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Vibrational spectral studies of dinicotinium sulfate

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ABSTRACT

This article describes the vibrational spectra of Dinicotinium sulfate. The Raman and infrared absorption spectra of Dinicotinium sulfate crystal containing two anions were recorded at room temperature and the vibrational assignments of the observed wave numbers are made. The presence of a carbonyl (C=O) group was identified and the two carbonyl groups are in different environment. The extensive intermolecular hydrogen bonding in the crystal has been identified by the shifting of bands due to the stretching and bending modes of the various functional groups. The sulfate group forms the anion. Its fundamentals continue to be degenerate except for the asymmetric bending mode and it suggests that the T_d symmetry of SO_4^{2-} group has not been affected in the crystal. Factor group analysis was also carried out for the Dinicotinium sulfate crystal to explore the possible vibrational modes.

KEYWORDS

Dinicotinium sulfate;
Infrared spectra;
Raman spectra;
Intermolecular hydrogen bonding;
Factor group analysis.

INTRODUCTION

All proteins are macromolecule because of their very high molecular weights. The small units of amino acid called monomer are the building blocks of proteins. Each amino acid is a nitrogenous compound having both an acidic carboxyl and a basic amino group. They are amphoteric in nature. In living system protein plays an important role in the structural organization. Many of the protein are named a functional protons because after serve as enzymes. Similarly Vitamins are also complex organic compounds whose preserve essential function of other physical depend activities.

The Nicotinic acid is a B vitamin and also known as niacin is a lipid, lowering agent widely used to treat hypertriglyceridemia by the inhibition of lipolysis in adipose tissue. The nicotinic acid is a complex[1] of 5-methylpyrazine-2-carboxylicacid and 4-oxide. The enzyme nicotinic acid mononucleotide adenylyltransferase is essential for the synthesis of nicotinamide in all living cells and in a potential target for antibiotics.

The study of sulfate minerals of Mars, supported by the discovery of Jarosite at Meridian plenum there is also the possibility of finding anhydrous sulfate minerals in the permafrost, located at the polar region. The studies of vibrational spectra of amino acid by FTIR and Raman spectroscopes are very much useful in obtaining information regarding molecular confirmation and the nature of hydrogen bonds in biologically important substance[2]. There have been several spectroscopic studies[3,4] of organic acid complexes of various nicotinic acid and the their derivatives.

In the present investigation the Dinicotinium sulfate crystal was analysed in Fourier transform infra red (FTIR) Raman spectra. Factor group analysis using the standard correlation method[5,6] has been carried out.

EXPERIMENTAL

The Dinicotinium sulfate crystal was obtained by crystallization from an aqueous solution of nicotinic acid and sulphuric acid in a 2:1 stoichiometric ratio. Slow evaporation of the mixture at room temperature produced colourless block-like triclinic crystal.

A Bruker IFS 66 V FTIR spectrometer was used for IR spectral measurements. The samples were prepared by the pellet technique and the spectrum was recorded in 4000-400 cm^{-1} range. Raman spectral measurements were made with FRA 106 Raman module. An air-cooled diode pumped Nd: YAG laser operated at 1064 nm and a power output of 200 mW was used as a source. The spectrum was recorded over the range 3500-50 cm^{-1}.

All the experiments were carried out at room temperature. For confirming the reliability of the data a Raman spectral measurements[7] were also made using the facility available in our laboratory. The argon-ion laser with the radiation wavelength of 488 nm was used in the source in the Spectra Physics model 2020-04S, which have a resolution of ~2-3 cm^{-1} by using suitable notch filter the Rayleigh line has been suppressed a grating monochromator displaced the reflected light and was detected with thermoelectrically cooled RCA Ga AS photomultiplier tube. The laser power was maintain at 20 mW

RESULTS AND DISCUSSION

In the infrared spectrum the C-H, N-H, O-H stretching lies in the region 2800-4000 cm^{-1} is more distinctive in Raman Effect. In the case of Dinicotinium sulfate the available functional groups are C-C ring, C-H, N-H-O, C=O, O-H-O, C-H out-of-plane and bending modes. The weak band at 2034 cm^{-1} is converted ascend stretching and out-of-plane stretching.

Crystal structure of dinicotinium sulfate

Dinicotinium sulfate, $2C_6H_6NO_2^+ . SO_4^{2-}$ the sulfate anion connects the nicotinic acid cations. The two nicotine cations are twisted from the pyridinium ring. The sulfate anion plays a vital role in stabilizing the structure of the crystal. Further, the cation and anions are connected by a system of hydrogen bonds. In the Dinicotinium sulfate crystal, one of the sulfate anion forms a strong O-H...O hydrogen bonds interlinked through N-H...O nicotinium anions forming an inversion-related closed hydrogen-bonded loop. The Dinicotinium sulfate belongs to the space group triclinic P_1^- contains two nicotinium $2C_6H_6NO_2^+$ as cations and SO_4^{2-} as anion in the asymmetric unit. The protons formed[8] in the sulphuric acid are transferred to the nicotinic acid forming two nicotinium cation. The C- N- C bond angle and the C-N bond distance in both cations confirm protonation on the N atom of the aromatic rings.

Analysis of vibrational modes of dinicotinium sulfate

There are 198 vibration modes excluding the three acoustic modes. It is distributed as $\Gamma=99A_g^R + 9A_u^{IR}$ this is presented in TABLE 1.

The A_g and B_g species are Raman active only. In contrast the other two vibration species A_u and B_u are infrared active only. The configuration of the Dinicotinium sulfate compound is shown in Figure 1.

The observed IR and Raman spectra are presented in Figure 2 & Figure 3.

The representing observed wave numbers together with the proposed assignments are given in TABLE 2.

Vibrational spectral analysis of dinicotinium cation

The cation Dinicotinium, $2C_6H_6NO_2^+$ compound has several functional groups such as O-H and N-H stretching vibration, C-H stretching, C=O, C=C, C-C, and O-H…O. These groups are expected to undergo changes in their intensity and position according to their environment. In the infrared spectrum the C-H, N-H, O-H stretching lies in the region 2800-4000 cm^{-1}. These are more distinctive in Raman spectra. The O-H stretching frequencies appears[2] as a medium band at 3205 cm^{-1}. The Carbonyl vibration is formed as a very strong band at 1731 cm^{-1}. Also a weak band occurs in the

TABLE 1: Factor group analysis of Dinicotinium sulfate (Crystal space group: P1- =Ci Z=2 Zb = 2)

Mode and degrees of Freedom for each species	Molecular symmetry	Site symmetry species C1	Factor group species C_i
	Vib 156	A	78 A_g + 78 A_u
2($C_6H_6NO_2$)$^+$	Trans 12	A	6A_g + 3A_u
168	Lib 12	A	6A_g + 3 A_u
	T_d		
		C_1	C_2
		A	9A_g+ 9A_g
$(SO_4)^{2-}$ Vibration	E 2F_2	A	
18			
Translational			
6	F1	A	3A_g +3A_g
Librations			
6	F2	A	3A_g + 3A_g

$$\Gamma SO_4{}^{2-}_{Int} + \Gamma SO_4{}^{2-}_{trans} + \Gamma SO_4{}^{2-}_{rot} = 15\,A_g{}^{R} + 15\,A_u{}^{IR}$$

$$\Gamma_{\text{Crystal}}^{\text{total}} = 99\,A_g{}^{R} + 99\,A_u{}^{IR} \qquad \Gamma \text{Acoustic} = 3A_u{}^{IR}$$

$$\Gamma \text{Optical}_{\text{Crystal}} = \Gamma \text{total}_{\text{crystal}} - \Gamma\text{acoustic} = 99A_g{}^{R} + 99\,A_u{}^{IR}$$

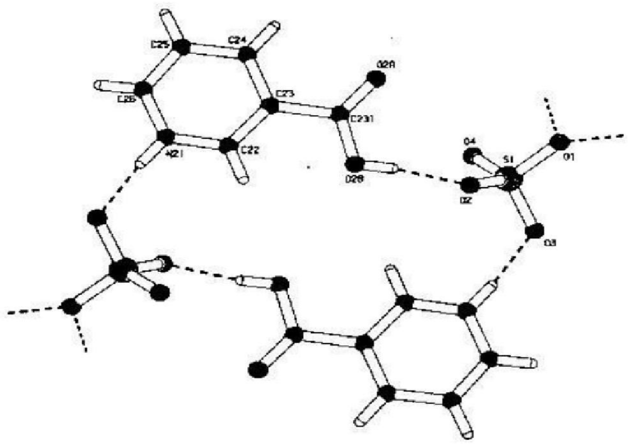

Figure 1 : Structural formula of Dinicotinium Sulfate

wave length region of 1659 cm^{-1}. The C=O stretching mode of vibrational occurs[9] at 1630 cm^{-1}. A strong band at 1396 cm^{-1} and O-H deformation-in plane is formed. In the wave length region of 1333 cm^{-1} a C-H deformation was also observed. The C-H wagging mode of vibration lies in the expected region of 669 cm^{-1} and 633 cm^{-1}. The C-O stretching mode is confirmed by the infrared line at 1134 cm^{-1} and a shoulder is formed in IR spectrum.

The O-H and N-H stretching vibrations and olefin C-H stretching vibration are occurring in the wavelength region of 3129 cm^{-1}. In the wavelength region of 3059 cm^{-1} region C-H stretching and cyclopropyl ring is

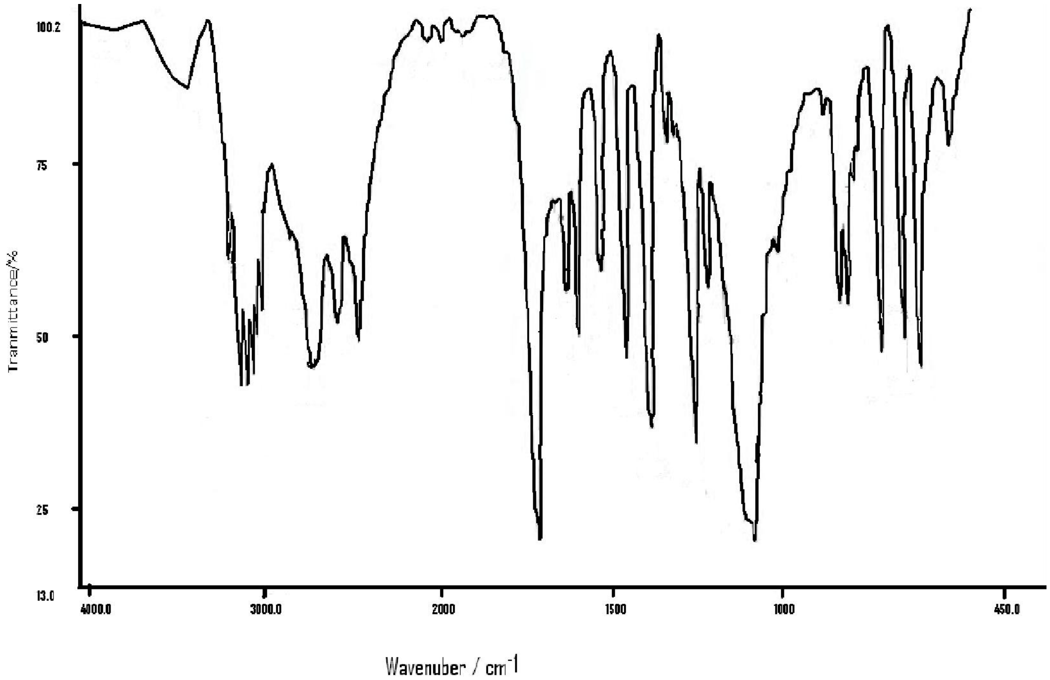

Fig:2 Infrared spectrum of Di(nicotonium)sulfate

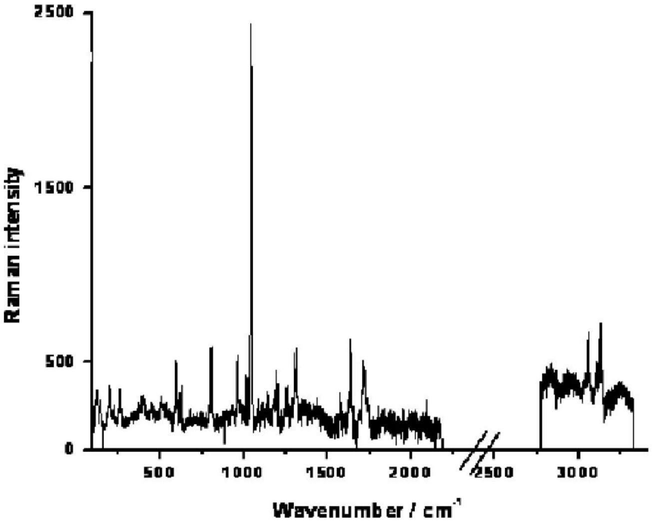

Figure 3 : Raman spectrum of Dinicotinium sulfate

TABLE 2 : Assignment of observed vibrational bands of ($\bar{\upsilon}$) for Dinicotinium Sulfate

Infrared ($\bar{\upsilon}$) cm^{-1}	Raman ($\bar{\upsilon}$) cm^{-1}	Assignment
3432 (w)		H2O
3205 (w)	3129 (s)	O-H str
3155 (v.s)		N-H str
3121 (s)		Olefinic C-H str
3083 (w)		C-H str
3059 (m)	3059 (s)	C-H str, Cyclopropyl ring
3024 (m)		C-H str
2859 (sh)		CH2 sym str
2734 (s)		CH2 sym str
2597 (s)		CH2 sym str
2471 (s)		C-H str
2034 (w)		C=O str, CNN O.P str
1975 (w)		C-H str
1936 (w)		C-H O.P bend
1913 (w)		C-H O.p bending
1790 (w)		Combination band
1731 (v.s)	1731 (v.s)	C=O str,
1659 (w)	1638 (s)	C=C str NH def, CN str
1630 (m)		C=O str
1602 (m)		C=C str
1531 (m)	1560 (sh)	N-H def, CN def
1464 (s)		C-H bending
1396 (s)		O-H def- in- 0.p
1333 (w)		C-H def
1315 (w)	1310 (m)	C-O str, CH def
1273 (v.s)		O-H def
1225 (m)		O-H def
1180 (m)	1199 (m)	O-H def, C-O str
1150 (m)	SO4^{2-} asy str	
1041 (v.s)	SO4^{2-} asy str	
1134 (sh)		SO4^{2-} o.p str
1107 (v.s)		C-O str
1027 (w)		SO4^{2-} str
1019 (w)		SO4 o.ph str
955 (m)	SO4^{2-} sym str	
881 (w)		C-H o.p bend
845 (m)		C-H str
806 (m)	C-H o.p.,aromatic	
823 (m)		C-H wag
733 (m)		=CH o.p wag
670 (m)		SO4^{2-} asy str
669 (sh)		SO4^{2-} bending
663 (s)		SO4^{2-} bending
617 (s)		SO4^{2-} asy str
613 (m)		C-C o.p ring def
592 (s)	592 (m)	SO4^{-} asy str
521 (m)		SO4^{2-} bending
262 (m)	Lattice vibration	
200 (m)	Lattice vibration	
139 (m)	Lattice vibration	
123 (m)	Lattice vibration	

asymmetric; br, broad; def, deformation; i.p., in-plane; i.ph., in-phase; m, medium; o.p., out-of - plane; o.ph., out- of –phase; rock, rocking; s, strong; sh, shoulder; str, stretch; sym, symmetric; tor, torsion; v, very; w, weak; wag, wagging.

formed, and the C=O stretching occurs at 1731 cm^{-1} The N-H deformation, C=C stretching are observed[10] in the Raman spectrum at 1638 cm^{-1}. The C-H stretching vibration and N-H deformation mode shouldering vibration can be made at1559 cm^{-1}. The medium bands due to the symmetry deformation, mode are appear in the wavelength region of 1310 cm^{-1}, the Raman spectrum is attributed[4] to with C-C stretching and C-C-O stretching mode are formed at 1250 cm^{-1}. The O-H deformation and C-O stretching vibrations are made[10] as a strong band at 1199 cm^{-1}. The N=O stretching, C-C-C- Stretching, vibration are made in the calculated[10] wave length region of 1150 cm^{-1} in the negotiate anion species.

Vibrational analysis of sulfate anion

Sulfate anion plays a important role in forming hydrogen bonds with both the cations and in stabilizing the crystal structure. In the free state the sulfate ion has T_d symmetry with its vibrational modes distributed as $A_1 + E + 2F_2$ where the A_1 and E species are Raman active only while the two F_2 species are both IR and Raman active. These mode[11] are expected to occur at 1104 (υ_3), 981(υ_1), 613(υ_4), 451(υ_2) respectively. The non-degenerate mode occurs at 1104 cm^{-1} is due to the symmetric mode of SO_4^{2-} group and it is expected to be the most intense and polarized in the Raman spectrum. It is a theoretically forbidden mode in the IR spectrum and usually occurs as a very weak line.

In Dinicotinium sulfate the symmetric bending mode of SO_4^{2-} group is formed at 592 cm^{-1} as a strong band in Infrared spectrum in the expected region and thus Raman forbidden mode is not excited. It is observed[12,13] as a medium symmetric bending mode 670 cm^{-1} and a strong symmetric bending mode at 613 cm^{-1}, 617 cm^{-1}. In the infrared spectrum and the weak symmetric bending mode at 592 cm^{-1}. The structural data shows that in the sulfate ion all the four bonds are equal in length. The SO_4^{2-} anion shows nearly tetrahedral (T_d) symmetry. The crystal is stabilized by extensive hydrogen bonding through three O atoms of the sulfate anions. However, the degeneracy of one of the triply degenerate modes of vibration (asymmetric bend) is only partially lifted. This confirms that the tetrahedral symmetry of sulfate ion is not distorted much in the crystal.

Hydrogen bonding

Amino acid in the crystalline state has an important feature which is the extensive hydrogen bonding that connects the molecules together. This hydrogen bonding gives the structures cohesion in three dimensions. It will cause a downshifting of stretching vibrational modes and up shifting of deformation modes.

The first type of hydrogen bonds is N-H...O bond involving O-H group of the Carboxylic group and oxygen atom of sulphate group of each of the molecular unit in the unit cell. There are three such bonds formed in the crystal. These bonds are very strong with the average O-H bond length being 0.82A^0 for both the residues this is reflected in the infrared spectrum of the compound where the O-H out of plane. These indicate that the liner distortion is much greater than the angular distortion.

The second category of hydrogen bonding is O-H-O bonds where the two residues of the cation are linked through the sulphate group. The hydrogen of the amino group is bonded with the oxygen of the sulphate group N-H bond length of 0.086A^0 and is considered as normal hydrogen bonds four such bonds in the various NH_2 vibrational modes.

The third category is the conjugated hydrogen bonds between the carboxyl oxygen of one cation and the amino hydrogen of the other N-H...O bond also formed which has length in the range of 2.641-2.528 A^o. There are three such bonds formed in the crystal in the residue. C-H distance is 0.093 A^o. These are normal hydrogen bonds and the effect is observed in the spectral data. The two protonated carboxylic group appear as a doublet with intense bands at 1630 cm^{-1} and 1731 cm^{-1} owing to the strong hydrogen bond in the C=O stretching wave number is shifted to a lower wave number at 1704 cm^{-1}. Due to these reasons the two-carboxyl group are observed in different environment in the crystal

CONCLUSION

The infrared and Raman spectral lines have been analysed and spectral wave numbers have been assigned for Dinicotinium sulfate. The C=O stretching is observed as a doublet. Extensive hydrogen bonding is responsible for the downshifting of the several stretching modes and the up shifting of many bending modes. The anion fundamentals continue to be degenerate except for the asymmetric bending mode. This suggests that the T_d symmetry of SO_4^{2-} group has not been affected in the crystal.

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