HB) or a soft (SB) base group [3]. The water dimer belongs to the HA/HB family, whereas the acetylene dimer ( $D_0 = 518\text{--}543 \text{ cm}^{-1}$ ) [4] or the propyne dimer ( $D_0 = 450\text{--}830 \text{ cm}^{-1}$ ) [5] belong to the SA/SB family. The later dimers were studied recently using the Helium NanoDroplet Isolation (HENDI) technique [5,6].

A quite complicated situation is encountered when considering the acetylene-water complex ( $\text{HC}\equiv\text{CH}\cdots\text{H}_2\text{O}$ ). On the one hand, the acetylene molecule can act either as a soft H-donor (SA) or -acceptor (SB) whether the C–H or the  $\text{C}\equiv\text{C}$  bond is considered. On the other hand, water is well known to be both a hard H-acceptor and a hard H-donor. Hence, isomers of the H-bonded  $\text{HC}\equiv\text{CH}\cdots\text{H}_2\text{O}$

complex may belong to two different families, SA/HB or HA/SB. This situation has been investigated in detail in argon matrix [7], pulsed supersonic slit jet [8], and quantum mechanical calculations using a hierarchy of theoretical methods MP2, MP4 and CCSD(T) [9]. All these studies converge on the SA/HB family where a terminal CH of acetylene is bonded to the O-atom of  $\text{H}_2\text{O}$ .

The propyne-water ( $\text{CH}_3\text{C}\equiv\text{CH}\cdots\text{H}_2\text{O}$ ) complex could be considered as rather similar to the acetylene-water complex. In fact, a much more intricate reality is revealed by the theoretical work of Lopes *et al.* from *ab initio* MP2 and DFT/B3LYP approaches using the 6–31++G(d,p) basis set [10]. This is due to the capacity of the  $-\text{CH}_3$  group of propyne to be a H-donor while the  $\text{C}\equiv\text{C}$  triple bond acts as a H-acceptor. Then,  $\text{H}_2\text{O}$  can both act as a H-donor and form a first H-bond with the  $\text{C}\equiv\text{C}$  triple bond and act as a H-acceptor and form another H-bond with the methyl group of propyne. Accordingly, Lopes *et al.* suggests that the propyne-water complex is stabilized as a quasi five-membered ring.

To our knowledge, no experimental work has been performed yet to investigate the structure of the  $\text{CH}_3\text{C}\equiv\text{CH}\cdots\text{H}_2\text{O}$  complex. This has motivated the pre-

sent work. In line with our previous studies on the acetylene and propyne dimers, we document here the absorption spectrum of the  $\text{CH}_3\text{C}\equiv\text{CH}\cdots\text{H}_2\text{O}$  complex hosted in helium droplets. The spectral regions that are investigated span the C–H stretch region  $\nu_1$  of propyne and the asymmetric stretch region  $\nu_3$  of water. The experimental work is complemented by *ab-initio* calculations.

## 2. Experiment

The experimental setup is the same as that used in our studies on the acetylene and propyne dimers [5,6]. Briefly, a beam carrying helium droplets is generated by a supersonic expansion. The backing pressure is 20 bar. The 5  $\mu\text{m}$  diameter nozzle is cooled down to 13.5 K. This produces helium droplets carrying  $\approx 7200$  atoms. Downstream the source chamber, the beam crosses successively two pickup regions where propyne and water molecules are deposited collisionally on the droplets. The beam then passes between the mirrors of a multi-pass assembly where a tunable infrared light beam is injected. The latter is produced by a tunable infrared optical parametric oscillator laser (linewidth 1 MHz). A mass spectrometer tuned to the mass of  $\text{He}_2^+$  is used to detect the helium droplets after the beam has left the interaction zone with the laser. Among the  $\text{He}_n^+$  cluster ions which characterize the ionization of a helium droplet, the  $\text{He}_2^+$  ion is that leading to the better signal-to-noise ratio (no impurity signal is indeed present at mass 8 u).

An experiment consists in monitoring the flux of helium droplets using the mass spectrometer, while scanning the infrared laser. Two ranges are reported below, 3328.5–3333.3  $\text{cm}^{-1}$  and 3729.0–3731.7  $\text{cm}^{-1}$ . The first one allows us to excite the  $\nu_1$  C–H stretch of the propyne moiety within the complex and the second one, the  $\nu_3$  asymmetric stretch of the water moiety. When the laser is tuned to a transition of a hosted species, the latter is excited ro-vibrationally and relaxes towards the droplet, which evaporates. Such an experiment allows us to record a kind of absorption spectrum of the hosted species. It runs as a standard HENDI experiment [11–15].

## 3. Experimental results

The absorption spectrum recorded when both propyne and water molecules are deposited on the helium droplet is shown as the green curve in Fig. 1. The horizontal scale of the figure shows two spectral regions 3328.5–3333.3  $\text{cm}^{-1}$  ( $\nu_1$  C–H stretch of propyne) and 3729.0–3731.7  $\text{cm}^{-1}$  ( $\nu_3$  asymmetric stretch of water). Actually, other spectral regions (3238.7–3241  $\text{cm}^{-1}$ ; 3621–3623  $\text{cm}^{-1}$ ; 3706–3709  $\text{cm}^{-1}$  and 3751.6–3754  $\text{cm}^{-1}$ ) were explored. They are not reported here since they revealed no signal that could be assigned to the propyne-water complex. The absence of bands in the spectral region 3751.6–3754  $\text{cm}^{-1}$  is especially important. According to previous works (for example [16,17]) it could be thought indeed that the band that is observed in the pre-

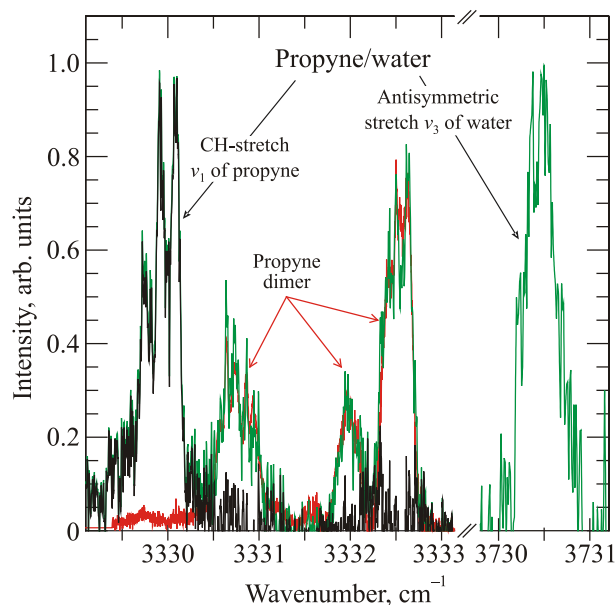


Fig. 1. (Color online) Absorption spectrum of the propyne/water mixture in helium nanodroplets (green curve). The red curve shows the propyne-only spectrum after the proper scaling. The black curve is the difference between both curves. The propyne-only spectrum does not contribute to the 3730–3731  $\text{cm}^{-1}$  spectral region and only the green curve appears in the right hand side of the figure. The assignments which label the spectral bands are justified in the text.

sent experiment near 3729  $\text{cm}^{-1}$  is associated with the water dimer rather than with the propyne-water complex as mentioned above. Actually, this is ruled out, because Kuyanov *et al.* [17] showed that two other bands located at 3752.6 and 3760  $\text{cm}^{-1}$  are associated with the water dimer but were not observed in the present experiment. Hence, we are left with the above assignment of the 3729  $\text{cm}^{-1}$  band to the propyne-water complex.

The red curve which appears in the left hand side of Fig. 1 is the spectrum measured in Ref. 5 when only propyne molecule is present on the droplet. It matches almost exactly the three bands centred at 3330.7, 3331.9 and 3332.5  $\text{cm}^{-1}$  which are observed in the green spectrum. They were assigned to the isomers  $m_1$  and  $m_2$  of the propyne dimer in Ref. 5. The latter are shown in Fig. 2. Note that a third isomer was found in Ref. 5. It leads to substantially redder absorption bands because its terminal CH groups are directly involved in H-bonds.

When subtracting the red curve from the green one in Fig. 1, the black curve is obtained. It documents selectively the absorption spectrum of droplets which carry both propyne and water molecules. A very structured band is observed. It has three sub-bands at 3329.75, 3329.90 and 3330.07  $\text{cm}^{-1}$ . Given this very distinct structure, we con-

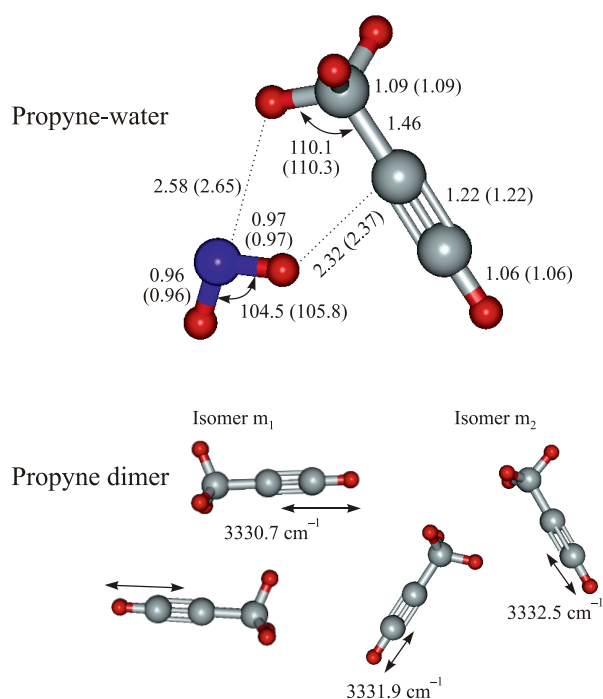


Fig. 2. (Color online) Optimized structures of the propyne-water complex (present work) and for comparison, that of isomers  $m_1$  and  $m_2$  of the propyne dimer (taken from Ref. 5). In the propyne-water complex, the dotted lines visualize the five member ring formed by the H-bonds and the numbers give the distances (in Å) and the angles (in degrees) which define the geometry (the calculation of Lopes *et al.* appears between parenthesis) [10]. For the propyne dimers, the double arrows show the direction of the transition dipoles and next to each one the corresponding absorption wavenumber.

sider that these absorption bands are due to the 1:1 propyne/water complex rather than larger propyne/water complexes which are likely associated with unstructured spectra.

#### 4. Discussion

Strikingly, the three sub-bands at 3329.75, 3329.90 and 3330.07  $\text{cm}^{-1}$  just assigned to the 1:1 propyne/water complex mimic the three sub-band structure of the 3332.5  $\text{cm}^{-1}$  band of the propyne dimer. The later was discussed in Ref. 5 as due to the bluest absorption of isomer  $m_2$ , i.e., to the C–H stretch excitation which is the less perturbed by the H-bond. This similarity suggests that the propyne-water complex is built similarly as the  $m_2$  isomer of the propyne dimer. Hence, water would act as the H-atom donor and would form a  $\text{OH}\cdots\pi$  bond with the CC triple bond of the propyne molecule (as an equivalent to the  $\text{CH}_3\cdots\pi$  bond in isomer  $m_2$ ). In such a configuration, the O-atom could be in the right position for acting as H-acceptor and form a second H-bond with the  $\text{CH}_3$  group of propyne. This would correspond to the structure with a quasi five-membered ring that was predicted theoretically by Lopes

*et al.* for the  $\text{CH}_3\text{C}\equiv\text{CH}\cdots\text{H}_2\text{O}$  complex [10]. This structure of the  $\text{CH}_3\text{C}\equiv\text{CH}\cdots\text{H}_2\text{O}$  complex is shown in Fig. 2. It is obtained from a similar calculation as that in Ref. 10 but a larger basis set is used. A full geometry optimization is performed at the MP2/aug-cc-pVTZ level using the MOLPRO package [18]. The geometry drawn in Fig. 2 agrees quantitatively with that of Ref. 10. This appears when comparing the distances calculated in the present work with those available from Ref. 10.

The present calculations allows us predicting the spectroscopic constants of the free propyne-water complex. They are listed in the left hand side of Table 1. No reference vibration is available for the present system to scale the calculated frequencies. The same scaling factor of 0.95594 as in our publication on the propyne dimer [5], is therefore used here. The predicted C–H stretch and OH asymmetric stretch become 3326.50 and 3742.74  $\text{cm}^{-1}$ , respectively. It is well documented that the origin of vibrational bands in HENDI experiment are weakly affected by the helium environment [12]. The predicted C–H stretch (3326.50  $\text{cm}^{-1}$ ) and OH asymmetric stretch (3742.74  $\text{cm}^{-1}$ ) frequencies can thus be directly compared to the band centres, estimated from Fig. 1 and listed in the right hand side of Table 1. The C–H stretch prediction matches accurately

Table 1. Spectroscopic constants of the propyne-water complex (in  $\text{cm}^{-1}$  except %a:%b:%c, which is dimensionless)

	Free complex (calculations without scaling factor)	Hosted complex (effective constants)
<b>Vibration</b>		
CH str.	3479.82	3329.82(1)
%a:%b:%c	0:100:0	0:100:0
$\text{H}_2\text{O}$ asym. str.	3915.25	3730.40(1)
%a:%b:%c	98:2:0	98:2:0
<b>Rotation</b>		
$A$	1.00	0.11(2)
$B$	0.48	0.0045(5)
$C$	0.33	0.0045(5)
$\Delta_K$		0.0005(3)
$\Delta_{JK}$		0.0006(5)
$\Delta_J$		0.0005(5)
$\Phi_K, \Phi_{KJ}, \Phi_{JK}, \Phi_J$		$5\cdot 10^{-6}$
Linewidth		0.06

Notes: %a:%b:%c are the percentages of a, b and c transition for exciting the relevant vibrational mode. The constants given for the free complex (middle column) are given by the MP2/aug-cc-pVTZ calculations without scaling factor. The effective constants given for the hosted complex (right column) are best fit values to get the agreement shown in Fig. 3 between simulation (red curve) and experiment (black curve). The number in parentheses is the uncertainty on the last digit of the effective constants.

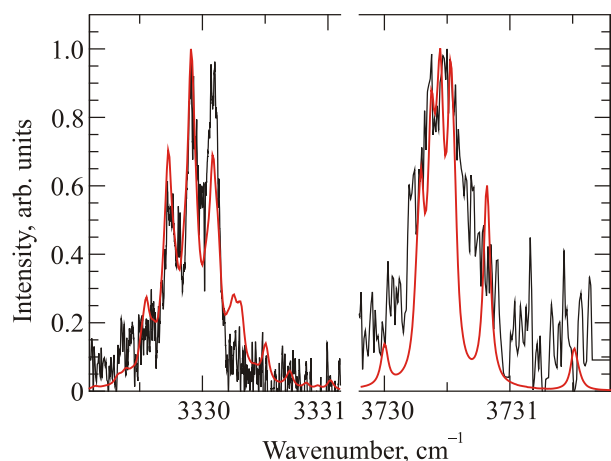


Fig. 3. (Color online) Fit of the absorption spectrum of the propyne-water complex hosted in helium nanodroplets. The experimental spectrum (in black) is taken from Fig. 1. The red curve is a simulation using the effective constants listed in Table 1.

the observed band centre within  $-3.32\text{ cm}^{-1}$ . For the OH asymmetric stretch, the prediction is only within  $+12.34\text{ cm}^{-1}$  from the observation. It must be mentioned that the scaling factor which is used is not well adapted to the water OH stretch mode, which is likely more anharmonic than the propyne CH stretch mode. Hence, we consider this agreement as satisfactory and assign the observed absorption bands to the propyne-water complex with the geometry shown in Fig. 2.

In contrast with vibrational frequencies, rotational constants are known to be dramatically affected by the helium environment in HENDI experiment [12]. To quantify this, we follow the same strategy as in Ref. 5 for the propyne dimer. Here, the propyne-water complex is assumed to behave as a rigid asymmetric top molecule. The two H-bonds which stabilize the complex and define its structure are not expected indeed to be dramatically affected by the helium environment. This assumption is indirectly justified by the discussion above on the vibrational constant that otherwise would be significantly different whether the complex is free or hosted in a helium droplet. Then, the absorption spectrum of the complex is simulated using the PGOPHER program suite [19]. Effective values are given to the rotational and distortion constants of the complex. This accounts phenomenologically for the effect of the helium environment on the rotation of the complex.

The effective constants used in the simulation are listed in Table 1. They were adjusted to ensure that the simulated spectrum fits the experimental spectrum. To limit the number of fit parameters, both the ground and excited vibrational states were described by the same set of rotational and distortion constants. The best fit spectrum is shown as the red curve in Fig. 3 and compared to the experimental spectrum in black. Note that sextic constants  $\Phi_K$ ,  $\Phi_{KJ}$ ,  $\Phi_{JK}$  and  $\Phi_J$  were included in the PGOPHER simulation.

This prevents troubles with the large effective values of  $\Delta_K$ ,  $\Delta_{JK}$  and  $\Delta_J$  which otherwise would force the energy of the rotational levels to decrease unrealistically at large values of  $J$  and  $K$ .

As mentioned above the value of the effective rotational and distortion constants listed in Table 1 carry a phenomenological information on the perturbation brought to the rotation of the complex, assumed to be rigid, by the helium environment. We first discuss this effect by comparing the effective rotational constants  $A$ ,  $B$  and  $C$  to those predicted for the free complex. The effective  $A$  constant is almost a factor 10 smaller than the  $A$  constant of the free complex and the effective constants  $B$  and  $C$  about a factor 100 smaller. This effect is qualitatively similar to that observed in Ref. 5 for the isomer  $m_2$  of the propyne dimer. However, it is quantitatively much larger. The decrease reported in Ref. 5 was only a factor 5 while here it is at least twice larger. Such a reduction of the effective rotational constants indicates that the helium environment slows down efficiently the rotation of the hosted species. This effect has been extensively reviewed [12,13,15]. It is interpreted as due to the increase of the moment of inertia of the rotating hosted species because a non-superfluid component of the droplet is driven into movement by the rotation of the hosted species itself.

The present observation of a much larger decrease of the rotational constants than observed in Ref. 5 for the propyne dimer is an indication that the non-superfluid helium component driven by the rotation of the propyne-water complex is heavier and has a larger extension than that driven by the propyne dimer. This is actually not too surprising since the large dipole moment of water can attract helium atoms into a non-superfluid component at a much larger distance than a propyne molecule.

The effective distortion constants  $\Delta_K$ ,  $\Delta_{JK}$  and  $\Delta_J$  which are read in Table 1 are of the same order of magnitude as those found in Ref. 5 for the propyne dimer. When compared to usual distortion constants of molecules in the gas phase, they are two or three orders of magnitude larger. This was observed already by many authors in HENDI experiments [12,13,15,20]. It received a full theoretical interpretation [21]. This phenomenon is due to a strong coupling between the higher rotational states of the molecule and the roton and maxon excitations of the superfluid helium phase.

It is interesting to bring together the value of  $\Delta_J$  for the propyne monomer in helium droplets ( $0.0005\text{ cm}^{-1}$ ) [5] with the values of  $\Delta_K$ ,  $\Delta_{JK}$  and  $\Delta_J$  for the isomers of the propyne dimer ( $0.0002$  to  $0.0008$ ) [5] and for the present propyne-water complex ( $0.0005$  and  $0.0006$  read in Table 1) in the same environment. They are in the same range. This suggests that the coupling with the roton/maxon excitation behaves in the same way, whatever the size of the hosted species.

## 5. Conclusion

The absorption spectrum of the propyne-water complex ( $\text{CH}_3\text{CCCH}\cdots\text{H}_2\text{O}$ ) is explored near the CH stretch region  $\nu_1$  of the propyne moiety. The vicinity of the asymmetric stretch  $\nu_3$  of the water moiety is also explored. The Helium NanoDroplet Isolation (HENDI) technique is used.

The observed spectrum is consistent with the structure of the complex that was predicted by Lopes *et. al.* [10]. The water molecule acts both as a H-atom donor towards the  $\text{C}\equiv\text{C}$  triple bond of propyne and as a H-atom acceptor from the  $\text{CH}_3$  group of propyne.

*Ab-initio* calculations at the MP2/aug-cc-pVTZ level are also performed in the present work. They fully agree with those of Lopes *et. al.* They are used to get an estimate of the spectroscopic constants of the free propyne complex. The latter are compared with effective constants which are determined when fitting the experimental spectrum by that simulated, assuming that the propyne-water complex behaves as a semi-rigid asymmetric top molecule. This allows us discussing the coupling between the hosted complex and the non-superfluid and the superfluid components of the helium droplet.

## Acknowledgment

This work received partial funding from Agence nationale de la Recherche (ANR-14-CE06-0019 — ESBODYR) and Triangle de la Physique (2010-004T — NOSTADYNE-2). E. Mengesha and A. Gutiérrez-Quintanilla acknowledge partial support from Eurotalent (2015 project #259) and Triangle de la Physique (2013-0436T — REACMAQ), respectively.

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## Пропін-водні комплекси, ізольовані в краплях гелію

A. Gutiérrez-Quintanilla, M. Briant, E. Mengesha, Marc-André Gaveau, J.-M. Mestdagh, B. Soep, L. Poisson

Проведено експеримент з гелієвою нанокрапельною ізоляцією (HENDI) для вивчення спектру поглинання комплексу пропін-вода ( $\text{CH}_3\text{CCH}\cdots\text{H}_2\text{O}$ ). Досліджено дві спектральні області: поблизу частот СН валентних коливань  $\nu_1$  пропінового фрагмента і поблизу частот антисиметричної моди  $\nu_3$  валентних коливань водного фрагмента. *Ab initio* розрахунки проведено на рівні MP2/aug-cc-pVTZ для оцінки спектральних констант вільного комплексу. Це забезпечило необхідні параметри для моделювання спектра поглинання комплексу і, таким чином, полегшило інтерпретацію експерименту. Спостережений спектр узгоджується зі структурою комплексу, де два водневі зв'язки між водою та пропінілом утворюють п'ятичленне кільце. Останнє було передбачено Lopes та ін. [*J. Mol. Struct.* **834**, 258 (2007)].

Ключові слова: гелієва нанокраплинна ізоляція, пропін, водневі зв'язки.

Пропин-водные комплексы, изолированные  
в каплях гелия

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Проведен эксперимент с гелиевой нанок капельной изоляцией (HENDI) для изучения спектра поглощения комплекса пропин-вода ( $\text{CH}_3\text{CCH}\cdots\text{H}_2\text{O}$ ). Исследованы две спектральные области: вблизи частот СН валентных колебаний  $\nu_1$  пропинового фрагмента и вблизи частот антисимметричной моды  $\nu_3$

валентных колебаний водного фрагмента. *Ab initio* расчеты проводились на уровне MP2/aug-cc-pVTZ для оценки спектральных констант свободного комплекса. Это обеспечило необходимые параметры для моделирования спектра поглощения комплекса и, таким образом, облегчило интерпретацию эксперимента. Наблюдаемый спектр согласуется со структурой комплекса, где две водородные связи между водой и пропином образуют пятичленное кольцо. Последнее было предсказано Lopes и др. [*J. Mol. Struct.* **834**, 258 (2007)].

Ключевые слова: гелиевая нанок капельная изоляция, пропин, водородные связи.