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Semiempirical Calculations of Singlet-Triplet and Triplet-Triplet Transitions

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Semiempirical calculations of the PPP-type with optimum values of parameters ($\gamma_{\mu\mu} = 8.2$ eV, $\beta^c = -2.5$ eV) reproduce fairly well the singlet-triplet (*S-T*) and triplet-triplet (*T-T*) excitation energies and oscillator strengths with conjugated hydrocarbons of various structural types. The usefulness of this parametrization is shown with anthracene. Moreover, the applicability of the Hückel's $N \rightarrow V_1$ energies for estimates of the *S-T* transitions is mentioned.

Electronic absorption spectra which are due to singlet-singlet transitions have been interpreted successfully by the semiempirical method of limited configuration interaction (LCI-SCF) [1, 2]. However, the results for *S-T* and *T-T* transitions obtained by the same procedure are not satisfactory. Relatively few attempts have been made to interpret these transitions theoretically (cf. e.g. [1, 3–5]) although relatively extensive experimental data are available in a literature. Moreover, the methods mentioned are only applicable either to *S-T* transitions (e.g. phosphorescence spectra) or to *T-T* transitions (obtained by the "flash photolysis" technique) and the agreement between calculated and experimental values is still not satisfactory.

Therefore, an attempt was made to find such a parametrization which leads to a reasonable agreement for both *S-T* and *T-T* spectra. The Mataga-Nishimoto approximation [6] was used for the approximation of electronic repulsion integrals and the values of the monocentric electronic repulsion integral, $\gamma_{\mu\mu}$, and of the core resonance integral, β^c, were treated as parameters, the values of which were adjusted to the first and second experimental *S-T* transition of benzene. The following optimum values were found: $\gamma_{\mu\mu} = 8.2$ eV, $\beta^c = -2.5$ eV. Using these parameters the energies of the triplet states and the oscillator strengths of *T-T* transitions were calculated for a representative set of conjugated hydrocarbons. One gets a considerable improvement in comparison to the standard PPP-parametrization. Not only do *S-T* and *T-T* transition energies agree satisfactorily with the experimental values but also the relative intensities of *T-T* transitions are reproduced fairly well.

For the sake of illustration the case of anthracene is mentioned more specifically. Recently results of careful measurements including very weak long-wavelength *T-T* transitions (down to 10 *kK*) have been published [7]. There is a fair agreement between theoretical data based on configuration interaction calculation (25 monoexcited configurations) and these experiments (Fig. 1). Theoretical data are indicated by vertical lines and transitions forbidden by symmetry by wavy arrows. Similarly encouraging results were obtained also with other hydrocarbons under study.

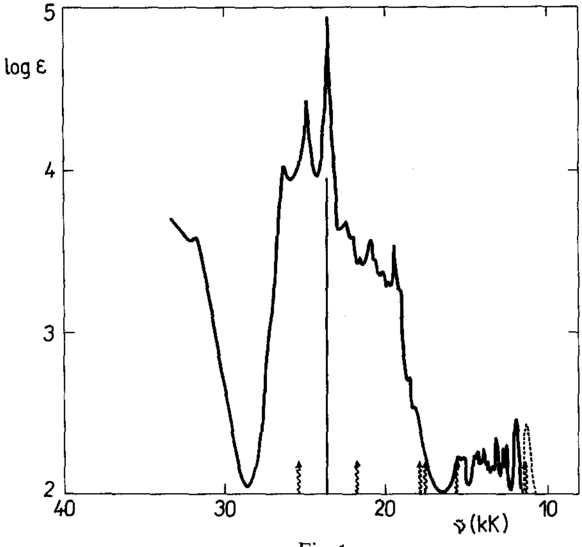

Fig. 1a

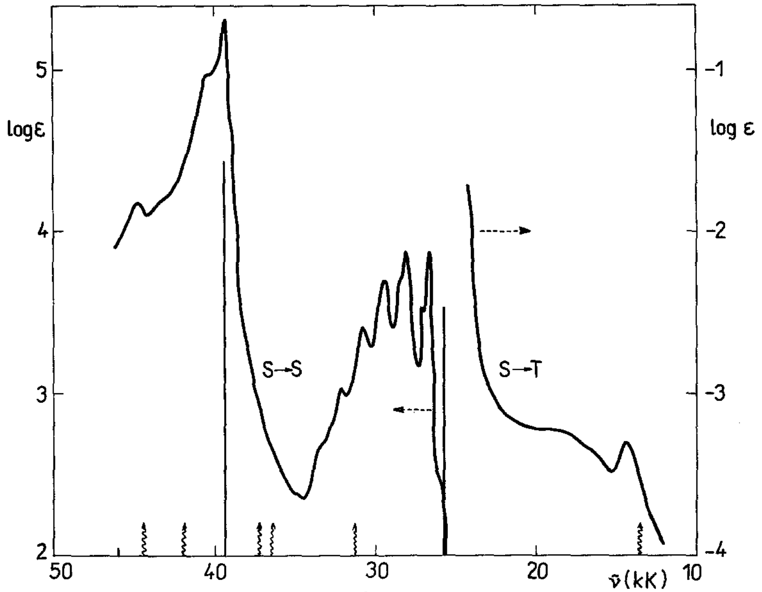

Fig. 1b

Fig. 1a and b. a *T-T* absorption curve (ethanol-methanol, 3 : 1; 113° K) according to Astier and Meyer [7]. b *S-S* absorption curve (ethanol) and *S-T* absorption curve (ethanol + ethyl iodide). Symbols: — allowed transitions, ⇝ forbidden transitions

Various theoretical estimates of the first *S-T* transition energy are summarized in the table. The usefulness of the prediction based on the Hückel's $N \rightarrow V_1$ energy and the failure of the conventional LCI-SCF values are worth-mentioning.

In Fig. 1 also data on the *S-S* and *S-T* transitions are included. (The singlet-triplet absorption curve was recorded in ethanol-ethyl iodide mixture.) Also here the theoretical data are in a fair agreement with the experimental spectra. It has to be added, however, that our parametrization fails to reproduce correctly the position of the (*S*-*S*) α-band in some benzenoid hydrocarbons (e.g. naphthalene, pyrene). Generally speaking a good agreement exists with numerous other *T*-*T* transitions; the error exceeds only quite exceptionally 0.2 eV.

More detailed description of the method used and numerical data for series of alternant and non-alternant systems are available from the authors. This information, a remark on applicability of the HMO method for the correlation of the *S*-*T* transition energies, and the configuration interaction with Roothaan's restricted open shell molecular orbitals will be published later.

Table. *Various theoretical estimates of the S-T transition energy (phosphorescence band) of anthracene and their absolute errors*

Method	E (eV)	$\lvert E - E_{\mathrm{exp}} \rvert$ (eV)
HMO[a]	1.95	0.11
LCI-HMO [8]	1.66	0.18
SCF [9]	1.68	0.16
LCI-SCF [9]	1.35	0.49
LCI-SCF-SC [9]	1.55	0.29
restricted SCF [10]	2.01	0.17
restricted SCF[b]	1.14	0.70
restricted LCI-SCF[b,c]	1.13	0.71
unrestricted SCF [11]	1.36	0.48
LCI-SCF[d] (new parametrization[f])	1.79	0.05
LCI-SCF[e] (new parametrization[f])	1.68	0.16
experimental value	1.84	—

[a] Calculated by means of the regresion line $\Delta\varepsilon^T(kK) = 12.19\,E(N \to V_1)\,(\beta) + 5.632$, where $\sigma = \pm 1.09\,kK$. $E(N \to V_1)$ stands for the energy gap between the highest occupied a lowest free Hückel π-molecular orbital.

[b] γ: Mataga-Nishimoto, $\gamma_{\mu\mu} = 10.84$ eV, $\beta^c = -2.318$ eV.

[c] Thirty nine monoexcited configurations (with respect to the triplet ground state).

[d] Sixteen monoexcited configurations (with respect to the singlet ground state).

[e] Twenty five monoexcited configurations (with respect to the singlet ground state).

[f] See text.

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