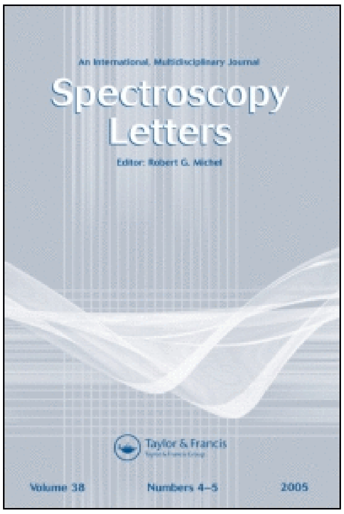

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# Vibrational Spectra of Indazole

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# VIBRATIONAL SPECTRA OF INDAZOLE

Key words: infrared, Raman, polarized spectra, indazole

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## ABSTRACT

The i.r. spectra of indazole have been measured from 4000 to 180 cm$^{-1}$; polarized spectra of single crystals have been also obtained. The Raman spectra of polycrystalline samples and solutions have been recorded and the polarization of many lines has been determined. Most vibrations have been assigned on the basis of the i.r. dichroism, Raman spectra and correlative arguments.

## 1. INTRODUCTION

The vibrational spectra of azoles have been the subject of several studies: on the contrary those of the corresponding benzazoles are by far less investigated. In particular, the i.r. and Raman spectra of pyrazole have been thoroughly investigated and detailed assignments have been proposed [1-6] whereas the data available for the corresponding benzo-derivative indazole are very scarce [7]. In order to remove these deficiencies the investigation of the vibrational spectra of this molecule was undertaken. In this paper we report the polarized i.r. spectra of single crystals and the i.r. and Raman spectra of polycrystalline solids and solutions. A vibrational assignment is proposed on the basis of the i.r. dichroic measurements and of the polarization of the Raman bands.

## EXPERIMENTAL

Indazole obtained from Fluka was used after repeated crystallisations. Single crystals were obtained by slow evaporation of methanol solutions. X-ray methods showed that the well developed plane of the crystals used in absorption measurements contained the a and b axes. The i.r spectra were recorded on a Perkin-Elmer 983G spectrophotometer. Polycrystalline samples were in the form of KBr pellets and Nujol mulls. Carbon tetrachloride was used to obtain i.r. spectra of solutions. Depolarization ratios were measured for methanol solutions. The measurements of the polarized spectra were carried out using a wire-grid polarizer and a beam-condenser. The Raman spectra were obtained with a SPEX Ramalog spectrometer using the 514.5 nm line of a Spectra-Physics model 165 $Ar^+$ laser for the excitation.

## RESULTS AND DISCUSSION

### Selection rules and spectral predictions

Crystals of indazole are monoclinic, space group $P2_1$ ($C_2^2$), with two molecules in the unit cell [8]. There are infinite chains of molecules connected by hydrogen bonds along the $2_1$ axis. The deviation from the planarity of one of the N atoms, ascribed to the hydrogen bond, is small enough to allow the choice of a $C_s$ symmetry for the discussion of the selection rules of the free molecule. With these assumptions, the selection rules for the indazole molecules and the crystal can be deduced from Table 1.

According to the above Table, each molecular fundamental should give two components in the crystal spectrum, active both in Raman and i.r., one being polarized along the b axis, the other in the ac plane. The A' and A" molecular fundamentals could be discriminated, to some extent, on the basis of the Raman polarization data of the solutions. Informations concerning the assignments of the i.r. bands can also be obtained from the consideration of their dichroism. The oriented gas model may be used to predict the behaviour in polarized light. For the isolated

TABLE 1

Selection rules for the free molecule and the unit cell of Indazole

| Molecule<br>$C_s$ | Site<br>$C_1$ | Unit cell<br>$C_2$ |
|---|---|---|
| A' 27 (i.r.,R) | A 39 (i.r.,R) | A 44 (5L)+$T_b$(i.r.,R) |
| A" 12 (i.r.,R) | | B 43 (4L)+$T_{ac}$(i.r.,R) |

L=Lattice modes

molecule, only the direction of the transition moments of the A" vibrations is fixed by symmetry and using the atomic coordinates given by Escande and Lapasset[8] the proportionality factors for the absorption intensities are

| | a | b | $c^*$($\perp$ab) |
|---|---|---|---|
| I(A") | 0.763 | 0.209 | 0.028 |

From these values it can be argued that, in the polarized i.r. spectra of the *ab* crystal plane, the A" out-of-plane modes should give the strongest component when the electric vector of the light is perpendicular to the *b* crystal axis. Bands showing a strong component parallel to the *b* axis or components of nearly equal intensity in both polarizations can be confidently assigned to in-plane modes.

## Vibrational assignments

The relevant i.r. and Raman data are collected in Table 2 together with the assignments.

The hydrogen bonding strongly affects the position and shape of the bands associated to the NH stretching mode. This fundamental is observed as a sharp i.r band at 3453 cm$^{-1}$ for the free molecule in $CCl_4$ solutions: in the solid state it appears as a strong, broad absorption with maximum at 3181 cm$^{-1}$, which moves to 2370 cm$^{-1}$ upon deuteration and undergoes a red shift of 10 cm$^{-1}$ on cooling to -140°C. The band is highly structured, in particular on the low frequency side, with several submaxima corresponding to combinations and overtones gainig intensity through Fermi resonance with the NH stretching fundamental. This fact makes difficult an unambiguous assignment of the CH stretching modes in the i.r. spectra. The assignment is easier for the Raman spectra where the intensity of the NH stretching band is very low. Keeping in mind the assignments of pyrazole[1-6], the polarized Raman band at 3104 cm$^{-1}$ can be assigned to the stretching fundamental of the CH of the pyrazole ring. The corresponding fundamentals for the benzene ring can be assigned to the Raman bands at 3088, 3070, 3041 and 3031 cm$^{-1}$.

TABLE 2

Experimental spectral data and assignments for indazole

| i.r. frequencies and polarization | | | Raman shift and polarization | | Assignment | |
|---|---|---|---|---|---|---|
| 3181 | s | ‖>⊥ | 3178 | vw,br | A' | ν NH |
| 3158 | s | ‖>⊥ | | | A' | |
| 3120 | m | ‖>⊥ | | | A' | |
| 3106 | m | ‖>⊥ | 3104 | m (p) | A' | ν CH (Pyrazole) |
| 3087 | m | ‖>⊥ | 3088 | mw | A' | ν CH ( Φ ) |
| | | | 3070 | ms (p) | | |
| 3071 | m | ‖>⊥ | { | | A' | ν CH ( Φ ) |
| | | | 3067 | ms | | |
| 3053 | m | ‖>⊥ | | | A' | |
| 3040 | m | ‖>⊥ | 3041 | w | A' | ν CH ( Φ ) |
| | | | 3031 | w | A' | ν CH ( Φ ) |
| 1622 | m | ‖>⊥ | 1623 | w (p) | A' | ν skeletal |
| 1585 | w | ‖>⊥ | 1584 | w (dp?) | A' | ν skeletal |
| 1509 | ms | ‖>⊥ | 1504 | w | A' | ν skeletal |
| 1486 | m | ‖>⊥ | 1488 | m (p) | A' | ν skeletal |
| 1444 | m | ‖=⊥ | 1443 | m | A' | ν skeletal |
| 1409 | w | ‖>⊥ | | | A' | |
| 1390 | sh | | | | | |
| {1382 | m | ‖>⊥ | 1389 | m (p) | A' | ν skeletal |
| 1357 | s | ‖=⊥ | 1359 | m (p) | A' | ν skeletal |
| 1315 | w | ⊥>‖ | 1315 | w (p) | A' | ν skeletal |
| 1305 | w | ‖>⊥ | | | A' | |
| 1285 | m | ‖>⊥ | 1284 | w (p) | A' | ν skeletal, δ CH |
| 1249 | m | ‖≥⊥ | 1248 | w (dp) | A' | δ CH, ν skeletal |
| 1205 | m | ‖>⊥ | 1203 | w (p) | A' | δ CH |
| 1171 | w | ‖>⊥ | | | A' | |
| 1150 | mw | ⊥ | | | | |
| {1144 | mw | ‖ | 1144 | vw | A' | |
| 1123 | m | ‖>⊥ | 1122 | w (p) | A' | δ CH |
| 1076 | ms | ⊥>‖ | 1077 | ms(p) | A' | δ CH |
| 1020 | w | ‖>⊥ | 1021 | w | A' | δ CH |
| 1004 | s | ‖=⊥ | 1002 | m (p) | A' | δ skeletal |
| 971 | * | ⊥ | | | (A") | τ CH |
| 951 | s | ‖ | 949 | w (p) | A' | δ skeletal |
| 941 | ms | ⊥ | 933 | m | A" | τ CH |
| 894 | mw | ‖>⊥ | 892 | w (p) | A' | δ skeletal |
| 870 | mw | ⊥>‖ | | | A" | τ CH |

TABLE 2 (cont.)

| i.r. frequencies and polarization | Raman shift and polarization | Assignment |
|---|---|---|
| 860 sh ⊥>∥ | 859 w | A" |
| 848 s ⊥>∥ | 846 w | A" τ CH |
| 805 w ⊥ | | |
| 785 m,br ⊥ | | |
| ** } | | A" τ NH |
| 768 ms ∥=⊥ | 769 vs(p) | A' δ skeletal |
| 746 vs ⊥>∥ | 751 vw | A" τ CH |
| 656 w ⊥>∥ | | |
| 616 m ∥>⊥ | 616 m (dp?) | A' δ skeletal |
| 563 w ⊥>∥ | 559 w | A" τ skeletal |
| 540 vw ∥=⊥ | 541 m (p) | A' δ skeletal |
| 510 vw ∥=⊥ | | |
| 470 vw ⊥>∥ | | A" τ skeletal |
| 436 m | | |
| {430 m ⊥>∥ | 427 vw | A" τ skeletal |
| 405 w | | |
| {400 w ⊥>∥ | 402 w (dp) | A" τ skeletal |
| 275 w ⊥>∥ | | A" τ skeletal |
| 240 vw | 238 w | |
| 225 vw | 223 vw(dp?) | A" τ skeletal |
| | 140 ms | lattice |
| | 126 ms | lattice |
| | 117 s | lattice |
| | 102 vs | lattice |
| | 87 m | lattice |
| | 63 w | lattice |
| | 42 vs | lattice |

* Observed only in the single crystal spectrum

** Evans hole

∥ Bands polarized parallel to the b crystal axis

⊥ Bands polarized parallel to the a crystal axis

s=strong, m=medium, w=weak; p=polarized, dp=depolarized

Φ=Phenyl; ν=stretching, δ=in-plane bending, τ=out-of-plane bending

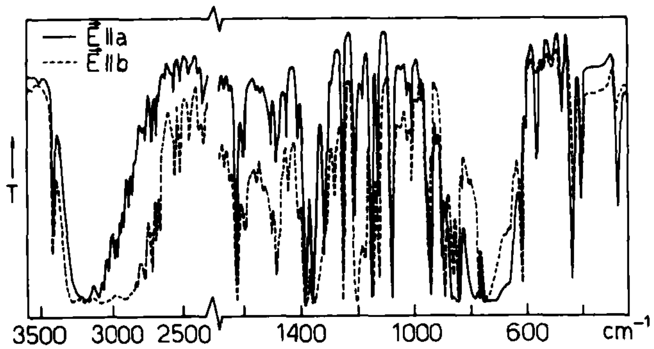

Fig. 1. Polarized i.r. spectrum of indazole, ab crystal plane

Fourteen A' fundamentals can be easily assigned to the Raman bands at 1623, 1488, 1389, 1359, 1315, 1284, 1203, 1122, 1077, 1002, 949, 892, 769 and 541 cm$^{-1}$ which are polarized in solution. The Raman lines at 1584, 1248 and 616 cm$^{-1}$, although depolarized, are also assigned to A' fundamentals on the basis of the behaviour of the corresponding i.r. bands with polarized light: in fact, they give either a prevailing component strongly polarized along the b axis, or two components with comparable intensity in both polarizations.

The available data don't allow an unambiguous attribution of the in-plane NH bending mode. Deuteriation does affect the position and intensity of several bands between 1500 and 1100 cm$^{-1}$, thus indicating a partial NH bending character for some of the fundamentals in this range. Moreover, the appearance of a rather broad band at 1031 $cm^{-1}$ in the i.r. spectrum of the N-deuterated compound suggest the assignment of the in-plane ND bending vibration to this frequency.

Concerning the out-of-plane fundamentals, the $\tau$NH mode is assigned to the broad absorption between 820 and 640 $cm^{-1}$ which disappears upon deuteriation giving a new band at 525 $cm^{-1}$. The dichroism parallel to the _a_ axis is consistent with this attribution, which is also supported by the observation that the absorption shape, particularly in the region 820-750 $cm^{-1}$, is strongly affected by cooling to liquid-nitrogen temperature. A $\tau$CH fundamental is also located in this range on the basis of the prevailing polarization parallel to the _a_ axis shown by the i.r. band at 747 $cm^{-1}$. The analysis of the shape of the absorption bands in this range shows that a resonance interaction does occur between the broad $\tau$NH and a combination tone. In fact, a transmission hole ( Evans hole[9] ) appears at ≈770 $cm^{-1}$, where a combination between the A' fundamental at 540 $cm^{-1}$ and the fundamental of A" species at 225 $cm^{-1}$ should occur. Moreover, the observation of a small, but significant, shift ( +6 $cm^{-1}$ ) of the $\tau$CH band at 747 $cm^{-1}$ upon deuteriation, suggests that also this mode does participate to this interaction through a three-level Fermi resonance mechanism.

Two $\tau$CH vibrations can be assigned to the i.r. bands at 941 and 870 $cm^{-1}$ which are clearly polarized along the a crystal axis. Correlative arguments based on the assignments for o-disubstituted benzenes [10] suggest that the remaining two $\tau$CH fundamentals should be located near 970 and 850 $cm^{-1}$, but no obvious candidates are found in these regions. The choice of the very weak band at 971 $cm^{-1}$, which is observed only in the single crystal spectra, and the strong band at 848 $cm^{-1}$ which shows a prevailing polarization along the a axis, but also a noticeable component polarized along the b axis, should be considered as tentative.

Three of the remaining A" fundamentals may be assigned to the i.r. bands at 563, 470 and 405 $cm^{-1}$ which are clearly polarized along the a axis. The assignment of the band at 405 $cm^{-1}$ is also supported by the depolarized character of its Raman counterpart. The choice of the bands at 270 and 225 $cm^{-1}$ is mainly suggested by correlative arguments based on the assignments of indole[11-13] and, for the latter mode, by the observation of a weak, likely depolarized Raman line at 223 $cm^{-1}$.

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