

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 Comment¹ on the paper of Ref. 2 makes the following main points: (1) the proper potential for the dimethylamino rotational motion about the $C_{\text{ipso}}-\text{N}$ bond must possess the proper symmetry; (2) the rotational angle τ 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 $V_2 \geq 3700 \text{ cm}^{-1}$ and $V_4 \leq -400 \text{ cm}^{-1}$ 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 $\text{DMABN}-d_6 0_0^0$ 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 $\nu = 0 \rightarrow 2$ torsional transition with a heretofore unobserved a' vibrational mode; and (4) Franck-Condon calculations can be employed to fit the $S_1 \leftarrow S_0$ 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 τ that the dimethylamino group makes with the aromatic ring changes upon $S_1 \leftarrow S_0$ excitation by ca. 30° ; (2) the potential for this motion is small $V_2 \sim 200 \text{ cm}^{-1}$ and $V_4 \sim 550 \text{ cm}^{-1}$; (3) Franck-Condon factor calculations can be employed to calculate the potential minimum shift upon $S_1 \leftarrow S_0$ 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 TICT² 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 small², large¹ 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.³ Our assignment of the features in the DMABN $S_1 \leftarrow S_0 0_0^0$ 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.

¹R. D. Gordon, J. Chem. Phys. **93**, 6908 (1990).

²V. H. Grassian, J. A. Warren, E. R. Bernstein, H. V. Secor, J. Chem. Phys. **90**, 3994 (1989).

³See Ref. 2 and Refs. 12, 13, and 14 contained therein. See also R. Howell, A. C. Jones, A. G. Taylor, and D. Phillips, Chem. Phys. Lett. **163**, 282 (1989).