

# Vibrational Dynamics of the CN Stretching in the Electronically Excited State by UV and Visible-Pump and Infrared-Probe Spectroscopy

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**Abstract:** We have carried out visible-pump infrared-probe measurements on a CN-containing coumarin in a protic solvent. The time-dependent changes of the infrared spectra are measured on a picoseconds time scale, likely because of vibrational cooling.

**OCIS codes:** (300.6530), (320.7120)

## 1. Introduction

Understanding of mechanisms of photochemical reactions in solution is one of the important problems in current chemistry. After photoexcitation to the electronically excited state of a solute molecule in solution, various relaxation processes occur such as vibrational energy relaxation or solvation dynamics. The fate of the excited state is strongly influenced by these relaxation processes, therefore, it is very important to understand these relaxation processes in detail. On the other hand, hydrogen-bonding liquids such as water and alcohol form characteristic network structures, which affect various properties of a solute molecule such as the electronic state and vibrational structures. In this work, we focus on the vibrational dynamics of a solute in the electronically excited state in alcohol solutions. The vibrational mode we investigate is the CN stretching mode of 3-cyano-7-hydroxy-4-methyl coumarin (C183m, Fig. 1). Generally, coumarin dyes change their permanent dipole moments largely by photoexcitation, causing change of the dielectric interaction between the dyes and surrounding solvents. We have carried out UV and vis-pump and infrared (IR)-probe spectroscopic measurements on this mode to examine influence of the solvent interactions on the vibrational dynamics of the solute.

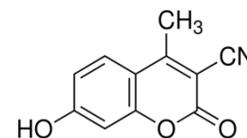


Fig. 1. C183m

## 2. Methodology

The pump pulse was generated by frequency-doubling of the output from a Ti:sapphire regenerative amplifier. The tunable IR pulse was generated by difference frequency mixing of the signal and idler from the optical parametric amplifier. The absorption changes were measured with an MCT (HgCdTe) array detector. The experiments were conducted using 100- $\mu\text{m}$ -thick liquid sample in a non-rotating cell.

## 3. Results and Discussion

Figure 2 shows the absorption spectrum of C183m in methanol in the UV-vis region. In this solvent, C183m exists as either a neutral form or an anionic form. We added a solution of  $\text{CH}_3\text{ONa}$  in methanol to the C183m solution so that a single species, the anion, exists in the sample. Figure 2 illustrates acid-base reactions of C183m in methanol. All the experiments are made for this anionic C183m.

We next measured the temperature dependence of the IR spectra of the CN stretching mode of C183m in methanol (Fig. 3). At room temperature (293K), the spectral lineshape was reproduced well by a single Gaussian function. It was found that the band peak shows a red shift and its shape becomes asymmetric with temperature increase. It is suggested that there are more than one component in this band, probably hydrogen-bonded and non-hydrogen-bonded CN stretching mode, and the free CN stretching band component increases with increasing temperature.

The transient IR spectra of the CN stretching band are shown in Fig. 4. There are a bleach centered at  $2225\text{ cm}^{-1}$  and a transient absorption at  $2180\text{ cm}^{-1}$ , and we fit the transient spectra with a sum of two Gaussian functions to

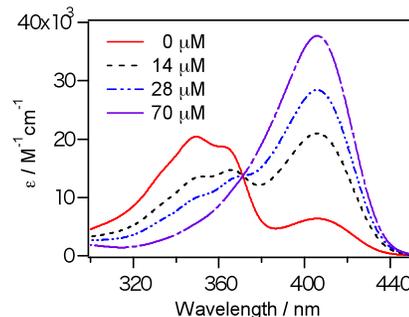


Fig. 2. UV-Vis absorption spectra of C183m in methanol. A solution of  $\text{CH}_3\text{ONa}$  in methanol is added. The concentrations of  $\text{CH}_3\text{ONa}$  are shown in the inset.

determine the peak wavenumber of the transient absorption component. The peak of the CN stretching mode shows a blue shift with delay time, and the time-dependence of this blue shift is reproduced well by a single exponential with a time constant of about 10 ps (Fig. 5). One of the possible mechanisms for this blue shift is vibrational cooling. Vibrational cooling resulted from anharmonic couplings between the high-frequency mode and some low-frequency modes. Just after the photoexcitation the local temperature around the solute is higher than the room temperature because of the dissipation of the excess energy, causing population in the higher vibrational states of the low-frequency modes. This vibrational cooling has been observed in several transient vibrational spectroscopic studies [1, 2]. Another possible mechanism for the blue shift is solvation dynamics [3, 4]. If the photoexcitation accompanies a large change of the dipole moment of the solute, dielectric response from the polar solvent causes the stabilization of the electronic and vibrational states of the solute. Depending on the directions of the permanent dipole moments of the  $S_0$  and  $S_1$  states and the charge distribution in the normal modes, the peak wavenumber shifts either the blue side or red side during the solvation dynamics.

We further carried out UV-pump and IR-probe measurement, where the third harmonics at 266 nm was used as a pump pulse. In this case the excess energy is about  $12450\text{ cm}^{-1}$ , which is much larger than that of the second harmonic excitation ( $1420\text{ cm}^{-1}$ ). The transient absorption spectrum at  $t = 0\text{ ps}$  is further blue-shifted compared to the second harmonic excitation case, and the time evolution of the blue shift can be described by a similar time constant to that of the vis-pump case. These results suggest that the blue shift is caused by vibrational cooling rather than solvation dynamics, since the total shift due to vibrational cooling depends on the excess energy whereas that due to solvation dynamics does not depend on it so much.

#### 4. Conclusion

We observed vibrational dynamics of the CN stretching of the  $S_1$  state C183m in methanol by sub-picosecond UV and visible-pump and IR-probe spectroscopy. The peak of the CN stretching band shows a blue shift in time, which is probably due to vibrational cooling.

#### 5. Reference

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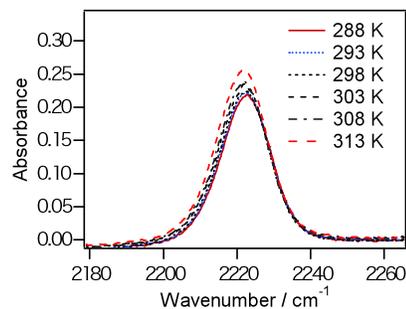


Fig. 3. Temperature-dependent IR spectrum of the CN stretching mode of C183m in methanol.

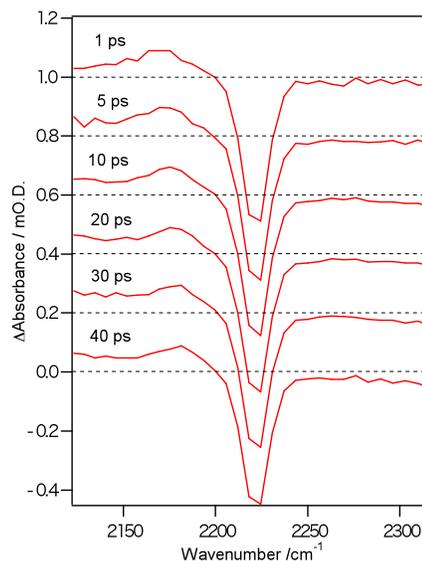


Fig. 4. Transient absorption spectra of C183m in methanol at different delay times.

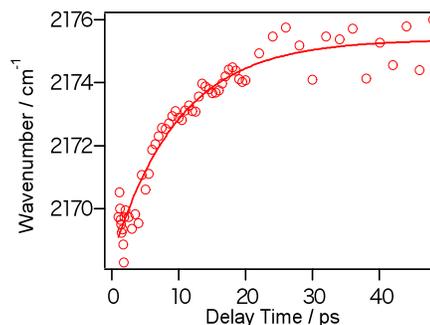


Fig. 5. The time evolution of the peak wavenumber of the CN stretching band of C183m in  $S_1$  measured by Vis-pump and IR-probe spectroscopy.