# Major Source of Intensity in the $n\pi^*$ Transition of Aromatic Carbonyls

Martin Vala, Jr.,[*1] and Jiro TANAKA

*Department of Chemistry, Nagoya University, Chikusa-ku, Nagoya*

(Received July 26, 1968)

The problem of the major source of intensity in the nominally orbitally forbidden, spin allowed $n\pi^*$ transitions in aromatic carbonyl compounds has been investigated by several authors.1-3) However, no conclusive evidence has been presented in support of either of the two most probable mechanisms: (1) Herzberg-Teller vibronic coupling and (2) delocalization of the carbonyl $n$ and/or $\pi^*$ orbitals onto the substituents.

We report here the main conclusions of our investigation on the polarized absorption spectrum of the spin-allowed $n\pi^*$ transition in single crystals of 4,4′-dichlorobenzophenone (DCBP) at room and liquid helium temperatures. Details of this work and further work on the singlet-triplet absorption and emission will be reported later.

Our major findings are discussed below. (1) The $n\pi^*$ transition is exclusively polarized in the carbonyl plane and parallel to the carbonyl axis. From this finding we may immediately reject vibronic coupling *via* non-totally symmetric b-type modes and magnetic dipole allowed transitions as possible source of intensity since a perpendicular-to-CO polarization is expected for these mechanisms. It is not possible to eliminate vibronic coupling *via* totally symmetric (a) vibrational modes, as they will have parallel-to-CO polarization. Indeed, there is evidence that several weaker vibronic bands observed in the structure-rich $n\pi^*$ band are gaining intensity in this manner. (2) The 0–0 transition is observed as a very sharp band ($\simeq 2$ cm$^{-1}$ wide) at 26552 cm$^{-1}$. A careful study of thick crystals (up to 2.5 mm) at room and liquid helium temperatures failed to reveal any absorption to the red of this band which could be assigned to a singlet-singlet transition. The 0–0 transition is followed by a long ($\simeq 10$ member) progression of broad vibronic bands of 38 cm$^{-1}$ spacing. These observations are strongly indicative of the intrinsic allowed electronic character of the $n\pi^*$ transition. (3) The appearance of a large number of sharp vibronic origins upon which are built 38 cm$^{-1}$ progressions of varying length is a prominent feature of the 4.2°K spectrum. We interpret these progressions as due to the totally symmetric in-phase torsional oscillations of the phenyl rings about their long axes. The fact that such oscillations can be observed in the $n\pi^*$ transition is direct experimental proof of the delocalization of the carbonyl $n$ and/or $\pi^*$ orbitals onto the phenyl rings.

We may write the wave function for the perturbed carbonyl $n$ and $\pi^*$ orbitals as:

$$\Psi_n{}^\dagger = \phi_n + \lambda_\pi{}'\psi_\pi{}'$$

$$\Psi_\pi{}^{*\dagger} = \phi_\pi{}^* + \lambda_\pi{}^{*\prime}\psi_\pi{}^{*\prime}$$

where $\phi_n$ and $\phi_\pi{}^*$ are the unperturbed carbonyl orbitals and $\psi_\pi{}'$ and $\psi_\pi{}^{*\prime}$ are the substituent pi orbitals. $\lambda_\pi{}'$ and $\lambda_\pi{}^{*\prime}$ are the first order mixing coefficients, for example:

$$\lambda_\pi{}' = \frac{\langle\phi_n|V|\psi_\pi{}'\rangle}{\varepsilon_n - \varepsilon_\pi{}'}$$

Here $\varepsilon_n$ and $\varepsilon_\pi{}'$ are the respective orbital energies. Now writing the transition moment integral to first order, we find:

$$\langle\Psi_n{}^\dagger|\vec{R}|\Psi_\pi{}^{*\dagger}\rangle =$$

$$\lambda_\pi{}^{*\prime}\langle\phi_n|\vec{R}|\psi_\pi{}^{*\prime}\rangle + \lambda_\pi{}'\langle\psi_\pi{}'|\vec{R}|\phi_\pi{}^*\rangle$$

Thus the $n\pi^*$ transition gains electronic allowed character from intramolecular CT transitions in so far as the perturbation coefficients are non-zero, *i. e.*, as long as there is finite overlap of the carbonyl orbitals with the phenyl orbitals. The intensity of the $n\pi^*$ transition is directly dependent on the magnitude of this mixing. Since the mixing is a first order effect, it will be inversely proportional to the energy separation between the $n\pi^*$ and intramolecular CT transition.

To further test this explanation we have determined the $n\pi^*$ intensities of three different compounds in this class, whose $n\pi^*$ and intramolecular CT transition energy separations are dissimilar. From these energy differences, we predict the $n\pi^*$ intensity to decrease in the order 4,4′-dimethoxybenzophenone > DCBP > benzophenone.3) Observation gave $f$=0.006, 0.004 and 0.0024, respectively, as predicted. This result leads to the overall conclusion of our work that the $n\pi^*$ transition in symmetric aromatic carbonyl compounds is formally electronically allowed and gains the major component of its intensity by mixing with the intramolecular CT transition.

---

[*1] National Science Foundation US-Japan Cooperative Science Program Fellow, 1966—1967. Present address: University of Florida, Department of Chemistry, Gainesville, Florida, 32601.

1) R. Shimada and L. Goodman, *J. Chem. Phys.*, **43**, 2027 (1965).

2) W. D. Chandler and L. Goodman, *ibid.*, **45**, 4088 (1966).

3) D. S. McClure and P. L. Hanst, *ibid.*, **23**, 1772 (1955).