

- 1 S. Paszyc, Photochemistry of nitroalkanes, *J. Photochem.*, 2 (1973/74) 183.
- 2 Tran-Dinh-Son and J. Sutton, *Int. J. Radiat. Phys. Chem.*, 5 (1973) 149.
- 3 S. Paszyc, H. Kozubek and B. Marciniak, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, XXV (12) (1977) 951.

## CORRELATED EXCITATIONS IN CONJUGATED MOLECULES

P. TAVAN and K. SCHULTEN

*Max-Planck-Institut für biophysikalische Chemie, D-3400 Göttingen (F.R.G.)*

The discovery of the forbidden  $2^1A_g$  state below the  $1^1B_u$  state in polyenes and diphenylpolyenes [1, 2] has revived the photochemistry of these molecules. The  $2^1A_g$  state is to be described as a concerted excitation of two  $B_u$  triplet states forming a covalent singlet spin wave in the polyene  $\pi$  system [2]. The low energy position of this state and its remarkable physical properties rationalize the photoactivity of polyenes. Spectroscopic work carried out in recent years has revealed the exact energy position of the  $2^1A_g$  state relative to the  $1^1B_u$  state in a series of polyenes and their derivatives. However, the observations were at variance with the early theoretical description [2] which has extended a PPP-CI treatment to include all double excitations in order to account for the triplet-triplet character of these states. We demonstrate now that these states also exhibit long range spin coupling of a quadruplet-quadruplet and quintet-quintet type extending over several adjacent ethylene units. This character must be accounted for by triple and quadruple excitations in a CI treatment to achieve the proper behaviour of the  $2^1A_g$ - $1^1B_u$  energy gap, an increase in going from butadiene (where the  $2^1A_g$  actually lies above the  $1^1B_u$  level) to decapentaene and a saturation from thereon [3].

Recently the idea has emerged that the *cis-trans* photoisomerisation of stilbene is governed by a higher excited  $^1A_g$  state which exhibits a minimum at the perpendicular conformation crossing the lowest excited  $^1B_u$  state upon bond rotation. An evaluation of the potential surfaces governing the photoisomerisation process (by a PPP-SCF-CI method) revealed that there indeed exists such a photochemically active  $^1A_g$  state which in the planar molecule lies about 1 eV above the lowest absorption band and involves the excitation of two electrons from the ground state [4]. Extensions of the calculations to the diphenylpolyenes demonstrate that this  $^1A_g$  state is related to the one-photon forbidden low lying triplet-triplet spin wave state of the polyenes [4]. Such a state is predicted to be photochemically active also in the visual chromophore (a protonated Schiff base of retinal) very much the same way as in stilbene.

The question arises how far covalent spin wave excitations extend in conjugated molecules. We have carried out a study of the polyazene spectra and have established that such states also exist in large numbers in these molecules. On the basis of extended PPP-SCF-CI calculations we predict energy level schemes which consistently account for the spectral data available and, in addition, contain some one-photon forbidden transitions yet unobserved [3].

- 1 B. S. Hudson and B. E. Kohler, *J. Chem. Phys.*, 59 (1973) 4984.
- 2 K. Schulten, I. Ohmine and M. Karplus, *J. Chem. Phys.*, 64 (1976) 4422.
- 3 P. Tavan, Thesis, Göttingen, 1978.
- 4 P. Tavan and K. Schulten, *Chem. Phys. Lett.*, 56 (1978) 200.