Relationes

Calculation of Oscillator Strengths for π-Electron Molecules

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A comparison of oscillator strengths calculated by the Mulliken and Rieke approximation and by the Hansen expression involving the geometric mean of the dipole-length and dipole-velocity formulae shows that the former method gives values twice as large as those from the latter method.

The choice of formula to be used in the calculation of oscillator strengths for π-electron molecules has been the subject of much discussion. In most calculations performed using the Pariser-Parr-Pople method, the Mulliken and Rieke approximation [1] is employed. This method does not require the calculation of any integrals, as only the diagonal elements of the dipole-length operator are included. However, the oscillator strengths obtained are usually larger than experimental values.

In recent calculations of the absorption spectra of a series of small aromatic molecules [2] and a number of purines and pyrimidines [3], the oscillator strengths were obtained from the geometric mean formula of Hansen [4] in which both dipole-length and dipole-velocity operators were used. This mean value has an advantage over its two component values in that the geometric mean formula contains no energy term; its disadvantage is in the need to calculate two sets of integrals. However, the oscillator strengths obtained are in reasonable agreement with experimental values [2, 3].

A comparison of oscillator strengths calculated by the Mulliken and Rieke method and by the Hansen method for the molecules previously studied [2, 3] showed that the values from the former method were twice as large as those from the latter method. All oscillator strengths calculated by the Mulliken and Rieke method were therefore multiplied by 0.5, and compared again with those from the Hansen method. For the twenty-one small aromatic molecules – azines, amino-pyridines, aminopyrimidines, phenylenediamines and dihydroxybenzenes – the largest difference between the two sets of values was 0.03, this being calculated for eight transitions with energies between 6.5 eV and 8.0 eV and with oscillator strengths greater than 0.30. The remaining eighty-seven transitions gave values which differed by up to 0.02 for oscillator strengths in the range of 0.0–0.60, the average difference being less than 0.01. Similarly, for the four bases of RNA – adenine, guanine, cytosine and uracil – the largest difference between the two sets of values was 0.04, this being calculated for three transitions with energies between 5.9 eV and 6.6 eV and with oscillator strengths greater than 0.30. The

remaining twenty-three transitions gave values which differed by less than 0.01 on average. Therefore the two sets of values were remarkably constant.

It is therefore proposed that the simpler Mulliken and Rieke method can be used to obtain oscillator strengths which are in close agreement with those obtained from the Hansen method, provided a factor of 0.5 is included in the expression.

References

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