

1 **Supporting Information**

2

3 **Impact of magnetic and electric fields on the free energy to form a calcium**
4 **carbonate ion-pair**

5

6 Ke Yuan^{1*}, Nikhil Rampal^{1,†}, Xuwei Du², Fangjun Shu³, Yanxing Wang³, Huiyao Wang²,
7 Andrew G. Stack¹, Paul Ben Ishai⁴, Lawrence M. Anovitz¹, Pei Xu²

8

9 ¹Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830, United States

10 ²Department of Civil Engineering, New Mexico State University, Las Cruces, NM 88003, United States

11 ³Department of Mechanical & Aerospace Engineering, New Mexico State University, NM 88003, United
12 States

13 ⁴Department of Physics, Ariel University, 40700 Ariel, Israel.

14 [†]Current Address: Quantum Simulations Group, Lawrence Livermore National Laboratory, CA 94550,
15 United States

16

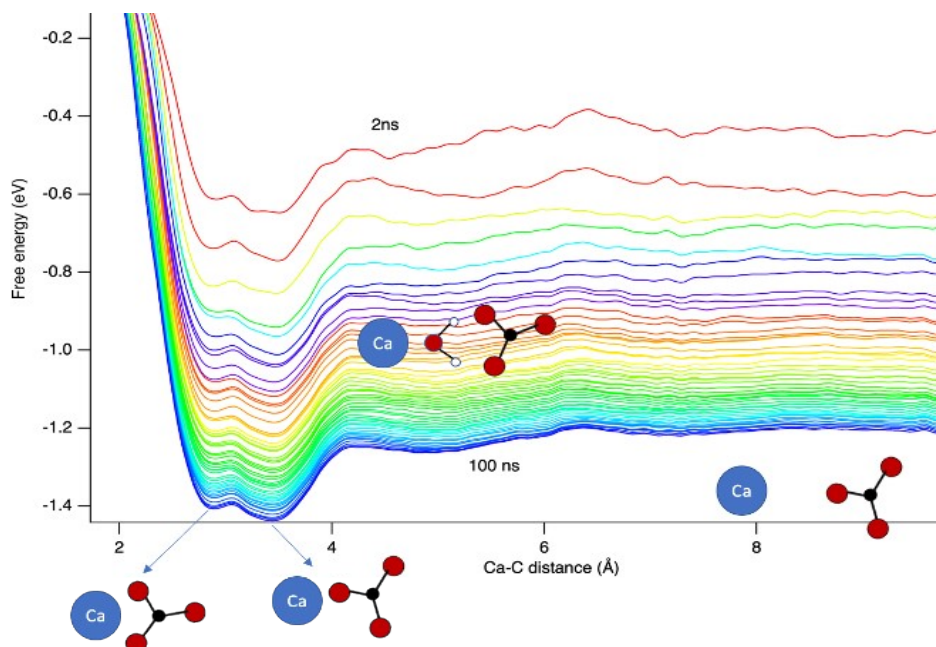
17

18

19

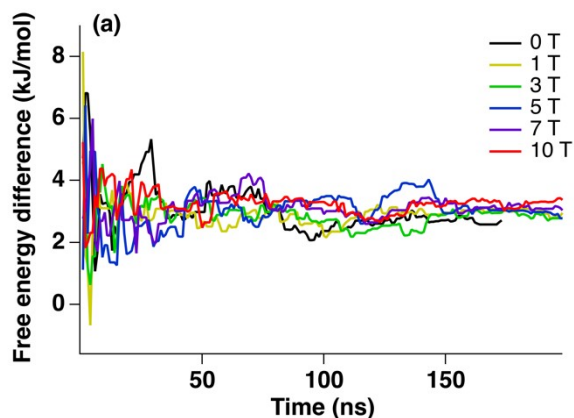
20

21

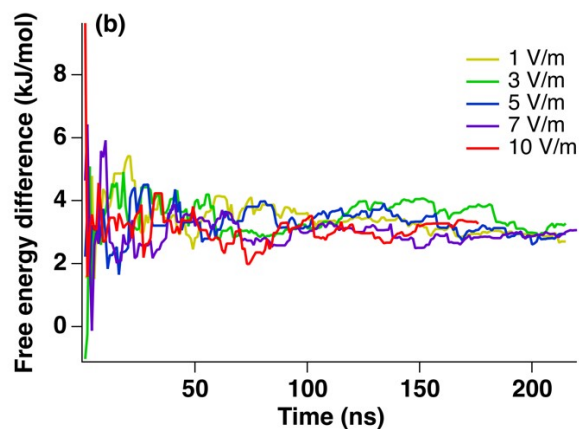


22
 23 **Figure S1.** Free energy profiles of forming a $[\text{Ca-CO}_3]^0$ ion pair in water at 300K without an
 24 external field. PMFs were plotted with increasing simulation time from 2 ns to 100 ns. Structures
 25 corresponding to different ion pair structures (contact, water-mediated, and non-contact ion pair
 26 or ions) are shown at different Ca-C distances.

27
 28
 29
 30
 31
 32
 33
 34



35



36

37 **Figure S2.** Changes in the differences of free energies of two close contact ion-pairs formed at
 38 Ca-C distances of 2.9 Å and 3.5 Å over time under a series of (a) magnetic and (b) electric fields.

39

40

41

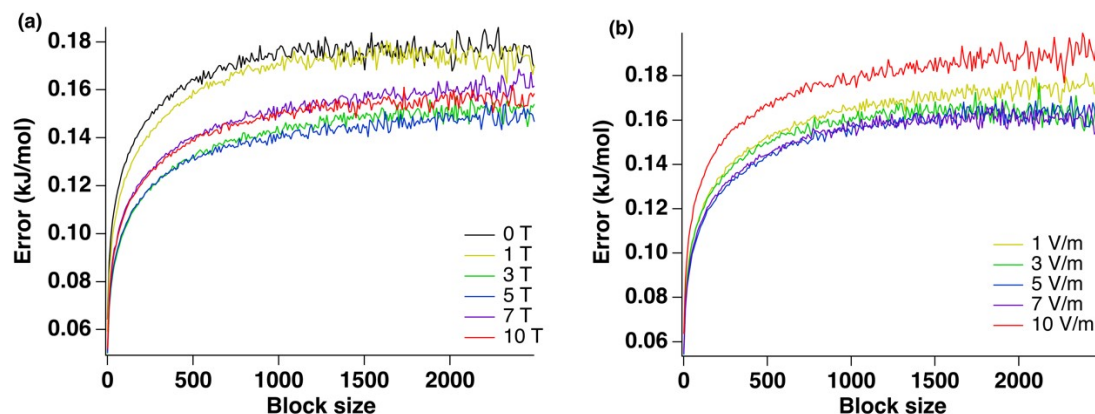
42 **Table S1.** Error analysis calculated based on the standard deviations of the free energy differences
 43 shown in Fig. S2 by using the last 25 ns of the data.

44

Magnetic field (T)	Error (kJ/mol)
0	± 0.10
1	± 0.10
3	± 0.12
5	± 0.11
7	± 0.10
10	± 0.10
Average	± 0.11
Electric field (V/m)	Error (kJ/mol)
1	± 0.09
3	± 0.14
5	± 0.09
7	± 0.09
10	± 0.06

Average ± 0.10

45
46
47
48
49
50



51
52
53
54
55
56
57
58
59
60
61
62
63
64

Figure S3. Estimated errors of the calculated PMFs under a series of magnetic and electric fields with increasing block size.

Table S2. Error analysis based on the averaged free energies with block sizes ranging from 2000 to 2500 in Fig S2.

Magnetic field (T)	Error (kJ/mol)
0	± 0.18
1	± 0.17
3	± 0.15
5	± 0.15
7	± 0.16
10	± 0.16
Average	± 0.16
Electric field (V/m)	Error (kJ/mol)
1	± 0.18
3	± 0.16
5	± 0.16
7	± 0.16
10	± 0.19

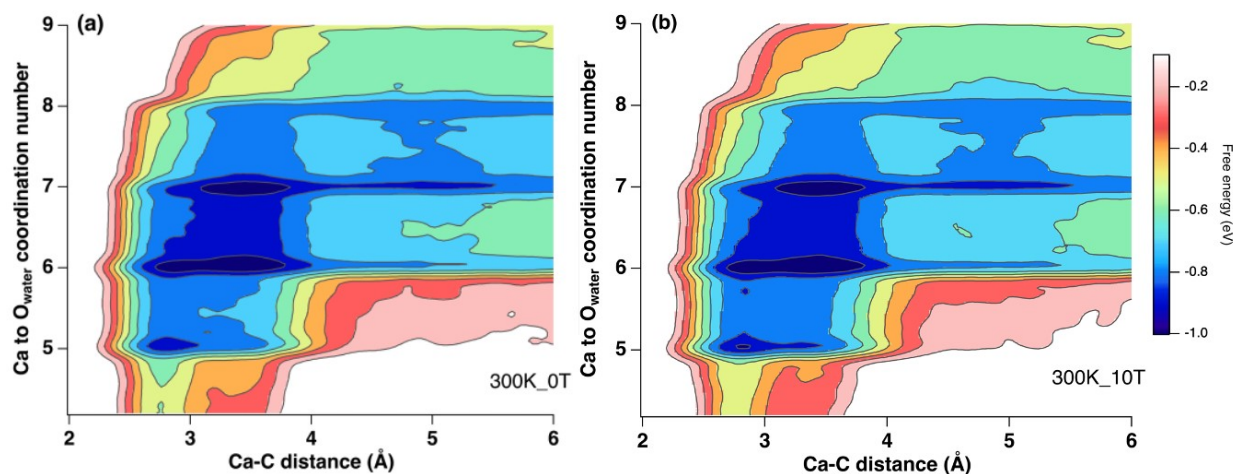
65
66
67
68
69
70
7172
73
74
75
76
77
78
79

Figure S4. Directly calculated 2D potential of mean force for formation of $[\text{Ca-CO}_3]^0$ ion-pair at 300 K under 0 T and 10 T. These directly calculated PMFs biased both the Ca-C distance and the CN of Ca to O_{water} and used a bias factor of 8, a bias height of 2.5 kJ/mol, and a simulation time of 100 ns.

Table S3. Free energy minima of forming contact and solvent-mediated $[\text{Ca-CO}_3]^0$ ion pairs at 300 K under a series of magnetic fields.

Magnetic field (T)	Contact ion-pair at 2.9 Å (± 0.16 kJ/mol)	Solvent shared ion-pair at 5.0 Å (± 0.16 kJ/mol)	Solvent separated ion-pair at 7.1 Å (± 0.16 kJ/mol)
300K			
0	-19.15	-5.26	-1.66
1	-19.28	-5.97	-1.85
3	-19.63	-6.03	-1.86
5	-19.91	-6.31	-1.87
7	-19.47	-5.68	-1.51
10	-19.47	-5.61	-1.47

82
83
84

85 **Computing the dissociation constants**

86

87 The pK_{diss} values were calculated based on two methods illustrated by Raiteri et al [1]. The energy
 88 difference method obtained the free energy difference directly from the free energy curves between
 89 the energy of forming the contact ion pair at ~ 3.5 Å and the energy of the fully dissociated ion
 90 pair at 14 Å. The pK_{diss} was calculated based on:

$$91 \quad pK_{diss} = \frac{\Delta F}{2.303RT} \quad (\text{Eq. S1})$$

92 The integration method takes a more rigorous approach based on statistical thermodynamics,
 93 where the free energy profiles were first aligned to the corresponding analytical solution, and then
 94 used the following equation based on Raiteri et al [1] to compute K_{diss} :

95

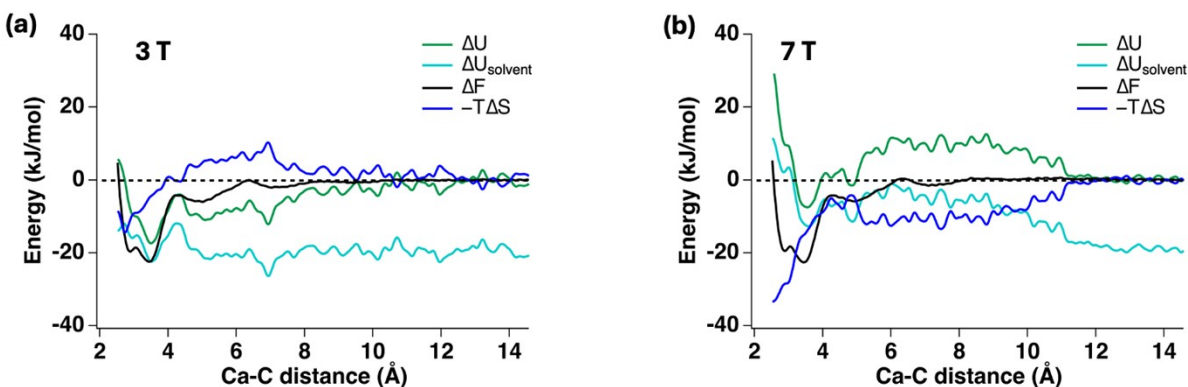
$$96 \quad K_{diss} = 4\pi C_0 \int_{R_0}^{R_1} \exp\left(-\frac{\phi(r)}{k_B T}\right) r^2 dr \quad (\text{Eq. S2})$$

97 where C_0 is a constant for the conversion of units from atoms/Å⁻³ to mol/L, R_0 is 2.0 Å and R_1 is
 98 14 Å. Details regarding the integration methods were reported in reference [1].

99

100

101



102

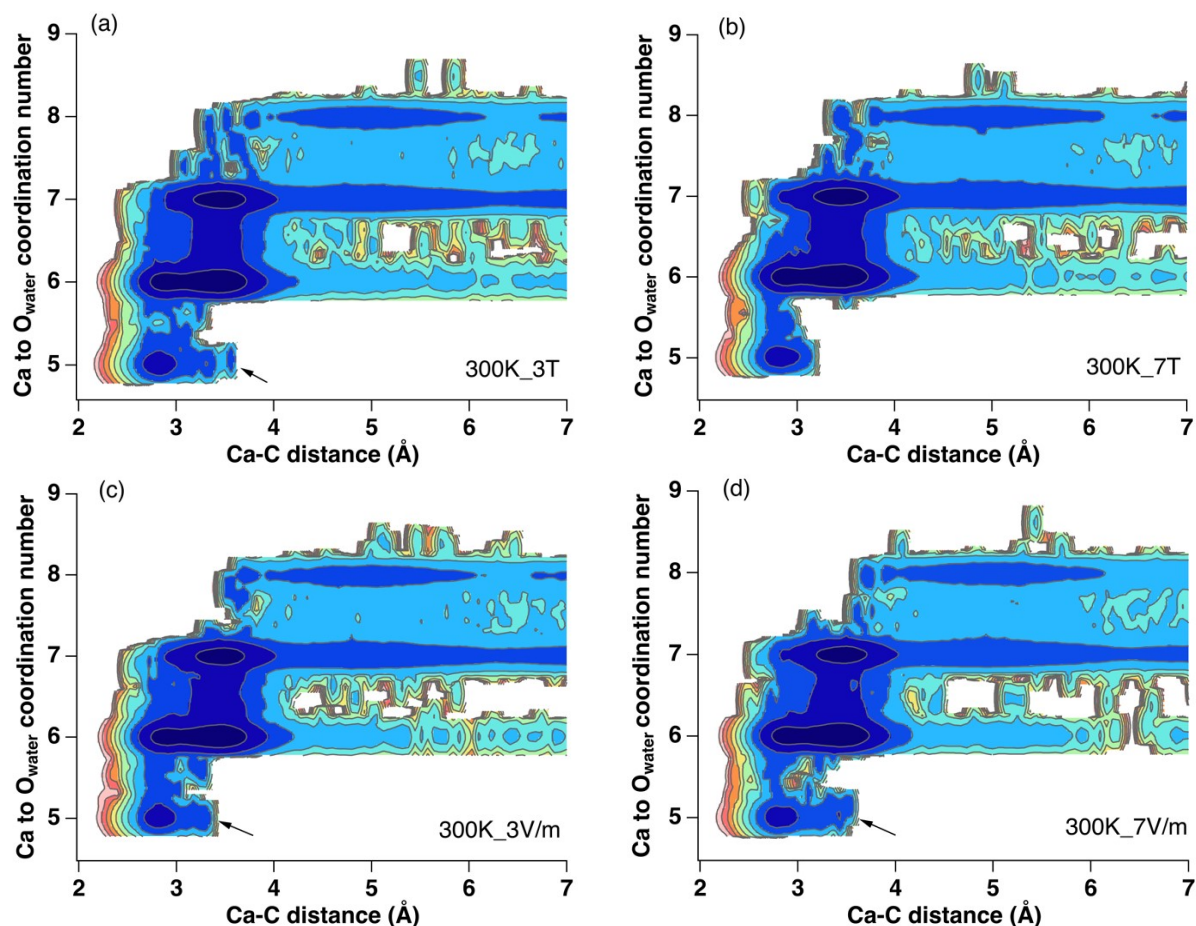
103

104 **Figure S5.** Deconvoluting the free energy (ΔF) into internal energy (ΔU), internal energy of solvent
 105 ($\Delta U_{solvent}$), and entropic terms ($-\Delta TS$) at 300K under (a) 3 T and (b) 7 T.

106

107

108



109

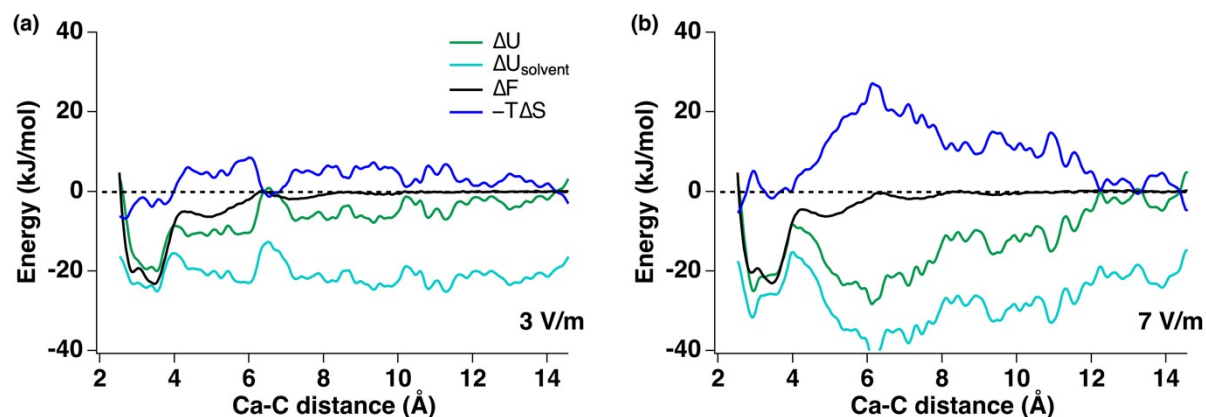
110

111 **Figure S6.** The reweighted 2D potential of mean force for the formation of $[\text{Ca-CO}_3]^0$ ion pair at
 112 300 K under (a) 3 T, (b) 7 T, (c) 3 V/m, and (d) 7 V/m. Arrows indicated new structures formed
 113 as contact ion-pairs under the external fields.

114

115

116



117

118 **Figure S7.** Deconvoluting the free energy (ΔF) into internal energy (ΔU), internal energy of solvent
 119 ($\Delta U_{\text{solvent}}$), and entropic terms ($-\Delta TS$) at 300K under (a) 3 V/m and (b) 7 V/m.

120

121

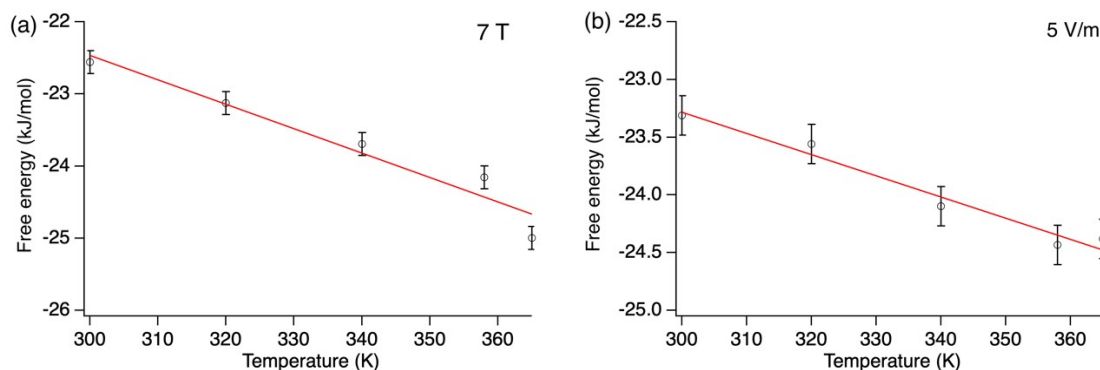
122

123 **Table S4.** Free energy minima of forming contact and solvent-mediated $[\text{Ca-CO}_3]^0$ ion-pairs at
 124 300 K under a series of electric fields.

Electric field (V/m)	Contact ion-pair (2.9 Å) (kJ/mol)	Solvent mediated ion-pair at 5.0 Å (kJ/mol)	Solvent mediated ion-pair at 7.1 Å (kJ/mol)
300K			
0	-19.1	-5.3	-1.7
1	-19.8	-6.3	-2.2
3	-20.2	-6.3	-1.9
5	-20.4	-6.2	-2.7
7	-20.4	-6.1	-1.9
10	-19.8	-6.2	-2.2

125

126



127

128 **Figure S8.** Determination of the free energy components from the linear fit. Fitting of the free
 129 energies calculated under a series of temperatures at (a) 7 T and (b) 5 V/m. R^2 values of the
 130 fitting are 0.94 and 0.97, respectively. Error bars associated with the free energy values are the
 131 standard deviations of the free energy minima at the last 25 ns of simulation (total simulation
 132 time for each free energy obtained at a specific temperature is about 150 ns).

133

134 **Table S5.** Free energy components (at 300 K) fitted based on Fig. S8. Finite difference referred to
 135 finite-difference temperature derivative method used to obtain most data in the manuscript and the
 136 linear fit referred to the data obtained from Fig. S8.

137

Methods	ΔF (kJ/mol)	ΔU (kJ/mol)	$-T\Delta S$ (kJ/mol)
Experiment* (0 field)	-18.0	8.7 ± 2.4	-26.7 ± 2.4
Finite difference (0 field)	-21.89	4.02	-25.91
Finite difference (7 T)	-22.56	-14.89	-7.67
Linear fit (7 T)	-22.47	-12.32	-10.15
Finite difference (5 V/m)	-23.31	-20.98	-2.33

Linear fit (5 V/m)	-23.28	-17.78	-5.50
--------------------	--------	--------	-------

138 *Experimental data from reference [2] by Kellermeier et al.

139

140 **Reference**

141 [1] Raiteri, P.; Demichelis, R.; Gale, J. D., Thermodynamically Consistent Force Field for Molecular
142 Dynamics Simulations of Alkaline-Earth Carbonates and Their Aqueous Speciation. *Journal of Physical
143 Chemistry C* **2015**, *119*, 24447-24458.

144 [2] Kellermeier, M., Raiteri, P., Berg, J. K., Kempter, A., Gale, J. D., & Gebauer, D. Entropy drives calcium
145 carbonate ion association. *ChemPhysChem* **2016**, *17*(21), 3535-3541.