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Electronic supplementary information for

The symmetric C-D stretching spectator mode in the $H+CHD_3 \rightarrow H_2+CD_3$ reaction and its effect on dynamical modeling

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I. Kinetic energy operators of the CZ_3 moiety.

The vibrational kinetic energy operator $\hat{K}_{CD_3}^{vib}$ in the 8D model reads

$$\begin{aligned}\hat{K}_{CD_3}^{vib} &= \frac{1}{8\rho^2}\left(\frac{3\sin^2\chi - 4\cos^2\chi}{\mu_x} + \frac{3\cos^2\chi - 4\sin^2\chi}{\mu_s}\right) \\ &-\frac{1}{2}\left(\frac{\sin^2\chi}{\mu_x} + \frac{\cos^2\chi}{\mu_s}\right)\frac{\partial^2}{\partial\rho^2} \\ &-\frac{1}{8}\left(\frac{1}{\mu_x} - \frac{1}{\mu_s}\right)\left(\frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{\partial}{\partial\rho}\frac{1}{\rho}\right)\left(\frac{\partial}{\partial\chi}\sin 2\chi + \sin 2\chi\frac{\partial}{\partial\chi}\right) \\ &-\frac{1}{4\rho^2}\left[\left(\frac{\sin^2\chi}{\mu_s} + \frac{\cos^2\chi}{\mu_x}\right)\frac{\partial^2}{\partial\chi^2} + \frac{\partial^2}{\partial\chi^2}\left(\frac{\sin^2\chi}{\mu_s} + \frac{\cos^2\chi}{\mu_x}\right)\right]\end{aligned} , \qquad \text{(S1)}$$

where the volume element $\sqrt{\mu_x\mu_s}\rho$ is incorporated and each term is written in either Hermitian or anti-Hermitian form. The reduced masses are $\mu_x = 3m_Z$ and $\mu_s = 3m_Z m_C/(3m_Z+m_C)$. In the 7D model, the CD bond length (ρ) is fixed at ρ_0 so that $\hat{K}_{CD_3}^{vib}$ is reduced to

$$\hat{K}_{CD_3}^{vib} = -\frac{1}{2\rho_0^2}\frac{\partial}{\partial\chi}\left(\frac{\sin^2\chi}{\mu_s} + \frac{\cos^2\chi}{\mu_x}\right)\frac{\partial}{\partial\chi} .$$

The rotational kinetic energy operator $\hat{K}_{CD_3}^{rot}$ reads

$$\hat{K}_{CD_3}^{rot} = \frac{1}{2I_A}\hat{\boldsymbol{j}}_2^2 + \left(\frac{1}{2I_C} - \frac{1}{2I_A}\right)\hat{j}_z^2 , \qquad \text{(S2)}$$

where $\hat{j}_z$ is the projection of the CD_3 rotational angular momentum $\hat{\boldsymbol{j}}_2$ along the ***s*** vector, and the principal moments of inertia I_A and I_C are defined as

$$I_A = \frac{3}{2}m_Z\rho^2\left(\sin^2\chi + \frac{2m_C}{m_C + 3m_Z}\cos^2\chi\right) , \qquad \text{(S3a)}$$

$$I_C = 3m_Z\rho^2\sin^2\chi . \qquad \text{(S3b)}$$

II. Basis representation

The basis functions in Eqn. (2) of the main text are given explicitly here. $f_{n_R}(R)$ is the sine discrete variable representation (DVR)[2] for the *R* coordinate,

$$f_{n_R}(R)=\sqrt{\frac{2}{R_2-R_1}}\sin\frac{n_R\pi(R-R_1)}{R_2-R_1}, \tag{S4}$$

where R_1 and R_2 are the grid boundaries. $\phi^r_{n_r}$, $\phi^\rho_{n_\rho}$, and $\phi^\chi_{n_\chi}$ are the potential optimized DVRs (PODVRs)[3] basis functions for the r, ρ, and χ coordinates, respectively. These basis functions are the eigenstates of the following one-dimensional (1D) reference Hamiltonians,

$$\hat{h}_r(r)=-\frac{1}{2\mu_r}\frac{\partial^2}{\partial r^2}+V_r^{ref}(r), \tag{S5a}$$

$$\hat{h}_\rho(\rho)=-\frac{1}{2}\left(\frac{\sin^2\chi_0}{\mu_x}+\frac{\cos^2\chi_0}{\mu_s}\right)\frac{\partial^2}{\partial\rho^2}+V_\rho^{ref}(\rho), \tag{S5b}$$

$$\hat{h}_\chi(\chi)=-\frac{1}{2\rho_0^2}\left(\frac{\sin^2\chi_0}{\mu_s}+\frac{\cos^2\chi_0}{\mu_x}\right)\frac{\partial^2}{\partial\chi^2}+V_\chi^{ref}(\chi), \tag{S5c}$$

where $V_r^{ref}(r)$, $V_\rho^{ref}(\rho)$ and $V_\chi^{ref}(\chi)$ are the corresponding one-dimensional reference potentials, obtained as the cuts of the PES in the asymptotic region with other coordinates fixed at the equilibrium values. ρ_0 and χ_0 are the equilibrium values of the CD_3 fragment in the CHD_3 reactant. An L-shaped representation[4] is used to divide the configuration space into asymptotic and interaction regions along the R and r DOFs. In the interaction region, N_R^{int} and N_r^{int} grid points are used in R and r DOFs, respectively, and in the asymptotic region, N_R^{asy} and N_r^{asy} grid points are employed.

The rotational basis functions that adapt the space inversion and permutation symmetry adapted are constructed by applying the projection operator P_{ii}^{Γ} onto the parity-adapted rotational basis function $\mathcal{Y}_{Jj_1j_2k}^{J_{tot}M\bar{K}\varepsilon}$, i.e. $y_{Jj_1j_2k}^{J_{tot}M\bar{K}\Gamma\varepsilon}=P_{ii}^{\Gamma}\mathcal{Y}_{Jj_1j_2k}^{J_{tot}M\bar{K}\varepsilon}$, where Γ labels the irreducible representations according to the isomorphic C_{3v} symmetry group. The parity-adapted rotational basis function $\mathcal{Y}_{Jj_1j_2k}^{J_{tot}M\bar{K}\varepsilon}$ reads

$$\mathcal{Y}_{J j_1 j_2 k}^{J_{tot} M \bar{K} \varepsilon}(\alpha,\beta,\gamma,\theta,\varphi,\theta_s,\varphi_s) = \sqrt{\frac{1}{2(1+\delta_{\bar{K},0}\delta_{k,0})}} \Big[\tilde{D}_{M,\bar{K}}^{J_{tot}}(\alpha,\beta,\gamma) Y_{j_1 j_2 k}^{J\bar{K}}(\theta,\varphi,\theta_s,\varphi_s) + \varepsilon(-1)^{J_{tot}+J+j_1+j_2+k} \tilde{D}_{M,-\bar{K}}^{J_{tot}}(\alpha,\beta,\gamma) Y_{j_1 j_2 -k}^{J-\bar{K}}(\theta,\varphi,\theta_s,\varphi_s) \Big] . \quad \text{(S6)}$$

Here M and K are the projection of the total angular momentum along the z-axis of the SF and BF frames, respectively (See Figure 1 of the main text for the definitions of the SF and BF frames.). $\bar{K} = |K|$ is the absolute value of K. The eigenvalue of the parity operator $\hat{\varepsilon}$ is denoted by ε. Rotational basis functions with even (ε=+1) and odd (ε=-1) parities transform according to different irreducible representations of the space inversion symmetry group. The overall rotation of the system is described by

$$\tilde{D}_{M,\bar{K}}^{J_{tot}}(\alpha,\beta,\gamma) = \sqrt{\frac{2J_{tot}+1}{8\pi^2}} D_{M,\bar{K}}^{J_{tot}}(\alpha,\beta,\gamma)^*, \quad \text{(S7)}$$

where $D_{M,K}^{J_{tot}}(\alpha,\beta,\gamma)$ is the Wigner rotation matrix. The internal rotational basis function $Y_{j_1 j_2 k}^{J\bar{K}}$ reads

$$Y_{j_1 j_2 k}^{J\bar{K}}(\theta,\varphi,\theta_s,\varphi_s) = \sum_m D_{\bar{K},m}^{J}(0,\theta,\varphi)^* \langle j_2 m j_1 0 | Jm \rangle \sqrt{\frac{2j_2+1}{4\pi}} D_{m,k}^{j_2}(0,\theta_s,\varphi_s)^* y_{j_1}^{0}(0,0), \quad \text{(S8)}$$

where the spherical harmonics $y_{j_1}^{0}(0,0)$ is associated with the orbital angular momentum $\boldsymbol{j}_1$ of Y in the CHD_3-fixed frame. $\sqrt{(2j_2+1)/4\pi} D_{m,k}^{j_2}(0,\theta_s,\varphi_s)^*$ is associated with the rotation of CD_3 in the CHD_3-fixed frame. m and k are the projections of the angular momentum $\boldsymbol{j}_2$ along the $\boldsymbol{r}$ and $\boldsymbol{s}$ vectors, respectively. The coupled angular momentum $\boldsymbol{J}$ in the CHD_3-fixed frame is obtained by coupling $\boldsymbol{j}_1$ and $\boldsymbol{j}_2$ using the Clebsch-Gordan (CG) coefficients $\langle j_2 m j_1 0 | Jm \rangle$.[5] $D_{\bar{K},m}^{J}(0,\theta,\varphi)^*$ results from the rotation of the CHD_3-fixed frame to the BF frame.

References:

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Table S1. Parameters used in the calculations (Atomic units are used if not otherwise indicated)

	Thermal flux eigenstates	Real-time propagation
Total time/time step		6000/10
Dividing surface	r_{TF} =3.0	R_{∞} =11.0
R	$R \in$ (3.0,16.0), N_R^{int} =30, N_R^{asy} =80	$R \in$ (3.0,16.0), N_R^{int} =30, N_R^{asy} =80
r	$r_1 \in$ (1.5,5.0) N_r^{int} =30, N_r^{asy} =6	$r_1 \in$ (1.5,5.0) N_r^{int} =30, N_r^{asy} =6
ρ	$\rho \in$ (1.5,3.0) N_{ρ} =3	$\rho \in$ (1.5,3.0) N_{ρ} =3
χ	$\chi \in$ (0.7,2.5) in rad. N_{χ} =6	$\chi \in$ (0.7,2.5) in rad. N_{χ} =12
J	$J \in (0,50)$	$J \in (0,50)$
j_1	$j_1 \in (0,42)$	$j_1 \in (0,42)$
j_2	$j_2 \in (0,24)$	$j_2 \in (0,24)$
j_z	$j_z \in (0,6)$	$j_z \in (0,6)$