Calculation of kinetic rate constants using high-level *ab initio* quantum chemical methods for planetary sciences and astrochemistry

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Existing photochemical models for the atmospheres of planetary bodies suffer from large errors when predicting the mole fraction profiles of various compounds. Global sensitivity analyses show that a major source of these model errors can be attributed to inaccurate rate coefficients for “key” radical–radical and radical–neutral reactions in low-temperature conditions. Accurate rate coefficients for key reactions thus improve the accuracy of photochemical models. Unfortunately, accurate experimental rate constants for such low-*T* reactions are difficult, if not impossible, to measure, and the lab data are affected by uncertainties in determining the absolute concentrations of radical species. Currently, the most common theoretical approach involves uncertainty extrapolation technique in which uncertainties in room-temperature rate constants are extrapolated to low-temperature conditions, resulting in large errors in the theoretical low-*T* rate constant data. To solve this existing problem, we are employing the two-transition-state (2TS) model developed by Klippenstein and coworkers to calculate high-level *ab initio* rate-constants for key low-*T* (*i.e.* 10–200K) reactions relevant to planetary atmospheres like that of Titan. In particular, we are investigating key reactions that have not yet been studied in the lab, and for which accurate rate coefficients are still unknown. Our calculated *ab initio* rate coefficients will be made available to the astrochemistry community via well-established free online kinetic databases (*e.g.* KIDA). These rate coefficients will be used by scientists in photochemical models to make accurate predictions of mole fraction profiles for planetary atmospheres and improve our understanding of the diverse chemistry of these bodies.

Keywords: Titan atmosphere, Low-temperature reaction kinetics, Ab initio quantum chemistry, Photochemical model, Plantery science, Astrochemistry

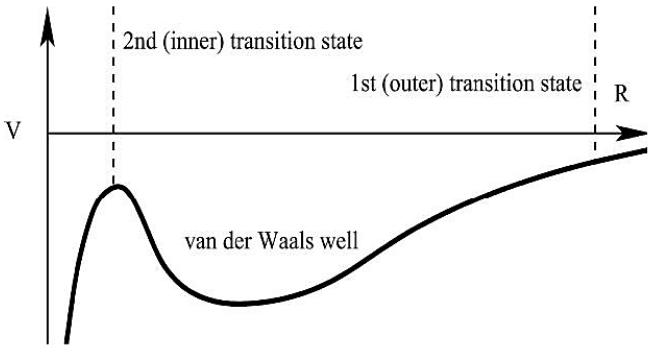

Figure 1. Schematic one-dimensional picture of the potential energy as a function of the reaction coordinate for a neutral–neutral reaction leading to bimolecular products. In its approach, the 2TS model incorporates both the 1st (outer) transition state for barrierless association reaction and the 2nd (inner) transition state for reaction path with a barrier. **Source:** Georgievskii and Klippenstein, 2007.

Table 1: Selected key reactions currently being investigated that are responsible for uncertainties in the mole fractions of major nitrogen species (left-most column) in low-*T* Titan conditions. Each reaction shown here has an absolute Rank Correlation Coefficient (RCC) value, a quantitative indicator of the sensitivity of model mole fractions on rate constants, greater than the chosen threshold of 0.2 at 100 km or above (right-most column). **Source:** Loison *et al.*, 2015.

Affected N Species	Key Reactions	|RCC| > 0.2
NH_3	$N(^4S) + NH_2 \rightarrow N_2 + H + H$	(100, 900) km
HNC	$N(^4S) + {}^3CH_2 \rightarrow HNC + H$	100 km
CH_2NH	$N(^2D) + CH_4 \rightarrow NH + CH_3$	900 km
CH_3C_3N	$^1CH_2 + CH_4 \rightarrow CH_3 + CH_3$	900 km
CH_3C_3N	$C_2N + H \rightarrow HCN + C$	900 km
C_2H_3CN	$CHCN + H \rightarrow C_2N + H_2$	900 km

