ORBITAL ANGULAR MOMENTUM IN LINEAR MOLECULES CONTAINING TRANSITION METALS

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Vibronic coupling arises in the Born-Oppenheimer approximation from the cross-term that appears when the second derivative operator for the nuclear kinetic energy acts on the product of an electronic and a nuclear wave function. This cross-term is usually handled as an effective operator which has matrix elements between vibrational levels of different electronic states. In unsymmetrical linear triatomic molecules these elements follow the selection rules $\Delta\Lambda = \pm 1$, $\Delta l = \mp 1$, $\Delta v_2 = \mp 1$, where ν_2 is the bending vibration. The most important effects occur in Π electronic states, because distant Σ^+ and Σ^- states affect the two Born-Oppenheimer components differently. If the Σ and Π electronic states are well separated the vibrational structure of the Π state can be treated as if there is an operator acting within the Π state that causes a quadratic splitting between its two components; this is the essence of the Renner- Teller effect. In transition metal-containing molecules the density of electronic states can be high enough for this approach to break down. Every electronic transition then contains intense "forbidden" vibrational bands, violating the usual selection rules, and large numbers of seemingly random perturbations occur. Examples will be drawn from the spectra of the metal methylidynes and hydroxides.