VALENCE-SHELL AND RYDBERG TRANSITIONS IN LARGE MOLECULES

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1. INTRODUCTION

The Rydberg \( (R) \) bands of most polyatomic molecules are located in the vacuum ultraviolet (VUV) spectral region, beyond 200 nm: in many cases, the lowest \( R \) bands are found between 200 and 120 nm (50,000–80,000 cm\(^{-1}\) or \( \sim 6-10 \) eV). While a few molecular spectra in this energy region have been known for a long time, the systematic conquest of this part of the VUV began only in the 1940's, with the work by W. C. Price and his colleagues [1]. A large number of VUV spectra have been measured in the last twenty years. Robin [2] has provided a comprehensive summary of the state of the VUV art, up to 1975. Shorter reviews are also available [3,4].

The scope of the present article prohibits any recapping of the earlier reviews. Instead, our intent is to provide a succinct account of the remaining difficulties and uncertainties, particularly those pertaining to the question of Rydberg/valence mixing.

Section 2 presents a general account of the problems associated with distinguishing between Rydberg states and valence states in molecules; Section 3 briefly surveys the connections between VUV spectroscopy and photochemistry; and, finally, Section 4 discusses the importance of Rydberg states in the spectroscopy of transition metal complexes.

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2. THE RYDBERG CONCEPT

For atoms, the definition of an $R$ state is simple: If the principal quantum number increases during a transition to a given excited state, that transition, and the resultant excited state, are termed "Rydberg". Thus, the corresponding spectral band is a member of an $R$ series and the size of the orbital of the excited electron is large in comparison to the size of the core.

For molecules, however, the definition of $R$ states is problematic.

2.1 The Hydrogen Molecule

For simple molecules, one might initially presume that correlation diagrams would offer a basis for a definition. Consider the well-known correlation diagram for homonuclear diatomics, as given by Herzberg [51], and apply it to the hydrogen molecule. Using LCAO-MO language, from the $1s$ atomic orbitals of the two hydrogen atoms we can build two molecular orbitals: Omitting normalization factors these are, of course, $\sigma_{gls} (l_{sa} + l_{sb})$ and $\sigma_{uls} (l_{sa} - l_{sb})$. Between these two levels a transition is possible, namely $\sigma_{uls} + \sigma_{gls}$. Since both the ground and excited states are built from atomically unexcited AO's, this transition is valence-shell (VS) and the molecular excited state is a VS state. However, the $\sigma_{uls}$ orbital correlates to $2p_\sigma$ in the unit-ed-atom (UA) approximation, and to $2p$ at the UA limit, with an increase in principal quantum number from 1 to 2. Thus, if we wish to maintain the atomic $R$-state definition, we must call the $\sigma_{uls}$ state "Rydberg", at least for short internuclear separations. This example illustrates well the difficulty inherent in the molecular Rydberg concept: Orbitals and states that are VS at normal distances may become $R$ at the UA limit, or approximately $R$ at short molecular distances. Mulliken calls this process "Rydbergization" [6].

Now, if the above electronic transition were the only one possible, the $H_2$ spectrum would consist of only two bands, a singlet and a triplet. However, infinitely many other transitions are of course possible (see [5], p. 340). And, therefore, the higher-energy molecular orbitals, which will be truly Rydberg at any molecular distance, must be built from AO's which are atomically excited. The lowest energy one of these higher MO's is the $\sigma_g 2s (2s_{sa} + 2s_{sb})$ orbital, which becomes $2s_\sigma$ at short molecular distances and $2s$ at the UA limit. The energy of this orbital may be either higher or lower than that of the $2p_\sigma$, depending upon the internuclear separation. Thus, the following question immediately arises: Which comes first, the $(2s_{sa} + 2s_{sb})$ orbital, a bonding combination built from higher AO's, or