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Efficient Calculation of Absorption Spectra in Solution: Approaches for Selecting Representative Solvent Configurations and for Reducing the Number of Explicit Solvent Molecules

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Table S1 Lennard-Jones parameters and partial charges of atoms in QB.

No.	Site	ε/k_b (K)	σ/Å	q/e
1	C	30.70	3.60	−0.149
2	C	55.00	3.20	0.085
3	C	55.00	3.20	−0.014
4	C	30.70	3.60	−0.135
5	C	30.70	3.60	−0.108
6	H	25.45	2.36	0.087
7	C	30.70	3.60	−0.022
8	H	25.45	2.36	0.101
9	H	25.45	2.36	0.105
10	C	30.70	3.60	−0.080
11	C	30.70	3.60	0.100
12	H	25.45	2.36	0.139
13	H	25.45	2.36	0.135
14	H	25.45	2.36	0.152
15	N	57.00	3.20	−0.195
16	CH_3	98.00	3.75	0.251
17	H	0.00	0.00	0.000
18	H	0.00	0.00	0.000
19	H	0.00	0.00	0.000
20	C	30.70	3.60	0.062
21	O	118.00	3.04	−0.514

1 Å = 0.1 nm

Table S2 Ground state and excited state charges of QB calculated from gas phase TD-CAM-B3LYP/6-311+G(*d*,*p*)

No.	Atom	q_{GS}/e	q_{ES}/e
1	C	−0.133	−0.066
2	C	0.113	0.098
3	C	−0.010	−0.011
4	C	−0.151	−0.050
5	C	−0.093	−0.095
6	H	0.098	0.114
7	C	−0.046	−0.145
8	H	0.088	0.115
9	H	0.102	0.107
10	C	−0.102	−0.114
11	C	0.066	0.016
12	H	0.120	0.086
13	H	0.115	0.106
14	H	0.130	0.109
15	N	−0.195	−0.260
16	C	−0.112	−0.124
17	H	0.123	0.108
18	H	0.123	0.109
19	H	0.105	0.103
20	C	0.097	0.123
21	O	−0.436	−0.330

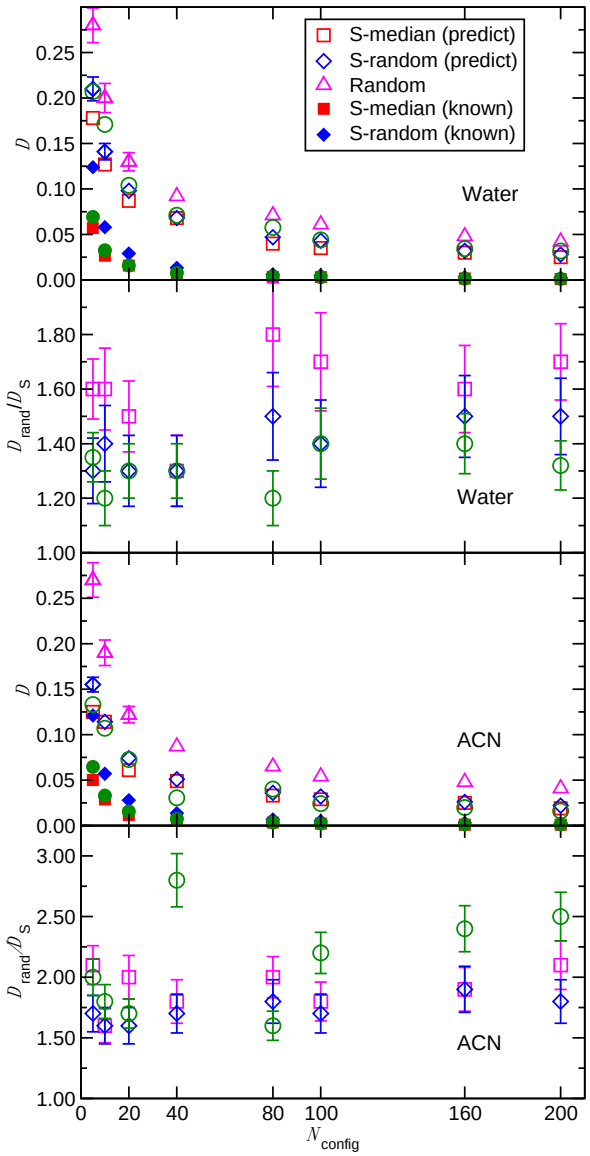

Fig. S1 *D* and *D values for three biased selection schemes based on predicted and pre-known excitation energies. Top: water; bottom: acetonitrile.**

As indicated by the data shown in Fig. S1, the performance of S-mean scheme is somewhat inconsistent. In a few cases (selecting 40, 100, 160, and 200 configurations for solvation in acetonitrile), it outperforms S-median and S-random. However, in many other cases, the S-mean scheme yields results that are less satisfactory than S-median, and sometime even worse than S-random. In contrast, the performance of the S-median scheme is more stable and consistent. Thus, we conclude that the S-median scheme is the best performing among the three biased schemes.

Table S3 *D* and *D values of different selection schemes for solvent water.**

Selection schemes	No. of configs	*D*	*D**
S-mean	5	0.207	0.0693
	10	0.171	0.0326
	20	0.104	0.0158
	40	0.071	0.00772
	80	0.058	0.00337
	100	0.044	0.00311
	160	0.034	0.00137
	200	0.032	0.00118
S-median	5	0.178 ± 0.003	0.05699 ± 0.00006
	10	0.127 ±0.007	0.02659 ± 0.00003

	20	0.087 ± 0.004	0.01570 ± 0.00011
	40	0.068 ± 0.004	0.00657 ± 0.00003
	80	0.040 ± 0.003	0.00342 ± 0.00002
	100	0.0350 ± 0.0018	0.00317 ± 0.000010
	160	0.0300 ± 0.0018	0.00153 ± 0.00004
	200	0.0250 ± 0.0012	0.00103 ± 0.00003
S-random	5	0.210 ± 0.013	0.124 ± 0.005
	10	0.141 ± 0.009	0.058 ± 0.002
	20	0.098 ± 0.006	0.0290 ± 0.0012
	40	0.068 ± 0.004	0.0132 ± 0.0006
	80	0.047 ± 0.003	0.0061 ± 0.0003
	100	0.043 ± 0.003	0.0052 ± 0.0002
	160	0.0320 ± 0.0018	0.0031 ± 0.00015
	200	0.0280 ± 0.0018	0.0024 ± 0.00013
Random	5	0.280 ± 0.019	
	10	0.200 ± 0.016	
	20	0.130 ± 0.010	
	40	0.092 ± 0.007	
	80	0.071 ± 0.006	
	100	0.061 ± 0.005	
	160	0.048 ± 0.004	
	200	0.042 ± 0.003	

Uncertainties are calculated from 95% confidence interval.

Table S4 D and D^* values of different selection schemes for solvent acetonitrile.

Selection schemes	No. of configs	D	D^*
S-mean	5	0.133	0.0646
	10	0.107	0.0330
	20	0.073	0.0155
	40	0.031	0.00741
	80	0.040	0.00355
	100	0.024	0.00243
	160	0.020	0.00129
	200	0.016	0.00140
S-median	5	0.125 ± 0.002	0.05010 ± 0.00008
	10	0.114 ± 0.005	0.0287129 ± 0.0000006
	20	0.061 ± 0.003	0.01162 ± 0.00004
	40	0.049 ± 0.003	0.006729 ± 0.000007
	80	0.0330 ± 0.0015	0.00331 ± 0.00004
	100	0.0290 ± 0.0013	0.00234 ± 0.000013
	160	0.0250 ± 0.0012	0.001003 ± 0.000008
	200	0.0190 ± 0.0011	0.000949 ± 0.000006
S-random	5	0.155 ± 0.008	0.121 ± 0.005
	10	0.114 ± 0.006	0.057 ± 0.003
	20	0.074 ± 0.004	0.028 ± 0.0014
	40	0.051 ± 0.003	0.0136 ± 0.0006
	80	0.036 ± 0.002	0.0068 ± 0.0004
	100	0.0320 ± 0.0017	0.0051 ± 0.0003
	160	0.0260 ± 0.0016	0.00310 ± 0.00017
	200	0.0220 ± 0.0013	0.00240 ± 0.00015
Random	5	0.270 ± 0.019	
	10	0.190 ± 0.014	
	20	0.122 ± 0.009	
	40	0.087 ± 0.007	

	80	0.065 ± 0.005
	100	0.054 ± 0.004
	160	0.048 ± 0.004
	200	0.041 ± 0.003

Uncertainties are calculated from 95% confidence interval.

Table S5 Average excitation energy of selected configurations.

Selection schemes	No. of configs	E_{ave}	
		Water	Acetonitrile
S-mean	5	2.1394	2.1148
	10	2.1179	2.1180
	20	2.1202	2.1268
	40	2.1351	2.1190
	80	2.1351	2.1157
	100	2.1405	2.1144
	160	2.1376	2.1173
	200	2.1347	2.1174
S-median	5	2.1320 ± 0.0019	2.1210 ± 0.0013
	10	2.1440 ± 0.0017	2.1130 ± 0.0012
	20	2.1397 ± 0.0008	2.1173 ± 0.0005
	40	2.1437 ± 0.0009	2.1170 ± 0.0004
	80	2.1364 ± 0.0007	2.1162 ± 0.0005
	100	2.1390 ± 0.0005	2.11640 ± 0.00019
	160	2.1385 ± 0.0003	2.1196 ± 0.0004
	200	2.1362 ± 0.0004	2.1179 ± 0.0005
S-random	5	2.135 ± 0.004	2.120 ± 0.002
	10	2.138 ± 0.002	2.118 ± 0.0015
	20	2.1370 ± 0.0017	2.118 ± 0.0010
	40	2.1360 ± 0.0011	2.1173 ± 0.0006
	80	2.1368 ± 0.0007	2.1181 ± 0.0005
	100	2.1364 ± 0.0008	2.1173 ± 0.0004
	160	2.1374 ± 0.0005	2.1176 ± 0.0005
	200	2.13690 ± 0.00014	2.1175 ± 0.0003
Random	5	2.134 ± 0.007	2.115 ± 0.006
	10	2.135 ± 0.005	2.118 ± 0.004
	20	2.136 ± 0.003	2.118 ± 0.003
	40	2.138 ± 0.002	2.118 ± 0.002
	80	2.1380 ± 0.0019	2.1190 ± 0.0016
	100	2.1380 ± 0.0015	2.1170 ± 0.0012
	160	2.1360 ± 0.0012	2.1180 ± 0.0011
	200	2.1360 ± 0.0010	2.1180 ± 0.0010

Uncertainties are calculated from 95% confidence interval.