

An potential energy surface for the O + O₂ reaction using neutral network approach

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Abstract. A new potential energy surface (PES) of the O₃ system was reported, based on the PESs reported by Dawes et al. and Schinke et al. The PES of O₃ reported by Dawes et al. was fitted using least square method based upon accurate high level ab initio points, and has been applied to many dynamics calculations. However, it is computationally slow and need lots of time to obtain the energy points from the PES. At the same time, the threshold of the ab initio points is low as 2.6 eV, relative to the minimum of the PES, which limits its application. On the contrary, the PES reported by Schinke et al. numerically is fast and extends to high energy. In this work, we first calculated the energy points from these two PESs. Then we fitted these energy points using PIP-NN approach. In this way, a revised version of the PES of O₃ was constructed and we used it to perform quantum reactive scattering dynamics calculation.

Keywords: Weak Interaction; Hydrogen Bond; ES IPT; Charge Redistribution.

1. Introduction

In recent decades, lots of theoretical and experimental studies have been focused on the ozone molecule because it plays a crucial role in the physics and chemistry of the earth atmosphere. [1-4] However, there are also some issues related to the ozone properties are still unsolved. For most molecules the isotope enrichment scales are related to the mass difference, but the case of ozone does not follow the rule as was observed in laboratory experiments, in the troposphere and stratosphere. Thus, it is a challenging work to interpret the anomalous isotope enrichment in atmospheric ozone. The accurate determination of the 3D ozone potential energy surfaces (PES) is a prerequisite for theoretical calculations explain the experimental phenomena.

There are several groups [5-8] reported the PESs of O₃. For example, Schinke and co-workers [5] reported the O₃ PES at icMRCI+Q/cc-pVQZ level in 2003 (SSB PES). About 5000 ab initio points were used in their calculations and the reaction scattering has been performed based on their PES. In 2013, Dawes and coworkers [6] reported a new full-dimensional and global PES of O₃ (DLLJG PES), which is an improved PES based on their previous PES and the long range electrostatic model of Leper et al. [9] In the DLLJG PES, least square method was adopted to fit the PES, thus it is very time consuming for obtaining the energy points in the dynamics calculations. There is rapid development using neural network (NN) method in the construction of PES in recent years. The PES using NN method is fast and robust, and only very limited energy points are required.

Although DLLJG PES is accurate, the threshold energy is low, about 2.6 eV relative to its minimum. On the other hand,

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the SSB PES is computationally fast and extends to high energy. Therefore, we can refit the PES using the NN method [10,11], based upon the energy points obtained from the SSB and DLLJG PES, to make it fast and extend to high energy, without losing the accuracy of the PES below energy 2.6 eV. For this purpose, permutationally invariant polynomial (PIP) NN method will be applied. PIP-NN approach has significant advantages, particularly for those molecules where several atoms are identical. It allows reducing significantly the number of energy points needed for constructing the PES, automatically accounting for the intrinsic molecular symmetry. The resultant PES is analytic and smooth everywhere in the configuration space. Gradients and Hessians of the potential energy function can also be computed analytically.

2. Method

For constructing the PES, we first calculated the required energy points with the SSB and DLLJG PES. In detail, for R and r direction, 100 energy points has been adopted in the region from 0.5 bohr to 22 bohr; in angle direction, from 0 to 90 degree, step with 10 degree. Then, using these energy points

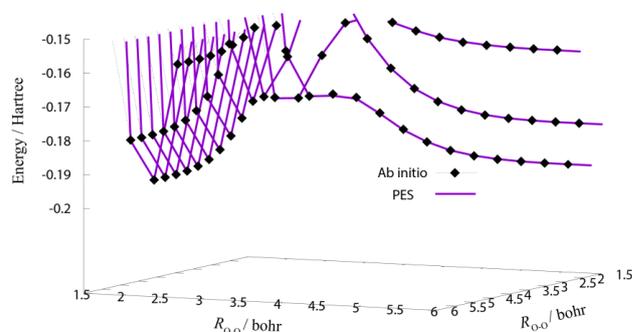


Fig. 1: The comparison between the “*ab initio*” points, which were obtained from the DLLJG PES and the new PIP-NN PES at the angle equal to 90 degree.

with the PIP-NN method the PES of O₃ was constructed. Here, we only have a brief introduce of PIP-NN method. The PIP-NN method [10,11] is widely used in the PES construction, such as H + MgH [12], O⁺ + H₂ [13], F + H₂ [14], Ne-C₂H₂ [15], OH⁺ + H₂ [16], H + CH₄ [17,18] reactions and so on. At first we transform the bond length to Q₁ = 1/r₁, Q₂ = 1/r₂ + 1/r₃, Q₃ = 1/(r₁*r₃), where r₁, r₂ and r₃ corresponds to the bond lengths, then we applied a feed backward neural network function with two hidden layer based on the Levenberg-Marquardt (LM) method. The functional form can be written as

$$y = b_1^3 + \sum_{k=1}^K (w_{1,k}^2 \cdot f^2(b_k^2 + \sum_{j=1}^J (w_{k,j}^2 \cdot f^1(b_j^1 + \sum_{i=1}^I (w_{j,i}^1 \cdot x_i)))))) \quad (1)$$

where I is the number of the ab initio points, J , K defines the number of neurons used for fitting, x_i ($i = 1, \dots, I$) are Q₁, Q₂, and Q₃ for a molecular configuration, the weights $w_{i,j}^l$ connect the i th neuron of ($l-1$)th layer and the j th neuron of l th layer, and the biases b_j^l determine the threshold of the j th neuron of l th layer, f^1 and f^2 are transfer functions. In present work, a neural network structure 3-30-30-1 is adopted in the calculation.

In order to have a better description for the PES in the asymptotic area, we fitted the PES with asymptotic energy as r or R little than 3.5 bohr; R or r larger than 8.0 bohr for every degree. Then, we connected the two PESs with a switch function which is written as

$$f(R) = \prod_n \left(1 - \frac{1}{2} \left(1 + \tanh \left(\frac{R_n - R_l}{R_w} \right) \right) \right) \quad (2)$$

where R_l is the position of the switch, and R_w is the constant of the switch strength.

After the construction of the PES using the PIP-NN method, we use it to perform the reactive scattering calculation by the time-dependent wave packet method with high-order split operator propagator. Then we compare the total reaction probabilities with those obtained using the

previous DLLJG PES.

3. Results and discussion

To In order to test the accuracy of present PES, we make a detail comparison between the DLLJG PES and present PES. First we make a comparison between the fitting result and the raw points which were obtained from the DLLJG PES. With angle equal to 90 degree, the comparison results are displayed in the **Fig. 1**. The agreement is good, suggesting that the PIP-NN method works well for this system.

The minimum energy reaction path of present PES and DLLJG PES are displayed in the **Fig. 2** for the angle equal to 30 and 180 degrees respectively. As seen in the plots, our present PES are in general good agreement with the DLLJG PES. However, there are small but detectable difference between these two PES at low energy, which may influences to the dynamics. Thus, we performed the dynamics calculation on these two PESs at total angular momentum $J = 0$ to check the accuracy of the new PES. In the calculation, same parameters as our previous work are used, which are able to give convergent results.[19]

Total reaction probabilities of the O + O₂ reaction based on the DLLJG PES and new PIP-NN PES are plotted in the **Fig. 3** as a function of collision energy. As seen in the figure, in general the probabilities calculated using the new PIP-NN PES are in good agreement with those using the PIP-NN PES. This indicates that present PES is accurate enough. However, this new PIP-NN PES is numerically fast and extends to high energy thus would be of applications of wider scope.

4. Conclusions

Based on the DLJG PES and SSB PES, a new revised PES is constructed for the O + O₂ reaction using the PIP-NN method. As comparing with previous PES, the new PIP-NN PES is numerical fast, and should be more accurate than the SSB PES. The new PES is compared in detail with the DLLJG PES. The

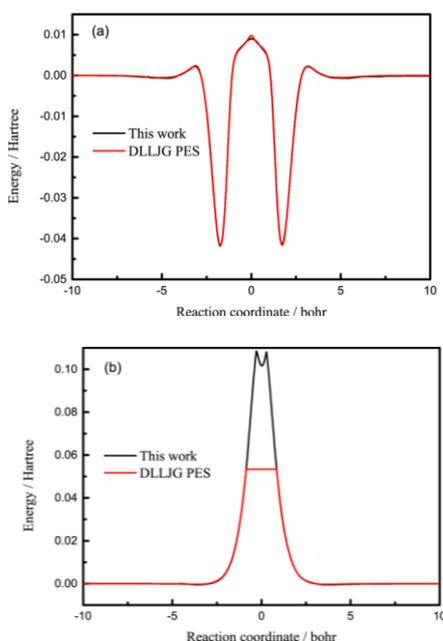


Fig. 2: The minimum energy reaction paths at the angle of 30 degree (a) and 180 degree (b) for present PIP-NN PES and DLLJG PES.

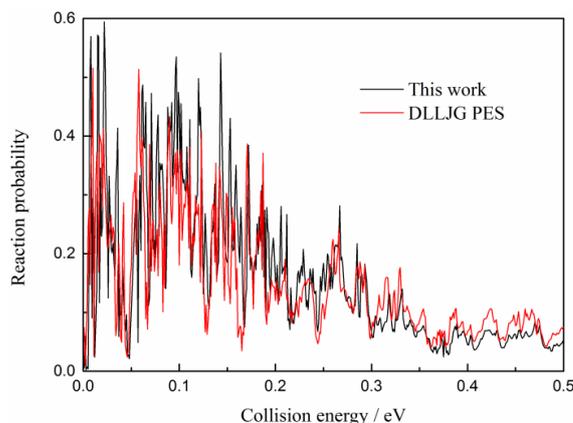


Fig. 3: The total reaction probabilities of the O + O₂ reaction based on present PES and DLLJG PES, respectively, at total angular momentum $J = 0$ in the collision energy range from 0 to 0.5 eV.

results indicated that in general the new PES is good agreement with the DLLJG PES. However, there are also some discrepancies at low collision energies. Reactive scattering calculation for the reaction of O + O₂ has been carried out based on the new PIP-NN PES and DLJG PES with total angular momentum J = 0. The dynamics results indicated that the difference between the two PESs is small.

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