ROVIBRONIC COUPLINGS IN A FOURFOLD DEGENERATE ELECTRONIC STATE OF AN OCTAHEDRAL MOLECULE : THE ν_3 BAND OF ReF_6.

M. REY, V. BOUDON, M. LOËTE, *Laboratoire de Physique de l'Université de Bourgogne, UMR CNRS 5027, 9 Av. A. Savary, BP 4780, F-21078 DIJON Cedex, France*.

The rhenium hexafluoride (ReF_6) molecule has the particularity to possess an incomplete electronic d subshell. This open-shell system belongs to the O_h group and exhibits a very large spin-orbit coupling leading to a fourfold degenerate electronic ground state of symmetry G'_g. This implies complex couplings between electronic and nuclear motions (vibronic couplings) and between electronic, nuclear and rotational motions (rovibronic couplings) which considerably complicate calculations. Many years ago, some abnormalities in the spectrum of the triply degenerate ν_3 band of symmetry F_{1u} (the absence of the usual PQR pattern for such an isolated band, for instance) was attributed to a dynamical quadratic Jahn-Teller effect [a]. But all the theoretical vibronic models developed up to now give matrices with very large sizes when adding the rotational part and this leads in practice to inextricable problems. To solve this, we propose a systematic tensorial development in the $SU(2) \otimes C_I \supset O_h^S$ group chain for the construction of the effective rovibronic Hamiltonian[b,c]. This new theoretical model is based on a polyad scheme and allows a simultaneaous treatment of the four vibronic sublevels

$$F_{1u} \otimes G'_g = E'_{1u} \oplus E'_{2u} \oplus 2G'_u \; .$$

The corresponding rovibronic energies are obtained by block-diagonalizing the full Hamiltonian for the considered vibronic polyad. The size of each rovibronic block is thus finite. In a previous study, we have successfully tested this model for an electronic triplet state ($V(CO)_6$) [d]. Here, we report in a similar way the low resolution band profile of the ν_3 band of ReF_6 and show the agreement between the observed [e] and calculated spectrum.

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