Density-Functional Methods for the Study of the Ground-State Vibrations of the Guanidinium Ion

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ABSTRACT

Sixteen density functional methods (including four hybrid methods) with the 3-21G and the 6-31G(d, p) basis set of atomic functions are used to predict the structure and vibrations of the guanidinium ion $C(NH_2)_3$. The study was done with the ion both in a vacuum and in an aqueous solution. To account for the solvation effect on the vibrating behavior of the ion, the solvent was modeled in two ways of increasing complexity: First, the guanidinium was inserted into a cavity of a continuous medium (dielectric constant ε 78) and, second, six explicit water molecules were considered around the ion and the whole aggregate inserted into the cavity of the continuum. The conformation corresponding to the energy minimum is predicted to have D_3 symmetry rather than D_{3h}. The harmonic vibrational frequencies obtained have a mean absolute deviation from the experimental data of about one-half the value achieved by pure Hartree–Fock methods. Isotopic substitution calculations were also carried out and shifts obtained are in good agreement with experience and so are the assignments of the observed bands to the vibrational normal modes. The study of the solvent effect shows the existence of modes that are not affected by hydration and some improvement in the values predicted, especially for low-frequency vibrations.

Introduction

The guanidinium ion, $C(NH_2)_3$, has been the subject of a wide variety of theoretical and experimental studies 1–9 . The importance of guanidine and its derivatives comes from its presence as a substructure in many compounds with relevant biochemical activity, as, e.g., the creatine, the pyrimidine bases of DNA, and the terminal side chain of the amino acid arginine, whose functions are strictly related with the physicochemical properties of that chemical species. In the field of

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protein chemistry, the importance of the guanidinium ion is noteworthy. The salt bridges established are essential for the characterization of the structure and function of the proteins. About 40% of such pairs of ionic groups within proteins involve guanidinium–carboxylate salt bridges and are now quite well documented [10, 11]. From a purely theoretical point of view, the guanidinium ion has attracted the attention of chemists, due to its peculiar properties. In fact, this is a carbocation with an unusual stability which makes guanidine one of the strongest organic basis (pK_a 13.6). This stability has been attributed to the π-electron delocalization in the planar cation [1]; however, in more recent studies, it was concluded that the high basicity of the guanidine is not caused by the resonance stabilization of the guanidinium, but, rather, by strong hydrogen bond interactions of the ion with the molecules of the solvent [8, 12]. The solvation of the guanidinium and the possibility of the formation of the ion pair in solution have been the subject of previous theoretical studies, as a model for the pairing of two arginines, usually found at the surface of proteins [13, 14]. This unusual type of contact between like-charged species seems to play an important role in the recognition and guidance in protein reactivity [15, 16].

The guanidinium ion is, therefore, widely used as a simple model for compounds with biological activity, and a good characterization of its physicochemical properties must be achieved to validate that approximation; besides, the comparison of the calculated parameters with experimental data constitutes a very good test of the theoretical formalism employed.

In the Hartree–Fock (HF) theory, the energy of a closed-shell system with n orbitals is given by

$$E \quad V \quad 2\sum_{i}^{n}\langle i\,\hat{h}^{N}\,i\rangle \quad 2\sum_{i,j}^{n}J_{ij} \quad \sum_{i,j}^{n}K_{ij}, \quad (1)$$

where V is the nuclear repulsion energy, the second term gives the one-electron energy (kinetic and potential), the third represents the Coulomb repulsion of the electrons, and the last term is the exchange energy which has no classical meaning but results from the quantum nature of the electrons as fermion particles. In this theory, the movement of the electrons is not correlated, which may explain the lack of success in some calculated molecular properties [17]. An alternative strategy is that provided by density functional (DF) theory where the Kohn–Sham equations [18] are solved. The resulting energy expression is

$$E \quad V \quad 2\sum_{i}^{n}\langle i\,\hat{h}^{N}\,i\rangle \quad 2\sum_{i,j}^{n}J_{ij} \quad E_X \quad E_C, \quad (2)$$

where E_X and E_C are the exchange and correlation energies, respectively, which are functionals of the electronic density, ρ, and eventually of the gradient of the density, $\nabla\rho$:

$$E_{X\ C} \quad \int f_{X\ C}(\rho, \nabla\rho)\, d\tau. \quad (3)$$

The DF methods [19, 20] differ from each other in the functional used for each energy term (exchange and correlation) and in the possible combinations of both. The growing popularity of these methods as a tool for calculating molecular properties is due to their inclusion of some electronic correlation effects with a low computational effort. As a consequence, application of DF methods to relatively large molecular systems and comparative studies with standard HF methods have been growing in the literature [21–31]. Andzelm and Wimmer [25], e.g., calculated equilibrium geometries, vibrational frequencies, bond dissociation energies, and dipole moments for a set of typical organic and for small inorganic molecules. They found good agreement between their results and those obtained by standard HF and MP2 methods [32]. Johnson et al. [26] reported a comparative study of six different DF methods, calculating some physicochemical properties for a set of 32 small neutral molecules. They used the 6-31G(d) basis set of atomic functions and, for comparison, they carried out calculations also by other standard HF methods. They concluded that, with the basis set employed, the calculated equilibrium geometries and dipole moments compare with experimental data as well as those obtained by more expensive conventional ab initio methods. The vibrational frequencies compared favorably with the ab initio results, whereas for atomization energies, there are even two DF methods which give much better agreement with experimental data. Application of DF methods to open-shell systems [27] has also revealed better performance of these methods, when compared with HF and MP2, to predict some properties of diatomic molecules. More recently, Qin and Wheelar [31] calculated the structure, electronic spin density ratios, harmonic vibrational frequencies, and deuterium isotopic vi-

brational frequency shifts for the phenoxyl radical, using unrestricted HF, MP2, and a variety of DF and hybrid HF DF methods. They concluded that for this open-shell system DF methods show, again, good agreement with experimental data and with more expensive methods.

Nowadays, the DF methods are more and more employed and useful for the study of molecular systems but the choice of functionals is not simple because rules are not established. The choice of adequate functionals for a good description of this particular chemical species is needed to be able to study larger molecular systems with biological interest where the guanidinium ion is present. In this article, an evaluation is made of different DF methods for the calculation of the conformation and properties of the guanidinium ion. A comparison with standard HF and MP2 results, on the one hand, and with experimental data, on the other, is presented.

Methods

All quantum mechanical calculations were carried out by using the Gaussian92 DFT 33 package of programs. The basis set of atomic functions employed throughout this work is the 3-21G. This choice is based on previous calculations of vibrational frequencies in a set of molecules made by Pople et al. 34 at the Hartree–Fock level. In that work, it is concluded that expansion of the basis set to the 6-31G(d) would not show an improvement in the calculated vibrational frequencies, when compared with experimental data. To justify the use of the smaller 3-21G basis set at the DF level, geometries and harmonic frequencies of the guanidinium ion were also calculated using the expanded basis set 6-31G(d, p), which includes p polarization functions in the hydrogen atoms and d functions in all the other atoms. The results show the same behavior for the calculated properties of the ion, thus justifying the use of the smaller basis set. As referred above, the DF methods differ in the functionals used for both the exchange and correlation terms of Eq. (2) and possible combinations of them. The exchange functionals used in this study include Slater's local density approximation 35 (abbreviated S) with an exchange scale factor of 2 3; the X_α functional, which is an older simplified version developed by Slater 35, 36 with a different value for the exchange scale factor (abbreviated XA) and, at last, the Becke's functional 37 which includes a gradient correction (abbreviated B). The correlation functionals considered here are the local spin density form of Vosko, Wilk, and Nusair (VWN) 38 ; the gradient-corrected functional of Lee, Yang, and Parr (LYP) 39 ; the local (nongradient-corrected) functional of Perdew (PL) 40 , and Perdew's 1986 functional (P86) with gradient corrections 41 . These functionals were combined to give 12 different methods: S-null, B-null, and XA-null, respectively, the Slater, Becke, and X_α exchange functionals without correlation contribution, and the B-LYP, B-P86, B-PL, B-VWN, S-LYP, S-P86, S-PL, S-VWN, and XA-LYP methods, which are combinations of the exchange and correlation functionals mentioned above. In addition, four hybrid methods, which use a mixture of Hartree–Fock exchange with DF exchange–correlation functionals, were also tested. The present work shows the results obtained with the first hybrid method proposed by Becke 42 with equal contributions of the HF exchange and the Slater exchange functional without correlation (BHandH); the same as the precedent but with the LYP 39 correlation added (BHandHLYP); Becke's three parameter exchange–correlation functional with Perdew's gradient correction for correlation (B3P86) 43 ; and Becke's three-parameter exchange–correlation functional with the LYP correlation included (B3LYP) 39, 43 .

To improve the calculated frequencies corresponding to Raman active vibration modes, when compared to resonance Raman spectra of aqueous solutions of guanidinium salts, an attempt to model the solvent was made in two steps: First, the ion was inserted into a cavity of a continuous medium, with the dielectric constant ε 78, and an Onsager type of self-consistent reaction field model (SCRF) 44 was applied. There are also other methods that include solvent effects through an SCRF technique 45 and, recently, a combination with DF methods was successful in studying reactions with small molecules 46 . However, the objective was to study the solvent effect in a semiquantitative way and the Onsager-type model seems appropriate to include the electrostatic long-range interactions of the ion with the bulk. In the second step, to account for the local effect of the solvent, six explicit water molecules were considered around the guanidinium ion. Initially, the water molecules were located around the plane of the ion with their oxygen atoms pointing toward the hydrogen atoms; then, a total relaxation of the aggregate, with the SCRF treatment, was carried

out using the 3-21G basis set of atomic functions with the density functional B-PL method.

Results and Discussion

STRUCTURE

Table I presents some geometrical parameters for the guanidinium ion obtained with several DF methods using both the 3-21G and 6-31G(d, p) basis set and, for comparison, some HF and experimental results [47, 48]. In general, the bond lengths and bond angles predicted by DF methods compare well with the range of values obtained by experiment. The B-null method shows the highest prediction for the C—N bond length, but still inside the experimental range. For the N–H bond, some comparison with experiment is possible due

TABLE I
Optimized geometrical parameters for the guanidinium ion, obtained with several DF and HF methods.[a]

Method	Geometrical parameter					
	rCN	rNH	∠(C — N — H)	∠(N — C — N)	∠(C — N — H — H)	∠(H — N — C — N)
DF / B-null (3-21G)	1.371	1.033	121.3	120.0	180.1	163.4
[6-31G(d, p)]	1.365	1.026	121.2	120.0	180.1	163.7
DF / B-LYP (3-21G)	1.352	1.023	121.3	120.0	180.2	163.9
[6-31G(d, p)]	1.348	1.017	121.3	120.0	180.1	163.7
DF / B-P86 (3-21G)	1.350	1.023	121.3	120.0	180.3	163.7
[6-31G(d, p)]	1.345	1.017	121.3	120.0	180.1	163.6
DF / B-PL (3-21G)	1.355	1.019	121.3	120.0	180.0	163.9
[6-31G(d, p)]	1.350	1.013	121.4	120.0	180.1	163.9
DF / B-VWN (3-21G)	1.352	1.017	121.4	120.0	180.0	164.3
[6-31G(d, p)]	1.347	1.011	121.4	120.0	180.1	164.0
DF / S-null (3-21G)	1.351	1.040	121.2	120.0	179.9	159.9
[6-31G(d, p)]	1.347	1.034	121.2	120.0	180.1	162.6
DF / S-LYP (3-21G)	1.334	1.030	121.2	120.0	180.0	161.3
[6-31G(d, p)]	1.331	1.025	121.1	120.0	180.4	162.5
DF / S-P86 (3-21G)	1.332	1.031	121.3	120.0	179.9	160.7
[6-31G(d, p)]	1.328	1.025	121.0	120.0	178.8	160.3
DF / S-PL (3-21G)	1.336	1.026	121.4	120.0	180.0	162.6
[6-31G(d, p)]	1.332	1.020	121.2	120.0	180.1	163.1
DF / S-VWN (3-21G)	1.334	1.024	121.4	120.0	179.9	162.6
[6-31G(d, p)]	1.330	1.018	121.2	120.0	180.1	163.2
DF / XA-null (3-21G)	1.336	1.027	121.4	120.0	179.7	162.1
[6-31G(d, p)]	1.333	1.021	121.2	120.0	180.0	162.9
DF / XA-LYP (3-21G)	1.319	1.019	121.4	120.0	179.7	162.1
[6-31G(d, p)]	1.317	1.013	121.1	120.0	180.1	162.9
DF / BHandH (3-21G)	1.320	1.010	121.6	120.0	180.1	169.8
[6-31G(d, p)]	1.317	1.005	121.3	120.0	181.1	168.6
DF / BHandHLYP (3-21G)	1.328	1.006	121.6	120.0	180.0	170.4
[6-31G(d, p)]	1.324	1.001	121.3	120.0	180.6	169.6
DF / B3LYP (3-21G)	1.30	1.015	121.4	120.0	179.1	166.9
[6-31G(d, p)]	1.336	1.010	121.3	120.0	178.9	165.5
DF / B3P86 (3-21G)	1.336	1.014	121.5	120.0	180.0	166.6
[6-31G(d, p)]	1.332	1.008	121.3	120.0	180.1	164.8
HF / 3-21G	1.324	1.000	121.8	120.0	180.0	180.0
HF / 6-31G(d, p)	1.321	0.995	121.4	120.0	180.0	180.0
MP2 / 6-31G(d)[8]	1.334	—	—	120.0	180.0	165.1
Expt.[47, 48]	1.32 to 1.37	1.00 to 1.02	118.2 to 123.3	120.0	180.0	180.0

[a] Distances in angstroms and angles in degrees; refer to Figure 1.

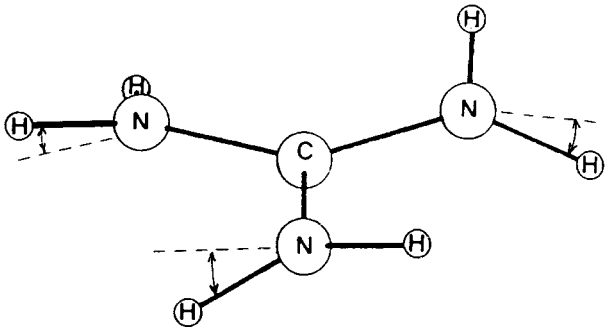

FIGURE 1. Structure of the guanidinium ion $[C(NH_2)_3)]^+$ (refer to Table I).

to neutron diffraction techniques which is the case, e.g., for the determination of the structure of L-arginine dihydrate crystals by Lehmann et al. 48 . In this case, the agreement with experiment is still excellent, with the N—H bond length slightly overestimated, around 0.01 Å, when correlational functions are not included or with the methods using the Slater (S) exchange functional. Concerning the bond angle C—N—H, all the results fitted well within the range of experimental values and the N—C—N angle was predicted to be 120° by all the methods. In general, the use of the expanded basis set 6-31G(d, p) did not bring any significant change to these results. The C—N and the N—H bond lengths were systematically reduced by 0.004 and 0.006 Å, respectively. The C—N—H bond angle suffered only slight reductions (around 0.2°) and the angle of torsion H—N—C—N, which reflects the rotation of the NH_2 group, exhibited variations up to 2.7°. It has always been assumed by theoreticians and experimentalists that the guanidinium group was planar. A good justification was the stabilization gain by delocalization of the charge which is favored by that particular geometry. In fact, this is predicted at the HF 6-31G(d, p) level, but, as stressed by Gobbi and Frenking 8 , the inclusion of corrections to the electronic correlation, as, e.g., with MP2 6-31G(d) methods, leads to a minimum in the potential energy hypersurface with D_3 symmetry rather than D_{3h}. The planar constraint used with DF methods leads to one imaginary frequency; however, total relaxation of the ion structure results in the distorted geometry with D_3 symmetry, whose parameters are shown in Table I. In all the optimized geometries, the nonhydrogen atoms remain in the same plane; the still planar NH_2 groups (note that the angle of torsion (C—N—H—H is always around 180°) are rotated around the C—N bonds from 10° to 20°, as one can see from the values of the dihedral angle H—H—C—N. It is important to stress that all the DF methods employed in this study are able to reproduce the D_3 symmetry of the energy-minimum geometry for the guanidinium ion, as it may also be obtained by HF methods incorporating some electronic correlation such as Møller–Plesset perturbation theory at second (MP2), third (MP3), and fourth order (MP4) 8, 32 .

FREQUENCIES

The harmonic vibrational frequencies calculated at the Hartree–Fock level is well known to be systematically overestimated by about 12% when compared to the experimental fundamental frequencies 34 . Nevertheless, the application of an empirical correction factor must be done with care because neither all the normal modes may follow that statistic nor it will be true for all the molecular systems. For the special case of the guanidinium ion, it is clear from Figure 2 that there is a random dispersion of the calculated values, especially for the low vibrational frequencies, when compared with experimental values 49 . For example, the experimental 820 cm ^{1} frequency is even underestimated. Figure 2 does also show how useless it is to increase the basis set. The mean absolute error (MAE) for the set of calculated harmonic frequen-

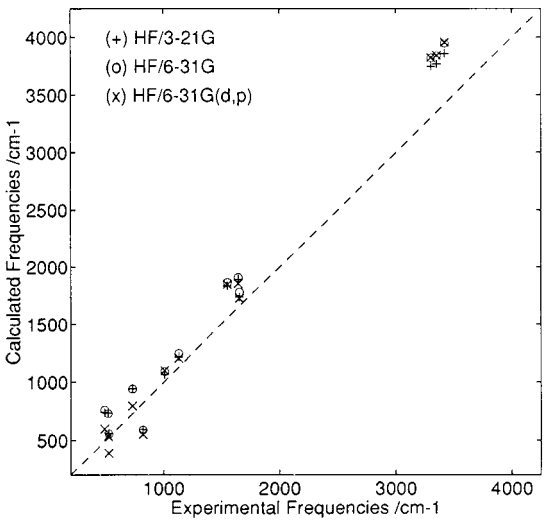

FIGURE 2. Plot of the experimental observed frequencies vs. calculated by the HF method with the 3-21G, 6-31G, and 6-31G(d, p) basis set of atomic functions.

cies was 19, 20, and 15%, respectively, for the 3-21G, 6-31G, and 6-31G(d, p) basis set. The small improvement of 4% in the results when the basis set is expanded from 3-21G to 6-31G(d, p) does not justify the increased amount of computational work. Besides that, the more favorable statistics for that basis set is due only to three particular low-frequency vibrations, namely, the 533.5 cm ^{1} (error 3%), 795.8 cm ^{1} (error 9%), and 596.7 cm ^{1} (error 22%), which are predicted using the smallest basis set with values 733.8 cm ^{1} (error 41%), 943.7 cm ^{1} (error 29%), and 739.6 cm ^{1} (error 51%), respectively. On the other hand, the 526 and 820 cm ^{1} experimental frequencies, which are attributed to the CN_3 angle deflection (E) and NH_2 twist (E) modes, respectively, are better predicted by the smaller basis set 556 cm ^{1} (E); error 5.7% and 592 cm ^{1} (A_2); error 27.7%) than by the 6-31G(d, p) (388.7 cm ^{1}; error 26.1% and 551.0 cm ^{1}; error 32.8%). Concerning the higher-frequency vibrations, the 3-21G basis set shows a slightly better performance than that of the bigger expanded basis set.

The extrapolation of the above conclusions to the DF methods must be done with care because the dependence of the calculated vibrational frequencies on the basis set employed can be different. Recently, Rauhut and Pulay applied a set of 11 scaling factors to DF force fields and calculated with success the vibrational frequencies of 31 simple organic molecules [50]. For the particular case of the guanidinium ion, the uncorrected vibrational frequencies obtained with the 3-21G basis set and the corresponding isotopic shifts for the deuterated species $C(ND_2)_3$ are shown in Table II. Table III presents, for the same vibration modes of the guanidinium ion, the frequencies obtained with the 6-31G(d, p) basis set. A comparison plot of these two groups of results with experimental data is presented in Figure 3, where the worst predictions of the hybrid methods are excluded for simplicity. This last plot shows that the quality of the results is not significantly improved when the expanded basis set is employed. For the three highest frequencies, the deviation from experimental data is even bigger, on the other hand, the two lowest frequencies show a decreasing of the associated error but, now, the values are underestimated. Therefore, further calculations throughout this work were done with the 3-21G basis set as a compromise between accuracy and time of computational work. All the frequencies are assigned to normal modes belonging to irreducible representations of the molecular symmetry point group D_3. The molecular system will have, therefore, eight normal modes of symmetry E (Raman and IR allowed), four with symmetry A_1 (Raman allowed), and another group of four A_2 (IR allowed). Comparison with experimental data is also possible, based on the values compiled by Sension et al. [49]. Values corresponding to the NH_2 asym. str. (A_2), NH_2 rock (A_2), and NH_2 twist (A_1) modes are not compared with experience once they belong to the A_2, A_2, and A_1 representations of the D_{3h} point group, respectively, which are inactives assuming that molecular symmetry. However, within the D_3 symmetry, these normal modes are predicted to yield experimental bands around 3560 cm ^{1} (IR), 1070 cm ^{1} (IR), and 325 cm ^{1} (Raman), respectively. The first two bands are predicted with low intensity and, perhaps, are superimposed with those arising from the corresponding E normal modes, namely, NH_2 asym. str. (E) and NH_2 rock (E), for which the calculated values of frequencies are always similar within a same method; the latter band appears in a very low frequency region and is predicted also with low intensity.

Figure 4 presents a comparison plot of the calculated frequencies with the available experimental data. It is clearly shown that the DF methods do give results in much better agreement with experimental data than do those obtained with the HF 3-21G method. The MAE goes now from 8.1 to 9.7% (exception for the value 11.2% of the XA-LYP method), about one-half the values obtained with the HF methods. On the other hand, the results obtained with the four hybrid methods are not included in Figure 4 because they gave the worst results, yet with lower MAE than HF methods: 14.9, 14.4, 11.6 and 10.7% for BHandH, BHandHLYP, B3P86, and B3LYP, respectively. However, those using the Becke's three-parameter exchange–correlation functional, and especially the B3LYP method, have shown a performance comparable with the pure DF methods.

The statistics presented for the DF methods are not uniformly distributed along the spectra; below 700 cm ^{1}, the vibrational frequencies are predicted with higher relative errors (between 8 and 30%), in clear contrast with the higher frequencies which present errors between 0 and 9%. In spite of that, the low-frequency band at 526 cm ^{1}, associated to the CN_3 angle deflection (E), is predicted with reasonably small errors for all the DF methods (around 9%). Noteworthy is the exceptional results given by the hybrid methods for this particular

vibration; those two using Becke's three-parameter exchange–correlation functional present an error of 5%, and those two using the older Becke's BHandH scheme show errors of 1 and 2%, respectively, with and without LYP correlation added.

The analysis of the vibrational frequencies and associated errors must be done with care to avoid erroneous conclusions. For example, the 490 and 820 cm ^{1} bands of the guanidinium spectra have been assigned to the NH_2 wag (out-of-plane) (E'' D_{3h}) and NH_2 twist (E'' D_{3h}) modes, respectively 49, 51 . However, if these two bands are reversely assigned, a slightly better agreement with experimental data will be achieved with the present results, as shown in Figure 5. Despite the smaller errors obtained, the analysis of the isotopic shifts will not support this supposition, as referred to below.

Although all the DF methods have shown, in general, a very good performance in predicting the vibrational frequencies of the guanidinium ion, the excellent results obtained with the B-null and S-null methods for the three highest frequencies is noteworthy. Figure 4 shows that, for the three highest-frequency vibrations, those good results are clearly distinct from a group of overestimated predictions for all the other DF methods. These excellent results are due, maybe, to error cancellation because harmonic frequencies are compared directly with experimental frequencies, which are anharmonic. In fact, as already stressed by Rauhut and Pulay 50 , the overestimation of the bond lengths, which leads to a decrease of force constants, cancels the general overestimation in frequencies. The effect is especially important for those vibrations for which anharmonicity is large, as is the case of the NH_2 stretching modes. Among all the DF methods, B-null and S-null are those which present larger overestimations for the N—H bond length of the guanidinium ion (see Table I). For the frequencies between 700 and 2000 cm ^{1}, all the methods are consistently good, with the exception of the NH_2 twist (E) mode; the hybrid methods show, in this range of frequencies, a performance similar to all the other pure DF methods, with a clear advantage for those using Becke's three-parameter exchange–correlation functional. Concerning the low-frequency vibrations, the fitting with experimental data is not so successful; the percentage errors show now values in the range 29–33%, 16–28%, and 8–12% for, respectively, the NH_2 twist (E), the NH_2 wag (A_2), and the NH_2 twist (A_1) modes.

Isotopic substitution constitutes a very useful tool for the correct assignment of a vibrational spectra of a compound. In this work, isotopic frequency calculations were carried out with the substitution of all the six hydrogens by deuterium atoms. The results have shown, again, a general agreement with experimentally observed values. All modes shift to lower frequency upon total deuteration of the guanidinium ion; Table II presents, for all the DF methods considered, the corresponding isotopic shifts in parentheses. This overall tendency was expected because isotopic substituion changes the masses of the vibrating atoms but the force constants remain approximately the same. However, the magnitude of the frequency shifts differ for each mode; the vibrations involving a large amount of hydrogen motion are supposed to suffer a greater shift than those of essentially C and N motions. For example, the highest frequencies, corresponding to NH_2 stretching-type modes, are predicted to be greatly influenced by isotopic substitution. On the other hand, frequencies corresponding to CN_3 angle deflection and CN_3 stretching modes are almost insensitive to H D isotopic changes. These results, in general, are in good agreement with experimental observed shifts. Surprisingly, the consistency of the results for the NH_2 twist (E) mode (293 9 cm ^{1}, against the experimental value 197 cm ^{1}) shows that the change in assignment for the two bands 820 and 490 cm ^{1}, proposed above, was not correct, although providing smaller errors for the predicted frequencies (see Fig. 5).

SOLVATION

The influence of the solvent on the vibrational frequencies of the guanidinium was studied in two steps: First, the ion was placed in a spherical cavity made in a continuous medium with dielectric constant ε 78. This should account for the long-range electrostatic interactions of the ion with the bulk. Results are shown in Table IV for those frequencies for which comparison with Raman spectroscopy data from aqueous solution of guanidinium salts is possible 49, 52 . The ion did not show any structural change when it was inserted in the cavity but vibrations felt the perturbation to some extent. In general, the vibrational frequencies shifted toward lower values, but the different modes were not affected in the same manner. Comparison with the gas-phase values shows that the totally symmetric NH_2 scissors and CN_3

TABLE II

Theoretical (3-21G basis set) and experimental vibration frequencies (cm ^{1}) for the $C(NH_2)_3^+$ and isotopic shifts for the deuterated species $C(ND_2)_3^+$.

	Vibrations: description, symmetry, frequencies (isotopic shifts)															
Method	NH_2 twist (A_1)	CN_3 angle def (E)	NH_2 twist (E)	NH_2 wag (E)	NH_2 wag (A_2)	CN_3 angle def (A_2)	CN_3 sym str (A_1)	NH_2 rock (A_2)	NH_2 rock (E)	CN_3 deg str (E)	NH_2 deg scissors (E)	NH_2 scissors (A_1)	NH_2 sym str (E)	sym NH_2 str (A_1)	NH_2 asym str (E)	NH_2 asym str (A_2)
B-null	321	466	536	542	604	668	919	1054	1079	1522	1637	1675	3333	3349	3440	3436
	(91)	(52)	(176)	(106)	(150)	(38)	(75)	(214)	(201)	(31)	(442)	(413)	(926)	(926)	(891)	(893)
B-LYP	314	473	552	582	628	712	964	1064	1103	1582	1660	1697	3423	3440	3530	3527
	(86)	(45)	(186)	(117)	(151)	(53)	(84)	(207)	(206)	(22)	(50)	(412)	(950)	(950)	(915)	(917)
B-P86	322	473	555	601	637	726	974	1063	1107	1596	1661	1694	3445	3462	3555	3552
	(90)	(43)	(190)	(123)	(150)	(64)	(87)	(203)	(208)	(17)	(454)	(410)	(957)	(956)	(922)	(924)
B-PL	334	481	562	593	638	716	956	1078	1111	1576	1679	1718	3455	3472	3564	3559
	(114)	(51)	(195)	(131)	(161)	(52)	(80)	(218)	(209)	(29)	(455)	(422)	(959)	(959)	(924)	(925)
B-VWN	318	483	558	592	637	723	962	1082	1115	1585	1686	1724	3474	3491	3583	3578
	(92)	(51)	(186)	(122)	(154)	(52)	(81)	(217)	(209)	(28)	(456)	(422)	(965)	(964)	(928)	(929)
S-null	394	461	551	619	624	718	973	1041	1078	1624	1559	1625	3312	3330	3420	3417
	(118)	(35)	(194)	(130)	(141)	(83)	(95)	(186)	(204)	(48)	(399)	(382)	(917)	(918)	(886)	(888)
S-LYP	380	469	564	655	641	763	1015	1052	1098	1684	1585	1647	3396	3415	3504	3501
	(111)	(36)	(201)	(139)	(141)	(101)	(106)	(180)	(207)	(39)	(411)	(378)	(940)	(940)	(908)	(911)
S-P86	394	466	568	673	645	771	1023	1047	1097	1699	1580	1642	3413	3432	3524	3521
	(115)	(28)	(208)	(144)	(136)	(115)	(108)	(173)	(208)	(36)	(412)	(375)	(944)	(944)	(913)	(915)
S-PL	341	472	560	648	643	768	1008	1056	1105	1677	1603	1669	3432	3451	3540	3537
	(98)	(37)	(196)	(135)	(142)	(94)	(100)	(184)	(208)	(44)	(413)	(390)	(951)	(951)	(917)	(920)
S-VWN	345	476	564	657	648	776	1014	1062	1110	1687	1610	1676	3450	3469	3558	3555
	(101)	(39)	(199)	(139)	(144)	(47)	(101)	(186)	(209)	(45)	(416)	(392)	(956)	(956)	(922)	(925)
XA-null	359	475	563	648	644	763	1004	1060	1105	1672	1600	1666	3407	3426	3516	3512
	(105)	(39)	(198)	(136)	(143)	(92)	(99)	(188)	(109)	(46)	(412)	(390)	(943)	(943)	(912)	(913)
XA-LYP	378	483	581	692	662	804	1045	1071	1123	1732	1622	1686	3488	3508	3597	3593
	(112)	(38)	(207)	(148)	(142)	(114)	(110)	(178)	(212)	(38)	(421)	(385)	(965)	(965)	(932)	(934)
BHandH	217	516	581	716	699	887	1068	1109	1177	1770	1705	1789	3619	3641	3729	3723
	(61)	(62)	(187)	(149)	(149)	(107)	(103)	(207)	(220)	(58)	(435)	(422)	(1002)	(1001)	(965)	(968)
BHandH	225	522	582	696	689	864	1045	1123	1180	1697	1771	1815	3640	3661	3749	3743
LYP	(67)	(67)	(182)	(148)	(144)	(79)	(93)	(229)	(219)	(25)	(481)	(438)	(1009)	(1008)	(969)	(972)
B3LYPa	269	497	568	636	664	787	1003	1092	1139	1637	1711	1750	3527	3546	3635	3631
	(79)	(56)	(187)	(132)	(152)	(69)	(89)	(219)	(213)	(22)	(466)	(423)	(980)	(980)	(943)	(946)
B3P86	281	497	570	658	673	803	1014	1093	1145	1652	1717	1751	3555	3574	3666	3661
	(83)	(53)	(189)	(139)	(150)	(82)	(91)	(213)	(216)	(15)	(472)	(422)	(986)	(985)	(949)	(951)
HF	179	556	592	740	734	944	1067	1159	1219	1736	1836	1893	3744	3767	3856	3849
(D_{3h})	(51)	(136)	(126)	(155)	(157)	(67)	(176)	(184)	(223)	(40)	(494)	(464)	(1038)	(1037)	(996)	(1000)
Expt.[49]	—	526	820	490	519	729	1009	—	1133	1659	1555	1649	3304	3353	3422	—
	(—)	(76)	(197)	(—)	(—)	(7)	(90)	(—)	(207)	(65)	(390)	(380)	(899)	(930)	(847)	(—)

TABLE III
Theoretical [6-31G(d, p) basis set] and experimental vibration frequencies (cm ^{1}) for the $C(NH_2)_3^+$.

	Vibrations: description, symmetry, frequencies															
Method	NH_2 twist (A_1)	CN_3 angle def (E)	NH_2 twist (E)	NH_2 wag (E)	NH_2 wag (A_2)	CN_3 angle def (A_2)	CN_3 sym str (A_1)	NH_2 rock (A_2)	NH_2 rock (E)	CN_3 deg str (E)	NH_2 deg scissors (E)	NH_2 scissors (A_1)	NH_2 sym str (E)	sym NH_2 str (A_1)	NH_2 asym str (E)	NH_2 asym str (A_2)
B-null	328	472	546	261	358	642	951	1016	1064	1621	1519	1629	3409	3423	3528	3526
B-LYP	341	477	560	324	413	656	991	1022	1081	1662	1550	1643	3498	3514	3620	3618
B-P86	341	476	560	332	421	659	1001	1020	1082	1550	1676	1638	3511	3526	3535	3634
B-PL	337	483	559	316	407	662	985	1037	1090	1667	1561	1665	3528	3543	3650	3648
B-VWN	339	485	562	322	413	665	990	1040	1095	1568	1675	1670	3548	3563	3671	3668
S-null	346	464	551	361	443	647	996	983	1047	1493	1657	1573	3386	3402	3505	3503
S-LYP	362	471	565	398	481	661	1034	989	1060	1505	1716	1585	3467	3485	3590	3588
S-P86	413	470	568	415	490	654	1042	992	1058	1496	1733	1574	3473	3491	3601	3599
S-PL	341	474	562	392	478	667	1028	1000	1070	1526	1708	1607	3499	3517	3623	3621
S-VWN	340	476	563	398	484	671	1033	1003	1074	1532	1716	1613	3518	3536	3642	3640
XA-null	353	477	564	390	473	665	1023	1001	1069	1523	1701	1604	3477	3495	3601	3599
XA-LYP	351	480	572	418	502	682	1059	1006	1080	1535	1760	1616	3562	3580	3688	3686
BHandH	266	515	588	423	532	740	1091	1064	1147	1633	1805	1729	3690	3710	3820	3816
BHandHLYP	245	520	587	386	502	740	1073	1083	1159	1657	1786	1762	3716	3735	3845	3841
B3LYP	318	496	572	364	460	693	1029	1051	1115	1596	1720	1693	3597	3614	3723	3720
B3P86	330	494	573	377	471	694	1041	1051	1117	1598	1735	1690	3621	3638	3750	3748
Expt. [49]	—	526	820	490	519	729	1009	—	1133	1659	1555	1649	3304	3353	3422	—

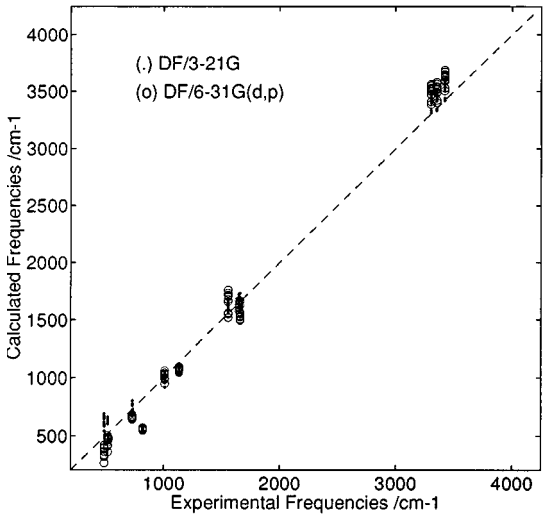

FIGURE 3. Plot of the experimental observed frequencies vs. calculated by pure DF methods with the 3-21G and the 6-31G(*d*, *p*) basis set of atomic functions.

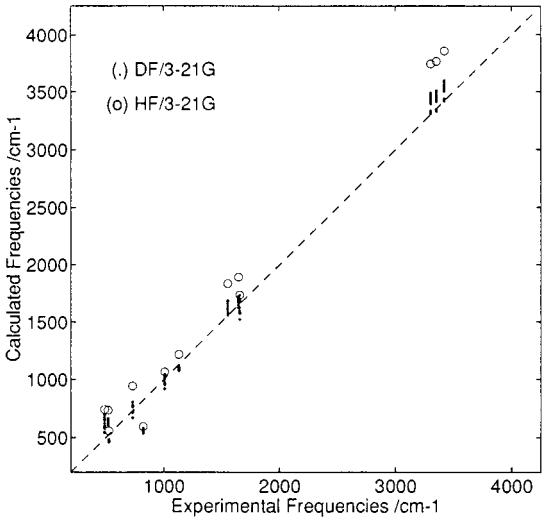

FIGURE 4. Plot of the experimental observed frequencies vs. calculated by pure DF and HF methods with the 3-21G basis set of atomic functions.

stretching modes are quite insensitive to the inclusion of this solvation contribution, in contrast with the CN_3 angle deflection (A_2) and CN_3 deg. stretching (E) modes with an average frequency shift of 37 and 16 cm ^{1}, respectively. This was to be expected due to the spherical symmetry of the cavity shape. It seems that the SCRF did not reduce the errors of the predicted frequencies in a systematic way and shows an improvement only for those modes for which the gas-phase frequen-

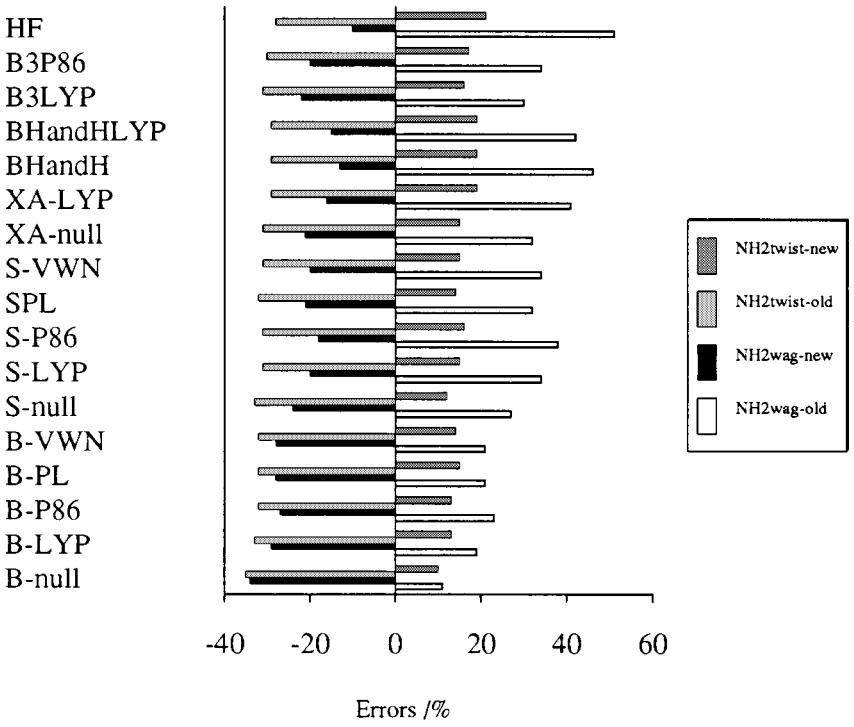

FIGURE 5. Bar chart of the errors obtained for the frequencies of the NH_2 twist (E) and NH_2 wag (E) modes, when they are assigned to the 820 and 490 cm ^{1} observed bands, respectively, (old) and when they are reversely assigned (new).

TABLE IV

Theoretical (3-21G basis set) and experimental vibration frequencies (cm ^{1}) for the guanidinium ion in the SCRF and deviations from gas-phase values.

	Vibrations: description, symmetry, frequencies (deviations)								
Method	CN_3 angle def (E)	NH_2 twist (E)	NH_2 wag (E)	CN_3 angle def (A_2)	CN_3 sym str (A_1)	NH_2 rock (E)	CN_3 deg str (E)	NH_2 deg scissors (E)	NH_2 scissors (A_1)
B-null	463 (3)	536 (0)	540 (2)	658 (10)	920 (1)	1072 (7)	1508 (14)	1630 (7)	1675 (0)
B-LYP	471 (2)	550 (2)	580 (2)	691 (21)	964 (0)	1097 (9)	1569 (13)	1651 (9)	1697 (0)
B-P86	468 (5)	554 (1)	596 (5)	697 (29)	974 (0)	1100 (7)	1584 (12)	1648 (13)	1694 (0)
B-PL	478 (3)	560 (2)	589 (4)	692 (24)	956 (0)	1104 (7)	1561 (15)	1671 (8)	1718 (0)
B-VWN	481 (3)	556 (2)	589 (3)	700 (23)	962 (0)	1109 (6)	1571 (14)	1679 (7)	1725 (0)
S-null	457 (4)	549 (2)	613 (6)	684 (34)	973 (0)	1072 (6)	1607 (17)	1554 (5)	1623 (0)
S-LYP	466 (3)	565 (1)	652 (3)	722 (41)	1015 (0)	1095 (3)	1664 (20)	1581 (4)	1647 (0)
S-P86	461 (5)	567 (1)	668 (5)	724 (47)	1023 (0)	1092 (5)	1679 (20)	1576 (4)	1642 (0)
S-PL	470 (2)	560 (0)	645 (3)	730 (38)	1008 (0)	1101 (4)	1658 (19)	1599 (4)	1669 (0)
S-VWN	472 (4)	562 (2)	652 (5)	736 (40)	1014 (0)	1105 (5)	1667 (20)	1605 (5)	1676 (0)
XA-null	471 (4)	562 (1)	644 (4)	725 (38)	1004 (0)	1100 (5)	1653 (19)	1595 (5)	1666 (0)
XA-LYP	479 (4)	579 (2)	686 (6)	760 (44)	1045 (0)	1119 (4)	1712 (20)	1618 (4)	1686 (0)
BHandH	517 (1)	582 (1)	716 (0)	835 (53)	1068 (0)	1177 (0)	1751 (19)	1704 (1)	1789 (0)
BHandH LYP	520 (2)	579 (3)	686 (10)	814 (50)	1045 (0)	1180 (0)	1690 (7)	1759 (12)	1815 (0)
B3P86	496 (1)	571 (1)	656 (2)	760 (43)	1014 (0)	1144 (1)	1648 (4)	1703 (14)	1751 (0)
B3LYP	497 (0)	567 (1)	635 (1)	750 (37)	1003 (0)	1139 (0)	1631 (6)	1700 (11)	1750 (0)
Expt.[52]	536	810	425	732	1015	1120	1670	1565	1015

cies were overestimated. The CN_3 angle def. (E) and CN_3 deg. str. (E) modes showed a very good improvement in their frequency values, especially for those methods using the Slater's exchange functional (S).

The suspicion that some of the closest molecules of the solvent could have the biggest effect on the vibration modes of the ion led to the inclusion of six explicit water molecules in an attempt to model the first hydration shell. Figure 6 shows the structure of the aggregate obtained with the DF B-PL (3-21G) method, after a total geometry optimization, and Table V presents the corresponding geometrical parameters. The geometry of the ion shows

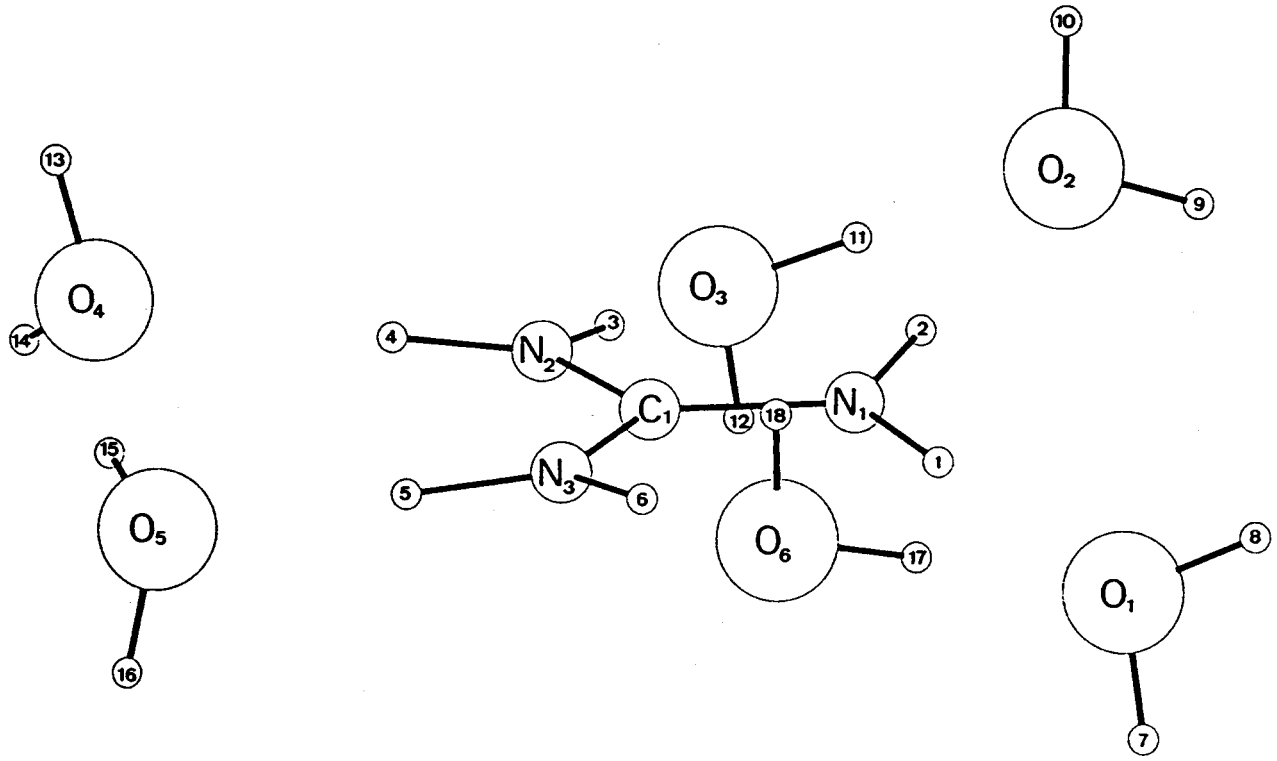

FIGURE 6. Optimized structure of the aggregate $[C(NH_2)_3)]^+(H_2O)_6$ obtained with the DF / B-PL (3-21G) method (refer to Table V).

only a slight deviation from the D_3 symmetry; however, the whole aggregate has no symmetry, due to the positions adopted by the water molecules. The torsion of the NH_2 groups is not so pronounced when compared with the geometry of the ion in the vacuum (now, around 10° out of the nonhydrogen atoms plane). The water molecules are located in two different planes, pointing their oxygen atoms toward the hydrogens of the ion, three of them with a distance around 1.7 Å and the other group of three water molecules with distance to hydrogens around 2 Å. That difference is due to hydrogen bonds established between two neighbor water molecules (WO—HW around 1.75 Å). The analysis of the modes and the correspondence to the isolated guanidinium vibrations were difficult because of the contamination by water vibrational modes. However, Table VI shows some preliminary results obtained with the DF B-PL (3-21G) method for those vibrational modes that did not include too much contamination and for which the correspondence to the previously defined modes was possible. The CN_3 sym. str. (A_1) and the CN_3 deg. str. (E) were shown to be quite insensitive to the presence of the solvent. Note that a change of assignments of the latter one with the NH_2 deg scissors (E) would give better agreement with experience, but the above analysis made in the gas phase led to the conclusion that the bands observed at 1670 and 1565 cm^{-1} have been correctly assigned. For the NH_2 wag (E), e.g., the inclusion of the solvent shows poor quality results, with the frequency being even more overestimated. For the high-frequency range, the predictions are also overestimated but, here, the percentage errors are smaller. However, for the low-frequency range, the CN_3 angle def. (E) and NH_2 twist (E) results are very satisfactory once the absolute errors were reduced from 10.2 to 8.8% and from 30.6 to 11.1%, respectively.

Conclusion

Several density functional (DF) and hybrid Hartree–Fock density functional (DF HF) methods were employed in this work to study the structure and vibrations of the peculiar charged system which is the guanidinium ion. All the DF methods predicted a geometry for the energy min-

TABLE V

Optimized geometrical parameters[a] obtained with the DF / B-PL (3-21G) method for the aggregate $[C(NH_2)_3]^+(H_2O)_6$.

Guanidinium ion					
$r(C-N_1)$	1.382	$\angle(H_1N_1C_1)$	121.1	$\angle(H_1N_1C_1N_3)$	9.4
$r(C_1-N_2)$	1.357	$\angle(H_2N_1C_1)$	120.2	$\angle(H_2N_1C_1N_2)$	11.4
$r(C_1-N_3)$	1.342	$\angle(H_3N_2C_1)$	122.2	$\angle(H_3N_2C_1N_1)$	11.3
$r(N_1-H_1)$	1.015	$\angle(H_4N_2C_1)$	120.1	$\angle(H_4N_2C_1N_3)$	8.0
$r(N_1-H_2)$	1.024	$\angle(H_5N_3C_1)$	121.0	$\angle(H_5N_3C_1N_2)$	6.9
$r(N_2-H_3)$	1.054	$\angle(H_6N_3C_1)$	122.0	$\angle(H_6N_3C_1N_1)$	8.1
$r(N_2-H_4)$	1.021				
$r(N_3-H_5)$	1.053				
$r(N_3-H_6)$	1.054				
Water molecules					
$r(O_1-H_7)$	1.005	$r(O_4-H_{13})$	0.992	$\angle(HO_1H)$	106.0
$r(O_1-H_8)$	1.001	$r(O_4-H_{14})$	1.004	$\angle(HO_2H)$	106.2
$r(O_2-H_9)$	1.004	$r(O_5-H_{15})$	1.016	$\angle(HO_3H)$	105.7
$r(O_2-H_{10})$	1.001	$r(O_5-H_{16})$	0.994	$\angle(HO_4H)$	107.0
$r(O_3-H_{11})$	1.030	$r(O_6-H_{17})$	1.019	$\angle(HO_5H)$	106.5
$r(O_3-H_{12})$	1.004	$r(O_6-H_{18})$	1.001	$\angle(HO_6H)$	105.8
Aggregate					
$r(O_1-\!\!-\!\!-H_1)$	2.062	$r(O_1-\!\!-\!\!-H_{17})$	1.763		
$r(O_2-\!\!-\!\!-H_2)$	2.070	$r(O_2-\!\!-\!\!-H_{11})$	1.748		
$r(O_3-\!\!-\!\!-H_3)$	1.713	$r(O_4-\!\!-\!\!-H_{13})$	1.760		
$r(O_4-\!\!-\!\!-H_4)$	2.037				
$r(O_5-\!\!-\!\!-H_5)$	1.718				
$r(O_6-\!\!-\!\!-H_6)$	1.724				

[a]Distances in angstroms and angles in degrees; refer to Figure 6.

imum with symmetry D_3, rather than D_{3h}, in clear agreement with other more expensive ab initio calculations with corrections for the electronic correlation. Isotopic shifts were also analyzed upon substitution of all the hydrogen atoms by deuterium atoms, and good agreement with experimental data was obtained. The 3-21G basis set of atomic functions was shown to be adequate for the calculation of the harmonic vibrational frequencies of the ion. The mean absolute error for the pre-

TABLE VI

DF / B-PL (3-21G basis set) vibration frequencies (cm ^{1}) for the guanidinium ion with different solvation levels

	Vibrations: description, symmetry, frequencies							
Solvation level	CN_3 angle def (E)	NH_2 twist (E)	NH_2 wag (E)	CN_3 sym str (A_1)	NH_2 rock (E)	CN_3 deg str (E)	NH_2 deg scissors (E)	NH_2 scissors (A_1)
Gas phase	481	562	593	956	1111	1576	1679	1718
SCRF	478	560	589	956	1104	1561	1671	1718
6 H2O + SCRF	583	720	855	951	1225	1576	1757	1814
Expt.[52]	536	810	425	1015	1120	1670	1565	1670

dicted DF frequencies is about one-half of that obtained by standard Hartree–Fock methods. The methods which show a slightly better performance are those using the Slater's exchange functional especially when combined with LYP or VWN correlation functionals. The hybrid DF HF methods showed slightly worst results but still better than pure HF methods, especially those using the Becke's three-exchange–correlation functional.

The vibrational behavior of the guanidinium ion showed some change upon inclusion of solvent effects. The results, although preliminary, show the existence of modes that are not affected by hydration due to their symmetry. For low-frequency vibrations, some improvement in the results was achieved, especially for the CN_3 angle def. (E) and the NH_2 twist (E) modes, when comparison is made with Raman spectroscopy data of aqueous solutions of guanidinium salts.

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