DFT study of vibronic properties of d^8 (Ni-, Pd-, and Pt-) phthalocyanines

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By means of density functional theory, we have studied the electronic structure and vibronic properties of single neutral NiPc, PdPc, and PtPc molecules and their singly and doubly ionized cations and anions. In particular, the vibronic couplings and reorganization energies of all systems are compared. Partitioning of the reorganization energy, corresponding to the photoelectron spectra of the first and second ionizations of studied molecules, into normal mode contributions shows that the major contributions are due to several vibrational modes with a1g symmetry and energies lower than 1600 cm^{-1}. The results reveal that the reorganization energy due to the singly positive ionization in the studied molecules is up to about one order of magnitude less than other reorganization energies. This makes these metal phthalocyanines, from the perspective of intramolecular reorganization energies, attractive as electron donor for intramolecular electron transfer in electron acceptor-donor systems. © 2013 American Institute of Physics.

I. INTRODUCTION

Metal phthalocyanines (Fig. 1), a class of weakly semiconducting organic dye molecules, have attracted considerable attention due to their electronic, optical, and structural properties. The wide range of their application includes chemical sensors,1–3 devices using photoelectric conversion,4 hetero-junction organic solar cells,5,6 optoelectronic devices,7–9 and data storage.10 Especially, their application in photoconductive and photovoltaic response is promising.11–13 Particularly, the photoinduced electron transfer in a system composed of fullerenes as electron-acceptor molecules covalently linked to phthalocyanines as photoactive donors has been observed.14

Better understanding of the influence of molecular structures of the donors and acceptors on photoinduced electron transfer reaction rates helps to improve the capture and storage of solar energy. In π-conjugated systems, the electronic transport properties are manipulated by the strong coupling between geometric and electronic structure.15–17 The electronic transport is efficient when the electronic coupling between adjacent molecules is maximized and the reorganization energy is minimized.18–21 Small reorganization energies in electron transfer reactions result in acceleration of the charge separation process and deceleration of the charge recombination process. We consider only the intramolecular reorganization energy, which originates from the change in optimized geometry of the molecule due to the gain or loss of electrons.22–24 Density functional theory (DFT) has already been employed to study the decomposition of the reorganization energy in several organic molecules, including indolocarbazoles and several triarylamine derivatives, among the normal modes, i.e., in the internal coordinate space, in order to identify the molecular segment which has most contributions to the reorganization energy.25 In case of metal-free phthalocyanines, the charge transport in their liquid crystalline phase has been investigated calculating the reorganization energy.26 By means of DFT, we study the electronic structure and vibronic properties of single neutral NiPc, PdPc, and PtPc molecules and their singly and doubly ionized cations and anions. The results point to a collective interaction of several vibrational modes with the molecular electronic structure rather than one particular mode.

The gas-phase experiments of the reactions that remove/donate electrons from/to the molecules which are singly or even multiply charged, e.g., buckminsterfullerene,27 provide a perspective to the fundamental process of electron transfer. The double-electron transfer reaction has been previously observed between triply charged buckminsterfullerene, and the polycyclic aromatic hydrocarbon molecules anthracene, corannulene, benzo[rst]pentaphene, and pyrene.28,29 Besides, the stability of doubly ionized cations of metal phthalocyanines have been already reported.30 Therefore, we have also considered the double ionization in our study.

II. COMPUTATIONAL METHODS

At the DFT level of theory, we previously31 performed geometry optimization for D_{4h} symmetric single neutral molecules of NiPc, PdPc, and PtPc, along with singly and doubly charged cations and anions of all molecules. We showed that ionization shrinks the HOMO-LUMO gap of the studied molecules. In the current study, those DFT calculations, which utilized the hybrid functional B3LYP32–34 and def-TZVP basis set,35,36 are extended to the determination of vibrational frequencies and normal modes. The calculations were performed with TURBOMOLE 5.10.37,38 Moreover, we performed similar calculations with def2-TZVP39 basis set and def2-ecp40 effective core potential which includes relativistic effects for heavy transition metals (Pd and Pt). These
calculateds of the electronic structure give very similar results. In Tables I and II, we compare the energies of the frontier molecular orbitals and the HOMO-LUMO gap energies for both basis sets.

To calculate the reorganization energy, we consider two potential energy surfaces for electronic states 1 and 2 which correspond to the neutral state and the ionized state of the molecule. The intramolecular reorganization energy $\lambda$ consists of two terms called relaxation energies\textsuperscript{21, 41, 42}

$$\lambda = \lambda^{(1)} + \lambda^{(2)},$$

where $\lambda^{(1)}$ is the difference of energies of state 1 in geometries 1 and 2, in which the geometry $i$ denotes the molecular geometry optimized in state $i$. Similarly, $\lambda^{(2)}$ is the difference of energies of state 2 in geometries 1 and 2 (see Fig. 2). Expanding the potential energies of the neutral and the ionized states in a power series of the normal coordinates indicates how each vibrational mode contributes to the reorganization energy.\textsuperscript{42} The Huang-Rhys factors are the contribution coefficients which equal the square of so-called vibronic coupling constants ($g^2$). Similar to our previous study,\textsuperscript{43} the Huang-Rhys factors corresponding to reorganization energies $\lambda^{(1)}$ and $\lambda^{(2)}$ were calculated by projecting the deformation pattern onto the vibrational modes of the relevant neutral and charged molecules, respectively. The normal modes of the neutral and ionized states are generally related by a transformation consisting of a translation and a rotation. The rotation matrix is the so-called Duschinsky matrix\textsuperscript{44} which describes the mixing of the normal modes. We calculated the Duschinsky matrices by the DUSHIN program.\textsuperscript{31}

III. RESULTS AND DISCUSSIONS

The results of projecting the deformation pattern onto the vibrational modes based on DFT/B3LYP calculations with def2-TZVP and def2-ecp effective core potential for NiPc are shown in Figs. 3–6 (for the comparison of the results of both basis sets for all studied molecules, see the supplementary material\textsuperscript{47}), where the relaxation energies $\lambda^{(1)}$ and $\lambda^{(2)}$ are partitioned into contributions from the vibrational modes. In these figures, the panels on the left show the Huang-Rhys factors related to $\lambda^{(1)}$ where the deformation pattern is projected onto the vibrational modes of the relevant neutral molecule, whereas the panels on the right show the Huang-Rhys factors related to $\lambda^{(2)}$ where the deformation pattern is projected onto the vibrational modes of the relevant ionized molecule. The total relaxation energies, obtained from the normal mode analysis, are shown in Table III. Our calculations show that all vibrational modes contributing to the reorganization energy have $a_{1g}$ symmetry. Moreover, the vibronic features of

<p>| TABLE I. Energy (eV) of calculated frontier molecular orbitals for NiPc, PdPc, and PtPc. |
|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|</p>
<table>
<thead>
<tr>
<th>HOMO-1/HOMO-2 (e$_g$)</th>
<th>HOMO (a$_{1u}$)</th>
<th>LUMO/LUMO+1 (e$_g$)</th>
<th>HOMO-LUMO gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiPc</td>
<td>−6.772</td>
<td>−5.117</td>
<td>−2.908</td>
</tr>
<tr>
<td>PdPc</td>
<td>−6.586</td>
<td>−5.200</td>
<td>−2.923</td>
</tr>
<tr>
<td>PtPc</td>
<td>−6.360</td>
<td>−5.236</td>
<td>−2.902</td>
</tr>
<tr>
<td>NiPc</td>
<td>−6.657</td>
<td>−5.176</td>
<td>−2.944</td>
</tr>
<tr>
<td>PdPc</td>
<td>−6.626</td>
<td>−5.255</td>
<td>−2.972</td>
</tr>
<tr>
<td>PtPc</td>
<td>−6.435</td>
<td>−5.292</td>
<td>−2.960</td>
</tr>
</tbody>
</table>

$^a$B3LYP.

$^b$Reference 31.
Moreover, Table IV shows that, in each of the studied (dashed lines), geometry deformation \( \lambda \) as a function of molecular geometry \( Q \).

FIG. 2. Schematic view of potential energy surfaces for two electronic states (1, right) contributing to the relaxation energies \( \lambda^{(1)} \) and \( \lambda^{(2)} \).

\( \lambda^{(1)} \) and \( \lambda^{(2)} \), corresponding to the molecules NiPc, PdPc, and PtPc with the same ionization, are roughly similar regardless of the central metal atom. This can be understood by noting that the influence of the central metal atom on the vibrational modes, contributing to the reorganization energy, is negligible. It can also be noted that the DFT calculations of reorganization energies and vibronic couplings with both basis sets give very similar results.

Except for singly negative ionizations, the reorganization energy \( \lambda \) decreases when the atomic number of the central metal atom increases. In positive ionizations, the difference \( \Delta \lambda \) of the relaxation energies is less than 0.3 meV, which shows that the curvature of the PES of the molecule has been changed only slightly due to the ionization. This value is larger for negative ionizations (Table IV). Moreover, Table IV shows that, in each of the studied molecules, the reorganization energy due to the geometry deformation in singly charged cations is up to about one order of magnitude less than the reorganization energy due to other degrees of ionization, which clarifies why metal phthalocya-

nines have the potential of playing a role as electron donor for intramolecular electron transfer in acceptor-donor systems (e.g., see Ref. 14).

Besides, the partitioning of the relaxation energy into normal mode contributions shows that the major contributions are due to several vibrational modes with wave numbers lower than 1600 cm\(^{-1}\), except two CH stretching modes in the range of 3100–3400 cm\(^{-1}\) which have negligible contribution to the relaxation energy. In positive ionizations, the main contribution to the relaxation energy comes from high-energy vibrations and the contribution from low-energy vibrations to \( \lambda \) is negligible. This high-energy contribution is in fact distributed over several vibrational modes with wave numbers in the range of 1000–1600 cm\(^{-1}\). For NiPc\(^{-1}\), there is a very elongated mode in the low-energy region which makes the contribution of other vibrational modes to the reorganization energy negligible. For other negative ionizations, although there are very elongated modes in the low-energy region (between 200 and 350 cm\(^{-1}\)), the contribution of other vibrational modes above 350 cm\(^{-1}\) is still significant.

The difference in the relaxation of negatively and positively ionized molecules can be discussed on the basis of the electronic structure of molecular orbitals through which the vibrational relaxations occur. Positively charged molecules are formed by emptying the HOMO. As the HOMO possesses \( \pi \)-electron character, a positively charged molecule is relaxed via the vibrational excitations involving \( \pi \)-electrons (1000–1600 cm\(^{-1}\), related to stretching modes of C=C and C=N). As the amount of charge increases (doubly ionized states), more \( \pi \)-electrons are involved in the relaxation process. This is seen as the increased contribution of frequencies in the range of 1000–1600 cm\(^{-1}\) (related to stretching modes of C=C and C=N). When an electron is added to the molecule, its degenerate LUMO and LUMO+1, which possess a certain \( d_{yz}/d_{xz} \) (14%) character, are occupied. Thus, the metal N in-plane bond bending in the range of 200–350 cm\(^{-1}\) may be involved in the relaxation of negatively ionized states as seen in the Huang-Rhys factors. It has been shown before for purely aromatic molecules that high frequency stretching modes of C=C are primarily involved in the relaxation during hole/electron transport.\(^{45,46}\) Adding a heteroatom like S into the carbon chain of conjugated systems seems to strongly influence the low frequency modes of C–C bonds.\(^{45,46}\)

FIG. 3. The Huang-Rhys factors of the vibrational modes of neutral NiPc (left) and NiPc\(^{+1}\) (right) contributing to the relaxation energies \( \lambda^{(1)} \) and \( \lambda^{(2)} \), due to the geometry deformation in singly positive ionization.
TABLE III. The relaxation energies $\lambda^{(1)}$ and $\lambda^{(2)}$ in meV, due to the geometry deformation in singly and doubly charged cations and anions of the molecules NiPc, PdPc, and PtPc.

<table>
<thead>
<tr>
<th></th>
<th>Doubly negative ionization</th>
<th>Singly negative ionization</th>
<th>Singly positive ionization</th>
<th>Doubly positive ionization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda^{(1)}$</td>
<td>$\lambda^{(2)}$</td>
<td>$\lambda^{(1)}$</td>
<td>$\lambda^{(2)}$</td>
</tr>
<tr>
<td>NiPc</td>
<td>121 118</td>
<td>207 193</td>
<td>19 19</td>
<td>66 66</td>
</tr>
<tr>
<td>PdPc</td>
<td>130 128</td>
<td>29 29</td>
<td>18 18</td>
<td>63 63</td>
</tr>
<tr>
<td>PtPc</td>
<td>137 134</td>
<td>31 31</td>
<td>18 18</td>
<td>63 63</td>
</tr>
</tbody>
</table>

**FIG. 4.** As Fig. 3, but for NiPc (left) and NiPc$^{-1}$ (right), singly negative ionization.

**FIG. 5.** As Fig. 3, but for NiPc (left) and NiPc$^{+2}$ (right), doubly positive ionization.

**FIG. 6.** As Fig. 3, but for NiPc (left) and NiPc$^{-2}$ (right), doubly negative ionization.
The efficiency of these results can be checked by measuring the vibrational structure of the first and second ionization peaks of the ultraviolet photoelectron spectroscopy spectra for NiPc, PdPc, and PtPc. In order to improve our results, we computed the Duschinsky rotation matrices of normal modes. There is only mixing of one pair of $a_g$ modes among the vibrations for cations, anions, and dianions of the studied molecules. There is only mixing of one pair of $a_g$ modes in NiPc$^{2+}$ (around 1140–1210 cm$^{-1}$), whereas two pairs of $a_g$ modes (around 1140–1210 cm$^{-1}$ and 1410–1470 cm$^{-1}$) of PdPc$^{2+}$ and PtPc$^{2+}$ are mixed. In all cases, the mixing of the modes is less than 20% (detailed in the supplementary material[37]). Therefore, neglecting the mixing of a few vibrational modes is still reasonable.

### IV. CONCLUSION

We have presented a DFT study of the reorganization energy for the first and second ionizations of NiPc, PdPc, and PtPc molecules. Since, in each of these molecules, the reorganization energy due to singly positive ionization is less than other counterparts, from the perspective of intramolecular reorganization energies, the results indicate that d$^8$ metal phthalocyanines, can better play the role of an electron donor, rather than an electron acceptor, in intramolecular electron acceptor-donor systems, although for a complete conclusion, the intermolecular reorganization energies, which are beyond the aim of our study, should also be taken into account. The partitioning of the reorganization energy into normal mode contributions shows that the major contributions are due to several vibrational modes lower than 1600 cm$^{-1}$. The only exception is NiPc$^{-1}$, for which there is a very elongated mode in the low-energy region which makes the contribution of other vibrational modes in the reorganization energy negligible. Moreover, there is only mixing of a few $a_g$ modes in the region of 1000–1600 cm$^{-1}$ among the vibrations contributing to the reorganization energy for anions and dications of the studied molecules, excluding NiPc$^{-1}$, due to the Duschinsky rotation. The DFT calculations with effective core potential which considers relativistic effects give very similar results to those without effective core potential.

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**TABLE IV.** The reorganization energy $\lambda$ and absolute difference of the relaxation energies $\Delta\lambda$, in meV, due to the geometry deformation in singly and doubly charged cations and anions of the molecules NiPc, PdPc, and PtPc.

<table>
<thead>
<tr>
<th></th>
<th>Doubly negative ionization</th>
<th>Singly negative ionization</th>
<th>Singly positive ionization</th>
<th>Doubly positive ionization</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda$</td>
<td>$\Delta\lambda$</td>
<td>$\lambda$</td>
<td>$\Delta\lambda$</td>
</tr>
<tr>
<td>NiPc</td>
<td>239</td>
<td>3</td>
<td>400</td>
<td>13</td>
</tr>
<tr>
<td>PdPc</td>
<td>258</td>
<td>3</td>
<td>58</td>
<td>0</td>
</tr>
<tr>
<td>PtPc</td>
<td>271</td>
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<td></td>
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<tr>
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<tr>
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<tr>
<td>PtPc</td>
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<td>2</td>
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</table>

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47See the supplementary material at http://dx.doi.org/10.1063/1.4773014 for the comparison of the results of both basis sets for all studied molecules.