

ARTICLE

Raman Spectra of 1,2,4-Triazole-3-carboxylate Solution

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Raman spectra of 1,2,4-triazole-3-carboxylate (TC^- anion) and its ring-deprotonated derivative (dpTC^{2-} dianion) in aqueous solutions were measured respectively. The density functional theory (DFT) calculations were performed using MN15 functional and PCM solvent model to investigate their structures, as well as the vibrational frequencies and Raman intensities. With the aid of the calculated spectra, all the observed Raman bands of dpTC^{2-} were clearly assigned, when taking into account the deuteration shifts. Moreover, various protonic tautomers of TC^- anion were compared in the present theoretical calculations, and 2H-tautomer was found more stable. The experimental Raman spectrum of TC^- solution was roughly consistent with the calculated spectrum of the monomeric 2H-tautomer of TC^- , but some splits existed for a few bands when compared to the calculated spectra, which might be contributed by the hydrogen-bonding dimers of TC^- .

Key words: 1,2,4-Triazole-3-carboxylate, Raman spectra, Density functional theory, Deprotonation

I. INTRODUCTION

Triazoles have attracted much attention because of their important applications in various areas [1–13]. In bio-medical engineering, the triazole-ring is always utilized as the fundamental structure of many clinical drugs, *e.g.*, ribavirin, fluconazole, anastrozole, es-tazolam, and so on. Moreover, the triazole derivatives are extensively used as the corrosion inhibitors for metal/alloy protection [7–10]. In recent years, the prosperity of click-chemistry also makes the triazole derivatives be active subjects in synthetic chemistry [11–13].

Surface-enhanced Raman scattering (SERS) of triazole derivatives has been intensively studied to reveal the anti-corrosion mechanism of these compounds [14–25]. Various structural and bonding information on surfaces, such as adsorption orientation [14, 22, 24], self-assembled monolayer formation [22], competitive adsorption [20], and the influence of electrode potentials [20–22, 24, 25], were investigated. Through comparing the Raman spectra of these compounds in solutions and the SERS spectra, the assignments of the observed SERS bands were obtained, and then the interactions between the adsorbents and substrates were discussed [14–18, 24, 25].

It is well-known that Raman spectra in solutions are useful in disclosing the solute-solute/solute-solvent in-

termolecular interaction and the influences of solvent on quantum state energies of solute [25–29]. Wrzosek *et al.* performed Raman spectroscopy and DFT calculations on 3-sulfur derivatives of 1,2,4-triazole (TS) in solid state and in aqueous solutions at different pH values [25]. It was found that the solid sample consisted of the 3,3'-disulfide of the triazole dimer, while the disulfide bridge was broken in solutions. Interestingly, in solutions at various pH values, TS can exist in different molecular structures, *e.g.*, thiolate anions, thiol-thione tautomers, and a mixture of neutral thiol-thione tautomers and TS-thiol ring cation [25]. Meng *et al.* utilized vibrational spectroscopy and DFT calculation to study the environment-dependent conformation of 3-amino-1,2,4-triazole [26]. The dimers dominated in solid, but the monomers were the major component in polar solvents. The observed differences in vibrational frequency and intensity of Raman bands were mainly attributed to the perturbation of the intermolecular hydrogen bonding between amino-triazole and the protonic solvents.

Carboxylic substitution is a common strategy to modulate the electronic properties of organic compounds. Carboxylic substituted triazoles have been applied in biomedicine [3–6] and corrosion inhibition [10]. The plentiful nitrogen and oxygen atoms in triazole carboxylates provide versatile ways to combine metal atoms, making them be the useful ligands for constructing the coordinate co-polymers or the metal organic framework materials with novel structures [29–35]. Yurdakul and Tanribuyurdu performed the DFT calculations of the molecular geometry, relative energy,

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and vibrational properties of several tautomers of 1,2,4-triazole-3-carboxylic acid (TCA), and the conclusions agreed with the FT-IR and Raman spectra of TCA measured in solid form [36]. As far as we know, the Raman spectra of triazole carboxylates in solutions have not been investigated yet, although their structures and properties in solutions are of great significance to understand the action mechanisms of the relative drugs and to optimize the hydrothermal syntheses conditions of the relative organometallic or coordination materials. Herein, we have measured the Raman spectra of 1,2,4-triazole-3-carboxylate and its deuterated derivatives in neutral and alkaline conditions. With the aid of the DFT calculations, the vibrational bands have been assigned, and their contributors have been discussed. All the conclusions can provide the detailed information of intermolecular hydrogen bonding.

II. EXPERIMENTS

TCA (>97%) was purchased from Sigma-Aldrich and was used without further purification. Similar to other aromatic organic acids, the solubility of TCA in water was quite small (about 0.007 mol/L at room temperature). Thus, TCA was dissolved in two different NaOH aqueous solutions in the present experiments. In the first solution, 56.4 mg (0.0005 mol) TCA was completely dissolved into 1.0 mL of 0.5 mol/L NaOH aqueous solutions. The final pH value was about 7.0, indicating the occurrence of acid-alkaline neutralization. Thus, TCA was expected to exist as triazole carboxylate (noted as TC^- hereafter). In the second solution, 56.5 mg TCA was completely dissolved in 1.0 mL of 1.2 mol/L NaOH aqueous solutions. The final pH was about 13.0, indicating a strong alkaline environment. Thus, TCA should undergo the deprotonation for the triazole ring (T-ring), and the major component became the deprotonated species and was marked as dpTC^{2-} dianion for convenience. In both solutions, the concentration of TCA was the same as 0.5 mol/L. Similarly, two deuterated solutions were prepared by using heavy water (D_2O , 99.5%) and NaOD (95%). To promote the isotope substitution, the solution was sealed in a small bottle, and was water-bath incubated at 75 °C for 12 h. As the results, for TC^- in the first solution, the H10 atom on the N atom and the H7 atom attached on C5 atom were replaced by deuterium, and hence the isotope substituted sample was denoted as d- TC^- . The deuterated dpTC^{2-} (marked as d- dpTC^{2-}) was prepared by adding excessive NaOD to remove deuterium on the N atom of T-ring. The structures of TCA, three main tautomers of TC^- , and dpTC^{2-} , are shown in FIG. 1.

Raman spectra were recorded with a LABRAM-010 Raman spectrometer equipped with an air-cooled CCD detector, where a 600 grooves/mm grating was used. The emission line at 488.0 nm of an Ar^+ ion laser was utilized as the excitation source with the power 3.5 mW

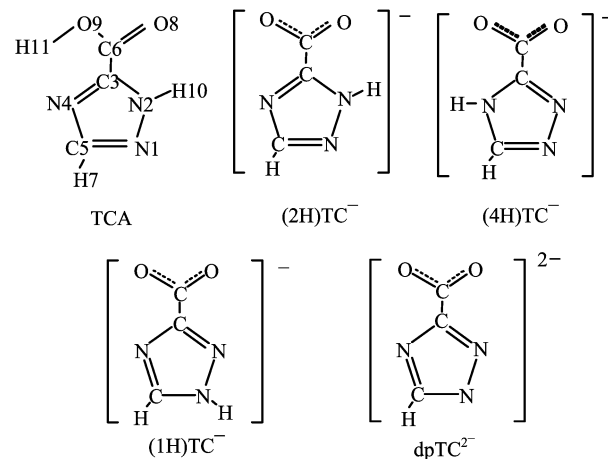


FIG. 1 Structural sketch with atomic labels for 1,2,4-triazole-3-carboxylic acid (TCA), three tautomers of 1,2,4-triazole-3-carboxylate anion (TC^-), and the deprotonated 1,2,4-triazole-3-carboxylate dianion (dpTC^{2-}).

on the samples. The acquisition time of the CCD detector was typically 100 s for Raman measurements. The spectra were baseline-subtracted.

All the DFT calculations were carried out using Truhlar's hybrid meta-NGA exchange-correlation functional MN15 [37]. The standard 6-311++G(d,p) basis sets and the PCM solvent model were employed in the present calculations. The optimized structures of TCA and its derivatives were obtained without symmetry constraint. Based on the optimized geometries, the analytic frequency calculations were performed to confirm their features of the global energy minimums, and to calculate the harmonic vibrational frequencies and the corresponding Raman activities. As the frequency scaling factor of the PCM-MN15/6-311++G(d,p) method was not found in literature, we conducted an auxiliary optimization-frequency calculation for benzene at the same level of theory. The calculated frequencies were then compared to the well-known 20 experimental frequencies of benzene in the region of $<1700 \text{ cm}^{-1}$ [38], which gave a frequency scaling factor of 0.9818. This value was used in the present study. All the DFT calculations were performed with the Gaussian 16 program [39].

The relative Raman intensity was converted from the calculated Raman activity using the following formula derived from the basic theory of Raman scattering [40, 41]:

$$I_i = \frac{f(\nu_0 - \nu_i)^4 A_i}{\nu_i [1 - \exp(-h c \nu_i / k_B T)]} \quad (1)$$

where ν_0 is the frequency of excitation light, ν_i and A_i are the harmonic frequency and Raman activity of the normal mode, h , c , and k_B are the well-defined fundamental constants, and f is a suitably chosen intensity normalization factor independent of normal modes.

Based on the calculated Raman intensities and harmonic frequencies, the Raman spectra were simulated with Lorentzian line-shapes with a FWHM of 6 cm^{-1} . Assignments of vibrational frequencies were carried out by inspecting the atomic displacements of the corresponding normal modes in conjunction with the potential energy distribution (PED) analyses. The PED calculations were done with Jamróz's VETA 4.0 program [42, 43].

III. RESULTS AND DISCUSSION

A. Raman spectra of TCA in solutions at different alkalinity

The spectral contributors of TCA in solutions at different pH values can be changed from TC^- in a neutral aqueous solution to dpTC^{2-} dianion in strong alkaline environment. Thus, the changes of Raman spectra of TCA in $\text{NaOH}/\text{H}_2\text{O}$ solution were specially paid attention to with the increase of alkalinity. In the prepared neutral solution, the initial concentrations were 0.5 mol/L for both TCA and NaOH . By gradually adding 0.024 mL of 2.5 mol/L NaOH aqueous solution into the 1 mL solution of TCA, Raman spectra were measured as shown in FIG. 2(a). With the increase of NaOH concentration, the 1063 , 1263 , 1353 , and 1453 cm^{-1} bands were gradually enhanced, while the 983 , 1108 , 1279 , 1341 , and 1424 cm^{-1} band intensities reduced, which responded to the transformation from the TC^- anion to the ring-deprotonated dpTC^{2-} dianion. Thus, these Raman bands must be contributed by dpTC^{2-} dianion and TC^- anion. Two strong bands at 1453 and 1263 cm^{-1} in strong alkaline environment were not observed in neutral solution, and thus they could be used as the characteristic bands for dpTC^{2-} dianion. Similarly, the band at 1424 cm^{-1} in neutral solutions could be considered as the spectral marker for TC^- anion, as it almost completely disappeared in strong alkaline solutions.

Since the 1453 cm^{-1} band of dpTC^{2-} and the 1424 cm^{-1} band of TC^- are well separated from the other bands, their intensity changes can reflect the transformation from TC^- to dpTC^{2-} with the increase of alkalinity. FIG. 2(b) plots the intensity changes of the bands at 1453 and 1424 cm^{-1} vs. the molar concentration ratio of $[\text{NaOH}]/[\text{TCA}]$. From the unchanged stages in FIG. 2(b), the complete transformation from the TC^- anion to the dpTC^{2-} dianion can be estimated to occur at the $[\text{NaOH}]/[\text{TCA}]$ ratio of ~ 2.05 . Moreover, as shown in assignment of the vibrational bands in the following sections, all the bands in FIG. 2(a) can be attributed to dpTC^{2-} and TC^- , implying that TCA exists only as the conformations of dpTC^{2-} or TC^- in aqueous solution.

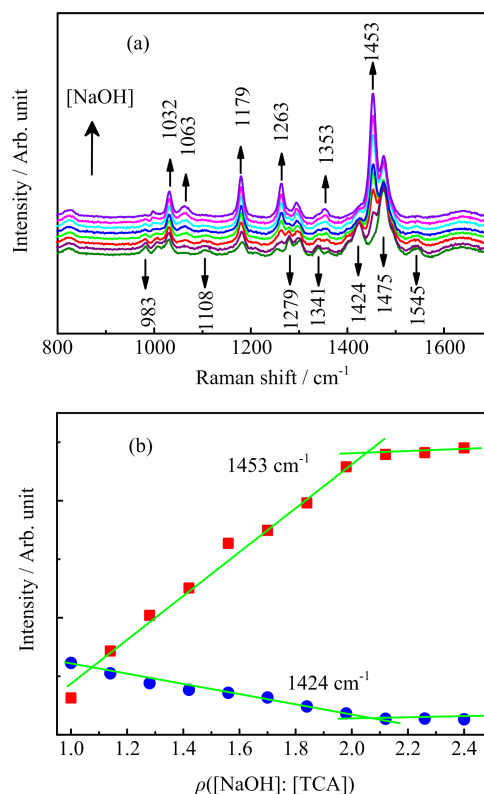


FIG. 2 (a) Raman spectra with step-by-step adding 0.024 mL NaOH solution (2.5 mol/L) into 1 mL the alkaline solution of TCA. The initial concentration of TCA is 0.5 mol/L in alkaline solutions; (b) intensities of the two bands at 1453 and 1424 cm^{-1} vs. the molar concentration ratio of $[\text{NaOH}]/[\text{TCA}]$.

B. Assignments of the Raman bands for dpTC^{2-} dianion

FIG. 3 shows the experimental and calculated Raman spectra of dpTC^{2-} dianion and its H7-deuterated derivative d-dpTC^{2-} in solutions. Both the concentration ratios, $[\text{NaOH}]/[\text{TCA}]$ and $[\text{NaOD}]/[\text{TCA}]$, were 2.4 for the solutions of TCA in $\text{NaOH}/\text{H}_2\text{O}$ and $\text{NaOD}/\text{D}_2\text{O}$ solutions. As shown in FIG. 3 (a) and (b), the spectrum of $\text{NaOD}/\text{D}_2\text{O}$ solution is almost identical to that of $\text{NaOH}/\text{H}_2\text{O}$, whatever for the peak positions and intensity patterns. The only difference exists at 1580 cm^{-1} where a weak band is observed in the $\text{NaOD}/\text{D}_2\text{O}$ solution, and its counterpart may be masked by the broad H_2O bending band (centered at $\sim 1640\text{ cm}^{-1}$) in the $\text{NaOH}/\text{H}_2\text{O}$ solution. The lack of isotopic effect provides an unambiguous evidence that in strong alkaline environment, TC^- undergoes deprotonation for the labile hydrogen atom (H10) on the N-atom of T-ring. FIG. 3(c) shows the recorded Raman spectrum of H7-deuterated sample, d-dpTC^{2-} , in alkaline $\text{NaOD}/\text{D}_2\text{O}$ solution ($[\text{NaOD}]/[\text{TCA}]=2.4$). The evident differences can be observed in FIG. 3(a) when compared with FIG. 3(c).

Based on the optimized geometries of dpTC^{2-} and d-

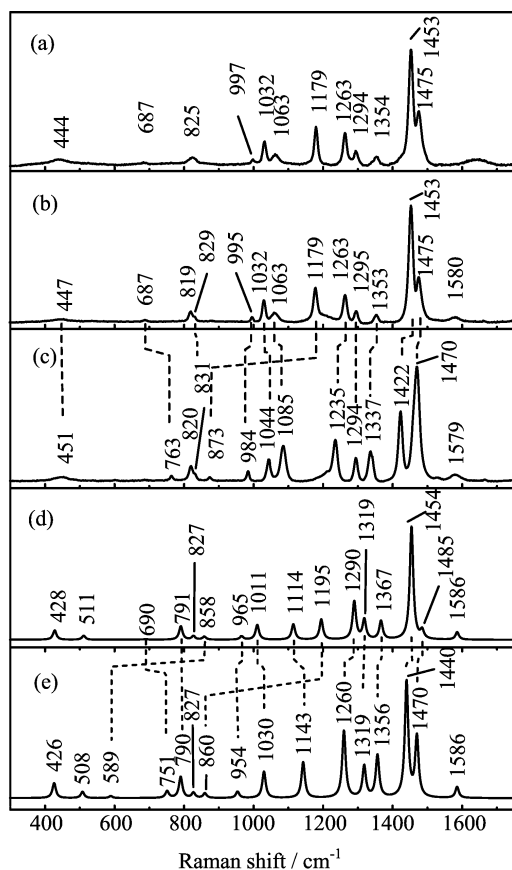


FIG. 3 Experimental (a, b, c) and calculated (d, e) Raman spectra of dpTC^{2-} and d-dpTC^{2-} . (a) dpTC^{2-} in $\text{NaOH}/\text{H}_2\text{O}$ solution, (b) dpTC^{2-} in $\text{NaOD}/\text{D}_2\text{O}$ solution, (c) d-dpTC^{2-} in $\text{NaOD}/\text{D}_2\text{O}$ solution; (d) dpTC^{2-} and (e) d-dpTC^{2-} .

dpTC^{2-} dianions at the PCM-MN15/6-311++G(d,p) level, their Raman spectra are simulated and displayed in FIG. 3 (d) and (e), respectively. The structure parameters, including bond lengths, bond angles, and dihedral angles of dpTC^{2-} dianion and $(2\text{H})\text{TC}^-$ (the most stable tautomer of TC^- anion) are listed in Table S1 of the supplementary materials. To our surprise, the simulated spectrum of dpTC^{2-} in FIG. 3(d) agrees very well with the experimental Raman spectrum in FIG. 3(a), except for a little weak intensity of the 1475 cm^{-1} band. For d-dpTC^{2-} , the agreement between the experimental and calculated spectra is also obtained as shown in FIG. 3 (c) and (e). Table I summarizes the spectral assignments of the major Raman bands for dpTC^{2-} and d-dpTC^{2-} . The PEDs of dpTC^{2-} are also provided in Table I.

According to the calculated PEDs, the Raman bands in the region of $1050\text{--}1650\text{ cm}^{-1}$ are contributed by the T-ring in-plane bond stretching, CO stretching of the COO^- group, and in-plane C5H7 bending modes. The $\text{C6O8}/\text{C6O9}$ anti-phase stretching of the COO^- group contributes the weak band at 1586 cm^{-1} for

dpTC^{2-} or d-dpTC^{2-} in FIG. 3 (d) and (e), which agrees well with the experimental data of 1580 cm^{-1} for dpTC^{2-} and 1579 cm^{-1} for d-dpTC^{2-} . The strong 1475 cm^{-1} band of dpTC^{2-} and its counterpart in d-dpTC^{2-} (at 1470 cm^{-1}) are attributed to the T-ring $\text{N1C5}/\text{C5N4}$ anti-phase stretching vibration, whose frequencies are calculated as 1485 cm^{-1} and 1470 cm^{-1} for dpTC^{2-} and d-dpTC^{2-} , respectively. Although the Raman intensity of this band is underestimated in calculations, the PCM-MN15 level of theory does correctly predict an impressive intensity increase of this band upon H7-deuteration. Moreover, the strong band at 1453 cm^{-1} for dpTC^{2-} and that at 1422 cm^{-1} for d-dpTC^{2-} in the experimental spectra are attributed to the $\text{N2C3}/\text{C3C6}$ anti-phase stretching strongly coupled with the N2C3N4 bending as well as the C6O8 stretching. This vibration was calculated at 1454 cm^{-1} for dpTC^{2-} and 1440 cm^{-1} for d-dpTC^{2-} , respectively, and both of them were the strongest in the simulated Raman spectra of FIG. 3 (d) and (e). The 1353 , 1295 , and 1263 cm^{-1} bands of dpTC^{2-} in FIG. 3(b) are assigned to the $\text{N2C3}/\text{N1C5}$ anti-phase stretching, $\text{C3N4}/\text{N4C5}$ anti-phase stretching, and $\text{N4C5}/\text{C5N1}$ in-phase stretching, respectively. The former two also strongly coupled with $\text{O8C6}/\text{C6O9}$ in-phase stretching of COO^- group. The calculated frequencies of them are 1367 , 1319 , and 1290 cm^{-1} , and the Raman intensities also closely resemble the experimental results. As shown in FIG. 3 and Table I, the calculated H7-deuteration shifts of these three modes are 11 , 0 , and 30 cm^{-1} , respectively, also well consistent with the observed values (16 , 1 , and 28 cm^{-1}) in experiments.

The C5H7 in-plane bending of dpTC^{2-} is calculated to appear at 1195 cm^{-1} , which is contributed by the stretching vibrations of N1N2 , N1C5 , and N4C5 bonds (Table I). Experimentally, a strong band at 1179 cm^{-1} was observed for dpTC^{2-} , but no band was detected nearby for d-dpTC^{2-} . This experimental peak is assigned to the C5H7 in-plane bending mode of dpTC^{2-} . The C5H7 in-plane bending mode is expected to show dramatic red-shift upon H7-deuteration, and according to PCM-MN15 calculation it shifts to 860 cm^{-1} . The weak band at 873 cm^{-1} of d-dpTC^{2-} in FIG. 3(c) may be contributed by this mode. The measured down-shift of 306 cm^{-1} upon H7-deuteration is well consistent with the DFT prediction (335 cm^{-1}). Meanwhile, both theoretical and experimental results show an intensity decrease for this mode upon H7-deuteration.

The band at 1063 cm^{-1} of dpTC^{2-} in FIG. 3(b) is assigned to N1N2 stretching, which is calculated at 1114 cm^{-1} in FIG. 3(d). The H7-deuteration causes an unusual upward shift for this mode by 22 cm^{-1} and 29 cm^{-1} , respectively, according to the experiment and the calculation. In addition, both the experiments and the calculations manifest an increase in Raman intensity upon H7-deuteration. By inspecting the atomic displacements of corresponding modes, we found that the N1N2 stretching is severely coupled with the C5-H7

TABLE I Experimental and calculated Raman frequencies (in cm^{-1}) of dpTC^{2-} and d-dpTC^{2-} dianions, as well as the potential energy distributions (PEDs) of dpTC^{2-} .

Experiment ^a		Calculated ^b		Assignment of dpTC^{2-} (PED ^c /%)
dpTC^{2-}	d-dpTC^{2-}	dpTC^{2-}	d-dpTC^{2-}	
		3169	2349	$\nu\text{C5H7}(99)$
1580(m)	1579(m)	1586	1586	$\nu\text{C6O8}(-46)$, $\nu\text{C6O9}(46)$
1475(s)	1470(vs)	1485	1470	$\nu\text{N1C5}(21)$, $\nu\text{N4C5}(-17)$, $\nu\text{N4C3}(-20)$, $\delta\text{N1C5H7}(-19)$
1453(vs)	1422(vs)	1454	1440	$\nu\text{N2C3}(-27)$, $\nu\text{C3C6}(22)$, $\nu\text{C6O8}(-13)$, $\delta\text{N2C3N4}(13)$
1353(m)	1337(s)	1367	1356	$\nu\text{N2C3}(46)$, $\nu\text{N1C5}(-16)$, $\nu\text{C6O9}(-14)$
1295(m)	1294(s)	1319	1319	$\nu\text{N4C3}(44)$, $\nu\text{C6O8}(-18)$, $\nu\text{C6O9}(-12)$, $\text{N4C5}(-10)$
1263(s)	1235(s)	1290	1260	$\nu\text{N4C5}(47)$, $\nu\text{N1C5}(42)$
1179(s)	873(w)	1195	860	$\delta\text{H7C5N1}(45)$, $\nu\text{N1N2}(-18)$, $\nu\text{N4C5}(-16)$, $\nu\text{N1C5}(11)$
1063(m)	1085(s)	1114	1143	$\nu\text{N1N2}(73)$, $\delta\text{N1C5H7}(15)$
1032(s)	1044(s)	1011	1030	$\delta\text{N4C3N2}(39)$, $\nu\text{N4C3}(24)$, $\nu\text{N2C3}(12)$
995(w)	984(m)	965	954	$\delta\text{C5N1N2}(87)$
		858	589	$\tau\text{H7C5N1N2}(84)$, $\tau\text{C3C5N2N1}(-11)$
829(sh)	831(sh)	827	827	$\tau\text{C6O9O8C3}(-64)$, $\tau\text{C3C6N2N4}(20)$, $\tau\text{C3N2N4C5}(14)$
819(m)	820(m)	791	790	$\delta\text{O9C6O8}(64)$, $\delta\text{N4C3N2}(-14)$
687(vw)	763(w)	690	751	$\tau\text{C3C5N2N1}(84)$, $\tau\text{H7C4N1N2}(13)$
		676	681	$\tau\text{C3N2N4C5}(69)$, $\tau\text{C6O9O8C3}(-24)$
		511	508	$\delta\text{O8C6C3}(59)$, $\tau\text{C6C3N2}(-24)$
447(w)	451(w)	428	426	$\nu\text{C6C3}(51)$, $\delta\text{O9C6O8}(-27)$, $\delta\text{N4C3N2}(-17)$
		243	240	$\delta\text{C6C3N2}(61)$, $\delta\text{O8C6C3}(28)$
		207	201	$\tau\text{C3C6N2N4}(73)$
		69	68	$\tau\text{O8C6C3N4}(99)$

^a vs: very strong, s: strong, m: medium, w: weak, vw: very weak, sh: shoulder peak. Solvent: D_2O .

^b Frequency scaling factor of 0.9818 was used.

^c ν : bond stretching, δ : in-plane bending, τ : out-of-plane torsion, +/−: symbol represents in-phase/anti-phase changes of the internal coordinates.

in-plane bending for dpTC^{2-} , whereas this type of coupling is very weak for d-dpTC^{2-} . Thus, the blue isotopic shift of this mode and the increase of Raman intensity are attributable to the considerable change of the normal mode composition after H7-deuteration.

The Raman bands in the region less than 1050 cm^{-1} involve in-plane and out-of-plane deformations of T-ring, OCO bending of the COO^- group, and relative motions between T-ring and COO^- group. The 1032 cm^{-1} band of dpTC^{2-} in FIG. 3(b) is assigned to the T-ring in-plane deformation involving mainly N4C3N2 bending, corresponding to the 1011 cm^{-1} band in the calculated spectrum of FIG. 3(d). The H7-deuteration causes a blue shift for this mode by 12 cm^{-1} , which is comparable with the calculated value 19 cm^{-1} . The atomic displacements of this mode show that the C5–H7 in-plane bending is coupled with the T-ring deformation, but the phase is opposite for dpTC^{2-} and d-dpTC^{2-} . This may be responsible for the blue-shift of this mode by H7-deuteration. The band of dpTC^{2-} at 995 cm^{-1} in FIG. 3(b) is also a T-ring in-plane deformation mode, which involves mainly the C5N1N2 bending. This mode is calculated to appear

at 965 cm^{-1} and shows 11 cm^{-1} red-shift upon H7-deuteration, well consistent with the experiments.

The Raman band at 819 cm^{-1} in FIG. 3(b) is due to the O9C6O8 bending of COO^- group, which is calculated at 791 cm^{-1} . The weak shoulder band at 829 cm^{-1} in FIG. 3(b) is attributed to an out-of-plane vibration of T-ring, involving mainly the out-of-plane motion of C3 atom. The low-frequency band at 447 cm^{-1} in FIG. 3(b) is attributed to the translation of the COO^- group relative to the T-ring, along the direction of C3–C6 bond. The C3–C6 bond stretching contributes a large PED (51%) to this mode.

C. Raman spectra of TC^- anion

TC^- has three main protonic tautomers, denoted here as $(2\text{H})\text{TC}^-$, $(1\text{H})\text{TC}^-$, and $(4\text{H})\text{TC}^-$, respectively, in which the labile hydrogen atom is attached on N2, N1, and N4 atoms. In principle, TC^- might have another four tautomers (see FIG. S1 in supplementary materials), in which the hydrogen atom is attached on the O8 or O9 atoms. But in view that the $\text{p}K_a$ val-

TABLE II Calculated energies (E in atomic unit), Gibbs free energies (G in atomic unit), relative energies (ΔE in kcal/mol), relative Gibbs free energies (ΔG in kcal/mol) of dpTC^{2-} , TC^- tautomers, and dimeric TC^- .

	E	G	ΔE^a	ΔG^a
dpTC^{2-}	-429.56379	-429.54513		
Tautomers (2H) TC^-	-430.04700	-430.01512	0.00	0.00
TC^- (4H) TC^-	-430.04247	-430.01138	2.84	2.35
(1H) TC^-	-430.04142	-430.01028	3.51	3.04
Dimeric TC^-				
Dimer 1	-860.11421	-860.03133	0.00	0.00
Dimer 2	-860.10889	-860.02735	3.34	2.50
Dimer 3	-860.10609	-860.02412	5.10	4.53
Dimer 4	-860.10466	-860.02353	5.99	4.89
Dimer 5	-860.10546	-860.02355	5.49	4.88
Dimer 6	-860.10428	-860.02273	6.23	5.39

^a Relative to (2H) TC^- for TC^- tautomers or to the Dimer 1 for TC^- dimers.

ues of carboxylic acids are larger than those of azoles, these four carboxylic-acid type tautomers are unlikely to co-exist with (2H) TC^- /(1H) TC^- /(4H) TC^- in solution. The PCM-DFT calculations also confirm that free energies of the four carboxylic-acid type tautomers are higher than (2H) TC^- by at least 4.96 kcal/mol. Thus, the four carboxylic-acid type tautomers will not be discussed in the following sections. The optimized geometry parameters of (2H) TC^- , (1H) TC^- , and (4H) TC^- are summarized in Table S2 of the supplementary materials. Using the optimized geometries, their relative energies and Gibbs free-energies are calculated and listed in Table II. Based on the relative free energies, the Boltzmann distributions of the three tautomers are determined to be 97.6% for (2H) TC^- , 1.8% for (4H) TC^- , and 0.6% for (1H) TC^- , indicating that the overwhelming majority of TC^- anions exists as (2H) TC^- at room temperature.

The simulated Raman spectra of (1H) TC^- , (4H) TC^- , and (2H) TC^- are displayed in FIG. 4 (a, b, c), respectively. FIG. 4(d) shows the experimental Raman spectrum of TC^- in aqueous solution. Among the three tautomers, the calculated spectrum of (2H) TC^- agrees better with the experimental spectrum. The slight differences seem not to be caused by the contributions of different tautomers, as the thermal distribution-weighted average spectrum in FIG. 4(e) is nearly identical to that of (2H) TC^- alone in FIG. 4(c).

FIG. 5 shows the experimental spectra of TC^- in aqueous solution and its deuterated derivative d- TC^- in D_2O , together with the calculated spectra of (2H) TC^- and d-(2H) TC^- . An initial impression can be obtained that some bands in experiments can be considered as split doublets of the single peaks in the calculated spectra. As discussed in the following section, the formation

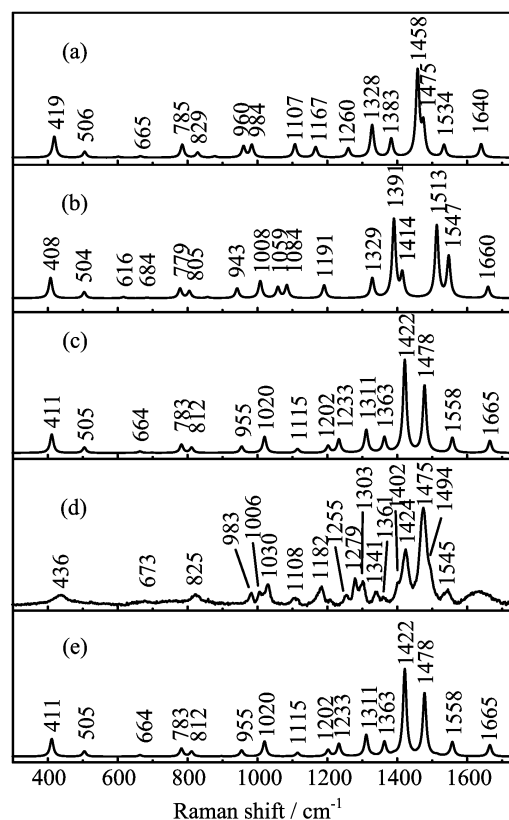


FIG. 4 The calculated Raman spectra of TC^- : (a) tautomer (1H) TC^- , (b) tautomer (4H) TC^- , (c) tautomer (2H) TC^- . (d) The experimental Raman spectrum of TC^- in aqueous solution. (e) Tautomer-distribution-weighted average spectrum.

of dimer in solutions could contribute to the band splitting. In Table III, the correlation between the experimental frequencies of TC^- and d- TC^- and the calculated frequencies of (2H) TC^- and d-(2H) TC^- are listed, as well as the PED results of (2H) TC^- .

Based on Tables III, the assignments of the observed Raman peaks are obtained. The weak bands at 1619 cm^{-1} observed in the D_2O solution of d- TC^- are attributed to the anti-phase O8C6/C6O9 stretch of COO^- group. Compared to that of dpTC^{2-} , this mode shows a quite large blue-shift (by 39 cm^{-1}), owing to the interaction between the O8 and H10(D10) atoms. In FIG. 5(a), the weak and broad peak at 1545 cm^{-1} of TC^- corresponds to the calculated band at 1558 cm^{-1} which is mainly contributed by the stretching of N4C3 and N1C5 bonds. The doublets at $1475/1494$ (shoulder), $1424/1402$ (shoulder), $1361/1341$, and $1303/1279\text{ cm}^{-1}$ correspond to the calculated peaks of (2H) TC^- at 1478 , 1422 , 1363 , and 1311 cm^{-1} in FIG. 5(c). According to the calculated PEDs and atomic displacements, the bands at 1478 and 1422 cm^{-1} in the calculated spectrum of FIG. 5(c) are assigned to the T-ring in-plane skeleton vibrations involving the stretches of the N2C3

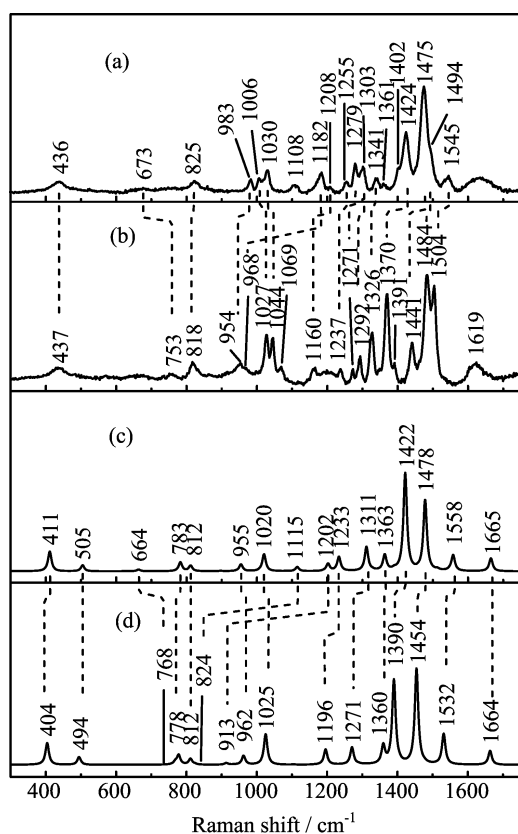


FIG. 5 The experimental Raman spectra of (a) TC^- in H_2O solution, (b) d-TC^- in D_2O solution; and the calculated Raman spectra of (c) $(2\text{H})\text{TC}^-$, (d) $\text{d-}(2\text{H})\text{TC}^-$.

and N4C3/N1C5 bonds. The peak at 1363 cm^{-1} is attributed to the in-phase O8C6/C6O9 stretch coupling with the N4C3 and N1C5 stretches, and that at 1311 cm^{-1} comes from the N1C5/C5N4 anti-phase stretch.

The observed $1006/1030\text{ cm}^{-1}$ doublet in FIG. 5(a) is considered to correlate to the calculated band at 1020 cm^{-1} in FIG. 5(c), which is attributed to the T-ring in-plane deformation involving N2C3N4 bending and in-phase N4C3/N2C3 stretch. Like dpTC^{2-} , the in-plane deformation mode shows blue-shift upon deuteration. The band at 983 cm^{-1} in FIG. 5(a) is also a T-ring in-plane deformation mode but involves mainly the C5N1N2 bending. The bands at 825 , 673 , and 436 cm^{-1} in FIG. 5(a) are assigned, respectively, to the O8C6O9 bending, C3N2N4C5 out-of-plane torsion, and the translation of COO^- group relative to the T-ring.

D. DFT calculations on dimers of TC^-

As mentioned above, in comparison with the calculated spectra of $(2\text{H})\text{TC}^-$ and $\text{d-}(2\text{H})\text{TC}^-$, some double splits were observed in the experimental spectra of TC^- and its deuterated derivatives. In contrast, dpTC^{2-} exhibits almost one-to-one correspondence between the

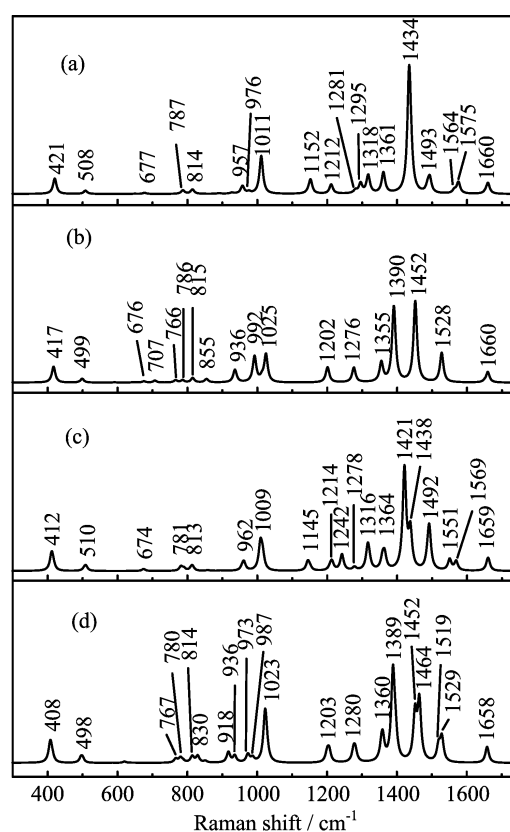


FIG. 6 The calculated Raman spectra of (a) dimer 1, (b) deuterated dimer 1, (c) dimer 2, and (d) deuterated dimer 2.

calculated and experimental bands. Thus, a reasonable presumption is drawn that the hydrogen-bonding interaction of the labile H10 atom on T-ring with neighboring molecules can cause the unusual double splits for TC^- . Using Raman/IR spectroscopy and DFT calculations, Meng *et al.* confirmed that 3-amino-1,2,4-triazole exists as monomers in solution but as dimers with hydrogen-bonding in solid state [26]. Taking into account that TC^- contains three nitrogen and two oxygen atoms, the dimer formed by hydrogen-bonding could not be ruled out. The dimerization, if presents, would surely have strong effect on the Raman spectra. Especially, for a homodimer the local vibrational modes of the two molecules can couple with each other [44]. This so-called vibrational exciton coupling can cause double split of IR or Raman bands.

To verify this assumption, the structures of probable hydrogen-bonding dimers of TC^- were optimized and are shown in FIG. S2 of the supplementary materials. Then the electronic energies and Gibbs free energies of them were calculated and are listed in Table II too. The two most stable dimers (dimers 1 and 2) are homodimers composed of two $(2\text{H})\text{TC}^-$ anions. In dimer 1, two $(2\text{H})\text{TC}^-$ anions are connected by two $\text{N-H}\cdots\text{O}$ hydrogen bonds, while in dimer 2 one $\text{N-H}\cdots\text{O}$ and

TABLE III Correlation of the experimental Raman frequencies (in cm^{-1}) of TC^- and d-TC^- anions and the calculated ones of $(2\text{H})\text{TC}^-$ and d-(2H)TC^- , together with the PED results of $(2\text{H})\text{TC}^-$.

Experiment ^a		Calculated ^b		Assignment of $(2\text{H})\text{TC}^{2-}$ (PED/%)
TC^- in H_2O	d-TC^- in D_2O	$(2\text{H})\text{TC}^-$	d-(2H)TC^-	
		3593	2643	$\nu\text{N2H10}(100)$
		3224	2393	$\nu\text{C5H7}(99)$
	1619(br)	1665	1664	$\nu\text{O9C6}(-55)$, $\nu\text{O8C6}(40)$
1545(m) ^c	1504(s)	1558	1532	$\nu\text{N4C3}(34)$, $\nu\text{N1C5}(-15)$, $\nu\text{C3C6}(-10)$, $\delta\text{H10N2N1}(12)$, $\delta\text{H7C5N4}(-10)$, $\delta\text{N2C3N4}(-10)$
1494(sh), 1475 (vs)	1484(vs), 1441(s)	1478	1454	$\nu\text{N2C3}(42)$, $\nu\text{N1C5}(13)$, $\delta\text{H7C5N4}(11)$
1424(s), 1402(sh)	1391(sh), 1370(vs)	1422	1390	$\nu\text{N4C3}(-22)$, $\nu\text{N1C5}(-15)$, $\delta\text{H10N2N1}(14)$
1361(w), 1341 (m)	1326(s)	1363	1360	$\nu\text{O8C6}(-33)$, $\nu\text{O9C6}(-20)$, $\nu\text{N1C5}(16)$, $\nu\text{N4C3}(17)$
1303(m), 1279(m)	1292(m), 1271(w)	1311	1271	$\nu\text{N4C5}(35)$, $\nu\text{N1C5}(28)$, $\nu\text{N1N2}(-10)$
1255(m)	1237(w)	1233	1196	$\nu\text{N1N2}(-28)$, $\delta\text{H10N2N1}(24)$, $\nu\text{N2C3}(-14)$
1208(w)	1160(w)			
1182(m,br)	968(w,sh) 1069(w)	1202	913	$\delta\text{H7C5N4}(42)$, $\nu\text{N4C5}(37)$
1108(w)		1115	824	$\nu\text{N1N2}(39)$, $\delta\text{H10N2N1}(32)$
1030(m), 1006(m)	1044(s), 1027(s)	1020	1025	$\delta\text{N2C3N4}(42)$, $\nu\text{N4C3}(17)$, $\nu\text{N2C3}(16)$
983(m)	954(m,br)	955	962	$\delta\text{C5N1N2}(78)$
		897	589	$\tau\text{H7C5N4C3}(84)$, $\tau\text{C3N2N4C5}(12)$
		812	812	$\tau\text{C6O9O8C3}(64)$, $\tau\text{C3C6N4N2}(19)$, $\tau\text{C3N2N4C5}(-12)$
825(br)	818(br)	783	778	$\delta\text{O8C6O9}(65)$, $\delta\text{N2C3N4}(-13)$
		695	497	$\tau\text{H10N2N1C5}(62)$, $\tau\text{C3C5N2N1}(-29)$
673(w,br)	753(vw)	664	768	$\tau\text{C3N2N4C5}(49)$, $\tau\text{H10N2N1C5}(22)$, $\tau\text{H7C5N4C3}(-10)$, $\tau\text{C6O9O8C3}(10)$
		627	634	$\tau\text{C3C5N2N1}(54)$, $\tau\text{H10N2N1C5}(15)$, $\tau\text{C6O9O8C3}(-14)$, $\tau\text{C3N2N4C5}(-12)$
		505	494	$\delta\text{O8C6C3}(62)$, $\delta\text{C6C3N4}(21)$
436(w)	437(w)	411	404	$\nu\text{C3C6}(50)$, $\tau\text{O8C6O9}(-24)$, $\tau\text{N2C3N4}(-17)$
		201	193	$\delta\text{C6C3N4}(66)$, $\delta\text{O8C6C3}(-30)$
		198	190	$\tau\text{C3C6N4N2}(73)$, $\tau\text{C3N2N4C5}(12)$
		76	60	$\tau\text{O8C6C3N2}(94)$

^a Raman spectra excited at 488 nm.^b scaling factor of frequency is 0.9818.

one $\text{N-H}\cdots\text{N}$ hydrogen bonds connect two monomers. The other dimers (dimers 3–6) have the higher Gibbs free energies than dimer 2 by 2.0–2.9 kcal/mol, and thus they are less stable. The binding free energies, defined as the Gibbs free energy of the dimer minus the sum of that of two $(2\text{H})\text{TC}^-$ monomers, are -0.68 kcal/mol for dimer 1 and 1.82 kcal/mol for dimer 2, respectively. Although the binding energy of dimer 2 is slightly positive, it may exist in solution in view of the high concentration of TC^- in experiments.

FIG. 6 displays the simulated Raman spectra of dimers 1 and 2 as well as their deuterated derivatives. The vibrational frequencies and Raman activities are listed in Table S3 of the supplementary material. For most of vibrational modes of dimer 1, the excitonic splits induced by dimerization are

small and typically vary less than 6 cm^{-1} . Only the N4C3/N1C5 anti-phase stretch and H10 in-plane bending modes, whose frequencies were 1558 and 1233 cm^{-1} in $(2\text{H})\text{TC}^-$ monomer, show evident splits in dimers 1 as $1575/1564\text{ cm}^{-1}$ and $1295/1281\text{ cm}^{-1}$, respectively. For dimer 2, only the N4C3/N1C5 anti-phase stretch and N4C3/N1C5 in-phase stretch show large splits into $1569/1551\text{ cm}^{-1}$ and $1438/1421\text{ cm}^{-1}$, respectively. Therefore, some other unknown factors, besides dimerization, should be responsible for the observed band splitting in experiments.

We noticed that, in addition to excitonic splits, many Raman bands of dimers 1 and 2 show considerable shifts in comparison to their counterparts in the monomeric $(2\text{H})\text{TC}^-$. Thus, the double splits in Raman spectra of TC^- could be explained by co-existence of monomers

and dimers (presumably as Dimer 1) in solutions. This deduction is acceptable, especially taking into account the small binding energy of dimer 1.

IV. CONCLUSION

Raman spectra of TC^- anion and dpTC^{2-} dianion in $\text{H}_2\text{O}/\text{D}_2\text{O}$ solutions were measured and analyzed with the aid of the density functional theory at the MN15/6-311++G(d,p) level and PCM solvent model. Based on the optimized geometries, the frequencies and Raman activities of various vibrational modes were calculated. Then the Raman spectra of TC^- anion and dpTC^{2-} dianion were simulated to compare with the experimental data.

For dpTC^{2-} and its deuterated derivative, the experimental Raman spectra were greatly consistent with the simulated spectra of the monomer. All dominant vibrational bands in spectra were well assigned.

Various protonic tautomers of TC^- anion were checked with DFT calculations. The 2H-tautomer was found more stable than the others, and overwhelmingly dominated in solutions at room temperature. Interestingly, the experimental Raman spectrum of TC^- anion was roughly consistent with the simulated spectrum of 2H-tautomer of TC^- , but double splits were observed for a few Raman bands. The stable hydrogen-bonding dimers of TC^- were suggested to exist in solution, and the dimer-monomer equilibrium was inferred to be responsible for the splits.

Supplementary materials: DFT calculated structural parameters and structural sketches of the studied species are shown.

V. ACKNOWLEDGEMENTS

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