CALCULATIONS OF PHOTO-IONIZATION CROSS SECTIONS FOR DIATOMIC MOLECULES.

by

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SUMMARY.

In this thesis we present calculations of photo-ionization cross sections for the diatomic molecules N_2, O_2 and NO. These are expected to have important astrophysical applications.

The necessary formulae and the justification of the one electron approach for evaluating electronic matrix elements for many-electron systems are given in Chapter 1, where an attempt is also made to survey briefly the relatively well known field of atomic calculations. The Chapter concludes with a resume of previous theoretical work on photo-ionization cross sections for molecules.

In Chapters 2 and 3 the electronic wave functions needed for the evaluation of the matrix elements are presented and discussed. It is apparent that approximate methods must be used for both the initial and final states. S.C.F.-L.C.A.O.-M.O. wave functions are found most convenient for the bound states and analytic expressions for these M.O.'s are derived for the case of Slater type A.O.'s, using prolate spheroidal co-ordinates. For the first attempt at calculations of the cross sections,

Flannery and Opik's final state model is chosen by analogy with Coulomb waves which are a first approximation for atomic calculations.

The first parts of Chapter 4 are concerned with the evaluation of the electronic matrix elements with the initial and final states of Chapters 2 and 3. In the final part, a calculation of the cross section using plane wave final states is presented for a $1\pi_g$ electron, this approach not being pursued in subsequent numerical work.

The results of the calculations for fixed nuclei reveal several interesting features. Each bound state orbital type has a characteristic cross section curve and this is explained. In the high energy behaviour of the cross sections for $1\pi_g$ and $3\sigma_g$ orbitals, we observe peaks which are interpreted as the basis of Cohen and Fano's "shoulder" effect. We also incorporate changes in the parameters for π M.O.'s and also in the amount of hybridization for σ M.O.'s and discuss their effects.

The inclusion of the vibrational eigenstates is considered necessary in the evaluation of the cross

sections near threshold and in Chapter 6 we develop formulae for the cross section using the Franck-Condon factor approximation. Comparison with experiment reveals that our approach is reliable for the $1\pi_g$, $1\pi_u$ and $3\sigma_g$ orbitals of N_2 and O_2 (if occupied). For the transitions to $O_2^+(a^4\Pi_u, A^2\Pi_u)$ an anomalous effect is found near threshold but for all $2\sigma_g$ and $2\sigma_u$ orbitals, the model meets with a radical failure which is discussed in detail. Before the total cross sections for N_2 and O_2 are discussed, we investigate the validity of the Franck-Condon factor approximation in the case of photo-ionization of the $1\pi_g$ electron (of zero kinetic energy) in O_2. We find the variation of the electronic transition moment with internuclear separation and reach the conclusion that the Franck-Condon factor approximation is valid to within a few percent.

In Chapter 7 we evaluate the electronic matrix elements for the 2π electron of nitric oxide. We find that much computational work can be avoided with an approximate approach which proves reliable near threshold.

Finally in Chapter 8, general conclusions are given with a discussion of possible methods for further work in this field.

STATEMENT

This thesis contains no material which has been accepted for the award of any other degree and to the best of my knowledge and belief, contains no material previously published or written by another person except where due reference is made in the text.

H. C. TUCKWELL

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