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Modified statistical model for the $CH^+ + H \rightarrow C^+ + H_2$ reaction

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Recent experiments [1] on the reaction of CH^+ with H present an interesting challenge for a theoretical interpretation. In view of the existence of a deep well in the potential energy surface (PES) of CH_2^+, the reaction is expected to proceed via the formation of a long-lived complex. However, the measured rate coefficient exhibits a strong decrease at low temperatures, which neither quasiclassical trajectory calculations [2,3] , nor quantum mechanical methods [3] using a full PES can explain.

It can be reasonably conjectured that the reduction of the reactivity is related to the presence of potential barriers in the near collinear configurations C-H-H and H-C-H, which hinder the formation of a complex. In this work, we investigate the possibility of an alignment of rotationally cold CH^+ along the CH^+-H axis using the notion of adiabatic rotation [4] or pendular [5] states. The largest alignment was found for the adiabatic rotation state labeled with $(j,\Omega)=(0,0)$ and to a somewhat lesser degree for the (1,1) and (1,0) states (Ω is the modulus of the projection of the rotational angular momentum $\boldsymbol{j}$ on to the collision axis. Thermal rate coefficients in Fig.1 are determined by standard statistical theory [6,7], using only polarization interactions in the reactant and product channels, but with a few possible energy-dependent restrictions on the reactivity of particular (j,Ω)-states.

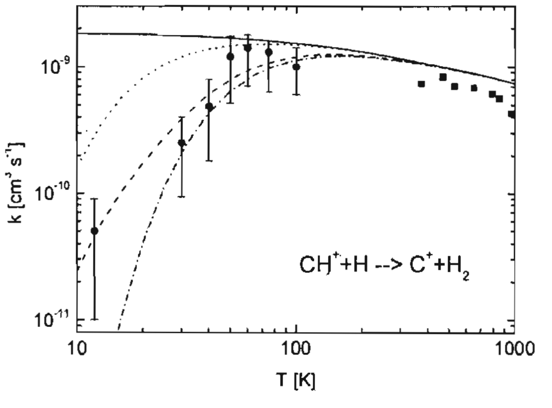

Fig.1. *Thermal rate coefficient as a function of temperature. Experimental results: circles [1] and squares [8]. Results of standard statistical theory: full line includes all (j,Ω) states of CH^+ and is in agreement with [2]. The dotted line excludes contribution of the (0,0) state assumed to be non-reactive due to alignment at collision energies $E_c<2B$ (B is the rotation constant of CH^+). The dashed line excludes contributions of (0,0) state for $E_c<6B$ and (1,1) states for $E_c<4B$ and the dot-dashed line excludes contributions of (0,0) state for $E_c<6B$ and (1,1) and (1,0) states for $E_c<4B$.*

Our calculations suggest that a very strong alignment occurs for the $j=0$ state and a large partial alignment of the $j=1$ states. This can explain very satisfactorily the main characteristics of the experimental rate coefficients. Of course a more sophisticated study is required in order to take into account of (and possibly re-examine) the detailed form of the PES close to linearity.

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