Raman spectra of solid films—V. Chloroaluminum, chlorogallium and chloroindium phthalocyanine complexes

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(Received 26 November 1985; in final form 26 February 1986; accepted 26 February 1986)

Abstract—Raman spectra of evaporated thin solid films (200 nm thickness) are studied using excitation frequencies in resonance and near resonance with the absorption red band of Al, Ga and in phthalocyanine. Depolarization ratios measured on thin films are also discussed.

INTRODUCTION

The electrooptical and photoreceptive properties of thin-film phthalocyanine (Pc) derivatives are now the object of intense spectroscopic studies prompted by the potential use of these organic films as active components in modern technologies. The basic aim of spectroscopic studies of thin Pc films is to provide information about the molecular structure and its perturbations due to the interactions between neighboring π -electron systems of Pc molecules. Specific spectroscopic techniques would also disclose important aspects of the molecular organization and long range order in submicron films. Most notably, reflection absorption infrared spectroscopy [1] (RAIS) and polarization studies of Raman bands [2] have been used to probe the long range molecular orientation. In this report we present a study of molecular vibrations observed in the Raman spectra (RS) and resonance Raman spectra (RRS) of AlPcCl, GaPcCl and InPcCl. Depolarization ratios of a number of Pc Stokes lines in solid films are presented and discussed.

EXPERIMENTAL

The AIPcCl was purchased from Eastman Chemicals. The GaPcCl and InPcCl were synthesized by reacting the metal chloride with phthalonitrile in quinoline. All Pcs were purified by the train sublimation procedure [3]. Thin films were deposited from a tantalum boat onto Corning glass and quartz plates in a Balzers vacuum system at a pressure of 10⁻⁶ Torr. The film thickness of 200 nm was monitored with an Inficon XTM quartz crystal oscillator. Raman shifts were analyzed using a microcomputer-controlled system described elsewhere [4]. Polarization measurements were carried out using a polarization rotator (Spectra Physics model 310-21) mounted on the 164 argon and krypton ion lasers. Scattered light was analyzed using a linear polarizer and scrambled before entering the Spex 1403 spectrometer. In our polarization notation we follow the following convention [5, 6]. The scattering plane is the xz plane. Illumination is always along the positive z-axis and observation along the x-axis. The plane of incidence (plane containing the normal to the thin solid film and the incoming laser beam) is also the scattering plane. i.e. the xz plane. Light polarized perpendicular (y-direction) to the plane of incidence is said to have S polarization, and light polarized (x-direction) parallel to the plane of incidence is said to have P polarization. There are four polarized

components that can be measured in this geometry: I_{yy} , I_{\parallel} (or SS component of the scattered intensity); I_{zy} , I_{\perp} (or SP component); I_{yx} (or PS component) and I_{zx} (or PP component). For a typical control experiment with CCl₄ the depolarization ratio $\rho = SP/SS$ of the 314 cm⁻¹ line is 0.75. Alternatively, the ratio $\rho = PS/SS$ is also equal to 0.75. These two geometries represent the conventional methods for taking the depolarization ratio of liquids.

In PORTO's notation [5] i(kl)j to describe scattering intensities, the symbols inside the parentheses are the polarization of the incident (k) and scattered light (l), while the symbols outside the parentheses are the propagation directions of the incident (i) and scattered light (j).

Therefore Z(YY)X = SS Z(YZ)X = SPZ(XY)X = PS

Z(XZ)X = PP.

The experimental geometry was such that the laser beam and the normal to the film surface formed a 60° angle. The absorption maxima observed for evaporated films of all compounds studied are listed in Table 1.

RESULTS AND DISCUSSION

RS of chloroaluminum, gallium and indium Pc have not been reported. LINSKY et al. [7] have studied a series of metallated Pcs, and listed M-Cl stretching vibrations from i.r. spectra. The molecular model for AlPcCl, GaPcCl and InPcCl would belong to a $C_{4\nu}$ symmetry point group with 168 normal modes. The number of fundamentals of each irreducible representation are $23A_1 + 19A_2 + 21B_1 + 21B_2 + 42E$. There are 107 Raman active vibrations $(A_1, B_1, B_2 \text{ and } E)$. The Pc molecule would have 67 stretching vibrations, including 16 C-H stretches that are not observed in the RS. Stretching vibrations with the highest relative intensity in the RS are probably due to breathing vibrations of isoindole and the macrocycle (nine in total), and stretching vibrations of conjugated C-N and C-C bonds. The C-N bond stretching of the pyrrole group would be red shifted by the coordination with the metal atom. The analysis of the observed Raman frequencies uses RR data, polarized spectra and characteristic frequencies of molecular moieties.

Resonance Raman spectra

RRS of 200 nm evaporated films on a quartz substrate are presented in Figs 1-3. Observed Raman



Fig. 1. Resonance Raman spectrum of a 200 nm chloroaluminum Pc film on quartz. 50 mW of 647.1 nm laser light and spectral bandpass of 5 cm⁻¹.



Fig. 2. Same as Fig. 1 only for chlorogallium phthalocyanine.

Table 1. Absorption spectra of 200 nm evaporated Pc films

| | Soret band | Red band |
|--------|------------|----------------|
| AlPcCl | 350 nm | 654-760 nm |
| GaPcCl | 360 nm | 672 and 742 nm |
| InPcCl | 362 nm | 668 and 730 nm |

shifts and relative intensities are listed in Table 2. The phthalocyanines are a classical example of strong RR scattering from the Herzberg–Teller mechanism with a general enhancement of A_1 , B_1 , B_2 and E modes. The

absence of overtones in the observed spectra rules out Franck-Condon scattering.

The characteristic macrocycle breathing vibration shows a trend of decreasing frequency value with increasing atomic weight of the central metal atom $(681 \text{ cm}^{-1} \text{ in AlPcCl}, 678 \text{ cm}^{-1} \text{ in GaPcCl} and$ $671 \text{ cm}^{-1} \text{ in InPcCl}$. This trend was also seen in PbPc (672 cm^{-1}) and SnPc (681 cm^{-1}) [8]. RRS of InPcCl closely parallel the observed spectra for PbPc [8]. In both cases the strongest RR band in the 1400–1600 cm⁻¹ region is observed below 1500 cm⁻¹: 1484 cm⁻¹ for PbPc and 1497 cm⁻¹ for InPcCl. Complementary information about Pc molecular vibrations was obtained by polarization measurements



Fig. 3. Same as Fig. 1 only for chloroindium phthalocyanine.

| AIPcC1 | | GaPcCl | | InPcCl | |
|------------|-----------|------------|-------------|------------|-----------|
| Wavenumber | Intensity | Wavenumber | Intensity | Wavenumber | Intensity |
| 58 | Shoulder | .58 | (13) | 59 | (13) |
| | | 72 | (8) | | |
| 106 | Shoulder | | | 138 | (7) |
| 178 | (16) | 169 | (7) | 174 | (9) |
| 237 | (6) | 245 | (12) | 219 | (19) |
| 251 | - añ | 289 | (5) | 240 | `(2)́ |
| | () | 346 | ଶ୍ | 267 | (7) |
| | | | (-) | 312 | (2) |
| 427 | (3) | 427 | (3) | 349 | (4) |
| 485 | (21) | 487 | (15) | 480 | (35) |
| | (=-) | 511 | â | 516 | (S) |
| 591 | (21) | 592 | (<u>)</u> | 589 | (17) |
| 681 | (100) | 678 | (48) | 671 | (86) |
| 001 | (100) | 701 | (4) | 0/1 | (00) |
| | | 719 | - Ch | | |
| | | 735 | (5) | | |
| 752 | (52) | 750 | (33) | 747 | (32) |
| 782 | (10) | 779 | (7) | 780 | (6) |
| 831 | (12) | 847 | (5) | 834 | (12) |
| 957 | (24) | 955 | (24) | 938 | (40) |
| 201 | (=) | 100 | (4-1) | 1008 | (2) |
| | | 1040 | (5) | 1030 | (a) |
| 1072 | (6) | 1085 | | 1087 | - A |
| 1100 | (14) | 1108 | | 1107 | (1) |
| 1147 | (37) | 1147 | (20) | 1142 | 200 |
| (14) | (37) | 1167 | (1) | 1161 | (4) |
| 1101 | (14) | 1188 | (8) | 1106 | (10) |
| 1212 | (8) | 1214 | (0) | 1212 | (10) |
| 1308 | (22) | 1306 | (15) | 1303 | (19) |
| 1343 | (54) | 1341 | (48) | 1340 | (82) |
| 1273 | (24) | 1369 | (6) | 1427 | (39) |
| 1455 | (30) | 1453 | (39) | 1447 | (18) |
| 1528 | Shoulder | 1528 | (100) | 1497 | (100) |
| 1539 | (93) | 1.520 | (100) | 1585 | (2) |
| 100 | (25) | | | | (4) |

Table 2. Vibrational frequencies observed in the RRS obtained with the 647.1 nm laser line

of the thin solid films, and are discussed in the following section.

Polarized spectra of thin films

KOBAYASHI et al. [9] using high resolution electron microscopy have shown that the growth of Pc films includes formation of molecular columns (onedimensional crystal). The packing of Pc molecules may give rise to highly oriented films, which can therefore be probed by polarized light. Using the 514.5 nm laser line along the positive direction of the z-axis and collection optics along the x-axis, all four SS, SP, PS and PP spectra were recorded. Large differences in relative intensities are seen between SS and SP spectra. This is illustrated in Fig. 4 for InPcCl. Notable changes can also be seen in the PS spectrum when compared with the PP spectrum displayed in Fig. 5. However, SS and PP (SP and PS) spectra are similar. Polarization data can be interpreted assuming that there exists a predominant molecular orientation in the Pc thin films. Depolarization ratios (SP/SS) for each of the irreducible representations of the symmetry point group can then be calculated and compared with experimental values [2, 10]. Detailed accounts of these calculations will be given in a separate communication. Model computations show that depolarization ratios



Fig. 4. Preresonance Raman spectra of InPcCl excited with 100 mW of 514.5 nm S-polarized laser light. Upper trace corresponds to the spectrum obtained when the analyzer is set to select P-polarized scattered light. Lower trace corresponds to the spectrum obtained when the analyzer is set to select S-polarized scattered light.



Fig. 5. Same as Fig. 4 only for P-polarized laser excitation light.

| GaPcCl | | InPcCl | | Symmetry and interpretation | |
|------------|-----------|------------|-----------|--------------------------------|--|
| Wavenumber | ρ | Wavenumber | ρ | | |
| 245 (12)* | 0.95 | 219 (18) | 0.59 | | |
| | | 480 | SP active | Isoindole deformation | |
| 592 (37) | SS active | 589 (17) | SS active | <i>A</i> , | |
| 678 (59) | 0.07 | 671 (74) | 0.11 | A_1 macrocycle breathing | |
| , , | | 683 (12) | 1.08 | | |
| | | 741 (14) | 0.33 | <i>A</i> ₁ | |
| 779 (13) | 0.51 | 784 (24) | 0.54 | • | |
| 846 (27) | SS active | 834 (40) | 0.19 | <i>A</i> ₁ | |
| 1009 (6) | SS active | | | A, | |
| 1039 (16) | 0.83 | 1030 (23) | 0.77 | - | |
| 1108 (13) | 1.07 | 1107 (24) | 1.03 | | |
| 1147 (8) | 1.18 | 1134 | SP active | | |
| 1188 | SP active | | | | |
| 1306 | SP active | | | | |
| 1341 (52) | 0.14 | 1338 (75) | 0.32 | A_1 pyrrole stretch | |
| | | 1342 | SP active | | |
| 1407 (15) | SS active | 1367 (41) | SS active | <i>A</i> ₁ | |
| 1433 (12) | SS active | 1422 (38) | 0.29 | A | |
| | | 1427 | SP active | | |
| | | 1447 (9) | 1.41 | | |
| 1453 (14) | 0.91 | 1459 | SP active | | |
| 1492 | SP active | 1497 | SP active | Pyrrole stretch | |
| 1528 (100) | 0.15 | 1502 (100) | 0.18 | A ₁ pyrrole stretch | |
| . , | | 1554 (4) | SS active | $A_1 C_2 N$ aza-group stretch | |
| 1592 (15) | 0.36 | 1585 (17) | 0.63 | A, benzene stretch | |
| 1611 (16) | 0.87 | 1613 (21) | 0.81 | Benzene stretch | |

Table 3. Polarization ratios ($\rho = SP/SS$) measured on 200 nm films with the 514.5 nm laser line.

*Numbers in parentheses are relative intensities.

(SP/SS) for the A_1 symmetry type would not produce a value larger than 0.7, considering all possible molecular orientations or experimental geometries. On this basis all Raman bands for which the ratio SP/SS > 0.7can be assigned to a symmetry type other than A_1 type. On the other hand, strongly polarized Raman bands (SP/SS < 0.7) are most probably related to A_1 type. Numerical results and symmetries are shown in Table 3. The assignments of A_1 species are in excellent agreement with previous polarization studies of RR bands in liquids for the PtPc molecule [11].

It is very interesting to notice that Raman bands that are SP active alone, or bands whose relative intensity is increased in the SP spectrum compared to the SS spectrum, are also seen in the RR spectrum. For instance, the SP active bands at 1188 cm⁻¹ in the InPcCl spectrum are also observed in the corresponding RRS. Since it is known that the Herzberg-Teller mechanism enhances the intensity of B_1 , B_2 and E symmetry types, it can be concluded that the nonresonant SP and PS spectra carry important information about B_1 , B_2 and E types of molecular vibrations. Clearly, this information surfaces as a consequence of extended molecular orientation in the phthalocyanine films.

CONCLUSIONS

The RRS of AlPcCl, GaPcCl and InPcCl follow the classical rule of a Herzberg–Teller enhancement of A_1 , B_1 , B_2 and E symmetry types without any evidence of

overtone series. Polarization studies of Pc thin films confirm the model of a film with a large degree of molecular organization. Distinct SS and SP spectra are obtained, and the SP spectrum is dominated by Raman bands of non-totally symmetric vibrations. This aspect of the work is being developed to be applied to studies of solvent-induced aggregation of thin solid films.

Acknowledgements—The authors would like to thank C. K. HSAIO and PETER KAZMAIER for providing us with chloroindium and chlorogallium phthalocyanine, respectively. Financial assistance from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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