

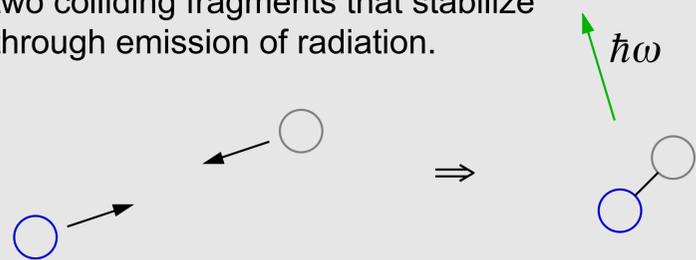
Formation of NaCl through radiative association: Computations accounting for non-adiabatic dynamics

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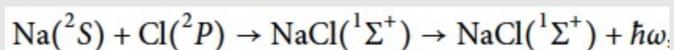
The formation of sodium chloride (NaCl) molecules through radiative association is studied computationally. It is found that non-adiabatic couplings affect the formation cross section by several orders of magnitude at energies in the meV range (Gustafsson JCP 153, 114305 (2020)). This is important for studies of interstellar objects where NaCl is abundant, for example the Egg Nebula (Ginsburg et al. APJ 872, 54 (2019)).

Introduction

Radiative association is molecule formation from two colliding fragments that stabilize through emission of radiation.



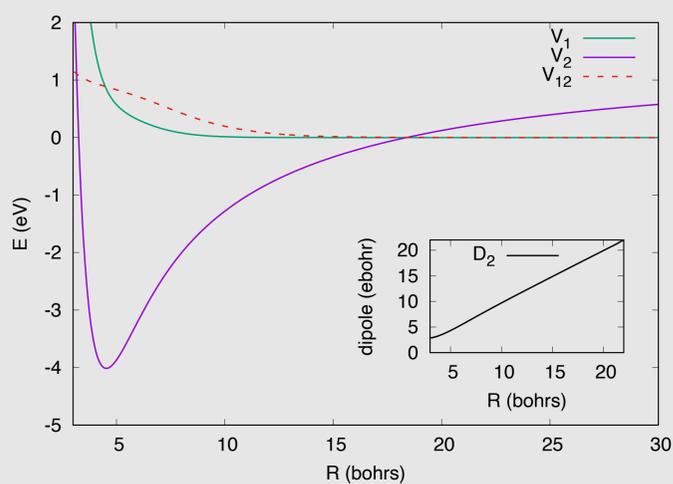
Radiative association of neutral diatomic molecules has not been possible to study in laboratory experiments yet. Since radiative association contributes to the chemical evolution in the interstellar medium, it is important to obtain computed formation rates. In this work we focus on the reaction



which may involve a non-adiabatic coupling.

Theoretical approach

There are several methods to compute radiative association for formation of diatomic molecules. They are based on classical or quantum collision theory, and typically they are one-dimensional, uncoupled problems. NaCl is a textbook example of a molecule where a non-adiabatic coupling exists.



NaCl($^1\Sigma^+$) potential energies for the atomic, $V_1(R)$, and ionic, $V_2(R)$, states, respectively. $V_{12}(R)$ is the coupling. The inset shows the dipole moment, $D_2(R)$, for the ionic state. The data comes from Giese and York JCP 120, 7939 (2004).

To account for these we solve the coupled Schrödinger equation (see e.g. Tchang-Brillet et al. JCP 96, 6735 (1992)).

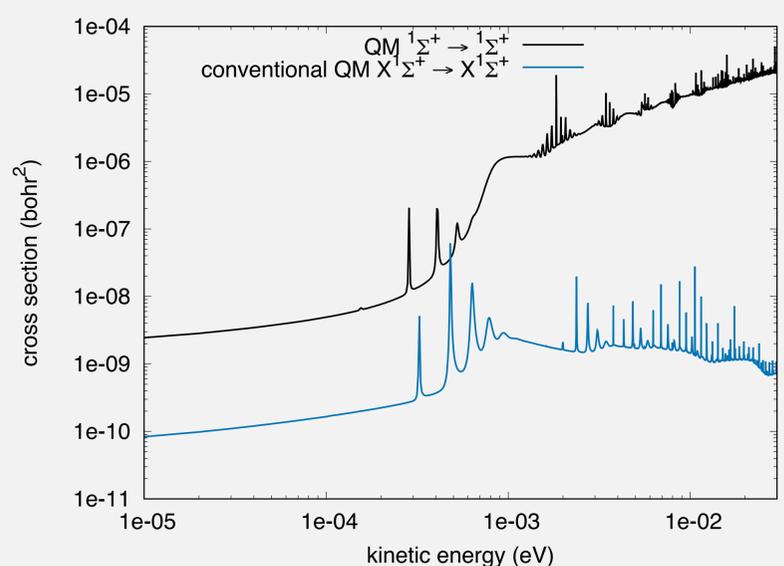
$$\frac{d^2}{dR^2} \mathbf{F}(R, E, J) + \frac{2\mu}{\hbar^2} [EI - \mathbf{V}(R, J)] \mathbf{F}(R, E, J) = 0$$

$$\mathbf{V}(R, J) = \begin{bmatrix} V_1(R) + \frac{\hbar^2 J(J+1)}{2\mu R^2} & V_{12}(R) \\ V_{12}(R) & V_2(R) + \frac{\hbar^2 J(J+1)}{2\mu R^2} \end{bmatrix}$$

\mathbf{F} = continuum wave function
 J = dumbbell angular momentum
 E = kinetic collision energy
 μ = reduced mass of the diatom

The cross section for molecule formation is computed as the matrix element of the dipole D_2 between the continuum wave function \mathbf{F} and a bound state wave function, computed on the ionic potential V_2 .

Results



Cross sections for forming NaCl through approach on the lowest $^1\Sigma^+$ state. The QM curve (black) is computed with non-adiabatic couplings and compared here with conventional QM, i.e. single channel quantum dynamics, in blue.

The cross sections show resonances, i.e. sharp peaks on a smooth baseline. In the single channel case those are shape resonances, which stem from tunneling through the centrifugal barrier to reach quasibound states. In the coupled case they come also from the coupling, which can mediate pathways to quasibound states on the ionic, V_2 , potential.

By Boltzmann averaging the temperature dependent rate constant up to 30 K can be computed from the cross section data.

Outlook:

Need: coupled calculations for NaCl up to the eV range, so that formation rates at temperatures of several hundred Kelvins can be computed

Challenge: sufficient number of energy points to resolve the resonances

Game plan: parallelization of the code and other performance improvements

