Calculations on Electric-Field-Induced Shifts in Ultraviolet Absorption Spectra: The Significance of Doubly Excited Configurations

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Calculations on the cation-induced shifts in the UV spectrum of the terphenyl mononegative ion suggest that the spectra of the ions of alternant hydrocarbons, as compared with those of the molecules, are rather insensitive to electric field perturbations. This feature only shows up if one includes enough (doubly) excited configurations to allow for the polarization of the excited states involved in the optical transitions.

Berechnungen über die von Kationen verursachten Verschiebungen im UV-Spektrum des mononegativen Terphenylions deuten darauf hin, daß die Spektren der Ionen alternierender Kohlenwasserstoffe im Vergleich zu denen der Molekeln gegen vom elektrischen Feld hervorgerufene Störungen ziemlich unempfindlich sind. Dies kommt nur dann zum Ausdruck, wenn man in den Berechnungen genügend (doppelt) angeregte Konfigurationen mit einbezieht, um auch die Polarisation der an den optischen Übergängen beteiligten Anregungszustände zu erfassen.

Des calculs sur les déplacements – provoqués par le cation – dans le spectre ultraviolet de l'ion mononégatif de terphényle indiquent que les spectres des ions d'hydrocarbures alternants, à côté de ceux des molécules, sont assez insensibles aux perturbations du champ électrique. On ne trouve ce résultat que dans le cas où l'on introduit un nombre suffisant de configurations excitées (doublement) pour tenir compte de la polarisation des états excités liés aux transitions optiques.

Introduction

A very large amount of experimental data are available about shifts in the UV spectra of aromatic hydrocarbon ions due to the association with the alkali counter ions [1]. They provide information about the existence of different types of ion pairs and about the thermodynamic properties relevant to the equilibria between them [2, 3]. Several calculations on these UV shifts, based on different models for the ion pairs, have been carried out but so far they have not yielded any conclusive information about the structure of the ion pairs observed experimentally.

Originally, the calculations reported in this paper were aimed at determining structural properties of the ion pairs by comparing the observed shifts with the shifts calculated for a range of a priori chosen structures. The results of the calculations indicate that this attempt was not very successful. Nevertheless, they show some interesting features which we think worthwhile reporting.

Results and Discussion

For the calculations on terphenyl use was made of the Pariser-Parr-Pople procedure. The spectral shifts were considered to be due to the Coulomb interaction between the alkali ion and the π-electron system of the anion.

They were obtained by comparing the strongly allowed long-axis polarised transitions between the ground and excited states as calculated by configuration interaction: first under the π-electron Hamiltonian, H_π and, second under $H_\pi + \Omega$, where Ω is the one-electron operator representing the Coulomb interaction between the monopositive point charge and the π-electrons of the terphenyl mononegative ion. In calculating the matrix elements of Ω in the basis of atomic $2 p_z$ orbitals, χ_p, we use a point-charge approximation:

$$\langle \chi_p | 1/R_{p+} | \chi_p \rangle = 1/r_{p+}$$

where r_{p+} is the centre-to-centre distance between the alkali ion and the carbon atom p. In Figs. 1-3 the calculated shifts in the position of the bands are shown for different positions of the cation relative to the anion. The results are based on the choice of a basis of 4, 11 and 18 configurations. As the results are obtained by diminishing each diagonal term of the variation matrix by the energy shift ΔE^0 of the ground state before configuration interaction, the graphs only represent relative level shifts, which is sufficient for spectral purposes.

A comparison of the calculated data summarised in Fig. 3 with the experimental data of the shifts in the UV spectrum of the terphenyl mononegative ion caused by the sodium ion (see the Table) yields an estimate of the cation-anion distance of only 3-4 Å. If such small distances are involved indeed the assumption that the cation can be represented by a point charge is not justified: contributions to the local field at the anion due to charge separation in the solvent molecules coordinating the cation no longer are negligible. Consequently, the original idea to use the calculations as a guide for determining the structure of the ion pairs turns out to be unrealistic. Nevertheless, the calculations as such show an interesting qualitative result: the ion spectrum is only sligthly sensitive to Coulomb type perturbations.

The band shifts in symmetrical molecules may be considered to originate from a difference in polarizability between the ground state and the excited state involved in the optical transition, rather then from a difference in zero-order charge distribution. It is obvious that in performing potential energy calculations such as the ones reported here one should include a sufficient number of excited configurations to allow for polarisation, not only of the ground state, but also of the excited states involved in the optical transition. Calculated approximate values of $\Omega_{ij}/\Delta E_{ij}$ between the lowest four configurations (i) and all relevant singly and doubly excited configurations (j) up to 6 eV from the ground state suggest that no drastic changes in the results are to be expected when the

Table. *Experimental data concerning the UV spectra of the free solvated and the associated terphenyl anion*

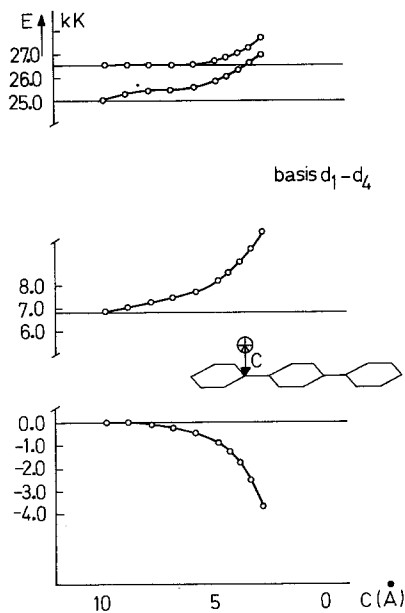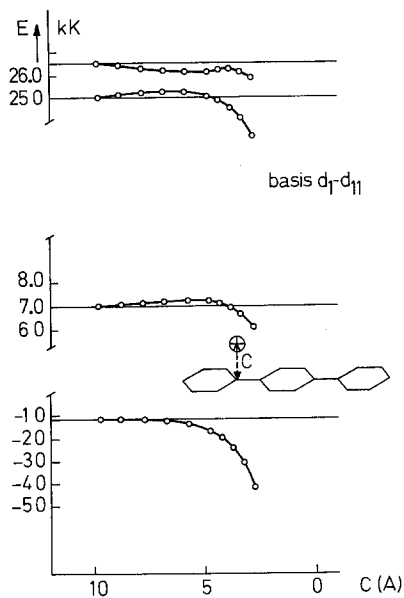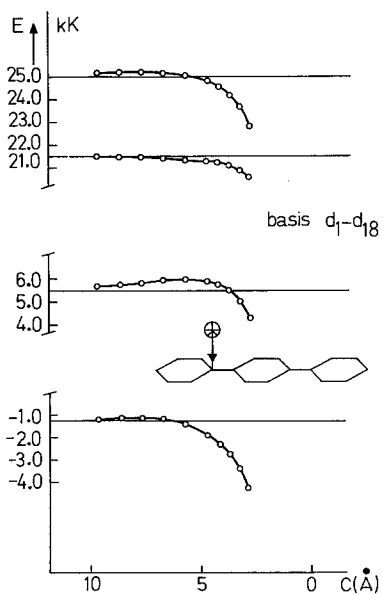|	Band position free terph. anion	Band position ass. terph. anion
first band	11.0 kK	12.0 kK
second band	20.7 kK	21.6 kK
third band	22.4 kK	23.2 kK

Fig. 1

Fig. 2

Fig. 3

Figs. 1-3. Level shifts vs. cation-anion position. Fig. 1. Basis of four configurations. Fig. 2. Basis of eleven configurations. Fig. 3. Basis of eighteen configurations

configurational basis is extended beyond these 18 configurations. In previous calculations [4, 5, 6, 7] and recent calculations by Labhart [8] the authors do not seem to have extended the configuration interactions far enough in their calculations of the polarizabilities of the excited states. Although our calculations refer to a centrally symmetric field, qualitatively the results will also hold for a homogeneous fields with gradient along the long axis of the molecule. Hence, we may expect polarizabilities of the ground state and excited states of the terphenyl ion to be very much alike, as becomes also evident from the influence of the alkali ion on the optical spectrum, which leads to blue shifts of only about $1000 \, cm^{-1}$, while field gradients as large as about $0.4 \, eV$ per Å occur. For neutral molecules the effect turns out to be quite different. Labhart's measurements on electro-optical phenomena [8, 9, 10] in polyene molecules show that spectral shifts can occur which, per unit field gradient, are almost one order of magnitude larger than the ones we calculated for the terphenyl anion, which is due to the fact the excited states involved have polarizabilities one order of magnitude larger than the ground state. It is obvious that this difference in behaviour between molecules and ions is due to the fact that the separation between the ground state and the lower excited states of the ions is much lower than for the corresponding neutral molecule. For the polyphenyl ions strongly allowed transitions (long axis polarised) are observed in the infra-red. As a consequence, the groundstate of the ion itself has already a polarizability of almost one order higher than that of the ground state of the corresponding molecules [11]. For the molecules this is quite different. Here the ground state is much farther separated from the lower excited states, so that the effect brought about by the electric field will be appreciably smaller. For the excited states of the molecule which arise form long axis polarised transitions, however, the influence of the electric field along the axis of the molecule will be comparable with that for the ground state or excited state of the ion, since here the excited states which mix in under influence of the field are much closer.

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