

SUPPLEMENTARY MATERIAL

Micro-solvation of CO in water: Infrared spectra and structural calculations for $(D_2O)_2$ -CO and $(D_2O)_3$ -CO

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COMPUTATIONAL METHODOLOGY

To locate the stable structures of both $(D_2O)_2$ -CO and $(D_2O)_3$ -CO molecular clusters we followed this procedure. First, for each of these two kinds of molecular clusters, 100 different starting geometries were generated by randomly distributing the corresponding monomers (i.e. the D_2O and CO molecules) upon the surface of a sphere having the radius of a few Angstroms. Then, on each of these geometries a full optimization was performed, i.e. the geometries of each monomers in the molecular cluster were allowed to relax. On each of the optimized structures thus obtained, the calculation of the Hessian was carried out to confirm that the corresponding geometry corresponds to a true minimum on the PES. Each one of these steps was performed at B2PLYP-D3BJ level of theory in conjunction with the m-aug-cc-pVTZ basis set.¹

For computing the CBS limit of the binding energies, two different extrapolation schemes were used, both composed of several single point energy calculations carried out on the optimized geometries obtained at B2PLYP-D3BJ level of theory in conjunction with the m-aug-cc-pVTZ basis set. For the composite schemes, the aug-cc-pVNZ basis sets with $N= T, Q$ and 5 were employed.^{2,3} Additional calculations were carried out using the cc-pCVTZ basis set.⁴

The first composite scheme, labelled as CBS-1, is based on separate extrapolation of the CBS limit for the Hartree-Fock (HF-SCF) energy, $E_{CBS}(\text{HF-SCF})$ and for the correlation energy computed at MP2 level of theory, $E_{CBS}(\text{corr})$. For $E_{CBS}(\text{HF-SCF})$ the expression proposed by Fenner⁵ was used, while for $E_{CBS}(\text{corr})$ the following inverse cubic function was used:

$$E_{CBS}(corr) = \frac{N^3 E_N^{corr} - (N-1)^3 E_{N-1}^{corr}}{N^3 - (N-1)^3}.$$

The CBS limit was expressed as:

$$E_{CBS} = E_{CBS}(HF - SCF) + E_{CBS}(corr)$$

The effects due to higher-order electron correlation past the MP2 level of theory was taken into account as the difference between the CCSD(T) and MP2 single point energies, computed using the aug-cc-pVTZ basis set.

$$\Delta_{MP2}^{CCSD(T)} = E_{CCSD(T)} - E_{MP2}$$

For computing the core-valence (CV) corrections, two calculations were performed at MP2 level and using the cc-pCVTZ basis set, correlating all the electrons, E_{ae-MP2} , and within the frozen-core approximation, E_{fc-MP2} .

$$\delta_{MP2}^{CV} = E_{ae-MP2} - E_{fc-MP2}$$

The CBS-1 limit was therefore given as

$$E_{CBS-1} = E_{CBS}(HF - SCF) + E_{CBS}(corr) + \Delta_{MP2}^{CCSD(T)} + \delta_{MP2}^{CV}$$

The second composite scheme, labelled as CBS-2, is based on using the 4-5 inverse polynomial extrapolation for the CBS energy at MP2 level,^{6,7} according to the following expression:

$$E_{CBS} = E_N(MP2) + \frac{b}{(N+1)^4} + \frac{c}{(N+1)^5}$$

The corrections due to higher-order electron correlation past the MP2 level of theory, and those due to CV effects, are computed as in CBS-1.

On the basis of these two extrapolation schemes (and taking into account the inclusion of zero-point vibrational correction), the most stable isomers of $(\text{D}_2\text{O})_2\text{-CO}$ and $(\text{D}_2\text{O})_3\text{-CO}$ among the different structures optimized were therefore identified. These two isomers were further optimized at CCSD(T)-F12c level of theory employing the VTZ-F12 and VDZ-F12 basis sets for $(\text{D}_2\text{O})_2\text{-CO}$ and $(\text{D}_2\text{O})_3\text{-CO}$, respectively. Anharmonic corrections were computed (within the framework of VPT2 theory and employing a reduced dimensionality scheme) using the m-aug-cc-pVTZ basis set and the B2PLYP-D3BJ and B3LYP-D3BJ functionals for $(\text{D}_2\text{O})_2\text{-CO}$ and $(\text{D}_2\text{O})_3\text{-CO}$, respectively.

All the DFT-D3BJ calculations were performed using the ORCA suite of programs,⁸ while MOLPRO was used for CCSD(T*)-F12c computations;^{9,10} single point energy calculations were carried out using the Gaussian suite of quantum chemical programs.¹¹ Geometry optimizations were carried out using the *TightOpt* criteria as implemented in the Orca software.

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Optimized geometries (Angstrom) for (D₂O)₂-CO at B2PLYP-D3BJ/m-aug-cc-pVTZ level of theory

Geo #1

O	1.622847	-1.147135	-0.100131
D	0.717759	-1.469857	-0.053644
D	2.080711	-1.575062	0.627735
O	0.815533	1.620769	0.080635
D	1.352517	2.247904	-0.407638
D	1.265664	0.769125	-0.015727
C	-2.148802	0.263367	-0.021961
O	-1.503859	-0.667673	0.017127

Geo #2

O	3.184234	-0.652575	0.000170
D	3.712497	-0.401283	0.762621
D	3.712542	-0.401217	-0.762229
O	0.824212	1.093692	0.000100
D	0.002354	0.596186	0.000048
D	1.524999	0.428229	0.000132
C	-2.293791	-0.156094	-0.000137
O	-3.407151	-0.351786	-0.000239

Geo #3

O	-1.753910	-1.139366	-0.102068
D	-0.810431	-1.322000	-0.015634
D	-2.175881	-1.626294	0.609776
O	-0.893528	1.585447	0.083084
D	-1.423694	0.779900	-0.005631
D	-1.358134	2.253610	-0.424746
C	1.373468	-0.596175	0.014192
O	2.338354	-0.009602	-0.012131

Optimized geometries (Angstrom) for (D₂O)₃-CO at B2PLYP-D3BJ/m-aug-cc-pVTZ level of theory

Geo #1

C	-1.887305	0.548357	-0.055951
O	-2.853309	-0.031168	-0.137439
O	0.982512	1.831276	0.069691
D	1.047221	2.396277	0.843355
D	0.079574	1.482672	0.077903
O	2.474441	-0.506361	-0.120431
D	2.951774	-0.532175	-0.952564
D	2.085733	0.386276	-0.067218
O	-0.052213	-1.689620	0.153355
D	-0.033812	-2.533708	0.608793
D	0.881101	-1.428821	0.057338

Geo #2

C	1.953123	0.547254	-0.137574
O	2.621973	-0.306533	0.180859
O	-0.756893	-1.259900	-1.089140
D	-1.002931	-1.288242	-0.148381
D	-1.189451	-2.008326	-1.504978
O	-1.291944	-0.310001	1.460115
D	-2.016230	-0.283953	2.088494
D	-1.353749	0.509803	0.934175
O	-1.146186	1.493853	-0.642888
D	-0.254439	1.853496	-0.661620
D	-1.070968	0.656083	-1.129436

Geo #3

C	-2.972141	-0.410827	-2.012870
O	-3.453384	-0.109090	-2.989400
O	1.170521	-1.624118	0.887910
D	1.724245	-2.264098	1.339644
D	1.112993	-0.852925	1.478764
O	0.083108	0.574168	2.225853

D	-0.126512	0.762689	3.142786
D	-0.714172	0.157753	1.847437
O	-1.595442	-1.157729	0.872419
D	-1.983832	-0.980573	0.010071
D	-0.745385	-1.595249	0.697386

Geo #4

C	-1.685950	-1.054714	0.198649
O	-2.699516	-1.294242	-0.237052
O	3.342534	-0.724293	-0.450699
D	3.555350	-0.252286	-1.258308
D	2.548909	-0.290845	-0.107375
O	0.985713	0.404753	0.844767
D	0.257260	-0.232072	0.818997
D	1.237545	0.475868	1.769829
O	-1.153660	1.921707	-0.336409
D	-0.271706	1.729660	0.008984
D	-1.053575	2.702538	-0.884927

Geo #5

C	-2.458665	-0.953527	-1.443108
O	-3.307817	-1.660455	-1.679196
O	2.086023	1.268387	0.992525
D	2.192642	0.589519	1.661867
D	1.161037	1.208215	0.691205
O	2.474711	1.098466	-1.761577
D	2.981849	1.804127	-2.168589
D	2.654115	1.159167	-0.806296
O	-0.116168	1.231845	-0.690349
D	0.595136	1.186922	-1.351333
D	-0.762862	0.567333	-0.945150

Geo #6

C	0.978824	-2.036319	0.429083
O	1.993007	-2.507696	0.593977
O	-0.992593	0.644713	0.736542
D	-0.249102	0.575243	1.359303
D	-1.065938	-0.237269	0.362312
O	1.590239	0.909214	1.825248
D	1.607869	1.598040	1.136783
D	1.918414	1.326823	2.624575
O	0.765599	2.574956	-0.231654
D	0.971327	2.654185	-1.165188
D	-0.017645	1.998110	-0.170982

Geo #7

C	-2.737332	0.430235	-0.343360
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O	-3.707299	1.001289	-0.247173
O	-0.019934	-1.308447	-0.941313
D	0.533731	-1.399860	-0.148540
D	-0.786340	-0.790275	-0.678257
O	2.378256	-0.481702	-2.036943
D	1.433562	-0.698636	-1.926714
D	2.674257	-0.979509	-2.802052
O	2.332657	-1.386371	0.600244
D	2.657703	-1.045119	-0.252011
D	2.740739	-0.841605	1.276120

Geo #8

C	-0.702320	-0.054020	2.062443
O	-0.411833	-1.141570	2.159385
O	-0.280641	0.518891	-0.832033
D	-0.704813	1.367698	-0.652080
D	-0.432748	0.337857	-1.768591
O	-0.532181	-0.242916	-3.650429
D	0.346473	-0.440299	-3.985662
D	-1.038817	-1.048566	-3.782531
O	-1.469372	2.688763	0.666560
D	-0.995997	3.480190	0.933677
D	-1.277752	2.033972	1.349261