QUADRATIC VIBRATION-ROTATION CONSTANTS $\gamma^{\beta}_{r,s}$ AND SEMI-EXPERIMENTAL $^{32}S^{16}O_2$ EQUILIBRIUM GEOMETRY

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Probably the most precise geometrical nuclear configuration of a semi-rigid molecule can be obtained through the wide-spread technique combining experimental values of rotational constants $B^{\beta}_{v}(\beta = x, y, z)$ (obtainable from high-resolution MW spectra) and non-empirical values of linear and quadratic vibration-rotation constants α^{β}_{r} and $\gamma^{\beta}_{r,s}$ plus a small electronic correction obtained through the rotational **g**-tensor ($\Delta B^{\beta}_{g} = (m_e/m_p) g^{\alpha\alpha} B^{\alpha}_{e}$):[1]

$$B^{\beta}_{v} = B^{\beta}_{e} - \sum_{r} \alpha^{\beta}_{r} \left(v_r + \frac{1}{2} \right) + \sum_{r \geq s} \gamma^{\beta}_{r,s} \left(v_r + \frac{1}{2} \right) \left(v_s + \frac{1}{2} \right) + \ldots \qquad (1)$$

While linear constants α^{β}_{r} can be trivially calculated using the second-order perturbation theory (VPT2), the evaluation of the quadratic constants γ^{β}_{rs} requires a number of complex rotational commutators and this problem was never solved systematically. Only a few experimental studies for the $^{32}S^{16}O_2$ molecule included evaluation of γ^{β}_{rs}. [2] [3] The theoretical research include an early work by Brown[4] and a recent review by Demaison *et al*.[5]

We propose the systematic procedure for evaluation of $\gamma^{\beta}_{r,s}$ using the fourth-order canonical Van Vleck perturbation theory (CVPT4). This approach is largely based on evaluation of vibrational and rotational commutators using the normal ordering of ladder operators of angular momentum.[6] The values of $\gamma^{\beta}_{r,s}$ can be obtained by comparing the operator form of the vibrationally transformed Hamiltonian $\hat{H}^{(4)}$ with the corresponding theoretical terms,

$$H_{vib-rot} = \sum_{\beta}^{xyz} J^2_{\beta} \left(B^{\beta}_{e} - \sum_{r} \alpha^{\beta}_{r} a^{\dagger}_{r} a_r + \sum_{r \geq s} \gamma^{\beta}_{rs} a^{\dagger}_{r} a_r a^{\dagger}_{s} a_s + \ldots \right). \qquad (2)$$

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