Femtosecond Isomerization of Crystal Violet in Alcohols

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Abstract: The temporal rise of the spectral bleaching of crystal violet (CV) in alcohol solutions was studied using femtosecond pump-probe spectroscopy with tunable pump pulses. From the pump-wavelength dependence of transient differential absorption (ΔOD) spectra, we concluded that CV has two ground states. The isomerization rate, not dependent on solvent viscosity, was ∼500 fs at 295 K. This shows that the structural difference between the isomers is not as large as a phenyl ring rotation, which has been regarded as the origin of the ground-state isomers. We proposed a ground-state model of CV, in which the molecular structure of CV has D_3 or C_3 symmetry, based on molecular orbital calculations. Our model explains not only our findings but also almost all of the previous findings that seemed to conflict with each other over the last 50 years.

Introduction

The identification of molecular structure and the observation of dynamics in organic molecules have long been one of the main subjects in chemistry.[1,2] Recently, direct observation of ultrafast (sub-ps to fs) conformational change in the ground or excited state has become possible owing to advances in ultrashort-pulse lasers.[3,4]

Crystal violet, tris(*p*-(dimethylamino)phenyl)methyl ion, is one of the triphenylmethane dyes for which there are many studies concerning molecular structures,[5−7] electronic states,[8−12] and relaxation dynamics of electronic excited states.[13−20] The visible absorption spectrum of CV in solution appears to be composed of two bands, and their origin was interpreted in three ways: (1) resolution of vibronic structures coming from one electronic state,[21] (2) electronic transition from one ground state to two excited states,[8−10,12] and (3) the existence of two isomers or two ground states.[22−25]

Lewis and co-workers[22] proposed two ground-state conformational isomers in thermal equilibrium as an origin of the two absorption bands. One was a propeller structure (D_3 symmetry), in which three phenyl rings are tilted in the same direction. The other was a distorted propeller structure (C_2 symmetry) for which one of the phenyl rings is tilted in the opposite direction. This model was based on the observation that the shorter wavelength band was diminished and the longer wavelength band was enhanced with decreasing temperature in alcoholic solutions. This observation argues against the possibility of a resolved vibronic structure as an assignment of the shorter wavelength band. Furthermore, similar intensity exchange between the two bands under high pressure[24,25] was explained within the framework of this model.

However, several theoretical studies indicated that the two bands originate from electronic transitions from one ground state to two excited states. The D_3-symmetry conformer was confirmed by X-ray diffraction studies of crystal samples,[5] resonance Raman studies,[7,12,21] and magnetic circular dichroism measurements.[6] On the other hand, the C_2-symmetry conformer has not been identified.

Korppi-Tommola and co-workers[10] questioned whether the distorted-propeller conformer is concerned only with stereoscopic structural changes because they observed no change in the absorption spectra of CV in solution except in alcohols when the temperature was decreased. They explained the origin of the two bands by lifting the degeneracy of the S_1 state due to solvation in polar solvents and by the formation of an ion pair with counteranion in nonpolar solvents. The fact that the spectral change at low temperature is observed only in alcohols was interpreted as follows. Reducing the temperature results in a decrease in alcohol monomers and an increase in alcohol dimers. If only the alcohol monomers can solvate with CV,

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the decrease in the alcohol monomers causes a decrease in dye cations whose S_1 state splits into two electronic states. The idea that the interaction of the alcohol monomer with the CV could split the degeneracy of the S_1 state was recently supported by Lueck and co-workers.[12] They calculated the effects of an external negative charge or dipole on the transition energies of parafuchsin, tris(*p*-aminophenyl)methyl ion, which is a D_3-symmetry triphenylmethane dye like CV. According to their calculations, an isolated D_3-symmetry triphenylmethane dye has the doubly degenerated S_1 state. However, the degeneracy of the S_1 state could be lifted by a symmetry-breaking perturbation due to a negative charge or a dipole near one of the amino groups. The calculation showed that the split of the S_1 state becomes larger when the negative charge increases or is close to the dye cation. This explains that the split of the two bands in nonpolar solvents is larger than that in polar solvents. In addition, they calculated both the energy difference and the potential barrier between the propeller structure and the distorted-propeller structure; the latter structure was larger in energy ($\sim$5000 cm^{-1}) than the thermal energy ($\sim$200 cm^{-1}) at room temperature. This shows that the population of the distorted-propeller type would be small at room temperature. Furthermore, they measured the polarization dependence of fluorescence spectra and resonance Raman spectra.[12] The fluorescence spectra of tri-para-substituted triphenylmethane dyes like CV were a mirror image of the longer wavelength absorption band. The fluorescence anisotropy depends on excitation wavelengths. These observations showed that the shorter wavelength band and the longer wavelength band are assigned to different electronic transitions. In the resonance Raman study, the assignment of normal modes was more consistent with D_3 than with C_2 symmetry. Moreover, the depolarization ratio of observed Raman bands agreed with the lifting of degeneracy of the S_1 state. These findings suggest that the symmetry breaking due to the perturbation of solvents or counteranions lifts the degeneracy of the S_1 state. Hence, the fluorescence spectra and the resonance Raman spectra support the idea that the absorption spectrum of CV is assigned to the transitions from one ground state to two excited states.

The studies of relaxation dynamics of CV in solution have also been done by the picosecond pump-probe technique.[13,15,23,26,27] They observed that the recovery of bleaching probed on the red side of the bleaching spectrum is faster than that probed on the blue side. This observation was interpreted as being due to the existence of either of the two ground states[23] or to two excited states having different nonradiative decay rates.[27] However, Ben-Amotz and Harris[15] interpreted that the apparent faster relaxation at the red side of the bleaching spectrum would be due to stimulated emission gains concomitant with the bleaching. Besides that observation, there was no excitation and observation-wavelength dependence of the bleaching recovery. From this, only one ground state and one excited state are enough to explain the observed bleaching recovery dynamics.

Although there have been several studies concerned with the ground state conformers of CV, it is not yet known whether the ground state of CV is homogeneous or inhomogeneous. Almost all of the studies indicating that only the propeller species exists argued against the asymmetry propeller structure. However, they failed to explain the temperature and the pressure dependence of the absorption spectrum of CV, which are the strong evidence for the existence of two ground states. On the other hand, only the temperature and the pressure dependence of the absorption spectrum have supported the idea of the two ground states. Thus, there has been no model to explain comprehensively the previous data. Our basic idea is that the structures of the ground states do not necessarily have to be limited to the conformational isomers proposed by Lewis and co-workers[21] even if we consider more than one ground state.

The spectral hole-burning technique is useful to confirm whether the absorption spectrum is homogeneous or inhomogeneous. As described above, the relaxation dynamics of CV in the picosecond region has been studied.[13,14,23,26,27] However, no study has paid attention to the temporal rise with photobleaching of the absorption spectrum of CV. We have found evidence that the absorption spectrum is inhomogeneous from the early part of the transient photobleaching.

The purposes of this paper were (1) to confirm whether the absorption spectrum of CV is homogeneous or inhomogeneous by the femtosecond hole-burning technique and (2) to propose a model that explains both our findings and the previous data that was followed by the mutually conflicting conclusions. This model is equivalent to a novel class of isomers, which should be called “solvation isomers” in solution.

Experimental Section

We used several alcoholic solutions of CV (methanol, ethanol, *n*-propenol, *n*-butanol) as samples. Crystal violet (chloride) purchased from Nakalai-Tesque (Kyoto, Japan) was GR grade and was used without further purification. We confirmed that there was only one spot on thin layer chromatography. The solvents were spectrosol grade supplied by Dojin (Tokyo, Japan). The sample concentration was 5×10^{-4} M. No spectral change was observed in absorption for methanol solutions of CV over the concentration range from 10^{-3} to 10^{-5} M. This shows no aggregation of CV in the solvents used. The samples were circulated through a quartz cell (0.5 mm thickness) to avoid persistent bleaching.

A femtosecond dye laser system and a femtosecond pump-probe spectrometer were described elsewhere.[28] Thus, we provide only the essential details here. Light pulses generated from a colliding pulse mode-locking dye laser (620 nm, 50 fs, 100 MHz) were amplified with a four-stage dye amplifier (620 nm, 800 μJ/pulse, 120 fs, 10 Hz). The amplified light pulses focused on D_2O in a quartz cell (1 cm optical length) result in white light continuum by self-phase modulation, and 4% of the white light continuum was used as probe and reference pulses. The rest passed through an interference filter (5 or 10 nm full width at half maximum). The wavelength-selected pulses amplified with a two-stage dye amplifier were used as pump pulses. The energy of the pump pulse was about 100 μJ/pulse. The diameter of the pump pulse on the sample was about 2 mm. Polarization of the pump pulses and the probe pulses was parallel (p-polarization). The pump wavelengths were tunable from 548 to 620 nm. The pump wavelengths used here were 548, 558, 583, and 598 nm. The shape of transient ΔOD spectra were identical with that when the pump intensity was decreased to 1/10. The transient ΔOD spectra were corrected for the group delay of the probe pulses.

We measured the steady state absorption spectrum of CV in ethanol from 295 to 30 K. The reason why ethanol was used instead of methanol as a solvent is that ethanol is hard to poly-crystallize compared to methanol. The concentration of the sample used was 1.0×10^{-5} M. The absorption spectra were corrected for the volume contraction ratio of ethanol. The light source was a tungsten lamp. The detection system was the same as that of the pump-probe measurement. The cryostat we used was a Cryodriver 3.0 (Edwards High Vacuum International, Crawley, England). The experimental temperatures were 295, 200, 125, 100, 80, 58, and 30 K. The accuracy of the temperatures was ±0.5 K.

We also studied the effects of a solvent molecule on the molecular structure of CV by molecular orbital calculations. The solvent molecule was methanol. The calculation method used was MNDO-PM3 (Modi-

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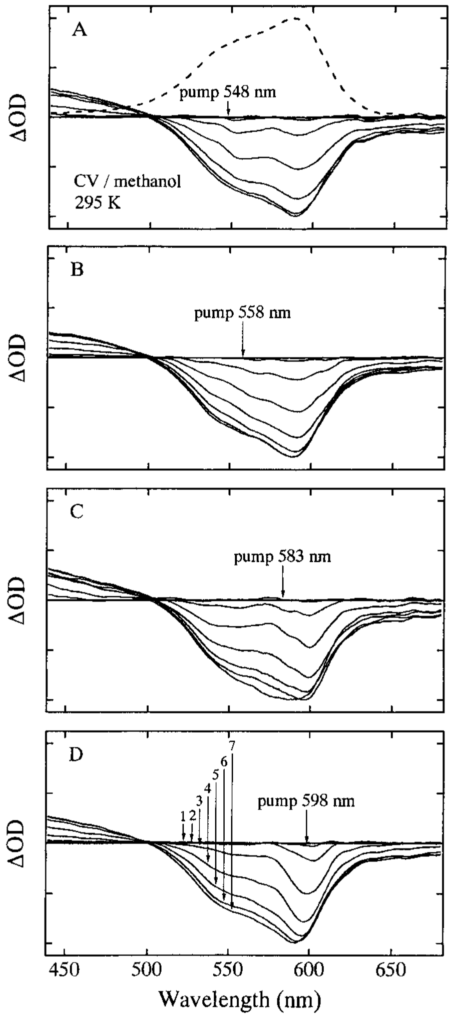

Figure 1. The transient differential absorption spectra (ΔOD) of CV in methanol at 295 K. The probe delay is from −600 (1) to 600 fs (7) at an interval of 200 fs. The bleaching maxima of (A), (B), (C), and (D) in optical density are −1.48, −1.52, −1.01, and −1.23, respectively. The absorption spectrum of CV is shown in part A with a broken line.

fied Neglect of Diatomic Overlap, Parametric Method 3)[29] with the program MOPAC Version 6. At first we calculated the structure and the total energy of a free CV. Following that, we calculated the equilibrium location of a methanol molecule, the structure of CV, plus the total energy of CV and a methanol molecule, when the methanol molecule was brought close to CV. Transition energies of CV were calculated using CNDO/S-CI (Complete Negelect of Differential Overlap/Spectroscopic-included Configuration Interaction).[30] A hundred lowest energy one-electron-excited configurations were taken into account for the CI calculations. A new γ ($\gamma = e^2/(R_{rs} + ka_{rs})$)[31] was used for the two-centered electron repulsion integral. The k value that reflected the experimental data of the absorption bands was 2.75. Even when $k = 1$ or ordinary NM-γ was used, final results were not affected essentially except absolute values of absorption wavelength.

Results

In Figure 1 we show a steady state absorption spectrum and transient ΔOD spectra of CV in methanol. The steady state absorption spectrum, shown in the upper part of Figure 1A, has a peak at 590 nm and a shoulder at 550 nm. The steady state absorption spectrum of CV in other normal alcohols was similar to that in methanol. The time range of transient ΔOD shown in Figure 1 was from −600 to 600 fs, corresponding to the temporal rise seen with bleaching.

The transient ΔOD spectra can roughly be divided into three regions: (1) in the shorter wavelength region than the absorption band (≤500 nm), where transient absorption was dominantly observed; (2) within the absorption band (500−620 nm), where bleaching was mainly observed; and (3) in the longer wavelength region than the absorption band (≥620 nm), where stimulated emission gain was dominant. The shape of the bleaching spectrum at 600 fs was almost identical to the absorption spectrum, so that the stimulated emission gain and transient absorption would overlap less on the bleaching spectrum.

For all of the pump wavelengths, a spectral hole at 600 nm and a spectral hole at 550 nm were observed, each of which corresponds to the absorption peak and the shoulder, respectively. The pump light at 548 nm and that at 598 nm resonate with the absorption band at 550 nm and that at 600 nm, respectively. It should be noted that the holes did not shift when pumped at 558 or 583 nm, both of which are out of resonance with the two holes.

Although the location of the holes was independent of the pump wavelengths, the temporal rise of the holes was dependent on the pump wavelengths. When pumped at 548 or 558 nm, the two holes appeared simultaneously (Figures 1A and 1B). When pumped at 598 nm, however, the hole at 550 nm appeared slower than that at 600 nm (Figure 1D). In addition, the hole at 600 nm shifted toward a shorter wavelength with time. We show the time evolution of the bleaching probed at 550 nm and that at 600 nm when pumped at 548 or 598 nm in Figure 2. Specifically, when pumped at 598 nm, the bleaching at 550 nm appeared with a time delay. In Figure 2C, we introduced a delay time for the rise of the bleaching τ_d into the fitting function as $1 - e^{-t/\tau_d}$. The calculated delay time was 500 fs. The origin of the time delay will be discussed in the following section.

Moreover, we measured delayed bleaching at 550 nm pumped at 598 nm in several normal alcohols to investigate the viscosity dependence of the delay time as shown in Figure 3. The delay time observed was practically 500 fs irrespective of the solvent used. In addition, even if the temperature of the sample increased from 283 to 313 K, the delay time was virtually constant.

The absorption spectra of CV in ethanol at several temperatures are shown in Figure 4. The absorption peak was 590 nm. With decreasing temperature, the shoulder at 550 nm was reduced whereas the peak was enhanced at all temperatures. These observations agree with the previously reported data.[22] It should be noted that the shoulder did not disappear completely even at 30 K.

The results of the molecular orbital calculation are summarized in Tables 1−3. From the calculation, a free CV exhibits the D_3 propeller structure. When a methanol molecule is close to a CV, there are two stable methanol locations. One is 3.712 Å above the central carbon, and the other is 4.101 Å above one of the nitrogens. The structure of the CV in both cases remains that of D_3 symmetry (Table 1). The average distance between methanol molecules in the liquid phase was estimated to be 4.0656 Å from the specific gravity assuming the uniform distribution of methanol molecules in the solution. One of the calculated data (4.101 Å) is almost the same as this value (4.0656 Å). However, when a cation is dissolved in a polar solvent, the solvent molecules would highly solvate the cation. It is reasonable to expect that the distance between the CV cation and solvent molecules is shorter than the average methanol-to-methanol distance in pure methanol, which is almost the same

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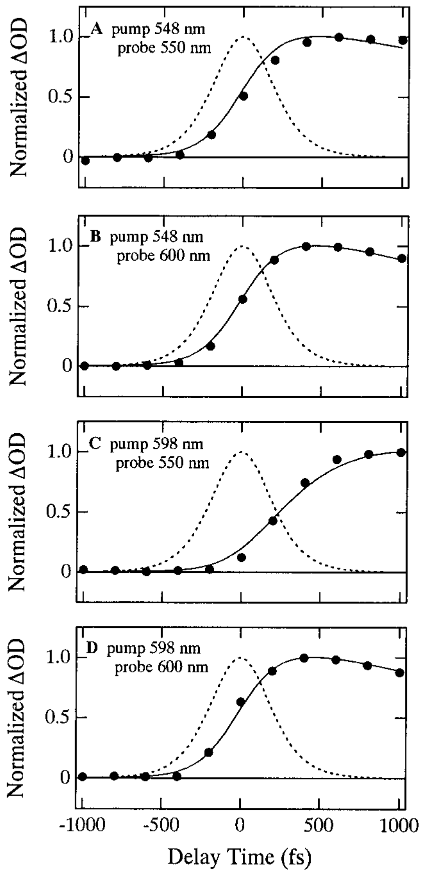

Figure 2. The time evolution of the spectral bleaching of CV in methanol at 295 K. The solid circles are the experimental data. The dotted line represents the response function, the shape of which is assumed to be a sech^2 function. The full width of the half maximum of the response function was about 450 fs. The solid lines are theoretical fits. The bleaching recovery times were 1.7 ps, which agrees with the previously reported data,[14,16] and 6.5 ps. A flattened top feature in the time evolution profile near 1000 fs was observed. This feature was interpreted in terms of a relaxation mechanism with one intermediate state other than the lowest excited singlet state.[14,16]

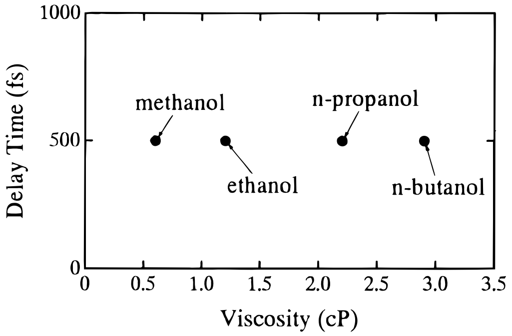

Figure 3. The rise delay time of the bleaching at 550 nm when pumped at 598 nm as a function of solvent viscosity. The viscosity data were reported in ref 15.

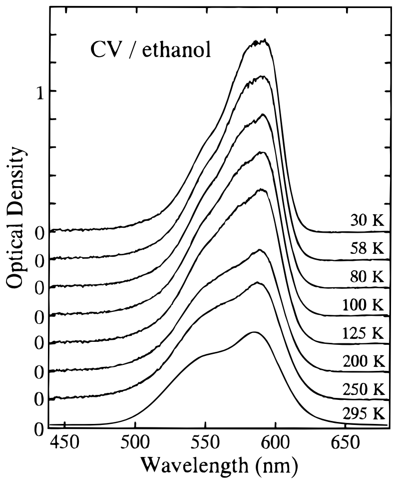

Figure 4. The temperature dependence of the absorption spectrum of CV in ethanol. The enhancement of the total OD with decreasing temperature may be due to the change of the refractive index of ethanol.

Table 1. Calculated Equilibrium Point of a Methanol Molecule on CV and Structure of CV

location of methanol	distance (Å)[a]	symmetry	total energy (eV)[b]
	∞	D_3 (planar)	−4377.72
central carbon	3.712	D_3 (planar)	−4377.81
nitrogen	4.101	D_3 (planar)	−4377.81

[a] The distance from oxgen of methanol to CV. [b] Total energy of CV and a methanol molecule.

Table 2. Calculated Structures of CV When a Methanol Distance Is Fixed at 2.0 Å

location of methanol	distance (Å)[a]	symmetry
central carbon	2.0 (fixed)	C_3 (pyramidal)
nitrogen	2.0 (fixed)	D_3 (planar)

[a] The distance from oxygen of methanol to CV.

Table 3. Calculated Absorption Bands and Oscillator Strength of CV[a]

symmetry	λ_1 (nm)/f	λ_2 (nm)/f
D_3 (planar)	546.2/0.88	534.5/0.70
C_3 (pyramidal)	562.0/0.77	550.1/0.71

[a] λ_1, λ_2 = absorption band. f = oscillator strength.

as the calculated CV-to-methanol equilibrium distance. Moreover, MNDO calculations tend to underestimate the interaction between molecules,[29] so that the calculated value of the methanol equilibrium distance would be longer than the real value. Thus, we calculated total energy and the structure of CV when a methanol molecule was closer to CV than the calculated equilibrium distance. When a methanol molecule is located at 2.0 Å above the central carbon, the structure is stable when the central carbon is 0.157 Å above the original sp^2 plane. In this case, the CV takes the C_3 pyramidal structure, while even if a methanol is located 2.0 Å above one of the nitrogens, the structure of the CV remains that of D_3 symmetry (Table 2). Calculated absorption bands of CV were shown in Table 3. When CV has D_3 symmetry, calculated absorption bands are 546.2 and 534.5 nm from lowest energy. When CV is deformed into C_3 symmetry, we obtained red-shifted bands at 562.0 and 550.1 nm. In the calculations of the absorption bands, no effects of a methanol other than the point-charge perturbation were taken into account.

Discussion

Inhomogeneity of the Absorption Spectrum of CV. We have already concluded that the observed transient ΔOD spectra is free from coherent artifacts and transient Raman gains.[28] Thus, we should consider the temporal rise of the spectral bleaching dependent on the pump and probe wavelengths as an inherent process in CV. If the ground state of CV is homogeneous, that is, the ground state is common for all electronic transition, a decrease in the population in the ground state results in a decrease in all electronic transition intensities. Consequently, the bleaching should rise simultaneously irrespective of the

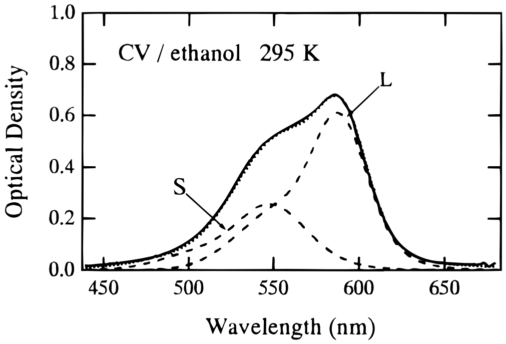

Figure 5. Gaussian deconvolution of the absorption spectrum of CV in ethanol at 295 K. The solid line represents the experimental data. The broken lines are the calculated spectra, each of which is composed of two Gaussians. The dotted line is the sum of the calculated spectra.

pump and probe wavelengths. We did similar pump-probe experiments for nile blue and cresyl violet, both of which are more rigid molecules than CV. There was no pump wavelength dependence in their transient ΔOD spectra. Our observations in Figures 1 and 2 unambiguously prove the inhomogeneity of the ground state of CV in alcohols.

To interpret the observed bleaching dynamics, it is necessary to divide the inhomogeneous absorption spectrum into homogeneous components. The procedure to resolve the spectrum is as follows. The exchange of the intensity ratio between the shoulder and the peak in the absorption spectrum with decreasing temperature is assumed to be due to the modification of the thermal equilibrium between two ground states. We also assume that most of the CV are in the lower ground state at 30 K. On the other hand, the S_1 state would be 2-fold degenerated according to the molecular orbital calculations of electronic states.[8,9,12] Furthermore, it was suggested that interaction of a polar solvent molecule or a counteranion with a CV breaks the symmetry of the CV, thus lifting the degeneracy of the S_1 state.[10,12] Hence, the absorption spectrum of CV at 30 K would be composed of two electronic transitions from one ground state to the split two S_1 states. For this reason, we fit two Gaussian curves on the absorption spectrum at 30 K. On the other hand, two isomers, each of which has the S_1 state split into two electronic states, should exist at room temperature. Thus, the absorption spectrum at room temperature should be composed of four Gaussians.

The result of the curve fitting for the absorption spectrum of CV in ethanol at room temperature is shown in Figure 5. The longer wavelength component denoted by L was well represented with two Gaussians whose maximum were 589 and 561 nm, respectively. The shorter wavelength component denoted by S was also composed of two Gaussians whose maximum are 550 and 524 nm, respectively. These two components overlap considerably around 550 nm. The energy difference between the two ground states was estimated to be about 200 cm^{-1} from the Arrhenius plot of the absorption intensity ratio between the two components. This value agrees well with that reported by Lewis and co-workers.[22] According to the energy difference, the population ratio between the two ground states is 9.7×10^{-3} from the Boltzmann factor at 30 K. This shows the adequacy of the assumption that there is little population in the higher energy ground state at 30 K.

The observed bleaching dynamics should be explained with a model that has two ground-state isomers, each of which has two excited states. In Figure 6, we illustrate population dynamics when pumped at 548 or 598 nm. The pump light of 548 nm excites both ground states because the two absorption components overlap around 550 nm. Consequently, the bleaching should be caused all over the absorption spectrum. Similarly, the pump light of 558 nm also excites both isomers. On the other hand, when pumped at 598 nm, only the lower-energy isomer would selectively be excited. Thus, only the longer wavelength component L would bleach and therefore the populations of the two ground state isomers would depart from thermal equilibrium. Note that the bleaching spectrum at 0 fs (marked with 4) in Figure 1D resembles the longer-wavelength component in shape shown in Figure 5. If the potential barrier from the higher energy ground state to the lower energy ground state is comparable to kT at room temperature, the population of the higher-energy isomers can transfer to the lower ground state within a few picoseconds assuming $10^{12}-10^{13}$ s^{-1} as the pre-exponential factor of the rate process. Thus, the ground states of CV would quickly be in thermal equilibrium. The decrease in population of the higher ground state after the population transfer causes bleaching of the shorter wavelength absorption component. The delay time (500 fs) of the rise of the bleaching at 550 nm when pumped at 598 nm is ascribable to the population transfer time based on the above model.

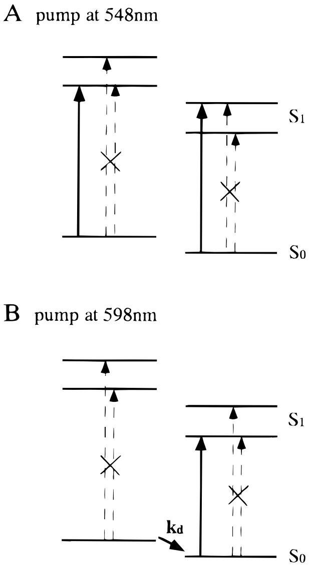

Figure 6. The energy level scheme of CV in alcoholic solutions. The arrows with solid lines represent electronic transitions by pump light or the population transfer from the higher ground state to the lower ground state. The arrows with broken lines are electronic transitions by probe light. × means the *saturation* of the transition. k_d is the isomerization rate, which is calculated at 1/500 $(\text{fs})^{-1}$ by the curve fitting shown in Figure 2.

We determined that the absorption spectrum of CV is inhomogeneous in several normal alcohols used, providing more direct evidence for the existence of ground-state isomers of CV between which we observed the population transfer. To support our interpretation further, we must explain the previously reported data that proposed the homogeneity of the absorption spectrum by means of our model.

A Model for the Ground-State Isomers of CV. The propeller structure of D_3 symmetry has already been identified as a ground-state structure of CV.[5,6,7] As another structure, the distorted propeller type with rotation of the phenyl rings having C_2 symmetry was proposed.[22] Although this structure is easily expected from the molecular structure of CV, there was no evidence for the C_2 structure. Furthermore, several studies[6−7,10,12] argued against this structure.

The origin of the ultrafast non-radiative relaxation of triphenylmethane dyes in the excited state is believed to be due to the torsional motion of the phenyl rings.[32] The bleaching recovery rate of CV depends sensitively on the solvent viscosity.[15] If the structural difference between the two isomers is due to the rotation or the torsion of the phenyl rings, the population transfer between the two isomers, or the change of structure, as well as the non-radiative relaxation rate of the excited state should become slower with increasing solvent viscosity. However, the rise time of the bleaching at 550 nm when pumped at 598 nm is practically constant even when the solvents were changed from methanol to *n*-butanol (Figure 3). The viscosity of butanol is about five times larger than that of methanol. The bleaching recovery time in butanol is about four times longer than that in methanol.[15] The insensitivity of the rise time to the solvent viscosity shows that the structural change between the two isomers is independent of, or at least not so sensitive to, solvent viscosity. In other words, no large structural change like the torsion of the phenyl rings is needed to account for the difference between the two isomers of CV.

In general, it should be considered that a large-amplitude vibrational mode with low frequency ($\leq$1000 cm^{-1}) would be concerned with the isomerization of ground states.[33] Moreover, the isomer of CV should have a structure especially affecting the shape of the absorption spectrum in the visible region. According to an expectation from the molecular structure of CV, the bending mode of the bonds from the central carbon to the three phenyl rings is a possible large-amplitude vibration except for the torsional motion of phenyl rings. The structural change accompanied by this vibration would be less affected by solvent viscosity than the torsional motion of the phenyl rings. Thus, we propose another ground-state structure of CV whereby the three bonds on the central carbon are bent with D_3 symmetry structure. Such a pyramidal structure has C_3 symmetry. The possibility of that CV takes a pyramidal structure was pointed out by Matsuoka and Yamaoka, although they were not able to experimentally identify any ground-state isomers.[34] We will discuss how CV can assume the pyramidal structure.

Because only D_3 symmetry was confirmed by the X-ray diffraction study of crystal samples,[5] the effects of solvent alcohol should be taken into account as the cause of the inhomogeneity of the ground state of CV. It is well-known that liquid alcohol forms a network (monomers and higher structures) by hydrogen bonds.[1,35] A CV solvated with alcohol is surrounded by a network of alcohol molecules. The CV could have two or more solvation forms interacting with alcohol molecules. We suppose that only a monomer alcohol can solvate with CV cation, which was previously discussed by Korppi-Tommola and co-workers.[10] A monomer−dimer equilibrium of alcohols modifies the solvation equilibrium between monomer alcohol and a CV cation. Therefore, we propose a model of the ground state of CV as shown in Figure 7. When an alcohol molecule is solvated with a CV near the central carbon, the central carbon would be pulled toward the alcohol molecule. Thus, the CV may become a pyramidal structure. When the solvation between the central carbon and the alcohol molecule breaks, the CV has the propeller structure. Because the CV solvated with an alcohol should have rather lower energy, the pyramidal structure corresponds to the isomer of lower energy and the propeller structure corresponds to the isomer of higher energy. In both structures, other alcohol molecules should locate near one of the amino groups. The effect of a symmetry-breaking perturbation due to an interaction with alcohol molecules would cause the splitting of the degenerated S_1 state.[12] As a result, the absorption spectrum of each ground state would be composed of two absorption bands.

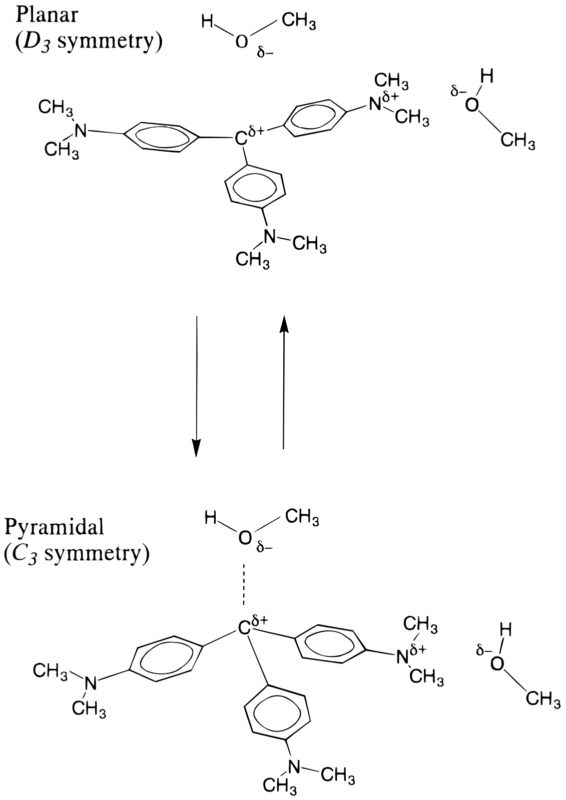

Figure 7. The proposed model of the ground state structures of CV in alcohols discriminated by solvation equilibrium between an alcohol molecule and a CV cation.

The results of our molecular orbital calculations showed that when a methanol molecule is located at 2.0 Å above the central carbon CV has the C_3 pyramidal structure. Moreover, the calculated absorption bands for both D_3 and C_3 symmetry almost agree with the absorption bands for the S component and L component shown in Figure 5, respectively. Although many solvent molecules really surround a CV, this result strongly supports the possibility of CV having the pyramidal structure in alcohols.

Assuming the isomerization of CV is along the coordinate of the bending mode of the bonds from the central carbon to the three phenyl rings, we computed the height of the potential barrier for the structural change from the propeller type to the pyramidal one. According to the resonance Raman studies,[7] the frequency of the bending mode of the bond from the central carbon to the three phenyl rings is 335 cm^{-1}. From this value the frequency of the collision to the potential barrier along this vibration is estimated to be 1.004×10^{13} s^{-1}. Using the isomerization time (500 fs), the potential barrier was computed to be about 320 cm^{-1}. This value is comparable to kT at 295 K (205 cm^{-1}). Using these parameters, the population transfer time at 283 K and that at 313 K were computed to be 508 and 435 fs, respectively. This explains the difficulty in discriminating between the population transfer time at 295 K and that at 283 or 313 K with our femtosecond spectrometer.

The reason why the C_3 symmetry structure has not been confirmed by resonance Raman studies for CV in alcohol is probably as follows. The wavelengths of the Ar$^+$ laser used for excitation in the resonance Raman studies[7,12,21] were at the shorter edge of the absorption band, so that the excitation lights resonate only the D_3 symmetry isomer. In the X-ray diffraction studies[5] the sample was not solution but crystal, so that the C_3

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symmetry isomer could not be confirmed. The molecular orbital calculations[12] only denied the distorted propeller isomer and show a lifting of the degeneracy of the S_1 state. The results rather support our model that involves the split S_1 state. The time-resolved bleaching studies, which only concern the bleaching recovery dynamics, were not able to confirm the presence of isomers. The bleaching recovery times we observed, however, agree with the previous data.[15−18]

Conclusion

The femtosecond pump-probe measurements presented in this work revealed the presence of the ground-state isomers of CV in alcohols and directly observed the isomerization between them. We found that the isomerization of CV takes ∼500 fs. This ultrafast isomerization rate did not depend on the solvent viscosity. This shows that the structural difference between the ground states is not as large as that caused by torsion of the phenyl rings. The molecular orbital calculations support the idea that CV would have not only the D_3 propeller structure but also the C_3 pyramidal structure solvated with alcohol molecules. The analysis of temperature dependence of the steady state spectrum showed that the absorption spectrum of each isomer is composed of two electronic transitions. Concluding our findings, we propose the solvation isomers whereby CV in alcohols has D_3 or C_3 symmetry. Furthermore, our model successfully explains almost all of the previously reported conflicting data on the issue of the homogeneity or inhomogeneity of the ground state of CV. Our study shows the usefulness of the pump and probe technique with tunable pump pulses in confirming the inhomogeneity in molecular structure of flexible organic molecules and observing the isomerization in the ground state even when the potential barrier is comparable to the thermal energy of the room temperature.

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