

FT-IR RAMAN STRUCTURE, VIBRATIONAL FREQUENCY ANALYSIS OF FLURO BENZYL CHLORIDE BASED OF DFT METHODCALCULATION

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ABSTRACT: Spectroscopy is a technique that uses the interaction of energy with a sample to perform an analysis. The data that is obtained from spectroscopy is called a spectrum. a spectrum is a plot of the intensity of energy detected versus the wavelength (or) mass or momentum or frequency, etc.

Key Words: FT-IR, FT-Raman, Spectroscopy.

I. INTRODUCTION

Infrared and raman spectroscopic techniques from its early beginning continues to be a complementary fertile research tool in the hands of physicists and chemists. In recent years, Fourier transform (FT) spectroscopy techniques enjoy the advantages over the conventional IR and Raman spectroscopy due to the very intensive developments of FT-IR and FT-Raman spectroscopy and hence attracted much interest by offering some unique features. The ultimate performance of any infrared spectrometer is determined by measuring its signal-to-noise ratio (snr). This is best achieved by ft infrared spectrometers. The improved snr's available with FT-IR makes it to become the instrument of choice for obtaining infrared spectra.

Frequency precision, good spectral subtractions and high resolution are difficult to achieve with conventional Raman spectroscopy. Hence a new technique, in which the Raman module is an accessory to an FT-IR spectrometer, called FT-Raman spectroscopy. FT-IR and FT-Raman technique has been found to be a useful in increasing the spectral sensitivity and thus yielding new information about the atomic or molecular species, or the functional group that exist in the sample.

II. METHODS AND MATERIALS

2.1 Experimental details

The fine sample of fluoro benzyl chloride was obtained from sigma aldrich chemical company, uk, with a stated purity 99% and it was used as such without further purification. The ft-raman spectrum of fluoro benzyl chloride was recorded using 1064mm line of region 3500-100cm⁻¹ on thermo election corporation model nexus spectrometer equipped with ft-raman module accessory. The ft-ir spectrum of the title compound recorder region 400-400cm⁻¹ on perkin-ehlmer spectrometer in kbr pellet.

2.2 Computational details

The combination of vibrational spectra with quantum chemical calculation is effective for understanding the fundamental mode of vibration of the compound. The structural characteristics, stability and energy f the compound under investigation are determined by one parameter (b3) exchange part and the lee-yang -parr (lyp) correlation functional, using 6-31g (d,p) and 6-311 g(d,p) basis sets with gaussian 09 program package. The cartesian representation of the theoretical force constant has been computed as the fully optimized geometry by assuming the molecule belongs to c point group symmetry. The transformation of the force field from cartesian to internal local symmetry coordinates, the scaling, the subsequent normal coordinates analysis (nac) calculation of potential energy distribution (pdes) has been done on a pc with version v7.0-g77 of the molvib program written by sundi

2.3 Molecular Geometry

The molecular structure of fluoro benzyl chloride having cs point group symmetry. The global minimum energy obtained by b3lyp/6-31 g (d,p) and 6-31 + g (d,p) basis sets for respectively. The calculation optimized geometrical parameters obtained in this study for the title compound are compared with the experimental values and presented in table-1.

The detailed description of vibrational modes can be given by means of normal coordinates analysis. For this purpose, the full set of 48 stranded internal coordinates the title compound is presented table-2. From this a non-redundant set of local symmetry coordinates has been constructed by suitable liner combination of internal coordinates following the recommendations of pulay and fogarasi

III. RESULTS AND DISCUSSION

Mullikan atomic charges

1	C	-0.062266
2	C	-0.133401
3	C	-0.498623
4	C	-0.127277

5	C	-0.014113
6	C	-0.093746
7	H	-0.074351
8	H	-0.075340
9	H	-0.049045
10	H	-0.050717
11	F	-0.445392
12	C	-0.564887
13	H	-0.005721
14	H	-0.006728
15	Cl	-0.452545

S.No	Observed frequency(cm^{-1})		Calculation frequency $\nu_i(\text{cm}^{-1})$	Force constant	IR indensity (km mol^{-1})	Raman activity $\text{A}^0 \text{amu}^{-1}$	Assignmet co-ordinates
	FT-IR	FT-Raman					
1.	3228(s)	3218(w)	3241	0.0039	2.2834	5.6749	vCH
2.	3118(ms)	3144(s)	3228	0.0494	2.0241	9.3156	vCH
3.	2942(vw)	2983(s)	3220	0.1987	0.4094	4.0108	vCH
4.	1996(w)	1776(s)	3218	0.2238	2.3111	5.2223	vCH
5.	1908(vw)	1654(vw)	3203	0.1673	3.2520	0.9851	vCH
6.	1872(s)	1478(w)	3146	0.4052	2.3432	0.3202	vCH
7.	1768(vw)	1383(s)	1648	0.4127	1.3975	6.3440	vCH
8.	1718(ms)	1342(ms)	1629	1.1539	2.5483	3.5653	vCH
9.	1692(vw)	1276(s)	1544	1.0270	10.3502	17.8425	vCC
10.	1660(vs)	1238(ms)	1534	1.3909	63.8793	46.8497	vCC
11.	1644(vs)	1172(s)	1495	1.2744	25.6920	23.6594	vCC
12.	1628(s)	1090(vw)	1364	0.5938	46.1349	2.5858	vCC
13.	1493(vs)	1032(vs)	1335	2.0308	15.2915	10.5365	vCC
14.	1478(s)	988(w)	1329	0.6145	25.5080	2.7113	bHCH
15.	1415(vs)	944(vw)	1277	0.7373	0.5236	4.2357	bCH
16.	1388(s)	878(w)	1230	0.8258	12.7249	2.3557	bCH
17.	1362(vs)	792(vw)	1194	0.7884	11.0445	1.9906	bCH
18.	1324(vs)	744(s)	1170	1.7110	8.5229	11.3372	bCH
19.	1292(vw)	676(s)	1116	0.8755	1.1374	0.8954	bCH
20.	1283(s)	642(vs)	1039	3.8767	1.2513	28.3029	bCH
21.	1242(vs)	621(s)	1031	1.2291	3.0206	5.4868	vCF
22.	1182(s)	604(vw)	979	0.9175	0.4657	7.5422	r-trigid
23.	1176(vw)	593(ms)	953	1.5824	14.9181	34.3242	r-symd
24.	1134(s)	564(s)	941	1.0717	2.2118	4.6118	r-asymd
25.	980(vs)	532(ms)	895	1.1144	37.8514	51.3343	bClCH
26.	918(ms)	478(vw)	831	4.3857	54.4214	41.9262	π CF
27.	882(s)	453(ms)	768	5.1194	5.0491	7.5531	λ CH
28.	848(vw)	432(vw)	732	1.5748	2.6970	0.3722	λ CH
29.	773(vs)	392(w)	674	3.8990	18.2026	3.1228	λ CH
30.	738(vs)	324(ms)	583	1.6470	13.1707	10.8094	λ CH
31.	712(vs)	298(ms)	545	2.8763	24.8113	3.9830	t-rigid
32.	694(s)	263(s)	539	8.4527	19.7757	41.3879	t-symd
33.	683(vw)	244(vw)	469	8.6292	49.2295	44.3350	t-asymd
34.	642(s)	212(vw)	434	6.1577	7.1452	83.4525	vecl
35.	576(vs)	191(s)	291	6.5732	2.2342	42.4379	vecl
36.	482(s)	184(ms)	265	6.7437	0.7818	58.9229	bccl
37.	432(vw)	164(s)	251	6.7179	7.5820	63.7348	t-rigid
38.	396(vw)	144(w)	102	6.6994	0.4902	80.0839	t-symd
39.	322(s)	132(w)	33	6.7937	6.7697	1.6631	t-asymd

Table: FT-IR, FT- Raman DFT structure, vibrational frequency analysis of fluro Benzyl chloride

3.1 Vibrational assignment

The title of compound belongs to c_s symmetry, consists of 14 atoms and its 39 normal modes which are distributed amongst the symmetry species $3n-6=22 a'$ (in-plane bending) + $8 a''$ (out plane bending). The detailed vibrational assignments of fundamental modes of fluoro benzyl chloride along with observed and calculated frequencies, Raman activity, force constant, infrared intensities, and normal mode description are in table.

3.2 C-H vibrations

C-H vibrations the fluoro benzyl chloride gives rise to the six C-H stretching, four C-H inplane-bending and four out-plane-bending vibrations corresponding to $C_2-H_7, C_4-H_8, C_5-H_9, C_6-H_{10}$ and fluoro benzyl chloride. The C-H stretching frequency is normally lies between 3228 and 2983cm^{-1} . In this region, the bands are not affected appreciably by the nature of substituent. Hence in our present study, the FT-IR bands observed at $3228, 3118\text{cm}^{-1}$ are assigned to C-H stretching vibrations and the counter part FT-Raman observed at 3241 , and 3144cm^{-1} . The c-h in-plane bending vibrations are usually expected to occur in the region $1400-2000\text{cm}^{-1}$ and these vibrations are very useful for characterization purpose.

Hence, in our present investigation, the FT-IR bands observed at 1478 and 1032cm^{-1} are assigned as C-H in-plane bending vibration, the same vibrations. The frequencies of the C-H out-of plane bending vibrations which occur in the region $1000-700\text{cm}^{-1}$ are mainly determined by the number of adjacent by the nature of substitutions normally. The experimentally observed wave number which was also confirmed by the ped.

3.3 C-C vibrations

The ring C-C stretching usually vibrations, know as semi-circular stretching usually occur in the region $1380-1280$ and $1600-1238\text{cm}^{-1}$ respectively. The C-C stretching vibrations of fluoro benzyl chloride are observed at 1644 and 1172cm^{-1} in the FT-IR spectrum and FT-Raman spectrum. In accordance with above literature data in our present study, the bands for c-c stretching vibrations are observed at $1654, 1776$ and 2983cm^{-1} spectrum. These observed frequencies show that the substitutions in the ring to some extent about the mode of vibrations. The comparison of the theoretically computed values are to be in good agreement with theoretical values obtained by b3lyp method.

3.4 C-Cl vibrations

The C-Cl stretching vibrations, generally, give strong band in the region $600-800\text{cm}^{-1}$. The vibrational coupling with other groups may result in the absorption to as high as 878cm^{-1} . Based on this, the ft-raman band 564cm^{-1} has been assigned to cl stretching vibration which was also confirmed by the ped.

3.5 C-F vibrations

The C-F stretching vibrations, generally, give strong band in the region $1000-1400\text{cm}^{-1}$. The vibrational coupling with other groups may result in the absorption to as high as 988cm^{-1} . Based on this, the FT-Raman band 642cm^{-1} has been assigned to cl stretching vibration which was also confirmed by the ped.

3.6 Mulliken atomic charges

The bonding capability of a molecule depends on the electronic charges on the chelating atoms. The atomic charges values have been obtained by the mulliken population analysis. To the reliability of our results, the mulliken population analysis of fluoro benzyl chloride has been calculated using b3lyp/6-31+g(d,p) and b3lyp/6-31g+(d,p) basis sets.

IV. CONCLUSION

The vibrational properties of fluoro benzyl chloride have investigated by FTIR and FT-Raman spectroscopies and were based on DFT calculation at the b3lyp/6-31+g(d,p) level. The assignments of the most of the fundamentals of the title compound provided in this work are quite comparable and unambiguous. The close agreements obtained between calculated. The observed frequencies, the results confirm the ability of the methodology applied for interpretation of the vibrational spectra of the title compound in the solid phase. The frequencies calculated with b3lyp/6-31+g(d,p) method which are in a better agreement with the experimental ones are superior to those calculated with b3lyp/6-31+g(d,p) method.

REFERENCES

- [1] Smekal, the quantum theory of dispersion, naturwissenschaften, 11, 873 (1923).
- [2] Compton, a quantum theory of the scattering of x-rays by light element physics
- [3] C.v. Raman and k.s. Krishnan, the optical analog of the compton effect, 121, 711 (1928)
- [4] G. Landsberg and I. Mandelstam, a novel effect of light scattering in crystals, naturwissenschaften, 16, 557 (1928).
- [5] C.v. Raman and k.s. Khrishnan, the production of new radiations by light scattering, proc. Roy. Soc. (London), 122, 23, (1929).
- [6] R.n. Jones, analytical applications of vibrational spectroscopy? A historical review, european spectroscopy news, 72, 10 (1987).
- [7] H.I. Welsh, m.f. Crawford, t.r. Thomas, and g.r. Love, raman spectroscopy of low-pressure gases and vapors, can. J. Phys., 30, 577 (1952).
- [8] T.h. Maiman, stimulated optical radiation in ruby, nature, 187, 493 (1960).
a. S.p.s. Porto and d.l. Wood, ruby optical maser as a raman source, j. Opt. Soc. Am., 52, 251 (1962).
- [9] T. Hirschfeld and d.b. Chase, ft-raman spectroscopy: development and justification, appl. Spectrosc., 40, 133 (1986).
- [10] W.s. Boyle and g.e. Smith, charge coupled semiconductor devices, bell system tech. J., 49, 587 (1970).
- [11] S.b. Dierker, c.a. Murray, j.d. Legrange and n.e. Schlotter, characterization of order in langmuir-blodgett monolayers by unenhanced raman spectroscopy, chem. Phys. Lett., 137, 453 (1987).
- [12] S.m. Angel, t.f. Cooney, and h.t. Skinner, applications of fiber optics in nir raman spectroscopy, in modern techniques in raman spectroscopy, j.j. Laserna (ed.), wiley, chichester, 1996.

- [13] G.e.f. Lundell, the chemical analysis of things as they are, industrial and engineering chemistry (analytical edition), 5, 221 (1933).
- [14] E.j. Woodbury and w.k. Ng, ruby laser operation in the near ir, proc. I.r.e., 50, 2367 (1962).
- [15] M. Delhay and m. Migeon, effet raman, c.r. Acad. Sci. Paris, 262, 1513 (1966).
- a. M. Fleischmann, p.j. Hendra and a.j. Mcquillan, raman spectra of pyridine adsorbed at a silver electrode, chem. Phys. Lett., 26, 163 (1974).

