

Electronic supplementary material S3 to

**High resolution spectroscopy of asymmetric top molecules in nonsinglet electronic states: The  $\nu_3$  fundamental of chlorine dioxide ( $^{16}\text{O}^{35}\text{Cl}^{16}\text{O}$ ) free radical in the  $X^2B_1$  electronic ground state**

Nonzero matrix elements of the  $^{(4)}H_{sp-rot}^v$  spin-rotational operator:

$$\begin{aligned} \langle NK\gamma, SJ | ^{(4)}H_{sp-rot}^v | NK\gamma, SJ \rangle &= \{ \Delta_N^s N^2 (N+1)^2 + \Delta_K^s K^4 \\ &+ (\Delta_{KN}^s + \Delta_{NK}^s) K^2 N (N+1) + \delta_{K,1} [ \delta_N^s N^2 (N+1)^2 + \delta_K^s N (N+1) ] (-1)^\gamma \} \\ &\times \frac{J(J+1) - N(N+1) - S(S+1)}{2N(N+1)}, \end{aligned} \quad (1)$$

$$\begin{aligned} \langle NK\gamma, SJ | ^{(4)}H_{sp-rot}^v | NK + \pm 2\gamma, SJ \rangle &= \{ 2\delta_N^s N (N+1) + \delta_K^s [K^2 + (K \pm 2)^2] \} \\ &\times [(1 - \delta_{K,0})(1 - \delta_{K,2}\delta_{\Delta K,-2}) + \sqrt{2}(\delta_{K,0} + \delta_{K,2}\delta_{\Delta K,-2})] \frac{J(J+1) - N(N+1) - S(S+1)}{4N(N+1)} \\ &\times \{ (N \mp K)(N \pm K + 1)(N \mp K - 1)(N \pm K + 2) \}^{1/2}, \end{aligned} \quad (2)$$

$$\begin{aligned} \langle N - 1K\gamma, SJ | ^{(4)}H_{sp-rot}^v | NK\gamma' \neq \gamma, SJ \rangle &= -(\Delta_K^s K^2 + \Delta_{NK}^s N^2 - \delta_{K,1}(-1)^\gamma \delta_K^s N) \\ &\times \frac{K}{2N} \left\{ \frac{(N^2 - K^2)(N - J + S)(N + J + S + 1)(S + J - N + 1)(N + J - S)}{(2N - 1)(2N + 1)} \right\}^{1/2}, \end{aligned} \quad (3)$$

$$\begin{aligned} \langle N - 1K\gamma, SJ | ^{(4)}H_{sp-rot}^v | NK + \pm 2\gamma' \neq \gamma, SJ \rangle &= -\frac{\delta_K^s}{4N} \{ (K + \pm 2)(N \mp K - 2) + K(N \mp K) \} [(1 - \delta_{K,0})(1 - \delta_{K,2}\delta_{\Delta K,-2}) \\ &+ \sqrt{2}(\delta_{K,0} + \delta_{K,2}\delta_{\Delta K,-2})] \left\{ \frac{(N \pm K + 1)(N \mp K - 1)(N \pm K)(N \pm K + 2)}{(2N - 1)(2N + 1)} \right\}^{1/2} \\ &\times \{ (N - J + S)(N + J + S + 1)(S + J - N + 1)(N + J - S) \}^{1/2}. \end{aligned} \quad (4)$$