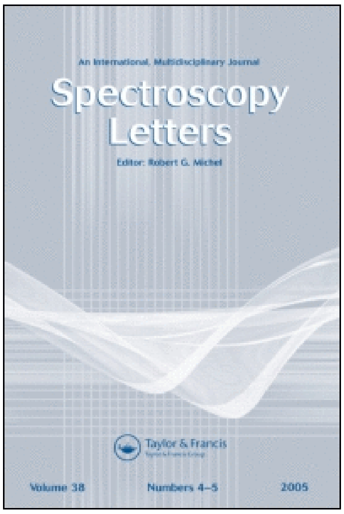

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VIBRATIONAL SPECTRA AND ASSIGNMENTS FOR 3,4-DIBROMOTHIOPHENE

Key words: 3,4-Dibromothiophene, Infrared and Raman spectra, Vibrational analysis.

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ABSTRACT

The infrared spectrum of 3,4-dibromothiophene has been studied from 4000 to 200 cm^{-1}. The Laser Raman spectrum has also been recorded and depolarization values have been measured. An assignment of the 21 fundamental vibrations is proposed based on group frequency correlations, Raman polarization data and comparison with the spectra of parent and some halogeno-substituted molecules.

INTRODUCTION

For several years our group has been engaged in the vibrational study of halogeno derivatives of heterocyclic pentatomic molecules. Inside of these general topics, a particular attention has been devoted to the study of the vibrational spectra of the bromine derivatives of Thiophene. We have already studied the vibrational spectra of 2-bromothiophene[1] and 3-bromothiophene[2]; more recently, we have developed a normal coordinate analysis with the overlay tecnique, which gave us the possibility of obtain accurate force fields for these two molecules[3]. Moreover, we have also established the vibrational assignments of 2,3-dibromothiophene and of 2,3,5-tribromothiophene[4].

This article deals with the vibrational assignment of 3,4-dibromothiophene on which there are not, up to date, literature information. The aim was that of extending our comparative analysis in this field to other bromine derivatives of thiophene; we also intend to use the assignment of the vibrational motions of this molecule as a basis for the understanding of its crystal spectrum at low temperature[5].

EXPERIMENTAL

The molecule (a commercial product from Aldrich), was purified by double distillation under vacuum; its purity, cheked by G.L. chromatography, was higher than 99%.
The infrared spectra were recorded with a Perkin-Elmer model 983 grating spectrometer using conventional cells for liquid samples.

Raman spectra were recorded with a Jobin-Yvon Ramanor HG 2S double holographic monochromator, using the 514.5 nm radiation from a Spectra-Physics model 164-06 Argon ion laser, as excitation source.

Frequencies for both infrared and Raman spectra are accurate to 1 cm^{-1}. They are reported in Table 1 with the proposed assignment.

TABLE 1

INFRARED AND RAMAN SPECTRA OF 3,4-DIBROMOTIOPHENE

INFRARED	RAMAN		ASSIGNMENT
3111 vs	3114 vs	0.30	ν(CH) A_1, B_1
1473 s			ν(ring) B_1
1392 ms	1394 vs	0.15	ν(ring)A_1
1329 vvs	1329 s	0.15	ν(ring)A_1
1308 sh			849 + 457
1207 vw	1202 vw	0.30	849 + 357
1155 w	1158 vw	0.75	δ(CH) B_1
1113 ms	1114 vs	0.30	δ(CH) A_1
908 vs	911 w	0.75	ν(ring) B_1
882* w			γ(CH) A_2
849 s	849 vvs	0.05	ν(ring) A_1
783 vvs	785 vw	0.75	γ(CH) B_2
703 vw			δ(ring) B_1
679 vw			457 + 223
649 s	649 m	0.20	δ(ring) A_1
605 vw			356 + 254
457 m	458 w	0.70	γ(ring) B_2
395* mw			γ(ring) A_2
376 vw	377 m	0.70	ν(CBr) B_1
356 mw	357 vvs	0.20	ν(CBr) A_1
	254 s	0.75	γ(CBr) A_2
223 m	224 w	0.75	δ(CBr) B_1
	169 ms	0.74	γ(CBr) B_2
	116 vs	0.60	δ(CBr) A_1

ν: stretch, δ: i.p. bending, γ: o.o.p. bending

*: from crystal spectrum

RESULTS AND DISCUSSION

3,4-dibromothiophene is supposed to be a planar molecule, in analogy with the parent molecule[6] and 2,5-dibromothiophene[7]; therefore it follows the selection rules of the C_{2v} point group symmetry. The 21 fundamental motions are distributed among the representations of this point group as: $8A_1(IR,\ R_p) + 7B_1(IR,\ R_{dp}) + 3A_2(R_{dp}) + 3B_2(IR,R^{dp})$.

The assignment here proposed is based on the followings: (i) the analogy with previous assignments on bromine derivatives of thiophene. (ii) the polarizability and the depolarization ratios of the Raman lines. (iii) the examination of the relative band intensities in the infrared absorption and in the Raman spectra. In the following section comments will be made only on certain particuliar features.

IN-PLANE VIBRATIONS

Identification of the 8 totally-symmetric normal modes is very easy: they correspond to very intense and polarized Raman lines at 3111, 1392, 1329, 1114, 849, 649, 357, 116 cm^{-1}. The bands at 3111 and 1114 cm^{-1} are assigned to $\nu(CH)$ and $\delta(CH)$ modes; the bands at 1392 and 1329 cm^{-1} correspond to the ring stretching modes. These attributions are straightforward and do not require any particular discussion: it is well known that the relevant vibrations give rise to localized group frequencies in the heteroaromatic compounds with pentatomic rings scarcely influenced by the presence of substituents in the ring[4,9].

The two modes associated with the C-Br bonds, are assigned to the frequencies at 357 cm^{-1} $\nu(CBr)$ and at 116 cm^{-1} $\delta(CBr)$, on the basis of the normal coordinate calculations of3-bromo thiophene[3]. Such an assignment finds also support on the fact that the line at 357 cm^{-1} is the more intense in the Raman spectrum of 3,4-dibromothiophene, as one should expect considering the large polarizability associated with thestretching of the C-Br bonds. The two remaining frequencies at 849 and 649 cm^{-1} are therefore associated with the ν_3 and ν_8 motions as in thiophene, where they fall at 833 and 606 cm^{-1} respectively[9].

The assignment of the fundamental frequencies of B_1 species is more difficult, expecially for some low frequency modes, in that there are not objective and certain criteria for their discrimination from the motions of B_2 species. The vibrations $\nu(CH)$, $\delta(CH)$ and $\nu(ring)$ are assigned on the basis of the same considerations developed for the corresponding totally symmetric motions. We must still assigne the two ring vibrations (stretch and bend) and the two motions regarding the substituent atoms. The two ring motions of B_1 symmetry, in thiophene at 871 and 750 cm^{-1}, are attributed to the infrared absorptions at 908 and 703 cm^{-1}. In the same region we observe another absorption at 783 cm^{-1}, which is the more intense band in the infrared spectrum and corresponds to a weak and depolarized Raman line. However, in agreements with the literature data by Peron et al.[8], we retain that such absorption should be correlated with the $\gamma(CH)$ vibration of the B_2 species. The two motions ν(CBr) and δ(CBr) foreseen to fall at lower frequencies, are thus associated with the absorptions at 376 and 222 cm^{-1}.

OUT-OF-PLANE VIBRATIONS

The three A_2 species vibrations are inactive in the infrared absorption spectrum and should correspond to depolarized Raman lines. On the basis of these considerations we have attributed the depolarized Raman line at 254 cm^{-1} to the γ(CBr) motion. The vibration γ(CH) was localized at ca. 900 cm^{-1} in thiophene; we have tentatively assigned this mode to the absorption at 882 cm^{-1} which is observed only in the infrared crystal spectrum of 3,4 dibromothiophene at liquid nitrogen temperature[5]. For the attribution of the A_2 γ(ring) mode, we have selected the IR band at 395 cm^{-1} which is observed only in the crystalline IR spectrum of the sample, as the preceeding one.

Among the three B_2 fundamentals, the γ(CH) motion has already been assigned (see above). The γ(ring) mode, at 465 cm^{-1} in 2,5-dibromothiophene[6,7] and at 452 cm^{-1} in tetrabromothiophene[9], has been correlated in 3,4-dibromothiophene with the medium intense infrared absorption at 457 cm^{-1} which has a corresponding depolarized Raman line at 458 cm^{-1}. For the attribution of the γ(CBr) motion the possible candidate is the depolarized Raman line at 169 cm^{-1}.

CONCLUSIONS

The analysis of these data and the comparison with the vibrational spectra of various bromo-derivatives of thiophene, selenophene and tellurophene show that it is impossible to rationalize any effect on the vibrational frequencies clearly dependent from the variations on the halogeno-ring and/or halogeno-heteroatom electronic interactions depending on the position of the halogen atoms in the heterocyclic ring.

It follows that the vibrational spectra and the relevant force fields of the bromo derivatives of thiophene, seem to be essentially determined by effects due to the mass of substituents. These mass effects are mainly localized on the motions involving the C-Br bonds and are not spried over the whole molecule as observed in the case of the halogeno derivatives of haromatic compounds.

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