

激發態鹼金族及鹼土族原子與小分子碰撞之理論 計算研究

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I. Abstract

In this research work, we calculated the ground state and excited states PES of Be + H₂, Be + CH₄, Na + CH₄ and Na + N₂. For the first three, we focused on the pathways of chemical quenching, while the last one is a physical quenching. Be(¹P) + H₂ → BeH + H occurs via a near C_{2v} intermediate in the 2A' state, where H-H = 1.4 Å for a better overlap between Be 2p_y and H₂ σ*. In the reaction of Be(¹P) + CH₄ → BeH + CH₃, the C_{3v} pathway has large 1A' and 2A' gap and thus is difficult for a non-adiabatic transition. The reaction is also likely to be a near C_{2v} one. Then the ground state Be will insert into one of the C-H bonds. While the anti-C_{3v} is not possible in Mg(¹P) + CH₄ → MgH + CH₃, it will be a possible pathway for Be(¹P) + CH₄ because Be is smaller. We used the same method to treat Na(4²P) + CH₄, but the 2A' and 1A' gap is always large, thus it is not likely to produce NaH.

In the physical quenching of Na(3²P) + N₂ → Na(²S) + N₂*, our result shows that it is also very likely via a near C_{2v} intermediate.

在這個研究計劃中我們計算了 Be + H₂, Be + CH₄, Na + CH₄ and Na + N₂ 基態及數個激發態的碰撞位能面。前三者主要是在尋找可能的化學反應途徑，最後一個則是非彈性碰撞。Be(¹P) + H₂ → BeH + H 是經由一個近 C_{2v} 的 2A' 中間物，其中 H-H = 1.4 Å，如此 Be 2p_y 和 H₂ σ* 可以形成較佳的軌域重疊。在 Be(¹P) + CH₄ → BeH + CH₃ 中 C_{3v} 抽取是不太可能，因為 1A' 與 2A' 始終間隔太大，以致難以進行 non-adiabatic transition。這個反應也是一個近 C_{2v} 的插入式反應，在轉至基態後鈹會插入其中一個 C-H 鍵。在 Mg(¹P) + CH₄ → MgH + CH₃ 中，anti-C_{3v} 無法進行反應，但是鈹比較小，所以也可以。我們以同樣的方式來處理 Na(4²P) + CH₄，但是 1A' 與 2A' 始終間隔太大，所以大概

很難生成 $\text{NaH} \cdot \text{Na}(3^2\text{P}) + \text{N}_2 \rightarrow \text{Na}(^2\text{S}) + \text{N}_2^*$ 也應經由近 C_{2v} 的插入式碰撞。

II. Key Words: potential energy surface, quenching, insertion, abstraction, side-on attack, end-on attack.

III. Introduction and Purpose

The collision between an excited IA or IIA atom with a small molecule has attracted physical chemists due to its simplicity for understanding fundamental dynamical theories. The reactions of these kinds of metals with alkanes or alkenes are also important in petroleum and catalytical industries. Further more, these kinds of collisions also occur in galaxies. In the early 1980's Breckenridge found that MgH resulted from $\text{Mg}(3^2\text{P}) + \text{H}_2$ had bimodal rotational distribution.¹⁻² It was suggested that the low J products came from an end-on attack of Mg^* , while the high J product came from a side-on attack. Later on the experiments showed that the bimodality had no obvious isotope and temperature effect.³ Chaquin et. al.⁴ also showed a 43 kcal/mol barrier for the end-on attack in their PES calculations. It is now known that either low or high J product are all resulted from side-on, a near C_{2v} attack. The reaction goes through an intermediate on the $2\text{A}'$ surface where H-H is about 1.5 Å for a better overlap between the metal $2p_y$ and H_2 σ^* . The bimodality is exit channel controlled on the $1\text{A}'$ surface. The reaction of Li^{*5} and Na^{*6} with H_2 is similar. Here, we tried to study the reaction

between $\text{Be}(^1\text{P})$ and H_2 for a comparison.

Breckenridge also found that MgH from $\text{Mg}(3^2\text{P}) + \text{CH}_4$ ⁷ also had bimodal rotational distribution. Chaquin's calculations⁸ indicated that direct abstraction of H by the metal via a C_{3v} pathway is not likely due to a barrier and a large gap between $2\text{A}'$ and $1\text{A}'$. But a near C_{2v} insertion followed by a distortion of methane would have almost no barrier. Chaquin's calculations also showed that $\text{Li}(2^2\text{P})$ would not react with methane. Several years ago, Kleiber did the experiment of $\text{Na}(4^2\text{P})$ with CH_4 , but did not find NaH .⁹ Thus, here we not only intend to obtain the PES of $\text{Be}(^1\text{P})$ with CH_4 , but also to obtain the PES of $\text{Na}^* + \text{CH}_4$.

The physical quenching of $\text{Na}(3^2\text{P})$ by N_2 had been intensively investigated in theories and experiments. Experiments showed that the peaked vibrational state of N_2 after collision is at $v' = 3$ or 4 .^{10,11} Habitz's¹² PES showed that the largest diabatic coupling occurs at Jacobian angle $\theta = 45^\circ$. Persico's¹³ PES showed that quenching would happen through a near C_{2v} intermediate on $2\text{A}'$. Poppe's PES¹⁴ showed that $\text{C}_{\infty v}$ collision also formed an intermediate. Here, we wanted to re-calculate the PES to ensure the pathways of quenching.

IV. Result and Discussion

We have calculated the potential curves of

Be(2^1P) + H₂ at $\theta = 1, 45$ and 89° and various H-H distances on the MRCI/ROOS basis set level. The $2A'$ well becomes deeper as θ increases from linear to perpendicular. This is because of the better overlap between Be $2p_y$ and H₂ σ^* . At $\theta = 89^\circ$, the well becomes deeper from $d(\text{H-H}) = 0.74$ (the equilibrium distance) to 1.4 \AA and then more shallow when $d(\text{H-H}) > 1.4 \text{ \AA}$. Thus, split of H-H up to 1.4 \AA will have the most efficient orbital overlap. We calculated the $3A'$ and $4A'$ potential curves. $3A'$ is $2p_z + \sigma$ asymptotically, which merges with $2A'$. Thus when one of the valence electrons of Be is excited to $2p$, it would have equal probability to move on $2A'$ and $3A'$. But there is a barrier on $3A'$ at $d(\text{Be-H}_2) = 2.2 \text{ \AA}$, which would need about 6000 K of experimental temperature to overcome it. Therefore we conclude that the pathway via $3p_z$ orbital will not be possible in a regular heat pipe reactor. We also obtained the $4A'$ surface, which is $4s + \sigma$ asymptotically and coupled with $3A'$ at $d(\text{Be-H}_2) = 1.7 \text{ \AA}$. Thus, Be at $4s$ can react with H₂ to form BeH. At $d(\text{H-H}) = 1.4 \text{ \AA}$ and short $d(\text{Be-H}_2)$, there are three non-adiabatic couplings. The one at $d(\text{Be-H}_2) = 1.3 \text{ \AA}$ is $1A'$ and $2A'$ coupling, the one at $d(\text{Be-H}_2) = 1.6 \text{ \AA}$ is $2A'$ and $3A'$ coupling and the most outer one is $1A'$ and $3A'$ coupling. When $d(\text{H-H})$ is small, there are only one coupling between $1A'$ and $2A'$. Also, as $d(\text{H-H}) > 1.4 \text{ \AA}$, these three coupling disappeared. We also obtained $1A'$ to $3A'$ for Li + H₂ at $d(\text{H-H}) = 1.4 \text{ \AA}$, but there is only $1A'$ - $2A'$ coupling. The reason here is that $3A'$ had been thought as a repulsive curve due to $3p_z + \sigma$. It is so asymptotically, but at short distance the $3a'$

and $4a'$ orbitals are so closed, where $4a'$ is $2p_y + \sigma^*$, and double excitation from $3a'$ to $4a'$ will occur. Therefore $3A'$ is also attractive. When H-H is too short or too long, $3a'$ and $4a'$ will not be too closed. Thus the $3A'$ well elevates and the three couplings disappear.

In Be(1^1P) + CH₄, our C_{3v} PES showed large $1A'$ and $2A'$ gap. Thus, it is not likely to react through this geometry. Since the reactants are on $2A'$ and the products are on $1A'$, there must be a non-adiabatic transition between these two states for the reaction to accomplish. We would like to find a geometry where $2A'$ and $1A'$ are very closed. When Be(1^1P) moves in along the dividing line of two C-H bonds to $d(\text{Be-C}) = 2.0 \text{ \AA}$, $2A'$ shows no obvious change but $1A'$ becomes repulsive. We then let Be rotate toward one of the hydrogen atoms (H_a) up to $d(\text{Be-H}_a)$ is nearly the equilibrium distance of a free BeH and CH₄ was kept not disturbed. Both $2A'$ and $1A'$ still showed no obvious change. Now we started to change CH₄ from T_d toward C_{3v} and let Be insert into C-H_a. At the beginning both $2A'$ and $1A'$ raised because breaking the C-H_a bond would need energy. Then $2A'$ formed a stable intermediate at $\angle\text{H}_a\text{BeC} \approx 90^\circ$, where $2A'$ and $1A'$ were very closed. We think that non-adiabatic transition can occur here. However, the $1A'$ energy still lowered beyond this angle up to $\angle\text{H}_a\text{BeC} = 180^\circ$. From the point of hybridization, ground state Be bonds to two moieties with its linear sp orbitals, while in its excited state, $2p_y$ is perpendicular to the sp orbital. That was why the $2A'$ and $1A'$

intermediate are at 90 and 180°. After the ground state CH₃-Be-H was formed, BeH left and the 1A' surface raised. However, in our calculations forming BeCH₃ is also exothermic. Our result shows that anti-C_{3v} is also a possible pathway, while it is not for the reaction of Mg* + CH₄. This could be due to the small size of Be. Be(³P) can proceed the same reaction as Be(¹P) does.

According to our private communication with Kleiber for his experiment of Na(4²P) + CH₄, in which no NaH was detected, we would like to understand the reason from PES. We treated this system with the same method for Be* + CH₄. Na(4²P) is the 8A' state. There is no direct coupling for 3A' to 8A' with 1A'. But transition state by state from 8A' to 3A' is easy due to small gap among these states. The key point is at the gap between 2A' and 1A'. But according to our calculations, 2A' and 1A' cannot be too closed to each other. We think that this could be the reason that Kleiber did not find NaH.

Although the transition between 2A' and 1A' for the quenching of Na*(3²P) by N₂ could take place at $\theta = 90, 45$ or 0° , our result shows that the most possible geometry is still near C_{2v}. The intermediate has d(N-N) ≈ 1.2 Å, slightly larger than its equilibrium distance 1.06 Å. This is for a better overlap between Na 3p_y and N₂ π^* . However there is also a 1A' shallow well for the end-on linear approach. For the reaction between metal and H₂, we did not find this 1A' well. That would be due to the

π electron of N₂ delocalizing over the empty 3p_y of Na.

V. Self-Evaluation

We have completed the work of Be* + H₂ and Be* + CH₄ and is writing papers for them. Na* + CH₄ and Na* + N₂ are nearly finished. We would like to do a QCT for Na* + N₂ to compare the peaked vibrational state of N₂ after collision with experiments.

VI. References

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