

## On the near ultra-violet absorption spectra of some bromoxylenes

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(Received 19 April 1977, revised 11 July 1977)

In continuation of our work on the electronic absorption spectra of some substituted benzenes, the near ultra-violet absorption spectra of 1-Bromo-2,3-Xylenes (I), 1-Bromo-2,4-Xylenes (II) and 1-Bromo-2,6-Xylene (III) have been photographed on a Hilger Medium quartz spectrograph using absorption columns of length varying from 10 to 150 cms and varying the temperature of the absorbing vapour from 0°C to 150°C.

The spectra of all the molecules studied occurs approximately in the region 2820-2480 Å. The bands are rather sharp and degraded to the red. The molecular structure of compound III has approximately a  $C_{2v}$  symmetry while the other compounds belong to  $C_s$  symmetry and the transition corresponding to the  $B_{2u} \leftarrow A_{1g}$  of benzene is an allowed one in all the cases under the reduced symmetry. It is of  $B_1 \rightarrow A_1$  type in compound III and  $A^1 \leftarrow A^1$  type in the other two molecules. The spectra have been analysed with the help of the analysed infra-red data of these molecules (Shashidhar & Rao 1972) also with the help of the corresponding spectra of three isomers of Xylenes (Cooper & Spomer 1952, Cooper & Sastri 1952, Rao & Sastri 1952).

The study of the temperature effect on the band systems has facilitated the choice of the band at 37019, 36227 and 37202  $\text{cm}^{-1}$  in compounds I, II and III respectively as the 0, 0 band. Most of the observed bands in compound I could be interpreted in terms of three ground state fundamentals 472, 604, 765  $\text{cm}^{-1}$ ; seven excited state fundamentals 366, 526, 696, 982, 1026, 1160, 1226  $\text{cm}^{-1}$  and a difference frequency 66  $\text{cm}^{-1}$ . While the bands in compound II could be interpreted in terms of three ground state frequencies 475, 632, 766  $\text{cm}^{-1}$ ; seven excited state frequencies 391, 531, 693, 963, 1005, 1182, 1240  $\text{cm}^{-1}$  and two difference frequencies 28 and 63  $\text{cm}^{-1}$ . The observed bands in the spectrum of compound III could be accounted for in terms of two ground state fundamentals 456, 621  $\text{cm}^{-1}$ ; seven excited state fundamentals 365, 485, 651, 971, 1070, 1171, 1250  $\text{cm}^{-1}$  and a prominent difference frequency 41  $\text{cm}^{-1}$ .

One of the authors (PVS) is grateful to the University Grants Commission for the award of a fellowship.

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*Indian J. Phys.* **52B**, 226-228 (1978)

## Unrestricted Hartree Fock method and the level shifting technique

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(Received 28 February 1977)

Recently Saunders *et al* (1973) have developed an elegant strategy to achieve convergence in closed and restricted open-shell calculations where the traditional Roothaan method fails to reach a stationary point on the energy surface because of an unpredictable swapping of the orbitals spanning the occupied and virtual orbital spaces. This method is known as the level-shifting method. The purpose of the present note is to extend the method of open-shell SCF-MO-LCAO calculations in the unrestricted Hartree Fock formalism (Amos & Hall 1961) and to discuss some of the possible improvements in the methods of implementation of the scheme. Some of the general features of the method are also pointed out.

The first order energy change resulting from the independent variations of the  $\alpha$  and  $\beta$ -spin orbitals spanning the occupied subspaces ( $\psi_1^\alpha$ ,  $\psi_1^\beta$ ), onto the corresponding virtual sub-spaces ( $\psi_2^\alpha$ ,  $\psi_2^\beta$ ) can be shown to be equal to  $\delta E^{(1)}$  where,

$$\delta E^{(1)} = \delta E_\alpha^{(1)} + \delta E_\beta^{(1)} = 2 \sum_k \sum_i (H_{ki}^\alpha)^2 / H_{kk}^\alpha - H_{ii}^\alpha + 2 \sum_k \sum_i \frac{(H_{ki}^\beta)^2}{H_{kk}^\beta - H_{ii}^\beta} \quad (1)$$

where  $H^\alpha$  and  $H^\beta$  are the spin-polarised Hamiltonian operators in the molecular orbital basis,  $k$  sums over the occupied orbital space and  $i$  over the virtual orbital space respectively. For a smooth energy lowering, the energy denominators in  $\delta E_\alpha^{(1)}$  and  $\delta E_\beta^{(1)}$  must be negative, a constraint that is easily satisfied by adding fairly large shifting parameters  $b_\alpha$  and  $b_\beta$  only to the  $H_{ii}^\alpha$  and  $H_{ii}^\beta$  type of matrix elements (diagonal elements in the virtual orbital block) respectively. This condition can be incorporated in the unrestricted SCF-MO-LCAO