RENNER-TELLER COUPLING IN OPEN SHELL DIHYDRIDES: A COMPARISON OF THEORY WITH OPTICAL SPECTRA OF NEUTRAL AND IONIC MOLECULES

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The studies of the Renner-Teller coupling in isoelectronic series of the neutral dihydrides, started with the experiments of Dressler and Ramsay [a] on the absorption spectra of NH_2 and of ND_2 published in 1959, with a companion paper on the theory by Pople and Longuet Higgins [b]. Subsequently experiments on their ionic counterparts, e.g. H_2O+, were carried out, initially using photoelectron spectroscopy. However it was not until the period starting in 1965 to 1980 that methods for calculating the vibronic interaction between the half-states were derived and tested. Complications arise owing the the role of the linear degeneracy of the two half states in the formation of the rovibronic structure, and the effects of the increasing spin-orbit interaction in the series from NH_2 to SbH_2, and H_2O+ to H_2Se+ in facilitating fragmentation processes. Many of these molecular spectra were considered in great detail, but some, such as that of AsH_2, have had a less complete treatment of vibronic interaction, in part since the original study of its electronic spectrum took place in the period from 1966-67 before most of the vibronic coupling methods had been developed developed. We wish to show the interplay between the angular momentum effects caused by the large amplitude motion in a degenerate system, and those caused by a rapidly increasing spin-orbit coupling constant.

[a] Phil. Trans. Roy. Soc. 251,553(1959)
[b] Molec. Phys. 1,372(1958)