INFRARED AND ULTRAVIOLET SPECTROSCOPY OF JET-COOLED 2-BENZYLPHENOL: II. EVIDENCE FOR STATE-SPECIFIC DUSCHINSKY NORMAL MODE MIXING IN THE EXCITED STATE

CHRISTIAN MÜLLER, CHIRANTHA P. RODRIGO, TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084*.

Visual inspection of the Fluorescence Excitation Spectrum (FES) and the Single Vibronic Level Fluorescence Spectrum (SVLF) of the electronic origin of 2-benzylphenol reveals a lack of mirror-symmetry. Both spectra are dominated by long overtone and combination band progressions involving the symmetric and antisymmetric phenyl ring torsional vibrations of frequencies $\tilde{\nu}_1^{\mathrm{S}_1} = 29\,\mathrm{cm}^{-1}$ and $\tilde{\nu}_2^{\mathrm{S}_1} = 41\,\mathrm{cm}^{-1}$ in the S_1 state and $\tilde{\nu}_1^{\mathrm{S}_0} = 29\,\mathrm{cm}^{-1}$ and $\tilde{\nu}_2^{\mathrm{S}_0} = 45\,\mathrm{cm}^{-1}$ in the S_0 state, respectively. Yet, both spectra markedly differ in the relative intensities of these progressions. Moreover, the SVLF spectrum of the vibronic transition at $41\,\mathrm{cm}^{-1}$, assigned to the fundamental of the antisymmetric phenyl ring torsion in the S_1 state, shows astonishing resemblance to the SVLF spectrum of the electronic origin. These findings suggest that the symmetric and antisymmetric phenyl ring torsions mix considerably upon electronic excitation to the S_1 state, even though, at first sight, their frequencies do not change much from their ground state values.

In order to represent the vibronic intensity patterns of the FES and the SVLF spectra of the 0_0^0, 1_0^1 and 2_0^1 transitions satisfactorily, state-specific Duschinsky mixing was invoked. Two-dimensional Franck-Condon overlap integrals were calculated based on recursion relations between harmonic oscillator wavefunctions derived using the standard generating function approach[1]. Employing a single set of parameters, the quality of the least-squares fit to the FES and the SVLF spectrum of the 0_0^0 transition is excellent. However, for a satisfactory represenation of the SVLF spectra of the 1_0^1 and 2_0^1 transitions, smaller rotation angles had to be used. Previously, state-specific Duschinsky mixing was invoked to qualitatively account for intensity irregularities of torsional progressions in the FES and a SVLF spectrum of 2-phenylindole[2]. To the best of our knowledge, this is the first attempt to treat this effect quantitatively. This unusual circumstance arises because of the large amplitude motion and small barrier associated with hindered rotation of the two phenyl rings.

(1) P. T. Ruhoff, *Chem. Phys.*, **1994**, *186*, 355.
(2) W. E. Sinclair, H. Yu, D. Phillips, J. M. Hollas, *J. Chem. Phys.*, **1997**, *106*, 5797.