Collision-induced dissociation mechanisms of $[Li(uracil)]^+$

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Intramolecular $[Li(uracil)]^+$ potential energy surface (PES)

Figure 1 shows a contour plot for Li^+ orbiting around uracil calculated at the MP2(FC)/6-31+G(d) level of theory. The plot clearly shows the two minima at O4 (lower right corner, θ~120º) and O2 (lower left corner θ~0º) and the transition state connecting both (θ~60º). The AM1 contour plot fails to describe the main features of the energy landscape. Therefore the AM1 Hamiltonian is reparametrized to fit MP2(FC)/6-31+G(d) calculations. The resulting AM1 Hamiltonian is termed AM1 with specific reaction parameters (SRP). Only the parameters for H, Li and O have been optimized in the fitting. In practice the following function is minimized using the general optimization program SUPOPT:

$$f = \sum_i (X_i - X_i^{target})^2 \, \omega_i \qquad (1)$$

where X_i is a semiempirical molecular property of our system (an energy difference, the geometry of a stationary point or the frecuenies) and X_i^{target} is the corresponding target value, taken in our case from MP2(FC)/6-31+G(d) calculations. In our case we selected the energies for several values of R and θ (see Figure 1 and Table 1) and also some properties of the O4 and O2 minima (distances, angles and frequencies). The values of X in Table 1 correspond to the AM1-SRP optimized values. The AM1-SRP optimized parameters are collected in Table 2. Figure 1 shows how the reparametrized potential (AM1-SRP) nicely reproduces the MP2(FC)/6-31+G(d) features. Table 3 collects the energies of the main stationary points in the PES. Quite interestingly, the high energy isomer π and the transition state connecting O4 and O2 are also nicely reproduced by our AM1-SRP Hamiltonian, even though those structures are not included in the optimization procedure. Figure 2 compares the main geometrical features of the stationary points of Table 1. Overall, the AM1-SRP potential seems to account for the most important details of the $[Li(uracil)]^+$ PES.

LJ parameters for $[Li(uracil)]^+$

The LJ paremters σ and ε of the ion, needed in eq 6, are obtained by fitting a LJ potential for the interaction between Xe and $[Li(uracil)]^+$ to the intermolecular potential of Figure 3. In particular, for each distance between Xe and the center of mass of the cation a total of 10^4 configurations are generated by randomly rotating the molecular over its Euler angles to obtain an average intermolecular potential between both species. Figure 4 shows both the averaged intermolecular potential (black line), and the fitted LJ potential (red line). The resulting LJ parameters are: ε = 12.7 kcal/mol and σ = 5.6 Å.

Once the LJ parameters are determined, the collision integral $\Omega^{(2,2)*}$, which is a function of the reduced temperature $T^* = k_B T/\varepsilon$, is approximated by:[1]

$$\Omega^{(2,2)*} = (0.636 + 0.567\log_{10}T^*)^{-1} \tag{2}$$

$$\Omega^{(2,2)*} = (0.697 + 0.518\log_{10}T^*)^{-1} \tag{3}$$

$$\Omega^{(2,2)*} = 1.161(T^*)^{-0.14874} + 0.525\exp(-0.773T^*) + 2.162\exp(-2.438T^*) \tag{4}$$

Equation (2) is accurate within ±7% in the range $0.3 \le T^* \le 500$, Eq. (3) within ±2.5% in the range $3 \le T^* \le 300$, and Eq. (4) within ±0.16% in the range $0.3 \le T^* \le 100$.

Tables

Table 1 Molecular properties selected for the reparametrization of the AM1 Hamiltonian.

Property[a]	X	X^{target}	ω_i
D_e of O4	49.1	48.9	1
D_e of O4	45.0	45.5	1
$d_{\mathrm{Li\text{-}O4}}$ in O4	1.803	1.755	100
$d_{\mathrm{Li\text{-}O2}}$ in O2	1.811	1.760	100
$a_{\mathrm{Li\text{-}O4\text{-}C}}$ in O4	171.8	171.9	0.5
$a_{\mathrm{Li\text{-}O2\text{-}C}}$ in O2	174.3	173.8	0.5
Freq(30th) of O4	3098	3100	0.01
Freq(31st) of O4	3206	3200	0.01
Freq(32nd) of O4	3396	3400	0.01
Freq(33th) of O4	3402	3400	0.01
E(4,40)	42.5	42.0	1
E(4.3,40)	43.3	41.7	1
E(4.5,40)	44.4	42.1	1
E(7,40)	47.3	47.1	1
E(10,40)	48.7	49.0	1
E(4,50)	53.8	53.9	1
E(4.3,50)	50.2	50.2	1
E(4.5,50)	49.6	49.1	1
E(7,50)	47.9	48.0	1
E(10,50)	48.6	49.0	1
E(4,60)	56.2	57.0	1
E(4.3,60)	51.1	52.0	1
E(4.5,60)	50.1	50.4	1
E(7,60)	47.7	47.9	1
E(10,60)	48.6	48.9	1
E(4,70)	48.1	48.6	1
E(4.3,70)	45.9	45.9	1
E(4.5,70)	46.0	45.3	1
E(7,70)	46.9	46.9	1
E(10,70)	48.3	48.6	1
E(4,80)	31.3	32.6	1
E(4.3,80)	34.2	33.5	1
E(4.5,80)	36.6	34.8	1
E(7,80)	45.4	45.1	1
E(10,80)	47.9	48.1	1

[a] D_e is the dissociation energy in kcal/mol, d is a distance in Å, a is an angle in degrees, *Freq*(ith) is the ith frequency in cm^{-1} of the O4 minimum and $E(R,\theta)$ is an energy in kcal/mol (with respect to the O4 minimum) of a geometry defined by R (in Å), and θ (in degrees) defined in Figure 1.

Table 2 AM1-SRP optimized parameters

Parameter	Atom	Value
USS	H	-11.481457
ZS	H	1.178108
BETAS	H	-6.060738
GSS	H	13.038821
ALP	H	2.920401
USS	Li	-3.938666
UPP	Li	-4.680952
ZS	Li	0.732507
ZP	Li	0.823119
BETAS	Li	-1.124105
BETAP	Li	-1.282833
GSS	Li	12.136146
GSP	Li	5.721065
GPP	Li	5.626132
GP2	Li	5.679185
HSP	Li	0.859623
ALP	Li	1.367705
USS	O	-96.991556
UPP	O	-80.094474
ZS	O	3.108050
ZP	O	2.549183
BETAS	O	-29.014009
BETAP	O	-29.202568
GSS	O	15.258495
GSP	O	13.592248
GPP	O	16.023733
GP2	O	13.051632
HSP	O	0.997777
ALP	O	4.428909

Table 3 Computed relative energies (in kcal/mol) of the main stationary points of the $[Li(uracil)]^+$ system.

	MP2(full)[a]	MP2/6-31+G(d)	AM1-SRP
O4	0.0	0.0	0.0
O2	3.7	3.7	4.1
π	33.3	31.6	28.9
TSO4-O2[b]		27.9	25.7
Uracil + Li^+	49.6	48.9	49.1

[a] MP2(full)/6-311+G(2d,2p) single point calculations at the MP2(full)/6-31G(d) optimized geometries from Ref 2. [b] Transition state connecting the O4 and O2 isomers.

Table 4 Parameters for the two-body intermolecular potentials[a]

	A	*B*	*C*	*D*	*E*	*F*
Xe -C1	14225.136326763011	2.534784794299	-595.354860105615	4.300798169912	20.837054930692	15.909242298820
Xe-N8	65267.206166058968	3.036664627121	-1178.783217068830	5.356774767287	78.400984924714	13.299375724666
Xe-C3	28869.129269651166	2.987026578069	-780.213411008639	4.945167018757	36.730449580161	12.220949526914
Xe-N7	54992.446161930595	2.943749381596	-1128.583812958915	5.220550671881	173.212717820843	15.460329297890
Xe-C5	40173.943171253064	3.205236625634	-2396.006874588727	6.364959823140	65.693209947712	17.478755638182
Xe-C6	37601.016309414132	2.834998911791	-954.551501973627	6.089746308211	56.451637348635	15.054894422453
Xe-O2	58784.832871095336	3.153985773196	-1369.114309260721	6.346358237921	92.669704414842	18.552539345042
Xe-O4	45122.725989321509	2.944286775850	-2398.571749983254	7.183988643345	88.763897703127	18.261930042678
Xe-Li9	54362.191175536944	3.266206089313	-1288.326114460758	4.577266713812	23.394275583071	20.902950099506
Xe-H10	46485.505146050207	4.131020705136	-626.047016823445	6.874171254661	54.815288232770	18.079875564055
Xe-H11	28641.730917767516	3.571226619510	-805.234291279628	6.652424207191	138.389284774963	11.721250644858
Xe-H12	28010.423724406181	3.645804241498	-597.215658990459	6.993947831541	253.366134682155	13.223735601755
Xe-H13	52490.150322087691	4.044681676497	-950.874063491422	6.557204711283	895.175847217096	16.716527622582

Parameter *A* is given in kcal mol^{-1}, *B* in Å^{-1}, *D* and *F* are dimensionless. The units for *C* and *E* are such that the potential energy is in kcal mol^{-1}, with *R* in Å.

Figures

Figure 1. Contour plots for Li^+ around uracil computed at the MP2/6-31+G(d), AM1 and AM1-SRP levels of theory.

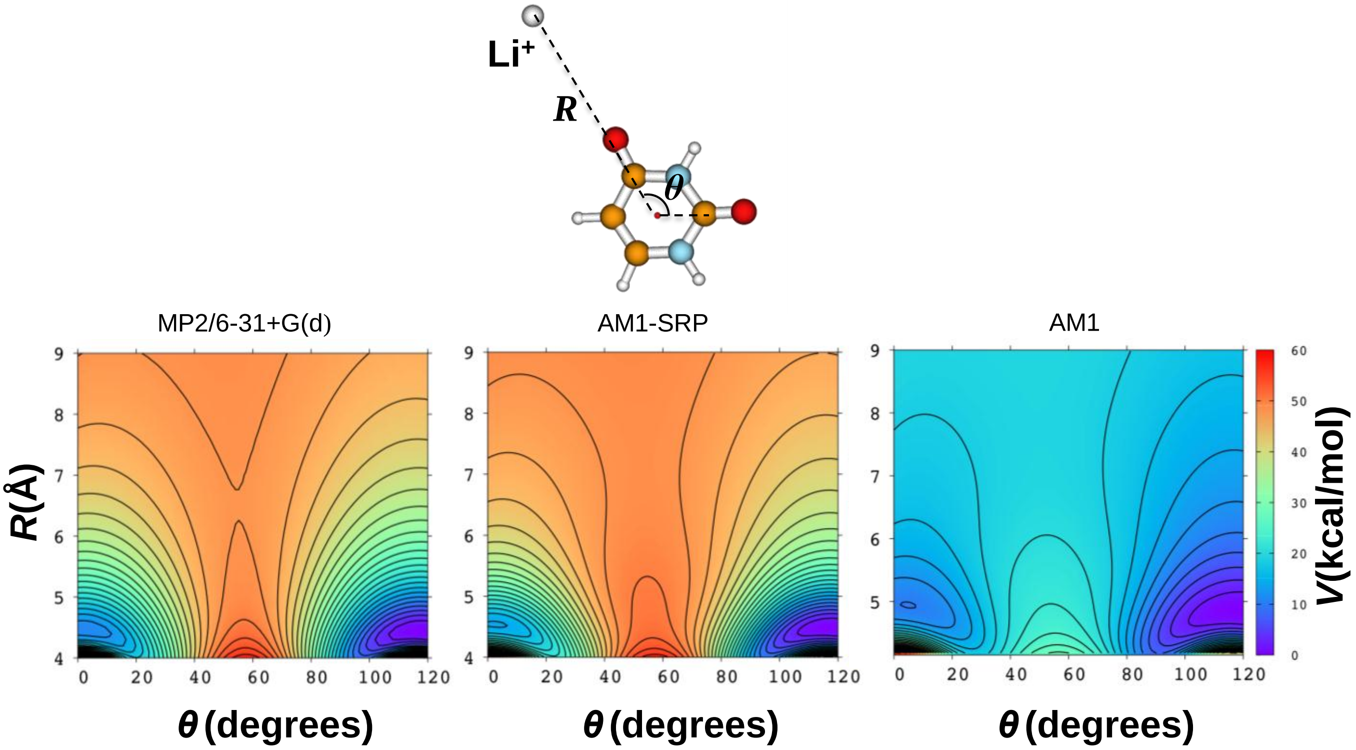


Figure 2. Stationary points found in our study for $[Li(uracil)]^+$ at the MP2/6-31+G(d) and AM1-SRP levels of theory. Distances are given in Å.

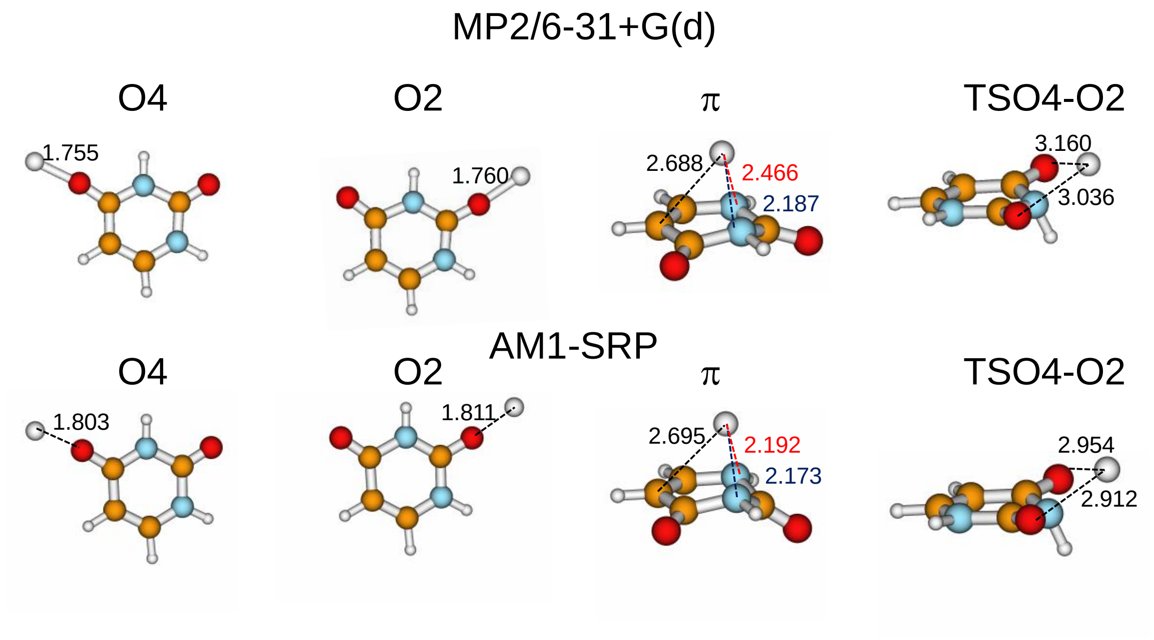


Figure 3. Analytical potential of eq 2 (solid lines) fitted to the RI-MP2(FC)/def2-QZVPP ab initio calculations (circles) for different orientations of Xe and $[\mathrm{Li(uracil)}]^+$.

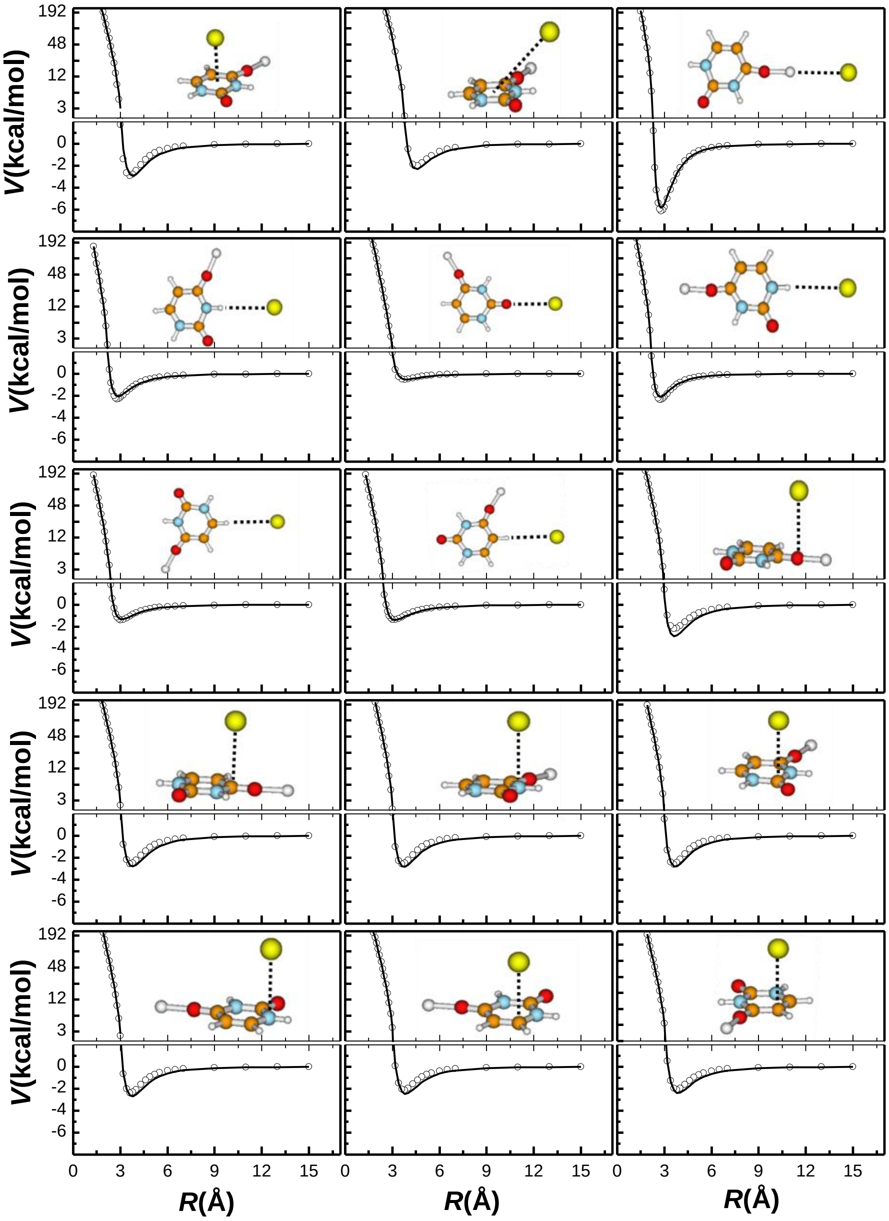
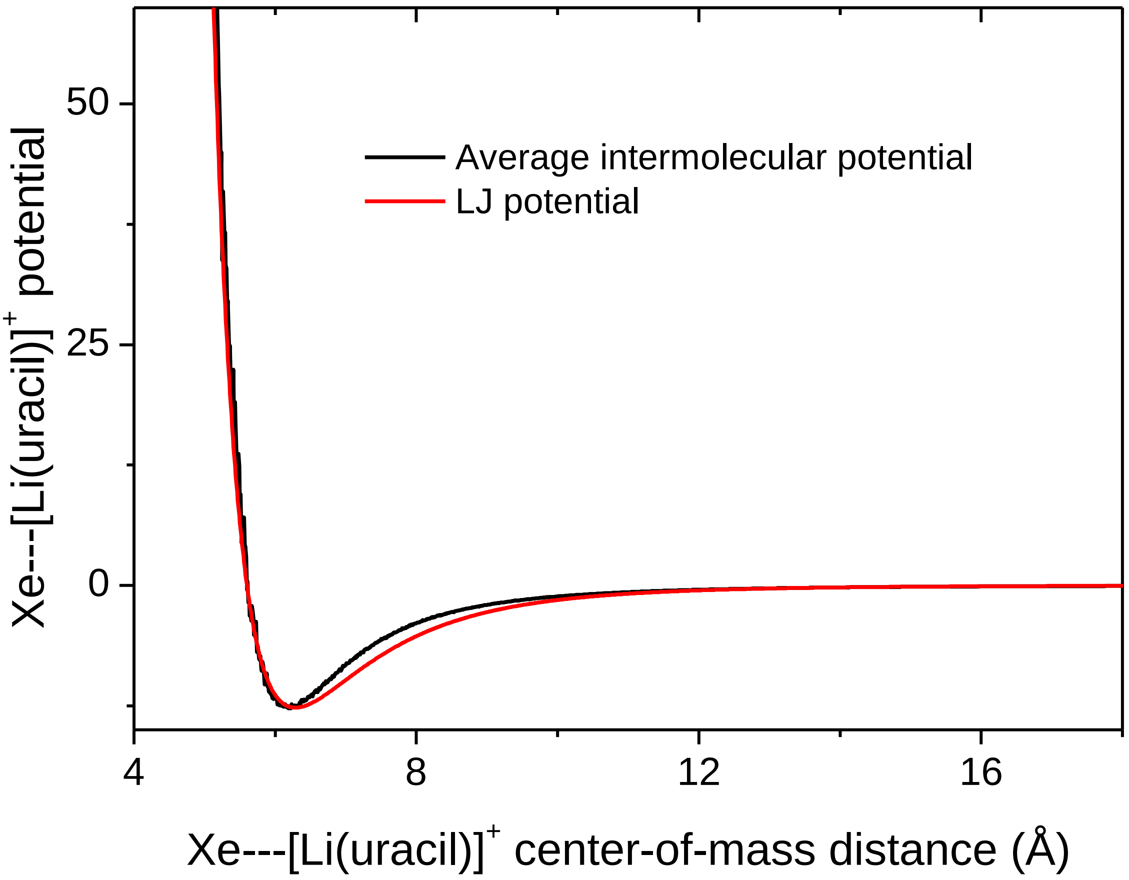


Figure 4. Average intermolecular potential and fitted LJ intermolecular potential for different Xe---[Li(uracil)]+ distances.



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