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VIBRATIONAL SPECTRA OF *t*-BUTYL ALCOHOL, *t*-BUTYLAMINE AND *t*-BUTYL ALCOHOL + *t*-BUTYLAMINE BINARY LIQUID MIXTURES

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ABSTRACT. Raman and FT-IR absorption spectra of *t*-butyl alcohol and *t*-butylamine pure components have been recorded in the liquid state in the region of 400-4000 cm^{-1}. The data obtained have been used to propose complete vibrational assignments for each of the liquid component and the structural features are discussed. Additionally, the Raman and infrared spectra of the binary liquid mixtures for the *t*-butyl alcohol/*t*-butylamine system have also been recorded. The variations in frequency shifts, intensities and line widths are discussed with a view to understanding the origin of such variations.

KEY WORDS: Infrared and Raman spectra, Binary solution, *t*-Butanol, *t*-Butylamine

INTRODUCTION

Vibrational spectra are, in general, sensitive to the local environment of a molecule, and information concerning the relative position of the molecule in quite a short time can be obtained from the spectra. Studies of the vibrational spectra of some organic amines such as cyclopentylamine [1], isopropylamine [2], *n*-propylamine [3], and *n*-butylamine [4, 5], have been reported in the last few years. Many organic alcohols have also been extensively investigated. We report here the Raman and FT-IR spectra of *t*-butyl alcohol and *t*-butylamine components in their liquid states. On the basis of the experimental data obtained we carried out a general assignment of the observed frequencies. The study of vibrational spectra of *t*-butyl alcohol (Bu^{t}OH) was undertaken to extend the work done earlier by Green and his co-workers [6] to other regions of vibrational spectra and the entire range of 400-4000 cm^{-1} was investigated. We are not aware of any previous spectroscopic work on binary system of *t*-butyl alcohol (Bu^{t}OH) and *t*-butylamine (Bu^{t}NH$_2$). It is therefore of interest to study such systems and to compare them with the corresponding pure components. In this work, a binary system involving mixtures of various compositions of Bu^{t}OH and Bu^{t}NH$_2$ was analyzed by means of the Raman band arising from stretching of the NH$_2$ functional group. Our previous work focussed on investigating the spectroscopic, thermodynamic and mass transport behaviour of pure as well as aqueous solutions of Bu^{t}OH and Bu^{t}NH$_2$ [7-9]. In this work such previous data are extended and consolidated with vibrational spectra of pure and binary mixtures of Bu^{t}OH and Bu^{t}NH$_2$.

EXPERIMENTAL

Materials and methods

t-Buty alcohol was supplied by Riedel-de Haën and *t*-butylamine by Aldrich. The stated purity of both solvents exceeded 99.0 mole %. The solvents were dried using thermally activated 3 Å molecular sieves. Binary mixtures were prepared by weighing appropriate amounts of the components into fine glass vials using a balance with accuracy ± 0.1 mg.

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Apparatus and procedures

Raman spectra were recorded with Jobin-Yvon V1000 spectrometer, a double monochromator instrument equipped with holographic gratings (1600 grooves per mm) for high resolution and good stray light rejection. A Spectra-Physics Model 2016 argon ion laser was used as the excitation source and non-lasing plasma lines were removed with a Laser III pre-monochromator. The Raman scattered radiation was detected with a gallium arsenide photomultiplier tube (PMT) which was cooled by a Peltier-effect device to *ca*. 250 K to reduce thermal noise. A spectralink module, connected to the PMT and interfaced to an IBM PC-compatible computer, provided photon counting, data acquisition and monochromator drive. Liquid samples in glass vials were attached to a motor drive unit situated in the macrochamber of the spectrometer. The vial was then spun to enhance the Raman signal and reduce the risk of sample decomposition. The Jobin-Yvon Prism software package was employed to operate the spectrometer. All data manipulations and spectral plotting were performed with the Spectra Calc software. The spectrometer was calibrated using the 514.5 nm line of the argon ion laser and the spectra were reproducible to ± 1 cm^{-1}. The spectral range covered was 4000-400 cm^{-1}. All the Raman spectra were recorded with samples at room temperature.

Mid-IR spectra were recorded on a Digilab FTS-60 Fourier transform infrared spectrometer employing a Globar source, a KBr beam splitter and an uncooled DTGS detector. The spectrometer was interfaced to a computer and a 68020 processor with Digilab software. The main body of the spectrometer was purged with dry nitrogen. Samples were examined as thin films using an attenuated internal reflectance (ATR) accessory. A clean dry Silicon ATR element was used to obtain a single-beam background spectrum. The ATR cell was then filled with a sample solution using syringe pressure and scanned to obtain absorbance spectra. The sample in the ATR cell was purged for at least 5 minutes with nitrogen gas before spectra were recorded. Between sample runs, the cell was flushed with water and acetone and then dried with ambient air. Thirty interferograms were collected, coadded, apodized with a triangular function and Fourier transformed to give spectra of 4 cm^{-1} resolution. Spectral manipulations were performed with the Spectra Calc program. All spectra reported here were obtained using a Silicon ATR cell at room temperature. The spectral range covered was 4000-1050 cm^{-1}.

RESULTS AND DISCUSSION

Vibrational spectral assignments of Bu^tOH and Bu^tNH_2 liquids

We report here the Raman and IR of Bu^tOH and Bu^tNH_2 in their neat liquid states. The Raman spectra are given in Figure 1 while the corresponding IR spectra of the liquids are shown in Figure 2. The Raman and IR bands observed for Bu^tOH along with their proposed assignments are listed in Table 1, and those of Bu^tNH_2 are in Table 2. Assignments were made on the basis of correlations with vibrations assigned in related molecules. In general, the assignments of the vibrations involving the amino group of Bu^tNH_2 follow those given for isopropylamine [2], *n*-butylamine [4], and the remaining vibrations follow the assignments given for *t*-butyl(*t*-butylimino)borane $(CH_3)_3CBNC(CH_3)_3$ and di-*t*-butylethyne $(CH_3)_3CCCC(CH_3)_3$ [10]. It is apparent from Figures 1 and 2 that the spectra of Bu^tOH are very similar to those of Bu^tNH_2. Obviously, the majority of bands arise from CH_3 stretching, wagging and rocking modes, and from CC_3 stretching, bending, etc. of the *t*-butyl groups. With three methyl groups in the molecule, there is a strong overlap (accidental degeneracy) in the CH_3 stretching, bending, rocking and torsional regions. The strong IR bands are commonly weak in Raman and vice versa. While most of the bands have been assigned as fundamentals, some remaining weak bands have been interpreted as combination bands or overtones.

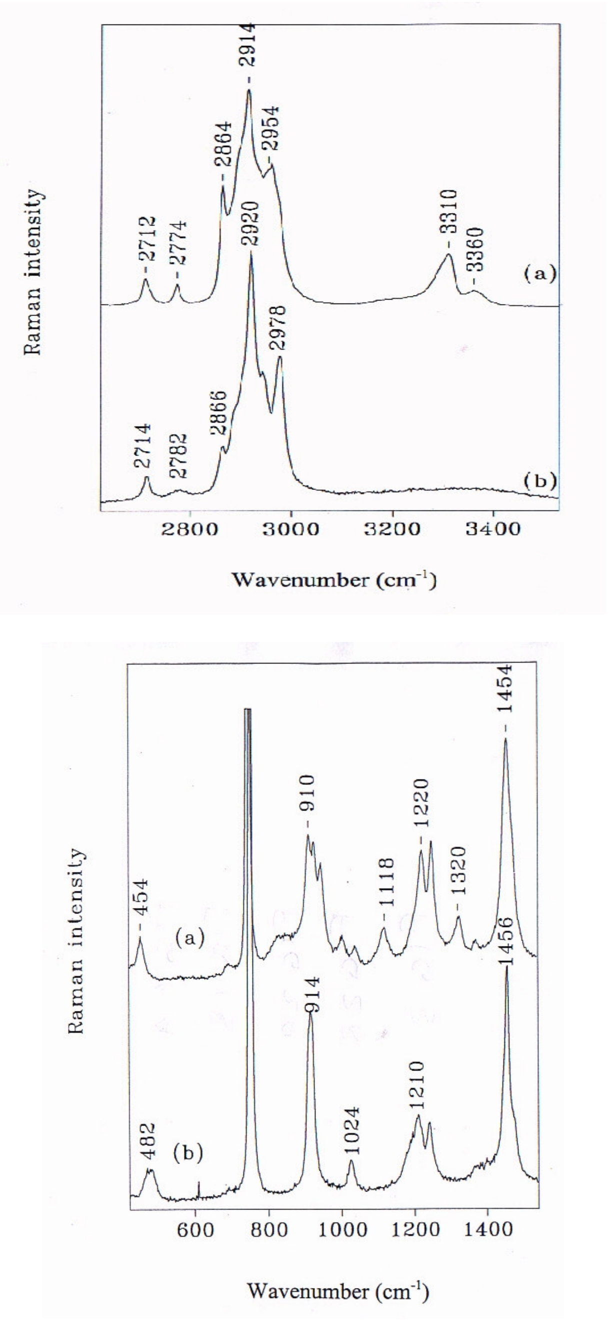

Figure 1. The Raman spectra of (a) *t*-butylamine and (b) *t*-butyl alcohol in the two regions: 2700-3500 cm^{-1} and 400-1500 cm^{-1}.

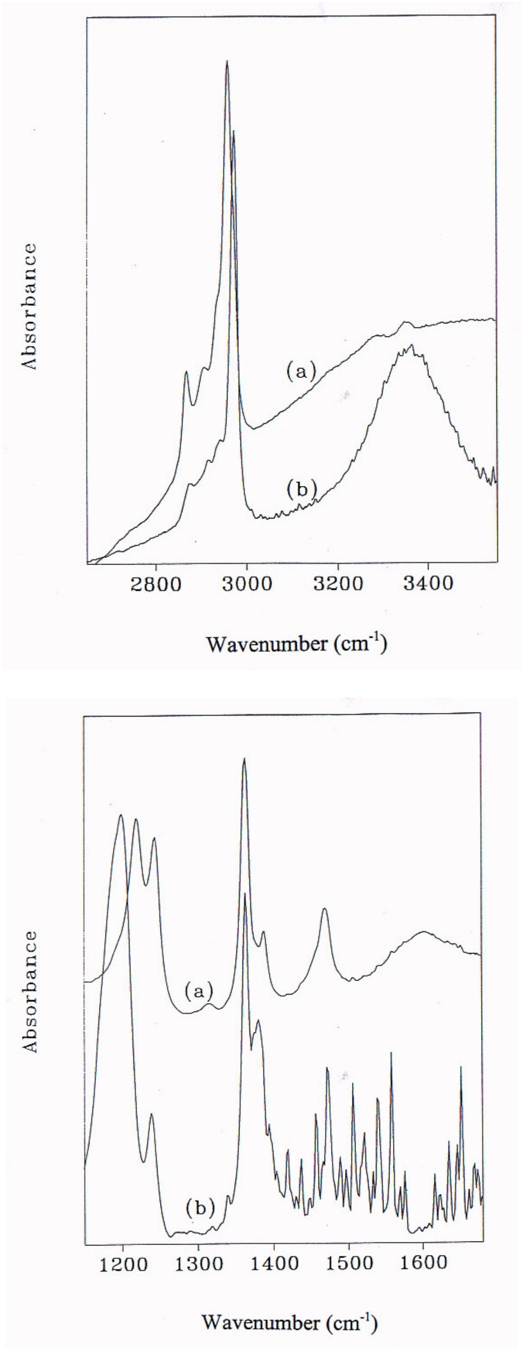

Figure 2. The infrared spectra of (a) *t*-butylamine and (b) *t*-butyl alcohol in the two regions: 2700-3500 cm^{-1} and 1150-1700 cm^{-1}.

Table 1. Observed frequencies (cm^{-1}) and vibrational assignments of Bu^tOH in neat liquid state.

Raman	IR	Assignment
3365 vw	3365 s	OH antisymmetric stretching
2978 m	2972 vs	CH_3 antisymmetric stretching
2944 w	2943 w	CH_3 antisymmetric stretching
2920 vvs	2917 vw	CH_3 symmetric stretching in Fermi resonance with CH_3 antisymmetric deformation
2866 m	2870 vw	CH_3 symmetric stretching
2772 m		combination band of CH_3 deformations
2710 m		overtone of CH_3 symmetric stretching deformation
1645 vw	1645 m	OH bending mode
1455 s	1455 vw	CH_3 antisymmetric deformation
1365 w	1364 s	CH_3 symmetric deformation
1240 m	1238 m	CC_4 skeletal streching
1210 m	-	out-of-phase C_3C-O antisymmetric stretching
1024 w	-	CH_3 rocking
915 s	-	CH_3 rocking
752 vvs	-	C_3C-O symmetric stretching mode

[*] Abbreviations used: m, medium; s, strong; v, very; w, weak; sh, shoulder; -, not detected due to the limited spectral range of Si ATR element.

Table 2. Observed frequencies (cm^{-1}) and vibrational assignments of Bu^tNH_2 in neat liquid state.

Raman	IR	Assignment
3360 m	3360 m	NH_2 antisymmetric stretching
3310 s	3310 w	NH_2 symmetric stretching
3190 sh	3200 sh	Overtone NH_2 scissoring
2960 m	2959 vs	CH_3 antisymmetric stretching
2914 vvs	2914 vw	CH_3 symmetric stretching in Fermi resonance with CH_3 antisymmetric deformation
2862 s	2868 m	CH_3 symmetric stretching
2774 m		combination band of CH_3 deformations
2712 vw		overtone of CH_3 symmetric stretching deformation (2 x 1364)
1600 vw	1603 m	NH_2 deformation (scissoring)
1454 s	1470 s	CH_3 antisymmetric deformation
1366 w	1364 s	CH_3 symmetric deformation
1322 w	1318 vw	NH_2 twisting
1244 m	1244 m	CC_4 skeletal streching
1220 m	1219 m	out-of-phase C_3C-N antisymmetric stretching
1114 w	-	CH_3 rocking
1034 w	-	CH_3 rocking
1000 w	-	C-N symmetric stretching
942 m	-	CH_3 rocking
922 m	-	C-C symmetric stretching
912 m	-	CH_3 rocking
746 vvs	-	C_3C-N symmetric stretching mode
454 w	-	CCN deformation

[*] Abbreviations used: m, medium; s, strong; v, very; w, weak; sh, shoulder; -, not detected due to the limited spectral range of Si ATR element.

Most of the Raman and IR bands of Bu^tOH coincided with those of Bu^tNH_2, because the modes associated with the *t*-butyl moiety of the Bu^tOH molecule, in general, are expected to have similar frequencies to the corresponding modes of Bu^tNH_2. There were a few exceptions, however: bands at 1320, 1114, 1000, 942 and 922 cm^{-1} observed in the Raman spectra of Bu^tNH_2, were surprisingly not visible in the Bu^tOH Raman spectra. The band at 1320 cm^{-1} weak in both the Raman and IR spectra is assigned to the NH_2 twisting vibration while the other weak band at 1000 cm^{-1} is assigned to the symmetric C-N stretching. The remaining three bands are assigned to the CH_3 rocking and C-C symmetric stretching [2, 4, 10]. The two bands observed at 1240 and *ca.* 1210 cm^{-1} in both Raman and IR spectra of Bu^tOH and Bu^tNH_2 molecules have similar intensities and thus suggest the presence of a Fermi resonance. The two bands observed at 2710 and 2772 cm^{-1} in the Raman spectra of both Bu^tOH and Bu^tNH_2 are missing in IR spectra. The 2710 cm^{-1} bands are assigned to a combination band of CH_3 deformations. It is worth noting that the broad and very weak bending modes of OH and NH_2 in Raman spectra are fairly strong in IR spectra. The vibrations are discussed below in two groups corresponding to a high-frequency region (3500-2800 cm^{-1}) and a low- and medium-frequency region (1800-400 cm^{-1}).

High-frequency region (3500-2800 cm^{-1})

In this region the vibrations corresponding to the O-H, N-H and C-H stretching modes should appear. These vibrations are of prime importance since they are well separated in frequency from the other fundamental modes. The characteristic IR pattern of liquid Bu^tNH_2 consists of two medium bands of approximately equal intensity. A shoulder on the low frequency side of the symmetric NH_2 stretching band near 3200 cm^{-1} is attributed to the first overtone of NH_2 scissoring enhanced by Fermi resonance interaction with the NH_2 symmetric stretching [11]. The strongest band at 3310 cm^{-1} in this region of the Raman spectrum is polarized and it is assigned to the symmetric NH_2 stretching mode while the weak depolarized band at 3360 cm^{-1} is assigned to the corresponding antisymmetric stretching mode. The overtone of NH_2 scissors shows very weak Raman scattering. In pure Bu^tOH liquid, however, only one broad O-H stretching vibration band appears in the high-frequency region centred around 3360 cm^{-1} which has an antisymmetric contour. The band is very strong in the infrared spectrum but very weak in the Raman spectrum. The 2800-3000 cm^{-1} frequency region comprises all fundamental vibrations due to the CH_3 stretching oscillators.

Medium and low-frequency region (1800-400cm^{-1})

Generally, bands occurring at the higher frequencies in this region correspond to all fundamental vibrations related with angular distortions such as bending and stretching vibrations involving the CH_3, NH_2 and OH skeletal groups. The amino group normally has three bending modes, the scissor, twist and wagging vibrations. The broad and fairly strong IR band at 1600 cm^{-1} of Bu^tNH_2 is assigned to the NH_2 scissoring vibrational mode and is absent in the Raman spectrum. The 1400-1500 cm^{-1} spectral regions of both Bu^tOH and Bu^tNH_2 show sharp distinct bands at about 1452 cm^{-1} which are assigned to CH_3 antisymmetric deformations. Since compounds containing quaternary carbon atoms (*t*-butyl group) exhibit vibrational modes in the 1200-1255 cm^{-1} region as a result of the CC_4 skeletal stretchings [12], the 1240-1250 cm^{-1} and 1210-1220 cm^{-1} bands of both Bu^tOH and Bu^tNH_2 are most likely due to similar vibrations involving the C_3C-N and C_3C-O moieties. In the Raman spectra of Bu^tNH_2 three fairly distinct bands appear around 920 cm^{-1} which are assigned to characteristic CH_3 rocking frequencies of *t*-butyl group skeletal stretching modes [10, 12]. In Bu^tOH, however, only one strong band appears in this region at 914 cm^{-1}. The strongest Raman band observed in the spectrum of Bu^tNH_2 is polarised and found at about 750 cm^{-1}. This band is attributed to the symmetric C_3C-N stretching mode. Similarly, this polarised Raman vibration at 752 cm^{-1} is the strongest line in the Raman spectrum of Bu^{t}OH liquid and is attributed to the in-phase C_3C-O stretching mode. The assignment is based on the fact that a similar band is observed for the in-phase CC_4 stretching mode in the same region in alkanes [13]. It is therefore important to note that this is in the same spectral region as observed for the symmetric stretching modes of quaternary carbon atoms, CC_4.

Vibrational spectra of Bu^{t}OH + Bu^{t}NH$_2$ mixtures

In order to present a comparison, the pure component spectra are reproduced in Figures 1 and 2. It should be pointed out that the values on the ordinate in the upper and lower part of the figures are on the same absolute scale. Comparison of the spectra of Bu^{t}OH with that of Bu^{t}NH$_2$ clearly show that the vibrations attributed to fundamental and skeletal vibrations of the *t*-butyl moiety such as CH_3, CC_4 stretching and bending vibration components exhibit similar intensities and frequency positions.

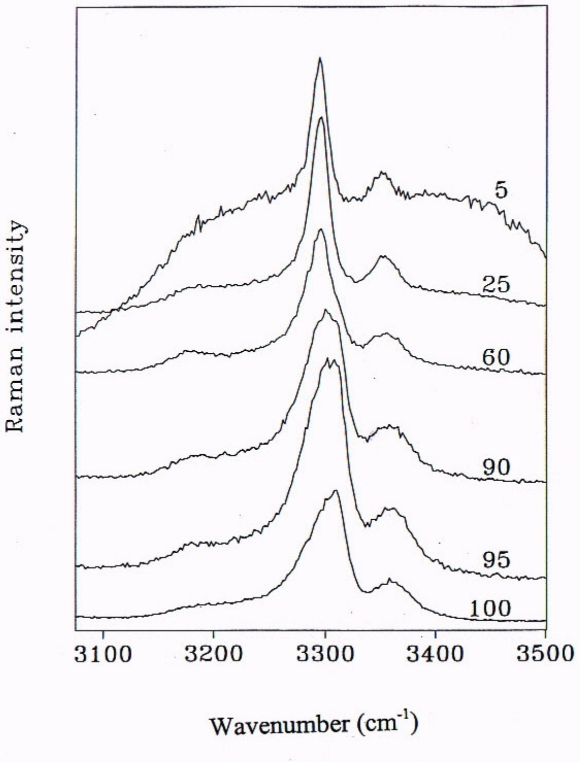

Figure 3. Effect on the Raman spectra of the NH_2 stretching modes of Bu^{t}NH$_2$ for Bu^{t}OH + Bu^{t}NH$_2$ mixtures as a function of concentration; moles % of Bu^{t}OH are noted on each curve.

In the region 3100-3800 cm^{-1} of the Raman spectra, however, Bu^tOH has a very weak band around 3365 cm^{-1} which is barely noticeable. On the other hand, in Bu^tNH_2, two distinct bands appear in this region. The stronger band at *ca*. 3310 cm^{-1} is due to the symmetric NH_2 stretching vibration, while the other band at 3360 cm^{-1} corresponds to NH_2 antisymmetric stretching vibration. The Raman spectra of Bu^tOH-Bu^tNH_2 systems with varying concentration of Bu^tOH in the spectroscopically significant region 3050-3500 cm^{-1} are reproduced in Figure 3. It can be seen that the intensity of the band around 3310 cm^{-1} decreases with addition of Bu^tOH. A new band appears at first as a shoulder at low concentrations of Bu^tOH. As the mole fraction of Bu^tOH increases, this shoulder develops into a band centred at 3294 cm^{-1} indicating probably partially covalent linear hydrogen-bonded complex formation of the type NH_2----O-H. This band thus is due to the amine-alcohol complex which is in agreement with earlier reports [14, 15]. Finally the 3294 cm^{-1} band dominates the spectrum at high concentrations of Bu^tOH, leaving the other band as a shoulder.

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REFERENCES

1. Kalasinsky, V.F.; Little, T.S. *J. Raman Spectros.* **1980**, 9, 224.
2. Durig, J.R.; Guirgis, G.A.; Compton, D.A.C. *J. Phys. Chem.* **1979**, 83, 1313.
3. Durig, J.R.; Beshir, W.B.; Godbey, S.E.; Hizer, T.J. *J. Raman Spectros.* **1989**, 20, 311.
4. Teixeira-Dias, J.J.C.; de Carvalho, A.E.B.; da Costa, A.M.A.; Lampreia, I.M.S.; Barbosa, E.F.G. *J. Spectrochim. Acta* **1986**, 42A, 589.
5. Auzanneau, I.; Combes, D.; Zwick, A. *J. Raman Spectrosc*. **1991**, 22, 227.
6. Green, J.L.; Lacey, A.R.; Sceats, M.G. *Chem. Phys. Lett*. **1987**, 137, 537.
7. Kipkemboi, P.K.; Easteal, A.J. *Indian J. Chem*. **2002**, 41A**,** 1139.
8. Kipkemboi, P.K.; Easteal, A.J. *Can. J. Chem*. **2002**, 80, 789.
9. Kipkemboi, P.K.; Kiprono, P.C.; Easteal, A.J. *Bull. Chem. Soc. Ethiop.* **2002**, 16, 187.
10. Klaeboe, P.; Bougeard, D.; Schrader, B.; Paetzold, P.; Von Plotho, C. *Spectrochim. Acta* **1985**, 41A, 53.
11. Perchard, C.; Perchard, J.P. *J. Raman Spectrosc.* **1977**, 6, 74.
12. McMurray, H.L.; Thornton, V. *Anal. Chem.* **1952**, 24, 318.
13. Daimay, L.V.; Colthup, N.B.; Fateley, W.G.; Grasselli, J.G. *Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, Inc.: New York; **1991**.
14. Baker, J.W.; Davies, M.M.; Gaunt, J. *J. Chem. Soc.* **1949**, 24, 1.
15. Saikia, B.; Suryanarayana, I.; Saikia, B.K. *Spectrochim. Acta* **1991**, 47A, 791.