

Supporting Information for Swalina *et al.*, “Solvation and Solvatochromism in CO₂ – Expanded Liquids. 3. The Dynamics of Nonspecific Preferential Solvation”

Analysis of DCS Atomic Charge Sets:

We present a comparison of the energetics observed for two different DCS atomic charge distributions employed in simulations of DCS in CH₃CN, CO₂, and the GXL mixture where $x_{\text{CO}_2} = 0.95$. The first charge set, which we will denote as S-AM1, is comprised of the scaled AM1 charges described in the Simulation Models and Methods section. The S₀ and S₁ charges for the second set have been calculated using the second-order approximate coupled-cluster method¹ including the resolution of the identity approximation (RICC2)^{2, 3} using the Turbomole⁴ program. The SVP basis set was used in conjunction with optimized auxiliary basis sets⁵ for the RI approximation. S₀ and S₁ charges were calculated with ESP fits using the method of Singh and Kollman⁶. This second set of charges is denoted as CC2. The CC2 and S-AM1 charge sets were both determined using the same planar *trans*-DCS structure.

Table SI-1: Properties of S₀ and S₁ *trans*-DCS.

<i>method</i>	μ_0 / D	μ_1 / D	ΔE / eV	f
AM1/CI	6.21 ^a (8.36) ^b	14.5 (20.97) ^b	3.38 ^a	0.96 ^a
RICC2	8.46	21.67	3.84	1.32
Experiment	7.0 ^c	21 ^c	3.29 ^d	0.6-0.8 ^e

^a Ref. ⁷ AM1 level.

^b Value determined from S-AM1 charge set.

^c Ref. ⁸

^d Ref. ⁷ From the absorption maximum in hexane.

^e Ref. ⁷ Range observed in various solvents.

Values of S₀ and S₁ dipole moments, excitation energies and oscillator strengths for DCS are presented in Table SI-1. The difference in S₀ and S₁ dipole moments calculated using the RICC2 approach, 13.2 D, is much closer to experiment than the value from AM1/CI, which differs from experiment by ~6 D. The S-AM1 charge set produces a dipole moment change which is similar to both the experimental and RICC2 values. Differences between the experimental values for the excitation energy, ΔE , and oscillator strength, f , compared to those calculated at the RICC2 level may be reduced by optimizing the ground state DCS structure at the same level of theory. Additional calculations to more precisely determine these trends may be undertaken, but for our present purposes, these RICC2 level calculations are sufficient.

Visual representations of the S-AM1 and CC2 charges for the S₁ and S₁ – S₀ differences are provided in Figure SI-1. The S₁ charge sets are very similar. The S₁ – S₀ charge difference sets (which are used to determine solute-solvent interactions for spectroscopic observables) possess qualitative similarities. A more quantitative comparison of all the charge sets is presented in Figure SI-2, which displays linear correlation plots between the S-AM1 and CC2 charges.

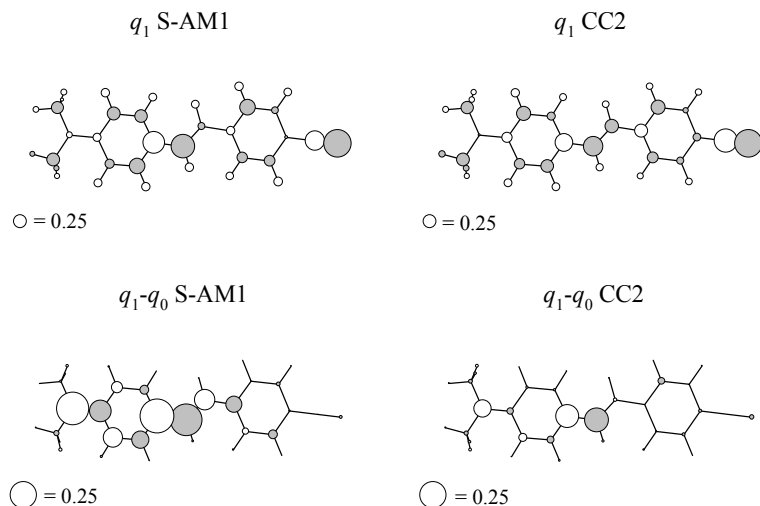


Figure SI-1

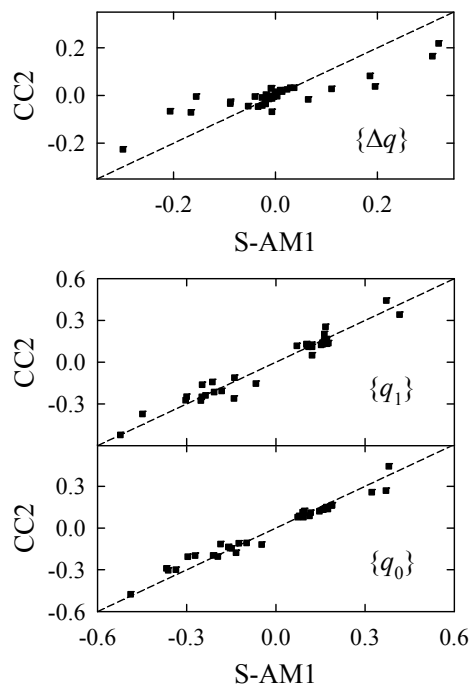


Figure SI-2.

Equilibrium molecular dynamics simulations of S_1 DCS in CH_3CN , CO_2 , and the $\text{CH}_3\text{CN}+\text{CO}_2$ solvent mixture ($x_{\text{CO}_2} = 0.95$) were conducted using the S-AM1 and CC2 DCS charge sets under the same conditions as described in the Simulation Models and Methods section of the present paper. Tabulated simulation parameters are provided at the end of this section. Energetics obtained with the two sets of charges are presented in Table SI-2.

The largest difference in the average solute–solvent electrostatic interaction, $\langle U_{\text{el}} \rangle_1$, between the S-AM1 and CC2 charge sets is for CO_2 – interactions between DCS and CO_2 are 18% higher for the S-AM1 charge set. For the CH_3CN and $x_{\text{CO}_2} = 0.95$ solutions, $\langle U_{\text{el}} \rangle_1$ differs by only 1-2% between the two charge sets. This seems reasonable considering that the S-AM1 set was scaled according to the Stokes shift for neat CH_3CN .

Table SI-2: Comparison of energetics simulated for the S_1 electronic state of DCS using the S-AM1 and CC2 DCS atomic charge sets. All values are in units of 1000 cm^{-1} .

	$\{q\}$	$-\langle U_{\text{el}} \rangle$	$-\langle \Delta U_{\text{el}} \rangle$	$\langle \delta \Delta U_{\text{el}}^2 \rangle / k_B T$
CH_3CN	S-AM1	8.53	3.77	3.36
	CC2	8.42	4.19	3.52
CO_2	S-AM1	2.94	0.907	0.849
	CC2	2.49	0.917	0.794
$x_{\text{CO}_2}=0.95$	S-AM1	5.55	2.46	2.60
	CC2	5.68	2.89	2.89

The solvent electrostatic interaction with the DCS $S_1 - S_0$ charge differences observed in S_1 , $\langle \Delta U_{\text{el}} \rangle_1$, are 10% (CH_3CN) and 15% ($x_{\text{CO}_2} = 0.95$) smaller for the S-AM1 charge set. For CO_2 , $\langle \Delta U_{\text{el}} \rangle_1$ differs by only 1% between the two charge sets. The larger $\langle \Delta U_{\text{el}} \rangle_1$ interactions observed for the CC2 set in solutions with CH_3CN may be due to the nature of the $\{\Delta q\}$ distribution – the S-AM1 set consists mainly of dipoles spread over the DCS framework, whereas the CC2 set contains a more localized positive charge on the dimethyl amino region (Figure SI-1). Linear response estimates for the Stokes shifts calculated from fluctuations of the solvent electrostatic interaction with the DCS $S_1 - S_0$ charge differences observed in S_1 , $\langle \delta \Delta U_{\text{el}}^2 \rangle_1 / k_{\text{B}}T$, differ by 5 – 10% between the two charge sets.

Time correlation functions for $\langle \Delta U_{\text{el}} \rangle_1$ observed in S_1 using the CC2 and S-AM1 charge sets for the three solvents are presented in Figure SI-3. The TCFs for the two charge distributions are remarkably similar. Thus, despite some small differences in individual charges, the CC2 and S-AM1 charge sets produce the same Stokes shift dynamics.

Overall, the scaled AM1 charges used for our GXL work are similar to ones obtained from high-level *ab initio* electronic structure calculations at the RICC2 level. Comparable solute-solvent electrostatic interactions were observed for both charge sets for simulations of DCS+ CH_3CN , CO_2 , and the $\text{CH}_3\text{CN}+\text{CO}_2$ mixture. Most importantly, both charge sets give rise to very similar Stokes shift dynamics. This correspondence validates our use of S-AM1 charges for the analysis presented in the paper. In future work, we nevertheless recommend use of the new CC2 charge set.

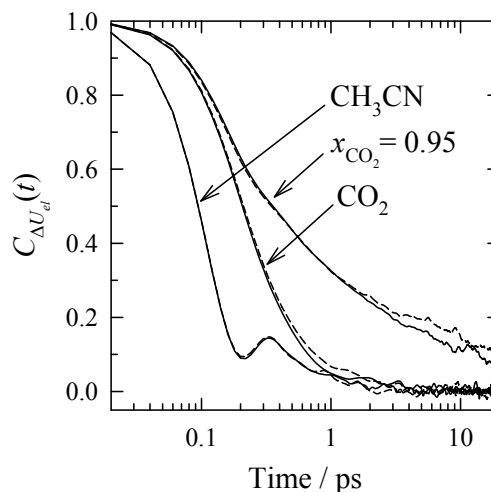


Figure SI-3. Time correlation functions for the electrical shift observed in S_1 electronic state of DCS. Dashed lines represent values obtained using the CC2 charge set.

References

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Table SI-3: Parameters used for DCS/CH₃CN+CO₂ GXL simulations. Atomic charges correspond to the CC2 charge set.

#	Symb.	Mol	$\varepsilon/k/K$	$\sigma/\text{\AA}$	Mass	q_0/e	q_1/e	$\Delta q/e$
1	CA	DCS	35.22	3.55	12.011	-0.107026	-0.111463	-0.004437
2	CA	DCS	35.22	3.55	12.011	-0.205502	-0.273615	-0.068113
3	CA	DCS	35.22	3.55	12.011	0.258182	0.254015	-0.004167
4	CA	DCS	35.22	3.55	12.011	-0.198068	-0.214318	-0.01625
5	CA	DCS	35.22	3.55	12.011	-0.109141	-0.1426	-0.033459
6	CA	DCS	35.22	3.55	12.011	-0.118075	-0.153105	-0.03503
7	HA	DCS	15.1	2.42	1.008	0.141761	0.129017	-0.012744
8	HA	DCS	15.1	2.42	1.008	0.137558	0.132766	-0.004792
9	HA	DCS	15.1	2.42	1.008	0.144898	0.124166	-0.020732
10	HA	DCS	15.1	2.42	1.008	0.140035	0.136884	-0.003151
11	CM	DCS	38.24	3.55	12.011	-0.298784	-0.260837	0.037947
12	CM	DCS	38.24	3.55	12.011	-0.146219	-0.372249	-0.22603
13	HA	DCS	15.1	2.42	1.008	0.150744	0.136347	-0.014397
14	HA	DCS	15.1	2.42	1.008	0.120616	0.146004	0.025388
15	CA	DCS	35.22	3.55	12.011	0.123326	0.3417	0.218374
16	CA	DCS	35.22	3.55	12.011	-0.177002	-0.247822	-0.07082
17	CA	DCS	35.22	3.55	12.011	-0.289086	-0.207125	0.081961
18	CA	DCS	35.22	3.55	12.011	0.26882	0.203065	-0.065755
19	CA	DCS	35.22	3.55	12.011	-0.302752	-0.274959	0.027793
20	CA	DCS	35.22	3.55	12.011	-0.135428	-0.162093	-0.026665
21	HA	DCS	15.1	2.42	1.008	0.134536	0.156885	0.022349
22	HA	DCS	15.1	2.42	1.008	0.164848	0.156203	-0.008645
23	HA	DCS	15.1	2.42	1.008	0.162144	0.166268	0.004124
24	HA	DCS	15.1	2.42	1.008	0.132036	0.141299	0.009263
25	CZ	DCS	75.48	3.65	12.011	0.444727	0.44346	-0.001267
26	NZ	DCS	85.55	3.2	14.007	-0.475828	-0.522593	-0.046765
27	NT	DCS	85.55	3.3	14.007	-0.115125	0.049934	0.165059
28	CT	DCS	33.21	3.5	12.011	-0.196612	-0.23859	-0.041978
29	HC	DCS	15.1	2.5	1.008	0.110019	0.125775	0.015756
30	HC	DCS	15.1	2.5	1.008	0.08752	0.117333	0.029813
31	HC	DCS	15.1	2.5	1.008	0.078135	0.110471	0.032336
32	CT	DCS	33.21	3.5	12.011	-0.204448	-0.249162	-0.044714
33	HC	DCS	15.1	2.5	1.008	0.087329	0.118257	0.030928
34	HC	DCS	15.1	2.5	1.008	0.113649	0.130175	0.016526
35	HC	DCS	15.1	2.5	1.008	0.078212	0.110508	0.032296
36	O	CO2	80.51	3.033	15.999	-0.3256	-0.3256	0
37	C1	CO2	28.13	2.757	12.011	0.6512	0.6512	0
38	O	CO2	80.51	3.033	15.999	-0.3256	-0.3256	0
39	Me	ACN	191	3.6	15.035	0.269	0.269	0
40	C2	ACN	50	3.4	12.011	0.129	0.129	0
41	N	ACN	50	3.3	14.007	-0.398	-0.398	0

Table SI-4: Coordinates for DCS and the S-AM1 charge set.

#	Symb.	x	y	z	q_0/e	q_1/e	$\Delta q/e$
1	C	12.6613038	8.83543481	-8.464155	-0.09843	-0.13901	-0.04059
2	C	12.7211476	7.46384332	-8.3192522	-0.29631	-0.30336	-0.00705
3	C	12.3423114	6.60795815	-9.3540603	0.32216	0.16668	-0.15548
4	C	11.9225342	7.178034	-10.558539	-0.27187	-0.20771	0.06416
5	C	11.8569622	8.54692936	-10.711574	-0.12472	-0.21347	-0.08875
6	C	12.2239619	9.38486397	-9.6629773	-0.0478	-0.06706	-0.01926
7	H	12.9505047	9.47943526	-7.6544791	0.16468	0.1578	-0.00688
8	H	13.0575814	7.04843983	-7.3863583	0.17486	0.1716	-0.00326
9	H	11.6641535	6.5495271	-11.389567	0.17186	0.15226	-0.0196
10	H	11.5333577	8.97105737	-11.643998	0.17317	0.17644	0.00327
11	C	12.411755	5.15080829	-9.1370452	-0.33642	-0.14102	0.1954
12	C	12.0942481	4.21820696	-10.029985	-0.14924	-0.44869	-0.29945
13	H	12.7163264	4.85568328	-8.1476959	0.16927	0.15689	-0.01238
14	H	11.9858287	4.5343602	-11.054271	0.14643	0.16914	0.02271
15	C	12.1559395	2.75950667	-9.8486186	0.09564	0.41574	0.3201
16	C	11.797476	1.920651	-10.898008	-0.134	-0.30015	-0.16615
17	C	11.8233288	0.54446922	-10.786212	-0.36799	-0.18257	0.18542
18	C	12.2174961	-0.0743169	-9.5939977	0.37032	0.16341	-0.20691
19	C	12.6049411	0.76914185	-8.5402834	-0.36203	-0.25212	0.10991
20	C	12.5714732	2.14005837	-8.6709754	-0.15967	-0.2479	-0.08823
21	H	11.4842781	2.35056155	-11.834171	0.16056	0.16985	0.00929
22	H	11.5337186	-0.0390333	-11.636674	0.18904	0.16239	-0.02666
23	H	12.9437983	0.35864781	-7.6106237	0.1881	0.16936	-0.01874
24	H	12.8964755	2.73452391	-7.836555	0.15811	0.15726	-0.00086
25	C	12.1605901	10.817446	-9.8245364	0.37994	0.37117	-0.00877
26	N	12.1100786	11.9459981	-9.9521561	-0.48866	-0.52288	-0.03422
27	N	12.2181795	-1.453309	-9.4551108	-0.18583	0.12188	0.30771
28	C	12.9060833	-2.0411587	-8.325836	-0.21075	-0.23655	-0.0258
29	H	12.8059737	-3.1158225	-8.3730586	0.11704	0.12032	0.00327
30	H	13.9680027	-1.7980619	-8.3030699	0.07895	0.0707	-0.00825
31	H	12.4622452	-1.7189581	-7.3918739	0.09252	0.12159	0.02907
32	C	12.087053	-2.2719333	-10.640892	-0.19537	-0.24903	-0.05366
33	H	12.8873632	-2.1053121	-11.361247	0.11316	0.10422	-0.00894
34	H	12.1011595	-3.3133505	-10.353706	0.09001	0.10309	0.01308
35	H	11.1404702	-2.0881949	-11.134239	0.07326	0.10973	0.03647

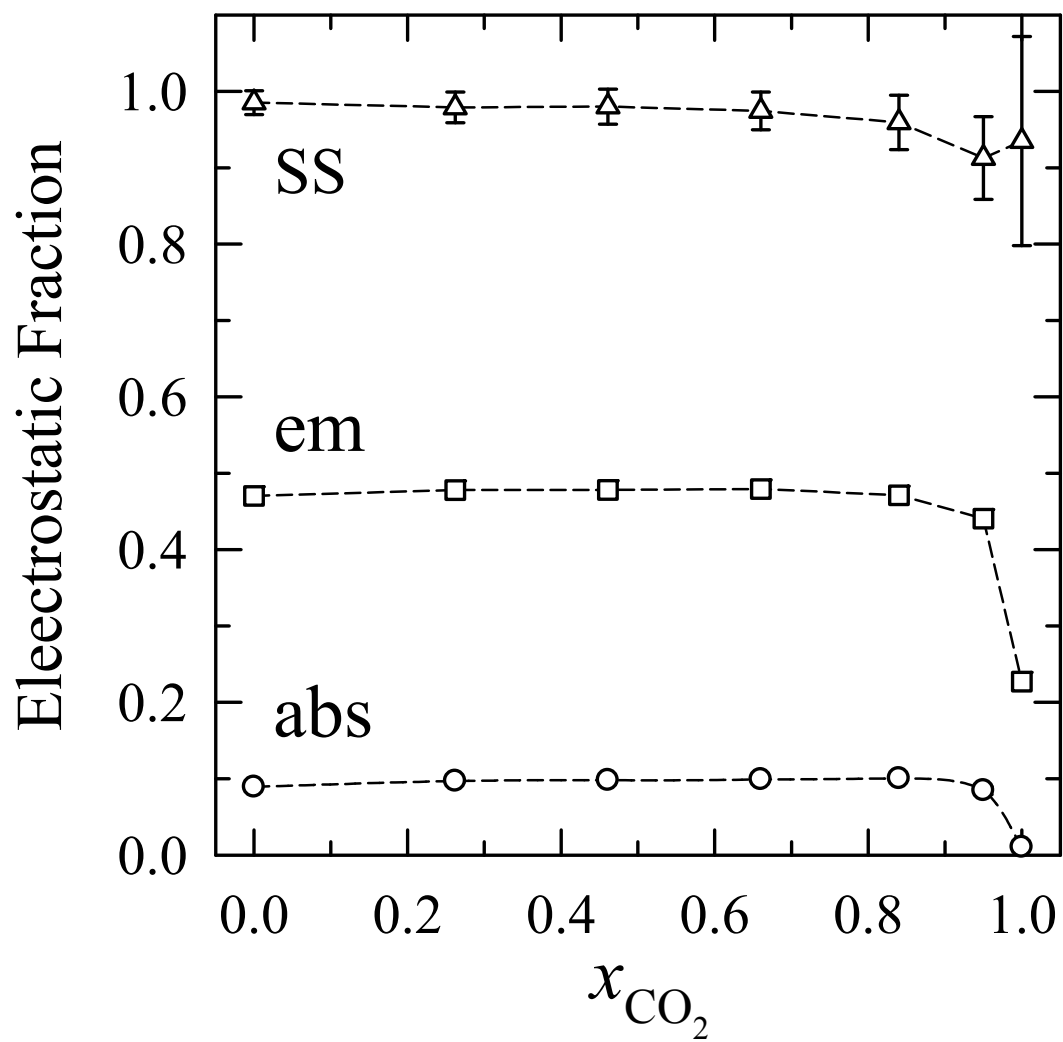
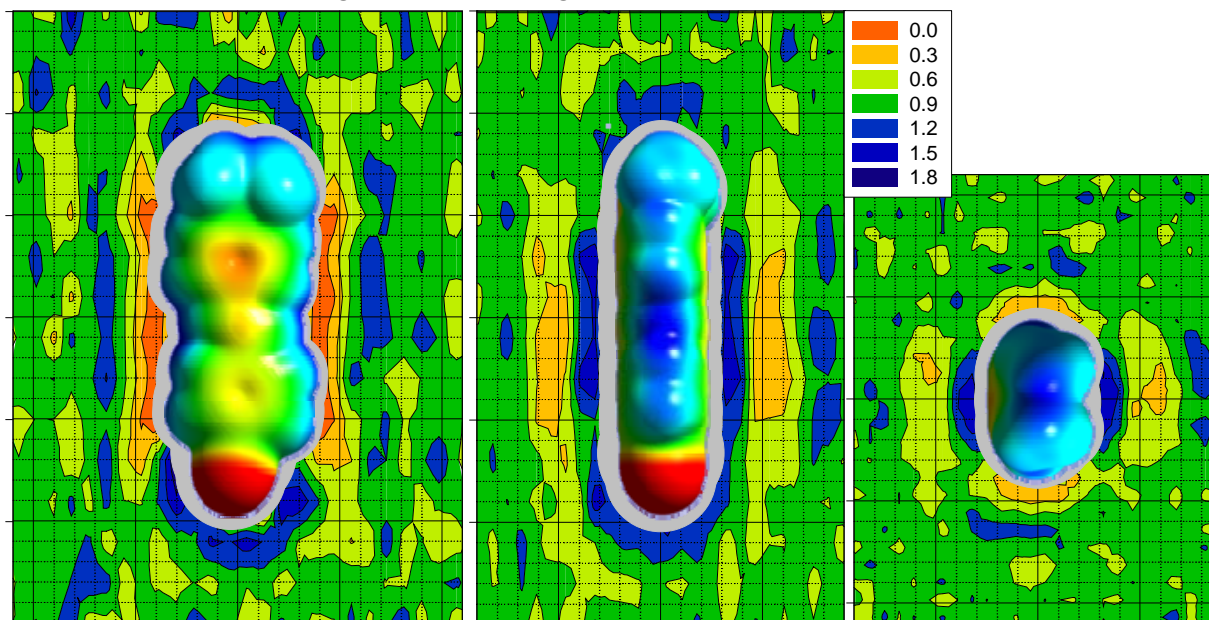


Fig. SI-4

Figure SI-4: Fraction of the simulated absorption (abs), emission (em), and Stokes shift (SS) contributed by electrostatic interactions as functions of composition.

CH₃CN – CH₃ Site Distribution



CH₃CN – N Site Distribution

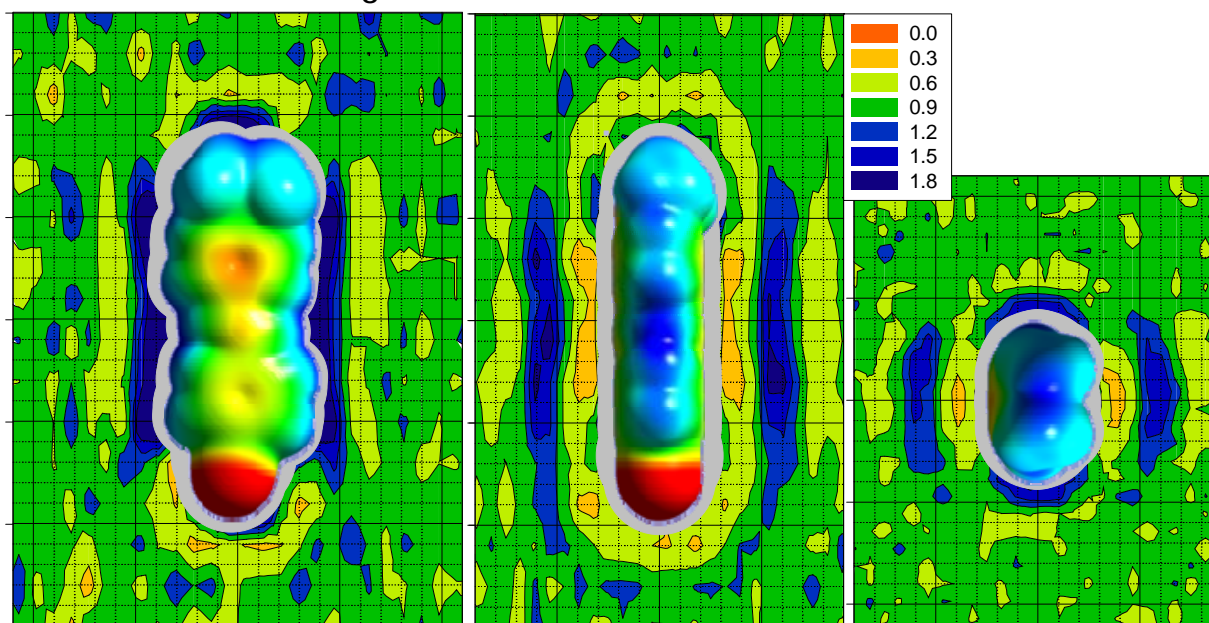


Figure SI-5: Enrichment factors of CH₃CN atoms observed in the $x_{\text{CO}_2} = 0.95$ system. These enrichment factors are defined as $(N_i(\vec{r})/\Sigma_i N_i(\vec{r}))/x_i$ where $N_i(\vec{r})$ denotes the number of atoms of type i at a location \vec{r} and x_i denotes the bulk mole fraction of such atoms. Molecule insets show an electrostatic map at the 0.004 au isodensity surface (see Fig. 10 and text).