MUTUAL CO-ASSIGNMENT OF THE CALCULATED VIBRATIONAL FREQUENCIES IN THE GROUND AND LOWEST EXCITED ELECTRONIC STATES

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The shifts of the molecular vibrational frequencies when going from the ground electronic state to the lowest excited electronic states pose some problems for the mutual co-assignment of the calculated vibrational frequencies in the different excited states. The *trans*-$C_2O_2F_2$ shift of the frequency of the symmetrical ν(C=O) stretching vibration between the S_0 and T_1 is 373 cm^{-1}.

The feasibility of mutual co-assignments of the vibrational frequencies in these electronic states has been demonstrated for *trans*-$C_2O_2F_2$. Matrices analogous to the Duschinsky matrix[a] were used to juxtapose the a_g vibrational frequencies of this molecule calculated at the CASPT2/cc-pVTZ level in the ground S_0 and excited triplet T_1 and singlet S_1 electronic states. The analog of the Duschinsky matrix D was obtained for this molecule using the equation $D = (L_I)^{-1} L_{II}$ where L_I and L_{II} are the matrices of the vibrational modes (normalized atomic displacements) obtained by solving the vibrational problems for the S_0 and T_1 electronic states, respectively. Choosing the dominant elements in columns of the D matrix and permuting these columns to arrange these elements along the diagonal of the transformed matrix D^* makes it possible to establish the correct mutual co-assignments of the calculated a_g vibrational frequencies of the *trans*-$C_2O_2F_2$ molecule in the S_0 and T_1 electronic states. The analogous procedure was performed for the *trans*-$C_2O_2F_2$ molecule in the T_1 and S_1 excited electronic states. The recent reassignments of the ν_2 and ν_3 calculated vibrational frequencies in the *trans*-$C_2O_2F_2$ molecule in the ground state were also obtained for the triplet T_1 and singlet S_1 excited electronic states.

The approach set forth in this text makes it possible to juxtapose the calculated vibrational frequencies of the same molecule in the different electronic states and to refine the assignments of these frequencies. This is essential in correctly analyzing the vibronic spectra of a molecule under investigation.

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[a] F. Duschinsky, *Acta Physicochim. URSS*, **7** (4), 551–566 (1937).