# Photoswitching of the Optical and Electrical Properties of One-dimensional $\pi$-Electron Systems

Nikolai Tyutyulkov* and Fritz Dietz
Wilhelm-Ostwald Institut für Physikalische und Theoretische Chemie, Universität Leipzig,
Johannisallee 29, D-04103 Leipzig
* Permanent adress: Faculty of Chemistry, University of Sofia, BG-1126 Sofia, Bulgaria
Reprint requests to Prof. F. D.; Fax: +49-341-97-36399,
E-mail: dietz@quant1.chemie.uni-leipzig.de

Z. Naturforsch. **57 a,** 89–93 (2002); received January 4, 2002

The photoswitching of the energy gap width of the isomeric forms of photoresponsive polymers with homonuclear photochromic diarylethene elementary units is investigated theoretically, taking into account the correlation correction. It is shown that a real switching of electrical conductivity (insulator ⇔ semiconductor or conductor) can not be realized with polymers with alternant homonuclear $\pi$-electron systems within the elementary unit. A change and tuning-in of the light absorption is possible in most cases.

*Key words:* Photoswitching; Photoresponsive Polymers; Band Structure.

## 1. Introduction

Suitable systems for the photoswitching of many physical (and may be chemical) properties are photochromic diarylethenes whose photocyclization gives dihydrophenanthrenes with a changed $\pi$-electron system and therefore changed properties [1]. If the reactive positions of the aryl groups are substituted with methyl (alkyl) groups, the dihydrophenanthrene photocyclization product is no longer sensitive to oxygen, and the reaction is reversible [2]. In this case the system has photochromic properties [3, 4]. The reversible photochemically induced valence tautomerism was also realized with more rigid compounds, the [2,2]-metacyclophanenes [5] and [2,2]-metacyclophanedienes [6] (see Fig. 1).

Recently, Mitchell [7] has shown that systems with up to three metacyclophanediene repetition units are multi-state switches of photochromic properties. Although some molecular [8 - 11] and oligomeric [12, 13] photochromic systems with photoswitchable redox potentials have been realized, only one example of a photochromic conjugated polymer (oligomer) with switchable electrical conductivity is known [14].

The aim of this paper is the design and tuning-in of photochromic conjugated polymers with switchable optoelectronic properties based on the energy spectra calculated with the band theory taking into account the correlation energy.

## 2. Objects of Investigation

The (model) polymers considered in this paper include the photochromic [2,2]-metacyclophanene ⇔ (dimethyl)-dihydrophenanthrene and [2,2]-metacyclophanediene ⇔ (dimethyl)-dihydropyrene systems, respectively, in the elementary unit (EU), shown in Figs. 2 and 3. All the polymeric systems **1** to **9** are alternant homonuclear compounds.

## 3. Computational Methods

### 3.1. *Band Gap Equation of Alternant $\pi$-Electron Systems*

The energy spectra of alternant $\pi$-systems with a singlet ground state can be calculated by means of the AMO (alternant molecular orbitals) version of the extended HF (EHF) method [15]. The energy gap (EG) of an arbitrary homonuclear alternant system is given by the formula [16, 17].

$$\Delta E(\mathrm{EHF}) = \left(\Delta_{\mathrm{corr}}^2 + \Delta E(\mathrm{HF})^2\right)^{1/2}. \quad (1)$$

0932–0784 / 02 / 0100–0089 $ 06.00 © Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com

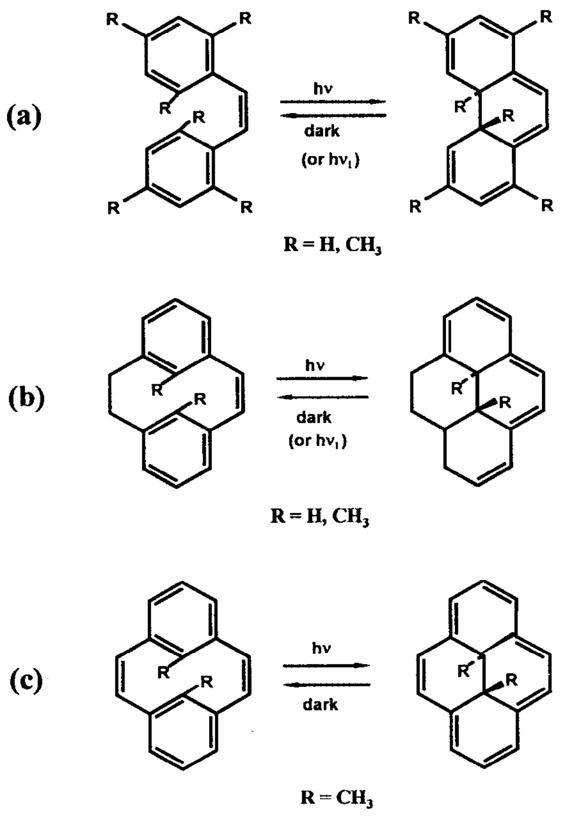

Fig. 1. Reversible photocyclization of (a) stilbenes, (b) [2,2]-metacyclophanenes, and (c) [2,2]-metacyclophanedienes.

In the Hubbard approximation [18, 19], (1) becomes

$$\Delta E = \left(\Delta_{\text{corr}}^2 + (\Delta_{\text{top}} + \Delta_{\text{geom}})^2\right)^{1/2}, \qquad (2)$$

where $\Delta_{\text{corr}}$ is the correlation correction, $\Delta_{\text{top}}$ is the EG in the "topological" approximation, that is, in the case that all bond lengths of the system are equal and all dihedral angles $\Theta$ are equal, and therefore all resonance integrals $\beta$ between adjacent $\pi$ centers are equal. The sum $\Delta_{\text{top}} + \Delta_{\text{geom}}$ expresses the EG calculated when taking into account the distortion of the bond lengths and optimized dihedral angles $\Theta$.

The correlation correction of EG is given by $\Delta_{\text{corr}} = 2\delta\gamma$, where $\gamma$ is the one-center Coulomb repulsion integral (Hubbard parameter [18, 19]) of the carbon $\pi$ centers. The dimensionless correlation parameter satisfies the equation

$$\delta M = \delta \sum_k \gamma / \left(\delta^2\gamma^2 + \beta^2 e_k^2\right)^{1/2}, \qquad (3)$$

where $M$ is the number of the $\pi$ centers and $e_k$ are the MO energies. Equation (3) has always a trivial solution $\delta = 0$; that is, the AMO energies coincide with the energies obtained in the one-electron HMO approximation. If $\delta \neq 0$, (3) takes the form

$$M = \sum_k \gamma / \left(\delta^2\gamma^2 + \beta^2 e_k^2\right)^{1/2}. \qquad (4)$$

From the inequality

$$1 = \frac{1}{M} \sum_k \gamma / \left(\delta^2\gamma^2 + \beta^2 e_k^2\right)^{1/2} < \frac{1}{M} \sum_k \gamma / |\beta e_k|$$

there follows the self-consistency condition

$$\left|\frac{\beta}{\gamma}\right| < \left|\frac{\beta}{\gamma}\right|_{\text{crit}} = \frac{1}{M} \sum_k \gamma / |\beta e_k|. \qquad (5)$$

That is, if the condition (5) is not fulfilled, (3) has no solution $\delta \neq 0$.

The MO energies $e_k$ (and the topological and geometrical components to the EG, (2)) in (4) were calculated using the HMO method by the numerical diagonalization of the corresponding matrix. If we adopt for the polymers a Bloch form of the wave vector $\omega_k \in [-\pi, \pi]$, the MO energies $e(\omega_k)$ are obtained by the numerical diagonalization of the matrix [20]

$$\mathbf{E}(k) = \mathbf{E}_0 + \mathbf{V} \exp(i\omega_k) + \mathbf{V}^+ \exp(-i\omega_k), \qquad (6)$$

were $\mathbf{E}$ is the energy matrix of the EU, $\mathbf{V}$ is the interaction matrix between neighbouring EUs ($\mu$-th and $\mu$+1-th), and $\mathbf{V}^+$ is the transposed matrix. The numerical results were obtained with the following set of standard parameters: $\beta = -2.4$ eV, $\gamma = 5.4$ eV, $\beta/\gamma = 0.44444$. These parameter values have been extensively employed for the description of the EG of many homonuclear $\pi$-electron systems for which $\Delta E$ is experimentally known. Using these parameters, quite resonable results could be achieved [15 - 19, 21 - 23].

### 3.2. *Geometry of the Polymers*

To estimate the geometry of the infinite polymers, an extended Su-Schrieffer-Heeger (SSH) model [24, 25] was used. In this approach, the SSH-PPP model [26] incorporates the linear electron-lattice coupling and a harmonic bond-strain potential as

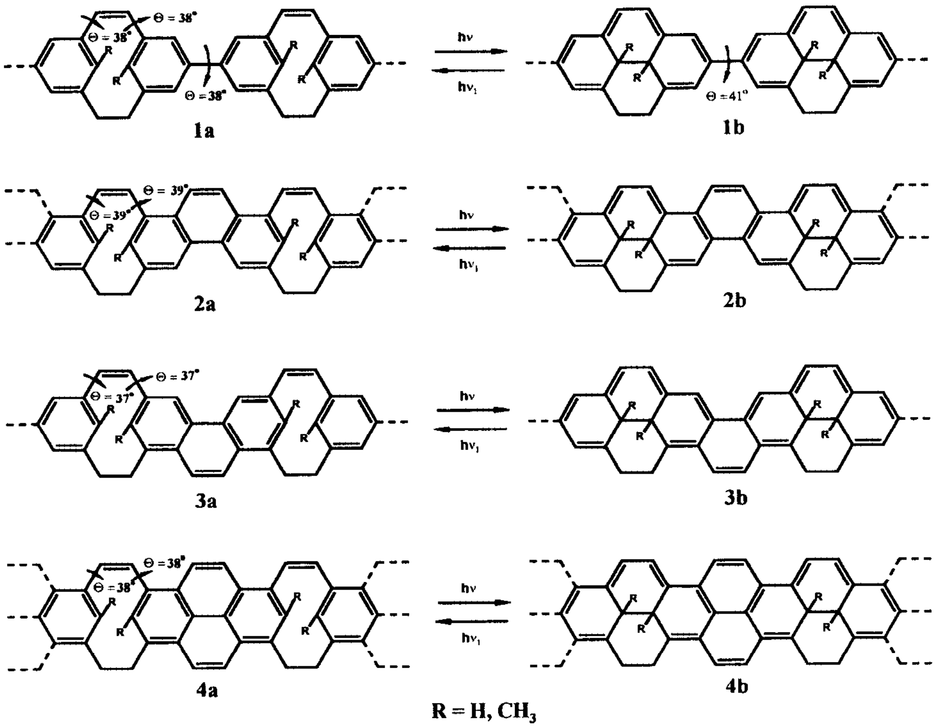

Fig. 2. Structures of polymers **1** to **4** with photochromic [2,2]-metacyclophanene – dihydrophenanthrene fragments.

Table 1. Energy gap components (in eV) of the investigated photochromic polymers (see Figs. 2 - 3) calculated by means of (2); all results are obtained with standard values of the parameters (Section 3).

| Polymer | $\Delta_{top}$ | $\Delta_{geom}$ | $\Delta_{corr}$ | $\Delta E$ | Polymer | $\Delta_{top}$ | $\Delta_{geom}$ | $\Delta_{corr}$ | $\Delta E$ |
|---|---|---|---|---|---|---|---|---|---|
| **1a** | 2.32 | 0.77 | [a] | 3.09 | **1b** | 0.15 | 0.80 | 2.16 | 2.36 |
| **2a** | 1.42 | 0.78 | 0.43 | 2.24 | **2b** | 0.78 | 0.55 | 1.69 | 2.15 |
| **3a** | 0.15 | 0.06 | 2.26 | 2.27 | **3b** | 1.52 | 0.75 | 0.19 | 2.28 |
| **4a** | 0.70 | 0.82 | 0.94 | 1.79 | **4b** | 1.41 | 0.44 | 1.82 | 2.59 |
| **5a** | 0.38 | 1.14 | 1.30 | 2.00 | **5b** | 0.38 | 0.47 | 2.18 | 2.34 |
| **6a** | 2.14 | 0.67 | 0.81 | 2.93 | **6b** | 0.90 | 0.27 | 2.12 | 2.42 |
| **7a** | 0.92 | 0.45 | 1.67 | 2.16 | **7b** | 0.98 | 0.42 | 2.00 | 2.44 |
| **8a** | 0.19 | 0.74 | 1.21 | 1.52 | **8b** | 0.19 | 0.02 | 1.88 | 1.89 |
| **9a** | 2.14 | 0.23 | 0.76 | 2.49 | **9b** | 0.00 | 0.10 | 2.14 | 2.14 |

[a] Equation (4) has no solution $\delta \neq 0$.

described in the SSH model, and the ($\pi$-) electron-electron interaction corresponding to the Pariser-Parr-Pople (PPP) approximation [27, 28]. The following parametrization was used: the electron-lattice coupling constant $\alpha = 3.21$ eV/Å, and the spring constant $K = 24.6$ eV/Å$^2$ [26].

For the two-center Coulomb repulsion integrals $\gamma_{ij}$ (to calculate the energy of the electron-electron interaction), the screened Mataga-Nishimoto approximation [29] was used ($\gamma_0 = 10.84$ eV):

$$\gamma_{ij} = e^2/(e^2/\gamma_0 + DR_{ij}), \tag{7}$$

where $D$ is the screening constant. The equilibrium geometry of the polymers was optimized containing oligomers with three repetition units by means of the AM1 method [30, 31].

For the calculation of the geometrical component of EG, $\Delta_{geom}$ in (2), the dependence of the resonance integrals between the neighbouring carbon atoms on the bond lengths $R$ and the dihedral angles $\Theta$ was calculated with Mulliken's formula [32]

$$\beta(R, \Theta) = \beta_0 S(R)/S(R_0) \cos \Theta, \tag{8}$$

where $S$ are the overlap integrals (calculated with $R_0 = 1.4$ Å and $Z_C = 3.25$).

## 4. Results and Discussion

In Table 1 are collected the topological, $\Delta_{top}$, geometrical, $\Delta_{geom}$, and the correlation correction, $\Delta_{corr}$,

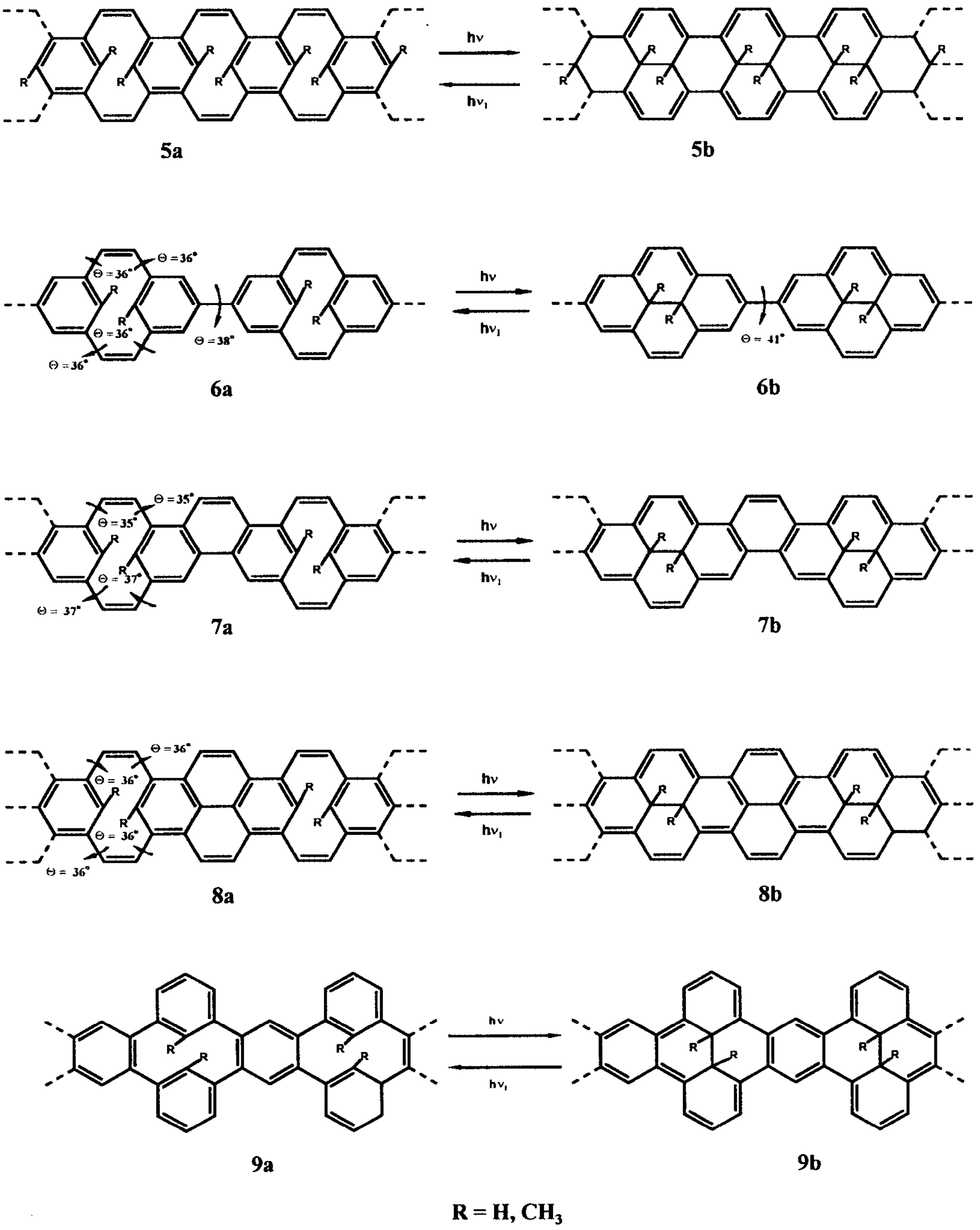

Fig. 3. Structures of polymers **5** to **8** with photochromic [2,2]-metacyclophanediene – dihydropyrene fragments, and structure of polymer **9**.

contributions to the width of the energy gap, $\Delta E$, of the open-ring (**1a** - **9a**) and closed-ring photoisomeric forms (**1b** - **9b**) of the model polymers investigated in this paper. A real switching of the optoelectronic properties is possible only in some cases, as can be seen from the values of $\Delta E$. The largest effect can be observed in cases when the EUs are linked flexible through single bonds in the polymers (**1a**/**1b** and

**6a**/**6b**). The EG of the closed-ring isomers is smaller at 0.7 and 0.5 eV, respectively, in relation to the open-ring isomers corresponding to an absorption in the longer-wavelength region. The more rigid the molecular structure of the polymers, the smaller is the effect of the change of the width of the EG at the isomerization reaction. A reverse effect, that means a longer-wavelength absorption of the open-ring isomer in relation to the closed-ring isomer, has been calculated in the case of polymers with the most rigid structure (**4**, **5**, **7**, **8**). In a few cases a negligible change of the width of the EG is observed at photocyclization (polymers **2**, **3**).

All the polymers **1** to **9** are formed from EUs which are alternant hydrocarbon fragments. Based on the results obtained with the Hubbard model using the AMO-EHF approximation, it has been shown [21] that the EG, $\Delta E$, of an arbitrary regular alternant one-dimensional $\pi$-system (polymer) having a singlet ground state, is different from zero. This means that these systems can have at best semiconductor properties but not metalic properties.

In summary, it can be generalized that a photoswitching of the electrical conductivity (insulator ⇔ conductor or at least semiconductor) is not possible using homonuclear photoresponsive polymers of the types investigated in this paper. One reason is the large correlation correction contribution, $\Delta_{\text{corr}}$, to the energy gap. If the topological and the geometrical components to the EG are small or nearly zero, e. g. polymer **3a**, a larger energy gap results by the correlation energy contribution $\Delta_{\text{corr}}$.

Therefore, a photoswitching of electrical conductivity in conjugated polymers could be realized only with heteronuclear polymers as has been shown by Mitchell et al. [14]. The calculation of the correlation correction for these types of compounds requires other formalisms.

### *Acknowledgement*

This work was supported by the Deutsche Forschungsgemeinschaft (N. T.).

[1] M. Irie, Chem. Rev. **100**, 1685 (2000).
[2] K. A. Muskat, D. Gegiou, and E. Fischer, Chem. Comm. **447** (1965).
[3] F. Dietz and A. V. Eltsov, in: A. V. Eltsov (Ed.), Organic Photochromes, Consultants Bureau, New York 1990.
[4] M. Irie, in: J. C. Crano, and R. Guglielmetti (Eds.), Photochromic and Thermochromic Compounds, Plenum Press, New York 1999, Vol. 1, p. 207.
[5] C. E. Ramey and V. Boekelheide, J. Amer. Chem. Soc. **92**, 3681 (1970).
[6] H. R. Blattmann, D. Meuche, E. Heilbronner, R. J. Molyneux, and V. Boekelheide, J. Amer. Chem. Soc. **87**, 130 (1965).
[7] R. H. Mitchell, Eur. J. Org. Chem. 2695 (1999).
[8] A. Yassar, C. Moustrou, H. K. Youssoufi, A. Samat, and R. Guglielmetti, Macromolecules **28**, 4548 (1995).
[9] A. Yassar, C. Moustrou, H. K. Youssoufi, A. Samat, R. Guglielmetti, and F. Garnier, J. Chem. Soc., Chem. Comm. 471 (1995).
[10] S. L. Gilat, S. H. Kawai, and J.-M. Lehn, Chem. Eur. J. **1**, 275 (1995).
[11] S. H. Kawai, S. L. Gilat, R. Ponsinet, and J.-M. Lehn, Chem. Eur. J. **1**, 285 (1995).
[12] F. Stellaci, C. Bertarelli, F. Toscano, M. Gallazzi, G. Zotti, and G. Zerbi, Advanced Mater. **11**, 292 (1999).
[13] F. Stellaci, F. Toscano, M. C. Gallazzi, and G. Zerbi, Synth. Metals, **102**, 979 (1999).
[14] M. J. Marsella, Z.-Q. Wang, and R. H. Mitchell, Organic Lett. **2**, 2979 (2000).
[15] P.-O. Löwdin, Phys. Rev. **97**, 1509 (1955).
[16] N. Tyutyulkov, I. Kanev, O. Kastano, O. E. Polansky, and H. Barentzen, Theor. Chim. Acta **55**, 207 (1980).
[17] N. Tyutyulkov and F. Dietz, Chem. Phys. **171**, 293 (1993).
[18] J. Hubbard, Proc. Roy. Soc. London **A276**, 238 (1963).
[19] J. Hubbard, Proc. Roy. Soc. London **A277**, 401 (1964).
[20] O. E. Polansky and N. Tyutyulkov, MATCH (Comm. Mat. Chem.) **3**, 149 (1977).
[21] N. Tyutyulkov, F. Dietz, D. J. Klein, W. A. Seitz, and T. G. Schmalz, Int. J. Quantum Chem. **51**, 173 (1994).
[22] F. Dietz, N. Tyutyulkov, S. Karabunarliev, J. Hristov, and K. Müllen, Polycyclic Aromatic Compounds **18**, 99 (2000).
[23] N. Tyutyulkov, G. Madjarova, F. Dietz, and K. Müllen, J. Phys. Chem. **B 102**,10183 (1998).
[24] W.-P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979).
[25] W.-P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. **B22**, 2099 (1980).
[26] S. Karabunarliev, M. Baumgarten, N. Tyutyulkov, and K. Müllen, Chem. Phys. **179**, 421 (1994).
[27] R. Pariser and R. H. Parr, J. Chem. Phys. **21**, 466, 767 (1953).
[28] J. A. Pople, J. Chem. Soc., Faraday Trans. **49**, 1375 (1953).
[29] N. Mataga and K. Nishimoto, Z. Phys. Chem. **13**, 140 (1957).
[30] J. J. P. Stewart, MOPAC 6.0, QCPE, No 455.
[31] SPARTAN Program System, PC Spartan plus, Wavefunction, Inc.: Irvine, CA, 1997.
[32] R. S. Mulliken, J. Chem. Phys. **46**, 497 (1949).