6-11-2020

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B. K. Kendrick
Los Alamos National Laboratory

M. Li
Temple University

H. Li
Temple University

S. Kotochigova
Temple University

J. F.E. Croft
University of Otago

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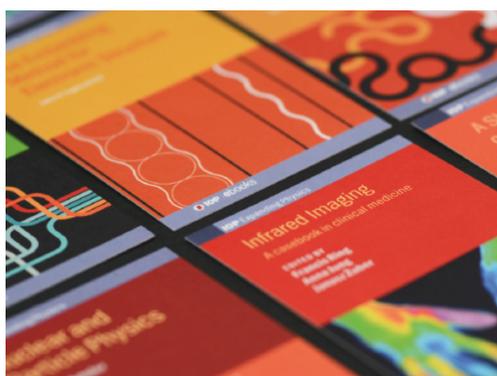See next page for additional authors

Authors

B. K. Kendrick, M. Li, H. Li, S. Kotochigova, J. F.E. Croft, and Balakrishnan Naduvalath

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To cite this article: B K Kendrick *et al* 2020 *J. Phys.: Conf. Ser.* **1412** 122016

Non-adiabatic quantum dynamics of the ultracold Li+LiNa→ Li$_2$+Na chemical reaction

B K Kendrick[1]*, M Li[2], H Li[2], S Kotochigova[2], J F E Croft[3] and N Balakrishnan[4]†

[1] Theoretical Division (T-1, MS B221), Los Alamos National Laboratory, Los Alamos, NM 87545, USA
[2] Department of Physics, Temple University, Philadelphia, Pennsylvania 19122, USA
[3] Department of Physics, University of Otago, Dunedin, New Zealand
[3] The Dodd Walls Centre for Photonic and Quantum Technologies, New Zealand
[4] Department of Chemistry and Biochemistry, University of Nevada, Las Vegas, NV 89154, USA

Synopsis   We report non-adiabatic dynamics of the Li+LiNa→Li$_2$+Na chemical reaction at cold and ultracold temperatures employing accurate ab initio electronic potential energy surfaces in a quantum dynamics formulation employing a diabatic representation. Results are compared against those from a single adiabatic ground state potential energy surface and a universal model based on the long-range interaction potential. We discuss signatures of non-universal behavior in the total rate coefficients as well as strong non-adiabatic effects in the state-to-state rotationally resolved rate coefficients.

Ultracold molecules, polar molecules in particular, are now at the forefront of precision spectroscopy, sensing, controlled studies of chemical reactions, quantum many-body physics, and quantum computing. Polar molecules comprised of heteronuclear alkali metal dimers such as KRb, NaK and LiNa have attracted considerable attention in recent years in controlled studies of chemical reactions. Electronically non-adiabatic effects are expected to play an important role in atom-dimer reactions involving these systems, e.g., K+KRb or Li+LiNa. These systems exhibit a conical intersection (CI) between the ground electronic state and the first excited doublet electronic state. The CI becomes accessible even for collision energies in the ultracold limit for ground state reactants. Explicit quantum calculations for these reactions remain a formidable challenge even for dynamics on a single adiabatic electronic potential surface.

Here, we report a first principles quantum dynamics study of non-adiabatic effects in Li+LiNa($v = 0, j = 0$) →Li$_2$(v', j')+Na reaction and compare results against a calculation that neglects non-adiabatic and geometric phase effects as well as that obtained using a universal model based on long-range forces. Details of the quantum dynamics method are given elsewhere [1]. Figure 1 compares non-thermal rate coefficients for total angular momentum quantum number $J = 0$ (s-wave scattering in the incident channel) from the two-state calculations

within a diabatic representation against a single surface calculation that excludes any geometric phase and non-adiabatic effects. The results correspond to even exchange symmetry (exchange of the two identical Li atoms). It is seen that the limiting values of the total and vibrationally resolved rate coefficients differ by factors of about 1.2 and 1.6. For rotational resolved rates, the results differ by an order of magnitude or more between 2-state and single surface calculations.
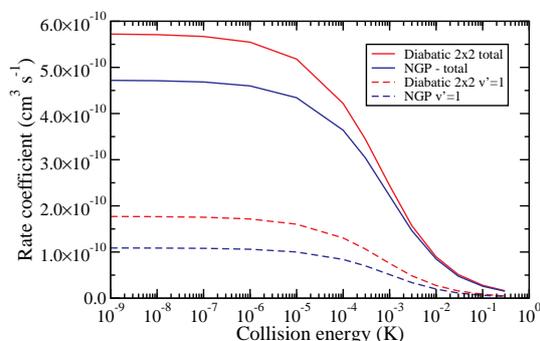

Figure 1. Rate coefficients for the Li+LiNa($v = 0, j = 0$) → Li$_2$(v')+Na reaction as a function of the collision energy. The diabatic 2×2 results correspond to the two-state calculation that implicitly accounts for the geometric phase effect. The NGP (no-geometric phase) result corresponds to a single ground state adiabatic potential. The results are for even exchange symmetry of the identical Li atoms and do not include nuclear spin-statistics factors.

References

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*E-mail: bkendric@lanl.gov
†E-mail: naduvala@unlv.nevada.edu