Reply to the Comment on: The torsional potential function of dimethylaminobenzonitrile and related compounds in their $S_1$ states

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Reply to the Comment on: The torsional potential function of dimethylaminobenzonitrile and related compounds in their $S_1$ states

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The preceding Comment on the paper of Ref. 2 makes the following main points: (1) the proper potential for the dimethylamino rotational motion about the $\text{C}_\text{ipso}$-$\text{N}$ bond must possess the proper symmetry; (2) the rotational angle $\tau$ which is zero in $S_0$ (a more or less planar conformation for the ring and the dimethylamino group) is ca. $\pm 25^\circ$ in $S_1$ (one CH$_3$-N bond roughly in the plane of the aromatic ring); (3) a large potential $V_2 \sim 3700$ cm$^{-1}$ and $V_4 \sim -400$ cm$^{-1}$ can be used to fit the complete set of spectroscopic data for the homologous five compound series if (and only if) one assumes that the DMABN-d$_6$ 0$^0_0$ transition is not observed; some of the transitions are assigned to first order forbidden bands, and a Fermi resonance is postulated for 3-DMABN for the $v = 0 \rightarrow 2$ torsional transition with a heretofore unobserved $a'$ vibrational mode; and (4) Franck-Condon calculations can be employed to fit the $S_1 \rightarrow S_0$ transition intensities.

Reference 2 draws the following main conclusions from the observed set of spectroscopic data for the five compounds studied: (1) the rotational angle $\tau$ that the dimethylamino group makes with the aromatic ring changes upon $S_1 \rightarrow S_0$ excitation by ca. $30^\circ$; (2) the potential for this motion is small $V_2 \sim 200$ cm$^{-1}$ and $V_4 \sim 550$ cm$^{-1}$; (3) Franck-Condon factor calculations can be employed to calculate the potential minimum shift upon $S_1 \rightarrow S_0$ excitation and thus the spectroscopic intensities; (4) an inversion potential can also be determined the parameters for which are as presented in Ref. 2; and (5) all the transitions are observed for these compounds even the DMABN-d$_6$ 0$^0_0$ transition (as suggested in Figs. 1 and 2), and no postulated Fermi resonances are required in the series.

The fit to experimental results presented in Ref. 2 seems dependent on fewer assumptions and moreover assigns many of the observed features (unassigned in Ref. 1) to a nitrogen inversion mode. Reference 2 also assumes that the torsion and inversion modes are independent. Aside from the assignment details, the major difference between the potentials of Refs. 1 and 2 is the size of $V_2$ and $V_4$. The potential of Ref. 2 is obtained in a weak perturbation limit; that is, the smallest potential is employed to get acceptable assignable eigenvalues for $S_1$ and then the concomitant eigenvectors are employed to "set" the $S_1$ potential minimum position ($\tau \sim 30^\circ$) with respect to the assumed $\tau = 0^\circ$ $S_0$ geometry.

While the potential of Ref. 1 has the correct symmetry, the potential of Ref. 2 fits the data set with fewer ad hoc assumptions and conditions. Neither potential seems consistent with the notion of a TICT excited state. The $S_1$ potential surface for this series of five compounds may be more complicated than presented in either Refs. 1 or 2 due to potential terms arising from twist/inversion interactions. Whether the potential $V(\tau)$ is small, large or indeed more properly nonseparable as $V = V(\tau,q)$, is still apparently an open question.

Finally, we point out that four previous publications have appeared on DMABN spectroscopy without assignment. Our assignment of the features in the DMABN $S_1 \rightarrow S_0$ spectrum as due to rotation and inversion degrees of freedom is not challenged by Ref. 1; in fact, our inversion/rotation separation is assumed. The only change suggested by Ref. 1 is in the potential.