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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). The 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.

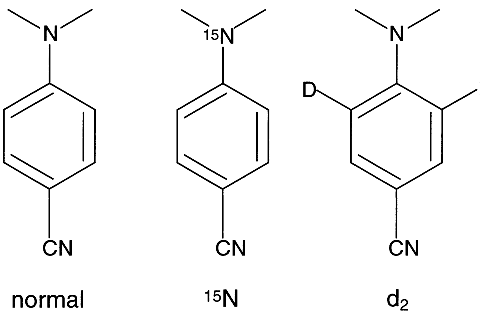
4-(Dimethylamino)benzonitrile (DMABN) is a representative of molecules having an electron donor (D) and acceptor (A) group at both ends of a conjugated π-electron system. Such D/A-substituted molecules sometimes show dual fluorescence in sufficiently polar solvents, and DMABN has attracted much attention as a prototype of such compounds. The dual fluorescence of DMABN is considered to originate from two emissive excited states: the locally excited (LE) state and the charge transfer (CT) state.[1–3] The LE state is generated immediately after very rapid relaxation from the optically excited (S_2) state, whereas the CT state is formed as the intramolecular charge transfer reaction proceeds.[4–9] The molecular structure of the CT state involved in this reaction, twisted or planar, is still under discussion.[10,11] In the charge transfer reaction of DMABN, the LE state is the precursor of the CT state. The molecular structure of the LE state, as well as that of the CT state, is an essential factor in the mechanism of the charge-transfer reaction.[6–9]

Recently, several research groups have investigated the excited state geometry of the LE and CT states of DMABN by using vibrational (infrared and Raman) spectroscopy.[12–19] We previously discussed the molecular structure of the CT state of DMABN[14,18] and of molecules with related structures,[19] by picosecond infrared spectroscopy in the fingerprint region. In one of those publications,[18] we recorded transient infrared spectra of DMABNs isotopically labeled in the peripheral (i.e., dimethylamino and cyano) groups. In this paper, we report infrared spectra of the ground, CT, and LE states of three DMABN and two isotope-labeled DMABNs, including a ring-deuterated species which was not measured previously.[14,18] The present results show that some of the experimental data and/or their interpretation reported for DMABN in the literature are questionable, especially for the LE state.[13,15,16]

Experimental

The experimental apparatus for measuring picosecond infrared spectra in the fingerprint region (1700–900 cm^{-1}) was basically the same as that described elsewhere.[20,21] The spectral data were taken at 4 cm^{-1} intervals. We made use of a method based on optically heterodyned detection of absorption anisotropy (OHDAA),[21] in order to detect very small infrared absorbance changes. Because of the characteristics of this OHDAA method, the transient species gives a positive induced band when the vibrational transition moment is parallel to the electronic transition moment, while it gives a negative induced band when the transition moments are perpendicular to each other. If the angle between the transition moment is the magic angle (54.7°), it gives no transient absorption band. In addition, of course, bleached absorption bands give peaks with the opposite signs to the induced bands. For molecules of C_{2v} symmetry, totally symmetric vibrational modes (a_1 species, in-plane) give positive transient absorption peaks, whereas non-totally symmetric modes (b_1 species, out-of-plane; b_2 species, in-plane) give negative peaks. Vibrational modes of a_2 species (out-of-plane) are not infrared active. This characteristic can help assignments of transient vibrational bands. In the conventional transient infrared absorption method, all the induced transient bands give bands with a common sign. This point must be recalled when transient absorption data obtained by OHDAA method is compared with those obtained by the conventional method. Static infrared spectra of the ground state molecules were recorded by a JASCO FT/IR-420 Fourier transform infrared spectrophotometer.

The isotopomers of DMABN measured in this study are the natural isotope-abundance sample (hereafter called "normal"), the dimethylamino nitrogen labeled compound (DMABN-^{15}N), and the 3,5-dideuterated molecule (DMABN-d_2). The chemical structures of these isotopomers are shown in Scheme 1. The normal and ^{15}N samples were synthesized as described previously.[22] DMABN-d_2 was obtained by refluxing DMABN (Aldrich) in D_2O containing D_2SO_4. The percentage of deuteration is larger than 95%, as determined by ^{1}H and ^{13}C NMR in comparison with DMABN. Acetonitrile and cyclohexane were used as solvents for the infrared measurements. These solvents (liquid chromatography grade) were purchased from Wako Pure Chemicals and used as received. The sample concentration was 7×10^{-2} mol dm^{-3} for acetonitrile solution and 2.7×10^{-2} mol dm^{-3} for cyclohexane solution.



Scheme 1.

Results and Discussion

1. Ground Electronic State. Static ground state infrared spectra for acetonitrile solutions of three isotopomers of DMABN (Scheme 1) are presented in Fig. 1. The spectra for the normal and ^{15}N species shown in this Figure are the same as those given in the previous papers.[18,22] The spectrum for DMABN-d_2 has a quite different spectral pattern as compared with those of the other two species. For the three isotopomers, the band frequencies, the results of the normal coordinate analysis, and the vibrational assignments based on this analysis are summarized in Table 1. In the case of the normal and ^{15}N species, the results are the same as those reported previously.[27] The method and the force field of the normal coordinate analysis employed in the previous work reasonably explain the vibrational bands observed for the d_2 species. Consequently, the infrared spectrum of the ground state of DMABN-d_2 obtained here confirms the validity of the our earlier vibrational analysis.[22]

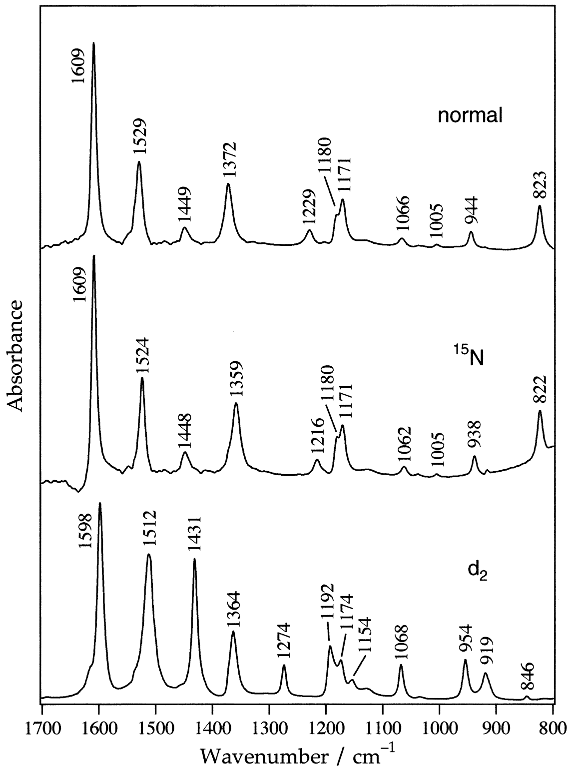


Fig. 1. Static infrared spectra of DMABN and the two isotope-labeled derivatives DMABN-d_2 and DMABN-^{15}N in the ground state, in acetonitrile solution at room temperature (concentration 0.07 mol dm^{-3}). Bands due to solvent have been numerically removed.

2. CT State. Transient infrared spectra of three isotopomers of DMABN in acetonitrile solution are shown in Fig. 2. The delay time between the pump and probe pulses was set at 16 ps. The transient species observed at this delay time is considered to be the CT state. The spectra for the normal and ^{15}N species are identical to those reported earlier,[18] as shown in Table 2.

The data for DMABN-d_2 are essentially consistent with the previous band assignments for normal DMABN and DMABNs isotopically labeled on dimethylamino group. A positive induced band at 1370 cm^{-1} of the d_2 species is considered to have an origin similar to that at 1425 cm^{-1} of normal DMABN (assigned to mode 18*a*/19*a* of Wilson notation[23]), which shows a low-frequency shift upon deuteration. Since the band at 1274 cm^{-1} of the ground state is due to an asymmetric vibrational mode, it gives a *negative bleached* absorption in the transient spectra. (As mentioned in the experimental section, negative peaks are coming from non-totally symmetric vibrational modes.) The sign of the peak is the same as that of a *positive induced* band due to the excited state.[18,21] The bleached band is clearly observed in the transient spectrum in cyclohexane solution (see Fig. 4). The positive transient band at 1277 cm^{-1} may include some contribution from the ground state asymmetric vibrational mode. However, from

Table 1. Infrared Band Frequencies (in cm^{-1}) of the Ground State of DMABN Isotopomers in Acetonitrile (see Fig. 1)

Normal		^{15}N		d_2		Assignment [a)]
Obsd	Calcd[a)]	Obsd	Calcd[a)]	Obsd	Calcd[a)]	
1609	1608	1609	1608	1598	1596	8*a*
1529	1517	1524	1512			18*a*,19*a*
				1512	1506	Me-ad
1449	1457	1448	1457			Me-sd
				1431	1433	Me-sd,18*a*,19*a*
1372	1353	1359	1336	1364	1344	C_{ring}–NMe_2
				1274	1269	3,14
1229	1237	1216	1223			N-Me
				1192	1174	C_{ring}–CN,18*a*; 3,19*b* [b)]
1180	1170	1180	1170			9*a*,C_{ring}–CN
1171	1161	1171	1161			Me-rc,1
				1174	1171	Me-rc,1
				1154		
				1068	1050	9*a*,12; Me-rc
1066	1051	1062	1047			Me-rc
1005	986	1005	986			12,19*a*
				954	938	N–Me
944	932	938	926			N–Me,1
				919	897	10*b*
				846	834	18*a*,9*a*
823	799	822	799			11

a) Based on normal coordinate analysis in Ref. 22. Calculated frequencies by B3LYP/6-31G(d) level. Abbreviations: 8*a* etc., Wilson notation for the benzene ring vibration; Me-ad, methyl group asymmetric deformation; Me-sd, methyl group symmetric deformation; Me-rc, methyl group rock.

b) Consists of two overlapping vibrational bands.

its very strong band intensity, it is obvious that the principal part of this band is coming from absorption by the CT state. This positive band due to the CT state may be attributed to the C_{ring}–NMe_2 single bond stretch, with a frequency almost the same as that observed for the normal species (1276 cm^{-1}). However, the benzene-ring vibrational modes, 18*a* and 19*a*, and the C_{ring}–NMe_2 stretch (see Fig. 3) are considered to be mutually hybridized to some extent. The low-frequency shift of the mode 18*a*/19*a* mentioned above (1425 cm^{-1} in the normal species to 1370 cm^{-1} in d_2) makes the frequency difference between the ring mode and the C_{ring}–NMe_2 stretch smaller, which may promote the hybridization among these modes. As a result, the mode hybridization in the d_2 species may be quite different from that in the normal species for the C_{ring}–NMe_2 stretch, although the frequency locations are apparently very close to each other.

In normal DMABN (and in DMABN–^{15}N as well), a band attributable to the ring mode 12 (Fig. 3) is observed at 959 cm^{-1}. In the d_2 species, no band corresponding to this mode is observed. This may be explained by hybridization of several vibrational modes as will be discussed in the following. For normal DMABN, vibrational oscillator strength may be concentrated on the mode giving the 959 cm^{-1} band. However, deuteration of the ring and consequent change of mode hybridization may cause dissipation of the vibrational oscillator strength into several vibrational modes. The intensity of each vibrational mode, to which the oscillator strength of mode 12 is distributed, may be lowered so significantly that they become virtually unobservable in the transient spectrum.

In the normal and ^{15}N species, strong bands are observed at 1220 cm^{-1}; these are attributed to the C_{ring}–CN stretch (and/or mode 9*a* of the ring). This vibrational mode is expected to shift to ca. 1200 cm^{-1} on deuteration, by analogy with the ground state. We can unfortunately not clearly observe the corresponding band in the transient spectrum of the CT state of the d_2 species. The ground state molecule gives bleached absorption bands around 1200 cm^{-1}, which possibly overlap with the C_{ring}–CN stretch of the CT state. The absence of the band is therefore consistent with the assignment of the band of the normal DMABN at 1220 cm^{-1}.

Kwok et al. have concluded that the CT state of DMABN has a twisted geometry,[17] since the observed frequencies of the C_{ring}–NMe_2 stretch and the C≡N stretch agree well with those of the CASSCF calculations.[24] However, it is necessary to examine the performance (i.e., accuracy) of the method of calculation, when molecular structure is discussed based on a comparison of experimental and quantum chemically calculated vibrational spectra. Previously, we have pointed out several serious disagreements between the observed and the calculated infrared spectra for the CT state of DMABN,[18] although the observed C_{ring}–NMe_2 stretching frequency has been well reproduced by the calculation. For example, the calculation fails to reproduce the band at 1425 cm^{-1} arising from a ring vibrational mode. In our opinion, the accuracy of the CASSCF calculations may have to be reexamined. The CT state spectrum of DMABN-d_2 observed in the present study may give useful data for that purpose. It is desirable to compare experimental infrared spectra observed for the CT state of various isotopomers of

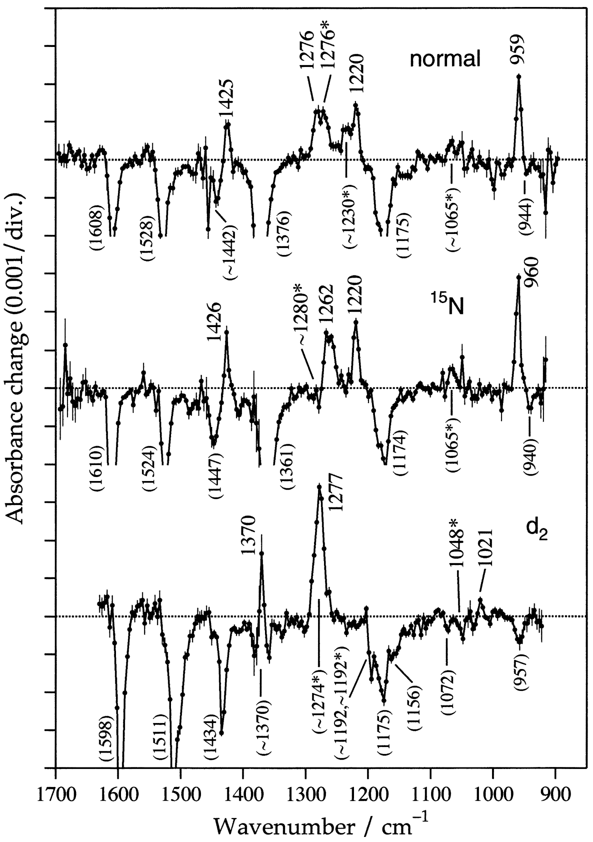


Fig. 2. Transient infrared spectra of DMABN and the two isotope-labeled derivatives DMABN-d_2 and DMABN-^{15}N in acetonitrile solution at room temperature (concentration 0.07 mol dm^{-3}) at 16 ps after excitation. Bleached bands arising from the ground state are indicated in parentheses. Negative bands due to non-totally symmetric vibrational modes (for both the ground and the excited states) are marked with asterisks.

Table 2. Infrared Band Frequencies (in cm^{-1}) of the Excited (CT and LE) States of DMABN Isotopomers in Acetonitrile (see Fig. 2) and Cyclohexane (Fig. 4)[a)]

Normal	^{15}N	d_2	Assignment [b)]
CT state			
1425	1426		18*a*,19*a*
		1370	18*a*,19*a*,C_{ring}–NMe_2
1276*	~1280*		3,14
		1277[c)]	C_{ring}–NMe_2,18*a*
1276	1262		C_{ring}–NMe_2
1220	1220		C_{ring}–CN
		1048*	
		1021	9*a*?
959	960		12
LE state			
1481*	1481*		
1415	1415	1416	
1399*	1398*	1398*	

a) Negative peaks arising from non-totally symmetric vibrational modes are indicated by asterisks.

b) See notes to Table 1 for abbreviations.

c) A bleached absorption band due to the ground state lies at very close frequency (1274 cm^{-1}).

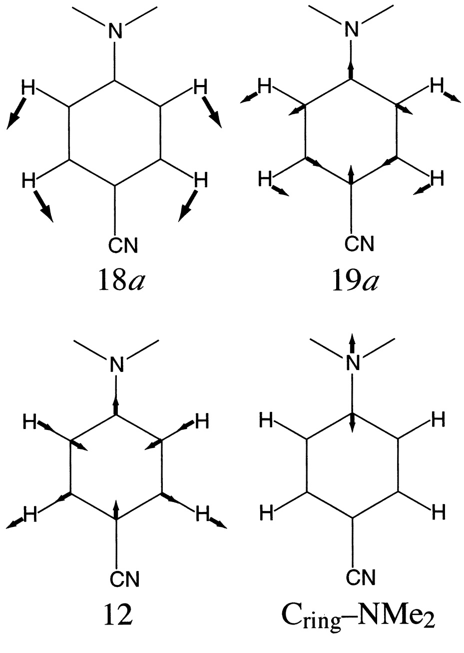


Fig. 3. Vibrational coordinates of DMABN.

DMABN with those obtained from quantum chemical calculations, not only for the C_{ring}–NMe_2 stretch and C≡N stretch but also for other bands, such as ring vibrational modes. The determination of the structure of the CT state based on calculations can be satisfactory only if a good agreement is obtained between the entire observed and calculated infrared spectra for the various isotope-labeled species investigated.

In our previous study,[18] it has been concluded that, in the CT state, (1) the C_{ring}–NMe_2 bond is of single bond character, and (2) the ring moiety is suggested to possess some quinoidality. The present result on DMABN-d_2 is consistent with that conclusion. A planar structure with the C_{ring}–NMe_2 bond of a double bond character is consequently not likely for the CT state of DMABN. Either one of the following two possibilities may be the right answer: the C_{ring}–NMe_2 bond is of single bond character due to torsional displacement, or, it retains single bond character for some reason despite a (nearly) planar structure. When an advanced theoretical calculation predicts accurately, in the future, the observed vibrational spectra including the ring modes, and/or if other kind of infrared data (mentioned in later section) are accumulated for the CT state, it will be well understood which possibility of the two is more realistic.

3. LE State. The optical transition from the ground state to the LE state of DMABN is associated with a transition moment perpendicular to the long molecular axis, and results in a relatively weak absorption band.[25] In solution, the LE state of DMABN is predominantly generated via relaxation from the S_2 state that has a larger oscillator strength than the transition to S_1.[8] The molecular structure of the LE state is an important factor in the mechanism of the intramolecular charge separation reaction. The following publications have appeared con-

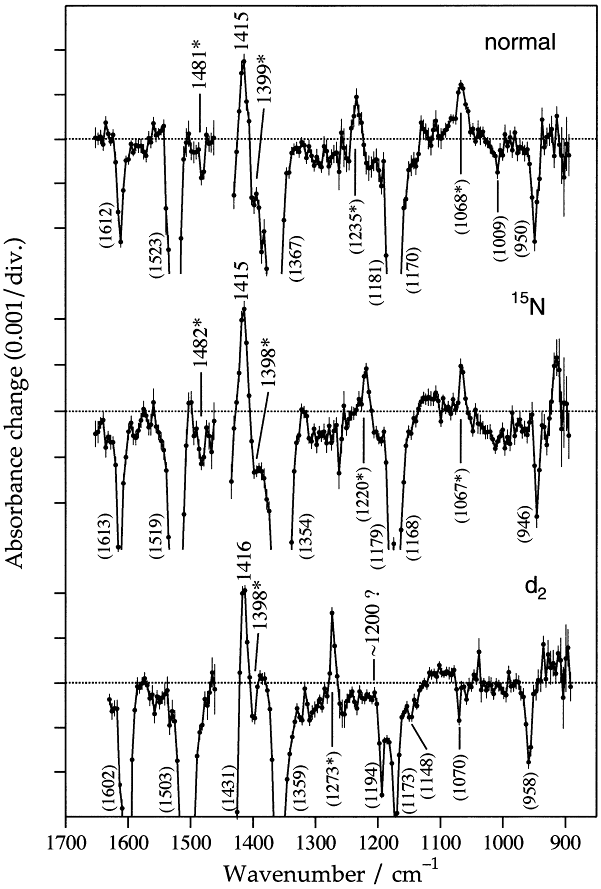


Fig. 4. Transient infrared spectra of DMABN and the two isotope-labeled derivatives DMABN-d_2 and DMABN-^{15}N in cyclohexane solution at room temperature (concentration 0.027 mol dm^{-3}) at 4 ps after excitation. Bleached bands arising from the ground state are indicated in parentheses. Negative bands due to non-totally symmetric vibrational modes (for both the ground and the excited states) are marked with asterisks.

cerning the LE state molecular structure.

In the gas phase, selective direct excitation from the ground state to a single vibronic level of the LE state is possible,[26–31] and the molecular structure has been discussed based on the band contour analysis. Kajimoto and coworkers have concluded that the dimethylamino group is planar and is twisted by 30° relative to the benzene plane (but the barrier height at 0° is found to be very small) in the gas phase, based on a rotational envelope analysis of the laser induced fluorescence spectrum.[27] Comparable results have been obtained in a recent study by Lommatzsch and Brutschy.[29] From a similar analysis, Salgado and coworkers have reached the conclusion that the amino twist angle is approximately 0°, whereas the planarity of dimethylamino group was not clearly established.[30] Although there are minor differences, the results of the gas phase experiments[26–31] agree on the point that the twist angle of the dimethylamino group is rather small.

In solution, a determination of the LE state structure is difficult, but several attempts have been made. Zachariasse and coworkers have proposed that inversion of the amino nitrogen is an important reaction coordinate in the relaxation process from the LE state to the CT state, based on an analysis of the fluorescence behavior of DMABN and related compounds in various solvents.[6–9] They explain the experimental results by assuming that the dimethylamino group is weakly pyramidalized in the LE state, similar to what has been found for the ground state. Kummrow and coworkers, on the other hand, have concluded that the LE state has a planar structure, based on comparison of observed and quantum chemically calculated infrared spectra.[13,16] Kwok et al. have supported the idea of a planar LE state from the observed Raman band frequencies.[15] However, the arguments concerning the LE state structure of DMABN in solution seem to be somewhat ambiguous and questionable, as will be discussed later in this section.

In Fig. 4, transient infrared spectra of the three isotopomers of DMABN in cyclohexane solution at a delay time of 4 ps are shown. Since these spectra were recorded shortly (4 ps) after photoexcitation, the transient species should be a singlet excited state. In cyclohexane solution, the CT state of DMABN is not formed and hence the transients observed in the spectra originate from the LE state. In the picosecond transient infrared spectra obtained, two (for DMABN-d_2) or three (for normal DMABN and DMABN-^{15}N) absorption bands due to the LE state are observed. In the normal and ^{15}N species, we find a negative peak at 1481 cm^{-1}, which may be attributed to a non-totally symmetric vibrational mode (see the experimental section). This band is not observed (or at least not clearly observable) for the d_2 species, possibly because of the strong bleached absorption band due to the ground state molecules. Except for this peak, the two other band positions (ca. 1415 and 1398 cm^{-1}) are almost identical for normal DMABN and the two isotope-labeled species. This clearly shows that the vibrational modes giving rise to these bands do not involve displacements of the amino nitrogen and of the 3- or 5-hydrogen or deuterium atoms of the benzene ring. It also indicates that the C_{ring}–NMe_2 single bond stretching vibration of the LE state is not observed in these spectra, because none of the bands shows a low-frequency shift upon ^{15}N-substitution in the dimethylamino group. We therefore attribute the bands at ca. 1415 cm^{-1} (positive peaks: totally symmetric mode) and ca 1398 cm^{-1} (negative peaks: non-totally symmetric mode) to vibrational modes with atomic displacements localized on the methyl groups and/or on the part of benzonitrile moiety adjacent to the cyano group (1-, 2-, or 6-carbons, 2- or 6-hydrogens of the ring or the cyano group itself).

Kwok et al. found a Raman band due to the LE state of normal DMABN at 1423 cm^{-1} in cyclohexane.[15] They have assigned this band to the C_{ring}–NMe_2 stretch, and from the vibrational frequency they concluded that the bond between the ring and dimethylamino group has considerable double bond character and that consequently the dimethylamino group is co-planar with the benzene ring. However, the only evidence they have shown for this band assignment is its 'strong intensity'. The infrared band at 1415 cm^{-1} we have found in the present measurement possibly arises from the same vibrational mode as that giving rise to the Raman band at 1423 cm^{-1}, taking into account the facts that the Raman spectral data of Kwok et al. were obtained at intervals of 10 cm^{-1} and that the band is quite broad.[15] Our present transient infrared data for the ^{15}N species show that the band at 1415 cm^{-1} is not due to the $\mathrm{C_{ring}}$–$\mathrm{NMe_2}$ stretch, as discussed above. If this infrared band (1415 cm^{-1}) corresponds to the Raman band at 1423 cm^{-1}, it would follow that the argument given by Kwok et al. for the planarity of dimethylamino group is not correct. Further discussion is needed on this point.

Chudoba et al. have reported the transient infrared spectrum of the LE state of DMABN in the wavenumber range between 2230 and 1270 cm^{-1}.[13,16] However, there seem to be questionable points concerning the LE state spectrum (at 1 ps delay) they have obtained, when we compare their spectrum with that presently recorded. In the spectrum of Chudoba et al., the LE state absorption bands between 1700 and 1400 cm^{-1} appear at the same frequencies as those observed for the ground state absorption bands. No bands have been found outside this wavenumber region. The three bands we have found here (1481, 1415, and 1399 cm^{-1}, see Table 2) were not observed. If they have failed to detect these three bands because of their weak intensities, then the "LE state bands", which they have found at the same positions as the ground state bands, must be very strong. In that case, we should observe strong transient infrared bands due to the LE state in our transient spectra, at the same frequencies as the ground state vibrational transitions, with signs of the peaks opposite to them. We do not find, however, such bands in the spectra shown in Fig. 4. Chudoba et al. obtained the infrared spectrum of the LE state of DMABN by numerical subtraction of the ground state contribution from the transient spectrum including the bleached absorption bands. In this method of obtaining the LE state spectrum, parameters such as the pump power density at the sample point are needed, but these are sometimes difficult to estimate accurately. Even if these parameters were accurately known, the problems of nonlinear effects such as depletion and generation of hot molecules still remain; such difficulties were not taken into account. They mentioned[16] that 'multiphoton absorption' was actually observed at very short delay times. Furthermore, effects of transient absorption anisotropy for polarized light were not considered. The 'infrared bands' of the LE state they have found at the same position as the ground state bands are probably due to artifacts coming from the numerical treatment of the spectra.

Kummrow et al. have performed vibrational analysis and infrared intensity calculations for the LE state of normal DMABN, based on the ab initio CASSCF method.[13,16,24] They have reported the results of the vibrational analysis for pyramidal and planar geometries of the dimethylamino group (with the twist angles fixed at 0°). For the pyramidal dimethylamino geometry, no strong band other than the $\mathrm{C_{ring}}$–$\mathrm{NMe_2}$ stretch was predicted around 1400 cm^{-1}, and this result is not consistent with the infrared spectrum observed here. As for the planar geometry of the dimethylamino group, on the other hand, several strong bands have been calculated in the region between 1500 and 1400 cm^{-1} (there is no description about details of the mode and symmetry species in Refs. 13, 16, and 24). In our transient spectra in Fig. 4, data could not be obtained in the region around 1450 cm^{-1} because of interference from strong absorption by the solvent cyclohexane. For that reason it is difficult to compare the results of the calculation by Kummrow et al. with the transient infrared spectrum obtained in this work. It may be said that the observed spectrum is a little closer to the calculated result for the planar geometry than to that for the pyramidalized geometry, for they give a few infrared bands in 1400's of cm^{-1}. It is almost impossible, however, to make use of this fact as a criterion for determination of the structure in the LE state. At least from a quantitative point of view, the calculated vibrational frequencies and intensities are not in good agreement with the observed transient spectrum. The results described in this section show that accuracy of the CASSCF calculation[13,16,24] is not sufficient for the purpose of determining the LE state geometry of DMABN from the experimental vibrational spectra. A decision on the geometry of the LE state of DMABN can therefore not be made at present.

Concluding Remarks

In several previous studies, conclusions on the molecular structure of the LE and CT states of DMABN have been derived from only partial agreement between observed and calculated vibrational spectra. If a calculation does not well reproduce the entire observed spectrum, however, this may indicate that the method of calculation is not fully satisfactory. The excited state structures which follow from such calculations must therefore be considered to be ambiguous. In the fingerprint region between 1500 and 900 cm^{-1}, hybridization of vibrational modes is often substantial, and small cross terms of the force field sometimes have sizable effects on vibrational modes and frequencies. This is indeed the case for the ground state DMABN,[22] and probably also for the excited states. This means that the partial agreement between observed and calculated frequencies may be accidental in some cases. It is therefore essential that the overall feature of the observed spectrum is well reproduced by the calculations, before conclusions on excited state structures can be made. For the CT and LE states of DMABN, this criterion is unfortunately not fulfilled at present. Vibrational analysis based on more accurate quantum chemical calculations is hence desired.

In order to investigate the structure of excited DMABN by transient infrared spectroscopy, one may try a different method as described in the following. In transient infrared absorption experiments, two transition moments are involved in the optical process: an electronic transition moment for the pump process and a vibrational transition moment for the probe process. The angle between the two transition moments can be determined by polarization dependence measurements with linearly polarized pump and probe light (or qualitative information is obtained in a simple way by optically heterodyned detection of absorption anisotropy,[21] the method adopted in this study). Consequently, if we can observe a non-totally symmetric vibrational mode of the dimethylamino group of the excited molecule, such as the anti-symmetric N–Me stretch, and if we can photoexcite the molecule with a transition moment perpendicular to the molecular axis, then the twist angle of the dimethylamino group of the excited molecule can be estimated. Similarly, we can obtain an approximate value of the wagging angle, if the molecule is excited with an electronic transition moment parallel to the molecular axis and a vibrational mode such as the symmetric N–Me stretch is observed. To achieve this goal, observation and assignment of suitable vibrational bands is necessary, and appropriate pump wavelengths must be available. The method would require a very high sensitivity of transient absorption measurements and a wide wavelength tunability for the pump light source. To obtain such a very high sensitivity is not easy at present; it may need extremely high stability of the light source. As for the tunability of the pump light, it may be already feasible if we adopt a modern Ti:sapphire based laser system. The geometric structure of the CT and LE states of DMABN could be determined without ambiguity, when this method would become possible in practice.

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