

Molecular-level origin of the carboxylate head group

response to divalent metal ion complexation at the

air-water interface

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Molecular-level origin of the carboxylate head group response to divalent metal ion complexation at the air-water interface

We exploit gas-phase cluster ion techniques to provide insight into the local interactions underlying divalent metal ion-driven changes in the spectra of carboxylic acids at the air-water interface. This information clarifies the experimental findings that the CO stretching bands of long-chain acids appear at very similar energies when the head group is deprotonated by high subphase pH or exposed to relatively high concentrations of Ca²⁺ metal ions. To this end, we report the evolution of the vibrational spectra of size-selected $[Ca^{2+} \cdot RCO_2^{-}]^+ \cdot (H_2O)_{n=0 \text{ to } 12}$ and $RCO_2^{-} \cdot (H_2O)_{n=0 \text{ to } 14}$ cluster ions toward the features observed at the air-water interface. Surprisingly, not only does stepwise hydration of the RCO_2^- anion and the $[Ca^{2+} RCO_2^{-}]^+$ contact ion pair yield solvatochromic responses in opposite directions, but in both cases, the responses of the 2 (symmetric and asymmetric stretching) CO bands to hydration are opposite to each other. The result is that both CO bands evolve toward their interfacial asymptotes from opposite directions. Simulations of the $[Ca^{2+} RCO_2^{-}]^+ (H_2O)_n$ clusters indicate that the metal ion remains directly bound to the head group in a contact ion pair motif as the asymmetric CO stretch converges at the interfacial value by n = 12. This establishes that direct metal complexation or deprotonation can account for the interfacial behavior. We discuss these effects in the context of a model that invokes the water network-dependent local electric field along the C-C bond that connects the head group to the hydrocarbon tail as the key microscopic parameter that is correlated with the observed trends.

1/ Different between pH and divalent saltreduced deprotonation of carboxylic headgroupby observing on CO stretch2/ complex binding between first and secondhydration shell

3/a small comparison between Mg^{2+} and Ca^{2+}

Comparison between deprotonated of carboxylate by pH and salt



Two bands of C-OH and C=O split into COO⁻_{ss} (1413 cm⁻¹) and COO⁻_{as} (1551 cm⁻¹) by increasing pH and adding CaCl₂
 COO⁻_{as} (1551 cm⁻¹) by adding CaCl₂ is broader than pD 10.5, this might give a complex binding between Ca²⁺ with COO⁻ which is a question in this study.

Physical properties of isotopologues of water^[11]

Property	D ₂ O (Heavy water)	HDO (Semiheavy water)	H ₂ O (Light water)	
Melting point (standard pressure)	3.82 °C (38.88 °F; 276.97 K)	2.04 °C (35.67 °F; 275.19 K)	0.0 °C (32.0 °F; 273.1 K)	
Boiling point	101.4 °C (214.5 °F; 374.5 K)	100.7 °C (213.3 °F; 373.8 K)	100.0 °C (212.0 °F; 373.1 K)	
Density at STP (g/mL)	1.1056	1.054	0.9982	
Temp. of maximum density	11.6 °C	Unverified	3.98 °C ^[12]	
Dynamic viscosity (at 20 °C, mPa⋅s)	1.2467	1.1248	1.0016	
Surface tension (at 25 °C, N/m)	0.07187	0.07193	0.07198	
Heat of fusion (kJ/mol)	6.132	6.227	6.00678	
Heat of vaporisation (kJ/mol)	41.521	Unverified	40.657	
pH (at 25 °C) ^[13]	7.44 ("pD")	7.266 ("pHD")	7.0	
p <i>K</i> _b (at 25 °C) ^[13]	7.44 ("pK _b D ₂ O")	Unverified	7.0	
Refractive index (at 20 °C, 0.5893 µm) ^[14]	1.32844	Unverified	1.33335	

https://en.wikipedia.org/wiki/Heavy_water

The pD of heavy water is generally measured using pH electrodes giving a pH (apparent) value, or pHa, and at various temperatures a true acidic pD can be estimated from the directly pH meter measured pHa, such that pD+ = pHa (apparent reading from pH meter) + 0.41. The electrode correction for alkaline conditions is 0.456 for heavy water.

□Introduction to ion pair

Types of Ion Pairing







SIP CIP

2SIP

Schematic representations



Fully solvated ion-pair

Solvent-shared ion-pair Solvent-separated ion-pair Cation outer-sphere complex Contact ion-pair Cation inner-sphere complex Adrien P. A. Sthoer ,Doctoral thesis, Erictyrode group

2SIP : distant of two solvent molecules
SIP : solvent layer separates the ions
CIP : contact ion pair

https://en.wikipedia.org/wiki/lon_association

Coordination modes of the carboxylate moiety



D pH reduced deprotonation

\Box Ca²⁺ reduced deprotonation



U Without divalent metal

Frequency (cm⁻¹)

D₂ Predissociation Yield



 \Box With Mg²⁺

 \Box COO⁻ as is blue shift when binding with Mg²⁺ and increasing n cluster





Table S2. Carboxylate Stretching Band Positions of Hydrated *d*-OPr

$CD_3CD_2COO^{-} \cdot (H_2O)_n$	MP2/aug-cc-pVDZ	MP2/aug-cc-pVDZ	Gas-phase	Gas-phase
	scaled by 0.986	scaled by 0.986	cluster	cluster
			$(\pm 4 \text{ cm}^{-1})$	$(\pm 4 \text{ cm}^{-1})$
n	v _s ^{coo}	v_{as}^{COO}	v_s^{COO}	v_{as}^{COO}
0	1331	1600	1338	1613
1	1356	1583	1356	1591
2	1374	1589	1374	1588
3	1381	1578	1378	1586
4	1391	1564	1384	1576
5 (3:1)	1379	1590	1375	1599
5 (2:2)	1398	1561		
6	1396	1566	1387	1568
7			1387	1572
14			1405	1549

\Box n=5 has a particularly interesting of different binding with others





\Box d₃₁-PA on 0.3M of CaCl₂

□ calculated at the MP2/aug-cc-pVDZ level of theory for n=0-5

 \Box infrared multiple photon-induced dissociation (IRMPD) for n= 6, 10, 12

 \Box 1/ COO⁻ _{as} is blue shift

 \square 2/ water bending mode is red shift for n=1-5 but then blue shift

$[Ca2+CD_3CD_2COO^-]^+ \cdot (H_2O)_n$	MP2/aug-cc-pVDZ scaled by 0.986	MP2/aug-cc-pVDZ scaled by 0.986	Gas-phase cluster	Gas-phase cluster
	5	5	$(\pm 4 \text{ cm}^{-1})$	$(\pm 4 \text{ cm}^{-1})$
n	v_s^{COO}	v_{as}^{COO}	v_s^{COO}	v_{as}^{COO}
0	1459	1421	1461	1431
1	1465	1437	1460	1448
2	1458	1462	1458	1471
3	1453	1478	1453	1486
4	1453	1480	1451	1494
5	1445	1494	1451	1496
6	1458	1496	1446	1511
8	1447	1499	1447	1521
10	1424	1527	1444	1527
12	1446	1521	1448	1536
13			1439	1539

Table S3. Metal Carboxylate Stretching Band Positions of Hydrated d-[Ca²⁺·OPr⁻]⁺

\Box Ca²⁺ with carboxylate



\Box Mg²⁺ with carboxylate



1st hydration shell



A summary of different between pH and divalent salt reduced deprotonation of carboxylic headgroup by observing on 2 CO stretch



1) both systems closely approach the behavior of the bulk interface in the size range corresponding to filling the second hydration shell,

2) the 2 CO stretching features approach these asymptotes with opposite solvatochromic shifts

3) the shifts in the contact ion pair are opposite from those displayed by the bare ion.

