Integrated and dispersed photon echo studies of nitrile stretching vibration of 4-cyanophenol in methanol

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By means of integrated and dispersed IR photon echo measurement methods, the vibrational dynamics of C-N stretch modes in 4-cyanophenol and 4-cyanophenoxide in methanol is investigated. The vibrational frequency-frequency correlation function (FFCF) is retrieved from the integrated photon echo signals by assuming that the FFCF is described by two exponential functions with about 400 fs and a few picosecond components. The excited state lifetimes of the C-N stretch modes of neutral and anionic 4-cyanophenols are 1.45 and 0.91 ps, respectively, and the overtone anharmonic frequency shifts are 25 and 28 cm⁻¹. At short waiting times, a notable underdamped oscillation, which is attributed to a low-frequency intramolecular vibration coupled to the CN stretch, in the integrated and dispersed vibrational echo as well as transient grating signals was observed. The spectral bandwidths of IR absorption and dispersed vibrational echo spectra of the 4-cyanophenoxide are significantly larger than those of its neutral form, indicating that the strong interaction between phenoxide and methanol causes large frequency fluctuation and rapid population relaxation. The resonance effects in a paradisubstituted aromatic compound would be of interest in understanding the conjugation effects and their influences on chemical reactivity of various aromatic compounds in organic solvents. © 2009 American Institute of Physics. [DOI: 10.1063/1.3140402]

I. INTRODUCTION

Ultrafast vibrational dynamics of peptides and proteins are important phenomena in understanding the biochemical processes and protein functions, such as protein foldingunfolding, DNA-protein interaction, ligand binding mechanisms in enzyme, and so on.¹⁻⁹ However, conventional fluorophores or electron spin resonance probes could potentially perturb the natural processes due to their large sizes, and therefore, infrared probes such as amide I mode have been studied and found to be quite useful in determining secondary and tertiary structures of polypeptides.^{10–19} However, these infrared modes are so abundant in natural biomolecules such as proteins so that it was inevitable to use an isotopelabeling technique to investigate local and site-specific dynamics around an IR probe.²⁰⁻²⁸ In this regard, novel IR probes whose vibrational frequencies are in transparent regions of the IR spectra of biomolecular solutions have been sought by many research groups.²⁹⁻³⁶ Nitrile probe is one of them since it is quite small and its frequency is highly sensitive to local electric field that can fluctuate and change in time when the protein containing the IR probe undergoes conformational transitions.^{10,31,37–40} A few interesting applications of the IR spectroscopy utilizing such a small IR probe were performed by properly introducing the C-N probe into proteins, DNA, and enzyme substrates.^{5,19,37} Also, several theoretical studies on the solvatochromic frequency shifts of such small IR probes, such as nitrile-, thiocyanate-, and azido-derivatized amino acids, have been reported recently.^{29,30,41,42}

In order to understand the ability of the C-N probe to investigate hydrogen bonding dynamics, the vibrational properties and dynamics of C-N stretch mode such as vibrational lifetimes, spectral line-shapes, solvent inhomogeneity, and solute-solvent interaction-induced spectral diffusion should be studied experimentally and theoretically.^{29,30,43–45} Particularly, the solvation dynamics that is directly related to them can be studied by examining the frequency fluctuation correlation function,^{46–48} and the latter can be successfully retrieved from vibrational photon echo experimental data.⁴⁹ In the present work, we chose 4-cyanophenol (4CP) in methanol solutions and studied the C-N stretching vibrations. Depending on pH, it can be present in either neutral or anionic form. At a high pH, the 4-cyanophenoxide (4CX) anion is present in solution, and it has a resonant structure as can be seen below,



Thus, it turns out that the C–N stretch frequency of 4CX is about 15 cm^{-1} smaller than that of 4CP in protic solvents. Such a resonant structure is important in understanding

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chemical reactivities of disubstituted aromatic compounds with electron donating and accepting substituents, and the related phenomena have been called the resonance (or conjugation) effects. Therefore, studying vibrational dynamics of C-N stretch modes in both neutral and anionic 4CPs would provide fundamental information on the dynamics of surrounding solvent molecules as well as substituent conjugation effects. Here, the nitrile group serves as an IR probe reporting not only the solvent motions in the vicinity of the C-N group but also the solute-solvent interaction between parahydroxyl group or phenoxide oxygen atom and solvent molecules. For the present study, we used IR photon echo methods. Now, in Sec. II, the experimental and molecular dynamics (MD) simulation methods will be discussed. The results and discussions are presented in Secs. III and IV. The main results are summarized in Sec. V.

II. EXPERIMENTAL AND MD SIMULATION METHODS

A. Sample preparation

The 4CP solution sample was prepared by dissolving 4CP in methanol, and the 4CX solution sample was by dissolving the 4CP in methanol containing excess MeONa. The sample concentrations of 4CP and 4CX are 0.25 and 0.14 M, respectively. All reagents were purchased from Aldrich and used without further purification. The Fourier transform infrared (FTIR) absorption spectra were obtained at 2 cm⁻¹ resolution with FT/IR-4100 (Jasco). The optical densities of the samples for IR photon echo experiments were adjusted to be ~0.2 at the peak, and the sample cell and path length are CaF₂ and 25 μ m, respectively.

B. Infrared photon echo experiment

The IR pulses in the 5 μ m wavelength region were generated by using Ti:sapphire regenerative amplifier (Spectra Physics Spitfire), IR optical parametric amplifier, and difference frequency mixing. The generated pulses have an energy of $\sim 4 \mu J$, and its pulse duration is about 65 fs with full spectral width at half maximum of 250 cm⁻¹. The center frequency is 5.1 μ m (2230 cm⁻¹). Each IR pulse was divided into three beams $(\mathbf{k}_1, \mathbf{k}_2, \text{ and } \mathbf{k}_3)$ having the same polarization, and they are used to generate the IR echo signal field, which was then sent to a monochromator having a liquid N₂ cooled mercury cadmium telluride detector (IR Associates, Inc.). The focal length of the monochromator is 190 mm, and the groove density of the grating used in the present experiments was 150 lines/mm. The IR photon echo signal was measured at frequency ω_t . The time intervals between the first and second pulses and that between the second and third pulses are denoted as τ and T, respectively. The echo signal field propagating in the direction of $-\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ with \mathbf{k}_1 pulse arriving at the sample before/after \mathbf{k}_2 pulse is referred to as rephasing/nonrephasing signals. Then, the integrated photon echo signal $I(\tau, T, \omega_t)$ at ω_t is measured. This gives a complete set of T-dependent data at each frequency ω_t , and this is known as the dispersed stimulated three pulse photon echo signal.



FIG. 1. Infrared absorption spectra of nitrile stretching vibrations of 4CP and 4CX in methanol solutions. The symbols represent experimental data, and the solid curves are the spectra calculated by using the FFCFs that are retrieved from global fitting analyses of integrated photon echo signals.

C. MD simulation method

In order to make direct comparisons between the photon echo experimental results and the computational results on the C-N stretch frequency-frequency correlation function (FFCF), we carried out quantum mechanical/molecular mechanical (QM/MM) MD simulations, where the solute, either 4CP or 4CX, is treated with the semiempirical PM3 method. The entire QM/MM MD simulations were performed with the AMBER 9 program package. The force-field parameters of 4CP and 4CX for the MD simulations were newly obtained by using the Antechamber module in the AMBER 9.⁵⁰ For the 4CP and 4CX QM/MM MD simulations, 338 and 337 methanol molecules were used, a periodic boundary condition was imposed, and the long-range electrostatic interactions were taken into consideration with the particle-mesh Ewald method.⁵¹ Each composite system was energyminimized with the steepest descent method and the conjugate gradient method. Then, the system is equilibrated at constant pressure of 1 atm and at temperature of 298 K, where the MD simulation time step was 1 fs and the periodic box size was adjusted in a constant N-P-T condition. After an additional constant temperature PM3/MM MD simulation at 298 K for 200 ps in a constant NVT condition, 1 ns trajectory for each case was obtained, and the coordinates were saved for every 10 fs to numerically calculate the FFCF later.

III. RESULTS

A. IR absorption spectra

The IR absorption spectra of C–N stretching vibrations of 4CP in methanol and of 4CX in MeONa/MeOH solution are shown in Fig. 1, where the background absorption by solvent was removed. The absorption bandwidth of 4CP is 13.2 cm^{-1} and that of 4CX is 20.4 cm⁻¹. The extinction coefficients of 4CP and 4CX are 284 and 547 L mol⁻¹ cm⁻¹, respectively. The peak position of C–N stretch band of 4CP is shifted to lower frequency compared with that in water, though the corresponding spectrum in water solution is not shown here. In the case of the water solution, there is a shoulder band in the high frequency region, which is associated with the C–N stretch of 4CP with a methanol molecule



FIG. 2. DVE spectra of nitrile stretching vibrations of 4CP and 4CX in methanol solutions. The symbols represent experimental data, and the solid curves are the spectra calculated by using the FFCFs that are retrieved from global fitting analyses of integrated photon echo signals. The waiting time T is 200 fs in this case.

strongly hydrogen-bonded to the nitrogen atom's lone pair in the nitrile group. Its disappearance in the IR spectrum of 4CP in methanol suggests that the C–N group in 4CP does not make a stable and long-lasting hydrogen bond with methanol molecule. This is also confirmed by QM/MM MD simulations, which suggest that the number of hydrogen-bonded methanol molecules around the C–N group in 4CP and 4CX are 0.27 and 0.71, respectively. The two IR absorption spectra of 4CP and 4CX are well fitted with a single Gaussian function.

Once the FFCF of C–N stretch mode is determined by analyzing the IR photon echo data, the IR absorption spectrum can be calculated by Fourier-transforming the following linear response function:

$$J(t) = e^{-g(t) - i\omega_{10}t - t/2T_1},$$
(1)

where g(t) is the line-broadening function,⁵² ω_{10} is the fundamental transition frequency, and T_1 is the lifetime of the first excited state.

B. Dispersed vibrational echo (DVE) spectra

Even though the incident IR pulse frequencies are adjusted to be close to the C-N fundamental frequency, each pulse has sufficiently broad bandwidth to cover not only the fundamental 0-1 but also the 1-2 transitions. The DVE spectra over the range of ω_t from 2120 to 2300 cm⁻¹ were obtained for a varying T. All those DVE spectra show both the fundamental 0-1 and the 1-2 transition contributions. Figure 2 depicts the DVE spectra of 4CP and 4CX at T=200 fs. The DVE spectra at T > 200 fs are qualitatively similar to those at T=200 fs, except that their intensities decrease in time. At a very short time T (<200 fs), where the incident pulses overlap in time, the T-dependent DVE spectra show complicated behaviors, and they could originate from nonresonant solvent contributions such as solvent combination modes and from low-frequency intramolecular vibrations coupled to the C-N stretch. However, both DVE spectra and integrated photon echo signals at longer time T can be suc-



FIG. 3. Integrated photon echo signals vs the first delay time τ . Here, the waiting time *T* varies from 500 to 2000 fs. Those of 4CP and 4CX are plotted in figures (a) and (b), respectively. The power spectra of integrated photon echo signals (at *T*=0) are shown in (c) and the corresponding τ scan integrated photon echo signals are shown in the inset.

cessfully fitted by using a proper model for the FFCF as will be discussed in the following subsection. From the global nonlinear fitting analyses, we found that the overtone anharmonic frequency shifts of the C–N stretch modes of 4CP and 4CX in methanol are 25 and 28 cm⁻¹, respectively. Note that the 3 cm⁻¹ difference in the overtone anharmonic frequency shift of 4CX in comparison to that of 4CP is mainly caused by the resonance effect mentioned in the introduction.

C. Integrated photon echo

In Fig. 3, the integrated photon echo signals of 4CP and 4CX when the waiting time *T* varies from 500 to 2000 fs are



FIG. 4. Transient grating signals of 4CP and 4CX.

plotted. There appear quantum beatings at a short time T though they are not shown here. Except for such a short-time oscillatory component, the integrated photon echo data were successfully fitted by using frequency correlation functions for the C–N modes consisting of two exponentially decaying functions and a nearly impulsive contribution from solvent modes, i.e.,

$$\langle \delta \omega(t) \delta \omega(0) \rangle = A_1^2 \exp(-t/t_1) + A_2^2 \exp(-t/t_2) + b \,\delta(t).$$
(2)

It is assumed that the 1–2 transition and the 0–1 transition frequency fluctuations are strictly correlated with each other and that the same parameters except for T_1 can be used for calculating the line-broadening functions for both cases.⁵³ The T_1 relaxation times of the C–N vibrations in 4CP and 4CX were estimated by carrying out transient grating experiments, i.e., measurements of $I(\tau=0, \omega_t; T)$ signals, and found to be 1.45 and 0.91 ps, respectively (see Fig. 4). Despite that the transient grating measurements have been used to estimate the excited state lifetimes, the more accurate data can be obtained by carrying out spectrally resolved pump-probe experiments for longer time scale.⁵⁴

The nonlinear response function components associated with the rephasing and nonrephasing photon echo were discussed before, and they are 55,56

$$\begin{aligned} R_{1}^{(R)} &= P(1,0|1,T)e^{-i\omega_{10}(t-\tau)}e^{G_{R}(\tau,T,t)}, \\ R_{2}^{(R)} &= P(0,0|0,T)e^{-i\omega_{10}(t-\tau)}e^{G_{R}(\tau,T,t)}, \\ R_{3}^{(R)} &= -2P(1,0|1,T)e^{-t/T_{1}}e^{-i((\omega_{10}-\Delta)t-\omega_{10}\tau)}e^{G_{R}(\tau,T,t)}, \\ R_{1}^{(\mathrm{NR})} &= P(1,0|1,T)e^{-i\omega_{10}(t+\tau)}e^{G_{\mathrm{NR}}(\tau,T,t)}, \\ R_{2}^{(\mathrm{NR})} &= P(0,0|0,T)e^{-i\omega_{10}(t+\tau)}e^{G_{\mathrm{NR}}(\tau,T,t)}, \end{aligned}$$
(3)

$$R_3^{(\mathrm{NR})} = -2P(1,0|1,T)e^{-t/T_1}e^{-i((\omega_{10}-\Delta)t+\omega_{10}\tau)}e^{G_{\mathrm{NR}}(\tau,T,t)}$$

where the line-shape functions $G(\tau, T, t)$ are defined as

$$G_{R}(\tau,T,t) = -g(\tau) + g(T) - g(t) - g(T + \tau) - g(t + T) + g(\tau + T + t),$$

$$G_{NR}(\tau,T,t) = -g(\tau) - g(T) - g(t) + g(T + \tau) + g(t + T)$$

$$-g(\tau + T + t).$$
(4)

Here, the fundamental transition frequency is denoted as ω_{10} ; the diagonal anharmonicity is as Δ . The relevant transition dipoles, not explicitly shown here but included in *P* functions in Eq. (3), are assumed to be constant obeying μ_{21}^2 $= 2\mu_{10}^2$ for 4CP and $\mu_{21}^2 = 2.2\mu_{10}^2$ for 4CX. The factor of 2.2 in the latter was obtained by fitting. Its deviation from two indicates anharmonicity of the CN stretch in 4CX system. Also, note that the vibrational population relaxation process is taken into account by multiplying the following exponentially decaying function, $\exp(-(\tau+t)/2T_1)$, to the nonlinear response function. The $R_3^{(R)}$ and $R_3^{(NR)}$ terms that are associated with the excited state absorption contributions contain an additional e^{-t/T_1} term to account for the faster relaxation of the *overtone* state.

Now, for the series of integrated photon echo signals of 4CP at T=500, 750, 1000, and 2000 fs in Fig. 3(a), we carried out a global fitting analysis and found that the best set of fitting parameters is $A_1=0.46 \text{ ps}^{-1}$, $A_2=0.79 \text{ ps}^{-1}$, $t_1=0.38 \text{ ps}$, and $t_2=6.0 \text{ ps}$. For 4CX, they are $A_1=0.58 \text{ ps}^{-1}$, $A_2=1.3 \text{ ps}^{-1}$, $t_1=0.41 \text{ ps}$, and $t_2=6.5 \text{ ps}$. Using these parameters and ignoring the third impulsive term in Eq. (2), which originates from solvent, we could calculate the IR absorption spectra and the DVE spectra (see solid lines in Figs. 1 and 2, respectively).

IV. DISCUSSION

A. Vibrational dynamics of C–N stretch mode

The FFCF was assumed to be described as a sum of two exponential functions, and each component could represent the corresponding dynamical contributions in different time scales. The faster component of the FFCF retrieved from the 4CP photon echo signals decays in 0.38 ps and its preexponential factor A_1 is 0.46 ps⁻¹. This corresponds to a Gaussian width of 5.8 cm⁻¹. From these values, one can find that the fast component is in a fast modulation (motional narrowing) limit since $A_1t_1 < 1$. In the case of the 4CX, the decay constant t_1 of the faster component was estimated to be 0.41 ps, and its pre-exponential factor is 0.58 ps^{-1} , where the latter gives a Gaussian width of 7.2 cm^{-1} . The fast dynamics of C-N vibrations in 4CP and 4CX is related to the hydrogen bonding dynamics around a nitrile group and also consistent with the recent 2D IR experiments by Ghosh *et al.*⁴⁴

The slower component in the FFCF for 4CP is similar to that for 4CX, but that of 4CP is a bit more rapidly decaying. The decay constant t_2 in the case of 4CP is about 6 ps, whereas that of 4CX is 6.5 ps. The corresponding amplitudes (A_2) of 4CP and 4CX are approximately twice larger than those (A_1) of the fast components. The decay constants t_2 in these two cases are however comparatively larger than the typical spectral diffusion time of solvent methanol, where the

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latter was found to be about 2 ps in the related 2D IR photon echo experiment on benzonitrile by Ghosh et al.⁴⁴ Suppose that the FFCF of C-N stretch mode, even in our cases, is strictly determined by the solvent dynamics around the C-N probe. Then, the same 2 ps component should be present in our cases too. However, we instead observed approximately 6 ps dynamics in the cases of 4CP and 4CX in methanol. The difference between our molecular systems and previous ones (benzonitrile and cinnamonitrile) is the presence of O-H group at the paraposition with respect to the C-N group. Thus, the hydrogen-bonding dynamics around the parahydroxyl group or phenoxide oxygen atom seems to be important and strongly affects the fluctuating frequency of the C-N stretch mode via conjugated phenyl ring bridge. If the O-H group is ionized, i.e., 4CX, the electrostatic interaction between phenoxide anion and methanol would become strong, which in turn would make the local solvation structure is well defined and relatively rigid. This picture is again consistent with the presence of electronic resonance structures of 4CX. In summary, the solute-solvent interaction between the negatively charged oxygen atom in the 4CX and surrounding methanol molecules influences the C-N stretch frequency fluctuation through the conjugated phenyl ring bridge. This evidently shows a resonance effect present in this paradisubstituted aromatic compound.

B. Underdamped oscillations in the photon echo signals

In the integrated photon echo and transient grating signals, we found underdamped oscillating components. These can be caused by interferences between different nonlinear optical transition pathways that have different coherence frequencies.^{57–61} Such an oscillating behavior could be related to combination vibrations of the C-N stretch mode with low-frequency intramolecular modes or intermolecular hydrogen bond stretching vibrations. The power spectrum of the integrated photon echo signal (at T=0) of 4CP shows two peaks at ~100 and ~145 cm⁻¹ [see the inset of Fig. 3(c) for the τ -dependent integrated photon echo signals at T=0]. To elucidate the nature of these oscillatory components, the geometry optimizations and vibrational analyses of 4CP with B3LYP method at 6-311++G(3df, 2pd) level⁶² were performed, and the results suggest that the out-of-plane bending motion of the entire C–N group is a relatively low-frequency mode and its frequency is 101 cm⁻¹. In the case of 4CX (anion), we found only one low-frequency peak in the power spectrum of the integrated photon echo signal, and its frequency is about 125 cm⁻¹. The same B3LYP calculation shows that the out-of-plane bending of the C-N group has frequency of 92 cm⁻¹. However, it is not yet clear whether that is the only mode strongly coupled to the C-N vibrational transition. Currently, detailed studies on these quantum beats in the integrated photon echo signals are performed by using different solvents to elucidate the origin and to find out which low-frequency modes are anharmonically coupled to the C-N stretch.

C. Solvatochromism and FFCF

Although one can generate a QM/MM MD trajectory for a given composite solution,⁶³ it is not possible to directly calculate the vibrational FFCF from the trajectory itself. Thus, it was necessary to develop a theoretical model for a proper description of solvation-induced effects on vibrational spectra. It is the interaction between solute and solvent molecules that is responsible for numerous spectroscopic phenomena. Particularly, vibrational frequency shift induced by highly inhomogeneous local electric field produced by solvent molecules is known as the vibrational solvatochromism. Furthermore, the frequency fluctuation and its autocorrelation function are an essential ingredient for numerical simulations of one-dimensional and two-dimensional vibrational spectra. A general framework to describe the vibrational solvatochromism has been discussed recently,64 where the charge distribution of the solute interacting with solvent electric field is divided into multiple fragments. According to this theory, the frequency shift of a *j*th mode, which is denoted as $\Delta \tilde{\nu}_i(\phi)$, is given by the following expansion form in terms of distributed multipole moments of solute charge distribution:

$$\Delta \tilde{\nu}_{j}(\phi) = \sum_{x} l_{xj} \phi(\mathbf{R}_{x}) + \sum_{x} \mathbf{L}_{xj} \cdot \mathbf{E}(\mathbf{R}_{x}) + \sum_{x} \Lambda_{xj} : \nabla \mathbf{E}(\mathbf{R}_{x}) + \dots, \qquad (5)$$

where \mathbf{R}_x is the position of interaction site *x* of the solute charge distribution and ϕ and **E** represent the local electric potential and field, respectively, at the fragment site *x* due to the environment. Essentially, these distributed sites collectively act like an antenna sensing the local electric field around a solute.⁶⁵ The three coefficients in Eq. (5) are

$$l_{xj} = (\hat{F}_j q_x(\mathbf{Q}))_{\mathbf{Q}_0}, \quad \mathbf{L}_{xj} = -(\hat{F}_j \mathbf{p}_x(\mathbf{Q}))_{\mathbf{Q}_0},$$

and

$$\Lambda_{xj} = -\frac{1}{6} (\hat{F}_j \Theta_x(\mathbf{Q}))_{\mathbf{Q}_0}$$
(6)

with

$$\hat{F}_{j} \equiv \frac{1}{2M_{j}\omega_{j}} \left\{ \frac{\partial^{2}}{\partial Q_{j}^{2}} - \sum_{i} \frac{g_{ijj}}{M_{i}\omega_{i}^{2}} \frac{\partial}{\partial Q_{i}} \right\}.$$
(7)

Here, M_j , ω_j and Q_j are, respectively, the reduced mass, frequency, and coordinate of the *j*th normal mode. g_{ijj} is the cubic anharmonic coefficient. q_x , \mathbf{p}_x , and Θ_x are, respectively, the partial charge, dipole moment, and quadrupole moment of the charge distribution fragment *x*. The partial derivatives are evaluated at the equilibrium structure \mathbf{Q}_0 of an isolated molecule. The first term in Eq. (7) describes the nonlinear coordinate dependencies of distributed multipoles, whereas the second does the mechanical anharmonicity contributions to the vibrational solvatochromism.

Using this model and ignoring the distributed dipole, quadrupole, and higher multipole contributions, we found that the C–N frequency shift of nitrile-derivatized compounds in methanol solutions can be calculated as²⁹



FIG. 5. (Color online) FFCFs of the nitrile stretching vibrations. The FFCFs (solid lines) of 4CP and 4CX obtained from the QM/MM MD simulations and theoretical model in Eq. (8) are plotted in (a). The FFCFs (dashed lines) retrieved from the global fitting analyses of integrated photon echo signals are shown in the same figure (a) for the sake of comparison. The numerically simulated IR absorption spectra of nitrile stretching vibrations, which were obtained by using the FFCFs from the QM/MM MD simulations, are compared with the experimental data (open squares and circles).

$$\delta \widetilde{\nu} = \sum_{a=1}^{n} l_a \phi_a^{\text{MeOH}}.$$
(8)

The dimensions of $\delta \tilde{\nu}$, ϕ_a^{MeOH} , and l_a are cm⁻¹, cm⁻¹/e, and e, respectively. The fitted l_a parameters for N, C(CN), C(Me), N-atom's lone pair orbital site, N-atom's π -orbital site, and C-atom's π -orbital site, which were obtained from a multivariate least square fitting analysis of the MeCN/water clusters, were found to be 0.00521e, 0.0801e, -0.00182e, 0.00157e, -0.00167e, and -0.00896e, respectively for MeCN (see the inset of Fig. 5).²⁹ It is now assumed that the frequency shifts of the C–N stretching vibrations of 4CP and 4CX can be described with the same set of l_a parameters. In Eq. (8), the electrostatic potential ϕ_a at the *a* site is calculated as

$$\phi_a = \frac{1}{4\pi\varepsilon_0} \sum_m \sum_j \frac{C_{j(m)}^{\text{MeOH}}}{r_{aj(m)}},\tag{9}$$

where $C_{j(m)}^{\text{MeOH}}$ is the AMBER partial charge of the *j*th site of the *m*th methanol molecule and $r_{aj(m)}$ is the distance between the site *a* of 4CP or 4CX and the *j*th site of the *m*th methanol molecule. From the 1 ns PM3/MM MD trajectories for both composite systems, the ensemble averaged C–N stretch fre-

TABLE I. Amplitudes (A_j) and decay constants (t_j) of the two exponentially decaying functions used to model the FFCFs [see Eq. (2)].

	$A_1 (ps^{-1})$	t_1 (ps)	$A_2 (ps^{-1})$	<i>t</i> ₂ (ps)	
Experiments					
4CP (neutral)	0.46	0.38	0.79	6.0	
4CX (anionic)	0.58	0.41	1.3	6.5	
QM/MM MD simulations					
4CP (neutral)	0.82	0.21	0.54	3.8	
4CX (anionic)	0.92	0.24	0.67	5.1	

quency shifts are calculated by using the following expression, i.e., $\langle \delta \tilde{\nu} \rangle = \langle \tilde{\nu} \rangle - \tilde{\nu}_0 = \Sigma l_a \langle \phi_a \rangle$. From the C–N frequency trajectory $\delta \tilde{\nu}(t)$ obtained for 4CP or 4CX, the FFCF, M(t), defined as $M(t) = \langle \delta \omega(t) \delta \omega(0) \rangle$ with $\delta \omega(t) = 2 \pi c \{ \delta \tilde{\nu}(t) - \langle \delta \tilde{\nu} \rangle \}$, was calculated. The decaying patterns of FFCFs are not simply exponential, indicating that there are multiple decay components reflecting different solvent dynamics around the IR probe C–N group.

D. Comparisons between experimental and simulated FFCFs

In order to directly compare the FFCFs of C-N stretch modes in 4CP and 4CX retrieved from photon echo signals with those from QM/MM MD trajectories, we deliberately fitted to the numerically simulated FFCFs with two exponential functions [see Fig. 5(a)]. In Table I, the corresponding parameters obtained are presented. Experimentally estimated t_1 value of 4CP, which is 0.38 ps, is smaller than that of 4CX, which is 0.41 ps. Despite that the t_1 values from MD simulations are a bit smaller than the experimentally determined t_1 values, the simulations agree with the experimental one in a sense that the t_1 value for 4CX is slightly larger than that of 4CP. This tendency can be understood by comparing the hydrogen bond strength between 4CP and methanol with that between 4CX and methanol. For the anionic 4CX, the negative charge is delocalized over the molecule, and the partial charge of nitrile N-atom increases. The average atomic partial charges of 4CP and 4CX are summarized in Table II, and the atom types are shown in Fig. 6. The partial charge of the nitrogen atom in the C-N group increases by a factor of two when the 4CP is ionized to become the 4CX. Consequently, the hydrogen bond between C-N and methanol becomes strong in this case, and the solvation shell could be a bit more rigid, which can make the fast component associated with the short-time hydrogen bond dynamics relatively slow—note that t_1 and t_2 values for 4CX are slightly larger than those for 4CP in both experiments and QM/MM MD simulations. This can be confirmed by examining the average numbers of hydrogen-bonded (<2.5 Å) methanol molecules to the nitrile. We found that they are 0.27 and 0.71 for 4CP and 4CX, respectively. In Fig. 7(a), the angle (\angle CN---H) distributions of H-bonded methanol molecules around 4CP and 4CX are plotted. The peak positions are at around 160°, which indicate that the hydrogen bond is formed between methanol H-atom and nitrile's nonbonded electron pair orbital. This type of hydrogen bond was called σ -type, which

TABLE II. Average atomic partial charges (in electron's charge) of 4CP and 4CX in methanol solutions, which are obtained from the QM/MM MD trajectories. The corresponding atom types are shown in Fig. 6.

	Charge			
Atom type	4CP	4CX		
CA	-0.177	-0.328		
C5	-0.025	0.019		
H3	0.119	0.089		
HA	0.131	0.110		
C	0.132	0.362		
OH (O)	-0.243	-0.691		
НО	0.234			
C1	-0.176	-0.328		
H1	0.131	0.109		
C3	-0.026	0.019		
H2	0.119	0.089		
C4	-0.045	-0.220		
C2	-0.046	0.023		
N1	-0.128	-0.252		

induces a blueshift of the CN stretch frequency.²⁹ In addition, we examined the hydrogen-bonded methanol molecules around the OH group or O⁻ anion in 4CP and 4CX. The average numbers of H-bonding solvent molecules are 0.21 and 2.80, respectively. Furthermore, the calculated distributions show that the peak angles (\angle CO(H)---H) are close to 120°, indicating that a methanol molecule forms a hydrogen bond with the phenol (or phenoxide) oxygen atom's lone pair.

Next, the overall amplitudes $(A_1 + A_2)$ of the experimentally retrieved FFCFs for 4CP and 4CX, which are 1.25 and 1.88 ps^{-1} , respectively, are compared with the simulation results, which are 1.36 and 1.59 ps⁻¹, respectively. The agreements are acceptable. Again, the fact that the fluctuation amplitude of CN frequency for 4CX is larger than that for 4CP is related to the intermolecular hydrogen-bonding interactions at the two sites, CN and OH (or O^{-}). In Fig. 5(b), the nitrile stretch bands calculated with the QM/MM MD FFCFs for 4CP and 4CX are directly compared with the experimental data (open squares and circles in this figure)-note that the peak positions of the simulated IR spectra are shifted to match to the experimental ones for the sake of comparison. Overall, the QM/MM MD simulation with the electrostatic potential calculation model in Eq. (8) works reasonably well, and the general trends are consistent with the experimental ones. Despite the qualitative agreements between theory and



FIG. 6. (Color online) Atom types of 4CP and 4CX. The atomic partial charges that are obtained from the QM/MM MD simulation trajectories are given in Table II.



FIG. 7. (a) Distributions of the nearest (<2.5 Å) methanol H-atom around the CN nitrogen atom with respect to the H-bond angle (\angle CN---H). (b) Angle (\angle CO(H)---H) distributions of the hydrogen-bonded methanol molecules around OH group or O⁻ atom in 4CP and 4CX, respectively.

experiment, there are a few issues that need to be improved in the future. First of all, the QM/MM MD simulation utilizing semiempirical QM method may not be accurate enough to quantitatively describe these vibrational frequency fluctuation amplitudes. Second, the vibrational solvatochromic parameters $\{l_a\}$ used here were obtained by considering acetonitrile-water clusters, not 4CP (or 4CX) methanol clusters. Thus, these parameters are not optimized for the present systems. Third, the force-field parameters for 4CP and 4CX, which were determined by using Antechamber module in AMBER 9 program package, should be improved.

V. SUMMARY

In order to study vibrational dynamics of C–N stretch modes in both neutral and anionic 4CP in methanol, the integrated and dispersed IR photon echo experiments were carried out. Depending on the ionic state of the hydroxyl group substituted at the paraposition in this aromatic compound, the vibrational relaxation rates and lifetimes of the C–N stretch mode changes. This is one of the resonance effects on vibrational properties found in paradisubstituted aromatic compounds in organic solvents. As the molecule becomes anionic, the lifetime of the C–N stretch excited state becomes short. The slow component in the FFCF of the C–N stretching vibration of 4CX becomes important, and it reflects the hydrogen-bonding interaction dynamics of the negatively charged oxygen atom to which surrounding methanol molecules form strong H-bonds.

The experimentally retrieved FFCFs of 4CP and 4CX were directly compared with numerically simulated ones for those systems, which were obtained by combining a recent

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theoretical model for vibrational solvatochromism of nitrile stretching vibration with QM/MM MD simulations. The increased H-bond strengths between the C-N group and para-O⁻ atom in the 4CX and methanol molecules, in comparison to that between neutral 4CP and methanol, could be responsible for the short lifetime, large amplitudes of FFCF, and broad spectral bandwidth of the C-N stretching vibration of 4CX. The agreements between QM/MM MD simulation results and experimental findings indicate that the vibrational dynamics of such a small IR probe can be successfully described by using the theoretical model discussed here and before. In addition, it was shown that the C-N probe can provide information on the hydrogen-bonding dynamics of parasubstituted hydroxyl group. In order to provide detailed descriptions on the quantum beats observed in the integrated photon echo and transient grating signals, we are currently carrying out a series of experiments for the same molecular systems in a variety of different solvents.

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