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# Molecular structure and infrared spectra of guanidinium cation

## A combined theoretical and spectroscopic study

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### Abstract

The guanidinium cations seem to be very interesting chemical species which can be used in design of molecular complexes with exactly planed chemical and physical properties suitable for nonlinear optics (NLO).

The molecular structure of guanidinium cation  $\text{C}(\text{NH}_2)^+$  has been calculated with the aim of density functional (B3LYP) method with the extended 6-311 + G(df,dp) basis set. The calculated geometrical parameters of guanidinium cation in gas phase were compared with experimental data of other guanidinium compounds. The harmonic frequencies and IR and Raman intensities of  $\text{C}(\text{NH}_2)^+$  were calculated with the B3LYP method using 6-311 + G(df,dp) basis set. The calculated frequencies were compared with the experimental ones observed in vibrational spectra measured for three newly obtained compounds in which guanidinium cation is common component. The assignment of the experimental spectra has been made on the basis of the calculated potential energy distribution (PED).

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**Keywords:** Guanidinium cation; DFT; Vibrational spectra; Hydrogen bonds

### 1. Introduction

Fast development of hardware and constant improvement in computer coding make high-performance computational techniques a promising alternative to experimental studies. This is especially attractive when experimental data are not available or incomplete. The nowadays theoretical methods are used for small molecular systems and large biomolecules and biopolymers. Not surprisingly, the special attention in this study is focused on computational approach of DNA structure [1]. Recently a considerably progress is observed in quantum modeling of supermolecules. A reasonable first order approximation for the modeling of supermolecules is the assumption that they can be represented as a superposition of interactions of their smaller components (building blocks or bricks) [2].

The guanidine as a small molecule which can be used as building brick in supramolecular chemistry was selected as a significant example. This choice was not accidental. The guanidinium ion can form a broad family of hydrogen-bonded crystals and this cation is relatively simple. Additionally, the structure of

described compound is related to those of amides and proteins in which is considerable current interest.

The properties of guanidinium cations are independent from environment constituted from different chemical anions. In investigated complexes this cation is flat. In this configuration the  $\text{CN}_3$  group skeleton is very stable. The understanding of “rigidity problem” seems to be very important in designing of new compounds. The peculiar electronic structure should be explained by detailed theoretical study. We hope that these studies will be helpful in designing new compounds of this type where guanidinium cation is not planar and deformed. We hope that new complexes without inverse center having application in nonlinear optics become discovered.

The second purpose of this work is the comparison the experimental vibrational spectra with the results of theoretical calculations. The clear-cut assignment of all bands in the experimental spectra has been made on the basis of the calculated potential energy distribution (PED). The reliable assignment of all bands in the infrared spectrum is indispensable for an understanding of the spectral changes in the hydrogen-bonded complexes.

Our preliminary studies show that comparing the calculated results for molecule state close to gas phase with experimental observations in solid crystalline phase is allowed. Previously

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observed differences between experimental frequencies of bands arising from hydrogen bonds are included in the wide range [3,4] ( $3000\text{--}1400\text{ cm}^{-1}$ ). The detailed relationships between strength of hydrogen bond and observed frequencies for experimental data were presented by Novak [5] and Nakamoto [6]. I suppose that in investigated molecule two groups of bands can be distinguished. In most cases the calculated frequencies of bands originating from vibrations of guanidinium cation should be in good agreement with experimental values. The opposite situation is expected for bands which originate from vibrations involved in hydrogen bonds system. The frequencies of bands obtained for free chemical bonds (for example, N–H) in theoretical spectra are observed much higher than noticed in experimental spectra where hydrogen atoms are involved in hydrogen bonds. After comparative studies in the family of guanidinium compounds the relationship between chemical character of hydrogen bond (strength and directional properties) and noticed frequencies for suitable bands should be clear. This information can be used in design of new similar compounds.

## 2. Methods

### 2.1. Theoretical

The optimized equilibrium structure, harmonic frequencies, infrared intensities and Raman scattering activities of guanidinium cation have been calculated by the Restricted Hartree Fock (RHF) method and the density functional three-parameter hybrid model (DFT/B3LYP—Becke + Slater + HF exchange and LYP + VWN5 correlation) [7,8]. In these studies, the 6-311 + G(df,dp) basis set have been employed (the valence triple- $\zeta$  basis set, augmented by d,f, polarization functions on carbon and nitrogen; p,d, polarization functions on hydrogen atoms and enlarged by diffuse functions on all atoms). This level of theory gives good results in predicting vibrational spectra of small organic molecules [9].

The normal coordinate analyses have been carried out for guanidinium cation according to the procedure described and recommended by Fogarasi and Pulay [10]. The redundant set of 34 internal coordinates has been used. The frequencies of NH stretching and bending vibrations involved in hydrogen bond network were scaled by 0.92 (SF). This scaling factor is smaller than recently reported SF for the A–H stretching force constants [11]. The other harmonic frequencies were scaled by the factor of 0.983 determined in previous studies of similar organic systems [12]. The calculated potential energy distribution for  $\text{C}(\text{NH}_2)^+$  has enabled to make detailed assignments of experimental IR and Raman spectra of molecules where guanidinium cation is basic “brick” of investigated structure.

All calculation was performed with the GAMESS program [13] version from 12 December 2003 (R2) compiled under Linux operation system. This job was executed on PC Cluster consists of 1 server node with two 32-bit Intel Xeon processors running at 1.8 GHz and 3 GB RAM, 20 computing nodes with dual 32-bit Intel Xeon processors running at 2.8 GHz and 2 GB RAM, 9 computing nodes with dual 32-bit Intel Xeon processors running at 1.7 GHz and 1 GB RAM.

### 2.2. Experimental

The detailed vibrational studies on powder and monocrystal samples (IR-microscopic study) were performed for three new obtained compounds: guanidinium hydrogensulphate, guanidinium hydrogenselenate and diguanidinium hydrogenarsenate monohydrate. The guanidinium cation is a slightly deformed by chemical neighborhood and geometry and spectroscopic parameters can be compared with theoretical calculations. The experimental frequencies and band assignments for guanidinium cation are taken from previous studies [14–18]. These papers include detailed description of obtaining the crystals and specification of experimental method used during vibrational studies.

## 3. Results and discussion

### 3.1. Geometrical structure

The optimized geometrical bonds lengths of guanidinium cation are listed in Table 1, together with the experimental values for guanidinium compounds obtained from earlier X-ray crystallographic experiments. The theoretical and experimental angles for investigated molecule are presented in Table 2. The Fig. 1 shows the numbering of atoms.

The theoretical and experimental data indicate that the guanidinium ion is planar. In theoretical study the titled compound has  $D_{3h}$  symmetry. All C–N bonds distances are equal to 1.3424 Å, whereas the all N–H bonds lengths are equal to 1.0066 Å. The angles of C–N skeleton are identical and equal to  $120.0^\circ$ . It is characteristic that all H–N–H angles are identical and equal to  $115.9^\circ$ . The other C–N–H angles in molecule are equal to  $122.1^\circ$ .

According experimental X-ray data the planarity of investigated cation is conserved in all described compounds, but the geometrical parameters are different in each case. In guanidinium hydrogenselenate [15] the C–N bonds have different length. The length of one of these bonds is equal to 1.278 Å, the second to 1.307 Å and the longest bond is equal to 1.335 Å. Similar differences are observed for N–H bond. The length of the shortest bond is equal to 0.558 Å, whereas the longest one

Table 1  
The experimental and calculated by DFT method distances [Å] for guanidinium cation

Bond	GUSE	GUS	G2AS		B3LYP
			Molecule A	Molecule B	
C1–N2	1.287	1.304	1.335	1.319	1.3424
C1–N3	1.307	1.307	1.297	1.327	1.3424
C1–N4	1.335	1.324	1.313	1.337	1.3424
N2–H5	0.829	0.692	0.679	0.855	1.0066
N2–H8	0.558	0.960	0.740	0.826	1.0066
N3–H6	0.684	1.020	0.852	0.776	1.0066
N3–H9	0.694	0.690	0.720	0.850	1.0066
N4–H7	0.778	0.779	0.778	1.005	1.0066
N4–H10	0.750	0.591	0.926	1.009	1.0066

GUSE, guanidinium hydrogenselenate; GUS, guanidinium hydrogensulphate; GUAS, diguanidinium hydrogenarsenate monohydrate.

Table 2

The experimental and calculated by DFT method angles [°] for guanidinium cation

Angle	GUSE	GUS	G2AS		B3LYP
			Molecule A	Molecule B	
N4–C1–N3	119.4	120.4	120.2	119.2	120.0
N2–C1–N3	119.9	119.9	120.4	120.0	120.0
N2–C1–N4	120.6	119.7	119.5	120.7	120.0
H5–N2–C1	129.7	120.3	125.7	122.6	122.1
H5–N2–H8	105.8	120.9	114.2	120.9	115.9
H8–N2–C1	123.9	118.7	118.1	116.6	122.1
H6–N3–C1	107.1	113.2	117.9	114.2	122.1
H6–N3–H9	132.3	101.6	121.4	129.3	115.9
H9–N3–C1	120.6	144.7	115.2	116.1	122.1
H7–N4–C1	121.4	127.5	125.3	115.2	122.1
H7–N4–H10	125.6	115.2	112.9	135.4	115.9
H10–N4–C1	112.5	111.0	121.8	103.4	122.1

GUSE, guanidinium hydrogenselenate; GUS, guanidinium hydrogensulphate; GUAS, diguanidinium hydrogenarsenate monohydrate.

has the length of 0.829 Å. The hydrogen atom from the shortest N–H bond is involved in N–H···O type of hydrogen bond with distance of 2.902 Å. This is the shortest N–H···O bond in investigated complex. Surprisingly, the longest N–H bond with distance equals to 0.829 Å is engaged in medium hydrogen bond (2.989 Å), whereas in the longest N–H···O hydrogen bond (3.082 Å) the N–H bond with distance 0.695 Å is involved.

The all N–C–N angles are practically identical and equal to ca. 120°. Serious differences were noticed for H–N–H angles: H(5)–N(2)–H(8) angle is 105.8° and the value of H(6)–N(3)–H(9) is 132.3°.

The differences between C–N bonds distances are observed in guanidinium hydrogensulphate [18], too. The shortest C–N bond is equal to 1.304 Å, medium one has the length equal to 1.307 Å and the longest C–N bond distance is estimate to be

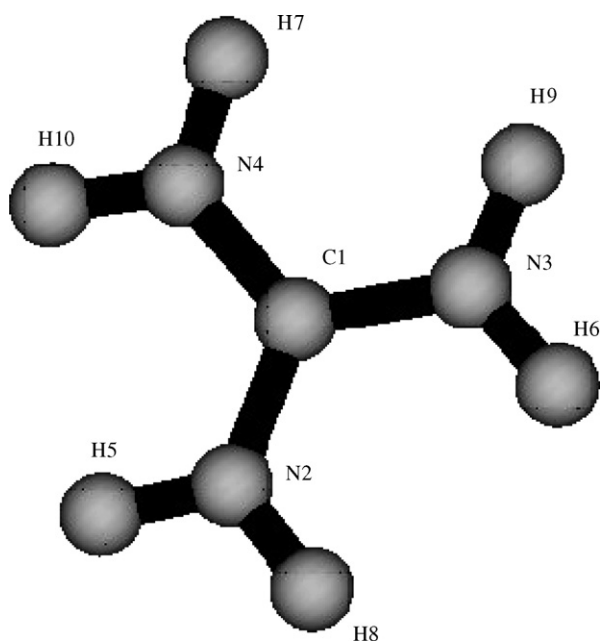


Fig. 1. The numbering of atoms in guanidinium cations.

1.324 Å long. The range of length values is smaller than in guanidinium hydrogenselenate complex. For N–H bonds the differences between lengths in two described crystals are bigger in the case of hydrogensulphate. The shortest bond has a slightly bigger value of length (0.591 Å) than in hydrogenselenate complex. The longest N–H bond is equal to 1.020 Å. The shortest N–H bond is involved in the longest N–H···O hydrogen bond with distance 3.054 Å. The N–H···O hydrogen bond with distance 2.990 Å is formed by the longest N–H bond (1.02 Å), whereas the shortest N–H···O bond distance is 2.908 Å. The medium N–H bond with distance 0.960 Å is involved in this chemical interaction.

The pronounce differences were observed for values of angles in guanidinium hydrogensulphate. Only skeleton N–C–N angles are very similar and equal to approximately 120°. The more interesting case is noticed for angle H(6)–N(3)–H(9). It is equal to 101.6°, only. Second unusual data are shown for H(9)–N(3)–C(1) angle (144.7°).

In diguanidinium hydrogenarsenate monohydrate [14] the two different guanidinium cations are present. In cations described as A the C–N and N–H bonds distances are similar as observed in guanidinium hydrogenselenate. For cation defined as B type the distances of C–N and N–H bonds are similar to those noticed for guanidinium hydrogensulphate. Generally we found that ion B has the longest C–N and N–H bonds.

In the longest N–H···O hydrogen bond in B guanidinium cation, N–H bond with distance 0.862 Å is involved. The shortest N–H···O hydrogen bond is formed by N–H bond with medium 0.850 Å, whereas the longest N–H bond equal to 1.009 Å is engaged in N–H···O bond with distance 2.972 Å.

Similar situation is observed for A type guanidinium cation. The medium N–H bond equal to 0.740 Å is involved in the longest N–H···O hydrogen bond (2.926 Å). As in B type molecule the shortest N–H bond is involved in hydrogen bond equal to 2.8502 Å. This is the shortest N–H···O hydrogen bond in guanidinium ion of A type.

Of course as in previous cases the skeleton N–C–N angles are very similar and equal to approximately 120°. More complicated situation is observed in the case of C–N–H and H–N–H angles. The suitable angles are not similar as in previously described crystals. In A type cation the H–N–H angles seem to be close to “ideal” case of theoretical structure where this angle was 115.9°. Another situation is noticed in the case of B type cation. The H–N–H angles are bigger than in model cation with  $D_{3h}$  symmetry. More differences between calculated and experimental data are observed for both A and B type ions for C–N–H angles.

The differences between theoretical geometrical parameters and experimental values should be explained by the formation of many hydrogen bonds in investigated crystals. These N–H–O hydrogen bonds have different length and angles.

It seems easy to understand that the drastic changes of distances are observed for N–H bonds, but similar diversity of bond length is noticed for C–N bonds which are involved in hydrogen bond network, indirectly. Generally the N–H bonds should be longer than in isolated guanidinium cation. The increase of distance of chemical N–H bonds should be proportional strength of N–H···O hydrogen bond. This trend is a little less clear in

case of carbon–nitrogen bonds. In this case the length of C–N bond should depend on the strength and to a large extent on the angles and directional properties of hydrogen bonds.

Similar problems concerning unambiguous interpretation of changes of angles in guanidinium cation involved in hydrogen bonds could be expected.

It should be noticed that direct comparison of theoretical geometric parameters with experimental results is very difficult. The calculation was performed for isolated molecule in gas phase, whereas in real crystals the bonds distances seem to be longer. It seems to be interesting that only two N–H bonds and two C–N bonds have length bigger than in theoretical model. Of course it is clear that comparison of theoretical model with experimental result directly is impossible but the monitoring of trends in the changes of these parameters is fruitful.

### 3.2. Mulliken and Lowdin population analysis

The Mulliken population analysis for guanidinium cation was performed by density functional method using 6-311 + G(df,dp) basis set. The results are presented in Table 3. The Fig. 2 shows the electrostatic potential (Fig. 2a) and atomic density (Fig. 2b). It is evidenced from this calculation that the total charge (+1) of the guanidinium cation  $\text{C}(\text{NH}_2)^+$  is not localized, but is disturbed among all atoms.

According to B3LYP calculation, the negative charge (−0.5272 e) is delocalized mainly between three nitrogen atoms: N2, N3 and N4. The positive charge is localized on C1 atom (0.5900 e). All hydrogen atoms are positively charged (0.3319 e). This distribution of charge seems to be symmetrical. It is clear that guanidinium cation is symmetrical on the basis of electrostatic charge distribution and formation of chemical bonds at each atom in this cation is in an equal degree probable.

Some differences in values of calculated charges are noticed between Mulliken and Lowdin population analysis. According to Lowdin calculation the negative charge is delocalized between N2, N3 and N4 atoms but these values are different: N2 and N3 atoms (−0.1075 e) and N4 (−0.1099 e). The positive charge is localized on C1 atom (0.2042 e). All hydrogen atoms are positively charged but these values are not the same for each hydrogen atom. For H6, H7, H8 and H10 charges are equal to ca. 0.1870 e, whereas for two atoms H5 and H9 these values

Table 3  
Mulliken and Lowdin charges (e) calculated for guanidinium cation

Atom	Charge	
	Mulliken	Lowdin
C1	0.5900	0.2042
N2	−0.5272	−0.1057
N3	−0.5272	−0.1057
N4	−0.5272	−0.1099
H5	0.3319	0.1847
H8	0.3319	0.1869
H6	0.3319	0.1870
H9	0.3319	0.1869
H7	0.3319	0.1847
H10	0.3319	0.1870

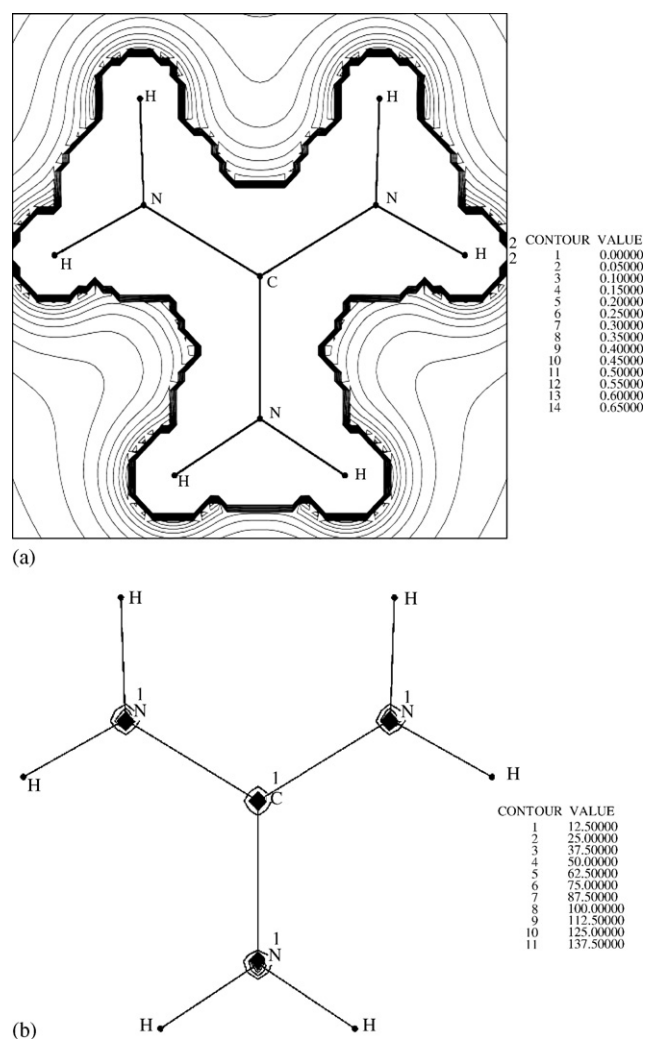


Fig. 2. (a) Electrostatic potential for guanidinium cation; (b) Atomic density calculated for guanidinium cation.

are equal to 0.1847 e. It results suggest that cloud of charge in investigated cation is not full symmetric, but is clear that charge is delocalized.

According to literature data [9] the net atomic charges obtained from Mulliken population analysis show extremely strong basis set dependence and they very considerably with the method employed in calculation. The full symmetrical distribution of charges in guanidinium ion in this approximation is questionable. It can be concluded that Lowdin atomic charges can be used for reliable description of the chemical properties of investigated ion, whereas the Mulliken charges have unrealistic values for this molecules. The inadequacy of Mulliken population analysis was noticed in other simple organic compounds with carbon and nitrogen atoms [9].

### 3.3. Vibrational spectra and their assignment

All theoretical frequencies, infrared and Raman intensities and potential energy distribution for guanidinium cation were obtained from B3LYP (UB3LYP) calculations using 6-311G(df,dp) basis set. In Table 4 all theoretical data are com-



Table 4  
The scaled calculated frequencies, IR and Raman intensities, PED% and the experimental frequencies of guanidinium cations

Frequency	IR intensity	Raman intensity	PED%	Calculated free guanidinium ion	GUS		GUSE		GUAS	
3442	217	43	N—H 50%	$\nu_{\text{asym}}\text{NH}_2$	3462 vs	$\nu_{\text{as}} \text{N—H} \cdots \text{O}$	3449 vs	$\nu_{\text{as}} \text{N—H} \cdots \text{O}$	3449 s	$\nu_{\text{asym}}\text{NH}_2$
3442	217	43	N—H 50%	$\nu_{\text{asym}}\text{NH}_2$	3348 vs	$\nu_{\text{sym}} \text{N—H} \cdots \text{O}$	3419 vs 3337 vs	$\nu_{\text{as}} \text{N—H} \cdots \text{O}$ $\nu_{\text{sym}} \text{N—H} \cdots \text{O}$		
3438	0	0	N—H 58%	$\nu_{\text{asym}}\text{NH}_2$						
3352	0	212	N—H 56%	$\nu_{\text{sym}}\text{NH}_2$	3278 vs	$\nu_{\text{sym}} \text{N—H} \cdots \text{O}$	3262 vs	$\nu_{\text{sym}} \text{N—H} \cdots \text{O}$		
3333	261	4	N—H 50%	$\nu_{\text{sym}}\text{NH}_2$			3212 vs	$\nu_{\text{sym}} \text{N—H} \cdots \text{O}$	3312 s	$\nu_{\text{sym}}\text{NH}_2$
3333	261	3	N—H 50%	$\nu_{\text{sym}}\text{NH}_2$			3175 vs	$\nu_{\text{sym}} \text{N—H} \cdots \text{O}$	3124 s	
					1861 v	Twisting NH <sub>2</sub>	1849 vw	Twisting NH <sub>2</sub>		
1686	0	30	H—N—H 56%, H—N—C 16%	$\sigma\text{NH}_2$	1566 m	$\delta\text{NH}_2$	1564 s	$\delta\text{NH}_2$	1563 w	$\delta\text{NH}_2$
1642	350	60	H—N—C 56%, N—C 11%, N—C—N 10%	$\sigma\text{NH}_2$	1554 m	$\delta\text{NH}_2$	1555 m	$\delta\text{NH}_2$	1556 w	$\delta\text{NH}_2$
1642	350	4	H—N—C 29%, H—N—H 20%, N—H 26%, N—C—N 18%	$\sigma\text{NH}_2$	1532 w	$\delta\text{NH}_2$	1539 m	$\delta\text{NH}_2$		
1625	234	2	H—N—C 60%, C—N 36%	$\nu_{\text{as}}\text{CN}$	1669 vs	$\nu_{\text{as}}\text{CN}$	1646 vs	$\nu_{\text{as}}\text{CN}$	1584 m	$\nu_{\text{asym}}\text{CN}$
1625	234	0	N—C—N 92%	$\nu_{\text{as}}\text{CN}$	1643 vs 1627 sh	$\nu_{\text{as}}\text{CN}$				
					1503 vw	$\delta\text{NH}_2$	1535 m	$\delta\text{NH}_2$	1503 w 1144 w	$\delta\text{NH}_2$ $\omega\text{NH}_2$
1089	28	2	H—N—H 38%, N—C—N 36%, H—N—C 16%	$\rho\text{NH}_2$			1098 vw	$\rho\text{NH}_2$		
1089	28	0	N—C 31%, N—H 30%, H—N—H 16%	$\rho\text{NH}_2$			1065 vw	$\rho\text{NH}_2$	1089 vw	
1050	0	0	H—N—C 72%	$\rho\text{NH}_2$						
1018	0	34	C—N 83%	$\nu_{\text{s}}\text{CN}$	1006 w 850 vs	$\nu_{\text{s}}\text{CN}$ $\omega\text{NH}_2$	1008 vw	$\nu_{\text{s}}\text{CN}$	1010 vw 821 m	$\nu_{\text{s}}\text{CN}$
804	0	0	N—C—N—H 82%	$\omega\text{CN}_3$	726 w 722 w	$\delta\text{CN}_3$ $\delta\text{CN}_3$	731 s	$\delta\text{CN}_3$	722 s	$\delta\text{CN}_3$
623	890	0	N—C—N—H 92%	$\omega\text{NH}_2$						
621	0	0	N—C—N—H 64%	$\omega\text{NH}_2$	595 sh	$\omega\text{NH}_2$			606 w	$\omega\text{NH}_2$
621	0	0	N—C—N—H 84%	$\omega\text{NH}_2$						
					583 sh					
557	0	0	N—C—N 73%	$\sigma\text{CN}_3$	579 vs	$\gamma\text{CN}_3$	573 m	$\gamma\text{CN}_3$		
557	0	0	N—C—N 36%, H—N—C 22%	$\sigma\text{CN}_3$			531 s		534 w 548 w	$\delta\text{CN}_3$
526	0	3	N—C—N—H 84%	$\tau\text{NH}_2$	551 sh					
526	0	4	N—C—N—H 97%	$\tau\text{NH}_2$						
					518 vs		523 s			
370	0	0	N—C—N—H 96%	tors.NH <sub>2</sub>						

The experimental data, sign and assignments are taken from refs. [14–18]. Abbreviations:  $\nu$ , stretching; s, symmetric; as, antisymmetric;  $\sigma$ , scissoring (symmetric in-plane);  $\rho$ , rocking (antisymmetric in-plane);  $\omega$ , wagging (symmetric out-of plane);  $\tau$ , twisting (antisymmetric out-of-plane); tors., torsion.

pared with experimental frequencies of recently reported three guanidinium complexes. In this table data presented are derived from guanidinium cation, only. In Fig. 3 are shown the eigenvectors for each calculated frequencies. Fig. 4 illustrates the theoretical infrared spectrum of guanidinium cation.

### 3.3.1. $\text{NH}_2$ vibrations

The  $\text{NH}_2$  stretching vibrations of guanidinium cations are observed in spectra of guanidinium complexes at various wavenumbers. The  $\nu_{\text{as}} \text{NH}_2$  were observed at 3449 and  $3419 \text{ cm}^{-1}$  for guanidinium hydroselenate (GUSE) and at  $3462 \text{ cm}^{-1}$  for guanidinium hydrosulphate (GUS). This

band for guanidinium hydrogenarsenate monohydrate (GUAS) was observed at  $3449 \text{ cm}^{-1}$ . In all measured spectra these bands are strong (GUAS) or very strong (GUSE and GUS). These IR intensities are in good agreement with theoretical approximation. The theoretical Raman intensities are medium. The bands originating from  $\nu_{\text{s}} \text{NH}_2$  vibrations were found in measured spectra in the range of  $3348\text{--}3212 \text{ cm}^{-1}$ . The intensities of these bands are specified as very strong (GUSE and GUS) and strong (GUAS).

From theoretical approach the  $\nu_{\text{as}} \text{NH}_2$  bands are observed at  $3783$  (scaled  $3442$ )  $\text{cm}^{-1}$  and  $3778$  (scaled  $3438$ )  $\text{cm}^{-1}$ , whereas the  $\nu_{\text{s}} \text{NH}_2$  bands are noticed at  $3684$  (scaled  $3352$ ) and  $3663$

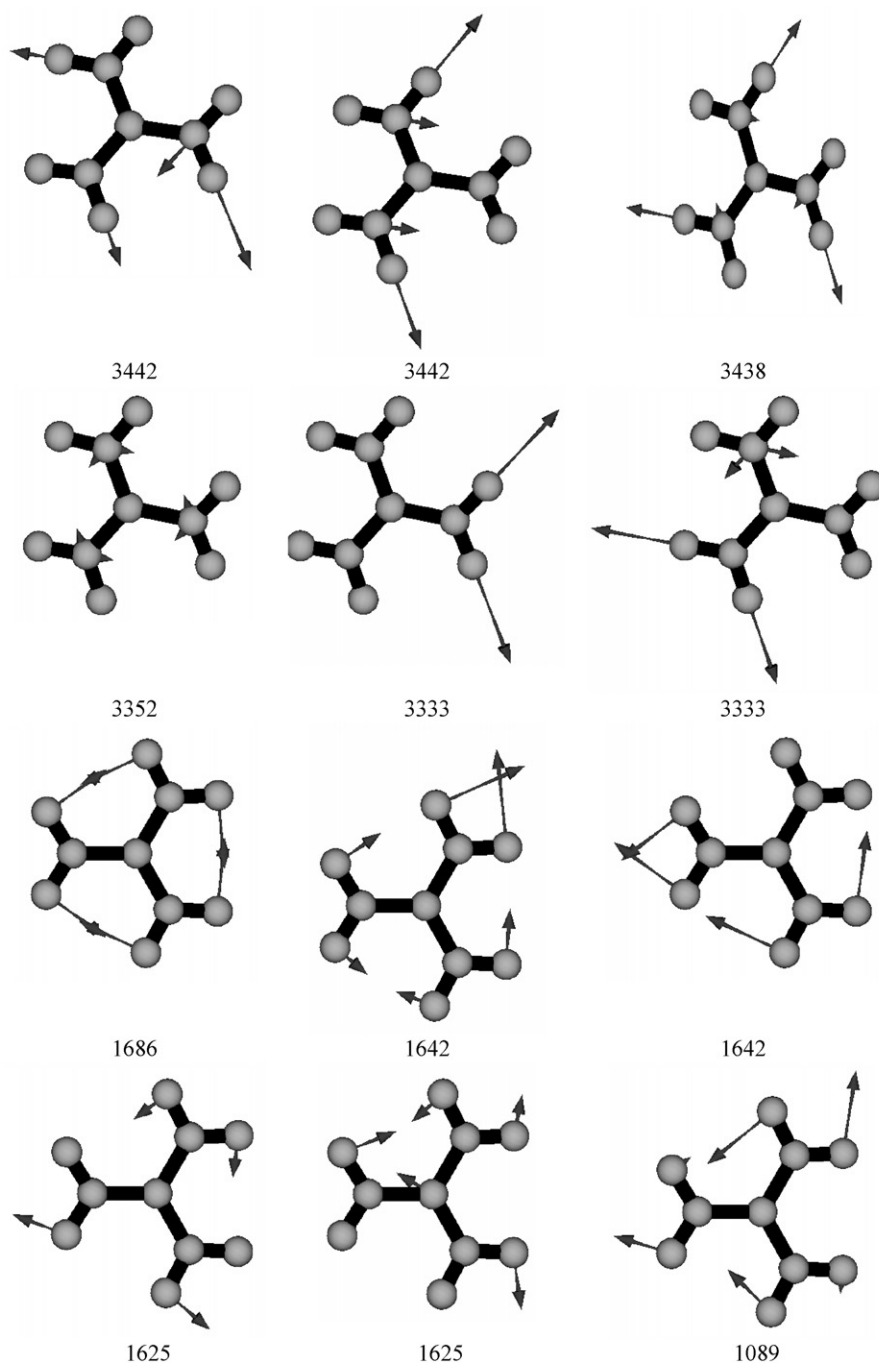


Fig. 3. The eigenvectors of displacement for calculated vibrations.

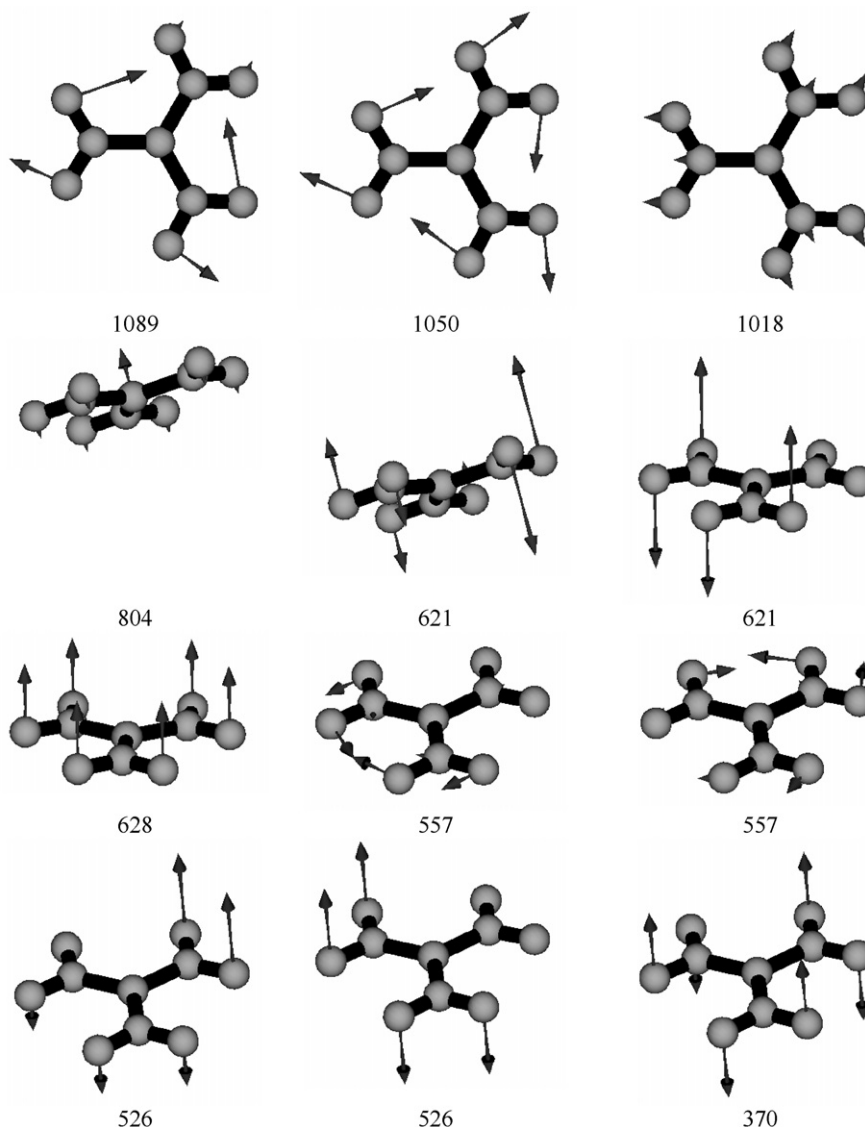


Fig. 3. (Continued).

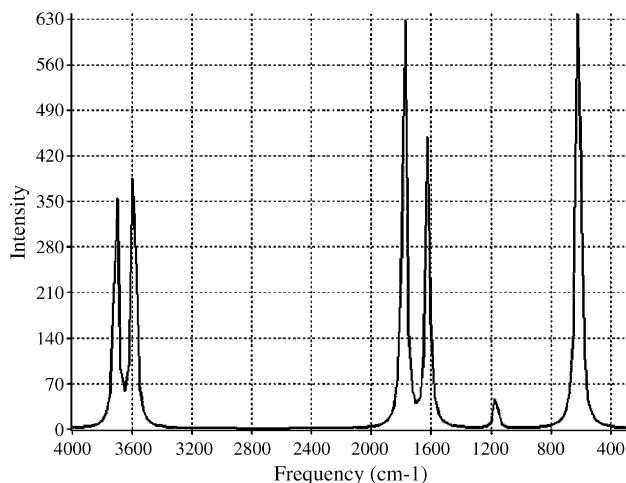


Fig. 4. Theoretical calculated infrared spectrum (without scaling) for guanidinium cation.

(scaled  $3333$ )  $\text{cm}^{-1}$ . The pronounced differences between theoretical calculations and experimental data results from the fact that our calculation was performed for isolated molecule in gas phase. In solid state the N–H bonds are involved in manifold of hydrogen bonds and van der Waals interactions between molecules in crystals. Unfortunately, the experimental infrared data for guanidinium ion in gas phase are inaccessible. In literature the experimental data for more or less similar compounds with  $\text{NH}_2$  chemical groups are described. The  $\text{NH}_2$  stretching frequencies of aniline and its cation are presented by Nakagana et al. [19] For neutral aniline these authors reported two absorption bands at  $3508$  and  $3422$   $\text{cm}^{-1}$  and assigned them to  $\nu_{\text{as}} \text{NH}_2$  and  $\nu_{\text{s}} \text{NH}_2$ , respectively. According to these data the N–H stretching vibrations should be shifted (redshift) by approximately  $20$ – $30$   $\text{cm}^{-1}$ .

Other frequencies for bands originating from N–H stretching vibrations were reported by Chakraborty and Manogaran [20]. In this paper the band assignment for the N–H stretching type of vibrations are included in the range of  $3265$ – $3109$   $\text{cm}^{-1}$ .



On the other hand with the used specific scaling factor (0.92) the frequencies are close to those originating from vibrational experiments. We believe that this specific scaling factor could be used as model for description of strength of hydrogen bonds in investigated crystals. The difference between theoretical and experimental frequencies may be expressed by special scaling factor. Similar value of this factor should inform about length and strength of hydrogen bonds formed directly by considered N–H chemical bonds. These observations require confirmation by other study.

The calculated PED has revealed that the NH<sub>2</sub> scissoring vibration of guanidinium cation contributes to two modes at 1686 and 1652 cm<sup>-1</sup>. In experimental spectra these bands are observed at lower frequencies in the range of 1566–1535 cm<sup>-1</sup>. In low temperature matrix experiment for chemical species with NH<sub>2</sub> group this band was observed at 1635 cm<sup>-1</sup> [21]. The intensity of band corresponding to symmetric deformation type of vibrations observed in our experimental data was medium. In theoretical calculation the intensity of band at 1686 cm<sup>-1</sup> was described as very weak in IR spectrum and medium in Raman. As very strong and weak was registered the band at 1625 cm<sup>-1</sup> in IR and Raman spectra, respectively. The distinct differences between experimental data and theoretical frequencies of bands connected with N–H chemical bonds may be additional evidence of involving of these bonds in N–H...O hydrogen bonds.

In our earlier experimental data the very weak bands at 1098, 1089 and 1065 cm<sup>-1</sup> were assigned to  $\rho$ NH<sub>2</sub>. Our theoretical calculation clearly indicates that those modes at 1089 and 1050 cm<sup>-1</sup> (weak in IR theoretical spectra) include considerable contribution from the NH<sub>2</sub> rocking vibrations, 54 and 57%, respectively. Furthermore, the calculated frequencies of these modes are in good agreement with the corresponding experimental values, when the special scaling factor (0.92) is used.

The NH<sub>2</sub> wagging types of vibrations in guanidinium cation are so strongly anharmonic that it is impossible to predict its frequencies within the frame of harmonic approximation. Such motion can be described by a symmetric double minimum potential, with the inversion barrier of approximately 500 cm<sup>-1</sup> [22,23]. In experimental spectra one weak band was observed at 606 cm<sup>-1</sup> in diguanidinium hydrogenarsenate monohydrate and the shoulder at 595 cm<sup>-1</sup> was recorded in guanidinium hydrogensulphate. The very strong band at 850 cm<sup>-1</sup> for guanidinium hydrogensulphate was assigned to NH<sub>2</sub> wagging vibrations, but this assignment is questionable.

The guanidinium cation is planar, therefore the frequencies of the NH<sub>2</sub> wagging type of vibration are noticed at higher wavenumbers [9]. Moreover, these frequencies are quite well predicted within the frame of harmonic approximation. These vibrations are assigned by Piest et al. [21] at 652 cm<sup>-1</sup>, and other authors assigned this mode at similar frequency, 656–658 cm<sup>-1</sup> [24]. Some authors suggest that frequency of band assigned to wagging type of vibration of NH<sub>2</sub> groups strongly depends on the method used in theoretical calculation [9]. According to this opinion the corresponding frequency is smaller (532 cm<sup>-1</sup>) when MP2 calculation method is used. Our calculated frequencies, 621 and 557 cm<sup>-1</sup> confirm their assignment. For these bands, similarly as other NH<sub>2</sub> vibrations 0.92 scaling factor

was used. It should be noticed that the band at 557 cm<sup>-1</sup> is the most intensive in whole infrared spectrum, whereas the band at 621 cm<sup>-1</sup> should be inactive in infrared and Raman spectra.

In experimental infrared spectra of guanidinium compounds the bands at 551 and 518 (GUS), 531 and 523 (GUSE) and at 548 and 534 cm<sup>-1</sup> (GUAS) were observed. The intensity of these bands is different: for GUS and GUSE crystals the intensities are strong, whereas for GUAS these bands were recorded as weak. These bands were not assigned on the basis of experimental spectra. According to theoretical calculations and PED analysis these bands are assigned to the twisting type of vibrations of NH<sub>2</sub> groups. The calculated frequency is 493 cm<sup>-1</sup> when 0.92 scaling factor was used or 526 cm<sup>-1</sup> for scaling factor equal to 0.983. These bands should not be active in infrared spectra.

Some problems were noticed for bands originating from torsional vibrations of NH<sub>2</sub> groups in guanidinium cation. Wojciechowski et al. [9] assigned to them two bands one at ca. 350 cm<sup>-1</sup> [21] and second at ca. 550 cm<sup>-1</sup>. Our theoretical study (our experimental IR spectra were measured in 4000–400 cm<sup>-1</sup> range) clearly indicates that band at 370 cm<sup>-1</sup> (scaled by 0.993) should be assigned to torsional vibration of NH<sub>2</sub> group.

### 3.3.2. C–N vibrations

The bands corresponding to C–N vibrations originate from symmetric and antisymmetric stretching and deformation vibrations of C–N bonds. In experimental infrared spectra of guanidinium hydrogensulphate the very strong bands at 1669 and 1643 cm<sup>-1</sup> were assigned to  $\nu_{as}$ CN. For guanidinium hydrogenselenate crystal the corresponding band was recorded at 1646 cm<sup>-1</sup>. One medium band at 1584 cm<sup>-1</sup> was assigned to  $\nu_{as}$ CN in diguanidinium hydrogenarsenate monohydrate. According to calculations the band at 1642 cm<sup>-1</sup> can be assigned to mode which represents complex vibration including the C–N stretching (36%) and in-plane NH bending components. The theoretical frequency of this mode agrees well with the experimental one. The intensity of the band corresponding to this antisymmetric stretching vibration should be strong in infrared and weak or very weak in Raman spectrum. The calculated activity is in good agreement with experimental data.

As revealed from the PED obtained for the guanidinium cation the symmetric stretching C–N vibration has the main contribution (73%) to the band at 1018 cm<sup>-1</sup>. According to theoretical results this band should be observed in Raman spectra, only. Its intensity should be medium. In experimental spectra this band is observed for all compounds. In IR spectra the intensity of this band is weak or very weak and its frequency is practically constant. In GUS this band is observed at 1006 cm<sup>-1</sup> whereas for GUSE at 1008 cm<sup>-1</sup> and for GUAS at 1010 cm<sup>-1</sup>. In Raman spectra this mode gives rise to the strongest band. It should be emphasized that our calculated frequency is in excellent agreement with experimental one. On the other hand the intensity of this band in theoretical calculations seems to be wrong. On the basis of these results the band is not active in infrared spectrum, but the intensity in Raman spectrum is described as medium only.

According to PED calculation the band at 804 cm<sup>-1</sup> should be assigned to wagging ( $\omega$ ) type of vibration of CN<sub>3</sub> group. This

band is not active in infrared spectra and in fact was not observed in experiment. Angell et al. [25] assigned band recorded at  $722\text{ cm}^{-1}$  to out-of-plane  $\text{CN}_3$  angle deformations (in IR spectra of guanidinium iodide and at  $724\text{ cm}^{-1}$  in infrared spectra of chloride analogue). These bands are not active in Raman spectra. It seems that the apparent disagreement between theoretical and experimental data suggest that the  $\text{CN}_3$  group is involved in interactions of hydrogen bond type. Very similar frequencies of  $\omega_{\text{CN}_3}$  were noticed for other compounds with C–N groups ( $755\text{ cm}^{-1}$  in experimental infrared spectrum of neutral aniline compound [9]), but in this case the theoretical frequency ( $752\text{ cm}^{-1}$ ) is very close to the experimental value.

In experimental spectra of guanidinium hydrogensulphate and hydrogenselenate analogue the bands at  $579\text{ cm}^{-1}$  (GUS) and  $573\text{ cm}^{-1}$  (GUSE) were recorded and assigned to in-plane  $\text{CN}_3$  angle deformation vibrations. Other bands were noticed at  $551\text{ cm}^{-1}$  (shoulder) and  $531\text{ cm}^{-1}$  for GUS and GUSE compounds, respectively. In experimental spectra of GUAS the weak bands are present at  $548$  and  $534\text{ cm}^{-1}$ . According to theoretical calculations the band at  $563\text{ cm}^{-1}$  was assigned to symmetric in-plane  $\text{CN}_3$  angle deformation vibrations. The PED analysis is in this case unambiguous, but on the basis of numerical calculations this band should not be active in vibrational spectra. This theoretical intensity calculation seems to be wrong. This band was observed by Angell et al. [25] in infrared and Raman spectra of guanidinium iodide ( $514\text{ cm}^{-1}$ ) and guanidinium chloride ( $525\text{ cm}^{-1}$ , IR;  $526\text{ cm}^{-1}$ , Raman). The agreement between experimental and theoretical results seems to be good taking into account the experimental conditions (vibrational spectra measured for solid state samples).

#### 4. Conclusions

The theoretical quantum approach and detailed vibrational study were performed for the guanidinium cation with the unrestricted B3LYP method. A planar structure of this molecule was affirmed. The planarity of the  $\text{CN}_3$  skeleton corresponds to  $\text{sp}^2$  hybridization of the carbon atom. The C–N bonds acquire partially double bond character of some delocalization of the lone pair electrons of the nitrogen atoms with the vacant p orbital of the carbon atom. This type of interaction would occur most efficiently if the nitrogen atoms exhibit  $\text{sp}^2$  hybridization, each C– $\text{NH}_2$  group then being planar and having a p-type lone pair which could be oriented parallel to the vacant orbital of the carbon atom. In such a case the guanidinium cation should have planar  $D_{3h}$  symmetry.

Good agreement has been obtained between the experimental and theoretical frequencies of guanidinium compounds, but for vibrations involved in hydrogen bond network the special scaling factor was applied. For the other vibrations the “standard” scaling factor can be used. It suggests that vibrations of investigated molecule belong to two groups: one is independent on chemical neighboring and second type of vibrations is sensitive to interactions with the environment. It seems to be clear that the difference between the scaling factors used by us and those reported in literature can be used as a measure of strength of hydrogen bonds in this and other similar chemical systems. On

the other hand, the comparison of experimental and theoretical spectra seems to be justified.

The clear-cut assignment of all bands in the spectra of guanidinium cation has been made on the basis of the calculated potential energy distribution for this molecule. Several discrepancies in the previous experimental vibrational assignment have been clarified. Some problems and differences were noticed during comparison of experimental and calculated intensities. Additionally, it should be noticed that the theoretical data are different than described in [26].

I hope that results presented in this work will be fruitful in further vibrational studies of the hydrogen bonded complexes of guanidinium cations and in design of new compounds with expected chemical and physical properties.

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