

## Vibrational spectroscopic studies of guanidinium hydrogenselenate $C(NH_2)_3 \cdot HSeO_4$

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### ABSTRACT

The vibrational wavenumbers of guanidinium hydrogenselenate were calculated using Gaussian03 software package at different levels and the fundamental modes are assigned. The predicted infrared and Raman activities are reported. The first hyperpolarizability is calculated and the guanidinium hydrogenselenate is an attractive object for future studies of non linear optics. The calculated wavenumbers and geometrical parameters are in agreement with the reported experimental values.

**Key words:** Guanidinium hydrogenselenate, HF, DFT calculations, hyperpolarizability.

### INTRODUCTION

Guanidinium complexes are biologically important due to their presence as a functional group in amino acids<sup>1-5</sup>. Their physical properties are of considerable interest with regard to the variety of applications in the field of ferroelectricity, biotechnology, medicine, etc. Bushiri *et al.*<sup>5,6</sup> and Fleck *et al.*<sup>7</sup> reported the structural and spectral studies of hydrated transition metal guanidinium compounds. Among the transition metal guanidinium complexes, zinc compound is the only anhydrous guanidinium sulphate<sup>7,8</sup>. Antony *et al.*<sup>9</sup> reported the spectroscopic properties of guanidinium zinc sulphate and ab initio calculations. The guanidinium ion, is relatively simple chemical species whose structure is related to those of amides and proteins in which there is considerable interest. Two part compound with organic cation and inorganic anion are intensively investigated. Recently many new compounds have been obtained

for using in nonlinear optics. Usually, these complexes are very stable and have good nonlinear optical properties. Good chemical and physical stability is connected with the existence of inorganic part in investigated compounds, whereas the organic part is responsible for non linear optical properties. Drozd *et al.*<sup>10</sup> reported the crystal structure, differential scanning calorimetry and vibrational low temperature investigations of the title compound. In the present work, we have calculated the geometrical parameters, vibrational wavenumbers and hyperpolarizability theoretically using Gaussian03 set of chemical codes and compared with reported values.

### Computational details

The vibrational wavenumbers were calculated using the Gaussian03 software package on a personal computer<sup>11</sup>. The computations were performed at HF/6-31G\* and B3LYP/6-31G\* levels of theory to get the optimized geometry (Fig. 1)

and vibrational wavenumbers of the normal modes of the title compound. DFT calculations were carried out with Becke's three-parameter hybrid model using the Lee-Yang-Parr correlation functional (B3LYP) method. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using analytic second derivatives to confirm the convergence to minima in the potential surface. The DFT hybrid B3LYP functional tends also to overestimate the fundamental modes; therefore scaling factors have to be used for obtaining a considerably better agreement with experimental data. Thus, a scaling factor of 0.9613 has been uniformly applied to the B3LYP and 0.8929 for HF methods calculated wavenumbers<sup>12</sup>. The observed disagreement

between theory and experiment could be a consequence of the anharmonicity and of the general tendency of the quantum chemical methods

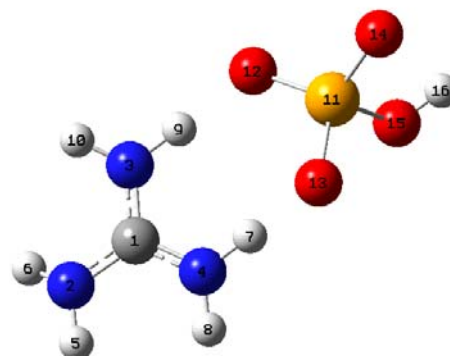


Fig. 1: Optimized geometry

Table 1: Geometrical parameters (DFT) of the title compound

Bond lengths (Å)		Bond Angles (°)		Dihedral Angles (°)	
C1-N2	1.3663	A(2,1,3)	119.1	D(3,1,2,5)	175.5
C1-N3	1.3282	A(2,1,4)	120.4	D(3,1,2,6)	28.5
C1-N4	1.3261	A(3,1,4)	120.5	D(4,1,2,5)	-5.8
N2-H5	1.0096	A(1,2,5)	118.7	D(4,1,2,6)	-152.7
N2-H6	1.0102	A(1,2,6)	118.0	D(2,1,3,9)	-176.6
N3-H9	1.0564	A(5,2,6)	115.1	D(2,1,3,10)	14.0
N3-H10	1.0095	A(1,3,9)	121.2	D(4,1,3,9)	4.6
N4-H7	1.0591	A(1,3,10)	119.5	D(4,1,3,10)	-164.8
N4-H8	1.0091	A(9,3,10)	118.4	D(2,1,4,7)	-167.1
H7-O13	1.6167	A(1,4,7)	120.9	D(2,1,4,8)	10.5
H9-O12	1.6304	A(1,4,8)	120.3	D(3,1,4,7)	11.7
Se11-O12	1.6522	A(7,4,8)	118.7	D(3,1,4,8)	-170.7
Se11-O13	1.6539	A(4,7,13)	173.9	D(1,3,9,12)	126.0
Se11-O14	1.6246	A(3,9,12)	174.7	D(10,3,9,12)	-64.5
Se11-O15	1.7987	A(12,11,13)	110.9	D(1,4,7,13)	88.4
O15-H16	0.9746	A(12,11,14)	116.7	D(8,4,7,13)	-89.2
		A(12,11,15)	103.4	D(4,7,13,11)	-127.3
		A(13,11,14)	116.0	D(3,9,12,11)	-147.1
		A(13,11,15)	103.9	D(13,11,12,9)	-1.4
		A(14,11,15)	104.0	D(14,11,12,9)	-137.2
		A(9,12,11)	115.9	D(15,11,12,9)	109.3
		A(7,13,11)	115.9	D(12,11,13,7)	24.2
		A(11,15,16)	102.9	D(14,11,13,7)	160.3
				D(15,11,13,7)	-86.3
				D(12,11,15,16)	123.4
				D(13,11,15,16)	-120.7
				D(14,11,15,16)	1.0

Table 2: Calculated (scaled) wavenumbers and assignments

HF/6-31G*			B3LYP/6-31G*			$\nu_{(IR)}$ ( $\text{cm}^{-1}$ )	$\nu_{(Raman)}$ ( $\text{cm}^{-1}$ )	Assign- ments
$\nu(\text{cm}^{-1})$	IR Intensity	Raman Activity	$\nu(\text{cm}^{-1})$	IR Intensity	Raman Activity			
3559	156.19	108.39	3571	69.76	87.79	3449		$\nu\text{OH}$
3559	88.00	39.26	3561	46.72	60.81	3419		$\nu_{as}\text{NH}_2$
3501	104.12	73.74	3521	49.93	95.48	3337		$\nu_{as}\text{NH}_2$
3495	121.65	37.18	3518	84.81	55.77	3262	3443	$\nu_{as}\text{NH}_2$
3445	74.89	72.59	3460	48.25	118.38	3212	3364	$\nu_s\text{NH}_2$
3065	241.07	244.91	2784	423.32	378.66	3175		$\nu_s\text{NH}_2$
2968	349.94	29.11	2642	125.66	15.16	2955		$\nu_s\text{NH}_2$
1731	7.45	1.54	1692	324.46	0.11	1734	1677	$\delta_{as}\text{NH}_2$
1692	455.29	4.92	1678	18.99	3.56		1661	$\delta_{as}\text{NH}_2$
1660	275.77	8.61	1633	220.51	10.88	1646		$\delta_{as}\text{NH}_2$
1603	94.83	0.60	1565	8.51	0.50	1564	1558	$\delta_s\text{NH}_2$
1569	211.09	2.30	1540	58.08	2.93			$\nu_{as}\text{CN}_3$
1147	16.04	0.84	1122	31.43	0.91			$\rho\text{NH}_2$
1125	31.57	0.97	1118	72.12	2.71			$\rho\text{NH}_2$
1090	720.43	0.79	1117	43.32	2.18	1098		$\rho\text{NH}_2$
1073	3.51	0.77	1056	0.28	2.79	1065		$\rho\text{NH}_2$
992	75.55	2.52	984	42.23	27.17	1008	1008	$\delta\text{OH}$
974	32.15	19.46	939	198.88	6.49	964		$\nu_s\text{CN}_3$
969	149.99	0.67	917	163.81	1.78		916	$\delta\text{OH}$
800	87.95	11.65	861	112.50	2.74		848	$\nu\text{SeO}_4$
772	52.65	9.12	838	13.84	2.20	833	832	$\nu\text{SeO}_4$
743	259.90	0.78	830	123.30	33.66	731	731	$\eta\text{CN}_3$
697	82.31	27.15	680	3.59	0.35	711	717	$\omega\text{SeO}_4\text{H}$
647	79.47	46.71	609	119.94	14.11	573		$\nu\text{SeO}_4$
616	385.31	1.19	551	20.50	2.21	531	530	$\omega\text{NH}_2$
563	2.89	3.11	515	133.61	2.02	523	526	$\delta\text{N}_3'$
								$\omega\text{NH}_2$
537	4.33	1.98	473	271.90	2.93			$\omega\text{NH}_2$
532	24.03	0.54	436	7.99	2.30		429	$\nu\text{SeO}_4$
503	3.00	1.97	399	98.54	4.47	415	417	$\delta\text{CN}_3$
357	168.47	9.12	386	49.14	2.45			$\delta\text{SeO}_4$
355	129.19	4.98	373	237.35	2.29		366	$\delta\text{SeO}_4$
323	81.62	6.58	348	33.84	3.44		352	$\delta\text{SeO}_4$
268	5.94	0.43	289	20.76	3.51		311	$t\text{NH}_2$
261	14.43	5.60	279	7.99	3.17			$\delta\text{SeO}_4$
256	22.98	5.45	203	57.82	0.62			$\delta\text{SeO}_4$
182	109.66	2.32	196	5.03	0.89			$\delta\text{SeO}_4\text{H}$
166	37.31	1.53	181	41.00	1.54			$\delta\text{CNH}_2$
147	19.84	4.54	162	13.80	3.72			$\delta\text{CNH}_2$
107	3.34	1.57	118	4.08	0.31		134	$\delta\text{CNH}_2$
59	6.22	0.06	69	9.36	1.46			$\gamma\text{SeO}_4$
41	0.03	3.06	34	0.81	3.17			$\delta\text{CNH}_2$
29	7.59	0.08	21	5.07	0.52			$\gamma\text{SeO}_4$

$\nu$ -stretching;  $\delta$ -in-plane deformation;  $\gamma$ -out-of-plane deformation;  $\omega$ -wagging;  $t$ -torsion; subscripts: as-asymmetric, s-symmetric. IR and Raman spectral data are taken from

to overestimate the force constants at the exact equilibrium geometry. The obtained geometrical parameters are given in Tables 1.

## RESULTS AND DISCUSSION

The calculated (scaled) wavenumbers and assignments are given in Table 2. The guanidinium ion vibrations are mainly due to NH and CN bonds. The fundamental modes of  $CN_3$  are expected<sup>1</sup> at 1041 and 1695, 717 and 498  $cm^{-1}$ . In associated aliphatic and alicyclic primary amines<sup>13</sup>, the  $NH_2$  asymmetric stretching vibration occurs at  $3365 \pm 25$   $cm^{-1}$  and symmetric stretching vibration in the region  $3290 \pm 30$   $cm^{-1}$ . The  $NH_2$  scissoring vibration<sup>14</sup> give rise to a broad band in the region  $1600 \pm 50$   $cm^{-1}$ . According to Roeges<sup>14</sup> the rocking/twisting  $NH_2$  mode is expected in the region  $1160 \pm 140$   $cm^{-1}$ . Drozd *et al.*<sup>10</sup> reported the  $NH_2$  vibrations at 3449, 3377, 1564, 1555  $cm^{-1}$  in the IR spectrum, 3443, 3314, 1558, 1549, 1098  $cm^{-1}$  in the Raman spectrum. The vibrations due to CN are reported at 1646, 1008, 731  $cm^{-1}$  in the IR spectrum and at 1661, 731  $cm^{-1}$  in the Raman spectrum<sup>10</sup>. The stretching vibrations of the Se-O bonds<sup>15</sup> appear in the region between 1000-800  $cm^{-1}$ . The SeO4 vibrations are reported at 953, 909, 876, 837  $cm^{-1}$  in the IR spectrum and at 916, 848  $cm^{-1}$  in the Raman spectrum<sup>10</sup>.

For the title compound, the DFT calculations give the bond lengths  $Se_{11}-O_{14}$ ,  $Se_{11}-$

$O_{12}$ ,  $Se_{11}-O_{13}$ ,  $Se_{11}-O_{15}$ ,  $C_1-N_2$ ,  $C_1-N_3$ ,  $C_1-N_4$  as 1.6246, 1.6522, 1.6539, 1.7987, 1.3663, 1.3282, 1.3261 Å where as the reported values are 1.6055, 1.6095, 1.6204, 1.7124, 1.2878, 1.3079, 1.3358 Å respectively<sup>10</sup>. Drozd *et al.*<sup>10</sup> reported the bond angles  $O_{14}-Se_{11}-O_{12}$ ,  $O_{14}-Se_{11}-O_{13}$ ,  $O_{12}-Se_{11}-O_{13}$ ,  $O_{14}-Se_{11}-O_{15}$ ,  $O_{12}-Se_{11}-O_{15}$ ,  $O_{13}-Se_{11}-O_{15}$ ,  $N_2-C_1-N_3$ ,  $N_2-C_1-N_4$ ,  $N_3-C_1-N_4$  as 116.1, 112.1, 110.5, 103.7, 107.1, 116.5, 120.1, 120.7, 119.5° whereas in the present case the corresponding values are 116.7, 116.0, 110.9, 104.0, 103.4, 116.0, 119.1, 120.4, 120.5°, respectively.

Analysis of organic molecules having conjugated  $\pi$ -electron systems and large hyperpolarizability using infrared and Raman spectroscopy has evolved as a subject of research<sup>16</sup>. The first hyperpolarizability ( $\beta_0$ ) of this novel molecular system is calculated using theoretically, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a  $3 \times 3 \times 3$  matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry<sup>17</sup>. The calculated first hyperpolarizability of the title compound is 2.8210  $\times 10^{-30}$  esu (B3LYP/6-31G\* methods). We conclude that the title compound is an attractive object for future studies of non linear optical properties.

## REFERENCES

1. Chakarborty, D., and Manogaran, S., *Ind. J. Chem.* **33A**: 969 (1994).
2. Sension, R.J., Hudson, B., and Callis, P.R., *J. Phys. Chem.* **94**: 4015 (1990).
3. Nemeč, I., Machackova, Z., Teubner, K., Cisarova, I., Vanek, P., and Micka, Z., *J. Solid State Chem.* **177**: 4655 (2004).
4. Carver, G., Spichiger, D., and Tregenna-Piggot, P.L.W., *J. Chem. Phys.* **122**: 124511 (2005).
5. Bushiri, M.J., Antony, C.J., and Fleck, M., *J. Raman Spectrosc.* **39**: 368 (2008).
6. Bushiri, M.J., Antony, C.J., and Fleck, *Solid State Commun.* **143**: 348 (2007).
7. Fleck, M., Bohar, I., and Tillmanns, E., *Solid State Sci.*, **6**: 469 (2004).
8. Morimoto, C.N., and Lingafelter, E.C., *Acta Cryst.* **26B**: 335 (1970).
9. Antony, C.J., Bushiri, M.J., Varghese, H.T., Panicker, C.Y., and Fleck, M., *Spectrochim. Acta* doi:10.1016/j.saa/2009.04.024.
10. Drozd, M., Baran, J., and Pietraszko, A., *Spectrochim. Acta* **61A**: 2775 (2005)
11. Frisch, M.J., *et al.*, *Gaussian03, Revision C.02.*, Gaussian Inc., Wallingford, CT (2004).
12. Foresman, J.B., in: Frisch, E., (Ed.),

- Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian*, Pittsburg, PA, (1996).
13. Segal, L., and Eggerton, F.V., *Appl. Spectrosc.* **15**: 112 (1961).
  14. Roeges, N.P.G., *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*, Wiley, New York (1994).
  15. Paetzold, R., and Amoulong, H., *Z. Anorg. Allgem. Chem.* **317**: 166 (1962).
  16. Tommasini, M., Castiglioni, C., Del Zoppo, M., and Zerbi, G., *J. Mol. Struct.* **480**: 179 (1999).
  17. Kleinman, D.A., *Phys. Rev.* **126**: 1977 (1962).