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NEUTRAL BENZ [A] PYRENE AND ITS RADICAL ION IN SOLID FILMS BY INFRARED SPECTROSCOPY

*Md Naziruddin Khan[1] and AS Al Dwayyan[2]
[1]King Abdullah Institute for Nanotechnology, King Saud University, Riyadh
[2]Department of Physics and Astronomy, College of Science, King Saud University
PO Box-2455, Riyadh-14511, KSA

ABSTRACT

The infrared spectra in the region 2000-400 cm^{-1}of benz [a] pyrene ($C_{20}H_{12}$) molecule and its radical ion doped in wax film are being discussed here. The harmonic frequencies and relative intensities of benz[a]pyrene molecule and cation obtained experimentally are compared to theoretically calculated values by density functional theory (DFT). The matrix effect, presence of some additional bands in wax film compared to Ar matrix spectra and the shifting of bands in the spectrum of cation are explicitly discussed. Excellent agreement in the spectral positions and strengths among experimental, DFT and in Ar matrix are observed.

Keywords: FTIR, PAH, wax films, DFT.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) form an important class of organic molecules which are prevalent in our surrounding. PAHs, some of which can undergo metabolic conversion to carcinogens, are widely dispersed in the environment, often in small quantities. There are many PAH derivatives which intensely fluorescent (Dwayyan *et al*., 2008; Khan, 2008). These molecules are currently of considerable practical interest since they are widely spread in the environment and are often harmful. Many PAHs belonging to the class of potentical carcinogenic aromatic (National Academy of Science, 1972) compounds are found in various environmental sources such as air, petroleum products, water and food etc Yurum (1988). PAHs are also one of the major classes of molecular species found in the interstellar medium (ISM) (Allamandola *et al*., 1989). Neutral and ionized PAH molecules are proposed as the carriers of a very common family of interstellar infrared fluorescence bands (Finlayson and Pitts, 1986; Allamandola *et al*., 1999; Hudgins, 2002).

Benz [a] pyrene/B[a]P is one of the most powerful cancer-producing parents. It is the first pure compound to be isolated and synthesized, and is subsequently found to be strongly carcinogenic in animals (Mahanama *et al*., 1994). Recently, a large number of PAHs, (Langhoff, 1996) their cation and anion are studied theoretically in view of astrophysical problems. Further, using matrix isolated technique, IR studied of some neutral PAHs from small to large size is reported (Hudgins and Sanford, 1998; Mottioda *et al*., 2003).

Since B[a]P is a strong carcinogen, the electronic spectra of B[a]P has been investigated by several workers (Birks, 1970; Pancir and Zahradnik, 1973; Yamaguchi *et al*., 1980) with different view points. Since B[a]P is an important contributor for interstellar infrared emission bands, the study of the vibrational spectroscopic properties of this molecule is very important. For last few years we have studied some PAHs by Photoacoustic Spectroscopy (Kumar *et al*., 1997; Garg *et al*., 1998) and UV-Visible Spectroscopy (Jain and Zaidi, 1988; Sharma *et al*., 1991). Recently, we have reported the Photoacoustic study of B[a] P in solid matrix (Garg and Zaidi, 1999). The electronic transitions are assigned as non-radiative transition with the help of MNDO/CNDO calculated values. We have also reported the vibrational spectra of anthracene and phenanthrene in solid wax matrix (Khan *et al*., 2002). Also, infrared spectra of bezantharacnce and chrysene molecule in wax film (Khan *et al*., 2006). Further, our group reported on pyrene in solid matrix (Khan *et al*., 2003). The results was analysed with theoretical values obtained by DFT. In continuation with above, here an attempt is made to have a detailed mid-infrared spectroscopic analysis of B[a]P molecule and radical ion in solid wax film. The measurement is made within the range of 2000-400 cm^{-1}.

EXPERIMENTAL DETAILS

We have adapted the technique developed by Peterkin (1971) for far-IR studies of powders for our mid-IR studies of PAHs. In his studies, Peterkin employed the technique of cold pressing and finely divided samples in a wax matrix having high melting point. This matrix does not have any absorption in the far-IR spectral range (40-400 cm^{-1}).

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*Corresponding author email: mnkhan_phy@yahoo.com

About 10g of wax or equivalent is placed in a 2 oz covered can. The whole is emerged in liquid nitrogen for several minutes, and then removed using an insulating material and vigorously hand – shaken for 20 second. The resulting powder is then shifted through a 20-mesh screen (or finer if desired) and kept at moderate to cool temperature until used. An appropriate amount of sample is placed in a stopper vial along with sufficient powdered wax to give the required thickness of final disk. The mixture should be well shaken to obtain a uniform sample. For the studies reported here, instead of cold-pressing the resultant finely-divided powder mixture, the fine mixture was heated into a furnace up to 70 ^{0}C at which temperature it melted. After 15-20 minutes, the PAH was homogeneously dissolved in the wax and the molten mixture was quickly cast between the two glass plates spaced about 0.1-0.5 mm apart. After cooling to the room temperature, the formed a very thin transparent film and was removed from glass plates. The wax matrix is almost transparent over the 2000-400 cm^{-1} spectral region. The transparent region of wax film in infrared is shown in figure 1.

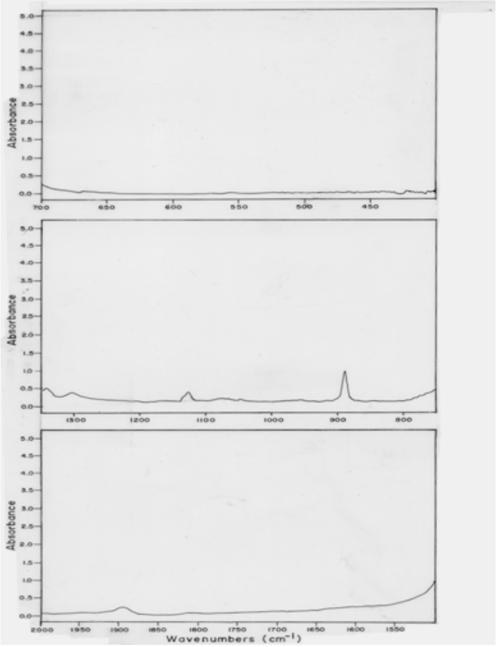

Fig. 1. The infrared spectrum of wax film in 2000-400 cm^{-1}.

Benz [a] pyrene was obtained from M/S Fluka AG (Switzerland) and solid wax was obtained from M/S Central Drug House (P) Ltd (India). An FT-IR spectrometer (Nicolet Instrument Corporation, USA. Model 410-IMPACT) was used to record the spectra of the sample. Radical ions of B[a]P were made after continuous exposure by UV radiation about 18hrs. A high-pressure mercury lamp 250W was used as a source of UV radiation. The glass envelope of the lamp was removed. Mid-Infrared spectra (2000-400 cm^{-1}) were collected using a DTGS detector/KBr beam splitter combination. All spectra reported here were measured at 1 cm^{-1} resolution.

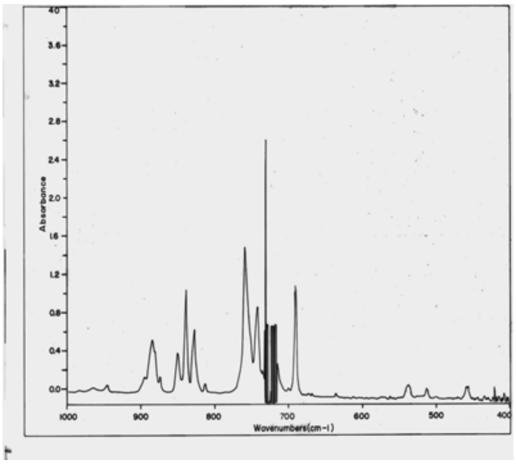

Fig. 2. Infrared spectrum of neutral benz [a] pyrene in 1000-400 cm^{-1}.

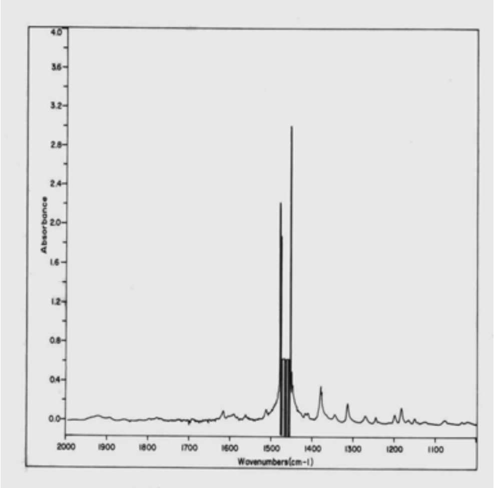

Fig. 3. Infrared spectrum of neutral benz [a] pyrene in 2000-1000 cm^{-1}.

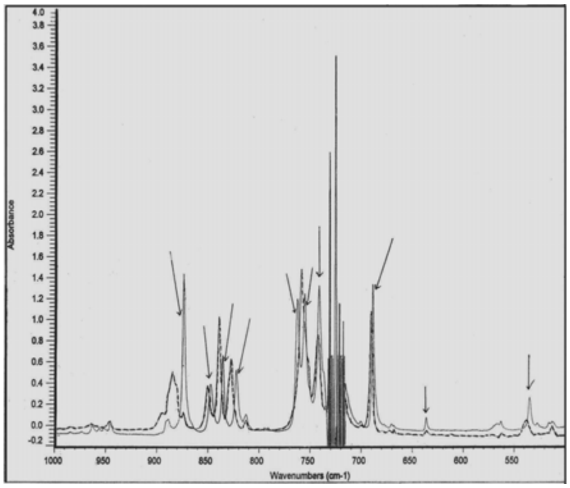

Fig. 4. Infrared spectrum of cation benz [a] pyrene in 1000-400 cm^{-1}.

Table 1. Infrared frequencies and relative intensities of neutral B[a]P.

Wax film	DFT (B3LYP/4-31G)[Bauschlicher]			Argon matrix	
Freq. cm^{-1}	Rel. int.	Freq. cm^{-1}	Rel. int.	Freq. cm^{-1}	Rel. int.
456.9	(0.08)	458.2	(0.05)		
512.1	(0.05)	515.3	(0.08)	512.5	(0.12)
-	-	524.9	(0.02)	527.1	(0.05)
537.2	(0.07)	535.2	(0.07)	534.9	(0.11)
560.0		(0.01)	568.7	(0.01)	
635.2	(0.01)	640.7	(0.09)	636.1	(0.09)
690.0	(0.75)	689.3	(0.24)	691.5	(0.34)
714.8	(0.16)	700.3	(0.02)	701.4	(0.03)
741.8	(0.55)	742.5	(0.30)	741.7	(0.34)
749.9	(0.24)	749.5	(0.05)		
758.3	(1.00)	758.7	(1.00)	760.9	(1.00)
-	-	760	(0.01)		
812.8	(0.04)	813.3	(0.10)	814.1	(0.13)
827.2	(0.30)			827.4	(0.34)
838.7	(0.72)	834.6	(0.89)	839.9	(0.17)
849.9	(0.25)	852.8	(0.35)	850.9	(0.30)
873.8	(0.09)	889.4	(0.03)	-	-
884.2	(0.36)	892.6	(0.48)	882.2	(0.45)
894.5	(0.09)	902.6	(0.24)	891.0	(0.03)
945.6	(0.04)	946.3	(0.05)	945.7	(0.02)
964.3	(0.01)	962.1	(0.01)		
1002.0	(0.01)	971.5	(0.01)		
1022.0	(0.01)	1019.4	(0.34)	1024.1	(0.04)
1035.0	(0.01)	1035.0	(0.04)	1038.4	(0.04)
1075.9	(0.01)	1077.7	(0.29)	1081.5	(0.02)
1149.8	(0.02)	1156.8	(0.02)	1150.9	(0.03)
-	-	1166.9	(0.02)	1165.6	(0.03)
1181.9	(0.08)	1180.6	(0.02)	1183.5	(0.16)
1198.5	(0.05)	1188.6	(0.15)	1194.9	(0.07)
-	-	-	-	1202.0	(0.05)
1245.1	(0.02)	1244.7	(0.01)	1239.6	(0.01)
-	-	1251.3	(0.07)	1246.0	(0.06)
1271.3	(0.02)	1275.3	(0.11)	1271.6	(0.08)
1312.8	(0.11)	1311.0	(0.02)	1315.3	(0.06)
1343.6	(0.02)	1340.6	(0.08)	1346.3	(0.02)
1376.5, 1378.0	(0.19)	1365.4	(0.011)	1388.9	(0.02)
1408.5	(0.02)	1402.0	(0.09)	1411.2	(0.07)
1416.1	-	(0.02)		1415.6	(0.02)
1420.6	(0.06)	1419.5	(0.09)		
				1429.5	(0.02)
1450.1	(0.18)	1453.6	(0.05)	1460.1	(0.03)
1475.2	(0.24)	1467.8	(0.03)	1467.3	(0.03)
1478.9	(0.08)	1488.0	(0.12)	1479.3	(0.04)
1512.3	(0.27)	1508.9	(0.07)	1498.5	(0.08)
				1516.1	(0.06)
1550.9	(0.04)				
1560.6	(0.01)	1566.5	(0.05)	1567.0	(0.06)
1586.7	(0.08)				
1590.0	(0.02)	1591.2	(0.04)	1592.8	(0.07)
1615.4	(0.04)	1618.7	(0.06)		

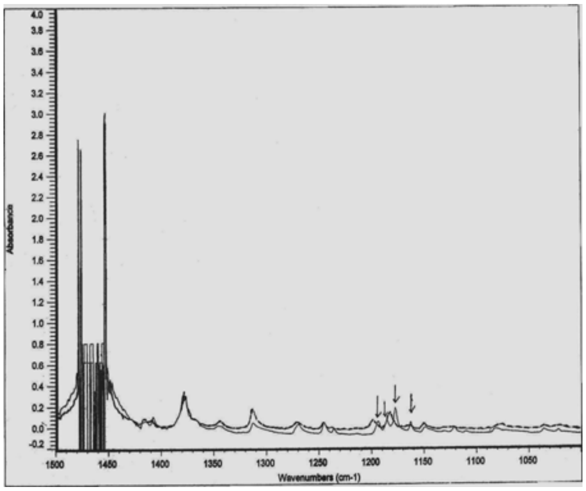

Fig. 5. Infrared spectrum of cation benz [a] pyrene in 1500-1000 cm^{-1}.

RESULTS AND DISCUSSION

The 2000-400 cm^{-1} infrared spectrum of B[a]P molecule in solid film is shown in figures 2 and 3. The frequency positions and relative strengths of the absorption bands are listed in table 1 and are compared with the theoretical values obtained by DFT method, and experimental data of Ar matrix. In general, the assignments are in good agreement with the theoretical values and also with the experimental results in Ar matrix. The most intense band of B[a]P molecule observes at 758.3 cm^{-1} is close to the predicted value 758.7 cm^{-1} . The observe band at 456.9 cm^{-1} in wax film is in close match with theoretical result 458.2 cm^{-1} . This band is not observed in Ar matrix. Majority of observed bands in 700-400cm^{-1}are agreed to theoretical predicted and Ar data. The additional band in film at 560.0 cm^{-1} in accordance with the predicted value at 568.7 cm^{-1}. In few cases, the relative intensities of two bands in both experiments appear in greater than theory i.e. 690.0, 741.8 (film), 691.5, 741.7 cm^{-1} (Ar) respectively. Two more bands in Ar at 527.1 cm^{-1} and 749.5 cm^{-1} are in accordance with the theoretical values at 524.9 cm^{-1} and 749.9 cm^{-1}, relative intensities of both bands are greater of predicted values. Mostly stronger bands of the B[a]P fall in C—H out of plane and C— C in plane bending region. A band in both the experiments appearing at 827 cm^{-1}, is not being predicted theoretically. The observed bands e.g. 873.8, 964.3 and 1002.0 cm^{-1} are additional in films which are in accordance with theoretical values. This may be due to the effect of interaction between the molecule and inert matrix. Most of the observed bands in the 1020-1200 cm^{-1} region basically are weak, some of them are found stronger in theory. Few bands of experiments in the1200-1400 cm^{-1} are different with theory values but their positions fall in close match. In general, the experimental results are found to be in close accordance with the predicted theoretical results.

The cation spectra of B[a]P are shown in figs. 4 and 5. The comparison of the band positions and their relative intensities between the experimental results and theoretical values, are systematically listed in table 2. The dotted line and the hard line in the spectra are indicated as neutral and cation respectively. Arrows in the figures are indicating all the cation spectra observed after exposure in UV light. Most of observed band positions of cation are in

Table. 2. Infrared frequencies and relative intensities of B[a]P cation.

Wax film Freq. (cm^{-1})	Rel. int.	DFT[Bauschlicher]		Argon matrix	
		Freq. (cm^{-1})	Rel. int.	Freq. (cm^{-1})	Rel. int.
534.3	(0.17)				
562.3	(0.04)	564.5	(0.14)		
688.2	(0.81)	688.2	(0.50)	685.2	(0.13)
741.0	(0.95)	756.5	(0.35)	747.2	(0.13)
755.0	(0.89)	758.7	(0.01)	755.2	(0.88)
762.1	(0.85)	763.4	(0.04)		
821.9	(0.35)	812.3	(0.02)	813	(0.09)
835.1	(0.40)	848.6	(0.36)		
847.0	(0.25)	848.6	(0.36)		
873.5	(1.00)	873.8	(0.07)	868.6	(0.08)
888.4	(0.05)				
		915.5	(0.15)	912.3	(0.17)
		933.8	(0.01)		
962.8	(0.04)	969.1	(0.01)		
		982.5	(0.04)	992.6	(0.08)
		1041.7	(0.02)		
1162.3	(0.05)	1154.7	(0.10)		
1176.8	(0.16)	1176.3	(0.05)		
1184.9	(0.07)	1188.7	(0.02)		
1193.2	(0.05)	1193.2	(0.15)		

accordance with the theory values. Among the cation bands, few are new and most of the neutral bands shift towards the higher frequency regions. In general, stronger cation spectra fall in C—C in plane bend and C—H out of plane bend region namely 688.2, 741.0, 755, 821.9 and 873.5 cm^{-1}. Some weak bands observed in C—H in plane bend regions. The mismatch in their band strengths between the theory and Ar cation are same also being observed in the spectra of cation doped in wax film.

CONCLUSIONS

Mid infrared spectra of neutral B[a]P and radical ions are measured in solid wax film in 2000-400 cm^{-1}. Wax film is an excellent matrix for the infrared study of PAHs in the 2000-400 cm^{-1} spectral region. Some new bands in the spectra of cation are observed in film, which are found to be in accordance with the DFT values. The experimental results are in good agreement with the theoretical values and the experimental Ar phase spectra.

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REFERENCES

Allamandola, LJ., Tielens, AGGM. and Barker, JR. 1989. Intersteller Polycyclic Aromatic Hydrocarbons: the Infrared Emission Bands, the Excitation-Emission Mechanism and the Astrophysical Implications. Astrophysical J. Suppl. Series. 71:733-775.

Allamandola, LJ., Hudgins, DM. and Sanford, SA. 1999. Modeling the Unidentified Emission with Combinations of Polycyclic Aromatic Hydrocarbons, Astrophys. J. 511:L115-L119.

Birks, JB. 1970. Photophysics of Aromatic Molecules, Wily Interscience London and New York.

Dwayyan, AS., Khan, MN., Algamdi, AA. and Deyeb, SS. 2008. Effect of DCCA on the optical and lasing properties of dye doped silica gels/ormosils. Canadian Journal of pure & applied sciencies. 2(1):221-226.

Finlayson-Pitts, BJ. And Pitts, JN Jr. 1986. Atmospheric Chemistry: Fundamentals and Experimental Techniques; Wiley & Sons, New York.

Garg, RK., Kumar, P., Ram, RS. and Zaidi, ZH. 1998. Photoacoustic Spectrsocopic Studies of mono substituted naphthalene molecules. Spectroscopy letters. 31(5):1013-1023.

Garg, RK. and Zaidi, ZH. 1999. Some carcinogenic polycyclic aromatic hydrocarbons by photoacoustic spectroscopy, SPIE Proceeding. 3853:82-86.

Hudgins, DM. and Sandford, SA. 1998. Infrared Spectroscopy of Matrix-Isolated Polycyclic Aromatic Hydrocarbons 1. PAHs containing 2 to 4 Rings, J. Phys. Chem. 102:329-343.

Hudgins, DM. 2002. Interstellar polycyclic Aromatic Compounds and Astrophysics. Polycyclic Aromatic Compounds. 22:469-488.

Jain, VK. and Zaidi, ZH. 1988. A re-Investigation of the electronic spectrum of perylene. Spectrochemica Acta Part A: Molecular spectroscopy. 44 (11):1159-1163.

Khan, MN., Kumar, P., Patel, BS. and Zaidi ZH. 2002. Infrared spectroscopic studies of PAHs in solid wax films: Anthracence and Phenanthrene, Spectroscopy Letters. 35:489-500.

Khan, MN, Dwayyan, AS. and Zaidi ZH 2006. Infrared spectroscopic Analysis of Chrysene and 12BZ in wax films, Chinese Physics Letters. 23:2407-2410.

Khan, MN. and Dwayyan, AS. 2008. Influence of solvent on the physical and lasing properties of dye-doped sol gel host. Journal of Luminescence. 128:1767-1770.

Khan, MN., Tyagi, A. and Zaidi, ZH. 2003. Studies of pyrene doped in solid wax film by Infrared Spectroscopy. Bulletin of Pure and Applied Science. 22D (2):159-164.

Kumar, J., Garg, RK., Prakash, Om., Ram, RS. and Zaidi, ZH. 1997. Photoacoustic spectroscopic studies of polycyclic aromatic hydrocarbons: Naphthalene cation. Spectroscopy letters. 30:1193-1200.

Langhoff, SR. 1996. Theoretical Infrared Spectra for Polycyclic Aromatic hydrocarbon Neutrals, Cations and Anions. J. Phys. Chem. 100:2819-2841.

Mahanama, KRR., Gundel, LA. and Daisay, JM. 1994. Selective Fluorescence Detection of Polycyclic Aromatic Hydrocarbons in Environmental Tobacco Smoke and Other Airborne Particles. International Journal of Environmental Analytical Chemistry. 56:289-309.

Mattioda, AL., Hudgins, DM., Bauschlicher, CW., Rosi, M. and Allamandola, LJ. 2003. Infrared Spectroscopy of Matrix-Isolated Polycyclic Aromatic Hydrocarbons 6. Polycyclic Aromatic Nitrogen Heterocycles and their cations, J. Phys. Chem. A 107:1486-1498.

National Academy of Sciences, Anonymous, 1972. Particulate polycyclic organic matter. National Academy of Sciences, Washington DC.

Pancir, J. and Zahradnik, R. 1973. Theoretical study of transitions from the first to higher excited singlet states, J. Phys. Chem. 77:121-123.

Peterkin, ME, 1971. Spectroscopic Tricks. Eds: Leopold, M. Plenum Pub. Corp. 3.

Sharma, AK., Jain, VK. and Zaidi, ZH. 1991. Effect of hydroxyl substituents on naphthalene. Acta Physica Hungarica. 70:109-113.

Yamaguchi, H., Tateishi, M and Muraoka, T. 1980. Electronic states of Benzo [a] pyrene. Linear and Magnetic circular Dichroism BaP as determined by X ray crystallography, Spectrochimica Acta A. 36(3):229-231.

Yurum, Y (Ed.). 1988. New Trends in Coal Science; NATO ASI Series, Series C: Mathematical and Physical Sciences; Kluwer Academic Publishers, Dordrecht. No. 244.