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Probing the early stages of solvation of *cis*-pinate dianions by water, acetonitrile, and methanol: a photoelectron spectroscopy and theoretical study†

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cis-Pinic acid is one of the most important oxidation products of α -pinene – a key monoterpene compound in biogenic emission processes. Molecular level understanding of its interaction with water in cluster formation is an important and necessary prerequisite for ascertaining its role in the aerosol formation processes. In this work, we studied the structures and energetics of the solvated clusters of *cis*-pinate (*cis*-PA^{2−}), the doubly deprotonated dicarboxylate of *cis*-pinic acid, with H₂O, CH₃OH, and CH₃CN by negative ion photoelectron spectroscopy and *ab initio* theoretical calculations. We found that *cis*-PA^{2−} prefers being solvated alternately on the two –CO₂[−] groups with increase of solvent coverage, a well-known solvation pattern that has been observed in microhydrated linear dicarboxylate dianion (DC_{*n*}^{2−}) clusters. Experiments and calculations further reveal an intriguing feature for the existence of the asymmetric type isomers for *cis*-PA^{2−}(H₂O)₂ and *cis*-PA^{2−}(CH₃OH)₂, in which both solvent molecules interact with only one of the –CO₂[−] groups, a phenomenon that has not been observed in DC_{*n*}^{2−} water clusters and exhibits that the subtle effect of the rigid four-membered carbon ring brought on the *cis*-PA^{2−} solvation. The dominant interactions between *cis*-PA^{2−} and solvent molecules form bidentate O[−]⋯H–O H-bonds for H₂O, O[−]⋯H–O and O[−]⋯H–C H-bonds for CH₃OH, and tridentate O[−]⋯H–C H-bonds for CH₃CN. The formation of inter-solvent H-bonds between H₂O and CH₃CN is found to be favorable in mixed solvent clusters, different from that between H₂O and CH₃OH. These findings have important implications for understanding the mechanism of cluster growth and the formation of atmospheric organic aerosols, as well as for rationalizing the nature of structure–function relationship of proteins containing carboxylate groups in various solvent environments.

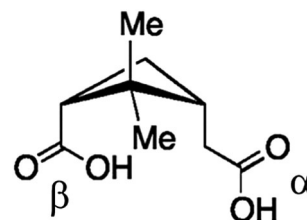
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Introduction

cis-Pinic acid (*cis*-PA), a C₉-dicarboxylic acid with a rigid, four-membered carbon ring linking two inequivalent carboxylic groups (α and β ; Scheme 1), is one of the several distinct oxidation products of α -pinene,^{1–7} which is the most abundant



Scheme 1 *cis*-Pinic acid.

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† Electronic supplementary information (ESI) available: The 20 K photoelectron spectrum of bare *cis*-PA^{2−} at 266 nm (Fig. S1); a comparison of experimental VDE value with calculated ones for the bare *cis*-PA^{2−} dianion at different theoretical levels (Table S1); a comparison of experimental VDEs to calculated ones and the relative energies (ΔE) of different isomers for the solvated *cis*-PA^{2−} clusters at different theoretical levels (Table S2); and Cartesian coordinates and energies of all isomers. See DOI: 10.1039/c5cp05974g

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emission from natural plants.^{5,8} With the upper limits of the partial vapor pressure of $(5.6 \pm 4.0) \times 10^{-8}$ Torr,³ *cis*-PA can be classified as a semivolatile organic compound (SVOC),^{7,9} and is found to play an important role in the formation of new aerosol particles.^{2–4,10} The contributions of those organic aerosol particles to the global aerosol budget have very complicated mechanisms with high uncertainties.^{10–19} Such complexity and uncertainty hamper the quantitative elucidation of their effects on the Earth's radiation balance.^{20–22}

With two carboxylic groups, *cis*-PA has the potential to form clusters with itself and other precursors like H₂O molecules.^{11,18,23,24} In the atmospheric environment, humidity is always one of the key parameters to drive the final stage of new particle growth and thus it would be important to investigate the fate of *cis*-PA in humid environments,²⁵ *i.e.*, the interaction of *cis*-PA with H₂O.

On the other hand, as a deprotonated conjugate base of a dicarboxylic acid, *cis*-pinate (*cis*-PA^{2−}) is also important in biochemistry²⁶ and synthetic chemistry,²⁷ and can be viewed as a simple model for peptide chains in slightly basic solutions. Thus a molecular understanding of its interactions with different solvents such as H₂O, CH₃CN, and CH₃OH will be helpful to address the protein functions and structures in various solvent environments.^{28–32}

In this work, we carried out a joint negative ion photoelectron spectroscopy (NIPES) and *ab initio* theoretical calculations on a series of size-selective *cis*-PA^{2−} solvated clusters to examine the early stages of the *cis*-PA^{2−} solvation with H₂O, CH₃CN, and CH₃OH. Unlike those dicarboxylates with linear and flexible aliphatic chains ([−]O₂C(CH₂)_nCO₂[−], DC_n^{2−}, *n* = 2–12) previously studied,^{33–38} *cis*-PA^{2−} contains a rigid, four-membered carbon ring with two inequivalent carboxylate groups (Scheme 1). Overall, we found that *cis*-PA^{2−} shows a similar solvation pattern compared to those of DC_n^{2−} interacting with water molecules, but subtle differences are unraveled. Meanwhile, we have systematically investigated *cis*-PA^{2−} solvation with CH₃CN and CH₃OH, two common nonaqueous solvents.^{32,39,40} This represents the first NIPES study of carboxylate solvation beyond solvent water, and reveals interesting and distinctly different solvation motifs that may help understand protein functions and structures in various solvent environments.

Experimental methods

The NIPES experiments were performed using a low-temperature, magnetic-bottle time-of-flight (TOF) photoelectron spectrometer, coupled with an electrospray ionization source and a temperature-controllable cryogenic ion-trap.⁴¹ The *cis*-pinate-solvent cluster dianions (*cis*-PA^{2−}(Sol)_{*m*}(H₂O)_{*n*}; Sol = CH₃CN and CH₃OH) were produced *via* electrospraying into the gas phase from a 0.1 mM solution of *cis*-pinic acid, dissolved in water/acetonitrile or methanol, with the solution pH value tuned to around 8 by adding ~100 mM aqueous NaOH solution dropwise. The produced ions were accumulated and collisionally cooled in the cryogenic 3D ion trap set to 20 K for 20–100 ms, minimizing the populations of high energy isomers and eliminating the extra features due to vibrational hot bands in the photoelectron spectra. The cold ions were then transferred into the extraction zone of a TOF mass spectrometer for mass and charge analyses.

During each NIPES experiment, the desired *cis*-PA^{2−}(Sol)_{*m*}(H₂O)_{*n*} dianions were mass-selected and decelerated before being photo-detached by an ArF laser beam (193 nm, 6.424 eV). The laser was operated at a 20 Hz repetition rate with the ion beam off

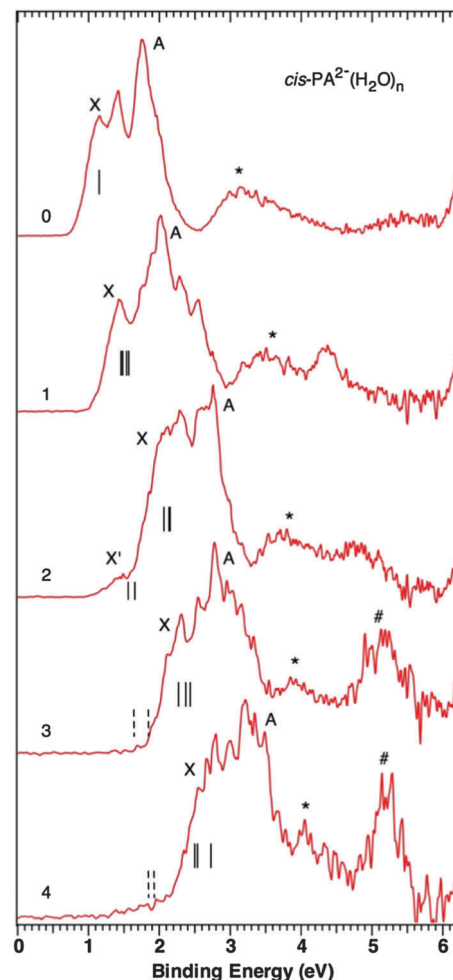


Fig. 1 The 20 K photoelectron spectra of *cis*-PA^{2−}(H₂O)_{*n*} (*n* = 0–4) at 193 nm. The solid and dashed vertical bars are the calculated VDEs from the lowest energy isomers (more symmetrically solvated ones aligning with band X) that are likely present in the experiments, and those high energy isomers (highly asymmetrically solvated) that are likely absent in the experiments, respectively.

at alternating laser shots to enable shot-by-shot background subtraction. Photoelectrons were collected at nearly 100% efficiency using the magnetic-bottle and analyzed in a 5.2 m long electron flight tube. The TOF photoelectron spectra were converted into electron kinetic energy spectra by calibration with the known NIPE spectra of I[−] and OsCl₆^{2−}. The electron binding energies (EBEs), given in the spectra in Fig. 1–3, were obtained by subtracting the electron kinetic energies from the detachment photon energy. The experimental vertical detachment energy (VDE) of each cluster anion was measured from the maximum of the first resolved peak in the respective NIPE spectrum.

Theoretical details

Quantum chemical calculations were performed using the Gaussian 09 program suite.⁴² Several methods, *i.e.* M06-2X, ωB97X-D, B3LYP, B3LYP, B3LYP, B3LYP, BP86, PBE, PW91, TPSS,

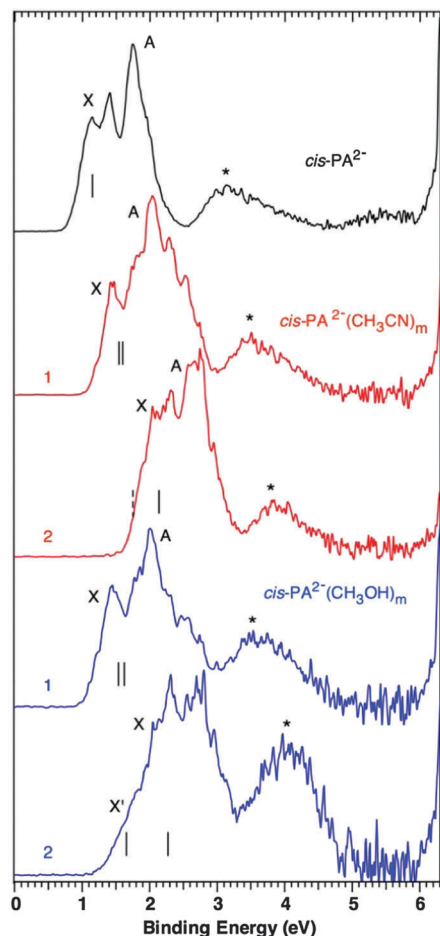


Fig. 2 The 20 K photoelectron spectra of $\text{cis-PA}^{2-}(\text{Sol})_m$ (Sol = CH_3CN and CH_3OH ; $m = 1$ and 2) at 193 nm. The solid and dashed vertical bars are the calculated VDEs from the lowest energy isomers (more symmetrically solvated ones aligning with band X) that are likely present in the experiments, and those high energy isomers (highly asymmetrically solvated) that are likely absent in the experiments, respectively.

and MP2, have been tested for the bare cis-PA^{2-} dianion (see Table S1 in the ESI[†]), showing that M06-2X/aug-cc-pVDZ and $\omega\text{B97X-D/aug-cc-pVDZ}$ yield better results than others. Furthermore, recent investigations have demonstrated that the M06-2X hybrid functional can reproduce well the photoelectron spectroscopic experiments of solvated carboxylate anions.^{24,43} Therefore, this functional was employed for the present calculations as well. The aug-cc-pVDZ basis set was used for all atoms. Structures were optimized using tight convergence criteria without any symmetry restrictions. Harmonic vibrational frequency analyses were carried out to confirm that the structures were real minima. Theoretical VDEs were calculated as the total energy differences between the dianions and the one-electron less monoanions both at the optimized geometries of the dianions. Relative energies obtained from the M06-2X/aug-cc-pVDZ optimization were almost the same as those from MP2/aug-cc-pVDZ//M06-2X/aug-cc-pVDZ single point energy calculations (Table S2, ESI[†]). Therefore, we will focus on the results obtained using M06-2X/aug-cc-pVDZ in the following parts.

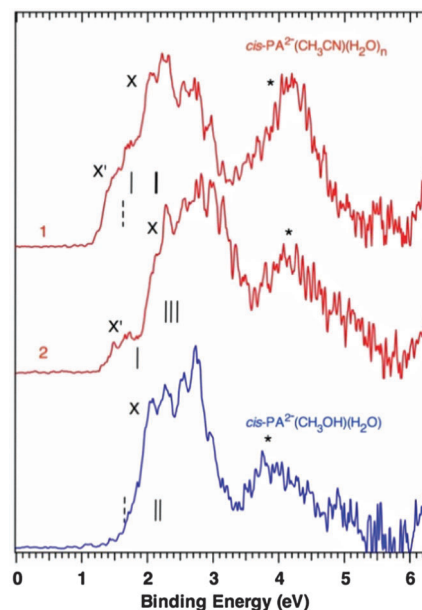


Fig. 3 The 20 K photoelectron spectra of $\text{cis-PA}^{2-}(\text{Sol})(\text{H}_2\text{O})_n$ (Sol = CH_3CN and CH_3OH ; $n = 1$ and 2) at 193 nm. The solid and dashed vertical bars are the calculated VDEs from the lowest energy isomers (more symmetrically solvated ones aligning with band X) that are likely present in the experiments, and those high energy isomers (highly asymmetrically solvated) that are likely absent in the experiments, respectively.

Results and discussion

Photoelectron spectroscopy

NIPE spectra of $\text{cis-PA}^{2-}(\text{H}_2\text{O})_n$ ($n = 0-4$). Fig. 1 shows the 20 K NIPE spectra of $\text{cis-PA}^{2-}(\text{H}_2\text{O})_n$ ($n = 0-4$) at 193 nm. The characteristic carboxylate $-\text{CO}_2^-$ X and A bands⁴⁴ are seen in both the spectra at 266 (Fig. S1 in the ESI[†]) and 193 nm (Fig. 1) for the bare cis-PA^{2-} . These bands arise from the removal of one electron from the highest occupied molecular orbital (HOMO) (mainly a σ^* in-plane antibonding orbital) and the HOMO-1 orbital (σ in-plane bonding combination) for the X doublet feature, and by detaching one electron from the HOMO-2 orbital with an out-of-plane antibonding p character for the A band, respectively.⁴⁵⁻⁴⁷ The weak broad band denoted “*” centered at ~ 3.0 eV EBE is a spectral feature ascribed to the detachment of the singly charged product monoanion or fragment anion by a second photon, as has been reported in previous studies.^{35,36,44,48} A strong signal with nearly 0 eV kinetic energy electrons is seen near the photon energy limit in the spectrum of cis-PA^{2-} . As suggested before,^{44,49} these zero kinetic energy photoelectrons are due to dissociative secondary autodetachment of the primary photodetached product of cis-PA^{2-} radical monoanions, which are expected to be highly unstable toward electron autodetachment and loss of CO_2 (decarboxylation).

The NIPE spectra of the solvated clusters $\text{cis-PA}^{2-}(\text{H}_2\text{O})_n$ in Fig. 1 show an overall similar spectral pattern compared to the bare solute with an incremental increase of EBE per water molecule (Table 1). A close examination of the spectra reveals interesting odd-even variations with the number of solvent water molecules for both EBE and spectral band shape. Upon solvation by one H_2O

molecule, the spectrum of $\text{cis-PA}^{2-}(\text{H}_2\text{O})_1$ shifts to high binding energy by 0.3 eV and becomes appreciably (by 30%) broader. This is because, when there is only one water molecule, either the α - or β -carboxylate group is solvated, resulting in two more inequivalent carboxylate ends, one $-\text{CO}_2^-$, and the other $-\text{CO}_2^-(\text{H}_2\text{O})_1$. The VDE of $\text{cis-PA}^{2-}(\text{H}_2\text{O})_1$ is measured from the $-\text{CO}_2^-$ end, which is only indirectly affected by the water molecule at the other end of cis-PA^{2-} . The contributions of these two inequivalent carboxylate ends with different EBEs also significantly broaden the overall spectral bandwidth. When the second solvated H_2O molecule is added, the VDE of $\text{cis-PA}^{2-}(\text{H}_2\text{O})_2$ is increased by 0.6 eV, and the spectral band becomes narrower relative to that at $n = 1$. This observation strongly suggests that the second water molecule solvates the un-solvated $-\text{CO}_2^-$ in the $n = 1$ cluster, resulting in two carboxylate ends both being solvated by one H_2O molecule, which reduces the chemical discrepancy of these two carboxylate ends and consequently narrows the spectral band. The VDE increase of $n = 2$ from $n = 1$, i.e., ΔVDE ($1 \rightarrow 2$, ~ 0.6 eV), reflects a direct solvation effect on the negative charge instead of an indirect charge-dipole stabilization for ΔVDE ($0 \rightarrow 1$, ~ 0.3 eV), and is expected to be larger. This odd-even effect seems recurring to $n = 3$ and 4, indicating an alternating solvation pattern for cis-PA^{2-} , similar to the solvation pattern observed for the aliphatic dicarboxylate DC_n^{2-} dianions.^{33–38} The above inference on solvation evolution reached from the analyses of the VDEs and spectral bands is also born out of our theoretical calculations (*vide infra*). It is notable that there is an additional weak X' band with low EBE = 1.45 eV in the $n = 2$ spectrum, suggesting the coexistence of multiple isomers for this cluster. Besides the X, A, and “*” bands, a high EBE spectral band “#”, which is obvious in $n = 3$ and 4 and discernible in $n = 1$ and 2, is also observed. The intensity of this band increases with water molecules. The nature of this band, as suggested before, is due to the ionization of solvent water molecules,^{35,36,50} whose ionization potential is significantly lowered by the presence of multiply charged negative ions in the vicinity. The VDEs of cis-PA^{2-} and its solvated clusters $\text{cis-PA}^{2-}(\text{H}_2\text{O})_n$ measured from the maxima (centers) of the first resolved bands are summarized in Table 1.

Table 1 The experimentally measured vertical detachment energies (VDEs) of $\text{cis-PA}^{2-}(\text{Sol})_m(\text{H}_2\text{O})_n$ clusters

Clusters	VDE (eV)	
	X	X'
cis-PA^{2-}	1.15 $\pm$ 0.05	
$\text{cis-PA}^{2-}(\text{H}_2\text{O})$	1.43 $\pm$ 0.05	
$\text{cis-PA}^{2-}(\text{CH}_3\text{CN})$	1.44 $\pm$ 0.05	
$\text{cis-PA}^{2-}(\text{CH}_3\text{OH})$	1.44 $\pm$ 0.05	
$\text{cis-PA}^{2-}(\text{H}_2\text{O})_2$	2.07 $\pm$ 0.10	1.45 $\pm$ 0.05
$\text{cis-PA}^{2-}(\text{CH}_3\text{CN})_2$	2.08 $\pm$ 0.05	
$\text{cis-PA}^{2-}(\text{CH}_3\text{OH})_2$	2.10 $\pm$ 0.10	1.60 $\pm$ 0.10
$\text{cis-PA}^{2-}(\text{H}_2\text{O})_3$	2.30 $\pm$ 0.05	
$\text{cis-PA}^{2-}(\text{H}_2\text{O})_4$	2.75 $\pm$ 0.10	
$\text{cis-PA}^{2-}(\text{CH}_3\text{CN})(\text{H}_2\text{O})$	2.07 $\pm$ 0.05	1.50 $\pm$ 0.10
$\text{cis-PA}^{2-}(\text{CH}_3\text{OH})(\text{H}_2\text{O})$	2.08 $\pm$ 0.05	
$\text{cis-PA}^{2-}(\text{CH}_3\text{CN})(\text{H}_2\text{O})_2$	2.29 $\pm$ 0.05	1.60 $\pm$ 0.10

NIPE spectra of $\text{cis-PA}^{2-}(\text{Sol})_m$ (Sol = CH_3CN and CH_3OH ; $m = 1$ and 2). The NIPE spectra of $\text{cis-PA}^{2-}(\text{CH}_3\text{CN})_m$ in Fig. 2 show a very similar trend in EBE and spectral bandwidth with the increase of the solvent molecules as $\text{cis-PA}^{2-}(\text{H}_2\text{O})_n$. The stepwise increase of EBE per CH_3CN , i.e. 0.3 and 0.6 eV for the first and second acetonitrile molecules, respectively, is identical within experimental uncertainties to what is observed in the case of water (Table 1); the spectral band for $m = 1$ is significantly broader than that for $m = 0$ and 2. These spectral revelations suggest a similar alternating solvation on the two $-\text{CO}_2^-$ ends of cis-PA^{2-} in CH_3CN as in H_2O .

Upon solvation by one CH_3OH , the spectrum of $\text{cis-PA}^{2-}(\text{CH}_3\text{OH})$ shifts to a higher EBE, again by ~ 0.3 eV (EBE = 1.44 eV, Table 1) relative to that of bare cis-PA^{2-} ; the spectral band is also similar to the clusters with one H_2O or one CH_3CN molecule discussed above. While the EBE for the main spectral band in $\text{cis-PA}^{2-}(\text{CH}_3\text{OH})_2$ is ~ 2.10 eV, similar to that with two H_2O or CH_3CN molecules, there exists a notable feature at EBE ~ 1.60 eV, with which the EBE is only slightly larger than that of $\text{cis-PA}^{2-}(\text{CH}_3\text{OH})$. This seems to suggest that besides the symmetric solvation with one CH_3OH molecule at each $-\text{CO}_2^-$ end, asymmetric solvation isomers with both CH_3OH molecules solvating one $-\text{CO}_2^-$ end may exist to give rise to this low EBE feature. Our theoretical calculations described below fully support the above predictions on $\text{cis-PA}^{2-}(\text{CH}_3\text{CN}/\text{CH}_3\text{OH})_m$ solvation.

NIPE spectra of $\text{cis-PA}^{2-}(\text{Sol})(\text{H}_2\text{O})_n$ (Sol = CH_3CN and CH_3OH ; $n = 1$ and 2). Fig. 3 shows the NIPE spectra of the mixed solvent clusters. The spectrum of $\text{cis-PA}^{2-}(\text{CH}_3\text{CN})(\text{H}_2\text{O})$ is notably broader than those of $\text{cis-PA}^{2-}(\text{CH}_3\text{CN})_2$ and $\text{cis-PA}^{2-}(\text{H}_2\text{O})_2$, in which besides a main spectral band with ~ 2.07 eV EBE, a low binding energy feature with significant intensity is shown at ~ 1.50 eV EBE. The presence of this low binding energy feature in the spectrum of $\text{cis-PA}^{2-}(\text{CH}_3\text{CN})(\text{H}_2\text{O})$ indicates that an isomer with both CH_3CN and H_2O solvating the same $-\text{CO}_2^-$ group in $\text{cis-PA}^{2-}(\text{CH}_3\text{CN})(\text{H}_2\text{O})$ is among the lowest energy structures that are accessible under the experimental conditions. For $\text{cis-PA}^{2-}(\text{CH}_3\text{CN})(\text{H}_2\text{O})_2$, besides the main band feature with EBE = 2.29 eV, it is unexpected to see a weak band with ~ 1.60 eV EBE, a value that is low enough that has to be derived from detaching a “naked” $-\text{CO}_2^-$ group. This observation suggests that a highly asymmetric solvation structure with all the solvent (two water and one acetonitrile) molecules solvating only one $-\text{CO}_2^-$ group in cis-PA^{2-} is also populated.

The main spectral band of $\text{cis-PA}^{2-}(\text{CH}_3\text{OH})(\text{H}_2\text{O})$ is similar to that in $\text{cis-PA}^{2-}(\text{H}_2\text{O})_2$ as expected; but considerably simpler than that of $\text{cis-PA}^{2-}(\text{CH}_3\text{CN})(\text{H}_2\text{O})$. Thus, the substitution of CH_3CN in $\text{cis-PA}^{2-}(\text{CH}_3\text{CN})(\text{H}_2\text{O})$ by CH_3OH in $\text{cis-PA}^{2-}(\text{CH}_3\text{OH})(\text{H}_2\text{O})$ results in distinct differences in the formation of H-bonding between CH_3CN and the $-\text{CO}_2^-$ group compared to that between $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ and the $-\text{CO}_2^-$ group. As it will become clear from our theoretical calculations described below, one CH_3CN molecule can form a triple H-bond *via* three H atoms in its methyl group with two oxygen atoms in the $-\text{CO}_2^-$ end, in contrast to solvent H_2O and CH_3OH , which mainly interact with the carboxylate oxygen atoms *via* forming bidentate

$\text{O}^{\ominus} \cdots \text{H}-\text{O}$ H-bonds for H_2O , and $\text{O}^{\ominus} \cdots \text{H}-\text{O}$ and $\text{O}^{\ominus} \cdots \text{H}-\text{C}$ H-bonds for CH_3OH .

Optimized structures

Considering that the solvent molecule forms H-bonds either with the α - or β -side $-\text{CO}_2^-$ group, each structure is labelled with $(x + y)$, where the values of x and y indicate the extent of solvation of each $-\text{CO}_2^-$ group. This alternative classification scheme will be helpful to compare the solvation pattern in the complexes containing more than one solvent molecule. For instance, iso A for $\text{cis-PA}^{2-}(\text{H}_2\text{O})_2$ in Fig. 4 is labelled $(1 + 1)$ and iso D $(2 + 0)$.

$\text{cis-PA}^{2-}(\text{H}_2\text{O})_n$ ($n = 1-4$). Fig. 4 shows the optimized structures of the low energy isomers for $\text{cis-PA}^{2-}(\text{H}_2\text{O})_n$ clusters. In the lowest energy isomer for the monohydrated cluster, the water molecule forms a bidentate H-bond with the α side $-\text{CO}_2^-$ (iso A). An alternative bidentate solvation on the β side $-\text{CO}_2^-$ gives rise to isomer B, which lies only 0.25 kJ mol^{-1} higher in energy. Isomers C and D, each consisting of a singly H-bonded water molecule that interacts with either β or α $-\text{CO}_2^-$, respectively, are calculated to be degenerate in energy by 15.65 and $15.66 \text{ kJ mol}^{-1}$ higher than isomer A. The calculated VDE values of isomers A–D are 1.57 , 1.49 , 1.47 , and 1.52 eV , respectively (Table 2), which all agree well with the experimental value of 1.43 eV . Since the two lowest-lying

Table 2 Comparison of experimental VDE values to calculated ones and relative energies (ΔE) of the isomers for $\text{cis-PA}^{2-}(\text{H}_2\text{O})_n$ ($n = 1-4$) at the M06-2X/aug-cc-pVDZ level. The isomers in bold are the ones which most likely exist in the experiments

Clusters	Isomers	ΔE (kJ mol^{-1})	VDE (eV)	
			Calc.	Exp.
$\text{cis-PA}^{2-}(\text{H}_2\text{O})$	iso A	0.00	1.57	1.43 ± 0.05
	iso B	0.25	1.49	
	iso C	15.65	1.47	
	iso D	15.66	1.52	
$\text{cis-PA}^{2-}(\text{H}_2\text{O})_2$	iso A	0.00	2.13	2.07 ± 0.10
	iso B	15.55	2.14	
	iso C	15.68	2.07	1.45 ± 0.05
	iso D	18.91	1.56	
	iso E	19.97	1.65	
$\text{cis-PA}^{2-}(\text{H}_2\text{O})_3$	iso A	0.00	2.28	2.30 ± 0.05
	iso B	0.48	2.42	
	iso C	1.54	2.38	2.75 ± 0.10
	iso D	19.79	1.84	
	iso E	19.86	1.65	
$\text{cis-PA}^{2-}(\text{H}_2\text{O})_4$	iso A	0.00	2.72	2.75 ± 0.10
	iso B	0.32	2.50	
	iso C	0.36	2.53	1.93
	iso D	27.45	1.93	
	iso E	28.38	1.84	

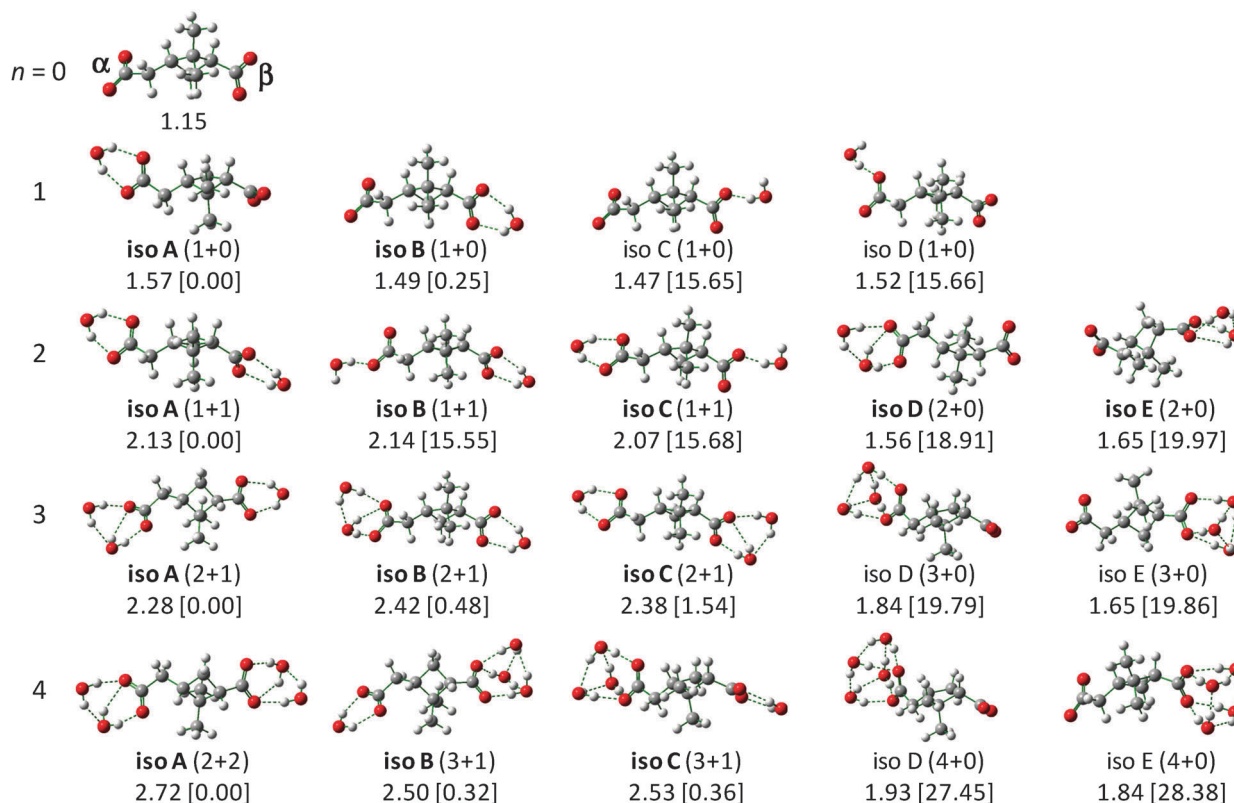


Fig. 4 M06-2X/aug-cc-pVDZ optimized structures of cis-PA^{2-} and $\text{cis-PA}^{2-}(\text{H}_2\text{O})_n$ clusters ($n = 0-4$ as indicated in the first column) (O, red; C, gray; H, light gray). The calculated VDEs (in eV) and relative energies (ΔE in kJ mol^{-1} , inside square brackets) are given. The isomers in bold are the ones which most likely exist in the experiments.

isomers A and B are almost energetically identical, both of them contribute to the experiments, indicating that essentially there is no preference of solvation at the α - or β -binding site. This holds true for the acetonitrile and methanol molecules as well (*vide infra*). The possible involvement of isomers C and D cannot be excluded, which is reminiscent of recent infrared photodissociation spectroscopy and *ab initio* molecular dynamics simulation on $\text{H}_2\text{PO}_4^-(\text{H}_2\text{O})$,⁵¹ in which large amplitude motions over a small barrier, involving the structures with the doubly and singly H-bonded water molecules, were reported. The energetics of the isomerization will be detailed in the Discussion section.

In the lowest energy isomer of $\text{cis-PA}^{2-}(\text{H}_2\text{O})_2$ (iso A), two water molecules are found to evenly distribute at the α - and β -sites (1 + 1), each forming a bidentate H-bond with the respective $-\text{CO}_2^-$ group (Fig. 4). Next energetically low-lying isomers B and C (+15.55 and +15.68 kJ mol^{-1}) feature one bidentate and one singly H-bonded water molecules interacting with β/α and α/β $-\text{CO}_2^-$, respectively. For isomers D and E, which are calculated to lie 18.91 and 19.97 kJ mol^{-1} above isomer A, each features two water molecules that form an inter-water H-bond and simultaneously solvate only one $-\text{CO}_2^-$ end (2 + 0). The calculated VDE of isomer A (2.13 eV) agrees excellently with the experimental VDE = 2.07 eV determined from the main peak (Table 2). Similar to the monohydrated case, isomers B and C, which feature one singly H-bonded water molecule on one $-\text{CO}_2^-$ end and one bidentate H-bonded water molecule on the other $-\text{CO}_2^-$ end, may also contribute to the main spectral band; and their calculated VDEs are in good accordance with the experimental value. In addition, isomers D and E with the (2 + 0) solvation configuration, are calculated to have VDEs of 1.56 and 1.65 eV, in agreement with the VDE of the minor peak X' (1.45 eV) (Fig. 1 and Table 1). Thus they are proposed to exist in the experiments as well and account for the X' band. This indicates that the inter-water H-bond is present even at $n = 2$.

For $\text{cis-PA}^{2-}(\text{H}_2\text{O})_3$, isomers A–C are almost energetically identical, in which two water molecules solvate one $-\text{CO}_2^-$ moiety and one water molecule solvates the other $-\text{CO}_2^-$ end (2 + 1). In isomers D and E, three water molecules make concerted efforts to solvate one $-\text{CO}_2^-$ either at the α - or β -site leaving the other $-\text{CO}_2^-$ “naked” (3 + 0), which are 19.79 and 19.86 kJ mol^{-1} above the lowest energy isomer A. The VDEs of isomers A–C are calculated to be 2.28, 2.42, and 2.38 eV, respectively, which are all in good agreement with the experimental value of 2.30 eV (Table 2). Therefore they are proposed to exist in the experiments and contribute to the observed spectrum. Isomers D and E, on the other hand, can be ruled out, because their calculated VDEs are 0.5 and 0.7 eV lower than the experimental VDE, and no appreciable low binding energy band is observed in the spectrum.

For $\text{cis-PA}^{2-}(\text{H}_2\text{O})_4$, the structure with each $-\text{CO}_2^-$ group solvated by two water molecules is calculated to be the lowest energy isomer (iso A, 2 + 2). The next lowest energy isomers B and C, in which three water molecules solvate one $-\text{CO}_2^-$ end and one water molecule solvates the other $-\text{CO}_2^-$ end (3 + 1), are found surprisingly favorable, almost degenerate with isomer A (only 0.32 and 0.36 kJ mol^{-1} higher in energy).

The calculated VDE of isomer A (2.72 eV) agrees best with the experiment (2.75 eV) (Table 2), while the calculated VDEs of isomers B and C (2.50, 2.53 eV) align reasonably to the rising portion of the spectrum (Fig. 1). Therefore we propose that isomers A, B, and C all contribute to the experimental spectrum. The most asymmetric isomers, D and E, in which all of the four water molecules form a H-bonded cage and solvate just one $-\text{CO}_2^-$ end (4 + 0), can be excluded under experimental conditions, because they are higher energy isomers (+27.45 and +28.38 kJ mol^{-1} , respectively) and their calculated VDEs are significantly smaller than the experimental value.

$\text{cis-PA}^{2-}(\text{CH}_3\text{CN})_m$ and $\text{cis-PA}^{2-}(\text{CH}_3\text{OH})_m$ ($m = 1$ and 2). For the $\text{cis-PA}^{2-}(\text{CH}_3\text{CN})$ cluster, the acetonitrile molecule is found to solvate one $-\text{CO}_2^-$ either at the α site (iso A) or the β site (iso B) *via* forming three H-bonds in-between methyl hydrogen atoms and the negatively charged $-\text{CO}_2^-$ group (Fig. 5), a distinctly different solvation motif compared to the water-carboxylate interaction. These two isomers are close in energy as expected. The calculated VDE values of isomers A (1.60 eV) and B (1.53 eV) are consistent with the experimental value of 1.44 eV (Table 3).

The lowest energy isomer of $\text{cis-PA}^{2-}(\text{CH}_3\text{CN})_2$ (iso A) features a symmetric solvation, *i.e.*, each $-\text{CO}_2^-$ is solvated by one triply H-bonded acetonitrile (Fig. 5). When both acetonitrile molecules solvate only one $-\text{CO}_2^-$ end (for instance, the β site, labeled iso B), the energy of this structure is significantly higher by 22.40 kJ mol^{-1} above isomer A. The VDE of isomer A reproduces the experimental value very well (Table 3), while the VDE calculated from the high energy isomer B is appreciably

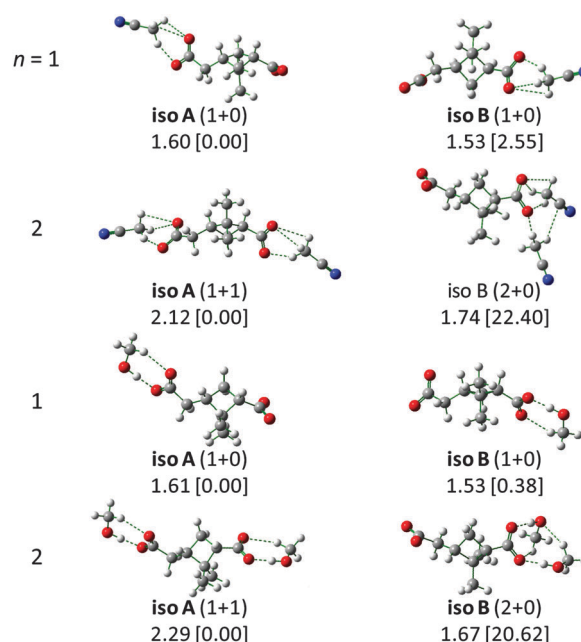


Fig. 5 M06-2X/aug-cc-pVDZ optimized structures of $\text{cis-PA}^{2-}(\text{CH}_3\text{CN})_m$ and $\text{cis-PA}^{2-}(\text{CH}_3\text{OH})_m$ clusters ($m = 1$ and 2, as indicated in the first column) (O, red; C, gray; H, light gray). The calculated VDEs (in eV) and relative energies (ΔE in kJ mol^{-1} , inside square brackets) are given. The isomers in bold are the ones which most likely exist in the experiments.

Table 3 Comparison of experimental VDE values to calculated ones and relative energies (ΔE) of the isomers for *cis*-PA²⁻(CH₃CN)_{*m*} and *cis*-PA²⁻(CH₃OH)_{*m*} (*m* = 1, 2) at the M06-2X/aug-cc-pVDZ level. The isomers in bold are the ones which most likely exist in the experiments

Clusters	Isomers	ΔE (kJ mol ⁻¹)	VDE (eV)	
			Calc.	Exp.
<i>cis</i> -PA ²⁻ (CH ₃ CN)	iso A	0.00	1.60	1.44 ± 0.05
	iso B	2.55	1.53	
<i>cis</i> -PA ²⁻ (CH ₃ CN) ₂	iso A	0.00	2.12	2.08 ± 0.05
	iso B	22.40	1.74	
<i>cis</i> -PA ²⁻ (CH ₃ OH)	iso A	0.00	1.61	1.44 ± 0.05
	iso B	0.38	1.53	
<i>cis</i> -PA ²⁻ (CH ₃ OH) ₂	iso A	0.00	2.29	2.10 ± 0.10
	iso B	20.62	1.67	

smaller than the experimental value. Hence, we suggest that isomer A is present in the experiments, but not isomer B.

The overall solvation pattern of *cis*-PA²⁻(CH₃OH)_{*m*} is very similar to that of *cis*-PA²⁻(CH₃CN)_{*m*} depicted above. For the mono-solvated *cis*-PA²⁻(CH₃OH) cluster, the optimized structures with the methanol molecule bound at the α (iso A) or β site (iso B) are energetically identical, which are stabilized by two H-bonds in-between the negatively charged -CO₂⁻ moiety with one methyl hydrogen atom (O⁻...H-C) and one hydroxyl hydrogen atom (O⁻...H-O) (Fig. 5). Optimization of the initial structure with three methyl hydrogen atoms coordinated to the -CO₂⁻ group converges to isomers A or B. The VDE values of isomers A and B are predicted to be 1.61 and 1.53 eV (Table 3), respectively, which are in good accordance with the experiment.

For *cis*-PA²⁻(CH₃OH)₂, the lowest energy isomer is found to have two methanol molecules each solvating one -CO₂⁻ end (Fig. 5, iso A). The next energetically low-lying isomer is the one with one -CO₂⁻ moiety (for instance, the β site, labeled iso B) solvated by two methanol molecules, which is 20.62 kJ mol⁻¹

higher in energy. The calculated VDE of the most stable isomer A (2.29 eV) is consistent with the experimental value of 2.10 eV. Isomer B might also be present in the experiments to account for the observed low binding energy threshold X' in the spectrum.

Mixed solvent *cis*-PA²⁻(CH₃CN)(H₂O)_{*n*} (*n* = 1 and 2) and *cis*-PA²⁻(CH₃OH)(H₂O) clusters. For the *cis*-PA²⁻(CH₃CN)(H₂O) mixed solvent cluster, two most stable structures are identified (Fig. 6, isomers A and B), in which each of the two -CO₂⁻ ends is separately solvated by one acetonitrile and one water molecule, respectively. The next low energy isomer C is found to feature a structure in which both acetonitrile and water molecules reside on one -CO₂⁻ end by forming two O⁻...H-O H-bonds with H₂O, and by formation of two O⁻...H-C (of methyl) H-bonds with CH₃CN, and one extra inter-solvent H-bond between O of H₂O and the third H of the methyl group in CH₃CN. Because totally five H-bonds are formed in isomer C, this structure is calculated to be quite favorable, only 7.81 kJ mol⁻¹ higher in energy than the global minimum. A third solvation scenario, in which the acetonitrile molecule solvates one -CO₂⁻ moiety by forming three O⁻...H-C (of methyl) H-bonds, and the water molecule binds to the N terminal of CH₃CN *via* the formation of a single N...H(OH) bond, is also identified (iso D). However, this structure is quite high in energy, lying 51.66 kJ mol⁻¹ above isomer A, and ~44 kJ mol⁻¹ above isomer C. The calculated VDEs of isomers A/B (2.12/2.11 eV) and isomer C (1.73 eV) (Table 4) align well with the EBE positions of the main spectral band X, and the low binding energy band X', respectively, suggesting that these isomers are all populated in the experiments. It is interesting to note that the X' band is significant, implying that the formation of H-bonded network in-between the acetonitrile and water solvents is preferred.

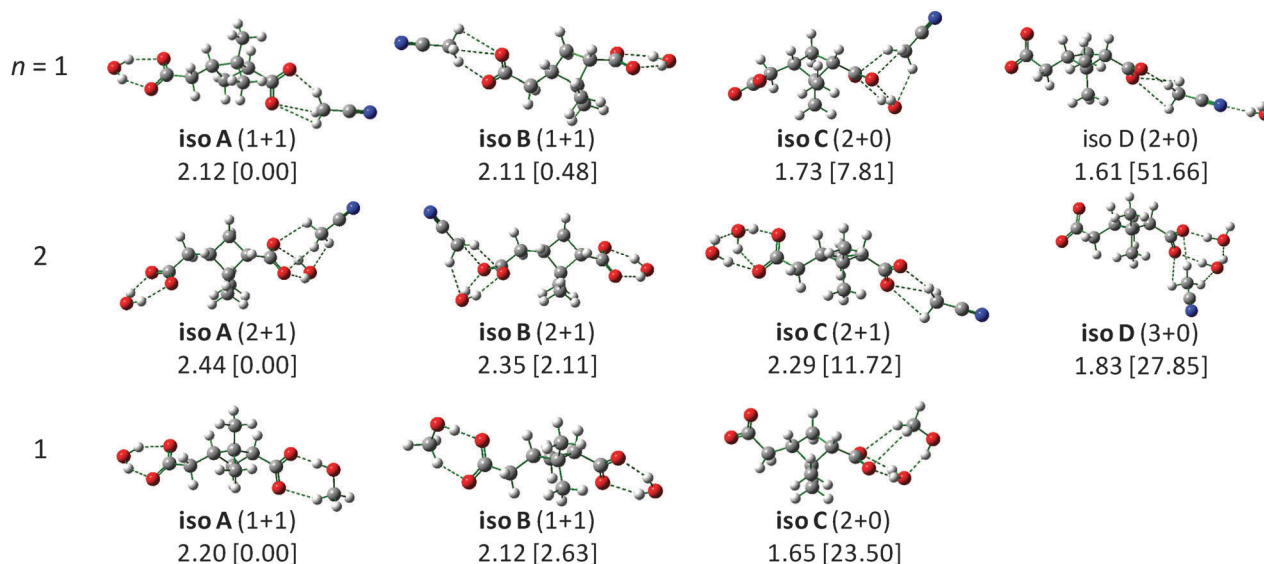


Fig. 6 M06-2X/aug-cc-pVDZ optimized structures of *cis*-PA²⁻(Sol)(H₂O)_{*n*} (Sol = CH₃CN and CH₃OH; *n* = 1 and 2, as indicated in the first column) (O, red; C, gray; H, light gray). The calculated VDEs (in eV) and relative energies (ΔE in kJ mol⁻¹, inside square brackets) are given. The isomers in bold are the ones which most likely exist in the experiments.

Table 4 Comparison of experimental VDE values to calculated ones and relative energies (ΔE) of the isomers for $cis\text{-PA}^{2-}(\text{CH}_3\text{CN})(\text{H}_2\text{O})_n$ ($n = 1, 2$) and $cis\text{-PA}^{2-}(\text{CH}_3\text{OH})(\text{H}_2\text{O})$ at the M06-2X/aug-cc-pVDZ level. The isomers in bold are the ones which most likely exist in the experiments

Clusters	Isomers	ΔE (kJ mol ⁻¹)	VDE (eV)	
			Calc.	Exp.
$cis\text{-PA}^{2-}(\text{CH}_3\text{CN})(\text{H}_2\text{O})$	iso A	0.00	2.12	2.07 ± 0.05
	iso B	0.48	2.11	
	iso C	7.81	1.73	1.50 ± 0.10
	iso D	51.66	1.61	
$cis\text{-PA}^{2-}(\text{CH}_3\text{CN})(\text{H}_2\text{O})_2$	iso A	0.00	2.44	2.29 ± 0.05
	iso B	2.11	2.35	
	iso C	11.72	2.29	1.60 ± 0.10
	iso D	27.85	1.83	
$cis\text{-PA}^{2-}(\text{CH}_3\text{OH})(\text{H}_2\text{O})$	iso A	0.00	2.20	2.08 ± 0.05
	iso B	2.63	2.12	
	iso C	23.50	1.65	

Adding a second water molecule to the naked -CO_2^- end of isomer C of $cis\text{-PA}^{2-}(\text{CH}_3\text{CN})(\text{H}_2\text{O})$ at the α - or β -site results in isomers A and B of the $cis\text{-PA}^{2-}(\text{CH}_3\text{CN})(\text{H}_2\text{O})_2$ cluster, respectively, which are predicted to be the lowest energy structures and are energetically nearly degenerate. Isomer C, in which two water molecules solvate one -CO_2^- moiety and one acetonitrile molecule solvates the other -CO_2^- , is identified and calculated to lie 11.72 kJ mol⁻¹ above isomer A. A third type of isomer, in which three solvent molecules form a solvent-cage and this cage solvates only one -CO_2^- group (isomer D), is also found and predicted to be 27.85 kJ mol⁻¹ higher in energy than isomer A. It can be seen from Table 4 that the calculated VDE values of three low-lying isomers A–C are 2.44, 2.35, and 2.29 eV, respectively, which are all close to the experimental VDE of 2.29 eV for the main spectral feature. The calculated VDE of isomer D is 1.83 eV, reasonably consistent with the experimental VDE of 1.60 eV obtained from the minor spectral band X'.

Similar to all clusters with two solvent molecules described above, the lowest-lying isomers A and B of $cis\text{-PA}^{2-}(\text{CH}_3\text{OH})(\text{H}_2\text{O})$ consist of methanol and water, each solvating one -CO_2^- group, respectively. The calculated VDEs of these two isomers, 2.20 and 2.12 eV, compare very well to the spectrum. The next low-lying isomer is identified to have an optimized structure, in which both methanol and water reside on the same side of the -CO_2^- end, forming four H-bonds with the negatively charged -CO_2^- group and one extra H-bond in-between these two solvent molecules (isomer C). This structure lies 23.50 kJ mol⁻¹ above isomer A, and its calculated VDE (1.65 eV) is appreciably smaller than the experimental VDE (2.08 eV). However, a close examination of the experimental spectrum (Fig. 3) indicated that the calculated VDE of isomer C falls in the onset region, suggesting that this asymmetrically solvated (2 + 0) isomer may also exist and contribute to the spectrum, albeit with very small population. Nevertheless, the contribution is much smaller than that for $cis\text{-PA}^{2-}(\text{H}_2\text{O})(\text{CH}_3\text{CN})$. The binding energies of CH_3CN and CH_3OH with $cis\text{-PA}^{2-}(\text{H}_2\text{O})$ are calculated to be 79.66 and 67.96 kJ mol⁻¹, respectively, exhibiting that the inter-solvent interactions of $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ is stronger than that of $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ in the complexes studied here, which support our experimental observation.

Discussion

Comparison of microhydration patterns between $cis\text{-PA}^{2-}$ and aliphatic dicarboxylates DC_n^{2-} – observing asymmetric solvation for the former

Since $cis\text{-PA}^{2-}$ is a dicarboxylate dianion, but linked by a rigid four-membered carbon ring and one methylene group (CH_2) between two -CO_2^- ends instead of by flexible aliphatic chains $\text{-(CH}_2)_n\text{-}$ in DC_n^{2-} ($\text{O}_2\text{C(CH}_2)_n\text{CO}_2^-$), it would be interesting to compare the solvation patterns between $cis\text{-PA}^{2-}$ of the current work and DC_n^{2-} that have been previously studied.^{34–37} As expected, both dianions show preference for alternating solvation on the two negatively charged -CO_2^- groups with solvent water molecules, resulting in the odd–even variations in the EBE and the spectral band shape with the addition of water as described above in detail. The broader and more complicated bands for clusters with odd number of water molecules than ones with even number of water molecules are due to the fact that the number of solvent water molecules interacting with two -CO_2^- ends differs by one in the former case, while equals the latter, which is significant for small hydrated clusters. This preference of solvation in a fashion as “symmetric” as possible is a direct consequence of the stronger $\text{CO}_2-\text{H}_2\text{O}$ interaction than the $\text{H}_2\text{O}-\text{H}_2\text{O}$ interaction. Interestingly, by comparing the experiments and calculations, we are able to assign the small feature (X') at low EBE in the spectrum of $cis\text{-PA}^{2-}(\text{H}_2\text{O})_2$ to the contributions of high energy (2 + 0) type isomers with both water molecules solvating only one -CO_2^- end. This asymmetric isomer has not been observed before for $\text{DC}_n^{2-}(\text{H}_2\text{O})_2$ clusters, showing the subtle effect of the rigid four-membered ring substituting the flexible aliphatic chains. For the larger $cis\text{-PA}^{2-}(\text{H}_2\text{O})_4$ cluster, we also found the existence of this type of asymmetrically solvated (3 + 1) isomers, *i.e.*, three water molecules solvate one -CO_2^- end and one water molecule solvates the other -CO_2^- end in the experiments; while only the (2 + 2) type solvated structures were exclusively found in the spectra of $\text{DC}_n^{2-}(\text{H}_2\text{O})_4$ clusters. The observation of high energy asymmetrically solvated isomers in $cis\text{-PA}^{2-}(\text{H}_2\text{O})_{2,4}$ but not in $\text{DC}_n^{2-}(\text{H}_2\text{O})_{2,4}$ may be indicative of the fact that barriers between symmetrically solvated clusters (global minima) and asymmetric ones (high energy) are significantly higher in $cis\text{-PA}^{2-}$ than in DC_n^{2-} , as a result of the rigid four-membered ring in backbone that links the two carboxylate ends in the former dianionic species. The isomerization barrier in-between the (1 + 1) and (2 + 0) structures for $cis\text{-PA}^{2-}(\text{H}_2\text{O})_2$ is estimated to be about 67 kJ mol⁻¹. It is worth pointing out that high energy isomers in several cluster systems were found to be kinetically trapped even at low temperatures.^{52–55}

Comparison of solvation patterns of $cis\text{-PA}^{2-}$ in different solvents

Distinctly different interaction motifs between the -CO_2^- group and various solvents are unraveled in this work. Specifically, H_2O interacts with the -CO_2^- group of $cis\text{-PA}^{2-}$ via a bidentate $\text{O}^-\cdots\text{H}-\text{O}$ H-bond, CH_3CN interacts with $cis\text{-PA}^{2-}$ through its methyl hydrogens by forming a tridentate $\text{O}^-\cdots\text{H}-\text{C}$ H-bond,

and CH₃OH interacts with *cis*-PA²⁻ by forming two H-bonds *via* its hydroxyl hydrogen O⁻⋯H-O and one of its methyl hydrogens O⁻⋯H-C with the -CO₂⁻ group. Interestingly, in the spectrum of *cis*-PA²⁻(CH₃OH)₂, we observed a low EBE band (X') which is assigned to a high energy isomer with an asymmetrically solvated structure (2 + 0). A similar (2 + 0) isomer is identified in the case of H₂O as well. However, for *cis*-PA²⁻(CH₃CN)₂, the (2 + 0) type isomer has higher energy and there is also no spectral evidence for its existence in the experiments. For the mixed solvent solvated *cis*-PA²⁻ clusters, we also observed distinct differences for inter-solvent interactions. Both experiment and theory support the existence of (2 + 0) and (3 + 0) type isomers for *cis*-PA²⁻(CH₃CN)(H₂O) and *cis*-PA²⁻(CH₃CN)(H₂O)₂, respectively, indicating that the inter-solvent H-bond interactions between CH₃CN and H₂O are very favorable. For the *cis*-PA²⁻(CH₃OH)(H₂O) clusters, however, the small contribution from the (2 + 0) structure cannot be ruled out. These observed differences in solvation stem from the delicate balance between solute-solvent and solvent-solvent interactions, and provide molecular level insights why proteins have different functions and structures in different solvent environments.^{28–31}

Conclusions

We studied the microsolvation of *cis*-pinate by H₂O, CH₃CN, and CH₃OH using NIPES and *ab initio* calculations. Both the spectral features and EBEs show an interesting odd-even effect, indicating that the solvents alternately solvate the two negative -CO₂⁻ groups preferably. A comparison between the experiments and calculations suggests that two types of isomers, *i.e.*, symmetric (1 + 1) and asymmetric (2 + 0), exist for both *cis*-PA²⁻(H₂O)₂ and *cis*-PA²⁻(CH₃OH)₂ clusters. The existence of asymmetric isomers in *cis*-PA²⁻, but not in DC_n²⁻, is likely due to kinetic reasons, *i.e.*, the barriers connecting symmetric and asymmetric structures are higher in the former.

For mixed H₂O/CH₃CN solvated clusters, the (2 + 0) and (3 + 0) types of high energy isomers may also be populated in the experiments as evidenced by the appearance of small low EBE features in the spectra, and supported by calculations which show good agreement between experimental and calculated VDEs based on these structures. For the *cis*-PA²⁻(CH₃OH)(H₂O) clusters, however, the small contribution from the (2 + 0) structure cannot be ruled out. This difference shows that the formation of inter-solvent H-bond interactions in-between H₂O and CH₃CN is much more favorable than that in-between H₂O and CH₃OH, and displays the delicate balance of solute-solvent and solvent-solvent interactions at work to determine the structures of solvated clusters. This study provides molecular level description of the interactions between carboxylate and three common solvents, and may shed light on the mechanism of cluster growth and the formation of atmospheric organic aerosols, as well as the different functions and structures of proteins in different solvent environments.

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