Asian Journal of Chemistry Vol. 21, No. 2 (2009), 1419-1424

Vibrational Assignments and Normal Coordinate Analysis of 2-Fluorenyl Methyl Ketone

G. ILANGO†, M. ARIVAZHAGAN*, V. BALACHANDRAN and R. JOHN XAVIER‡
Department of Physics, A.A. Govt. Arts College, Musiri-621 201, India
E-mail: brsbala@rediffmail.com

The FT-IR and FT-Raman spectra of 2-fluorenyl methyl ketone have been recorded. The observed frequencies were assigned to various modes of vibrations on the basis of normal coordinate calculations, assuming C_S point group symmetry. The potential energy distribution associated with normal modes is also reported here. The assignment of fundamental vibrations agrees well with the calculated frequencies.

Key Words: Vibrational spectra, 2-Fluorenyl methyl ketone, Normal coordinate analysis.

INTRODUCTION

Fluorene is one of a group of chemicals called polycyclic aromatic hydrocarbons (PAHs). Polycyclic aromatic hydrocarbons are often found together in groups of two or more. They can exist in over 100 different combinations. Polycyclic aromatic hydrocarbons are found naturally in the environment but they can also be synthesized. Polycyclic aromatic hydrocarbons are solid and range in appearance from colourless to white or pale yellow-green. Polycyclic aromatic hydrocarbons are obtained when products like coal, oil, gas and garbage are burnt. Fluorene is used to make dyes, plastics and pesticides. Fluorene and its derivatives are used in resinous products and dyestuffs[1].

Consideration of these factors motivated to study the vibrational aspects of the derivatives of fluorene. The FTIR and FT-Raman spectra of 2-fluorenyl methyl ketone are recorded and a complete vibrational analysis is proposed for the better understanding of physical and chemical properties of 2-fluorenyl methyl ketone.

Structural parameters and symmetry: The molecular structure of 2-fluorenyl methyl ketone is shown in Fig. 1. The molecule is assumed to have a C_S point group symmetry. The 28 atoms in 2-fluorenyl methyl ketone give rise to 78 normal modes of vibrations. These vibrations are distributed into 53a′ and 25a″ species, where a′ and a″ represents the in-plane and out-of-plane vibrations respectively. Since, the molecules are possessing a low symmetry the spectra will be more complex and hence, the interpretation of the spectral data is difficult.

---

†Department of Physics, MAM College of Engineering, Tiruchirappalli-621 105, India.
‡Department of Physics, H.H. Rajah's Govt. Arts College, Pudukkottai-622 001, India.

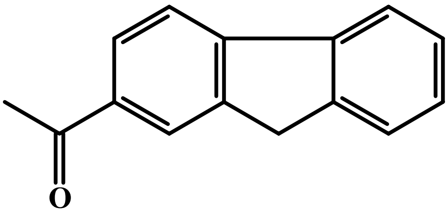

Fig. 1. Structure of 2-fluorenyl methyl ketone

EXPERIMENTAL

The reliability of the results of normal coordinate analysis depends on the availability of spectral data like frequencies. Spectral data of high precision can be obtained for the sample using the sophisticated spectroscopic equipments. With the advent of powerful monochromatic laser sources and photoelectric recording in both Raman and infrared instruments, spectra can be recorded in a short interval of time.

Pure sample of 2-fluorenyl methyl ketone in polycrystalline form was obtained from Lancaster Chemical Company, UK and was used as such without any purification. The Fourier transform infrared spectra of this molecule was recorded on Perkin-Elmer FT-IR model 1600 spectrophotometer in the region 4000-400 cm^{-1} and 500-50 cm^{-1} using KBr and polyethylene pellet technique, respectively. The FT-Raman spectra of the title compound as recorded on Bruker IFS 66V FT-IR spectrophotometer with FRA 106 FT-Raman attachment. The Nd:YAG laser operating at 200 mW power with 1064 nm excitation was used as source. The resolution of the recorded spectra is ± 1 cm^{-1}. The observed FTIR and FT-Raman spectral band of the 2-fluorenyl methyl ketone are given in Table-2.

RESULTS AND DISCUSSION

Force constants: The compound chosen in this study is highly complex and hence, difficult to estimate the values of various forces involved between various bonds. However, with the help of sophisticated softwares[2,3] for normal coordinate analysis of these complex systems are solved and the best fit force constants based on general valance force field (GVFF) are listed in Table-1.

The values of the force constants f_q and f_s are found to be 8.9011 m dyne Å^{-1} between carbon and oxygen for 2-fluorenyl methyl ketone. These values are in good agreement with the characteristic values of double bonded regions between the respective atoms. But, in the values of f_p between carbon and carbon for present compound are found to be 5.1896 m dyne Å^{-1}. These values suggests that these carbon atoms are involved in resonance hybridization and hence the values are in between the π and σ bonds. The interaction force constants are slowly introduced in the force constants refinement process in order to minimise the difference between the observed and calculated frequencies. Moreover, the computation of interaction

TABLE-1
POTENTIAL ENERGY CONSTANTS OF 2-FLUORENYL METHYL KETONE
(In the units of m dyne Å^{-1}, m dyne rad^{-1} and m dyne Å^{-1} rad^{-2})

Types of constants	Parameters	Coordinates involved	Values of 2-fluorenyl methyl ketone
Diagonal constant			
Stretching	f_D	C-H	5.0421
	f_d	C-C	3.2917
	f_p	C=C	5.1896
	f_q	C=O	8.9011
Bending	f_α	CCC	1.3715
	f_β	CCH	1.2154
	f_γ	CCO	0.9657
	f_σ	CCC	0.6314
Interaction constants			
Stretch-stretch	f_{Dd}	CH CC	0.6440
	f_{dp}	CC CC	-0.5431
	f_{dq}	CC CO	0.3997
	f_{DD}	CH CH	0.2308
	f_{dd}	CC CC	0.1371
Stretch-bend	$f_{d\alpha}$	CC CCC	0.0651
	$f_{D\alpha}$	CH CCC	0.0608
	$f_{q\beta}$	CO CCH	0.0435
	$f_{q\alpha}$	CO CCC	0.0271
Bend-bend	$f_{\alpha\beta}$	CCC CCH	0.0074
	$f_{\alpha\alpha}$	CCC CCC	0.0063
	$f_{\gamma\beta}$	CCO CCH	0.0049
	$f_{\beta\beta}$	CCH CCH	0.0063

force constants CCCO, CCCN stretch-stretch interactions for added to obtain reasonable frequency fit in the double bond region. The negative value of the interaction force constants f_{dp}, suggests that the electrons are delocalized near the bonds.

Vibrational assignments: The observed and calculated frequencies along with the assignments of fundamentals and potential energy distribution for present compound are given in Table-2.

C-H Vibrations: The substituted benzene gives rise to C-H stretching, C-H in-plane bending and C-H out-of-plane bending vibrations. The characteristic frequency of C-H stretching vibrations is around[4] 3100-3000 cm^{-1}. The presence of aromatic type structure is best recognized by the presence of C-H stretching vibrations and C=C vibrations. In these regions the bands are not much affected by the substitution pattern, the nature of the substitution and on the presence of conjugation with the double bonds of the ring. Hence, in this study FTIR and Raman bands appeared

TABLE-2
VIBRATIONAL ASSIGNMENTS OF FUNDAMENTAL FREQUENCIES (cm^{-1}) OF 2-FLUORENYL METHYL KETONE

Species	Observed frequency and intensity		Calculated frequency	Assignments (PED %)
	FTIR	Raman		
a'	3102 w	–	3100	C-H stretching (96)
a'	3090 w	–	3088	C-H stretching (98)
a'	3086 w	–	3084	C-H stretching (94)
a'	3071 w	–	3069	C-H stretching (98)
a'	–	3068 w	3066	C-H stretching (92)
a'	–	3051 w	3049	C-H stretching (94)
a'	3021 w	–	3019	C-H stretching (86)
a'	–	3001 w	2999	C-H stretching (88)
a'	2997 w	2999 w	2995	C-H stretching (90)
a'	2924 w	2925 w	2922	C-H stretching (92)
a'	–	2912 w	2910	C-H stretching (91)
a'	–	2901 w	2890	C-H stretching (89)
a'	1782 w	–	1781	C=O stretching (98)
a'	1677 s	–	1675	C=C stretching (97)
a'	–	1660 s	1658	C=C stretching (89)
a'	1611 vs	–	1609	C=C stretching (86)
a'	1605 ms	–	1603	C=C stretching (88)
a'	1486 w	1485 vw	1482	C-C stretching (97)
a'	1465 w	1466 vw	1462	C-C stretching (92)
a'	1450 ms	–	1447	C-C stretching (91)
a'	–	1430 vw	1427	C-C stretching (93)
–	1422 ms	–	–	CH_3 scissoring
a'	1395 ms	1397 w	1392	C-C stretching (89)
a'	1359 s	1360 w	1356	C-C stretching (90)
a'	1334 w	1335 ms	1331	C-C stretching (89)
a'	–	1302 w	1299	C-C stretching (88)
a'	1291 s	–	1288	C-C stretching (90)
a'	1266 vs	1268 s	1263	C-C stretching (87)
a'	1228 s	–	1225	C-C stretching (82)
a'	1194 w	1192 vw	1187	C-H in-plane bending (75)
a'	–	1180 vw	1173	C-H in-plane bending (74)
a'	1172 w	–	1165	C-H in-plane bending (72)
a'	1157 w	–	1150	C-H in-plane bending (71)
a'	–	1150 vw	1143	C-H in-plane bending (69)
a'	–	1127 w	1120	C-H in-plane bending (68)
a'	1119 w	–	1112	C-H in-plane bending (69)
–	1097 w	–	–	CH_3 rocking
a'	1081 w	–	1071	C-C in-plane bending (66)
a'	–	1068 w	1058	C-C-C trigonal bending (68)
a'	1058 w	–	1048	C-C-C trigonal bending (69)
a'	1049 w	–	1039	C-C-C in-plane bending (70)
a'	–	1035 w	1025	C-C-C in-plane bending (72)
a'	–	1026 w	1016	C-C-C in-plane bending (69)
a'	1017 w	–	1007	C-C-C in-plane bending (68)
a'	1000 w	–	990	C-C-C in-plane bending (65)
a'	–	960 vw	950	C-C-O in-plane bending (70)

Species	Observed frequency and intensity		Calculated frequency	Assignments (PED %)
	FTIR	Raman		
a'	954 ms	–	944	C-C-O in-plane bending (69)
a'	931 vw	–	925	C-C-H in-plane-bending (67)
a'	–	923 vw	917	C-C-H in-plane bending (66)
a'	898 w	–	889	C-C in-plane bending (71)
a'	876 w	–	867	C-C-H in-plane bending (70)
a'	859 w	–	850	C-C in-plane bending (70)
a'	850 vs	–	841	C-C in-plane bending (69)
a'	–	842 w	833	C-C in-plane bending (67)
a'	828 w	–	824	C-C in-plane bending (64)
a"	–	822 vw	816	C-H out-of-plane bending (61)
a"	773 vs	775 vw	767	C-H out-of-plane bending (60)
a"	–	763 ms	757	C-H out-of-plane bending (58)
a"	750 s	–	741	C-C-C out-of-plane bending (57)
a"	741 vw	–	732	C-C-C out-of-plane bending (56)
a"	–	719 vw	710	C-C out-of-plane bending (59)
a"	711 w	–	702	C-C-C out-of-plane bending (58)
a"	686 ms	–	678	Ring out-of-plane bending (58)
a"	678 w	674 w	666	C-C out-of-plane bending (56)
a"	639 vw	–	634	C-H out-of-plane bending (62)
a"	618 s	–	613	C-H out-of-plane bending (56)
a"	609 s	–	–	Skeletal deformation
a"	600 ms	–	592	C-C-C out-of-plane bending (57)
a"	548 vw	547 vw	539	C-C-C out-of-plane bending (56)
–	510 vw	–	–	CH$_3$ torsion
a"	484 w	–	477	C-C-C out-of-plane bending (55)
a"	472 w	–	465	C-C-C out-of-plane bending (56)
a"	460 vw	–	453	C-C-C out-of-plane bending (55)
a"	452 w	–	445	C-C out-of-plane bending (55)
a"	428 w	–	421	C-C out-of-plane bending (54)
a"	414 ms	–	408	C-C-C out-of-plane bending (54)
a"	–	321 vw	316	C-C-H out-of-plane bending (63)
a"	–	301 vw	296	C-C-H out-of-plane bending (62)
a"	258 ms	–	253	C-C-O out-of-plane bending (60)
a"	–	240 vw	235	C-C-O out-of-plane bending (59)
a"	183 vw	–	178	C-C-O out-of-plane bending (58)
a"	164 vw	–	160	C-C-O out-of-plane bending (57)
–	–	114 w	–	NO$_2$ torsion

PED = Potential energy distribution.

between 3102-2901 cm^{-1} in 2-fluorenyl methyl ketone have been designated to C-H stretching vibrations. The in-plane and out-of-plane bending vibrations of C-H group listed in Table-2 are made in analogy with the literature[5,6].

C-C Vibrations: Benzene has two degenerate modes e$_{2g}$ (1596 cm^{-1}) and e$_{1u}$ (1485 cm^{-1}) and two non-degenerate modes b$_{2u}$ (1310 cm^{-1}) and a$_{1g}$ (995 cm^{-1}) due to skeleton stretching of C-C bonds. Bonds between 1650 and 1400 cm^{-1} in derivatives of benzene are assigned to these modes. The actual positions are determined not so much by the nature of the substituents but by the form of substitution around the ring[7]. All the frequencies except that of the ring breathing mode (995 cm^{-1}) remain practically unaffected by substitution. In this study, the FTIR bands observed between 1677-1605 cm^{-1} in 2-fluorenyl methyl ketone are assigned to C=C stretching vibrations. The in-plane and out-of-plane bending vibrations of carbon atoms are found in the respective characteristic region and they are listed in Table-2.

CH_3 Group vibrations: The scissoring, rocking and torsional modes of CH_3 groups of 2-fluorenyl methyl ketone are found at 1422, 1097 and 510 cm^{-1}, respectively. The frequency assigned for CH_3 group vibration in this work are found to be in good agreement with literature values[8,9].

Conclusion

Thus, a complete vibrational assignment of 2-fluorenyl methyl ketone has been carried out using infrared and FT-Raman spectra on the basis of C_S point group symmetry. A good agreement is established between the observed and calculated frequencies for both in-plane and out-of-plane vibrations.

The potential energy distribution (PED) calculations regarding the normal modes of vibration provide a strong support for the frequency assignment on the highly molecules.

REFERENCES

1. M. Jones, Jr, Organic Chemistry, Norton & Company, New York (1997).
2. J. Mink and L.M. Mink, Computer Program System for Vibrational Analysis of Molecules, Erlangan (1983).
3. J.H. Schachtshneider, Vibrational Analysis of Polyatomic Molecules, FORTRAN IV Programmes, Technical Report, Shall Development Company, Emery Ville, California, Vol. 5 and 6 (1964).
4. S. Mohan and V. Ilangovan, *Indian J. Pure & Appl. Phys.*, **32**, 91 (1994).
5. C.N.R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York (1963).
6. R.M. Silverstein, G.C. Bassler and T.C. Morrill, Spectrometric Identification of Organic Compounds, John Wiley & Sons, New York (1991).
7. N. Jaggi and R.M.P. Jaiswal, *Indian J. Pure & Appl. Phys.*, **40**, 385 (2002).
8. V. Krishnakumar, K. Parasuraman and A. Natarajan, *Indian J. Pure & Appl. Phys.*, **35**, 1 (1997).
9. A. Anjaneyulu, Krishnamal and L. Bhatnagar, *Indian J. Pure & Appl. Phys.*, **27**, 75 (1989).

(*Received*: 21 February 2008; *Accepted*: 8 October 2008) AJC-6924