

# Experimental and Theoretical Investigations on the IR and Raman Spectra for CuPc and TiOPc

Serpil Harbeck and Hans-Georg Mack\*

*\*Institute of Physical and Theoretical Chemistry, University of Tübingen  
Auf der Morgenstelle 18, 72076 Tübingen, Germany  
E-mail: [hans-georg.mack@uni-tuebingen.de](mailto:hans-georg.mack@uni-tuebingen.de)  
(Author for correspondence)*

Vibrational IR and Raman powder spectra were recorded for copper phthalocyanine (CuPc) and titanyl (IV) phthalocyanine (TiOPc). Density functional theory (DFT) calculations have been used to predict the theoretical spectra and to assist reliable assignments of the experimental frequencies. There is, in general, a good agreement between experimental and theoretically predicted spectra. The best accordance between experiment and calculated wavenumbers was obtained in the case of the IR spectrum for CuPc (maximum deviations between experiment and theory (unscaled values) amount to less than  $20\text{ cm}^{-1}$ ). New assignments for the IR and Raman spectra for both molecules were done in order to establish the basis for further work on thin films.

## 1. Introduction

Metallophthalocyanines (MPcs) and their derivatives belong to one of the most intensively studied class of aromatic systems due to their interesting and unique physical and chemical properties. One can find them in a wide range of applications, from chemical sensors to electronics to various optical applications, e.g. colourants, optical data storage, solar cells, gas sensors, electrochromic displays, printers, liquid crystals, etc. In the literature a huge number of experiments with respect to characterisation of multiple phthalocyanine compounds, e.g. XPS, UPS, UV, IR, Raman, ellipsometry, etc., are reported. These investigations serve, f.i., for layer characterisation like film growth in special applications. Vibrational spectroscopy, especially IR and Raman, have proved to be most suitable techniques for the determination of structures of phthalocyanine thin layers.

CuPc is a planar non-polar molecule ( $D_{4h}$  symmetry), which possesses one unpaired electron (open shell situation), and, for this reason, it is chemically very reactive, especially against other radicals. On the other hand, TiOPc represents a closed shell system with non-planar structure ( $C_{4v}$  symmetry) and a large dipole moment. Both molecules constitute different systems with respect to their physical and chemical properties. Vibrational spectroscopy serves as an appropriate tool for characterising such properties. In the literature, there exists a large number of IR and Raman investigations on CuPc<sup>1-5</sup> and TiOPc.<sup>6-8</sup>

Theoretical calculations of the optical spectra for these molecules are rare. Numerous quantum chemical studies of the geometric and electronic structure of CuPc were published (see, for instance, Ref. 9-12, and citations therein), but no theoretical IR and Raman spectra were reported up to now. However, there are theoretical and experimental IR and Raman spectra of ZnPc.<sup>13, 14</sup> These authors also report an assignment of the experimental Raman spectrum for CuPc on the basis of the calculated spectra for ZnPc. In the case of TiOPc, to our knowledge, there are no theoretical investigations with respect to the geometric structure and vibrational spectra.

In this work, we present experimental (powder measurements) and theoretical IR and Raman investigations for CuPc and TiOPc. Vibrational frequencies are assigned on the basis of quantum chemical calculations using density functional methods, and according to data previously reported in the literature. Special attention is paid to the complete assignments of the vibrational spectra of the Pc powders, in which the molecules do not show any orientation. However, in the case of a film, the situation is different. Depending on the nature and on preparation conditions, the molecules are orientated in a preferred direction. In order to determine the molecular orientation, a thorough analysis of the vibrational spectra is necessary. This analysis in the literature mainly is done on the basis of C-H o.o.p. vibrations (around 730  $\text{cm}^{-1}$ ) in the IR spectrum. Especially in the case of Raman spectra, this analysis can be done only for the  $\alpha$ -modification of CuPc. For the other modifications or for other Pc molecules, e.g. TiOPc, it is not sufficient to look only at one single band. Therefore, the studies presented here, serve as preliminary investigations for further work aiming to a deeper understanding of complex layer growth, orientation and electronic properties of phthalocyanine molecules in thin films.

## 2. Experimental

### *Materials:*

Both CuPc and TiOPc were purchased from commercial sources (Syntec).

### *Raman Spectra:*

Raman spectra of both powders were recorded with a Horiba Jobin Yvon HR 800 spectrometer equipped with CCD and edge filter. The edge filter does not allow detecting of the anti-stokes bands, the lower end of the spectral edge being around 130  $\text{cm}^{-1}$ . A 532.14 nm green laser (double freq. Nd:YAG laser) was used as excitation source, the spectra were recorded with a resolution of 3.7  $\text{cm}^{-1}$  (grating 600 l/mm). The optimum measurement time amounted to 40 seconds. Each spectral region was recorded twice in order to avoid spikes, which lead to measurement artefacts in the spectra.

### *IR Spectra:*

DRIFT (**D**iffuse **R**eflectance **I**nfrared **F**ourier **T**ransform) spectra were obtained on an Equinox 55 Bruker spectrometer equipped with a MCT detector. Single channel spectra of the reference and sample were recorded with a resolution of 2  $\text{cm}^{-1}$  and performing 128 scans. Finely ground KBr powder was used as reference. The

samples (CuPc and TiOPc) were mixed and well ground with potassium bromide powder. The accompanying software (OPUS 4) was applied for calculation of the extinction spectra using the reference spectrum.

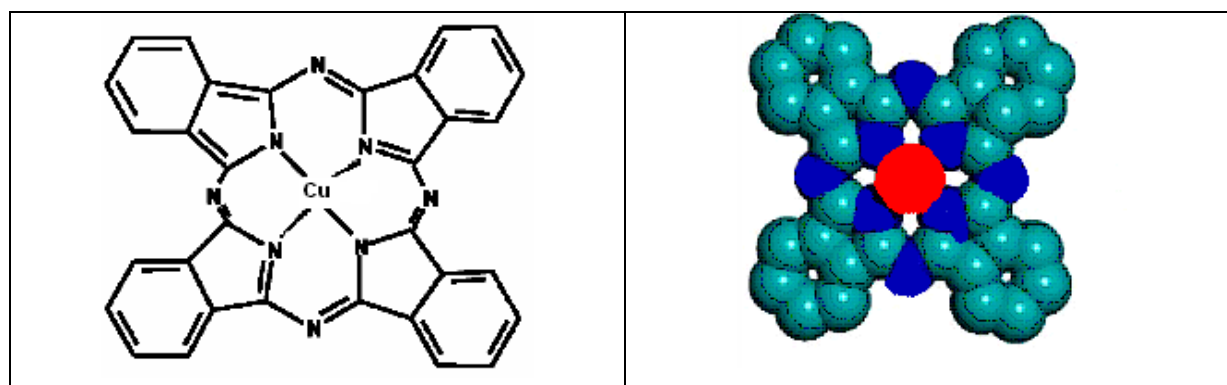
#### *Computational Details:*

Quantum chemical calculations at the density functional level of theory were carried out with the DMol<sup>3</sup> <sup>15</sup> and the Gaussian 03 <sup>16</sup> programs. In the case of DMol<sup>3</sup>, the gradient-correct exchange correlation BPW91 functional<sup>17</sup> was applied and an all-electron double numerical basis set (DNP) was used for the wave function expansion. The Gaussian 03 calculations were performed with the 3-parameter hybrid functional B3LYP as reported by Becke<sup>18</sup>, applying the standard 6-31G\* basis set. In the case of CuPc, a spin-unrestricted scheme was employed. In all calculations, the geometric structures of the molecules were fully optimized, maintaining D<sub>4h</sub> symmetry for CuPc and C<sub>4v</sub> for TiOPc. In all vibrational spectra obtained for the equilibrium ground states no imaginary frequencies were observed, all structures, therefore, represent true minima on the respective Born-Oppenheimer energy hypersurface. The vibrational normal modes were visualized with GaussView 2.1.<sup>19</sup>

### 3. Results and discussion

#### 3.1 Copper phthalocyanine

The planar copper phthalocyanine molecule consists of 57 atoms. The free CuPc molecule possesses D<sub>4h</sub> symmetry. Four isoindole groups are connected at the C atoms of the pyrroles through a nitrogen atom (aza group bridge). The copper atom is located in the centre of the molecule and coordinated to the nitrogen atoms of the pyrrole units (Fig. 1).



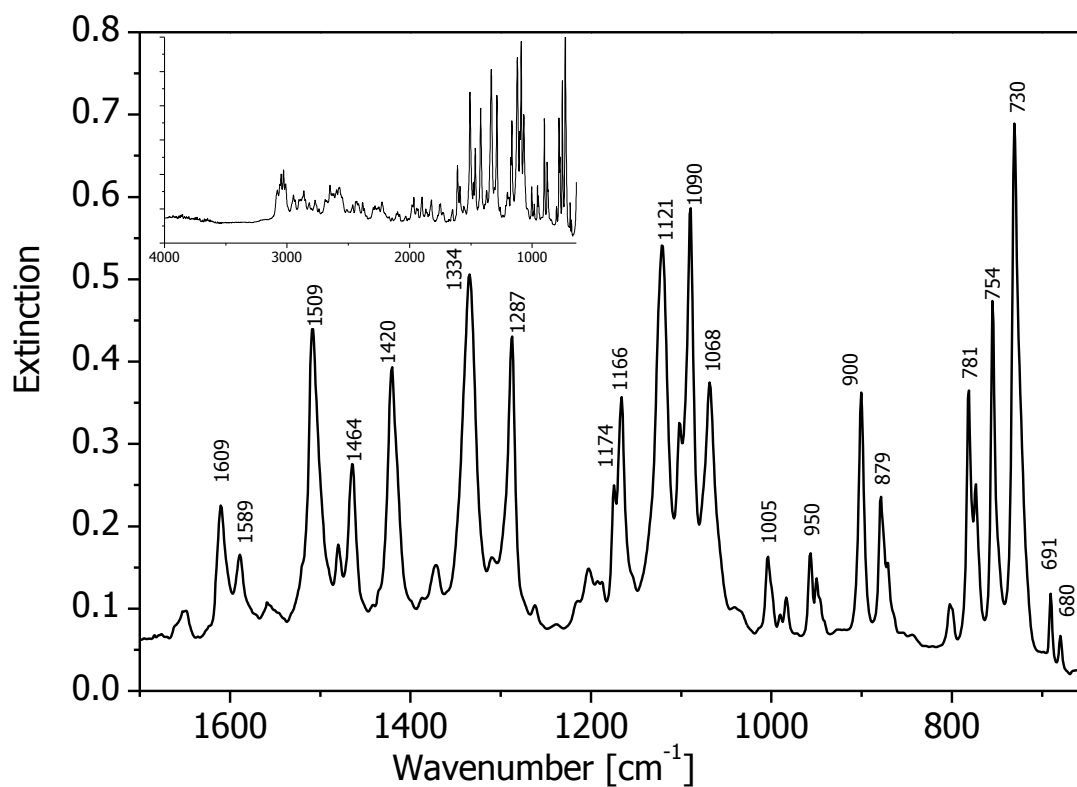
**Fig. 1** Molecular structure of copper phthalocyanine.

Copper phthalocyanine possesses 165 normal modes, which are either IR or Raman active. The irreducible representation for the vibrations is given as follows:

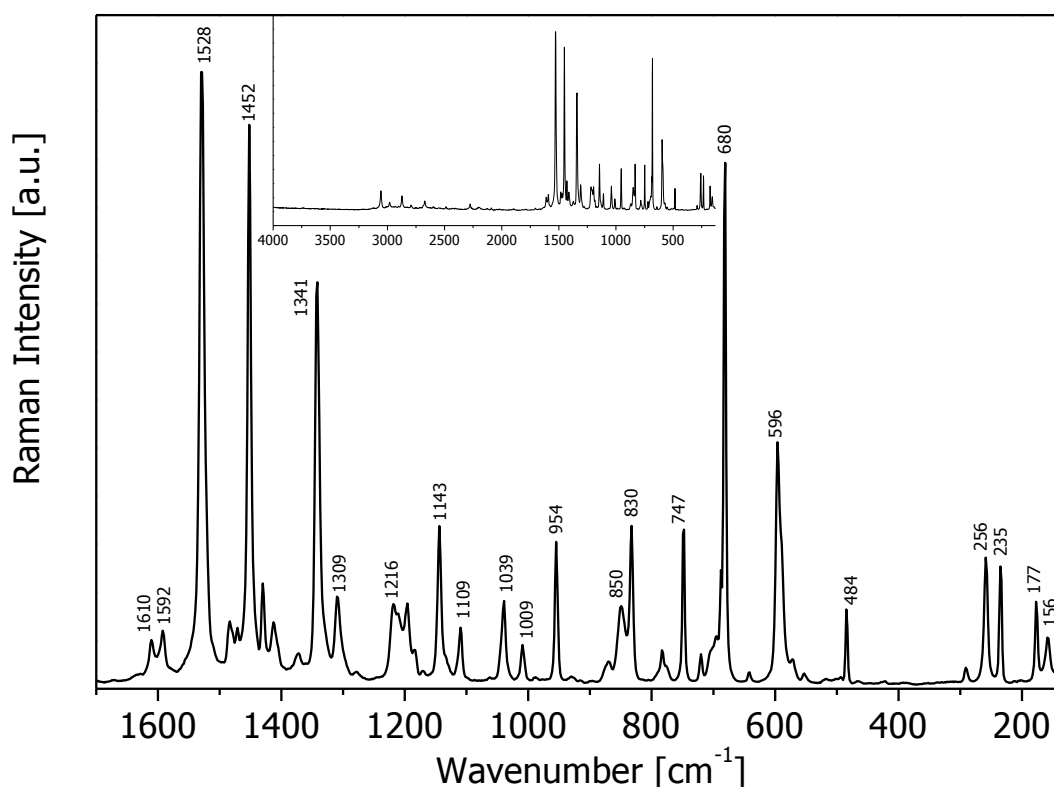
$$\Gamma_{\text{vib}} = 14A_{1g} + 13A_{2g} + 14B_{1g} + 14B_{2g} + (2x)13E_g + 6A_{1u} + 8A_{2u} + 7B_{1u} + 7B_{2u} + (2x)28E_u$$

where  $A_{1u}$  and  $E_u$  modes are IR and  $A_{1g}$ ,  $B_{1g}$ ,  $B_{2g}$  and  $E_g$  are Raman active. The  $A_{1g}$ ,  $B_{1g}$ ,  $B_{2g}$  modes represent in-plane vibrations and the doubly degenerated  $E_g$  modes are out-of-plane modes.

Figures 2 and 3 show the experimentally obtained DRIFT (spectral range 1700 to 630  $\text{cm}^{-1}$ ) and Raman spectra (1700-130  $\text{cm}^{-1}$ ). In both cases, the most intensive bands are labelled and the whole spectral ranges are given as inserts.



**Fig. 2** DRIFT spectrum of copper phthalocyanine powder. The spectral range 4000-630  $\text{cm}^{-1}$  is inserted in the picture.



**Fig. 3** Raman spectrum of copper phthalocyanine. The spectral range 1700-130  $\text{cm}^{-1}$  is inserted.

In Table 1, the most important and intensive experimental IR and Raman frequencies as well as their corresponding tentative assignments are collected. The assignments of the bands were carried out as follows:

- i. by comparison with data reported in the literature: for IR according to Ref. 1, 7, 20, 21 and for Raman on the basis of Ref. 4, 22, 23;
- ii. by means of theoretical predicted frequencies: B3LYP/6-31G\* and BPW91/DNP calculations for the IR spectrum, B3LYP/6-31G\* results in the case of the Raman frequencies;
- iii. by assistance of simulated vibrational pictures.

The attributions of the vibrations, which are labelled with \* indicate new assignments, those which agree with the literature, are marked in the table by a + sign and those, which do not agree, with a – sign. In the IR spectrum, the description of the vibrations at 1287, 1121, 1090, 1068, 1005, and 680  $\text{cm}^{-1}$  is different from that of the other authors. This might be mainly due to the fact, that the most extensive experimental work and attribution of bands were performed for sandwich-type lanthanide phthalocyanines.<sup>20</sup> In the case of the Raman vibrations, our assignments, to a large extent, follow the proposals of Gladkov et al.<sup>22</sup> These authors reported the Raman spectrum of the CuPc analogue ZnPc ( $\alpha$ -form). They separated their spectrum into seven spectral regions and compared the experimental wavenumbers to the frequencies obtained by a normal coordinates analysis. For the following bands, their description deviates from our assignment: 1195, 1143, 1039, and 954  $\text{cm}^{-1}$ . This might be explained by the fact, that the measurements presented in this work were carried out with untreated powder samples, whereas the data reported in the literature was obtained for certain modifications of CuPc and/or thin films.<sup>4, 22</sup> This is also

true for the IR investigations.<sup>1, 7, 21</sup> Furthermore, for these large molecules, it is hard to unambiguously attribute a band to a single normal mode. Due to the  $D_{4h}$  symmetry of CuPc, no common bands are expected in the IR and Raman spectra (exclusion principle). This is reflected by the experimental data, except for a few accidental overlap.

**Table 1** Assignment of bands observed in the IR and Raman Spectra of CuPc

DRIFT Band maximum [cm <sup>-1</sup> ]	Approximate description	Raman Band maximum [cm <sup>-1</sup> ]	Approximate description
over 3000 <sup>+</sup>	benzene C-H stretching	1610 <sup>+</sup>	benzene C-C stretching
1609 <sup>+</sup>	benzene C-C stretching	1592 <sup>+</sup>	pyrrole deformation
1589 <sup>+</sup>	benzene C-C stretching	1528 <sup>+</sup>	benzene and pyrrole C-C stretching
1509 <sup>+</sup>	pyrrole deformation	1481 <sup>+</sup>	aza stretching coupling with pyrrole C-N-C rocking
1479 <sup>+</sup>	isoindole stretching	1470 <sup>+</sup>	benzene C-C stretching
1464 <sup>+</sup>	isoindole stretching	1452 <sup>+</sup>	isoindole deformation (mainly pyrrole)
1420 <sup>+</sup>	isoindole stretching	1373 <sup>*</sup>	isoindole deformation (mainly benzene)
1372 <sup>+</sup>	isoindole stretching	1341 <sup>+</sup>	pyrrole deformation
1334 <sup>+</sup>	pyrrole C-C stretching coupling with aza rocking	1309	pyrrole deformation
1287 <sup>-</sup>	pyrrole C-C stretching	1244 <sup>*</sup>	pyrrole asym C-N stretching coupling with C-H i.p. <sup>a</sup> deformation
1191 <sup>*</sup>	isoindole stretching	1216 <sup>+</sup>	pyrrole stretching coupling with C-H i.p. deformation
1166 <sup>+</sup>	C-H deformation	1195 <sup>-</sup>	C-H deformation
1121 <sup>-</sup>	isoindole deformation	1143 <sup>-</sup>	C-H deformation
1090 <sup>-</sup>	pyrrole C-N asym. stretching	1109 <sup>*</sup>	benzene and inner ring i.p. deformation
1068 <sup>-</sup>	benzene C-C-C deformation	1039 <sup>-</sup>	C-H deformation
1005 <sup>-</sup>	benzene breathing	954 <sup>-</sup>	C-H o. o. p.
950 <sup>*</sup>	C-H o.o.p. <sup>b</sup>	850 <sup>+</sup>	macrocycle breathing
900 <sup>*</sup>	benzene deformation coupling with aza deformation	830 <sup>+</sup>	macrocycle breathing
879	aza stretching coupling with isoindole deformation	747 <sup>+</sup>	pyrrole o.o.p.
781 <sup>*</sup>	isoindole breathing coupling with isoindole deformation	702 <sup>+</sup>	benzene deformation
773 <sup>*</sup>	C-H o.o.p.	680 <sup>+</sup>	macrocycle breathing
754 <sup>+</sup>	Pc ring deformation	644 <sup>+</sup>	isoindole o.o.p.
730 <sup>+</sup>	C-H wagging	596 <sup>+</sup>	macrocycle breathing

680 <sup>-</sup>	benzene radial	570 <sup>+</sup>	benzene deformation
		484 <sup>+</sup>	macrocycle deformation
		290 <sup>*</sup>	isoindole o.o.p coupling with N-Cu-N rocking
		256 <sup>+</sup>	macrocycle breathing
		235 <sup>+</sup>	inner ring of the macrocyclus deformation (N-Cu-N)
		177 <sup>+</sup>	isoindole stretching
		156 <sup>+</sup>	isoindole o.o.p. coupling with benzene o.o.p.

<sup>a</sup> i.p.: in-plane. <sup>b</sup> o.o.p.: out-of-plane <sup>+</sup> Assignment in agreement with the literature. <sup>-</sup> Assignment not in agreement with the literature. <sup>\*</sup> Not assigned or mentioned in the literature.

The experimentally observed infrared frequencies and relative intensities together with the theoretically predicted values (BPW91/DNP and B3LYP/6-31G\*) are given in

Table 2. The best overall agreement with respect to the wavenumbers between experiment and theory is obtained by the BPW91/DNP method (DMol<sup>3</sup>). In contrast to this, the experimental intensities are generally reproduced better by the B3LYP/6-31G\* approach (GAUSSIAN 03). Comparison of experimental and theoretical results shows, that not all of the experimentally observed vibrations and their intensities can be related to the calculated data. The reason for the deviations of the theoretically predicted results from the experiment – both with respect to the wavenumbers and the intensities – might be as follows: All calculations (with both methods for both CuPc and TiOPc) were performed for a single molecule in the gas-phase at 0 K. On the other hand, the experiments were carried out on powder samples at room temperature and ambient atmosphere. This is also true for the other experimental spectra discussed below.



**Table 2** Experimental and calculated IR frequencies and intensities for CuPc

EXPERIMENTAL (DRIFT) FREQ./INT. <sup>a</sup> [cm <sup>-1</sup> ]		DMOL <sup>3</sup> (BPW91/DNP)		GAUSSIAN 03 (B3LYP/6-31G*)		SYM.
		FREQUENCIES [cm <sup>-1</sup> ]	INTENSITIES [km/mol]	FREQUENCIES [cm <sup>-1</sup> ]	INTENSITIES [km/mol]	
1609	<i>w</i>	1611	11	1664	13	<i>E<sub>u</sub></i>
1589	<i>vw</i>	1587	8	1642	11	<i>E<sub>u</sub></i>
1509	<i>s</i>	1503	41	1558	75	<i>E<sub>u</sub></i>
1479	<i>vw</i>	1478	37	1531	0,7	<i>E<sub>u</sub></i>
1464	<i>m</i>	1458	28	1518	20	<i>E<sub>u</sub></i>
1420	<i>s</i>	1413	48	1465	105	<i>E<sub>u</sub></i>
1372	<i>vw</i>	1379	157	1387	215	<i>E<sub>u</sub></i>
1334	<i>vs</i>	1318	51	1371	19	<i>E<sub>u</sub></i>
1287	<i>s</i>	1279	17	1329	45	<i>E<sub>u</sub></i>
1215	<i>vw</i>	1188	0.5	1226	4	<i>E<sub>u</sub></i>
1174 <sup>b</sup>	<i>m</i>					
1166	<i>s</i>	1157	103	1201	72	<i>E<sub>u</sub></i>
1121	<i>vs</i>	1119	103	1151	188	<i>E<sub>u</sub></i>
1102 <sup>b</sup>	<i>m</i>					
1090	<i>vs</i>	1096	0.01	1132	139	<i>E<sub>u</sub></i>
1069	<i>s</i>	1057	19	1095	58	<i>E<sub>u</sub></i>
1005	<i>w</i>	1010	17	1038	7	<i>E<sub>u</sub></i>
956 <sup>b</sup>	<i>w</i>					
950	<i>w</i>	935	5	963	3	<i>A<sub>2u</sub></i>
900	<i>s</i>	885	13	918	31	<i>E<sub>u</sub></i>
879 <sup>b</sup>	<i>m</i>					
801 <sup>b</sup>	<i>w</i>					
781	<i>s</i>	797	1	820	1	<i>E<sub>u</sub></i>
773	<i>m</i>	771	16	786	91	<i>A<sub>2u</sub></i>
754	<i>s</i>	746	33	770	55	<i>E<sub>u</sub></i>
730	<i>vs</i>	720	317	731	134	<i>A<sub>2u</sub></i>
690 <sup>b</sup>	<i>w</i>					
680	<i>vw</i>	635	2	653	4	<i>E<sub>u</sub></i>

<sup>a</sup> v: very, w: weak, m: medium, s: strong. <sup>b</sup> These experimental frequencies could not be identified with corresponding values of the calculations.

Experimental and theoretical Raman frequencies as well as the corresponding intensities of the bands are presented in

Table 3. The calculations were only done at the B3LYP/6-31G\* level of theory (GAUSSIAN 03), because in our current version of DMol<sup>3</sup> Raman intensities are not available. The Raman spectrum for CuPc calculated by the B3LYP/6-31G\* method is in better agreement with the experiment than the IR spectrum obtained by the same approximation, as can be seen from Tables 2 and 4.

**Table 3** Experimental and calculated Raman frequencies and intensities for CuPc

EXPERIMENTAL FREQ./INT. <sup>a</sup> [cm <sup>-1</sup> ]		GAUSSIAN 03 (B3LYP/6-31G*)		SYM.
		FREQUENCY S [cm <sup>-1</sup> ]	SCATTERING ACTIVITIES [Å <sup>4</sup> /AMU]	
1610	<i>w</i>	1644	153	A <sub>1g</sub>
1592	<i>w</i>	1611	16424	B <sub>1g</sub>
1528	<i>vs</i>	1526	120	B <sub>2g</sub>
1481	<i>w</i>	1499	369	B <sub>2g</sub>
1470	<i>w</i>	1478	113	A <sub>1g</sub>
1452	<i>vs</i>	1444	456	A <sub>1g</sub>
1428	<i>w</i>	? <sup>b</sup>	?	
1412	<i>w</i>	1397	1422	B <sub>1g</sub>
1373	<i>vw</i>	1389	2113	A <sub>1g</sub>
1341	<i>s</i>	1353	4966	B <sub>1g</sub>
1309	<i>w</i>	? <sup>b</sup>	?	
1216	<i>w</i>	1244	495	B <sub>2g</sub>
1210	<i>w</i>	1217	1186	B <sub>1g</sub>
1195	<i>vw</i>	1197	448	A <sub>1g</sub>
1143	<i>m</i>	1142	351	B <sub>2g</sub>
1109	<i>w</i>	1067	66	B <sub>2g</sub>
1039	<i>w</i>	1039	354	A <sub>1g</sub>
1009	<i>w</i>	996	0,16	E <sub>g</sub>
954	<i>m</i>	963	1	E <sub>g</sub>
871	<i>vw</i>	897	4	E <sub>g</sub>
850	<i>w</i>	859	148	A <sub>1g</sub>
830	<i>m</i>	795	96	B <sub>1g</sub>
781	<i>vw</i>	786	0.14	E <sub>g</sub>
774	<i>vw</i>	764	820	B <sub>1g</sub>
747	<i>m</i>	723	21	E <sub>g</sub>
703		702	6	B <sub>2g</sub>

680	vs	696	299	A <sub>1g</sub>
641	vw	645	1,8	E <sub>g</sub>
596	s	604	72,7	A <sub>1g</sub>
570	vw	568	0,7	B <sub>1g</sub>
484	w	493	98	B <sub>2g</sub>
290	vw	284	0,8	E <sub>g</sub>
256	m	260	71	A <sub>1g</sub>
235	m	239	31	B <sub>2g</sub>
177	m	174	18	B <sub>1g</sub>
156	w	125	13	E <sub>g</sub>

<sup>a</sup> v: very, w: weak, m: medium, s: strong. <sup>b</sup> These frequencies are missing in the calculation.

### 3.2 Titanyl phthalocyanine

The molecular structure of TiOPc is presented in Fig. 4. In contrast to CuPc, TiOPc is a non-planar molecule and it possesses a polar group (Ti=O) in the center of molecule, which slightly sticks out of the molecular plane.

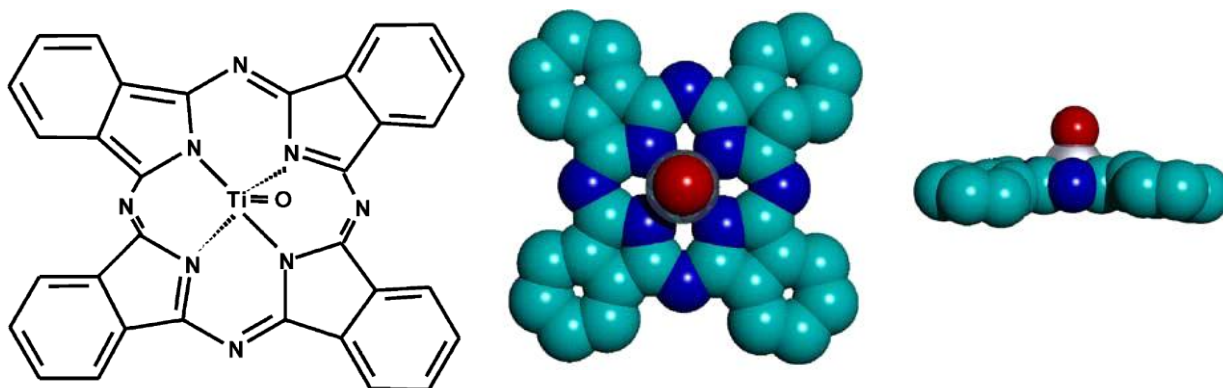


Fig. 4 Molecular structure of the TiOPc molecule.

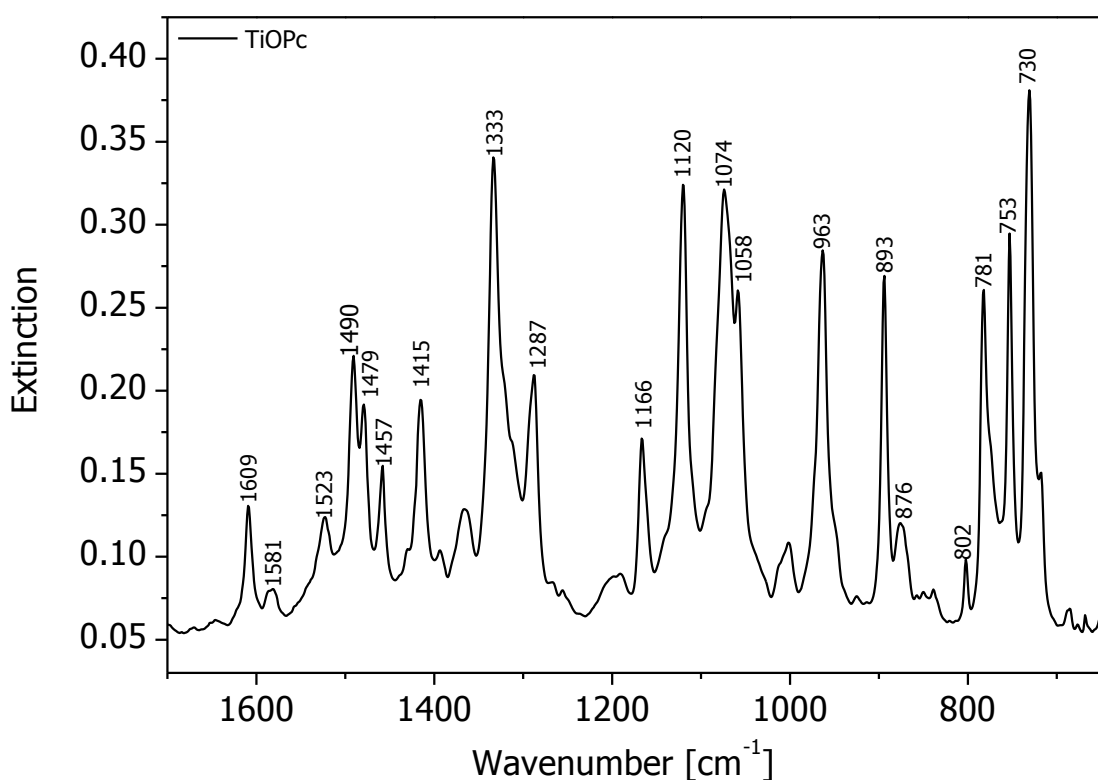
The symmetry of the molecule is C<sub>4v</sub> and it consists of 58 atoms, therefore, 168 normal modes of vibration are expected. The irreducible representation for the vibrations is:

$$\Gamma = 23A_1 + 19A_2 + 21B_1 + 21B_2 + (2 \times) 42E$$

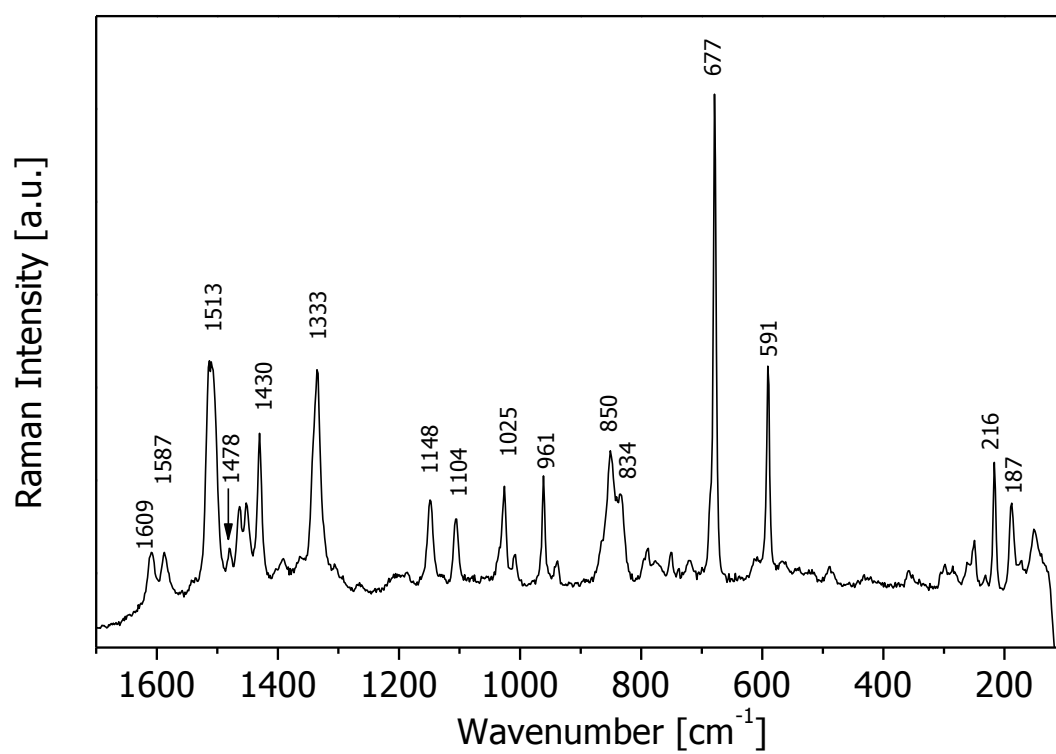
The A<sub>1</sub> and E modes are both Raman and IR active, while the B<sub>1</sub> and B<sub>2</sub> modes are only Raman active. The A<sub>2</sub> modes are neither Raman nor IR active.

In Fig. 5 and Fig. 6 the experimental DRIFT spectrum (spectral range 1700 to 640 cm<sup>-1</sup>) and the Raman spectrum (spectral range 1650 to 130 cm<sup>-1</sup>) of TiOPc pow-

der are shown. The most prominent features are labelled. Wavenumbers of both spectra as well as suggested assignments are collected in Table 4. As in the case of CuPc, the assignment was performed on the basis of literature data (for IR see References: 7, 20, 21; for Raman References: 7, 8) and assisted by our density functional calculations (IR: B3LYP/6-31G\* and BPW91/DNP; Raman: B3LYP/6-31G\*).



**Fig. 5** DRIFT Spectrum of Titanyl Phthalocyanine powder in the spectral range 1700 and 640 cm<sup>-1</sup>.



**Fig. 6** Experimental Raman spectrum of Titanyl Phthalocyanine in the spectral range 1650-130  $\text{cm}^{-1}$ .

**Table 4** Band assignment of the absorption bands of DRIFT and Raman spectrum of TiOPc

DRIFT Band maximum [cm <sup>-1</sup> ]	Approximate description	RAMAN Band maximum [cm <sup>-1</sup> ]	Approximatedescription
1609 <sup>+</sup>	benzene C-H stretching	1609	benzene stretching
1581 <sup>+</sup>	benzene C-C stretching	1587	aza C-N asym. stretching
1523	aza C-N sym. stretching coupling with pyrrole stretching	1513 <sup>-</sup>	aza C-N sym. stretching
1490	pyrrole stretching	1478 <sup>*</sup>	pyrrole deformation
1479	isoindole stretching	1452 <sup>+</sup>	benzene C-C stretching coupling with pyrrole stretching
1457	isoindole stretching	1430 <sup>-</sup>	isoindole deformation
1415	isoindole stretching	1333 <sup>+</sup>	pyrrole C-C stretching coupling with aza rocking
1366	isoindole stretching	1148 <sup>+</sup>	pyrrole stretching
1333 <sup>+</sup>	pyrrole C-C stretching coupling with aza rocking	1104 <sup>+</sup>	C-H deformation
1287 <sup>*</sup>	C-H deformation	1025 <sup>+</sup>	C-H deformation
1166 <sup>*</sup>	C-H deformation	1007 <sup>+</sup>	benzene breathing
1120 <sup>+</sup>	C-H deformation	961 <sup>*</sup>	Ti-O stretching
1074 <sup>+</sup>	C-H deformation	938 <sup>-</sup>	C-H o.o.p. <sup>a</sup>
1058 <sup>*</sup>	isoindole deformation coupling with aza stretching	850 <sup>+</sup>	macrocycle breathing
1003 <sup>*</sup>	benzene breathing	737 <sup>*</sup>	isoindole o.o.p.
963 <sup>+</sup>	Ti-O stretching	677 <sup>+</sup>	macrocycle sym. deformation
893 <sup>+</sup>	isoindole asym. deformation with coupling aza stretching	591 <sup>+</sup>	macrocycle breathing
876 <sup>*</sup>	isoindole deformation coupling with aza sym. stretching	250 <sup>*</sup>	macrocycle breathing
802 <sup>*</sup>	isoindole stretching coupling with N-Ti-N asym. stretching	216 <sup>*</sup>	inner ring deformation
781 <sup>*</sup>	isoindole o.o.p. <sup>a</sup>	187 <sup>*</sup>	isoindole o.o.p (weak)
753 <sup>+</sup>	ring deformation		

730 <sup>+</sup>	C-H wagging		
715 <sup>+</sup>	C-H wagging		

<sup>a</sup> o.o.p.: out-of-plane. <sup>+</sup> Assignment agreement with the literature. <sup>-</sup> Assignment does not agreement with the literature. <sup>\*</sup> Not assigned or mentioned in the literature.

The assignments of the IR bands are in good agreement with those proposed by other authors. However, the weak features at 1003, 948, 876, 802 and 781  $\text{cm}^{-1}$  are not described in the literature. These bands were assigned only according to the theoretically predicted frequencies and their corresponding visualized vibrational pictures. The band at 961  $\text{cm}^{-1}$  in the Raman spectrum is attributed to the Ti=O stretching vibration, in agreement with our DRIFT spectrum, with the IR data reported in Ref. 7 as well as with the calculations performed in this work. The vibration observed at 938  $\text{cm}^{-1}$  is assigned to a C-H out-of-plane vibration, according to the simulated vibrational picture. In contrast to this, Jennings et al.<sup>8</sup> relate the band at 938  $\text{cm}^{-1}$  in their Raman spectrum of amorphous TiOPc to the Ti=O stretching mode. Both our IR and Raman spectrum support our interpretation. In the case of TiOPc, in contrast to CuPc, there are vibrations which are both IR and Raman active, due to the  $C_{4v}$  symmetry of the molecule. An example is the Ti=O stretching mode, which appears at 963  $\text{cm}^{-1}$  in the IR spectrum and at 961  $\text{cm}^{-1}$  in the Raman spectrum. The IR band, however, is one of the most intensive bands in the spectrum, while the Raman feature is rather weak. The reason for this phenomenon is the large change in the dipole moment during the vibration, whereas the polarizability of the molecule is less affected.

**Table 5** Experimental and calculated IR frequencies and intensities for TiOPc

EXPERIMENTAL (DRIFT) FREQ./INT. <sup>a</sup> [ $\text{cm}^{-1}$ ]		DMOL <sup>3</sup> (BPW91/DNP)		GAUSSIAN 03 (B3LYP/6-31G*)		SYM.
		FREQUENCIES [ $\text{cm}^{-1}$ ]	INTENSITIES [ $\text{km/mol}$ ]	FREQUENCIES [ $\text{cm}^{-1}$ ]	INTENSITIES [ $\text{km/mol}$ ]	
1610	<i>m</i>	1619	10	1662	13	<i>E</i>
1581	<i>w</i>	1588	4	1638	7	<i>E</i>
1523	<i>w</i>	1510	0.1	1558	0.1	<i>A</i> <sub>1</sub>
1490	<i>s</i>	1504	8	1538	61	<i>E</i>
1479	<i>s</i>	1478	35	1514	37	<i>E</i>
1457	<i>m</i>	1464	59	1457	75	<i>E</i>
1415	<i>s</i>	1426	1	1435	10	<i>A</i> <sub>1</sub>
1366	<i>w</i>	1345	13	1384	10	<i>A</i> <sub>1</sub>
1333	<i>vs</i>	1298	100	1349	65	<i>E</i>
1287	<i>s</i>	1265	10	1326	25	<i>E</i>
1166	<i>s</i>	1183	7	1198	37	<i>E</i>
1120	<i>vs</i>	1150	49	1149	136	<i>E</i>
1074	<i>vs</i>	1107	111	? <sup>b</sup>	? <sup>b</sup>	
1058	<i>s</i>	1080	20	1090	17	<i>E</i>
1003	<i>w</i>	1000	12	1038	6	<i>E</i>
963	<i>s</i>	1002	121	1075	184	<i>A</i> <sub>1</sub>
948	<i>w</i>	944	0.3	965	0.08	<i>A</i> <sub>1</sub>
893	<i>s</i>	886	20	910	40	<i>E</i>
876	<i>w</i>	836	6	856	7	<i>A</i> <sub>1</sub>
802	<i>w</i>	797	5	818	6	<i>E</i>
781	<i>s</i>	768	8	795	46	<i>A</i> <sub>1</sub>
753	<i>s</i>	745	39	767	57	<i>E</i>
730	<i>vs</i>	717	279	739	0.1	<i>E</i>

<sup>a</sup> v: very, w: weak, m: medium, s: strong. <sup>b</sup> This frequency is missing in the B3LYP/6-31G\* calculations.



In Table 5, experimental and calculated (BPW91/DNP, B3LYP/6-31G\*) IR frequencies and intensities are collected. Both the frequencies and the intensities as obtained at the BPW91/DNP level of theory are in better agreement with the experiment than the respective values as predicted by the B3LYP/6-31G\* calculations. Differences between experiments and theory are due to the reasons as mentioned above in the case of CuPc.

In Table 6, experimental and theoretical Raman frequencies as well as the corresponding intensities of the bands are collected. As in the case of CuPc, the calculations were only performed at the B3LYP/6-31G\* level of theory (see above). The calculated Raman spectrum (frequencies as well as intensities) for TiOPc agrees better with the experiment than the IR spectrum obtained by the same theoretical method (see Tables 6 and 8).

**Table 6** Experimental and calculated Raman frequencies and intensities for TiOPc

EXPERIMENTAL FREQ./INT. <sup>a</sup> [cm <sup>-1</sup> ]		GAUSSIAN 03 (B3LYP/6-31G*)		SYM.
		FREQUENCIES [cm <sup>-1</sup> ]	SCATTERING ACTIVITIES[Å <sup>4</sup> /AMU]	
1609	w	1640	87	A <sub>1</sub>
1587	w	1593	17563	B <sub>2</sub>
1513	s	1558	784	A <sub>1</sub>
1478	vW	1478	273	B <sub>1</sub>
1463 <sup>b</sup>	w	?	?	
1452	w	1457	0.5	E
1430	s	1435	214	A <sub>1</sub>
1333	s	1343	4820	B <sub>2</sub>
1148	w	1216	1330	B <sub>2</sub>
1104	w	1138	432	B <sub>1</sub>
1025	w	1055	132	B <sub>1</sub>
1007	vW	1039	349	A <sub>1</sub>
961	w	1075	35	A <sub>1</sub>
938	vW	998	0.2	B <sub>1</sub>
850	vW	856	179	A <sub>1</sub>
737	vW	739	18	E
677	vs	691	322	A <sub>1</sub>
591	s	601	67	A <sub>1</sub>
250	vW	250	58	A <sub>1</sub>
216	w	215	15	B <sub>1</sub>
187	w	179	15	B <sub>2</sub>

<sup>a</sup> v: very, w: weak, m: medium, s: strong. <sup>b</sup> Frequency missing in the calculations.

Comparing the theoretical Raman spectra both for CuPc and TiOPc with the experiments, two outstanding deviations from the experiment are obvious: (1) in each case, the most intensive calculated band (1611 cm<sup>-1</sup> for CuPc and 1593 cm<sup>-1</sup> for TiOPc) corresponds to very weak bands in the experiments (1592 and 1585 cm<sup>-1</sup>, respectively); (2) on the other hand, very strong bands observed in the experimental spectra (the third intensive in the case of CuPc at 680 cm<sup>-1</sup> and the most intensive for TiOPc at 677 cm<sup>-1</sup>) appear in the calculated spectrum as very weak bands. As mentioned above, the reason for this fact is that the experimental conditions differ

from the assumptions underlying the calculations, i. e. single molecules in the gas phase at 0 K.

Additionally, the most intensive bands in IR and Raman spectra for both molecules could be identified. The intensities of the corresponding IR and Raman bands are rather different, especially in the case of the Ti=O stretching vibration, which is the only o.o.p mode in TiOPc. Therefore, it will be very helpful to characterise the molecules using both IR and Raman methods for polarisation measurements on thin films prepared by different experimental conditions, e.g. deposition rate, temperature, substrate or varying layer thickness. These factors significantly influence the orientation of the molecules.

## 4. Conclusion

In this work we completely characterised the vibrational spectra (IR and Raman) of CuPc and TiOPc, which show different structural and electronic properties. Complete assignments of the experimentally observed vibrational modes for these large molecules, which show complex spectra, were done with the help of density functional calculations. The results obtained for the powder spectra in this investigation will be essential for further work on ultra thin films (2-50 nm) and for the understanding of the film growth with respect to the orientation of the phthalocyanine molecules.

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