

Supplementary Material: "Theoretical modeling of molecules in weakly interacting environments: Trifluoride anions in argon"

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Grid-based sampling for the F_3^- -Ar potential

A part of the *ab initio* data set for the F_3^- -Ar interaction potential was collected with grid-based sampling. This was done by incrementally changing the following six coordinates: the trifluoride bond lengths, the F-F-F angle, the distance between the central F atom and the Ar atom ($r_{\text{F-Ar}}$) and the two angles used to define the orientation of the argon around the trifluoride (θ, ϕ). These are depicted in Figure 1.

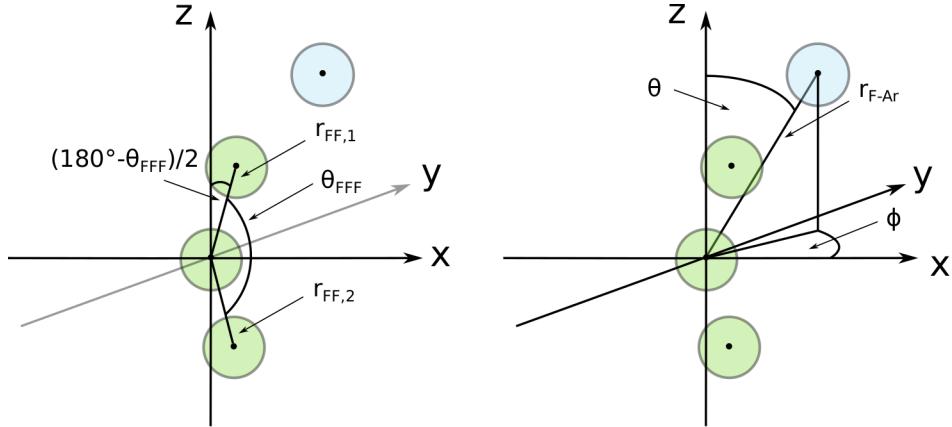


Figure 1: Coordinates included in the grid-based sampling.

For non-linear trifluoride configurations the grid-based sampling was employed to supply additional data in the region of strongest attractive interaction. Thus, the distance $r_{\text{F-Ar}}$ was varied between 4.0 Å and 5.5 Å with a step of 0.5 Å. The F-F bond lengths were incremented between 1.69 Å and 1.77 Å in steps of 0.02 Å, laying a focus on the bond length region close to equilibrium, while the intramolecular angle was set to 150°, 160° and 170°. The remaining two (orientational) angles were changed from 0° to 90° and 0° and 180° in steps of 30° and 60°, respectively. For linear trifluoride configurations the bond lengths were sampled with an irregular grid between 1.5 Å and 2.0 Å. The distance between the central F atom and the Ar atom was varied between 3.0 Å and 10.0 Å in steps of 0.5 Å and the polar angle θ was set to the values 0°, 5°, 15°, 25°, 35°, ..., 85°, 90°. The azimuthal angle ϕ is a redundant coordinate for the linear trifluoride and was thus not sampled. In total, the grid-based strategies comprised about 14000 data points.

Test scans for the F_3^- -Ar and F_3^- - Ar_2 potentials

The six test scans presented in Fig. 1 of the main text are obtained with the coordinate configurations listed in Table 1. The coordinate systems are defined as shown in Figure 1 above.

Table 1: Coordinate configurations for the potential scans shown in Fig. 1 of the main text. The row "panel" refers to the panel in Fig. 1 of the main text.

panel	F_3^- -Ar			F_3^- - Ar_2		
	3	4	5	3	4	5
$r_{\text{FF},1}$	1.930	1.723	1.820	scan	1.723	1.720
$r_{\text{FF},2}$	scan	1.723	1.690	1.723	1.723	1.750
θ_{FFF}	180.0	scan	175.0	180.0	scan	180.0
$r_{\text{F-Ar}}$	3.700	3.100	scan	3.523	3.100	scan
θ	63.0	90.0	1.0	124.6	90.0	60.0
ϕ	134	0	0	313.6	90.0	0.0
$r_{\text{F-Ar},2}$	-	-	-	4.853	5.105	3.600
θ_2	-	-	-	136.2	54.0	120.0
ϕ_2	-	-	-	67.2	83.1	0.0

Structural modeling and minima hopping runs

To model the matrix environment a trifluoride anion was placed at the center-of-mass of a cubic fcc $5\times 5\times 5$ super cell of 500 argon atoms. Then, the argon atoms were split in two groups: the 104 atoms closest to the guest and the remaining ones. The positions of the atoms in the latter group were fixed to retain a fcc crystal structure environment. Likewise, the trifluoride was treated as a linear rigid rotor. Depending on how many vacancy sites were examined zero, one or two argon atoms were removed from the trifluoride's vicinity. Then, the positions of the movable (inner) argon atoms and the orientation of the trifluoride as well as its center-of-mass position were rattled and loosely equilibrated with a local LBFGS relaxation. At this point, five minima hopping (MH) optimizations sharing a list of minima were started. In total, 1000 local minima were examined. The initial temperature was set

to 200 K. The molecular dynamics part of the MH runs was run with a time step of 1 fs and terminated as soon as the trajectory was found to be in a minimum for the second time. The local relaxation step was performed with the LBFGS method and a stopping force criterion of 0.05 eV/Å. The temperature and energy adjustment parameters were set to $\beta_1 = 1.1$, $\beta_2 = 1.1$, $\beta_3 = 1.0/1.1$, $\alpha_1 = 0.98$ and $\alpha_2 = 1.0/0.98$. The initial energy acceptance criterion was $E_0 = 0.5$ eV. After the MH optimizations the constraints on the trifluoride were lifted and the structures yielded by the MH runs locally reoptimized with the LBFGS method and a force criterion of 0.01 eV/Å. This part of the modeling procedure was carried out with the Atomic Simulation Environment.¹

The plane projection plots were generated with the trajectory analysis tool TRAVIS.²

Cohesive and vibrational zero-point energies

The cohesive energies were calculated by summing up the energies of the individual guest-host and host-host interactions. To account for the fact that the three trifluoride-argon models contain a differing number of argon atoms, the energy contribution of the Ar-Ar pairs was corrected in case of the MCX-1V and MCX-2V structures. In order to do this, for each removed rare gas atom the average binding energy of an argon atom in an argon bulk fcc crystal is added to the host-host energy contribution. The average binding energy is estimated from the pure $5 \times 5 \times 5$ fcc argon supercell by taking half of the interaction energy of a central argon atom with all other 499 rare gas atoms in the cell. The correction is 90 meV for each removed Ar atom.

The scheme is motivated by the circumstance that in matrix isolation the environment forms around the guest molecule. Thus, the rare gas atoms displaced by the trifluoride should become part of the argon bulk structure, instead of being fully removed from the frozen matrix.

The zero-point energies are obtained from harmonic normal mode analyses based on PES-2B. Only the degrees of freedom in the movable part of the structures are included, while the outer rare gas atoms remain frozen. However, for the single- and double-vacancy models the movable section is expanded by one and two argon atoms, respectively, to maintain comparability of the zero-point energies to the cell without vacancies.

Vibrational states of entrapped F_3^- based on PES-3B

Analogous to Fig. 4 in the main text, Figure 2 illustrates the nuclear densities for the fundamental vibrational states of the entrapped F_3^- described by PES-3B.

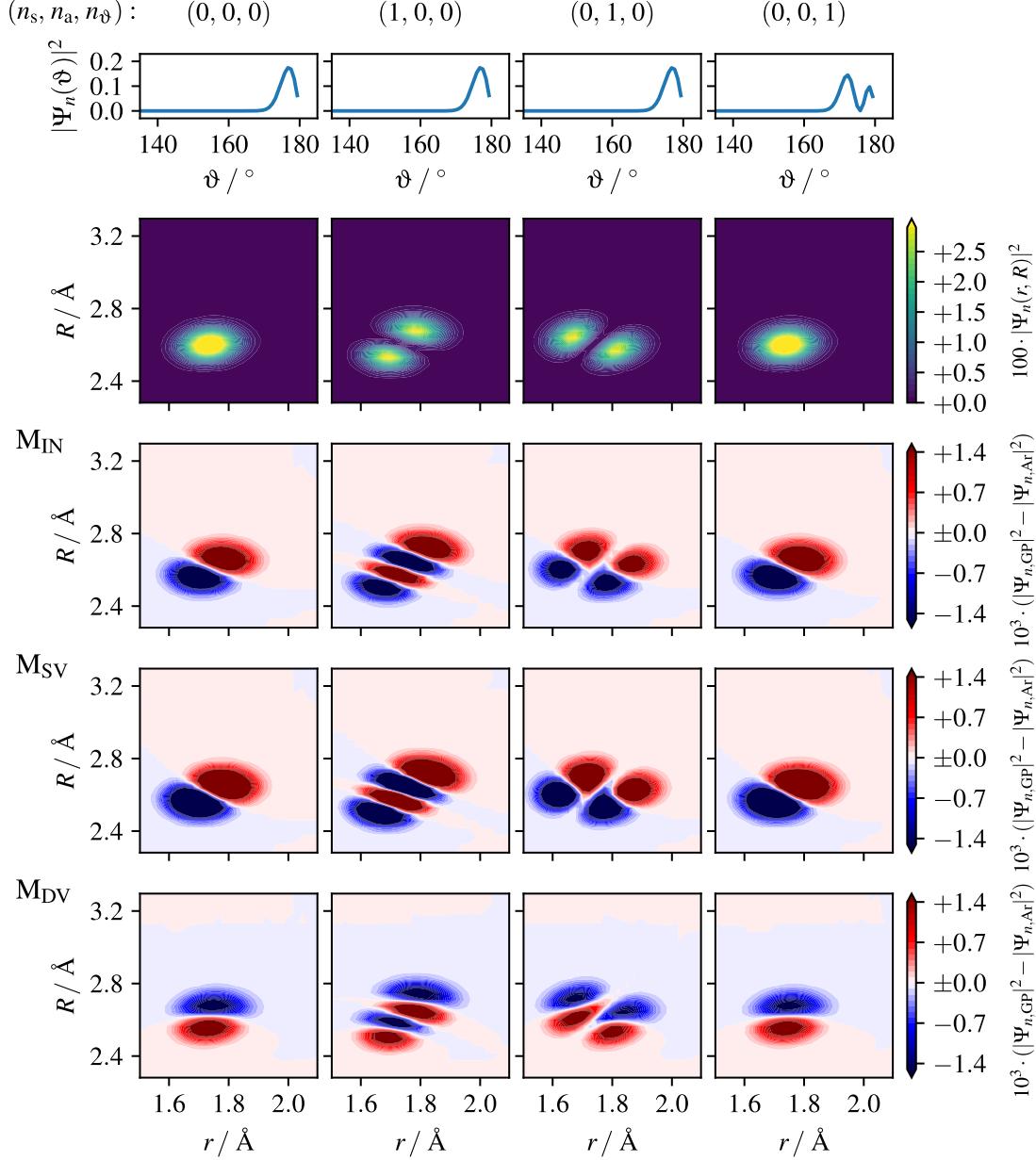


Figure 2: Nuclear densities of vibrational states of F_3^- in argon, obtained with PES-3B. Top two rows: Densities integrated along r and R (first row) and ϑ (second row) for the most stable structure of the MC1-0V cluster. Final three rows: Difference densities along r and R for the most stable minima of the MC1-0V (M_{IN}), MC2-1V (M_{SV}) and MC2-2V (M_{DV}) clusters, calculated with respect to the nuclear densities of free F_3^- .

References

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- (2) Brehm, M.; Thomas, M.; Gehrke, S.; Kirchner, B. TRAVIS – A free analyzer for trajectories from molecular simulation. *J. Chem. Phys.* **2020**, *152*, 164105.