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Ab initio HF and MP2 Study of the Atomic Charges in Some XY_4^{2-} Tetrahedral Anions – A Route to Model Hydrogen Bonding Proton Acceptor Abilities

Bojan Šoptrajanov,[1,2] Ljupco Pejov,[1] and Mira Trpkovska[1]

[1] Institut za hemija, PMF, Univerzitet “Sv. Kiril i Metodij”, P.O.B. 162, 91001 Skopje, Macedonia
[2] Makedonska akademija na naukite i umetnostite, Skopje, Macedonia

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Ab initio HF and MP2 Study of the Atomic Charges in Some XY_4^{2-} Tetrahedral Anions – A Route to Model Hydrogen Bonding Proton Acceptor Abilities[#]

Bojan Šoptrajanov,[1,2,]* Ljupco Pejov,[1] and Mira Trpkovska[1]

[1] Institut za hemija, PMF, Univerzitet "Sv. Kiril i Metodij", P.O.B. 162, 91001 Skopje, Macedonia
[2] Makedonska akademija na naukite i umetnostite, Skopje, Macedonia

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Abstract

Motivation. The problem of predicting the proton acceptor abilities of various species, as well as the understanding of the variety of factors influencing these abilities is of substantial importance for the interpretation of the IR spectra of hydrogen–bonded molecules in solid state.

Method. The proton acceptor abilities of some XY_4^{2-} anions (SO_4^{2-}, SeO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, CrO_4^{2-} and BeF_4^{2-}) were studied using *ab initio* quantum chemical methods and IR spectroscopy. The geometries of the anionic species were optimized at both HF SCF and MP2 (frozen core) levels of theory. The charge distribution for the optimized geometries was investigated using both the Mulliken scheme and the natural population analysis (NPA).

Results. Quantum–chemically computed partial atomic charges on Y atoms within various XY_4^{2-} tetrahedral species correlate well with the spectroscopically measured frequencies of the proton–donor ammonia molecule rocking modes. The results obtained using the quantum chemical methods were compared to the experimental spectroscopic results for several $[Cu(NH_3)_4]XY_4$ and $[Cu(NH_3)_4]XY_4\cdot H_2O$ species. Conclusions regarding the proton acceptor abilities of the XY_4^{2-} anions were mainly derived on the basis of the experimentally obtained IR frequencies of the $\rho(NH_3)$ modes.

Conclusions. The atomic charges on the Y atoms in a series of tetrahedral XY_4^{2-} species derived from *ab initio* HF/LANL2DZ and MP2/LANL2DZ densities with Mulliken as well as NPA charge–assignment schemes give a correct order of proton acceptor abilities of these anions, according to the spectroscopically obtained positions of the $\rho(NH_3)$ modes in a series of structurally similar $[Cu(NH_3)_4]XY_4$ and $[Cu(NH_3)_4]XY_4\cdot H_2O$ compounds. The *ab initio* (both HF and MP2) results are practically completely in line with the experimental observations, while the much simpler electronegativity–based approach fails to explain some of the spectroscopically observed trends.

Keywords. *Ab initio* charge distribution; Mulliken population analysis; natural population analysis; proton acceptor ability; hydrogen bonding.

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* Correspondence author; phone: ++398-2-117-055; fax: ++398-2-226-865; E-mail: bojan@robig.pmf.ukim.edu.mk.

1 INTRODUCTION

The proton acceptor ability of molecular and ionic species involved in hydrogen bonding has been a subject of many experimental and theoretical studies [1, 2 and references therein]. The concept of atomic charge, although relatively loosely defined, has often served as a quantitative measure of the proton acceptor ability. It has been shown [1] that atomic charges derived on the basis of electronegativity–based concepts failed to explain the spectroscopically determined order of the proton acceptor abilities of several tetrahedral species. On the other hand, despite the fact that it is a fundamental problem to calculate "the absolute values" of atomic charges on the basis of *ab initio* molecular wavefunctions, the predicted order of the proton acceptor abilities based on the first principles calculations were shown to be fully in line with experimental observations [3]. Continuing our previous studies of series of compounds containing intermolecular hydrogen bonds, we now report the theoretical results for the electric charges on the Y atoms of some XY_4^{2-} ions (and, by implication, the proton acceptor abilities of the ions) and compare them with the experimental data on $[Cu(NH_3)_4]XY_4$ and $[Cu(NH_3)_4]XY_4 \cdot H_2O$ type compounds.

2 EXPERIMENTAL AND COMPUTATIONAL DETAILS

The geometries of the XY_4^{2-} species were fully optimized at the Hartree–Fock (HF SCF) and second order Møller–Plesset perturbation theory (MP2) levels, using Schlegel's gradient optimization algorithm (computing the energy derivatives analytically) [4]. The MP2 study was performed within the frozen core (FC) approximation. In order to have consistent results for all species, the LANL2DZ basis set (D95 on the first–row elements [5] and Los Alamos ECP plus DZ [6–8] on Na to Bi) was used within both approaches. The stationary points found on the molecular potential energy hypersurfaces were tested using numerical harmonic vibrational analysis. The molecular charge distributions were partitioned among the atomic centers using both the Mulliken scheme [9] and the natural population analysis algorithm (NPA) [10]. Within the MP2 approach, the MP2 densities were used for population analysis. All calculations were performed using the Gaussian 94w series of programs [11,12].

The Fourier transform infrared spectra of solid $[Cu(NH_3)_4]XY_4$ and $[Cu(NH_3)_4]X'Y'_4 \cdot H_2O$ samples (where $XY_4^{2-} \in \{SeO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, CrO_4^{2-}\}$, while $X'Y'_4{}^{2-} \in \{SO_4^{2-}, BeF_4^{2-}\}$) were also studied. The spectra were recorded at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT) on a Perkin Elmer system 2000 FT–IR interferometer. A variable–temperature cell (Graseby Specac) was used for the low–temperature measurements.

3 RESULTS AND DISCUSSION

Although no symmetry restrictions were imposed during geometry optimizations, as expected, the minima on the anionic potential energy hypersurfaces correspond to T_d symmetry. The calculated HF and MP2 atomic charges for the optimized geometries of the XY_4^{2-} species using the Mulliken and NPA partition schemes are presented in Table 1, together with the experimentally obtained frequencies of the rocking NH_3 modes.

Although the weaknesses of the Mulliken charge–assignment scheme have been well documented [10 and references therein], it has been proved that it is valuable in predicting the trends, despite the “absolute values” of the atomic charges in series of molecular species. The overall consistence with the charges obtained on the basis of the natural population analysis (based on a deeper physical background), gives further support to the previous statement. Having in mind that the atomic charges cannot be uniquely determined either theoretically or experimentally, the conclusions about their values are often derived on the basis of the experimentally determined electrostatic properties (such as dipole moments). Since the symmetry of the XY_4^{2-} species in the solid phase often deviates only slightly from the ideal T_d one, the hydrogen bonding proton acceptor ability is of great importance for deriving such conclusions about the electrostatic properties, especially the atomic charges of the proton–accepting atoms. It should be mentioned at this point that, although being slight, a deviation from the ideal T_d symmetry exists for the XY_4^{2-} species in the members of the investigated series of compounds. The theoretical predictions, on the other hand, refer to an idealized T_d geometry, corresponding to the *ab initio* determined minimum on the anionic potential energy hypersurface. However, it was proved by a series of calculations that slight deviations in the geometry of the XY_4^{2-} species, although in principle affect (but only slightly) the actual values of the atomic charges, the trends are unchanged.

Table 1. Calculated Relative Atomic Charges (q/e) of the Y Atoms (O or F) in XY_4^{2-} Species by Mulliken (MPA) and the Natural Population Analysis (NPA) and the Experimentally Determined Frequencies of the Rocking NH_3 Modes

Species	MPA		NPA		$\tilde{\nu}(\rho NH_3)/cm^{-1}$
	HF	MP2	HF	MP2	
SeO_4^{2-}	–0.9749	–0.8968	–1.1951	–1.1462	743
CrO_4^{2-}	–0.7725	–0.6106	–0.8080	–0.5947	720
WO_4^{2-}	–0.9309	–0.7015	–1.1479	–0.9444	707
MoO_4^{2-}	–0.9003	–0.6705	–1.0611	–0.8377	703
SO_4^{2-}	–0.9317	–0.8632	–1.1068	–1.0711	730
BeF_4^{2-}	–0.7399	–0.6842	–0.9307	–0.9016	700

Of course, it would be valuable to draw conclusions about the strength of the interaction between the ammonia molecule and the XY_4^{2-} anion in the case of isomorphous series of compounds, where the matrix effects are practically equal. In such case, conclusions about the consistence between the theoretical predictions and the experimental results would be straightforward.

Although all of these compounds are not strictly isomorphous, the structures of particular pairs among them are rather similar, especially regarding the surrounding of the ammonia molecules and the hydrogen bonding networks. Namely, two members of the investigated series of compounds (the sulfate and tetrafluoroberrylate salts) are monohydrates [13], while the others are nonhydrous. The two hydrates crystallize in the same, orthorhombic system [13], but even they can not be considered as strictly isomorphous, since the unit cell of the tetrafluoroberrylate compound is approximately four times larger than that of the sulfate, and several other differences between the two crystal structures exist. According to the spectroscopic studies [14], the structures of the molybdate and the tungstate compounds are very similar, although definite conclusions regarding the isomorphism between them could not be inferred only on that basis. The selenate compound seems to be, on the other hand, structurally the most similar to the chromate one [15]. Thus, when deriving conclusions about the hydrogen bond strengths, it is convenient to divide the whole series of compounds into three structurally similar pairs.

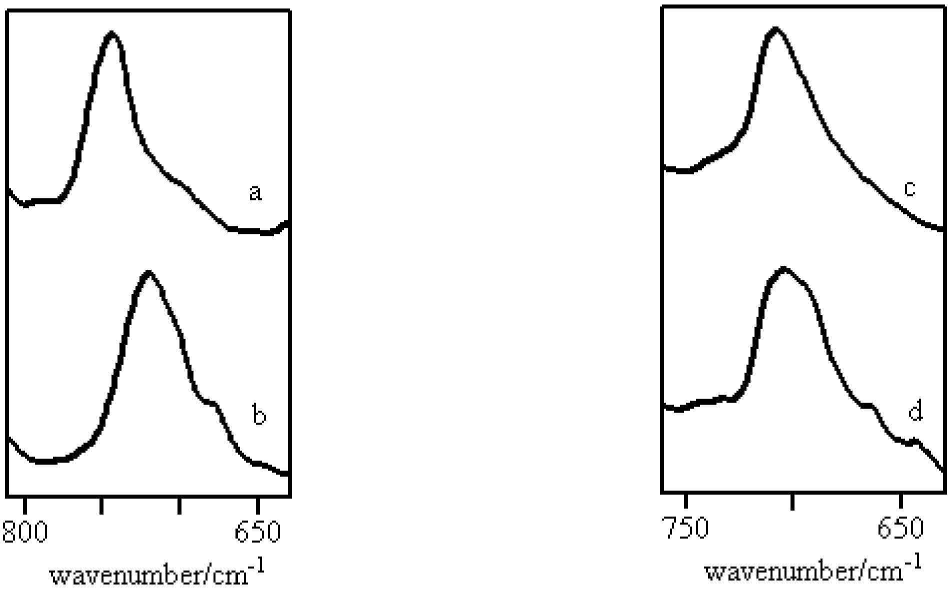

Figure 1. The region of appearance of the $\rho(NH_3)$ modes in the FT–IR spectra of the investigated series of compounds: a, $[Cu(NH_3)_4]SeO_4$; b, $[Cu(NH_3)_4]CrO_4$; c, $[Cu(NH_3)_4]WO_4$; d, $[Cu(NH_3)_4]MoO_4$.

The spectroscopic results invariably show that the frequencies of the $\rho(NH_3)$ vibrations strongly depend on the nature of XY_4^{2-} anion, as can be seen from Table 1. These are, on the other hand, a measure for the strength of the interactions (mainly with hydrogen bonding character) between the ammonia molecule and the anion [14,15]. Of course, the $\rho(NH_3)$ frequencies are also dependent on the strength of the M–N bonds, but in the investigated here compounds only one type of metal ion is present (Cu^{2+}) and, perhaps with the exception of the sulfate and tetrafluoroberrylate salts (where a water molecule is also coordinated to the metal), considerable differences in the M–N bond strengths are not expected. The much-pronounced dependence of the frequencies of the rocking NH_3 modes on the nature of the anion in series of salts containing the same cation was also studied by Müller *et al* [16]. Their results seem to invariably suggest that it is the proton acceptor ability of the anion that determines mostly the position of the bands due to these modes. On the other hand, the proton acceptor ability of the anions is governed by the charges of the proton accepting atoms. The region of appearance of the ρ(NH_3) modes in the IR spectra of the investigated series of compounds is shown in Figure 1. The analysis derived from both HF and MP2 electron densities, based on both the Mulliken and the NPA charge assignment schemes predict a considerably higher partial charge on the oxygen atoms in the selenate than on the chromate anion, slightly higher on the WO_4^{2-} oxygens than on the MoO_4^{2-} ones and, finally, *higher* on the SO_4^{2-} O atoms than on the F atoms in the BeF_4^{2-} species although, due to the much higher electronegativity difference between the Be and F atoms than that between the S and O atoms, the opposite trend would be expected. In line with the theoretical results, the ρ(NH_3) frequency is considerably higher in $[Cu(NH_3)_4]SeO_4$ than in $[Cu(NH_3)_4]SeO_4$, slightly higher in $[Cu(NH_3)_4]WO_4$ than in $[Cu(NH_3)_4]MoO_4$ and *higher* in $[Cu(NH_3)_4]SO_4{\cdot}H_2O$ than in $[Cu(NH_3)_4]BeF_4{\cdot}H_2O$. In other words, for the studied pairs of structurally similar compounds the rocking NH_3 frequencies follow closely the order of the calculated charges.

The conclusions about the relative hydrogen bond strengths in these compounds may be also derived on the basis of the ND stretching frequencies from the isotopically isolated NH_2D species. In fact, even more realistic results are expected to be obtained using values for these frequencies than the ones for the rocking NH_3 modes. Reliable results could be in principle obtained only for the selenate, chromate, molybdate and tungstate compounds, due to the impossibility of an exact and unambiguous assignment of the NH (ND) stretching bands in the two members which are crystalline hydrates. However, the situation is rather complicated in this series of compounds, since at least eight bands are expected to appear in this spectral region, on the basis of available structural data. The actual number of bands is, in fact, lower, indicating thus a significant overlap among the bands [14,15]. Some of the bands actually appear only as shoulders. It is, therefore, very complicated and uncertain to maintain a one to one correspondence between these bands even in the pairs of structurally similar compounds. Even a curve–fitting procedure combined with previous spectral deconvolution is not of practically any help, since it is well known that the curve–fitting algorithms are of little value in cases of bands that appear very close to each other, and are characterized with relatively large halfwidths. Definite conclusions about the hydrogen bond strengths in these compounds, basing on these data, could therefore be eventually derived only taking the position of the centroids of the features in the N–D stretching region. However, the last quantity is determined by other factors as well, so the conclusions would be loosely based. We therefore just briefly mention that in the case of the MoO_4^{2-} – WO_4^{2-} pair, the position of the ν(N–D) modes is in line with the previously derived conclusions on the proton acceptor abilities, while in the CrO_4^{2-} – SeO_4^{2-} pair the trend is opposite to the one predicted on the basis of position of the ρ(NH_3) modes. However, due to the previously explained reasons, we consider the experimental data regarding the ρ(NH_3) modes as more reliable for deriving conclusions about the proton acceptor abilities of the XY_4^{2-} species, especially appealing on the results of Müller *et al.* [16].

4 CONCLUSIONS

The atomic charges on the Y atoms in a series of tetrahedral XY_4^{2-} species derived from *ab initio* HF/LANL2DZ and MP2/LANL2DZ densities with Mulliken as well as NPA charge–assignment schemes, give a correct order of proton acceptor abilities of these anions, according to the spectroscopically obtained positions of the $\rho(NH_3)$ modes in a series of structurally similar $[Cu(NH_3)_4]XY_4$ and $[Cu(NH_3)_4]XY_4 \cdot H_2O$ compounds. This is not the case with the charges derived on the basis of the electronegativity concepts.

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