Aug. 11, 2018

ELECTRONIC SUPPLEMENTARY INFORMATION

Direct Diabatization Based on Nonadiabatic Couplings: The N/D Method

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(1) *Origin* files for visualizing the H_3-LIN and H_3-BENT examples

The electronic supplementary information includes two standalone files:

- H3_LIN.opj
- H3_BENT.opj

These are files produced by the Origin (version 9.3) software for interactive visualization of the H_3-LIN and H_3-BENT data shown noninteractively shown in Figs. 5 and 6, respectively. The files can be opened with the program *Origin* or with the freely distributed *Origin* Viewer program (https://www.originlab.com/viewer/).

(2) Comparison of *Molpro*-derived NAC and N/D-derived $\nabla\theta_{JK}$ for LiF

To compare the *Molpro*-derived NAC and N/D-derived $\nabla\theta_{JK}$, we used the LiF system presented in the manuscript ($\varepsilon = 160\ \mathrm{E_h^{-1}}$). The magnitudes of the NAC elements were calculated as described in the manuscript by using *Molpro* and eqs (15), (17), and (18), where $w_\rho = 1$ for both Li and F atoms. This results in the plot of $g_{12}(\mathrm{R_{LiF}})$ shown in Fig. S1(b) below and Fig 1(a) in the manuscript.

We fit rotation angle, $\theta_{12}(\mathrm{R_{LiF}})$ by employing the integral of the Cauchy–Lorentz distribution function, $f_{CL}(R_{\mathrm{LiF}})$:

$$f_{CL}(R_{\mathrm{LiF}}) = \frac{1}{\pi\gamma\left[1+\left(\frac{R_{\mathrm{LiF}}-R_0}{\gamma}\right)^2\right]}$$

$$F_{CL}(R_{\mathrm{LiF}}) = \int f_{CL}(R_{\mathrm{LiF}})\,\mathrm{d}R_{\mathrm{LiF}} = \frac{1}{2}+\frac{1}{\pi}\mathrm{atan}\left(\frac{R_{\mathrm{LiF}}-R_0}{\gamma}\right)$$

In the fit, the complementary F_{CL} function: $1 - F_{CL}(R_{\mathrm{LiF}})$, is used because $\theta_{12}(\mathrm{R_{LiF}})$ behaves like a vertical reflection of the integral. The derivative of the fitted $\theta_{12}(\mathrm{R_{LiF}})$ with respect to $\mathrm{R_{LIF}}$ is: $-f_{CL}(R_{\mathrm{LiF}})$. Since the range of $\theta_{12}(\mathrm{R_{LiF}})$ is 0 to $\pi/2$, the function was normalized before the fit. The two fit parameters, R_0 and γ were evaluated with *Excel* Solver: $R_0 = 5.73255$ Å and $\gamma = 0.27564$ Å. For comparison with $g_{12}(\mathrm{R_{LiF}})$, the absolute value of $f_{CL}(R_{\mathrm{LiF}})$ was multiplied by $\pi/2$ (to adjust to $\theta_{12}(\mathrm{R_{LiF}})$) and converted from $\mathrm{Å^{-1}}$ to $\mathrm{bohr^{-1}}$; the new function is $f'_{CL}(R_{\mathrm{LiF}})$. All of the curves described are plotted in Figure S1. The comparison between the

derivative of the rotation angle and the NAC is good. Around the state crossing ($R_{LiF} = \sim$5.7 Å), the $g_{12}(\mathrm{R_{LiF}})$ and $f'_{CL}(R_{\mathrm{LiF}})$ curves both show a large jump. In the $R_{LiF} < 4$ Å region, the $g_{12}(\mathrm{R_{LiF}})$ shows different behavior than the fit. This feature of $g_{12}(\mathrm{R_{LiF}})$ was purposely avoided in our N/D diabatization and this current fit, i.e., the diabats and the adiabats are close to equal.

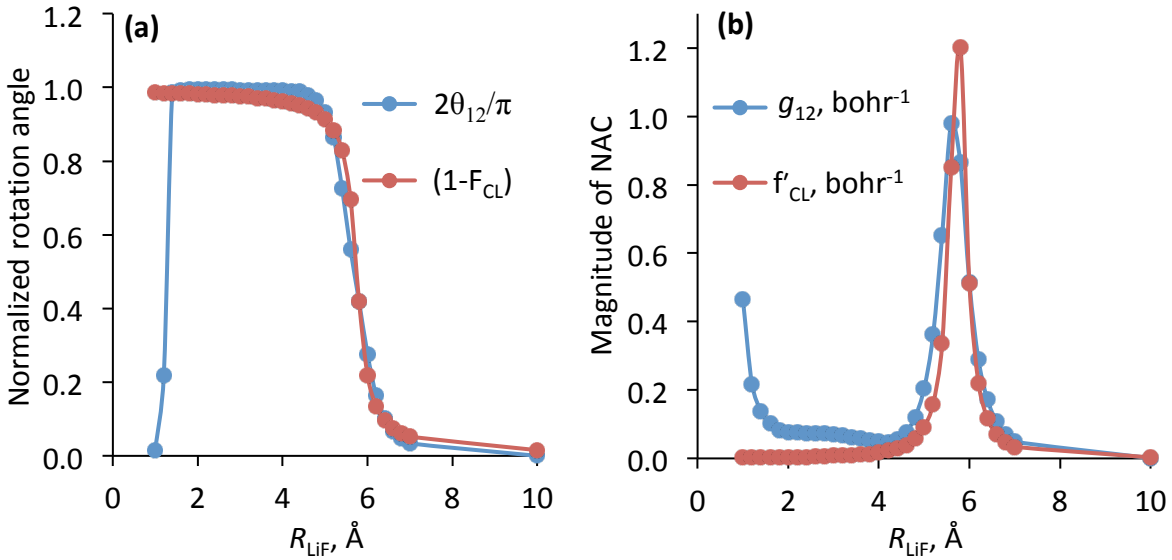

Fig. S1. Plot (a) shows the normalized rotation angle θ_{12} and its fit by the complementary $F_{CL}(R_{\mathrm{LIF}})$ function. Plot (b) compares g_{12} (magnitude of calculated NACs) with the f'_{CL} function (derivative of complementary $F_{CL}(R_{\mathrm{LIF}})$ function).