I. PARAMETERS OF THE MCTDH CALCULATIONS

In this supplementary section we list the technical details of multiconfiguration time-dependent Hartree (MCTDH) calculations presented in the letter. The calculations were done using the Heidelberg MCTDH package [1]. We used Jacobi coordinates, shown in Fig. 1, to represent the Hamiltonian of $HeLi_2$. The *ab initio* potential energy surfaces from Ref. [2] are given on a grid and are cast into the product form by using the POTFIT algorithm [3]. The two reduced masses entering the kinetic energy operator [4] are μ_r= 3.50 amu and μ_R= 3.1111 amu. The details on the used grids and propagation times are given below for each individual computation. To avoid the scattering of the outgoing wavepackets off the grid edge in the R and r coordinates we added a cubic complex absorbing potential (CAP) to the respective degrees of freedom. The CAP is given as $V_{cap}(R,r) = W^{(R)}_{cap}(R) + W^{(r)}_{cap}(r)$, where the potential along the coordinate z is

$$W^{(z)}_{cap}(z) = \begin{cases} 0, & z < z_{cap} \\ \frac{C_z}{z^3}, & z \geq z_{cap}. \end{cases} \tag{1}$$

with the CAP parameters listed in Tab I. To represent the Hamiltonian in Eq. 2 of the Letter we used the Discrete Variable Representaion (DVR) technique [5]. The grids, DVR types and the numbers of single particle functions used in full three dimensional calculation are given in Tabs. (II,III,IV). The grids, DVR types and the numbers of single particle functions used in two dimensional calculations are given in Tabs. (V – XII). The propagation time in all calculations is 100 ps, time step 1 fs. In the calculations we checked that the electron spectra are converged with respect to the following parameters: total propagation time, time step, grid step, and grid size.

[1] Current versions: 8.4.20 and 8.5.13 (2020). See http://mctdh.uni-hd.de/ for a description of the Heidelberg MCTDH package.

[2] A. Ghosh, L. S. Cederbaum, and K. Gokhberg, J. Chem. Phys **150**, 16409 (2019)

[3] A. Jäckle and H.-D. Meyer, J. Chem. Phys. **104**, 7974 (1996); D. Pelaez and H.D. Meyer, J. Chem. Phys. **138**, 014108 (2013)

[4] H. Meyer, Annu. Rev. Phys. Chem. **53**, 141 (2002)

[5] M. H. Beck, A.Jäckle, G.A.Worth H.-D.Meyer, Phys. Rep. **324**, 1 (2000).

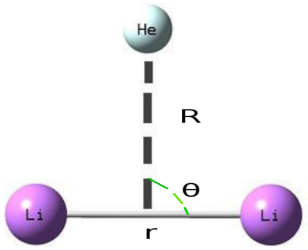

FIG. 1. Schematic representation of the $HeLi_2$ cluster and the Jacobi coordinates R, r, and θ used to compute nuclear dynamics. The coordinates stand respectively for the distance from He to the Li_2 center of mass, Li – Li distance, and the angle between the Li_2 molecular axis and the line connecting He with the center of mass of Li_2. From [2].

TABLE I. CAP parameters. All data are in a.u.

	R_{CAP} (C_R)	r_{CAP} (C_r)
He^+Li_2 ($^1\Sigma_g^+$)	89.0 (0.001084)	14 (0.372967)
He^+Li_2 ($^3\Sigma_u^+$)	89.0 (0.001084)	40 (0.001134)

TABLE II. MCTDH parameters used for the 3D propagation on the He^+Li_2 ($^1\Sigma_g^+$) PES.

mode	DVR	grid size	grid points
R	Sin DVR	0-50 $\AA$	417
r	Hermite DVR	1.6-8 $\AA$	54
θ	Restricted Legendre DVR	0-90°	45

TABLE III. MCTDH parameters used for the 3D propagation on the He^+Li_2 ($^3\Sigma_u^+$) PES.

mode	DVR	grid size	grid points
R	Sin DVR	0-50 $\mathring{A}$	417
r	Hermite DVR	2-24 $\mathring{A}$	183
θ	Restricted Legendre DVR	0-90°	45

TABLE IV. Number of single-particle functions (SPFs) used for the 3D MCTDH propagation on the He^+Li_2 ($^1\Sigma_g^+$) and He^+Li_2 ($^3\Sigma_u^+$) PES.

mode	SPF	SPF
	d[a]	f[b]
R	15	15
r	15	15
θ	15	15

[a]d represents the intermediate decaying states [b]f represents the double ionized final state

TABLE VI. MCTDH parameters used for the 2D propagation on the He^+Li_2 ($^1\Sigma_g^+$) PES along R and θ coordinates with r=2.69 Å.

mode	DVR	grid size	grid points
R	Sin DVR	0-50 $\mathring{A}$	417
θ	Restricted Legendre DVR	0-90°	45

TABLE V. MCTDH parameters used for the 2D propagation on He^+Li_2 ($^1\Sigma_g^+$) PES along R and r coordinates with $\theta = 0, \pi/2$

mode	DVR	grid size	grid points
R	Sin DVR	0-50 $\mathring{A}$	417
r	Hermite DVR	1.6-8 $\mathring{A}$	54

TABLE VII. MCTDH parameters used for the 2D propagation on the He^+Li_2 ($^3\Sigma_u^+$) PES along R and r coordinates with $\theta = 0, \pi/2$.

mode	DVR	grid size	grid points
R	Sin DVR	0-50 $\mathring{A}$	417
r	Hermite DVR	2-24 $\mathring{A}$	183

TABLE VIII. MCTDH parameters used for the 2D propagation on the He^+Li_2 ($^3\Sigma_u^+$) PES along R and θ coordinates with r= 4.18 Å.

mode	DVR	grid size	grid points
R	Sin DVR	0-50 $\mathring{A}$	417
θ	Restricted Legendre DVR	0-90°	45

TABLE IX. Number of single-particle functions (SPFs) used for the 2D MCTDH propagation on the He^+Li_2 ($^1\Sigma_g^+$) PES along R and r coordinates with $\theta = 0, \pi/2$.

mode	SPF	SPF
	d[a]	f[b]
R	15	10
r	15	10

[a]d represents the intermediate decaying states [b]f represents the double ionized final state

TABLE X. Number of single-particle functions (SPFs) used for the 2D MCTDH propagation on the He^+Li_2 ($^1\Sigma_g^+$) PES along R and θ coordinates with r=2.69 Å.

mode	SPF	SPF
	d[a]	f[b]
R	15	10
θ	15	10

[a]d represents the intermediate decaying states [b]f represents the double ionized final state

TABLE XI. Number of single-particle functions (SPFs) used for the 2D MCTDH propagation on the He^+Li_2 ($^3\Sigma_u^+$) PES along R and r coordinates with $\theta = 0, \pi/2$.

mode	SPF	SPF
	d[a]	f[b]
R	15	10
r	15	10

[a]d represents the intermediate decaying states; [b]f represents the double ionized final state

TABLE XII. Number of single-particle functions (SPFs) used for the 2D MCTDH propagation on the He^+Li_2 ($^3\Sigma_u^+$) PES along R and θ coordinates with r=4.18 Å.

mode	SPF	SPF
	d[a]	f[b]
R	15	10
θ	15	10

[a]d represents the intermediate decaying states [b]f represents the double ionized final state