RESEARCH ACTIVITIES II
Department of Molecular Structure

II-A Picosecond Transient Infrared Studies on Excited States of Donor-Acceptor Systems

Molecules having an electron donor and acceptor group at both ends of a conjugated π-electron system sometimes show characteristic photophysical behavior: dual fluorescence, for example. 4-(Dimethylamino)benzonitrile (DMABN) has attracted much attention as a prototype of such compounds. The photophysics of these compounds are thought to be closely related to excited state molecular structures. We have already published static/transient infrared studies on DMABN and isotopomers in the ground state and in the charge-transfer excited state [*J. Phys. Chem. A* **104**, 4182 (2000); *Chem. Phys.* **260**, 193 (2000); *J. Phys. Chem. A* **105**, 4182 (2001)]. As an extension of that, we have studied molecular structures of excited states of DMABN and analogues by means of picosecond infrared spectroscopy.

II-A-1 Picosecond Infrared Spectrum of 4-(Pyrrol-1-yl)benzonitrile: Structure of the Excited Charge-Transfer States of Donor-Acceptor Systems

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Picosecond transient infrared spectrum of the excited charge-transfer (CT) state of 4-(pyrrol-1-yl)-benzonitrile (PBN) has been recorded in the frequency range of 1700–920 cm^{-1}. The CT state of PBN gives several quite strong infrared bands. The band at 1219 cm^{-1} shifts toward high-frequency side with increasing delay time between pump and probe pulses. This frequency shift is attributed to vibrational relaxation. Some of the transient bands (1429, ~1290, 1219, and 964 cm^{-1}) are very close in frequencies to those observed for the benzonitrile moiety of the excited CT state of 4-(dimethylamino)benzonitrile (DMABN). This finding implies that benzonitrile groups of PBN and DMABN are decoupled from the electron donating (pyrrole or dimethylamino) groups, and it can be explained by the twisted intramolecular charge transfer model. To make this point clear, however, further discussion is necessary on the band assignments and on correlation between structure and spectral pattern.

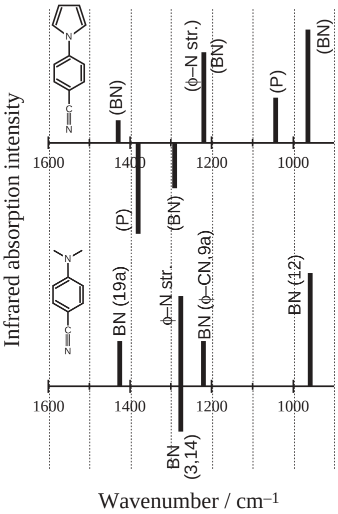

Figure 1. Transient infrared spectral patterns for the excited CT states of PBN (top) and DMABN (bottom). Tentative band assignments are given in parentheses for PBN. BN, mode of benzonitrile moiety; P, mode of pyrrole moiety.

II-A-2 Picosecond Infrared Spectra and Structure of Locally Excited and Charge Transfer Excited States of Isotope Labeled 4-(Dimethylamino)benzonitriles

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Infrared spectra of the ground, charge transfer (CT), and locally excited (LE) states of isotope-labeled 4-(dimethylamino)benzonitriles (DMABNs) in the region between 1700 and 900 cm^{-1} are reported. The isotopomers measured are normal DMABN, NC–C_6H_4–$^{15}NMe_2$ (dimethylamino nitrogen labeled DMABN), and NC–$C_6H_2D_2$–NMe_2 (3,5-dideuterated DMABN). Infrared spectrum of the excited CT state of DMABN-

d_2 is consistent with the previous band assignments for normal DMABN and DMABNs isotopically labeled on dimethylamino group. For the LE state of normal DMABN, three bands are observed at 1481, 1415, and 1399 cm^{-1}. This is in contrast with a previously reported transient infrared spectrum, where positions of bands due to the transient do not shift from the ground state ones. The band at *ca.* 1481 cm^{-1} is observed for normal and ^{15}N labeled DMABN, but not for DMABN-d_2. Except for this point, the band positions are almost identical for the three isotope-labeled species. The vibrational transitions observed at *ca.* 1415 and 1398 cm^{-1} are hence attributed to modes with atomic displacements localized on methyl groups and/or the part of the benzonitrile moiety adjacent to the cyano group or the cyano group itself. Quantum chemical calculations of the vibrational spectra for the CT and LE states of DMABN at present do not correctly reproduce the experimental spectra, which means that more accurate calculations are needed for a reliable analysis of these spectra.

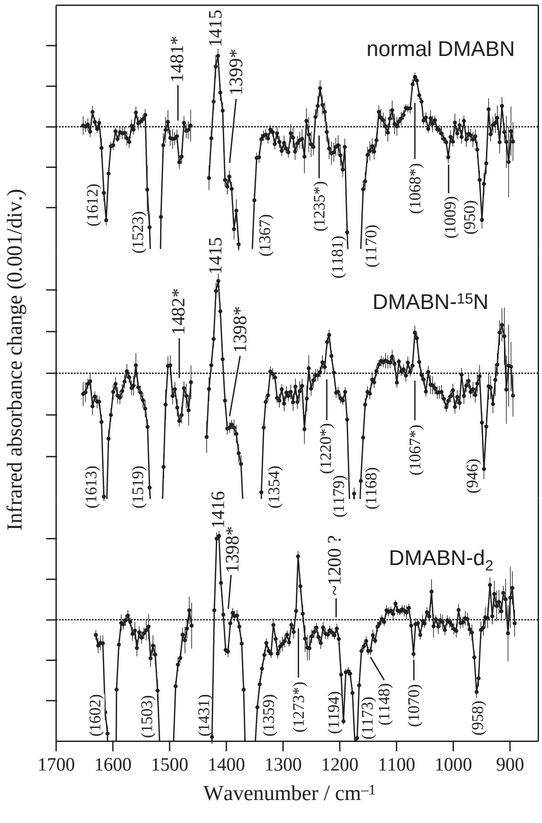

Figure 1. Transient infrared spectra of DMABN and the two isotope-labeled derivatives DMABN-d_2 and DMABN-^{15}N in cyclohexane solution at room temperature at 4 ps after excitation. Bleached bands arising from the ground state are indicated in parentheses. Negative bands due to non-totally symmetric vibrational modes (for both the ground and the excited states) are marked with asterisks.