# Supplementary Information

# Complexes of Alkali Metal Cations and Molecular Hydrogen: Potential Energy Surfaces and Bound States

Massimiliano Bartolomei,† Tomás González-Lezana,† José Campos-Martínez,†
Marta I. Hernández,*,† and Fernando Pirani‡

†*Instituto de Física Fundamental, Consejo Superior de Investigaciones Científicas (IFF-CSIC), Serrano 123, 28006 Madrid, Spain*

‡*Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Perugia, Italy*

E-mail: marta@iff.csic.es

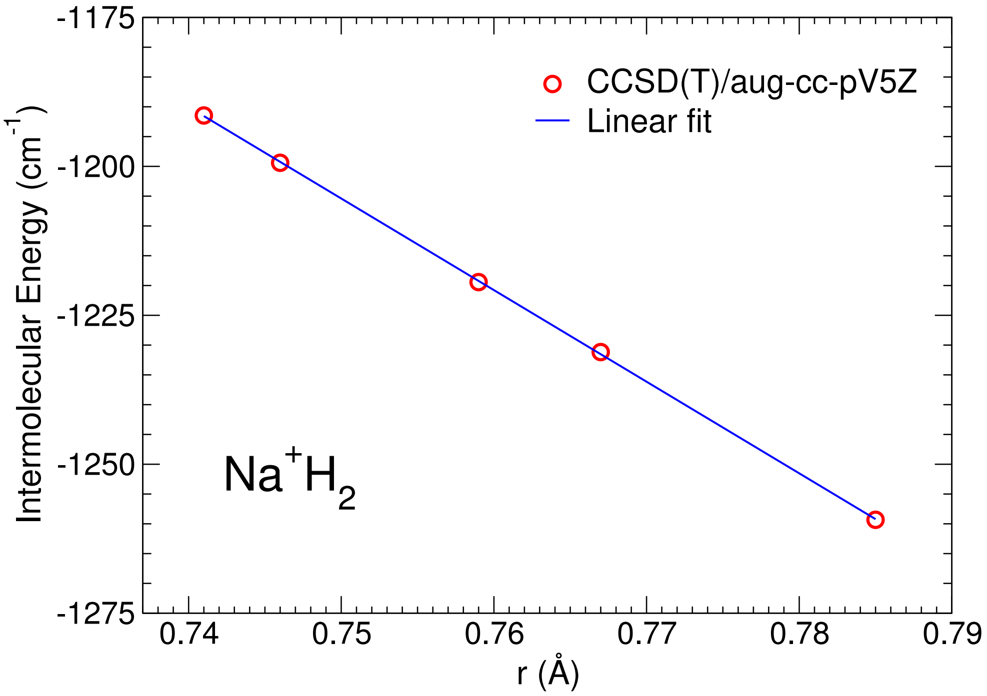

Figure S1: **Dependence of the Na$^+$-H$_2$ interaction energy with the H$_2$ intramolecular distance,** $r$**,** for an intermolecular distance $R$ fixed at 2.381 Å and perpendicular orientation ($\theta = 90^o$). Open red circles are CCSD(T)/aug-cc-pV5Z calculations (BSSE corrected) whereas blue line is a linear fit to these data. Absence of second and higher order polynomials in the expansion of the Na$^+$-H$_2$ interaction energy around the vibrationally averaged value of $r$ (in the present case, $r_0$= 0.76664 Å) gives supports to the estimation of the vibrationally averaged intermolecular potential by a calculation using the effective distance $r_0$. See main document for the theoretical framework of this analysis.

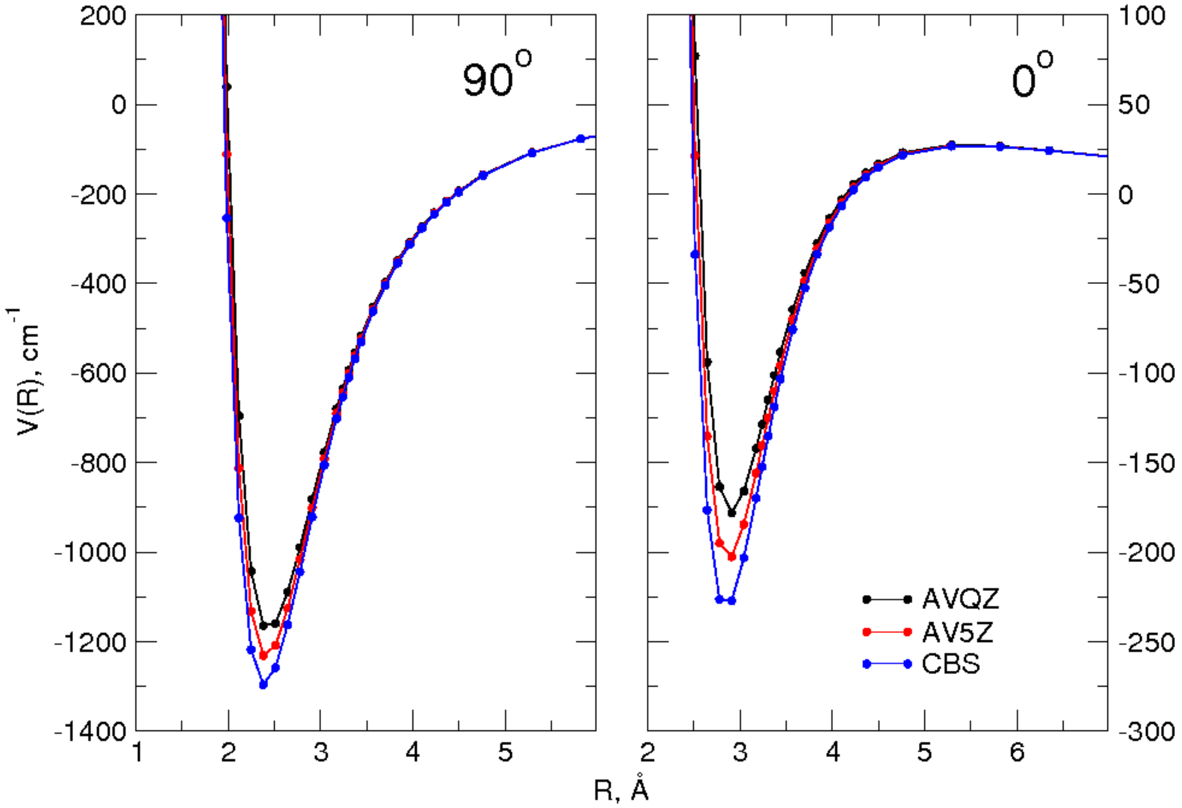

Figure S2: **Basis set dependence of the CCSD(T) interaction energies of $H_2$-$Na^+$:** Interaction energies ($cm^{-1}$) vs. intermolecular distance (Å) for the perpendicular ($\theta$=90$^o$, left panel) and parallel ($\theta$=0$^o$, right panel) configurations, by using the aug-cc-pVQZ (AVQZ) and aug-cc-pV5Z (AV5Z) bases as well as the complete basis set (CBS) estimation obtained using the extrapolation formulas of Halkier *et al* (Refs. 40, 41 of the main article). The internuclear distance in $H_2$ is fixed to $r_0$= 0.76664 Å. In the regions of the absolute minimum ($\theta$=90$^o$) and saddle point ($\theta$=0$^o$), the CBS interaction energies are about 5 and 10% larger in absolute value, respectively, than those obtained with the aug-cc-pV5Z basis set. In addition, it can be noticed that the extrapolation procedure leads to somewhat smaller equilibrium distances as well as more harmonic-like potentials around these stationary points.

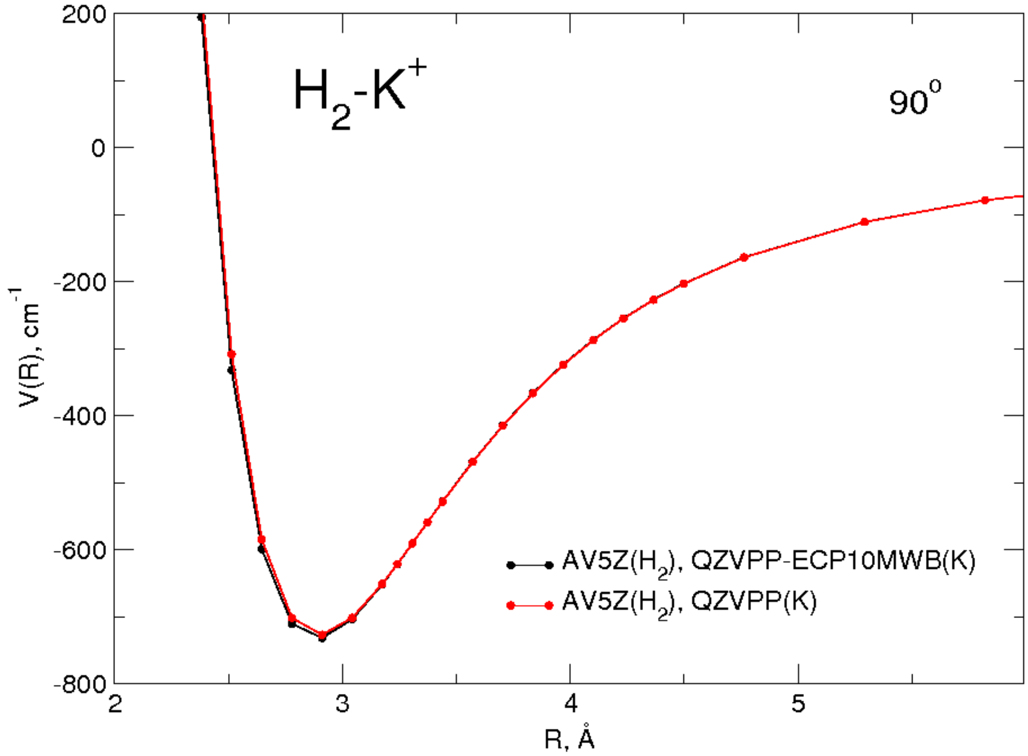

Figure S3: **Scalar relativistic effects in $H_2$-$K^+$:** CCSD(T) interaction energy ($cm^{-1}$) of $H_2$-$K^+$ as a function of the intermolecular distance (Å) for the perpendicular ($90^o$) configuration and $r_0$= 0.76664 Å, obtained by using the aug-cc-pV5Z (AV5Z) and def2-QZVPP set for $H_2$ and K, respectively (in red). Black curve refers to the inclusion of the ECP10MWB effective core potential (Ref. 42 of the main document). It can be seen that scalar relativistic effects, implicitly included through the effective core potential, lead to negligible variations (less than 1%) in the interaction energy around the minimum.

**Table S1: Comparison of the analytical intermolecular potentials (Eq.5 and Table 1 of the main article) with the *ab initio* energies, computed at intermolecular distances $R$ close to the minimum ($\theta = 90^o$) or the saddle point ($\theta = 0^o$). Except for the point close to the saddle of $K^+H_2$, the analytical potential accurately reproduces the *ab initio* energies.**

| | | $Na^+$ | $K^+$ | $Rb^+$ | $Cs^+$ |
|---|---|---|---|---|---|
| | $R$ (Å) | 2.381 | 2.919 | 3.175 | 3.374 |
| $\theta$= 90$^o$ | *Ab initio* energy (cm$^{-1}$) | -1296.3 | -738.2 | -601.6 | -502.9 |
| | Analytical energy (cm$^{-1}$) | -1302.8 | -740.1 | -602.5 | -499.3 |
| | $R$ (Å) | 2.910 | 3.307 | 3.572 | 3.704 |
| $\theta$= 0$^o$ | *Ab initio* energy (cm$^{-1}$) | -227.2 | -99.8 | -79.2 | -74.0 |
| | Analytical energy (cm$^{-1}$) | -229.4 | -103.9 | -80.4 | -73.9 |

**Table S2: Energy levels (in cm$^{-1}$) of Na$^{+}$H$_2$ and Na$^{+}$D$_2$. Inversion and H (D) nuclei permutation parities are $p_i$ and $p_j$, respectively and $J$ is the total angular momentum. Levels involved in the calculation of rotational constants (see main article) are indicated in bold face. Notice that there are not allowed states for $J = 0$ and $p_i = -1$ and that only energy levels below -10 cm$^{-1}$ are shown. Also note that results for D$_2$ have been obtained using the same intermolecular potential as that of Na$^{+}$-H$_2$ (i.e., using the effective H$_2$ intramolecular distance $r_0$=0.76664 Å)**

| $J$ | $p_i$ | $p$H$_2$ ($p_j = +1$) | $o$H$_2$ ($p_j = -1$) | $o$D$_2$ ($p_j = +1$) | $p$D$_2$ ($p_j = -1$) |
|---|---|---:|---:|---:|---:|
| 0 | +1 | -902.17319 | -451.52802 | -998.85340 | -643.36592 |
| 0 | +1 | -636.46801 | -238.68266 | -787.09354 | -461.35829 |
| 0 | +1 | -422.11654 | -76.24522 | -603.18983 | -307.03511 |
| 0 | -1 | —- | —- | —- | —- |
| 1 | +1 | -327.04572 | **-830.19787** | -598.19764 | **-964.95705** |
| 1 | +1 | -96.31009 | -560.83323 | -411.18756 | -752.58988 |
| 1 | +1 | — | -342.54904 | -251.47327 | -567.95497 |
| 1 | -1 | **-899.26684** | **-830.25604** | **-997.24428** | **-964.98589** |
| 1 | -1 | -633.85376 | -560.88738 | -785.59681 | -752.61651 |
| 1 | -1 | -419.82091 | -448.84840 | -601.81214 | -641.84232 |
| 2 | +1 | **-893.45768** | **-824.51028** | **-994.02705** | **-961.80049** |
| 2 | +1 | -628.62972 | -555.71592 | -865.57931 | -749.65316 |
| 2 | +1 | -624.17571 | -443.49321 | -782.60446 | -638.79622 |
| 2 | -1 | -624.17593 | **-824.33595** | -865.57932 | **-961.71403** |
| 2 | -1 | -351.07091 | -555.55368 | -652.01597 | -749.57331 |
| 2 | -1 | -321.51541 | -337.90325 | -595.10591 | -565.17786 |

**Table S3: As in Table S2, energy levels of $K^+H_2$ and $K^+D_2$.**

| $J$ | $p_i$ | $p\mathrm{H}_2$ ($p_j = +1$) | $o\mathrm{H}_2$ ($p_j = -1$) | $o\mathrm{D}_2$ ($p_j = +1$) | $p\mathrm{D}_2$ ($p_j = -1$) |
|---|---|---:|---:|---:|---:|
| 0 | +1 | -474.36020 | -163.49703 | -534.79911 | -286.63497 |
| 0 | +1 | -309.10445 | -33.46475 | -401.91554 | -176.39453 |
| 0 | +1 | -185.25554 | —- | -291.23713 | -88.69770 |
| 0 | -1 | —- | —- | —- | —- |
| 1 | +1 | —— | **-395.59107** | -229.54745 | **-499.38111** |
| 1 | +1 | —- | -225.72893 | -112.84478 | -365.42182 |
| 1 | +1 | —- | -97.01271 | -18.49171 | -253.52108 |
| 1 | -1 | **-472.45189** | **-395.62538** | **-533.76812** | **-499.39501** |
| 1 | -1 | -307.43086 | -225.76077 | -400.97042 | -365.43456 |
| 1 | -1 | -183.83976 | -161.73260 | -290.38330 | -285.66334 |
| 2 | +1 | **-468.63777** | **-391.84148** | **-531.70680** | **-497.34883** |
| 2 | +1 | -304.08691 | -222.43552 | -399.08096 | -363.55774 |
| 2 | +1 | -181.45050 | -158.20675 | -396.71568 | -283.72083 |
| 2 | -1 | -181.45022 | **-391.73864** | -396.71570 | **-497.30717** |
| 2 | -1 | —- | -222.34012 | -261.42172 | -363.51953 |
| 2 | -1 | —- | -94.12725 | -227.56692 | -251.80063 |

**Table S4: As in Table S2, energy levels of $\mathrm{Rb}^+\mathrm{H}_2$ and $\mathrm{Rb}^+\mathrm{D}_2$.**

| $J$ | $p_i$ | $p\mathrm{H}_2$ ($p_j = +1$) | $o\mathrm{H}_2$ ($p_j = -1$) | $o\mathrm{D}_2$ ($p_j = +1$) | $p\mathrm{D}_2$ ($p_j = -1$) |
|---|---|---:|---:|---:|---:|
| 0 | +1 | -378.30355 | -103.32321 | -429.95114 | -212.25493 |
| 0 | +1 | -235.46203 | —- | -314.61386 | -117.80786 |
| 0 | +1 | -134.01205 | —- | -221.51612 | -45.94778 |
| 0 | -1 | —- | —- | —- | —- |
| 1 | +1 | —- | **-296.32611** | -149.52369 | **-393.65791** |
| 1 | +1 | —- | -148.60833 | -48.44436 | -277.02357 |
| 1 | +1 | —- | -42.00241 | —- | -182.47609 |
| 1 | -1 | **-376.68358** | **-296.35474** | **-429.09589** | **-393.66830** |
| 1 | -1 | -234.06394 | -148.63482 | -313.83665 | -277.03306 |
| 1 | -1 | -132.85486 | -101.81321 | -220.82158 | -211.44678 |
| 2 | +1 | **-373.44562** | **-293.13982** | **-427.38587** | **-391.96926** |
| 2 | +1 | -231.27050 | -145.85211 | -312.28282 | -275.48778 |
| 2 | +1 | -130.54440 | -98.79570 | -289.60532 | -209.83104 |
| 2 | -1 | -79.31587 | **-293.05399** | -289.60532 | **-391.93810** |
| 2 | -1 | —- | -145.77274 | -171.59512 | -275.45931 |
| 2 | -1 | —- | -39.63383 | -147.87347 | -181.07572 |

**Table S5: As in Table S2, energy levels of $Cs^+H_2$ and $Cs^+D_2$.**

| $J$ | $p_i$ | $p$H$_2$ ($p_j = +1$) | $o$H$_2$ ($p_j = -1$) | $o$D$_2$ ($p_j = +1$) | $p$D$_2$ ($p_j = -1$) |
|---|---|---:|---:|---:|---:|
| 0 | +1 | -304.09432 | -61.77507 | -346.10385 | -157.72396 |
| 0 | +1 | -184.39008 | —- | -249.14045 | -78.88417 |
| 0 | +1 | -101.68803 | —- | -172.14264 | -20.28376 |
| 0 | -1 | —- | —- | —- | —- |
| 1 | +1 | —- | **-218.32607** | -88.00361 | **-308.59050** |
| 1 | +1 | —- | -93.68110 | —- | -210.07667 |
| 1 | +1 | —- | —- | —- | -131.39750 |
| 1 | -1 | **-302.70880** | **-218.35103** | **-345.37695** | **-308.59887** |
| 1 | -1 | -183.20507 | -93.70450 | -248.48328 | -210.08438 |
| 1 | -1 | -100.71995 | -60.47924 | -171.55937 | -157.03879 |
| 2 | +1 | **-299.93950** | **-215.59806** | **-343.92358** | **-307.15347** |
| 2 | +1 | -180.83756 | -91.34159 | -247.16946 | -208.77612 |
| 2 | +1 | -98.78742 | -57.88979 | -202.94901 | -155.66896 |
| 2 | -1 | —- | **-215.52320** | -202.94901 | **-307.12837** |
| 2 | -1 | —- | -91.27147 | -103.05153 | -208.75300 |
| 2 | -1 | —- | —- | -86.59941 | -130.21959 |

**Table S6: Properties of the $M^+$-$D_2$ bound states: Binding energies for *ortho* ($o$) and *para* ($p$) species and their difference, $\Delta(D_0) = D_0(o)$-$D_0(p)$; rotational constants $A$, $B$, $C$, $\bar{B}$, centrifugal distortion constants $\Delta_J$ and $\Delta_{JK}$ (with exponents indicated within parenthesis) and expected value of the $M^+$-$D_2$ distance for the ground vibrational state; stretching and bending frequencies $\nu_s$ and $\nu_b$. All values in $cm^{-1}$ unless otherwise specified. Note that present results have been obtained using the same intermolecular potential energy surfaces as those of $M^+$-$H_2$ (i.e., using the effective $H_2$ intramolecular distance $r_0$=0.76664 Å), except for the entry labelled with † which corresponds to a more consistent $Na^+$-$D_2$ interaction potential.**

| Complex | | $D_0(o)$ | $D_0(p)$ | $\Delta(D_0)$ | $\nu_s$ | $\nu_b$ | $A$ | $B$ | $C$ | $\bar{B}$ | $\Delta_J$ | $\Delta_{JK}$ | $\langle R \rangle$ (Å ) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Na^+$-$D_2$ | | 998.9 | 1024.8 | -25.9 | 211.8 | 355.5 | 33.08 | 0.8191 | 0.7902 | 0.8046 | 4.2(-5) | 7.5(-4) | 2.47 |
| | † | **986.0** | **1011.9** | **-25.9** | **210.2** | **354.4** | **33.14** | **0.8183** | **0.7894** | **0.8038** | **4.1(-5)** | **7.7(-4)** | **2.47** |
| | *a* | 923 | 949 | -26 | 196 | 336 | 33.34 | 0.8025 | 0.7746 | 0.7886 | 4.6(-5) | 7.8(-4) | 2.48 |
| | *b* | — | — | — | — | — | — | *0.8158* | *0.7870* | *0.8014* | *4.6(-5)* | *8.5(-4)* | *2.46* |
| $^{39}K^+$-$D_2$ | | 534.8 | 559.2 | -24.4 | 132.9 | 248.2 | 34.90 | 0.5225 | 0.50860 | 0.5156 | 2.8(-5) | 3.1(-4) | 3.00 |
| $^{85}Rb^+$-$D_2$ | | 430.0 | 453.5 | -23.5 | 115.3 | 217.7 | 35.86 | 0.4329 | 0.4225 | 0.4277 | 2.0(-5) | 1.5(-4) | 3.21 |
| $Cs^+$-$D_2$ | | 346.1 | 368.4 | -22.3 | 97.0 | 188.4 | 37.15 | 0.3677 | 0.3593 | 0.3635 | 1.7(-5) | -1.0(-4) | 3.46 |

† **Properties corresponding to extra *ab initio* calculations using $r_0$=0.759 Å(the average $r$ distance of the $D_2$ ground vibrational state) and a subsequent fit using the analytical functions of Eq. 5 of the main paper. The new interaction potential is identical to the $Na^+$-$H_2$ one (Table 1 of the main document) except for $\varepsilon^{\perp}$= 766.083 $cm^{-1}$, and the partial charge, $q_D$= 0.46137 a.u. (reproducing a new calculation of the quadrupole at the new intramolecular distance, $Q$ = 0.47457 a.u.);**

*a* Rovibrational states calculations of Ref. 20 of the main paper;

*b Rotationally resolved infrared spectrum of Ref. 20 of the main paper.*

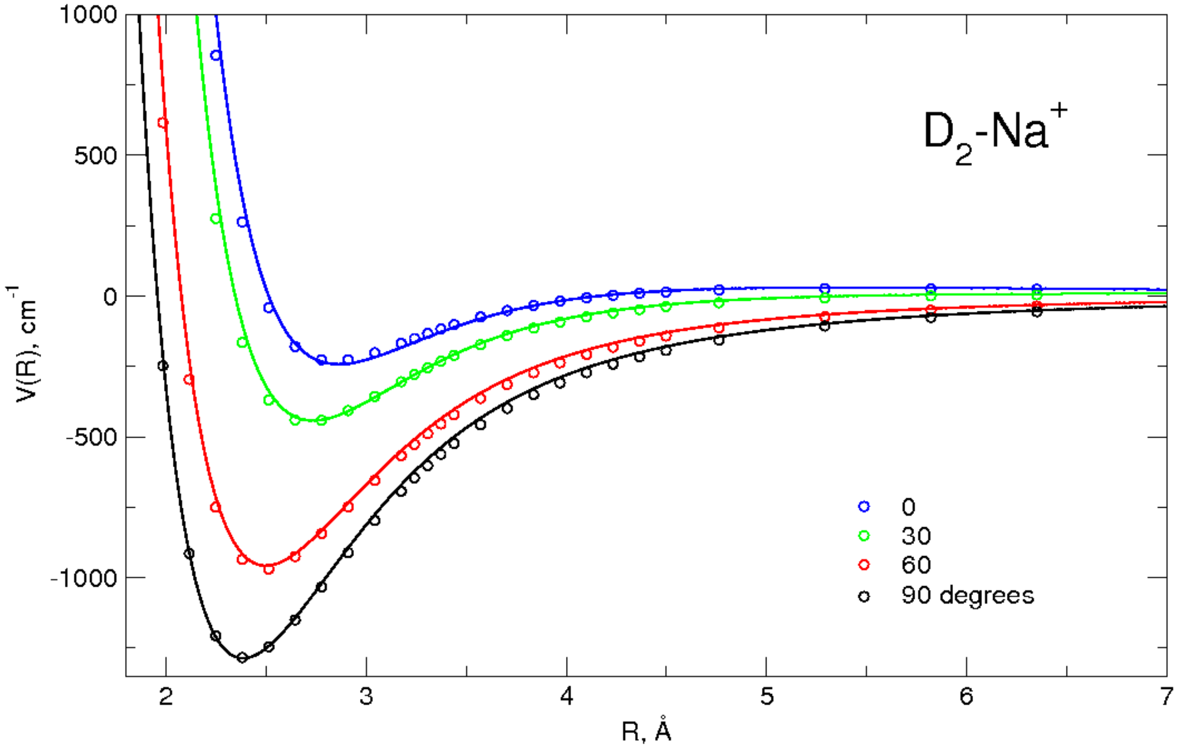

Figure S4: **Interaction potential for Na$^+$D$_2$:** As in Fig. 1 of the manuscript but for Na$^+$D$_2$, obtained from *ab initio* calculations using $r_0$= 0.7590 Å . The analytical PES shares all parameters of the Na$^+$-H$_2$ potential except for $\varepsilon^{\perp}$= 766.083 cm$^{-1}$ and $q_D$ = 0.46137 a.u.. Energies and intermolecular distances of this analytical potential are, for the minimum ($\theta = 90^o$), -1286.7 cm$^{-1}$ and 2.386 Å, and for the saddle point ($\theta = 0^o$), -242.1 cm$^{-1}$ and 2.863 Å, respectively.