Raman Tensor Calculation for Magnesium Phthalocyanine

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Abstract

We present ab-initio density functional (DFT) calculations of the vibrational spectra of neutral Magnesium phthalocyanine (MgPc) molecule and of its Raman scattering intensities.

1 Introduction

Organic materials are attractive for electronic industry, because they promise large versatility based on organic chemistry, low price based on very common elements used as building blocks and interesting mechanical properties. There is quite a vigorous research activity in organic materials for electrical applications - from insulators through semiconductors to conductors and even superconductors. Here we are concerned with metal phthalocyanines (MPc). Electronic structure calculations \cite{1} and recent experimental observation of the possibility to dope these materials by adding electrons \cite{2} resembles somewhat the situation of fullerenes. In our previous paper we speculated about possible phase diagrams for electron doped MgPc \cite{3}. While these possibilities are under active experimental considerations, we noticed that for the commonest experimental diagnostic, namely Raman scattering there is no reference calculation of either modes nor Raman intensities (with exception of ZnPc \cite{14}). In this paper we focused our interest on the vibrational properties of MgPc, which we wish to study ab-initio. While our final aim will be to compute spectra of doped and undoped molecules, this work will be restricted to neutral undoped MgPc, which has not been studied so far.

2 Technical details.

All our calculations were done using the PWscf software package \cite{4}, which is a plane-wave basis set DFT implementation. We used the LDA approximation
with Slater approximation for exchange and Perdew-Zunger functional for correlations effects. In order to lower the plane wave energy cut-off we used the non-local RRKJ3 ultra–soft pseudopotentials \cite{5}. The kinetic energy cut-off was 35Ry for the wave functions basis set and 280Ry for the charge density basis set. The plane-wave basis set assumed periodic boundary conditions. The unit cell had dimensions $21 \times 21 \times 11\text{Å}$, therefore including enough vacuum to represent the isolated molecule.

By energy optimization we found the equilibrium molecular structure with structural parameters as in Table 2. The molecule has $D_{4h}$ symmetry group and is planar. The electronic structure agrees well with former calculations of Liao et. al.\cite{1}. Some levels near the HOMO–LUMO gap are listed in the table 1.

We calculated the vibrational spectra of neutral, undoped MgPc by means of the density functional perturbation theory \cite{6}. The dynamical matrix was calculated in Cartesian coordinates. In the isolated molecule with $N$ atoms there are $3N - 6$ genuine vibrations while 6 modes corresponds to translation–rotational degrees of freedom with zero frequency. In reality due to periodic images of molecules there is a weak virtual interaction which can cause "libration" of the molecule at nonzero, even imaginary frequency. We eliminated these modes by transforming the dynamical matrix to internal coordinates and setting the corresponding dynamical matrix elements to zero. We checked that after this procedure we obtained eigenvectors of correct symmetry. Assignment of irreducible representation to all eigenvectors was done by projection on symmetry adapted bases of all linearly independent atomic displacement. For $N = 57$ atoms there are 165 vibrations

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

where $E_g$ and $E_u$ are two–fold degenerated modes. The calculated frequencies are summarized in Fig. 2.

The Raman intensity is related to the change of molecular polarizability due to the deformation introduced by the vibration. We calculated the polarizability derivatives with respect to deformations in the static limit.

With each vibrational mode $q_i$ is associated a Raman tensor $T^{\mu \nu}_{i}$ given by

$$T^{\mu \nu}_{i} = \frac{d \alpha_{\mu \nu}}{d q_i}$$

Here $\mu$, $\nu$ are Cartesian indices, $\alpha_{\mu \nu}$ is the polarizability tensor defined as $\alpha_{\mu \nu} = \frac{\partial^2 U}{\partial E_{\mu} \partial E_{\nu}}$, $U$ is the total energy and $E$ an external electric field. Therefore one has to calculate third derivatives of total energy $\frac{\partial^3 U}{\partial E_{\mu} \partial E_{\nu} \partial x_l}$. The energy derivatives with respect to atomic displacements are forces acting on atomic nuclei, and are calculated via the Hellman-Feynman theorem. We extracted the force dependence on electric field by numerical differences. Applied fields were $\pm 1 \times 10^{-3}$, $\pm 2 \times 10^{-3}$, $\pm 4 \times 10^{-3}$ a.u.. Details about application of electric field within periodic boundary conditions are the same as in Ref. 7. There
are alternative methods for the Raman tensor calculation using linear response theory \[8, 9\]. However, numerical derivative method with finite field is computationally less demanding for the present case, where moreover the implementation is very simple.

From the Raman tensor Eq. (1) we calculated for each mode the gas phase (angle averaged) Raman scattering cross section following \[10, 11\] in the form:

\[
\frac{d\sigma_i}{d\Omega} = \frac{(2\pi\nu_0)^4 h(n_i + 1)}{c^4} \frac{45\alpha'_i^2 + 7\gamma'_i^2}{8\pi\nu_i} \frac{4}{45}
\]

\[
\alpha'_i = \frac{1}{3} (T_{xx}^i + T_{yy}^i + T_{zz}^i)
\]

\[
\gamma'_i = \frac{1}{2} \left\{ (T_{xx}^i - T_{yy}^i)^2 + (T_{xx}^i - T_{zz}^i)^2 + (T_{yy}^i - T_{zz}^i)^2 + 6[(T_{xy}^i)^2 + (T_{xz}^i)^2 + (T_{yz}^i)^2] \right\}
\]

\[
n_i = \left[ \exp \left( \frac{h\nu_i}{kT} \right) - 1 \right]^{-1}
\]

\(\nu_0\) is frequency of incident light, \(n_i\) is equilibrium occupation number for the initial vibrational state \(i\) at the given temperature \(T\). The \(\alpha'\) and \(\gamma'^2\) are isotropic and anisotropic parts of the Raman tensor. Both are invariant under rotations. Formula (2) is valid for the most common experimental setup when incident ray, observed ray, and incident light polarization of electric field are perpendicular to each other.

The Raman tensor of a particular mode must belong to the same irreducible representation as that vibration mode. In a coordinate system connected to the molecule as indicated on Fig. 1 all symmetric tensors of second rank are divided according to irreducible representations in the form:

\[
A_{1g} : \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}, \quad B_{1g} : \begin{pmatrix} c & 0 & 0 \\ 0 & -c & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad B_{2g} : \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad E_g : \begin{pmatrix} 0 & 0 & e \\ 0 & e & f \\ e & f & 0 \end{pmatrix}
\]

(3)

Traceless irreducible representations possess only the anisotropic part, while the \(A_{1g}\) mode has both parts. Weights in front of \(\alpha'\) and \(\gamma'\) in formula (2) (45 and 7 respectively) can be changed by observation geometry, thus providing a way to (partially) assign symmetry to vibration eigenmodes (see for example Ref. [11]). We note that for the \(E_g\) representation it is possible to define a single independent parameter \(\sqrt{e^2 + f^2}\) because of the degeneracy and orthogonality of degenerated modes.

3 Results and discussion

In Table 2 we give our LDA optimized structure of MgPc. In comparison with data in references \[1, 12\] we see a reasonable agreement. The difference can be attributed to different density functional (GGA in Ref. \[1\]). LDA is known to slightly overbind in covalent bonds. Kohn-Sham orbitals energies (Tab. 1) are
given relative to vacuum zero taken as the SCF electrostatic potential far from the molecule. They are also in good agreement with Ref. [1] as far as we can read off values from fig. 2 of Ref. [1].

Vibrational spectra of various metal-phthalocyanines were experimentally measured [13] by means of Raman spectroscopy. In the case of ZnPc there is also a DFT calculation of the vibrational and Raman spectra [14]. In general the most intense peak was found to be in the interval 1500-1550 cm\(^{-1}\) depending on the central atom.

Our calculated vibration spectrum of MgPc is on Fig. (2). Above the frequency line for Raman active modes we write the corresponding non-zero component of Raman tensor as defined by Eq. (3). The simulated Raman spectrum according to formula (2) is shown on Fig. (3). To simulate spectrum for each intensity and frequency we added Gaussian with the spread $\sigma=5$ cm\(^{-1}\). We considered the low temperature limit ($n_i=0$) and low incident light frequency limit. Our most intense Raman scattering mode is at 1587 cm\(^{-1}\) with symmetry $B_{1g}$. This is similar to ZnPc which is at 1516 cm\(^{-1}\) with symmetry $B_1$.

The results of the presented calculation should be compared with Raman data of MgPc, as soon as available. It will also serve as a starting point for future work on the electron doped molecules [2].

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Table 1: Kohn-Sham eigenvalues spectra and irreducible representation of wavefunctions near the HOMO–LUMO gap. Note that $e_g$ and $e_u$ orbitals are two-fold degenerated.

| level     | KS-eigenvalue [eV] | symmetry |
|-----------|--------------------|----------|
| LUMO+1    | -2.241             | $b_{1u}$ |
| LUMO      | -3.692             | $e_g$    |
| HOMO      | -5.132             | $a_{1u}$ |
| HOMO-1    | -6.092             | $b_{2g}$ |
| HOMO-2    | -6.446             | $b_{2u}$ |
| HOMO-3-4  | -6.526             | $e_u$    |

Table 2: Structure of MgPc. Bond lengths are in Å, angles in degrees. Notations corresponds to labels on Fig. 1.
Figure 1: Schematic structure of the MgPc molecule. Orientation of coordinate system is important for definition of the Raman tensors by Eq. (3).
Table 2: Frequencies and independent Raman tensor components of neutral MgPc. Frequencies are in cm$^{-1}$, Raman tensor components in atomic units (distance in Bohr radii $a_0$, energy in Rydbergs, and electric fields units $e/a_0$).

Note that $A_{1g}$ has two independent components, the first is $a$ and the second $b$ following the notation in Eq.(3).
Figure 3: Calculated Raman spectrum of MgPc for very low excitation frequency and low temperature.