

ISSN 1996-3394

Asian Journal of
Materials
Science

FT-Raman Spectroscopic Study of Indian Bituminous and Sub-bituminous Coal

B. Manoj and A.G. Kunjomana
Department of Physics, Christ University, Hosur Road,
Bangalore-29 Karnataka, India

Abstract: In this study, Raman spectra in the 400 to 1800 cm^{-1} region were obtained for two different coal samples. The bands observed at 601 and 569 cm^{-1} were attributed to presence of Halloysite which was shifted to lower wave number with leaching. Intense bands observed at 569-640 cm^{-1} could also correspond to ring breathing vibration. Band due to Si-O perpendicular vibration is observed at 1090 cm^{-1} and is disappeared with HF leaching. The graphite band (1580 cm^{-1}) and the defect band (1350 cm^{-1}) were observed in the sample. Intensity of graphite band (G) was stronger in bituminous coal than sub-bituminous coal, where as the defect band was stronger in sub-bituminous coal with leaching. Presence of D-band was an indication of condensed Benzene rings in amorphous carbon and was comparatively stronger in sub-bituminous coal. Carbonyl bands were stronger in sub-bituminous coal than bituminous coal. The relatively strong band near 1695 cm^{-1} was attributed to carboxylic acid and relatively weak band at 1670 cm^{-1} was assigned to ketonic structures. Sub-bituminous coal sample was showing moderately higher absorption than bituminous coal. Samples having higher oxygen content had intense absorption band of carbonyl group compared to samples having lower oxygen content.

Key words: FT-Raman, bituminous coal, sub-bituminous coal, characterization, leaching

INTRODUCTION

Raman spectroscopy had been used extensively to characterize the structural features of carbonaceous matter since Tuinstra and Koenig (1970) first correlated Raman bands to structural parameters measured from XRD for polycrystalline graphite. Raman spectroscopy had also been applied to study the structural features of coal-derived products (Friedel and Carlson, 1972; Wang *et al.*, 1990). In these studies, the Raman spectral characteristics, mainly those of graphite (G) and defect bands (D) were used to investigate the coal structure and its correlation to other characteristics, e.g., the coal rank and the 'graphite' crystalline size parameters (Guedes *et al.*, 2010). Lasers in visible range, such as the Ar⁺ laser at 488 and 515 nm and the He-Ne laser at 623 nm, were often used, which easily excite strong fluorescence emission, distorting Raman spectra and resulting in difficulties in structural quantification (Schwan *et al.*, 1996).

Little work had been done using a NIR laser (1064 nm) to study coal/char structures. The Raman spectra of highly disordered carbonaceous materials such as amorphous carbon or

Corresponding Author: B. Manoj, Department of Physics, Christ University, Hosur Road,
Bangalore-29 Karnataka, India Tel: +91 80 4012 9340

coal chars differ considerably from that of 'ideal' polycrystalline graphite. Normally there was a large overlap of Graphite (G) and defect (D) band in disordered carbon material and more structural information was hidden in the 'overlap'. The Raman spectroscopy of clay minerals had received less attention due to the weakness of the Raman scattered signal, the photo-degradation of the sample and the occurrence of fluorescence which swamped the signal. The use of FT Raman spectroscopy offered the advantages of reduced fluorescence, improved signal to noise by co-adding of scans and the longer wavelength of light reduced sample degradation.

The application of infrared and Raman spectra to the study of intractable carbonaceous material had produced information valuable to researchers involved studies of the structure of coal. Spectral frequencies were principally assignable to functional groups but some of the important spectral features, not assignable to groups, had been involved in considerable conjecture concerning proper assignments (Jelicka *et al.*, 2006; Li *et al.*, 2006). In present study, the authors had obtained Raman results on two Indian Coals that showed two sharp lines in each sample in the range 1575-1620 and 1350-1400 cm^{-1} region. Other weak lines found in region were also assigned. The change of intensity of the spectral line with leaching was also investigated.

MATERIALS AND METHODS

Experiment was carried out during 2009-2010 at Department of Physics Christ University, Bangalore, India. Coal samples were obtained from two different sources; sub-bituminous coal from Godavari coal field and high volatile bituminous coal from Korba coal field by random picking. The samples, in as received condition, is powdered and dried in a dessicator to remove the absorbed water. Samples were leached with Concentrated HF (40, 30, 20 and 10%) for 24 h and washed with enormous amount of distilled water. The slurry was filtered and dried at about 80°C for removing the absorbed water and allowed to cool slowly in dessicator. The spectral measurements were carried out at Sree-Chitra Tirunal Institute for Medical Sciences and Technology, Thiruvananthapuram, Kerala, India.

Raman Spectroscopy

The Raman and infrared spectra were obtained using a Bruker RFS 100/S series FTIR spectrometer equipped with a Raman accessory. This comprised a Nd-YAG laser operating at a wavelength of 1064 nm and a Raman sampling compartment incorporating 180 degree optics. For analysis, about 20 g of the sample was crushed in to fine powder of about 5 μm in size. The Raman detector was a highly sensitive standard Ge detector and was operated at room temperature. Under these conditions Raman shifts were observed in the spectral range 1800-400 cm^{-1} . Raman spectra were obtained directly keeping the powdered sample in the incident beam 50 scan mode with a resolution of 4 cm^{-1} . Raman spectra were collected as single beam spectra and were not corrected for instrumental effects. A laser power of 200 mW was used. This power was low enough to prevent damage to the minerals, but was sufficient to produce quality spectra.

RESULTS AND DISCUSSION

Low Wavenumber Region (400-1200 cm^{-1})

The FT-Raman of coal in the <1200 cm^{-1} region is shown in Fig. 1 and 2; the coal minerals were characterized by very intense bands in the 200 to 1200 cm^{-1} region. These bands have been identified using conventional dispersive Raman spectroscopy

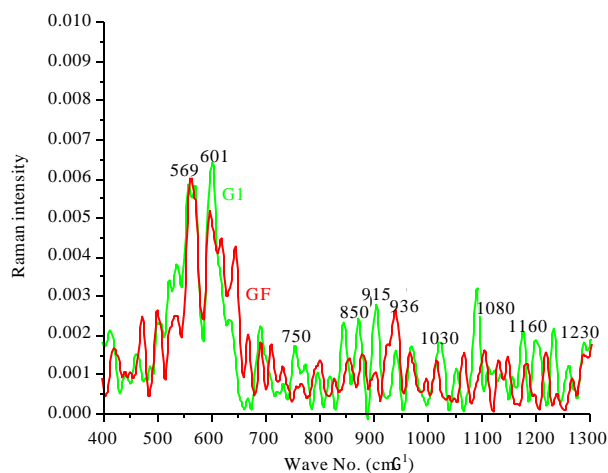


Fig. 1: FT Raman Spectra of sub-bituminous coal ($400\text{-}1200\text{ cm}^{-1}$) G1-Virgin sample, GH-HF leached sample

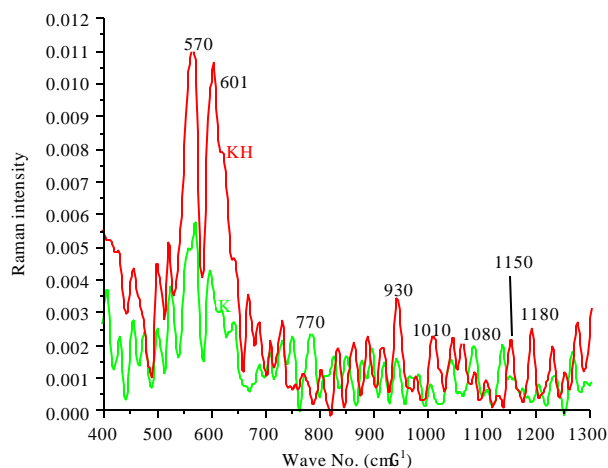


Fig. 2: FT Raman spectra of high volatile bituminous coal ($400\text{-}1200\text{ cm}^{-1}$) K1-Virgin sample, KH-HF leached sample

(Johnson *et al.*, 1986). Frost *et al.* (1993) assigned the same band to clay minerals in his FT Raman spectroscopy study on Kaolinite, Dickite and Halloysite. This part of the spectral region is very much sample dependent. The band had been attributed to Si-O-Si stretch (Ishii *et al.*, 1967). The band at 570 cm^{-1} was changed to lower wavelength of 561 cm^{-1} with HF leaching. The band at 602 cm^{-1} was also lowered with leaching. Intense bands observed at $569\text{-}640\text{ cm}^{-1}$ could also correspond to ring breathing vibration. With HF leaching, the intensity of this band is slightly decreased in sub-bituminous coal where as in the case of bituminous coal the intensity was increased. In the present study authors assigned this band in sub-bituminous coal due to the combined effect of minerals and ring breathing vibration,

where as in the bituminous coal this was due to ring breathing. This absorption increased in bituminous coal with leaching. Bands at 704, 752 and 785 are attributed for Kaolinite; 703, 744 and 792 for Halloysite and 744 and 794 cm^{-1} for Dickite to the Al-OH vibrations of surface hydroxyls. These bands were resolved in the Raman spectra but with less intensity. There were small peaks for Kaolinite and for Halloysite. It was again related to symmetry reduction. The in-plane bending vibrations of the surface hydroxyls in the kaolinite minerals lie at 936 cm^{-1} and inner hydroxyl at 915 cm^{-1} . These bands are strongly infrared active but are very weak in the Raman. These bands were very weak with HF leaching in both sub-bituminous and high volatile bituminous sample. Jelicka *et al.* (2006) observed the ring-plane bending modes of COO- at 811 and 773 cm^{-1} and 792 and 737 cm^{-1} for the COOH bending modes in mellitic acid. Present study also showed absorption spikes in region which was more pronounced in sub-bituminous coal than bituminous coal. With HF leaching intensity of this band decreased in both the samples. This was due to the removal of oxygenated functional group with leaching.

Kaolinites being a dioctahedral layer of silicates as opposed to tri octahedral possess lower effective symmetry thus imposing distortions on the tetrahedral sheet. Thus the intense infrared bands at 1014, 1036 and 1108 cm^{-1} for kaolinite were attributed to the perpendicular Si-O vibrations. These bands were weak in Raman but are observable as small spikes with maximum intensity at 1090 cm^{-1} .

Schwan *et al.* (1996) assigned the band at 1180 cm^{-1} to sp^3 -rich structures in amorphous carbon films. Nemanich and Solin (1979) assigned the bands at 1170 cm^{-1} to hexagonal diamond, nano-crystalline diamond or sp^3 -rich carbon structure. In the present study, a band at 1180 cm^{-1} represents the sp^2 - sp^3 carbonaceous structures in Indian coal. This structure was comparatively weaker in virgin coals, but with HF leaching intensity of this band increased marginally.

Li *et al.* (2006) in their studies on Victorian coal assigned the band at 960, 1230 and 1060 cm^{-1} to the contribution from ether and benzene resulted/accompanied structure respectively. In the present study these bands had weak intensity in the spectrum of both bituminous and sub-bituminous coal. The vibrational frequency below 900 cm^{-1} of coal had not yet been explored and there is no general agreement about the origin of the features observed at about 400-500 and 700-800 cm^{-1} in amorphous carbon-based systems like coal. The 460 and 720 cm^{-1} features showed a different behaviour with chemical leaching; the 460 cm^{-1} peak became stronger with HF leaching in both samples. Conversely, the 720 cm^{-1} feature did not show any appreciable change with leaching.

1300-1800 cm^{-1} Region

The FT-Raman of coal in the 1300-1700 cm^{-1} region is shown in Fig. 3 and 4. This region consists of so many peaks. Wang *et al.* (1990) investigated the structures of highly ordered carbonaceous materials with exciting laser in the visible range and identified the G band at 1585 cm^{-1} and D-band at 1350 cm^{-1} . Li *et al.* (2006) had been found that the D band position was dependent on the excitation laser wavelength (λ_o). i.e., the position of D-band will move from 1360 cm^{-1} at 488 nm to 1285-1327 cm^{-1} at the wavelength of 1064 nm. The Raman spectra of the coal samples do had two very broad bands at around 1580-1605 and 1300-1350 cm^{-1} (Fig. 3, 4) at the position of G and D bands as stated above. This G band may be due to presence of graphite crystalline structures or due to the aromatic ring breathing of alkene (C = C). In the present study the sub-bituminous coal had two well defined absorption at 1585 and 1605 cm^{-1} . With HF leaching this doublet was disappeared to a singlet. In the bituminous coal there was only a narrow band observed at 1605 cm^{-1} but with HF leaching

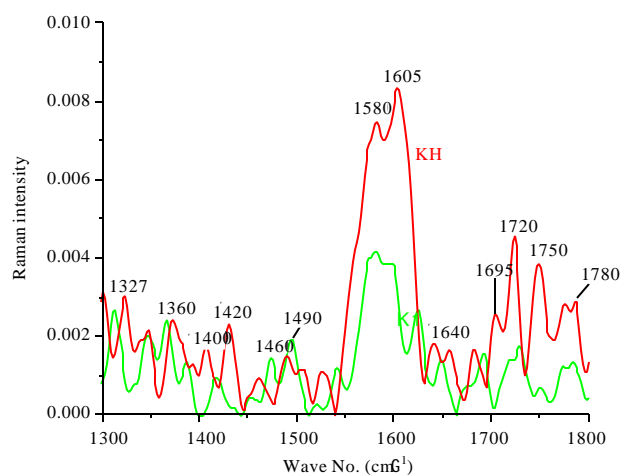


Fig. 3: FT Raman spectra of bituminous coal (1300-1800 cm^{-1}) K-Virgin sample, KH-HF leached sample

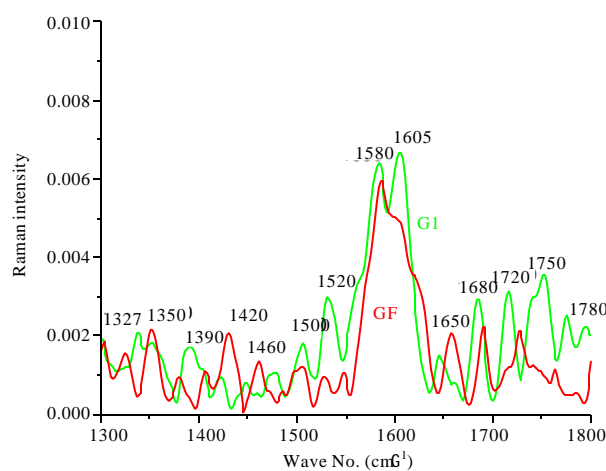


Fig. 4: FT Raman spectra of sub-bituminous (1300-1800 cm^{-1}) G1-Virgin sample GF-HF leached sample

this band was splitted in to two defined spikes with more intensity. This indicated that with increasing rank the graphite band becomes narrower. Bituminous coal and sub-bituminous coal are showing different result in this region. Schwan *et al.* (1996) assigned the D-band at 1355 cm^{-1} to benzene or condensed benzene rings in amorphous carbon.

Li *et al.* (2006) suggested that aromatics with a ring size of no less than 6 fused benzene rings gave peaks close to the D-band (Fig. 3, 4). Aromatics having 6 or more fused benzene rings but less than in graphite, will contribute to the observed D band in the Raman spectrum. D band will disappear as an infinite sized aromatic network such as the single graphite structure is formed (Tuinstra and Koenig, 1970; Li *et al.*, 2006). In the present study, the sample is showing weak but defined absorption in this region. This showed the

presence of fused benzene rings in the sample. This absorption was stronger for bituminous coal than sub-bituminous coal. This indicated that aromaticity increased with rank of the coal. With leaching, the absorption of this band marginally increased.

Very recent studies conducted by Guedes *et al.* (2010) reported narrowing of G band with increase in rank of coal. They also reported shift of D-band to lower wave number with increase of rank of coal. In the present study, authors observed narrowing of G-band in bituminous coal compared to sub-bituminous coal. But surprisingly with HF leaching, the doublet observed in sub-bituminous coal reduced to a singlet where as in bituminous coal, this band became in to two defined peak at 1580 and 1605 cm^{-1} along with increase of intensity.

Nemanich and Solin (1979) assigned a peak at 1490 cm^{-1} as semi-circle ring stretch or condensed benzene rings or contribution from the phonon density of states in finite crystal of graphite. Li *et al.* (2006) assigned three bands at 1540, 1465 and 1380 cm^{-1} to G_R band (standing for G right) V_R band (standing for valley right) and V_L band (standing for Valley left) respectively for the Victorian brown coal. Jelicka *et al.* (2006) assigned the band at 1550 cm^{-1} to the asymmetric stretch of the COO- units and the bands at 1468 and 1386 cm^{-1} to the symmetric modes from the same COO- groups. They assigned the band at 1676 cm^{-1} due to the acid COOH group C=O function. In the present study, Indian sub-bituminous coal had moderate absorption at 1540 and 1465 cm^{-1} compared to bituminous coal. These bands could represent aromatic ring systems typically found in amorphous carbon materials. A significant difference between the Raman spectra of sub-bituminous coal and bituminous coal was seen in this region. It was more prominent in sub-bituminous coal than bituminous coal. In sub-bituminous coal peaks correspond to COOH groups were present and with HF leaching its intensity was reduced drastically. Presences of oxygenated functional groups are normally more in low rank coals. In bituminous coal, may of this band did not show any change with leaching. The spikes observed in the bituminous coal were mainly due to graphite structure than carbonyl groups.

Li *et al.* (2006) assigned band at 1700 cm^{-1} to carbonyl (C=O) structure in the coal. This band was moderate in sub-bituminous coal in the present study. Starsinic *et al.* (1984) assigned the band at 1695 cm^{-1} to carbonyl groups, possibly ketones. The relatively strong band near 1695 cm^{-1} was attributed predominantly to carboxylic acid and a relatively weak band at 1670 cm^{-1} was assigned to ketonic structures. In the spectrum, sub-bituminous coal was having higher absorption than bituminous coal in the carboxylic region. It was clear that the samples having higher oxygen content have intense absorption band at 1695 cm^{-1} compared to samples having lower oxygen content.

CONCLUSIONS

FT Raman spectroscopy study of coal revealed the presence of more oxygenated functional groups along with graphite structure. Intense band for kaolinite was found at 601 and 569 cm^{-1} . The band had also been attributed to carbonyl group. The band at 570 cm^{-1} was changed to lower wavelength of 561 cm^{-1} with HF leaching. The band at 602 cm^{-1} was also lowered with leaching. The bands at 704, 752 and 785 were assigned for kaolinite; 703, 744 and 792 for halloysite and 744 and 794 cm^{-1} for dickite to the Al-OH vibrations of surface hydroxyls. These bands were resolved in the Raman spectra but of less intensity. Thus the intense infrared bands at 1014, 1030 and 1090 cm^{-1} for kaolinite were attributed to the perpendicular Si-O vibrations. These bands were weak in Raman but were observable as small spikes with maximum intensity at 1090 cm^{-1} . The Raman spectra of sub-

bitumionous coal sample had two very broad bands at around 1580-1602 cm^{-1} and this was due to the presence of Graphite structure and the doublet disappeared to a singlet of almost the same intensity with leaching. Where as in the bituminous coal these two bands were originally weak but become well defined absorption spikes with HF leaching. This indicated that with increase of coal rank the graphite band becomes weaker but with leaching the absorption becomes stronger. There are small spikes observed at 1300-1350 cm^{-1} due to Defect bands. This band was comparatively stronger in bituminous coal than sub-bituminous coal and showing a shift to lower wavenumber and intensity with leaching. The D-band at 1355 cm^{-1} was due to benzene or condensed benzene rings in amorphous carbon. Indian sub-bituminous coal had moderate absorption at 1520 and 1500 cm^{-1} compared to bituminous coal. In the spectrum, sub-bituminous coal was having higher absorption than bituminous coal in the carboxylic region. It was clear that the samples having higher oxygen content had intense absorption band at 1695 cm^{-1} compared to samples having lower oxygen content.

REFERENCES

- Friedel, R.A. and G.L. Carlson, 1972. Difficult carbonaceous materials and their infrared and Raman spectra- Reassignment for coal spectra. *Fuel*, 51: 194-198.
- Frost, R.L., J.R. Bartlett and P.M. Fredericks, 1993. Fourier transform Raman spectra of kandite clays. *Spectrochimica Acta A: Mol. Spectroscopy*, 49A: 667-674.
- Guedes, A., B. Valentim, S. Prieto, S. Rodrigues and F. Noronha, 2010. Micro-Raman spectroscopy of collotelinite, fusinite and macrinit. *Int. J. Coal Geol.*, 10.1016/j.coal.2010.06.002
- Ishii, M., T. Shimanouchi and M. Nakahira, 1967. Far infrared absorption of layer silicates. *Inorganica Chim. Acta*, 1: 387-392.
- Jelicka, J., H.G.M. Edwards and S.E.J. Villar, 2006. Raman spectroscopic study of mellite- A naturally occurring aluminium benzenehexacarboxylate from lignite-Claystone series of the tertiary age. *Spectrochimica Acta Part A.*, 65: 229-234.
- Johnson, C.A., J.W. Patrick and K.M. Thomas, 1986. Characterization of coal chars by Raman spectroscopy, X-ray diffraction and reflectance measurements. *Fuel*, 65: 1284-1290.
- Li, X., J. Hayashi and C.Z. Li-Fuel, 2006. FT-Raman spectroscopic study of the evolution of char structure during the pyrolysis of a Victorian brown coal. *Fuel*, 85: 1700-1707.
- Nemanich, R.J. and S.A. Solin, 1979. First and second order Raman scattering from finite-size crystals of graphite. *Phys. Rev. B.*, 20: 392-401.
- Schwan, J., S. Ulrich, V. Batori, H. Enhardt and S.R.P. Silva, 1996. Raman spectroscopy on amorphous carbon films. *J. Applied Physics.*, 80: 440-447.
- Starsinic, M., Y. Otake, Jr. P.L. Walker, P.C. Painter-Fuel, 1984. Application of FT-i.r. spectroscopy for COOH groups in coal. *Fuel*, 63: 1002-1007.
- Tuinstra, F. and J.L. Koenig, 1970. Raman spectrum of graphite. *J. Chem. Phys.*, 53: 1126-1130.
- Wang, Y., D.C. Alsmeyer and R.L. McCreery, 1990. Raman spectroscopy of carbon materials: Structural basis of observed spectra. *Chem. Mater.*, 2: 557-563.