The dynamic study of $Ca(3^1D) + RH \rightarrow CaH(X^2\Sigma^+) + R$ (R=H or CH_3)

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The reaction pathway and the nascent CaH product distribution in the reaction $Ca(3^1D) + RH \rightarrow CaH(X^2\Sigma^+) + H$ are obtained using a pump-probe technique. The Ca atom is first prepared in the 3^1D state by a two-photon absorption, and then in brief time delay the laser-induced fluorescence of the reaction product CaH is monitored. For $Ca + H_2$, the temperature dependence measurement yields a positive slope, indicative of the reaction occurrence without any potential barrier, but for $Ca + CH_4$, we found the energy barrier about 2700 cm^{-1}.

I. INTRODUCTION

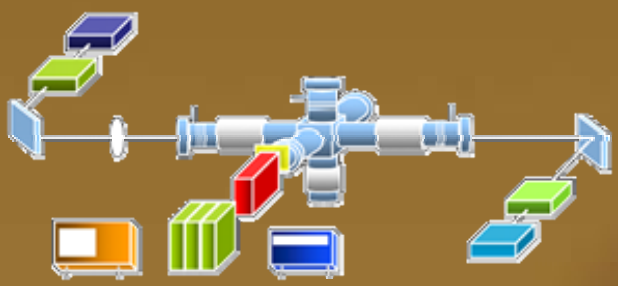
Activations of H–H, C–H, and C–C bonds by metal elements have attracted wide attention due to their concerns with catalytic and atmospheric chemistry and fuel exploration. Among them, the interaction between alkaline-earth metals and alkane hydrocarbons is actively focused on the following reaction channel by using a pump-probe technique:

$M^*(nsnp\ ^{1,3}P) + RH \rightarrow MH(\nu, N) + R.$

The energy required to initiate the reaction can be deposited in the electronic states of the metal atom *M with a pump laser source. Then the probe laser is applied after a brief time delay to monitor the *MH*v, *N* product distributions. In this manner, the nascent product distributions may be obtained even in a bulk system. The measurements of internal state distributions, energy disposal into the products, and vector-related information, combined with *ab initio* calculations of potential-energy surfaces PESs, may provide insight into the reaction dynamical complexity.**

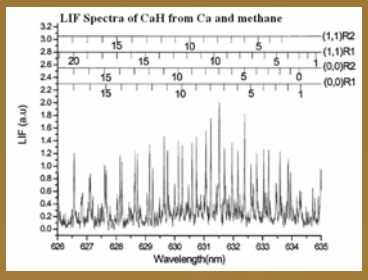
II. Experimental

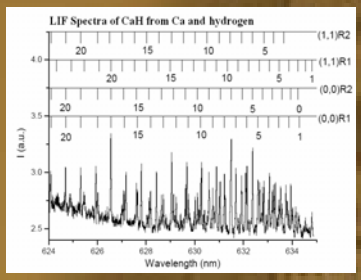
The pump-probe technique was composed of two tunable dye lasers. Each was pumped by an individual frequency-doubled Nd:YAG yttrium aluminum garnet laser operating at 10 Hz with a pulse duration of 5–8 ns. The pump laser, performed with a LDS 925 dye emitting at 915 nm, was used to prepare the Ca atom in the 3^1D^2 state via a two-photon absorption. After 20 ns delay, the probe-laser beam with a DCM dye was used to excite the laser-induced fluorescence LIF of CaH in the $B\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$ transition in the wavelength range of 626–635 nm. The spectral resolution was better than 0.1 cm^{-1}. The zero delay time was defined as the maximum temporal overlap between pump and probe pulses. A brief delay time avoided two-color multiphoton excitation processes and also ensured that the product population distribution was in a nascent state. The pump beam was directed through an 0.3 cm^2 pinhole and then focused with a 65 cm focal-length lens to the center of the reaction chamber, where it overlapped spatially with the unfocused probe beam counterpropagating through the other 0.3 cm^2 pinhole. The output energies after the pinholes were kept at about 1.1 mJ and 100 μJ for the pump and probe pulses, respectively.



III. Result & Discussion

1. Laser induced fluorescence spectrum

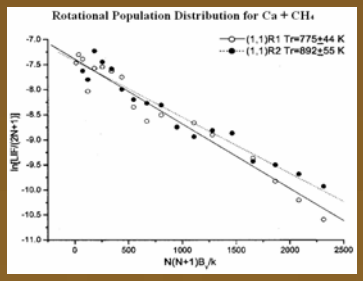


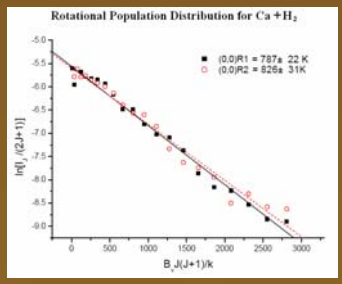


2. Rotational population distribution

The rotational population may be approximately characterized by a statistical thermal distribution. According to the equations , a plot of $\ln[I_J/(2J+1)]$ as a function of $B_vJ(J+1)/k$ in the CaH(v''=0) and (v'=1) distribution of each line yields a slope homologous to a Boltzmann rotational temperature T.

$$I_J = N_0 \frac{(2J+1)}{q} e^{\frac{-J(J+1)B_v}{kT}}$$

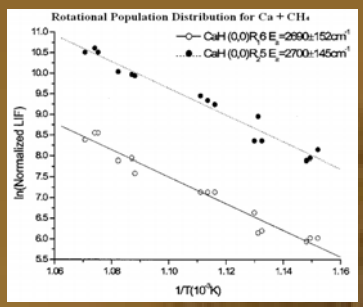


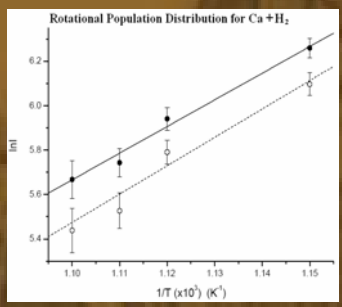


3. Temperature dependent

The rotational line intensities of CaH (0,0)$R_2$5 and (0,0)$R_1$6 were selected to be measured. Each peak area integrated and plotted against the reciprocal of the temperature on a logarithmic scale by Arrhenius plot .

$$\log k = \log A - \frac{E_a}{2.303\,RT}$$





IV Conclusions

The reaction pathway for $Ca(3^1D) + RH \rightarrow CaH(X^2\Sigma^+) + R$, R=$CH_3$ or H, has been investigated by using the pump–probe technique in combination with potential energy surface (PES) calculations. The nascent product distributions of CaH have been found with a Boltzmann rotational temperature of 1012 ± 102 K and 834 ± 70K for the v = 0 and 1 levels from $Ca + CH_4$, and 807 ± 38K and 684 ± 77K from $Ca + H_2$, respectively. For the reaction about $Ca + CH_4$ the Arrhenius plot of the rotational intensity versus the reciprocal of temperature yields a positive activation energy(2626±390cm^{-1}), indicating that the colliding process should cross a potential barrier , but for the reaction about $Ca + H_2$ we did not find any energy barrier. According to the PES calculations, the pathway is found to favor an insertion mechanism. $Ca(3^1D)$ approaches RH in C_{2v} or C_s symmetry.