Supplementary information

Quantum stereodynamics of the $Na(^2S) + NaLi(X^1\Sigma^+) \rightarrow Li(^2S) + Na_2(X^1\Sigma_g^+)$ reaction: effect of NaLi molecular alignment

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I. Reactant coordinate based TDWP method

The Hamiltonian of the system in reactant Jacobi coordinates can be expressed as:

$$\hat{H} = -\frac{\mathsf{h}^2}{2\mu_R}\frac{\partial^2}{\partial R^2} - \frac{\mathsf{h}^2}{2\mu_r}\frac{\partial^2}{\partial r^2} + \frac{\left(\hat{J}-\hat{j}\right)^2}{2\mu_R R^2} + \frac{\hat{j}^2}{2\mu_R R^2} + \mathrm{V}\left(R,r,\theta\right) \tag{1}$$

where μ_R and μ_r are the reduced masses corresponding to the atom-diatom distance R and diatomic bond length r, respectively. $\hat{J}$ is the total angular momentum operator of the $LiNa_2$ system and $\hat{j}$ is the rotational angular momentum operators of NaLi molecular. V is the potential energy that can be obtained by the three-dimensional PES.

The total wavefunction in the body-fixed (BF) frame is expand using a direct product basis:

$$\psi^{JMp}\left(R,r,\theta\right) = \sum_{n,v,j,K} F_{nvjK}^{JMp} u_n\left(R\right)\phi_v\left(r\right)y_{jK}^{JMp}\left(\theta\right) \tag{2}$$

where $u_n(R)$, $\phi_v(r)$ and $y_{jK}(\theta)$ are the translational, vibrational and rotational basis functions, respectively. The quantum number K, which represents the projection of the total angular momentum J onto the BF z-axis, ranges from 0 to J for even parity (p = +1) and from 1 to J for odd parity (p = -1).

The initial wave packet is constructed in the space-fixed (SF) frame as a product of the Gaussian wave packet $G(R)$ and initial rovibrational wavefunction $\phi_{v_0 j_0}\left(r,\theta\right)$. The $G(R)$ is defined as

$$G\left(R\right) = \left(\frac{2}{\pi\delta^2}\right)^{1/4} \exp\left[-\frac{\left(R-R_0\right)^2}{\delta^2} - i\sqrt{2\mu_R E_0}R\right] \tag{3}$$

where R_0, δ and E_0 represents the position, width and the mean collision energy of the initial wave packet, respectively.

The propagation of wave packet is performed using the second-order split-operator algorithm[1]. During the wave packet propagation, constructing an absorption potential effectively prevents the wave packet from being reflected at the grid edges. In our calculations, the absorption potential in the r and R directions is defined as a piecewise function:

$$D(x) = \begin{cases} \exp\left[-\Delta_t \cdot C_a \cdot \left(\dfrac{x-x_a}{x_b-x_a}\right)^2\right], & x_a \le x \le x_b \\ \exp\left[-\Delta_t \cdot C_b \cdot \left(\dfrac{x-x_b}{x_{\mathrm{end}}-x_b}\right)^2\right] \times \exp\left(-\Delta_t \cdot C_a\right), & x_b < x \le x_{\mathrm{end}} \end{cases} \tag{4}$$

The energy-dependent scattering matrix is calculated in the SF frame by applying the asymptotic boundary conditions：

$$S_{vjl\to v'j'l'}^{J\varepsilon}\left(E\right) = \frac{1}{\alpha\left(E\right)}\sqrt{\frac{k_f}{2\pi\mathsf{h}^2\mu_{R_f}}}h_{l'}\left(k_f R_{f\infty}\right)\left\langle \chi_{v'j'}\middle|\psi^{+}\left(E;R_{f\infty}\right)\right\rangle, \tag{5}$$

where $h_{l'}$ is the outgoing Riccati-Hankel function. k_f and $R_{f\infty}$ represent the wave vector in the exit

channel and the position of the project plane, respectively. $\chi_{v'j'}$ is product ro-vibrational wavefunction. The amplitude $\alpha(E)$ of the initial wave function at a specified collision energy is defined by

$$\alpha(E)=\sqrt{\frac{\mu_R}{2\pi\hbar^2 k_{vj}}}\int h_l(k_{vj}R)G(R)\mathrm{d}R\cdot \tag{6}$$

Finally, the S-matrix in the SF frame is then transformed into the helicity representation using the following relations：

$$S^J_{v'j'm',vjm}=S^J_{v'j'-m',vj-m}=\sqrt{\frac{(1+\delta_{m'0})(1+\delta_{m0})}{2}}\left[S^{J,+1}_{v'j'm',vjm}+S^{J,-1}_{v'j'm',vjm}\right], \tag{7}$$

and

$$S^J_{v'j'-m',vjm}=S^J_{v'j'm',vj-m}=(-1)^J\sqrt{\frac{(1+\delta_{m'0})(1+\delta_{m0})}{2}}\left[S^{J,+1}_{v'j'm',vjm}-S^{J,-1}_{v'j'm',vjm}\right], \tag{8}$$

where m denotes the projection of angular momentum along the quantization axis z at the direction of relative velocity. The state-to-state scattering amplitude can be calculated by

$$f_{vjm\to v'j'm'}(\vartheta,\phi,E)=\frac{1}{2ik_m}\sum\nolimits_J(2J+1)d^J_{mm'}(\vartheta)e^{i(m-m')\phi}S^J_{vjm\to v'j'm'}(E), \tag{9}$$

where ϑ is the polar angle and $d^J_{mm'}(\vartheta)$ is the Wigner's reduced rotation matrix. The azimuthal angle ϕ is constrained to zero throughout this study.

1 M. D. Feit, J. A. Fleck and A. Steiger, *J. Comput. Phys.*, 1982, **47**, 412-433.

II. The primary parameters employed in dynamical calculations

Table S1. Numerical parameters used in the TDWP calculations of the Na + NaLi ($v_0 = 0, j_0 = 1$) → Li + Na_2 reaction. Atomic units are used if not otherwise stated.

Parameter	Value
R	$R \in [0.3, 26.0]$, $N_R = 299$, $N_R^{Int} = 179$
r	$r \in [3.0, 30.0]$, $\nu_{Int} = 249$, $\nu_{Asy} = 11$
Rotational basis	$j_{Int} = 189, j_{Asy} = 89$
Initial wave packet	$R_0 = 18.0$, $\delta = 0.4$, $E_0 = 0.21$ eV
Absorbing potential	R: $C_a = 0.01$, $C_b = 0.04$, $R_a = 22.0$, $R_b = 25.5$ r: $C_a = 0.01$, $C_b = 0.04$, $r_a = 23.0$, $r_b = 29.5$
Propagation time	$T_{tot} = 300000$, $\Delta_t = 200$
Matching plane	$R_{0f} = 18.0$

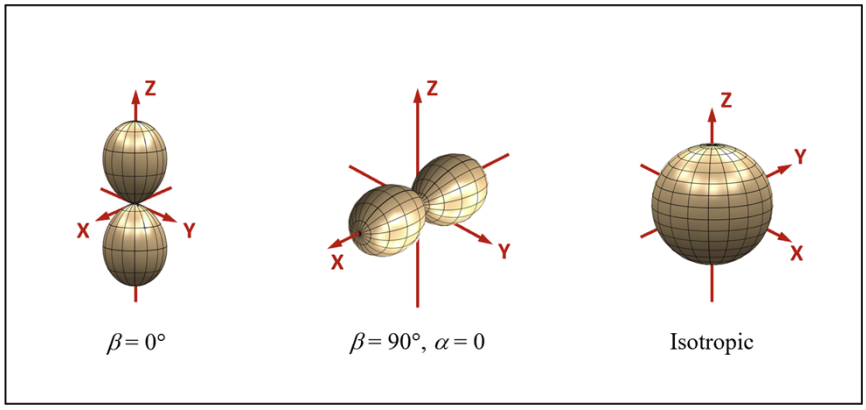

Fig.S1 The schematic of molecular bond axis distribution for different preparations.

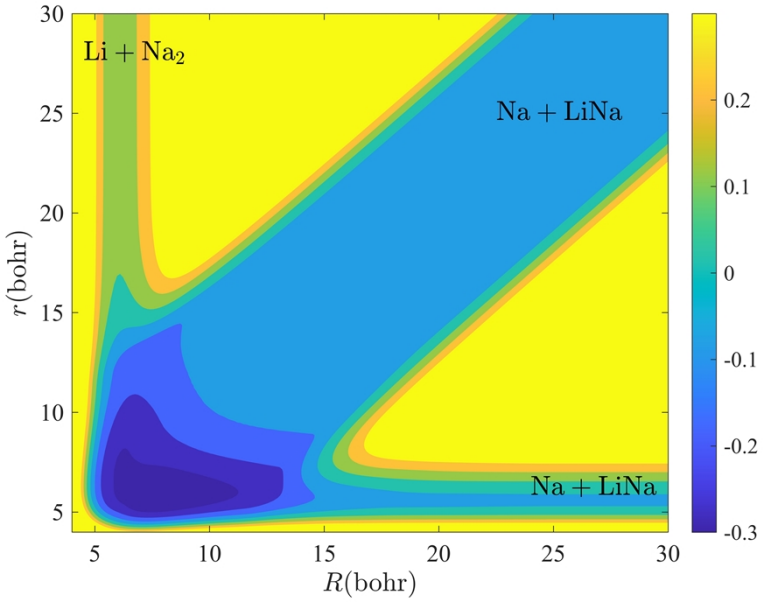

Fig.S2 Contour plot of the ground-state PES for the Na(^{2}S) + NaLi ($X^1\Sigma^+$) reaction in the Jacobi coordinate of the reactants.

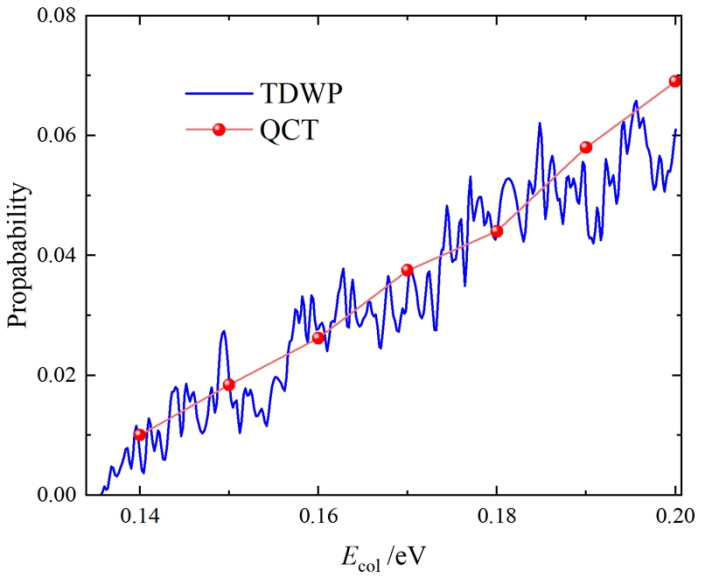

Fig. S3 Comparison of the reaction probabilities calculated by TDWP and QCT methods for the reaction Na + NaLi ($v_0 = 0, j_0 = 1$) → Li + Na_2 with total angular momentum $J = 0$.