Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Spin-paired Solvated Electron Couples in Alkali-Ammonia Systems

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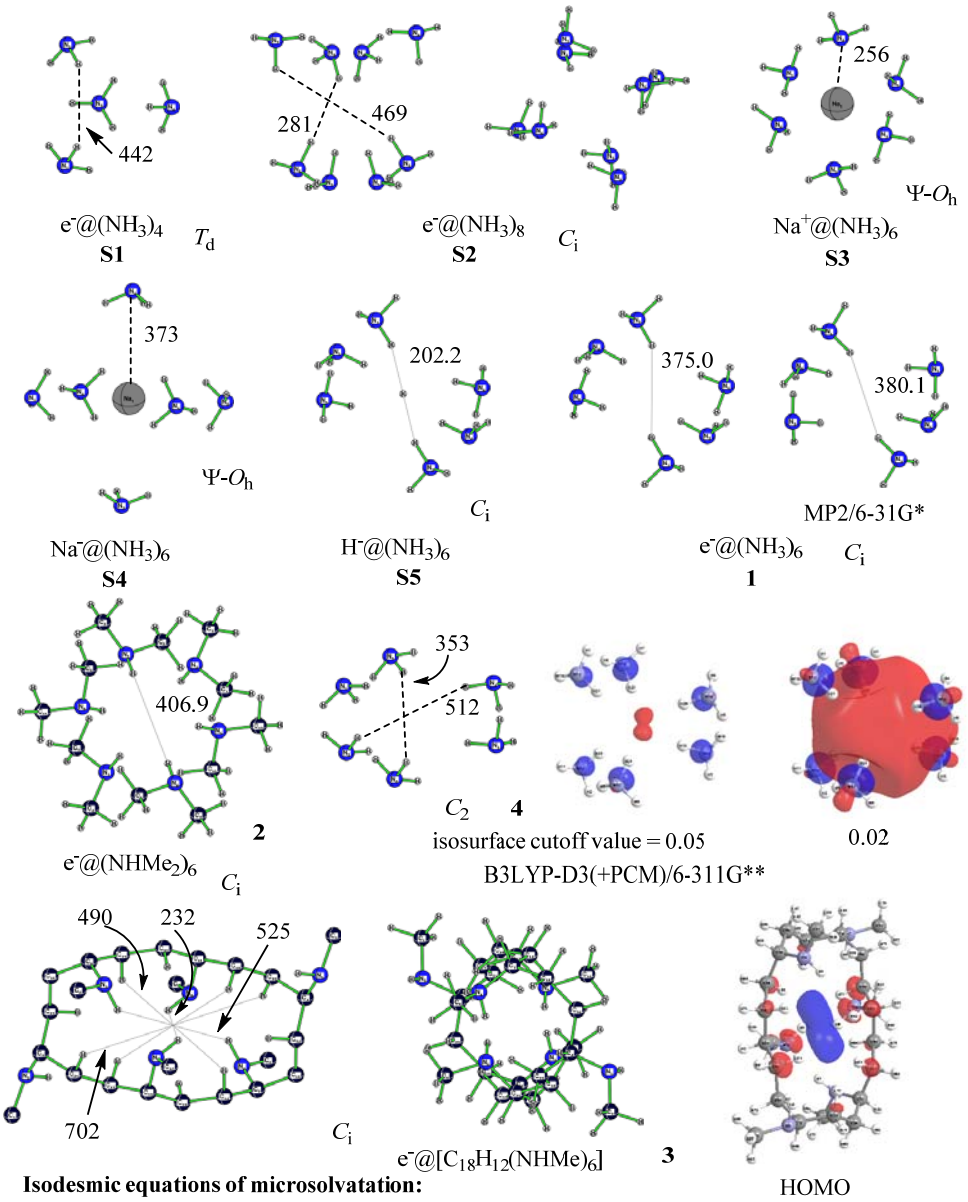


Isodesmic equations of microsolvatation:

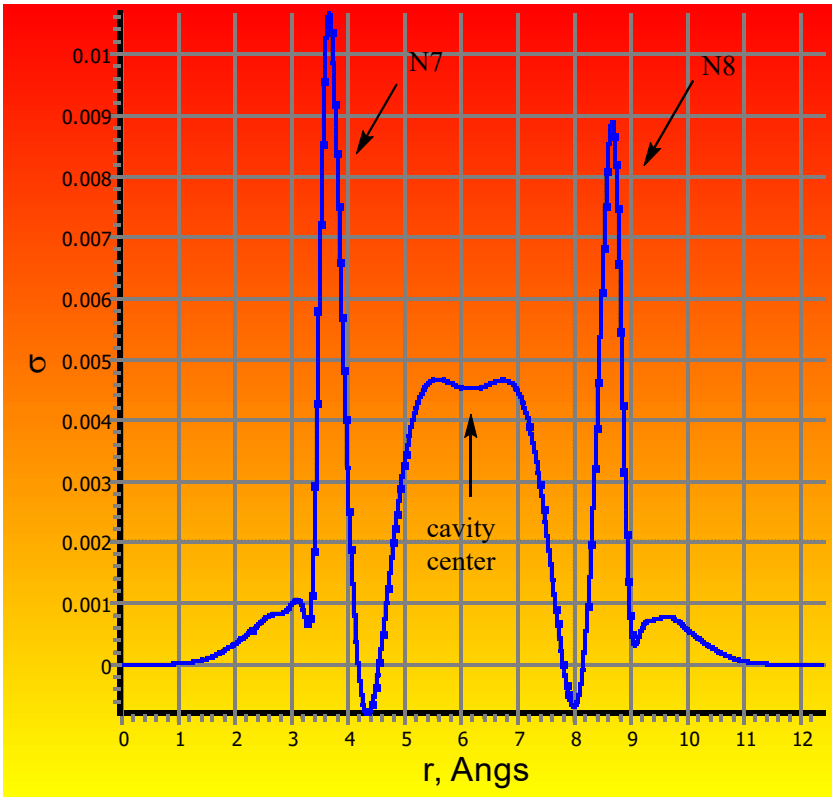
$Na_{am} + 8\,NH_3 \longrightarrow Na^+_{am} + e^-_{am}$ eq. 1 $\Delta H = 55.4$ kcalmol^{-1}

$Na_{am} + cage_{Na+} + cage_{e.-} \longrightarrow Na^+_{am} + cage_{Na} + e^-_{am}$ eq. 2 $\Delta H = 52.7$ kcalmol^{-1}

$2\,e^-_{am} + cage_{(2e)-2} \longrightarrow (2e)^{-2}_{am} + 2\,cage_{e.-}$ eq. 3 $\Delta H = 57.2$ kcalmol^{-1}

Figure S1. Geometries (with point group symmetries) and HOMOs (for **3** and **4**) at B3LYP/6-31G*, unless otherwise stated. Distances are given in pm. **S5** is the reactant connected to **TS7** in the text. Hydrogens of outwards pointing CH bonds in **3** are suppressed where appropriate. The pseudo-octahedral symmetry in **S3** and **S4** is actually an exact local O_h symmetry, when only nitrogen and sodium are considered. Below are the computed microsolvatation reactions given (strictly speaking, eq. 1 is not "isodesmic"). The "cage" species in eqs. 1-3 are the respective first solvent shells of the clusters referred to in the indices (computed as single points).

a)



b)

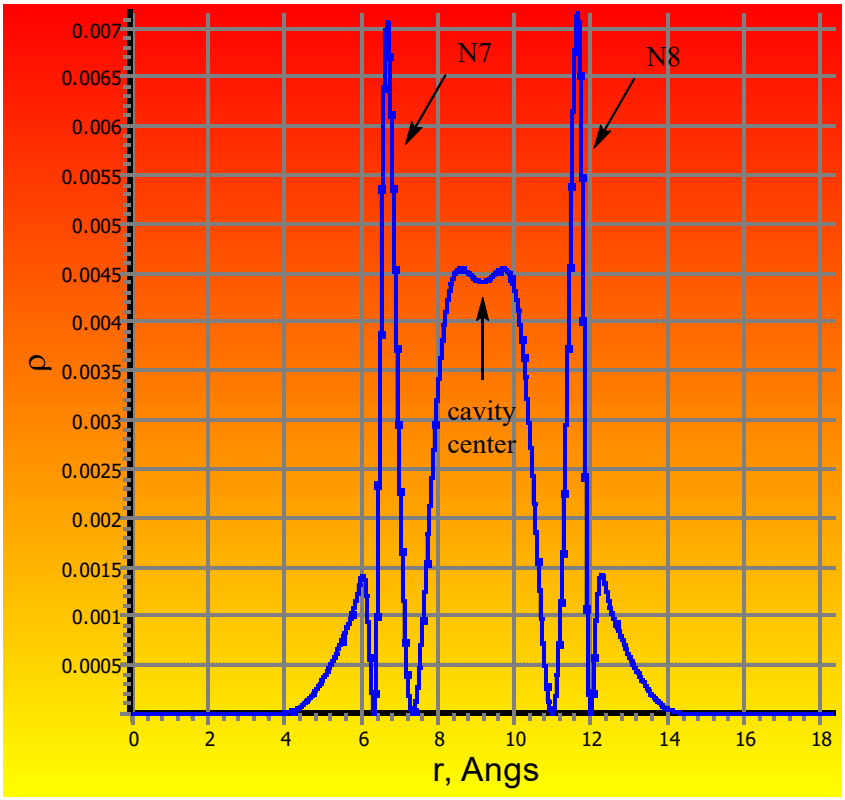


Figure S2. Spin density **a**) and SOMO (orbital #31) electron density **b**) of species **1**. The plots are contour lines along diametrically opposite ammonia nitrogen atoms. The numerical value of the spin and electron density in cavity center, respectively, are 0.0045 and 0,0044, normalized to unity (for the single excess electron) inside the given frame (in Å). Spatial integration would provide the fractional spin and charge located in the cavity.