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ARTICLE

## Fourier Transform Infrared and Raman Spectral Analysis of Isothiocyanic Acid Phenyl Ester

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### ABSTRACT

The FTIR and FTR spectra of isothiocyanic acid phenyl ester have been recorded in the regions 4000-200  $\text{cm}^{-1}$  and 4000-30  $\text{cm}^{-1}$ . The vibrational analysis has been carried out by assuming  $C_s$  symmetry. The observed frequencies were assigned to various modes of vibrations on the basis of intensity, frequencies from allied molecules and the normal coordinate calculations. The potential energy distribution associated with normal modes and also reported here. The assignment of fundamental vibrational frequencies for isothiocyanic acid phenyl ester agrees with the calculated frequencies.

### KEYWORDS

Vibrational spectra, Normal coordinate calculation, Isothiocyanic acid phenyl ester.

### INTRODUCTION

Isothiocyanic acid phenyl ester, is a colourless liquid. It is penetrating, irritating odor and readily volatilized with steam. It is soluble in alcohol and ether while insoluble in water. It has boiling point 221 °C and it is combustible [1-3]. It is irritant to tissue and toxic by ingestion and inhalation. It is used in medicine and organic synthesis. It is obtained by action of concentrated hydrochloric acid on sulfocarbonyl chloride by reaction of thiophosgene with aniline. Electronic absorption spectra of some monosubstituted benzenes in the vapour phase were investigated by Shashidhar [4]. The vibrational spectra of isothiocyanic acid phenyl ester have not been reported in the literature. Hence in the present study, the results and analysis for the FTIR and FT Raman spectra of this compound is reported. The assignments were further verified through normal co-ordinate calculations.

### EXPERIMENTAL

The FTIR spectra of isothiocyanic acid phenyl ester are recorded on Bruker IFS 66V FTIR spectrometer in the region 4000-200  $\text{cm}^{-1}$ . The FT Raman spectra of same compound is also recorded on the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.06  $\mu\text{m}$  line with a scanning speed of 30  $\text{cm}^{-1} \text{min}^{-1}$  of spectral width

of  $20 \text{ cm}^{-1}$ . The frequencies for all sharp bands were accurate to  $\pm 1 \text{ cm}^{-1}$ . The FTIR and FT Raman spectra of isothiocyanic acid phenyl ester are shown in Fig. 1.

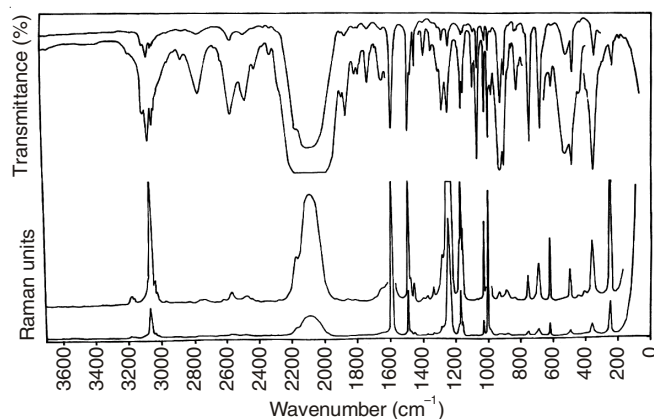


Fig. 1. FTIR and FTR spectra of isothiocyanic acid phenyl ester

**Theoretical considerations:** Isothiocyanic acid phenyl ester belongs to  $C_s$  point group having 36 normal modes of vibrations and they are distributed as  $G_{\text{vib}} = 28 a' + 8 a''$ . The vibrations of the type  $a'$  belongs to in-plane and those of  $a''$  belongs to out-of-plane. All the frequencies are assigned to various fundamental modes and compared with those obtained from some related molecules. The potential energy distribution is evaluated using the refined force constants to test the validity and precision of the present assignment. The close agreement between the observed and calculated frequencies confirms the validity of the present assignment.

**Normal coordinate analysis:** The method of normal coordinate analysis is necessary for the complete assignment of the vibrational frequencies of larger polyatomic molecules and for a quantitative description of the vibrations. The present work, SGVFF has been employed to express the potential energy. The normal coordinate calculations were performed by using the program of Fuhrer *et al.* [5] with suitable modifications for computing the G and F matrices and for adjusting a set of independent force constants. The structural parameters necessary for these compounds are taken from Sutton's Table [6] and structurally related similar molecules. The normal coordinate calculations have also been performed to obtain vibrational frequencies and the potential energy distribution for the various modes. In the normal coordinate analysis, the potential energy distribution from each internal coordinates to the total potential energy associated with particular normal coordinate of the molecule. The vibrational assignments for all the in-plane and out-of-plane vibrations of Raman and infrared frequencies are made on the basis of data available in the literature for related molecules, the intensities and potential energy distribution.

**Potential energy distribution:** The check whether the chosen set of assignments contribute maximum to the potential energy associated with normal coordinates of the molecules, the potential energy distribution (PED) has been calculated using the relation:

$$\text{Potential energy distribution} = \frac{F_{ii} L_{ik}^2}{\lambda_k}$$

where  $F_{ii}$  are the force constants defined by damped least square technique,  $L_{ik}$  the normalized amplitude of the associated element (i,k) and  $\lambda_k$  the eigen value corresponding to the vibrational frequency of the element k. The potential energy distribution contribution corresponding to each of the observed frequencies over 10 % are listed in the present work.

## RESULTS AND DISCUSSION

The observed and calculated infrared and Raman frequencies of isothiocyanic acid phenyl ester and the proposed assignments along with the associated potential energy distribution are listed in the Table-1.

**C-H stretching:** The C-H stretching frequency of phenyl ring is normally placed between  $3100$  and  $2800 \text{ cm}^{-1}$ . There are five C-H stretching modes in isothiocyanic acid phenyl ester. Hence the bands observed at  $3100$ ,  $3069$ ,  $3038$ ,  $2863$  and  $2760 \text{ cm}^{-1}$  are assigned to C-H stretching in benzene, which agrees the calculated frequencies. The potential energy distribution for C-H stretching frequency calculated at  $2859 \text{ cm}^{-1}$  shows that 82 % is contributed by C-H stretching vibration with a small contribution of about 12 % from C-C stretching band [7].

**C=C stretching:** For aromatic compounds, the most characteristic C=C stretching bands are at  $1650$ - $1450 \text{ cm}^{-1}$ . If there is no absorption in this region, it is a fair proof that the compound is not aromatic. The observed frequencies at  $1650$ ,  $1600$  and  $1494 \text{ cm}^{-1}$  are assigned to C=C stretching which agree with the calculated frequencies and literature values [8]. As per the potential energy distribution calculation, C=C stretching at  $1488 \text{ cm}^{-1}$  (calculated) contains 67 % of C=C stretching vibration with 21 % of CH stretching vibration.

**C-C stretching:** Skeleton vibrations involving carbon-to-carbon stretching within the ring absorb in the  $1300$ - $1000 \text{ cm}^{-1}$  region [9]. The modes corresponding to C-C stretching in benzene are assigned to the bands at  $1188$ ,  $1168$  and  $1081 \text{ cm}^{-1}$  in isothiocyanic acid phenylester.

**NCS vibrations:** Due to the stretching vibrations of  $-N=C=S$  group, a very strong band in the region  $2150$ - $1990 \text{ cm}^{-1}$  is observed. The very strong Raman band at  $2088 \text{ cm}^{-1}$  (calculated  $2082 \text{ cm}^{-1}$ ) has been assigned to  $N=C=S$  stretching vibration [10]. The potential energy distribution calculation indicates that this vibration is not pure mode whereas it is mixed mode with combination of 41 % of  $N=C=S$  stretching, 29 % of C-NCS stretching and 10 % of CC stretching. The C=S stretching vibration is assigned to  $1170 \text{ cm}^{-1}$ . N=C and C=S in-plane bendings are assigned to  $688$  and  $663 \text{ cm}^{-1}$ . Similarly C=S and N=C out-of-plane bendings are assigned to  $430$  and  $410 \text{ cm}^{-1}$  [10].

**In-plane and out-of-plane bendings:** The bands due to the C-H in-plane bending vibrations, which occur in the region  $1400$ - $1200 \text{ cm}^{-1}$ , are very useful for characterization purposes and may be very strong indeed. The observed frequencies at  $1450$ ,  $1400$ ,  $1369$ ,  $1350$  and  $1250 \text{ cm}^{-1}$  are assigned to C-H in-plane bendings, which agree with calculated frequencies [11]. The frequencies of C-H out-of-plane bendings vibrations are mainly determined by the number of adjacent hydrogen atoms on the ring and not very much affected by the nature of the substituent [12]. Normally these vibrations occur in the

TABLE-1  
OBSERVED, CALCULATED FREQUENCIES ( $\text{cm}^{-1}$ ), VIBRATIONAL ASSIGNMENTS AND  
POTENTIAL ENERGY DISTRIBUTION OF ISOTHIOCYANIC ACID PHENYLESTER

Species	Observed frequency/Intensity		Calculated wavenumber	Assignment	Potential energy distribution (%)
	Infrared	Raman			
a'	3100 w	–	3089	C-H stretching	88 $\nu(\text{CH})$
a'	3069 s	3069 vs	3062	C-H stretching	94 $\nu(\text{CH})$
a'	3038 s	3035 s	3036	C-H stretching	86 $\nu(\text{CH})$
a'	2863 w	–	2859	C-H stretching	82 $\nu(\text{CH})$ + 12 $\nu(\text{CC})$
a'	2760 m	2750 w	2755	C-H stretching	90 $\nu(\text{CH})$
–	2563 w	–	–	1400 + 1156	–
–	2480 m	–	–	1494 + 1000	–
a'	–	2088 vs	2082	N=C=S stretching	41 $\nu(\text{N=C=S})$ + 29 $\nu(\text{C-NCS})$ + 10 $\nu(\text{CC})$
a'	1650 m	–	1644	C=C stretching	81 $\nu(\text{C=C})$
a'	1600 s	1600 s	1604	C=C stretching	78 $\nu(\text{C=C})$
a'	1494 s	1494 vs	1488	C=C stretching	67 $\nu(\text{C=C})$ + 21 $\nu(\text{CH})$
a'	1450 w	1450 w	1442	C-H in-plane bending	84 $\beta(\text{CH})$
a'	1400 w	1400 w	1401	C-H in-plane bending	76 $\beta(\text{CH})$ + 21 $\beta(\text{CC})$
a'	–	1369 w	1358	C-H in-plane bending	86 $\beta(\text{CH})$
a'	1350 w	–	1342	C-H in-plane bending	80 $\beta(\text{CH})$ + 11 $\beta(\text{CC})$
a'	–	1331 w	1326	C-N stretching	69 $\nu(\text{CN})$ + 21 $\nu(\text{CC})$
a'	1250 s	1244 s	1246	C-H in-plane bending	79 $\beta(\text{CH})$ + 10 $\beta(\text{CC})$
a'	1169 m	1170 vs	1168	C=S stretching	72 $\nu(\text{C=S})$ + 17 $\nu(\text{CN})$
a'	1156 m	1156 s	1151	C-C stretching	86 $\nu(\text{CC})$
a'	1100 m	–	1108	C-C stretching	90 $\nu(\text{CC})$
a'	1075 vs	–	1061	C-C stretching	74 $\nu(\text{CC})$ + 19 $\nu(\text{CH})$
a'	1000 s	1000 vs	989	CCC trigonal bending	90 $\beta(\text{CCC})$
a''	988 m	–	978	C-H out-of-plane bending	84 $\eta(\text{CH})$
a''	925 vs	925 w	919	C-H out-of-plane bending	88 $\eta(\text{CH})$
a''	906 vs	–	902	C-H out-of-plane bending	76 $\eta(\text{CH})$ + 12 $\eta(\text{CC})$
a''	–	888 w	876	C-H out-of-plane bending	67 $\eta(\text{CH})$ + 30 $\eta(\text{CC})$
a'	863 w	–	858	CCC ring breathing	94 $\beta(\text{CCC})$
a''	825 m	830 w	822	C-H out-of-plane bending	62 $\eta(\text{CH})$ + 23 $\eta(\text{CC})$
a'	750 s	750 m	743	C-N in-plane bending	62 $\beta(\text{CN})$ + 31 $\beta(\text{CS})$
a'	688 s	688 m	680	N=C in-plane bending	60 $\beta(\text{C=N})$ + 34 $\beta(\text{CS})$
a'	–	663 m	654	C=S in-plane bending	53 $\beta(\text{C=S})$ + 38 $\beta(\text{CN})$
a'	619 m	619 m	612	CCC in-plane bending	82 $\beta(\text{CCC})$ + 12 $\beta(\text{CH})$
a'	525 vs	–	517	CCC in-plane bending	74 $\beta(\text{CCC})$ + 21 $\eta(\text{CH})$
a'	494 vs	494 m	488	CCC in-plane bending	89 $\beta(\text{CCC})$
a'	444 m	–	436	CCC in-plane bending	69 $\beta(\text{CCC})$ + 20 $\eta(\text{C-NCS})$
a''	–	430 w	421	C=S out-of-plane bending	55 $\eta(\text{C=S})$ + 28 $\eta(\text{N-C})$
a''	–	410 w	400	N=C out-of-plane bending	51 $\eta(\text{C=N})$ + 32 $\eta(\text{C=S})$
a''	–	356 w	342	CN out-of-plane bending	49 $\eta(\text{C-N})$ + 30 $\eta(\text{C=S})$

a' = in-plane vibrations; a'' = out-of plane vibrations; w = weak; m = medium; s = strong; vw = very weak; vs = very strong.

range 900-700  $\text{cm}^{-1}$ . The bands at 988, 925, 906, 888 and 825  $\text{cm}^{-1}$  are assigned to C-H out-of-plane bendings, which agree quite well with the calculated frequencies. CCC in-plane bending vibrations are assigned to 525, 494 and 444  $\text{cm}^{-1}$ .

## Conclusion

A complete vibrational spectra and analysis is reported in the present work for the first time for isothiocyanic acid phenyl ester. The close agreement between the observed and calculated frequencies confirms the validity of present assignment.

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