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ABSTRACT

According to the existing combustion mechanisms, the main reactions related to NO$_2$ have been investigated in this research. Based on the transition state theory, the YL method proposed by Yao and Lin is utilized to obtain both the anharmonic and harmonic rate constants in a canonical system, respectively. The anharmonic effect of these reactions is also examined by comparing the anharmonic rate constant with the harmonic rate constant. The calculations indicate that there is a junction between the anharmonic and harmonic rate constants, and the anharmonic rate is lower than the harmonic one at high temperature. The results show that the anharmonic effect is significant and cannot be ignored, especially at high temperature. Finally, inspired by the least square idea, the kinetics and thermodynamic parameters of reaction mechanism involving NO$_2$ are also given in fuel combustion processes.

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I. INTRODUCTION

Fuel combustion is considered to be the most widely used way to produce energy; however, it also releases a large number of exhaust gases, such as carbon monoxide (CO), nitrogen oxides (NO$_x$), and sulfur oxides (SO$_x$), to the atmosphere. Environmentally, the influence of NO$_x$ on the global climate has become a catchword in the discussion about the fuel combustion. NO$_x$ in the atmosphere contributes to photochemical smog, to the formation of acid rain precursors, to the destruction of ozone in the stratosphere, and to global warming.$^{1-3}$ Additionally, it is well known that fuel goes through intricate chemical reactions when it is combusting. Subsequently, the development of suitable approaches for reducing NO$_x$ emission has been drawn heavily on the comprehensive understanding of the chemical reaction mechanism involved in the formation and consumption of NO$_x$. Nevertheless, the combustion of fuel is a complex multidimensional and multiphase process, involving a variety of reactants and products. In addition, the practical combustion condition cannot be presented easily and precisely in an experimental environment. Considering the fact that many combustion mechanisms obtained by theoretical research are in agreement with the experimental results, it is popular for many studies to apply the method of numerical modeling to obtain the combustion mechanism, which provides a microperspective to understand the fuel combustion processes and explain related experimental phenomena. On the other hand, it is noteworthy that NO$_2$ consists of a larger portion of total NO$_x$ resulting from combustion sources, which suggests that a more complete understanding of the mechanism related to NO$_2$ in fuel combustion processes is indeed required.

The purpose of this study is to investigate the anharmonic effect and calculate the rate constants of the main reactions related to NO$_2$ when fuel is burning. Besides, the harmonic and anharmonic rate constants are calculated by the YL (Yao and Lin) method in the canonical cases.$^{4-9}$ In this method, the transition state (TS) theory, Laplace transformation, and inverse Laplace transformation are employed, and the Morse oscillator (MO) is chosen to describe the anharmonic effect. Notably, in order to confirm the results of the rate constants obtained, we compare the rate constants of the reaction NO + O$_2$ → NO$_2$ + O (R5)
calculated with the ones obtained via the Arrhenius equation and the kinetics parameters provided by experiment. According to that experiment, an experimental measurement of the species concentrations using four quartz sampling probes was performed for the combustion gas of a premixed CH$_4$-air flame under fuel-lean and slightly fuel-rich conditions. Additionally, four quartz sampling probes were different in the sample pressure, the cooling rate, and the surface to volume ratio. Furthermore, a platinum/platinum rhodium 13% thermocouple and an alumel/chromel thermocouple were used to measure the combustion gas temperature at the probe position and the sample temperature within the probe, respectively. In addition, in the experiment, the flow of the sample in the probe was laminar and assumed to be one-dimensional. What is more, the NO and NO$_2$ concentrations were measured by using a chemiluminescent analyzer with a molybdenum converter, and the stable species concentrations were measured by using gas chromatographs. Finally, based on the idea of the least square, this paper obtains the reaction mechanism referring to NO$_2$ through the rate constant calculated. This work will contribute to providing a microperspective for reducing NOx emission in fuel combustion processes.

II. THEORY AND CALCULATION DETAILS

A. Canonical case and TS theory

According to the TS theory proposed, the rate constant $k$ for unimolecular dissociation in the canonical case is calculated as follows:

$$k = \frac{k_B T}{h} \cdot \frac{Q^*(T)}{Q(T)} e^{-\frac{\Delta E}{RT}},$$

(1)

where $Q(T)$ and $Q^*(T)$ are the partition functions of the reactant and TS, respectively. Besides, $h$ is Planck’s constant, $k_B$ is the Boltzmann constant, $T$ is the system temperature, and $E$ represents the activation energy. The expressions of $Q^*(T)$ and $Q(T)$ are given as

$$Q^*(T) = \prod_{i} q_i^*(T),$$

(2)

$$Q(T) = \prod_{i} q_i(T),$$

(3)

where $N$ is the number of the vibrational modes for reactant, $q_i^*(T)$ is the $i$th vibrational partition function of TS, and $q_i(T)$ is the $i$th vibrational partition function of the reactant. In the light of Eqs. (1)–(3), it is clear that the partition function plays a prominent role in calculating the rate constant. Regularly, $Q^*(T)$ and $Q(T)$ are calculated in the harmonic oscillator approximation. However, the anharmonic effect in the calculation of rate constant is considered by employing the MO, and MO is taken as a simple form, expressed as follows:

$$E_{a} = \left( u_i + \frac{1}{2} \right) \hbar \omega_i - \chi \left( u_i + \frac{1}{2} \right)^2 \hbar \omega_i,$$

(4)

where $\omega_i$ represents the frequency of the $i$th vibrational mode, $\hbar = \frac{h}{2}\pi$, and $u_i$ is the vibrational quantum number of the $i$th vibrational mode. Moreover, the maximum of $u_i$ can be calculated from $u_{max} = \frac{1}{2^N} - \frac{1}{2}$. Besides, $\chi_i$ is the anharmonic constant for various molecules, which can be determined with the help of ab initio calculations.

Likewise, for bimolecular reaction, $A + B \rightarrow C + D$, in a canonical system, the rate constant $k$ can be given by

$$k = \frac{k_B T}{h} \cdot \frac{Q^*(T)}{Q(T)} e^{-\frac{\Delta E}{RT}},$$

(5)

where $Q(A)$ and $Q(B)$ represent the partition functions of reactants $A$ and $B$, respectively. Consequently, the rate constants can be obtained for unimolecular and bimolecular reactions.

B. Reaction mechanism

1. Thermodynamic and kinetics parameters

CHEMKIN software, which is broadly used in combustion reaction research, is a flexible and powerful tool for incorporating complex chemical kinetics. By making use of Gaussian 09 software program, the anharmonic and harmonic thermodynamic data and kinetics data of reactants can be obtained, respectively, to fit the input-file data style of CHEMKIN. These thermodynamic data include constant-pressure specific heat capacity ($C_p$), enthalpy ($H$), and entropy ($S$). Additionally, the thermodynamic parameters of the reaction mechanism, $a_1 - a_n$, can be calculated from the above data on the basis of the least square method; the details are shown in Refs. 9 and 16.

The calculation of the kinetics parameters in the reaction mechanism is achieved according to the Arrhenius equation,

$$k = A T^n e^{-\frac{E_a}{RT}},$$

(6)

where $k$ is the rate constant, $A$ is the pre-exponential factor, $E_a$ is the activation energy, $R$ is the universal gas constant (8.314 J/mol K), and $n$ is the temperature exponent. This paper obtained the kinetics parameters ($A$, $n$, $E_a$) of each reaction studied, using the same method as that in Refs. 7 and 9.

C. Ab initio calculations

Ab initio calculations are carried out by Gaussian 09 program. The geometry optimization of the reactants and TSs, the B3LYP method with the 6-311++G** basis set is utilized. The harmonic and anharmonic vibrational frequencies, which are calculated at the same level, are used for characterization of stationary points, zero-point-energy (ZPE) corrections, and the calculations of reaction rate constants according to TS theory. In order to confirm that TS connected smoothly to the reactants and products, intrinsic reaction coordinate (IRC) is traced at the same level. For the purpose of achieving higher accuracy, the single-point energies (SPEs) of the reactants, products, intermediates (IMs), and TSs are calculated by the CCSD(0)-6-311++G** method. In general, these data, such as the SPE, ZPE, optimized structures, and vibrational frequencies, are required when the rate constant is calculated by the YL method.
III. RESULTS AND DISCUSSION

According to the widely used fuel combustion mechanisms, we choose five main NO2 involved reactions (a)–(e) that were investigated in previous works. However, the research studies on the reverse direction are comparatively limited. In order to better understand the reaction mechanism related to NO2, the reverse direction of (a)–(e) should be laid emphasis on. These reverse reactions are as follows:

\[
\begin{align*}
\text{R1:} & \quad \text{N}_2\text{O} + \text{CO}_2 \rightarrow \text{NCO} + \text{NO}_2, \\
\text{R2:} & \quad \text{NO} + \text{OH} \rightarrow \text{NO}_2 + \text{H}, \\
\text{R3:} & \quad \text{NCO} + \text{NO} \rightarrow \text{CN} + \text{NO}_2, \\
\text{R4:} & \quad \text{NO}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{NO}, \\
\text{R5:} & \quad \text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{O}.
\end{align*}
\]
For (R1)–(R5), based on the values of the ZPE, barrier height, and SPE, the potential energy surfaces (PESs) were calculated, as displayed in Figs. 1–3, respectively. The energy of the reactant is set at 0 kcal/mol. The relative energies of TS1–TS13 and IMs are also given in Figs. 1–3, respectively. Besides, for (R1)–(R5), both the harmonic and anharmonic rate constants are calculated from 300 K to 4000 K in the canonical system, respectively, and the relationships between the anharmonic rate constant and the harmonic rate constant are plotted in Figs. 4–8 over the same temperature, respectively. The insets in Figs. 4, 7, and 8 are given to show exactly the position and existence of the junction between the anharmonic and harmonic rate constants. Additionally, this paper takes 300 K as the lower limit of temperature, as in the CHEMKIN program, in which the temperature zone of thermodynamic parameters of the input files is separated into high and low temperature zones, 300 K–1000 K and above 1000 K. In addition, to present the tendency of the difference between the anharmonic and harmonic rate constant changing with the increasing temperature better, 4000 K has been chosen as the upper limit of temperature. The calculated energy parameters [in reaction (R1)] of reactants, products, IMs, and TSs at...
FIG. 6. The canonical rate constants of reaction (R3) from 300 K to 4000 K.

FIG. 7. The canonical rate constants of reaction (R4) from 300 K to 4000 K.

CCSD/6-311++G"** level are shown in Table I, and the frequencies of the three transition states (TS1, TS2, and TS3) at the B3LYP/6-311++G"** level are shown in Table II. At CCSD/6-311++G"** level, the energy parameters of reactants, products, IMs, and TSs of reaction (R2) are shown in Table III, those of reaction (R3) are shown in Table IV, those of reaction (R4) are shown in Table V, and those of reaction (R5) are shown in Table VI. In addition, the experimental data of (R5) at temperature range from 2100 K to 4000 K are given in Fig. 8.

For reaction (R1), Fig. 1 displays the potential energy surface (PES) comprised by two IMs (IM1 and IM2) and three TSs (TS1, TS2 and TS3). It is clear that there is only one channel from reactants to products. Corresponding to reaction (R1), it is obvious that the harmonic and anharmonic rate constants increase with increasing temperature, and the harmonic and anharmonic rate constants are almost equal to zero when the temperature is below 1500 K in Fig. 4. On the other hand, the harmonic rate constant is larger than the anharmonic rate constant when the temperature is above 1300 K. For example, when the temperature is 1300 K, the harmonic rate constant [0.051 (cm$^3$/mol)/s] is 1.07 times that of the anharmonic one [0.047 (cm$^3$/mol)/s], and the harmonic rate constant [3.54 × 10$^{11}$ (cm$^3$/mol)/s] is 1.31 × 10$^3$ times that of the anharmonic one.
[2.70 × 10^{10} \text{ (cm}^3\text{/mol)/s}] at 4000 K. However, the anharmonic rate constant is larger than the harmonic one when the temperature is below 1100 K, which means that there is a junction occurring between 1100 K and 1300 K. It is also noteworthy that the difference between the harmonic rate constant and the anharmonic rate constant is not remarkable at low temperature, whereas the difference is obvious at high temperature.

For reaction (R2), the PESs are presented in Fig. 2, which contain three reaction channels (channels 1–3), four IMs (IMs 3–6), and seven TSs (TSs 4–10), totally. Figure 5 illustrates that the anharmonic and harmonic rate constants grow along with the rising temperature. What is more, the harmonic rate constant is higher than the anharmonic rate constant, and it is obvious that the difference between the harmonic and anharmonic rate constant becomes larger and larger with the increasing temperature. When the temperature is 300 K, the harmonic rate constant [4.69 × 10^{2} \text{ (cm}^3\text{/mol)/s}] is 4.08 times that of the anharmonic one [1.15 × 10^{2} \text{ (cm}^3\text{/mol)/s}]. When the temperature is 4000 K, the harmonic rate constant [2.32 \times 10^{10} \text{ (cm}^3\text{/mol)/s}] is 3.36 × 10^{5} times that of the anharmonic one [6.91 \times 10^{3} \text{ (cm}^3\text{/mol)/s}]. Apparently, the anharmonic effect of this reaction cannot be ignored.

The PES for reaction (R3) is presented in Fig. 3, which contains only one reaction channel and one TS (TS11). It is apparent that the anharmonic and harmonic rate constants grow with the increment of temperature in Fig. 6. In addition, it is obvious that the harmonic rate constant is larger than the anharmonic rate constant, especially at high temperature. To be more specific, when the temperature is 300 K, the harmonic rate constant [5.30 \times 10^{-5} \text{ (cm}^3\text{/mol)/s}] is 1.10 times that of the anharmonic one [4.84 \times 10^{-6} \text{ (cm}^3\text{/mol)/s}], and the harmonic rate constant [5.21 \times 10^{13} \text{ (cm}^3\text{/mol)/s}] is 2.76 times that of the anharmonic one [1.89 \times 10^{13} \text{ (cm}^3\text{/mol)/s}] at 4000 K. For this reaction, the anharmonic effect is significant, especially at high temperature.

For reaction (R4), Fig. 3 presents the PES for (R4), which includes one reaction channel and one TS (TS12). As seen in Fig. 7, it is distinct that the anharmonic and harmonic rate constants grow along with the rising temperature. The anharmonic and harmonic rate constants are approaching zero when the temperature is below 700 K. On the other hand, the anharmonic rate constant is larger than the harmonic one when the temperature is below 700 K. For instance, when the temperature is 300 K, the anharmonic rate constant [7.70 \times 10^{-32} \text{ (cm}^3\text{/mol)/s}] is 1.31 times that of the harmonic one [5.86 \times 10^{-32} \text{ (cm}^3\text{/mol)/s}], and the harmonic rate constant [2.33 \times 10^{-7} \text{ (cm}^3\text{/mol)/s}] is 1.02 times that of the harmonic one [2.28 \times 10^{-5} \text{ (cm}^3\text{/mol)/s}] at 700 K. However, the harmonic rate constant is larger than the anharmonic one when the temperature is above 900 K. For example, when the temperature is 900 K, the harmonic rate constant [1.04 \times 10^{-3} \text{ (cm}^3\text{/mol)/s}] is 1.36 times that of the anharmonic one [7.61 \times 10^{-1} \text{ (cm}^3\text{/mol)/s}], and the harmonic rate constant [2.66 \times 10^{14} \text{ (cm}^3\text{/mol)/s}] is 1.49 \times 10^{5} times that of the anharmonic one [1.78 \times 10^{12} \text{ (cm}^3\text{/mol)/s}] at 4000 K. Accordingly, there is a junction between the anharmonic and harmonic rate constant from 700 K to 900 K. All in all,

### Table I

The energy parameters of the reactants, products, IMs, and TSs of N_{2}O + CO_{2} → NCO + NO_{2} at the CCSD/6-311++G** level.

| Species            | SPE  | ZPE  | Barrier |
|--------------------|------|------|---------|
|                   | (kcal/mol) | (kcal/mol) | (kcal/mol) |
| N_{2}O + CO_{2}    | 14.241 30 | −2.337 10 × 10^{5} | ... |
| IM1                | 15.638 25 | −2.336 21 × 10^{2} | ... |
| IM2                | 13.055 64 | −2.335 83 × 10^{2} | ... |
| NCO + NO_{2}       | 10.007 10 | −2.335 59 × 10^{2} | ... |
| TS1                | 14.750 90 | −2.336 14 × 10^{2} | 96.78 |
| TS2                | 13.092 53 | −2.335 71 × 10^{2} | 49.92 |
| TS3                | 11.974 70 | −2.335 58 × 10^{3} | 24.06 |
TABLE II. The frequencies of the three transition states (TS1, TS2, and TS3) of N₂O + CO₂ → NCO + NO₂ (R1) at the B3LYP/6-311+G** level.

| Transition states of reaction R1 | TS1 | TS2 | TS3 |
|---------------------------------|-----|-----|-----|
| Units                           | cm⁻¹| cm⁻¹| cm⁻¹|
| Frequencies                     | Harmonic frequency | Anharmonic frequency | Harmonic frequency | Anharmonic frequency | Harmonic frequency | Anharmonic frequency |
| 1                               | 841i | 883i | 447i | 464i | 434i | 457i |
| 2                               | 1872 | 1826 | 1860 | 1832 | 1909 | 1972 |
| 3                               | 1666 | 1628 | 1605 | 1584 | 1898 | 1848 |
| 4                               | 1160 | 1129 | 1471 | 1435 | 1309 | 1290 |
| 5                               | 897  | 871  | 1015 | 994  | 1137 | 1108 |
| 6                               | 781  | 766  | 697  | 691  | 857  | 872  |
| 7                               | 636  | 622  | 642  | 635  | 749  | 745  |
| 8                               | 428  | 421  | 595  | 586  | 721  | 723  |
| 9                               | 398  | 386  | 568  | 560  | 588  | 592  |
| 10                              | 246  | 221  | 275  | 270  | 523  | 533  |
| 11                              | 175  | 163  | 272  | 268  | 343  | 366  |
| 12                              | 113  | 108  | 158  | 154  | 167  | 172  |

The anharmonic effect of this reaction cannot be ignored at high temperature.

The PES for reaction (R5), which consists of one channel and one TS (TS13), is displayed in Fig. 3. As depicted in Fig. 8, it is worth noticing that the anharmonic and harmonic rate constants are growing with the increasing temperature, and they are almost equal to zero when the temperature is below 700 K. Additionally, a junction occurs at about 1300 K. When the temperature is below 1300 K, the anharmonic rate constant is greater than the harmonic one. For

TABLE III. The energy parameters of the reactants, products, IMs, and TS of NO + OH → NO₂+H at the CCSD/6-311+G** level.

| Species     | SPE (kcal/mol) | ZPE (kcal/mol) | Barrier (kcal/mol) |
|-------------|----------------|----------------|--------------------|
| NO + OH     | 10.379         | −1.28769 × 10⁵ | ...                |
| IM3         | 12.653         | −1.28756 × 10⁵ | ...                |
| IM4         | 13.748         | −1.28797 × 10⁵ | ...                |
| IM5         | 12.594         | −1.28720 × 10⁵ | ...                |
| IM6         | 12.570         | −1.28726 × 10⁵ | ...                |
| NO₂ + H     | 5.514          | −1.28732 × 10⁵ | ...                |
| TS4         | 5.216          | −1.28644 × 10⁵ | 14.73              |
| TS5         | 10.779         | −1.28684 × 10⁵ | 62.54              |
| TS6         | 11.028         | −1.28695 × 10⁵ | 99.76              |
| TS7         | 9.871          | −1.28744 × 10⁵ | 35.80              |
| TS8         | 9.871          | −1.28754 × 10⁵ | 78.56              |
| TS9         | 6.236          | −1.28704 × 10⁵ | 90.88              |
| TS10        | 6.622          | −1.28718 × 10⁵ | 91.57              |

TABLE IV. The energy parameters of the reactants, products and TS of NCO + NO → CN + NO₂ at the CCSD/6-311+G** level.

| Species     | SPE (kcal/mol) | ZPE (kcal/mol) | Barrier (kcal/mol) |
|-------------|----------------|----------------|--------------------|
| NCO + NO    | 9.568          | −1.86478 × 10⁵ | ...                |
| CN + NO₂    | 8.584          | −1.86465 × 10⁵ | ...                |
| TS11        | 9.026          | −1.86444 × 10⁵ | 25.06              |

TABLE V. The energy parameters of the reactants, products, and TS of NO₂ + OH → HO₂ + NO at the CCSD/6-311+G** level.

| Species     | SPE (kcal/mol) | ZPE (kcal/mol) | Barrier (kcal/mol) |
|-------------|----------------|----------------|--------------------|
| NO₂ + OH    | 10.817         | −1.75864 × 10⁵ | ...                |
| HO₂ + NO    | 11.664         | −1.75842 × 10⁵ | ...                |
| TS12        | 12.739         | −1.75803 × 10⁵ | 61.07              |

TABLE VI. The energy parameters of the reactants, products, and TS of NO + O₂ → NO₂ + O at the CCSD/6-311+G** level.

| Species     | SPE (kcal/mol) | ZPE (kcal/mol) | Barrier (kcal/mol) |
|-------------|----------------|----------------|--------------------|
| NO + O₂     | 7.395          | −1.75449 × 10⁵ | ...                |
| NO₂ + O     | 5.514          | −1.75400 × 10⁵ | ...                |
| TS13        | 5.325          | −1.75396 × 10⁵ | 52.16              |
TABLE VII. The fitting results of kinetics parameters through anharmonic rate constants calculated at temperatures from 300 K to 4000 K. Reaction: $A$ is given in units of $(cm^3$/mol)$/$s and $E$ is given in units of (kcal/mol).

| Reaction | $A$   | $n$   | $E$   |
|----------|-------|-------|-------|
| R1 $N_2O + CO_2 \rightarrow NCO + NO_2$ | $9.02 \times 10^9$ | 1.67 | 98.08 |
| R2 $NO + OH \rightarrow NO_2 + H$ | $2.00 \times 10^{12}$ | 0.39 | 6.46 $\times 10^4$ |
| R3 $NCO + NO \rightarrow CN + NO_2$ | $1.38 \times 10^9$ | 1.55 | 25.20 |
| R4 $NO_2 + OH \rightarrow HO_2 + NO$ | $1.16 \times 10^{13}$ | 0.74 | 63.32 |
| R5 $NO + O_2 \rightarrow NO_2 + O$ | $1.34 \times 10^{10}$ | 1.65 | 53.62 |

TABLE VIII. The fitting results of kinetics parameters through harmonic rate constants calculated at temperatures from 300 K to 4000 K. Reaction: $A$ is given in units of $(cm^3$/mol)$/$s and $E$ is given in units of (kcal/mol).

| Reaction | $A$   | $n$   | $E$   |
|----------|-------|-------|-------|
| R1 $N_2O + CO_2 \rightarrow NCO + NO_2$ | 85.35 | 1.12 | 95.47 |
| R2 $NO + OH \rightarrow NO_2 + H$ | 68.00 | 4.23 | 5.53 $\times 10^4$ |
| R3 $NCO + NO \rightarrow CN + NO_2$ | $5.30 \times 10^7$ | 2.04 | 24.80 |
| R4 $NO_2 + OH \rightarrow HO_2 + NO$ | 0.59 | 4.97 | 59.49 |
| R5 $NO + O_2 \rightarrow NO_2 + O$ | 5.91 | 4.49 | 50.60 |

TABLE IX. The fitting results of thermodynamic parameters through anharmonic rate constants calculated at temperatures from 300 K to 1000 K.

| Reactant | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $a_5$ | $a_6$ | $a_7$ |
|----------|-------|-------|-------|-------|-------|-------|-------|
| NCO      | 3.04  | $0.87 \times 10^{-2}$ | $-0.93 \times 10^{-5}$ | $0.53 \times 10^{-8}$ | $0.13 \times 10^{-11}$ | $2.30 \times 10^3$ | 11.13 |
| NO       | 3.86  | $-0.29 \times 10^{-2}$ | $0.74 \times 10^{-5}$ | $-0.60 \times 10^{-8}$ | $0.17 \times 10^{-11}$ | $1.39 \times 10^3$ | 3.23 |
| NO$_2$   | 3.55  | $0.14 \times 10^{-2}$ | $0.85 \times 10^{-5}$ | $0.12 \times 10^{-7}$ | $0.44 \times 10^{-11}$ | $2.80 \times 10^3$ | 7.91 |
| OH       | 3.43  | $0.62 \times 10^{-3}$ | $-0.88 \times 10^{-5}$ | $0.23 \times 10^{-8}$ | $0.80 \times 10^{-12}$ | $2.67 \times 10^3$ | 1.74 |
| O$_2$    | 3.83  | $0.33 \times 10^{-2}$ | $-1.01 \times 10^{-5}$ | $0.98 \times 10^{-8}$ | $0.32 \times 10^{-11}$ | $1.15 \times 10^3$ | 2.30 |
| N$_2$O   | 2.41  | $0.105 \times 10^{-2}$ | $-1.22 \times 10^{-5}$ | $0.83 \times 10^{-8}$ | $0.24 \times 10^{-11}$ | $4.31 \times 10^3$ | 10.00 |
| CO$_2$   | 2.15  | $1.05 \times 10^{-2}$ | $-1.14 \times 10^{-5}$ | $0.72 \times 10^{-8}$ | $0.20 \times 10^{-11}$ | $10.70 \times 10^3$ | 3.79 |

TABLE X. The fitting results of thermodynamic parameters through anharmonic rate constants calculated at temperatures from 1000 K to 4000 K.

| Reactant | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $a_5$ | $a_6$ | $a_7$ |
|----------|-------|-------|-------|-------|-------|-------|-------|
| NCO      | 5.07  | $0.23 \times 10^{-2}$ | $0.11 \times 10^{-5}$ | $0.24 \times 10^{-9}$ | $0.20 \times 10^{-13}$ | $1.77 \times 10^3$ | 0.80 |
| NO       | 2.97  | $0.17 \times 10^{-2}$ | $-0.78 \times 10^{-6}$ | $0.17 \times 10^{-9}$ | $-0.13 \times 10^{-13}$ | $1.50 \times 10^3$ | 7.27 |
| NO$_2$   | 4.38  | $0.31 \times 10^{-2}$ | $0.15 \times 10^{-5}$ | $0.33 \times 10^{-9}$ | $0.28 \times 10^{-13}$ | $2.39 \times 10^3$ | 2.63 |
| OH       | 1.93  | $0.83 \times 10^{-3}$ | $-0.12 \times 10^{-6}$ | $0.11 \times 10^{-10}$ | $0.30 \times 10^{-14}$ | $5.40 \times 10^3$ | 12.4 |
| O$_2$    | 3.26  | $0.14 \times 10^{-2}$ | $-0.69 \times 10^{-6}$ | $0.15 \times 10^{-9}$ | $0.12 \times 10^{-13}$ | $1.66 \times 10^3$ | 4.46 |
| N$_2$O   | 4.37  | $0.35 \times 10^{-2}$ | $-0.16 \times 10^{-5}$ | $0.35 \times 10^{-9}$ | $0.28 \times 10^{-13}$ | $3.10 \times 10^3$ | 0.12 |
| CO$_2$   | 4.16  | $0.37 \times 10^{-2}$ | $-0.17 \times 10^{-5}$ | $0.37 \times 10^{-9}$ | $0.30 \times 10^{-13}$ | $3.32 \times 10^3$ | 0.63 |
TABLE XI. The fitting results of thermodynamic parameters through harmonic rate constants calculated at temperatures from 300 K to 1000 K.

| Reactant | \(a_1\) | \(a_2\) | \(a_3\) | \(a_4\) | \(a_5\) | \(a_6\) | \(a_7\) |
|----------|--------|--------|--------|--------|--------|--------|--------|
| NCO      | 3.04   | 0.87 \(\times 10^{-2}\) | 0.93 \(\times 10^{-5}\) | 0.53 \(\times 10^{-8}\) | 0.13 \(\times 10^{-11}\) | 2.30 \(\times 10^{3}\) | 11.13 |
| NO       | 3.86   | 0.29 \(\times 10^{-2}\) | 0.74 \(\times 10^{-5}\) | 0.60 \(\times 10^{-8}\) | 0.17 \(\times 10^{-11}\) | 1.39 \(\times 10^{3}\) | 3.23 |
| NO\(_2\) | 3.61   | 0.99 \(\times 10^{-3}\) | 0.90 \(\times 10^{-5}\) | 0.12 \(\times 10^{-7}\) | 0.43 \(\times 10^{-11}\) | 2.80 \(\times 10^{3}\) | 7.91 |
| OH       | 3.43   | 0.62 \(\times 10^{-3}\) | 0.88 \(\times 10^{-5}\) | 0.23 \(\times 10^{-8}\) | 0.80 \(\times 10^{-12}\) | 2.67 \(\times 10^{4}\) | 1.74 |
| O\(_2\)  | 3.83   | 0.33 \(\times 10^{-2}\) | 1.01 \(\times 10^{-5}\) | 0.98 \(\times 10^{-8}\) | 0.32 \(\times 10^{-11}\) | 1.15 \(\times 10^{3}\) | 2.30 |
| N\(_2\)O | 2.41   | 1.05 \(\times 10^{-2}\) | 1.22 \(\times 10^{-5}\) | 0.83 \(\times 10^{-8}\) | 0.24 \(\times 10^{-11}\) | 4.31 \(\times 10^{3}\) | 10.00 |
| CO\(_2\) | 2.15   | 1.05 \(\times 10^{-2}\) | 1.14 \(\times 10^{-5}\) | 0.72 \(\times 10^{-8}\) | 0.20 \(\times 10^{-11}\) | 10.70 \(\times 10^{3}\) | 3.79 |

TABLE XII. The fitting results of thermodynamic parameters through harmonic rate constants calculated at temperatures from 1000 K to 4000 K.

| Reactant | \(a_1\) | \(a_2\) | \(a_3\) | \(a_4\) | \(a_5\) | \(a_6\) | \(a_7\) |
|----------|--------|--------|--------|--------|--------|--------|--------|
| NCO      | 4.98   | 0.24 \(\times 10^{-2}\) | 0.12 \(\times 10^{-5}\) | 0.25 \(\times 10^{-9}\) | 0.21 \(\times 10^{-13}\) | 1.81 \(\times 10^{3}\) | 1.24 |
| NO       | 2.97   | 0.17 \(\times 10^{-2}\) | 0.78 \(\times 10^{-6}\) | 0.17 \(\times 10^{-9}\) | 0.13 \(\times 10^{-13}\) | 1.50 \(\times 10^{3}\) | 7.27 |
| NO\(_2\) | 4.29   | 0.32 \(\times 10^{-2}\) | 0.15 \(\times 10^{-5}\) | 0.34 \(\times 10^{-9}\) | 0.28 \(\times 10^{-13}\) | 2.41 \(\times 10^{3}\) | 3.09 |
| OH       | 1.93   | 0.83 \(\times 10^{-3}\) | 0.12 \(\times 10^{-6}\) | 0.11 \(\times 10^{-10}\) | 0.30 \(\times 10^{-14}\) | 5.40 \(\times 10^{3}\) | 12.4 |
| O\(_2\)  | 3.26   | 0.14 \(\times 10^{-2}\) | 0.69 \(\times 10^{-6}\) | 0.15 \(\times 10^{-9}\) | 0.12 \(\times 10^{-13}\) | 1.66 \(\times 10^{3}\) | 4.46 |
| N\(_2\)O | 4.37   | 0.35 \(\times 10^{-2}\) | 0.16 \(\times 10^{-5}\) | 0.35 \(\times 10^{-9}\) | 0.28 \(\times 10^{-13}\) | 3.10 \(\times 10^{3}\) | 0.12 |
| CO\(_2\) | 4.16   | 0.37 \(\times 10^{-2}\) | 0.17 \(\times 10^{-5}\) | 0.37 \(\times 10^{-9}\) | 0.30 \(\times 10^{-13}\) | 3.32 \(\times 10^{3}\) | 0.63 |

obtained through the anharmonic \(C_p\), \(H\), and \(S\) of reactants, are given in Tables IX and X, respectively. In addition, Tables XI and XII present the values of thermodynamic parameters, which are computed through the harmonic \(C_p\), \(H\), and \(S\) of reactants, respectively. Additionally, it is noticeable that there is no anharmonic effect on single atom or molecule with symmetrical configuration, so the harmonic thermodynamic parameters are made use of when filling the anharmonic fitting results for this kind of molecule or single atom. Likewise, the feasibility of this fitting method of thermodynamic parameters is also checked. In general, the deviation could be controlled within a reasonable extent. Consequently, this fitting method of thermodynamic parameters is reliable.

IV. CONCLUSIONS

In this research, a comparison is made between the harmonic rate constant and the anharmonic rate constant from 300 K to 4000 K for all reaction in this work. The results indicate that temperature has a strong effect on the rate constant. It is found that the values of the harmonic and anharmonic rate constants are very small when temperature is low. On the contrary, both of them are relatively large at high temperature. It is worth noting that although the harmonic and anharmonic rate constants increase as temperature grows, there is a difference between the increasing speed of the harmonic rate constant and that of the anharmonic rate constant, especially when the temperature is relatively high. On the other hand, for reactions (R1), (R4), and (R5), there is a junction occurring between the anharmonic and harmonic rate constants, and the anharmonic rate constant is larger than the harmonic one when the temperature is below the junction, whereas the harmonic rate constant is larger than the anharmonic one when the temperature is above the junction. In general, the anharmonic effect is significant at high temperature. Additionally, for (R5), the values of the anharmonic rate constant obtained by the YL method are closer to the experimental data than the harmonic rate constant at high temperature, which indicates that the YL method is also suitable for the calculation of the rate constant of the bimolecular reaction.

Furthermore, the results show that the fitting method utilized in this work provides a dependable way to calculate the kinetics parameters and thermodynamic parameters of the reaction mechanism through the rate constant. In a word, it is meaningful to investigate the anharmonic effect on the reaction mechanism via the anharmonic rate constant. The anharmonic reaction mechanism offers a new perspective for comprehending the chemical reactions referring to NO\(_2\) and taking steps to lower NO\(_x\) emission.

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