

## ARTICLE

Reaction of CH<sub>3</sub> with NO<sub>2</sub>Cong-yun Shi<sup>a</sup>, Feng Dong<sup>a</sup>, Shuo Sun<sup>b</sup>, Hao Zhang<sup>b</sup>, Li Guo<sup>a</sup>, Ji-kang Feng<sup>b\*</sup>, Fan-ao Kong<sup>a\*</sup>*a.* Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China; *b.* Institute of Theoretical Chemistry, College of Chemistry, Jilin University, Changchun 130023, China

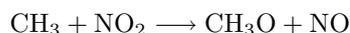
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The elementary reaction of the CH<sub>3</sub> radical with NO<sub>2</sub> was investigated by time-resolved FTIR spectroscopy and quantum chemical calculations. The CH<sub>3</sub> radical was produced by laser photolysis of CH<sub>3</sub>Br or CH<sub>3</sub>I at 248 nm. Vibrationally excited products OH, HNO and CO<sub>2</sub> were observed by the time-resolved spectroscopy for the first time. The formation of another product NO was also verified. According to these observations, the product channels leading to CH<sub>3</sub>O+NO, CH<sub>2</sub>NO+OH and HNO+H<sub>2</sub>CO were identified. The channel of CH<sub>3</sub>O+NO was the major one. The reaction mechanisms of the above channels were studied by quantum chemical calculations at CCSD(T)/6-311++G(df,p)//MP2/6-311G(d,p) level. The calculated results fit with the experimental observations well.

**Key words:** CH<sub>3</sub>+NO<sub>2</sub>, Time-resolved FTIR spectroscopy, Quantum chemical calculation, Reaction product, Reaction mechanism

## I. INTRODUCTION

Methyl radical is a key reaction intermediate of the oxidation of methane in the atmosphere and in combustion system [1]. The reaction of CH<sub>3</sub> radical with NO<sub>2</sub> is an interesting radical-radical reaction, which may provide an effective way to remove the harmful NO<sub>x</sub> species. Understanding the pathway and the mechanism of this reaction is significant both in basic science and in solving environmental problems. The experimental investigation of this reaction has been focused on the reaction kinetics thus far. Yamada and co-workers explored the CH<sub>3</sub>+NO<sub>2</sub> reaction in 1981 [2]. Using photoionization mass spectrometry, they determined that the rate constant of CH<sub>3</sub> decay was  $(2.5 \pm 0.5) \times 10^{-11}$  cm<sup>3</sup>/(molecule s) at 295 K. They reported that the only ion signal of the product was NO, so they suggested that the reaction is



Monitoring the temporal profile of the product CH<sub>3</sub>O by detecting laser-induced fluorescence, Biggs *et al.* and Wollenhaupt *et al.* measured the rate constant as  $(2.3 \pm 0.3) \times 10^{-11}$  and  $1.9 \times 10^{-11}$  cm<sup>3</sup>/(molecule s), respectively [3,4].

Theoretical studies on the reaction mechanism have been carried out by two groups. Based on the *ab initio* calculations at the level of CCSD(T)//MP2/6-311++G(2d,p), Yamaguchi *et al.* found that the pathway to form the intermediate CH<sub>3</sub>ONO is barrierless, and that the most important reaction pathway is to

produce CH<sub>3</sub>O+NO [5]. Recently, a detailed quantum chemistry calculation on the title reaction has been performed by Zhang *et al.* [6]. The reaction pathways of seven channels on the singlet potential energy surface (PES) have been studied at the B3LYP/6-311G(d,p) and MC-QCISD (single-point) levels. They concluded that CH<sub>3</sub>O+NO and H<sub>2</sub>CO+HNO are the most favorable product channels with comparable yields, whereas H<sub>2</sub>CO+HON are the less competitive products.

So far, only the reaction channel leading to the products of CH<sub>3</sub>O and NO has been identified experimentally. Searching evidence of other product channels thus becomes necessary in further experimental investigations. Here we report that by employing time-resolved Fourier transform infrared (TR-FTIR) emission spectroscopy the reaction products can be found. The vibrationally excited products OH, HNO and CO<sub>2</sub> were found for the first time. Three more reaction channels were thus identified. Unfortunately, some new reaction channels, which are found in the present experiment, have not been predicted by Zhang *et al.* and Yamaguchi *et al.* The fact shows that their theoretical studies on the reaction mechanism are not complete. We therefore perform a more comprehensive *ab initio* study at the CCSD(T)/6-311++G(df,p)//MP2/6-311G(d,p) level on the singlet states. An overall reaction mechanism involving the known reaction pathways, CH<sub>3</sub>O+NO and HNO+H<sub>2</sub>CO, and a new product channel CH<sub>2</sub>NO+OH are clarified and presented in this paper.

## II. EXPERIMENTAL AND THEORETICAL METHODS

The experimental apparatus was described in detail previously [7]. The apparatus consists of three parts: A KrF laser (Lambda Physik, LPX 305I, 248 nm, 150 mJ/pulse), a vacuumed reaction chamber and a

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TR-FTIR spectroscope (Nicolet, Nexus 800 or 870). The excimer laser beam was led into the reaction chamber to photolyze the precursor molecules. The  $\text{CH}_3$  radical was produced by the laser photolysis of the precursor molecules either  $\text{CH}_3\text{Br}$  or  $\text{CH}_3\text{I}$  at 248 nm. Mixed gases of methyl halides and  $\text{NO}_2$  flowed through the reaction chamber. The infrared emission from the vibrationally excited products was collected into the TR-FTIR spectroscope by a pair of gold-coated spherical mirrors (White cell), and was detected by an InSb (77 K) detector, which is sensitive in the region of  $1850\text{--}6000\text{ cm}^{-1}$ . The spectral resolution of the spectroscope was set at  $16\text{ cm}^{-1}$ .

The detailed reaction mechanism was investigated theoretically by quantum chemical calculations with Gaussian 03 program package [8]. The geometric structures and the vibrational frequencies of all the stationary points were calculated with 6-311(d,p) basis set at the MP2 level on the singlet potential energy surface. Intrinsic reaction coordinate (IRC) calculations were performed further to confirm that the transition states connecting the right minima at the same level [9]. More precise energies were ascertained by the CCSD(T)/6-311++G(df,p) calculations with inclusion of the MP2 zero point vibrational energies.

### III. RESULTS AND DISCUSSION

#### A. Products and reaction channels

The photolysis of methyl halides produces methyl radical almost exclusively at 248 nm [10(a)-(d)]. The absorption cross section of  $\text{CH}_3\text{Br}$  at 248 nm is about 20 times larger than that of  $\text{NO}_2$  [11], so the reaction of  $\text{CH}_3+\text{NO}_2$  is the dominant reaction in the photolysis of  $\text{CH}_3\text{Br}+\text{NO}_2$  system. In a reference experiment, no IR emission was observed in the photolysis of pure  $\text{CH}_3\text{Br}$  or  $\text{NO}_2$  lonely, so the system provides a neat spectral background for investigating the title reaction. Once the laser pulse irradiated the gaseous mixture of  $\text{CH}_3\text{Br}$  and  $\text{NO}_2$ , IR emissions appeared in the spectrum in a few microseconds. A time-resolved IR emission spectrum recorded by a fast scanned FTIR spectroscope (Nicolet, Nexus 800) at  $5\text{ }\mu\text{s}$  is shown in Fig.1(a). Several emission bands appear in the spectrum. Within  $5\text{ }\mu\text{s}$  and at the present pressure, about 60 collisions take place for each molecule. To assure that the species appeared in the spectrum are the nascent products of the reaction, we performed another experiment using a step-scanned FTIR spectroscope (Nexus 870) with  $1.5\text{ }\mu\text{s}$  resolution. The precursor molecule used was  $\text{CH}_3\text{I}$ . The partial pressure of methyl iodide and  $\text{NO}_2$  were 26 and 100 Pa respectively. For each molecule only seven collisions took place in the case. The same emission bands appeared in the spectrum too, which is shown in Fig.1(b). Therefore the observed species are the nascent products of  $\text{CH}_3+\text{NO}_2$  reaction definitely.

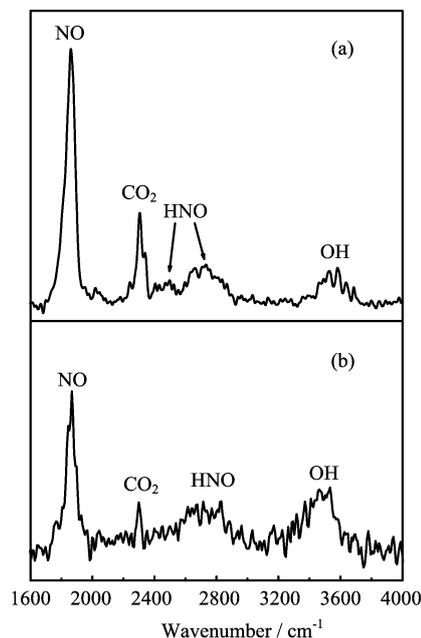


FIG. 1 Time-resolved IR emission spectra for the reaction  $\text{CH}_3+\text{NO}_2$  after KrF laser shining. (a) The emission spectrum of  $\text{CH}_3\text{Br}+\text{NO}_2$  system recorded at  $5\text{ }\mu\text{s}$  delay. The partial pressures of  $\text{CH}_3\text{Br}$  and  $\text{NO}_2$  are 90 and 170 Pa, respectively. (b) The emission spectrum of  $\text{CH}_3\text{I}+\text{NO}_2$  system recorded at  $1.5\text{ }\mu\text{s}$  delay. The partial pressures of  $\text{CH}_3\text{I}$  and  $\text{NO}_2$  are 26 and 100 Pa, respectively.

In Fig.1(a), a strong emission band from  $1750\text{ cm}^{-1}$  to  $2000\text{ cm}^{-1}$  is assigned to the nitrous oxide ( $v\rightarrow v-1$ ) emission. The real NO emission intensity of the vibrationally excited states could be much stronger than the appeared intensity, because the wavelength response of the InSb detector used in this experiment sharply cuts off at  $1850\text{ cm}^{-1}$ . It is noticed that both the NO ( $v\rightarrow v-1$ ) and HCO ( $\nu_3, v\rightarrow v-1$ ) species emit IR light at the same wavelength region. However we exclude that this emission band refers to the transition of HCO ( $\nu_3$ ). If HCO was formed in the reaction, the species would immediately undergo a rapid secondary reaction with  $\text{NO}_2$ , since the reaction rate is  $(2.34\pm 0.37)\times 10^6\text{ s}^{-1}$  at 170 Pa of  $\text{NO}_2$  [12-14]. This reaction could further produce vibrationally excited CO [15]. But no IR emission of CO was observed in our experiment. It is thus inferred that the secondary reaction  $\text{HCO}+\text{NO}_2$  does not exist. The emission band peaked at  $1860\text{ cm}^{-1}$  is thus assigned to the transitions of NO ( $v\rightarrow v-1$ ). Previously Yamada *et al.* found the ion signal of NO by a quadrupole mass spectroscopy in a complicate reaction system, where the  $\text{CH}_3$  radicals were generated by infrared multiphoton dissociation (IR MPD) of  $\text{C}_6\text{F}_5\text{OCH}_3$  [2]. The NO species might not be the primary product of the  $\text{CH}_3+\text{NO}_2$  reaction. In contrast, the NO observed in this experiment is the product of the elementary reaction firmly.

The band from  $2200\text{ cm}^{-1}$  to  $2380\text{ cm}^{-1}$  is attributed

to the emission of CO<sub>2</sub> ( $\nu_3$ ). The spectrum of CO<sub>2</sub> emission has been simulated. The population ratio of  $v=1, 2$  and  $3$  is  $1/2.3/1.3$ .

There are two broad humps between 2380 and 2550 cm<sup>-1</sup> and between 2550 and 2900 cm<sup>-1</sup> in the spectra. The bands are assigned to the (200)-(100) and (100)-(000) transitions of HNO, respectively [15,16]. However, since the  $\nu_1$  and  $\nu_5$  bands of H<sub>2</sub>CO are in the same wavelength [17], we do not exclude the existence of H<sub>2</sub>CO ( $\nu_1$  and  $\nu_5$ ) emissions.

Another broad band from 3320 cm<sup>-1</sup> to 3730 cm<sup>-1</sup> is assigned to the emission of OH radical. Figure 2 shows the rotational lines of  $v=1 \rightarrow v=0$  transition according to Polanyi's assignment [18]. The large splitting about 40 cm<sup>-1</sup> in the spectrum characterizes the large rotational constant  $B_e$  (18.9 cm<sup>-1</sup>).

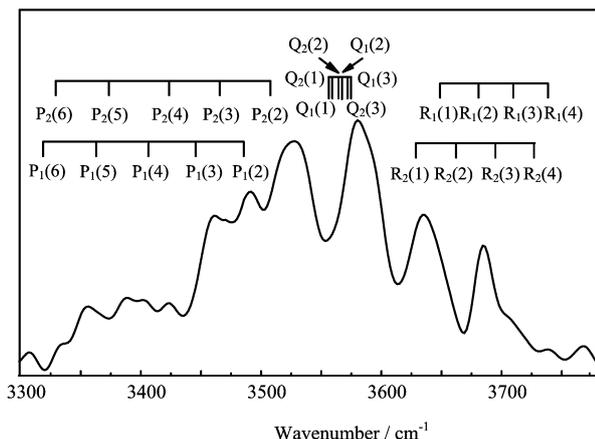
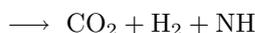
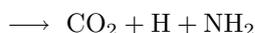
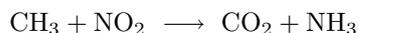


FIG. 2 Time-resolved IR emission spectrum for the reaction CH<sub>3</sub>+NO<sub>2</sub> after KrF laser shining. The emission spectrum of CH<sub>3</sub>Br+NO<sub>2</sub> system is recorded at 5  $\mu$ s delay. The partial pressures of CH<sub>3</sub>Br and NO<sub>2</sub> are 90 and 170 Pa, respectively. The band from 3320 cm<sup>-1</sup> to 3730 cm<sup>-1</sup> is assigned to the transition of OH ( $v=1 \rightarrow v=0$ ). The wavelengths of the rovibrational lines are indicated by bars in the figure.

The nascent vibrationally excited products of OH, CO<sub>2</sub>, NO and HNO were observed in our TR-FTIR spectrum. The fact indicates that the following reaction channels (1)-(3) occur, as one product of each channel has been identified in the experiment.



The channels (2) and (3) are found experimentally for the first time. There exist three thermal possible channels to produce CO<sub>2</sub>. They are in the following:



Unfortunately, we can not identify which channel takes place.

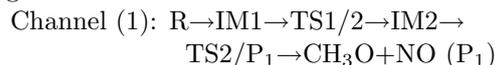
The channel (1) is the most favorable reaction channel. The area of the NO peak is larger than those of the CO<sub>2</sub> peak and OH hump. The actual yield of NO is much more than those of CO<sub>2</sub> and OH in our spectrum, since the InSb IR detector has a very low response to NO emission in the long wavelength. The comparisons are based on that NO, CO<sub>2</sub> and OH have almost comparable Einstein A factors [19-21].

## B. Reaction mechanisms

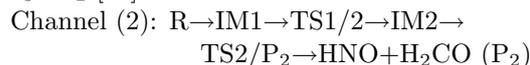
To understand the reaction mechanism of channels (1), (2) and (3), we performed quantum chemistry calculations at the level of CCSD(T)/6-311++G(df,p)//MP2/6-311G(d,p). The potential energy surface (PES) of the CH<sub>3</sub>+NO<sub>2</sub> reaction in singlet is shown in Fig.3. The MP2-optimized geometries for the reactants, the intermediates and the transition states are shown in the Fig.4.

According to our calculation results, we will discuss the reaction pathways of the three observed product channels. The calculated results show that many energy barriers in the reaction are slightly higher than the energy level of the reactants. In the present experiment, however, the reactants CH<sub>3</sub> generated in the UV photolysis are the hot species, which enable to overcome the barriers energetically.

The results of channels (1) and (2) are in agreement with Zhang's results and described briefly in the followings.

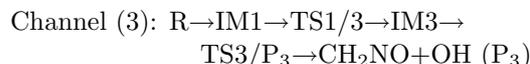


CH<sub>3</sub> radical attacks NO<sub>2</sub> molecules without energy barrier, forming an intermediate CH<sub>3</sub>NO<sub>2</sub> (IM1). Subsequently, the IM1 isomerizes to IM2 (CH<sub>3</sub>O-NO) via the transition state TS1/2. The cleavage of O-N bond in IM2 leads to the final products CH<sub>3</sub>O+NO (P<sub>1</sub>) via transition state TS2/P<sub>1</sub> with an energy barrier of 153.4 kJ/mol. The channel becomes the major contribution to the total reaction, because the energy barrier is the lowest among all the reaction channels. The formation mechanism is also supported by the photodissociation of CH<sub>3</sub>NO<sub>2</sub>. Lee indicates that CH<sub>3</sub>O+NO are the products of infrared multiphoton dissociation of CH<sub>3</sub>NO<sub>2</sub> [22].



Accompanying with H atom migration, the rupture of the CH<sub>3</sub>O-NO bond in IM2 (*trans*-CH<sub>3</sub>ONO) leads to the products HNO and H<sub>2</sub>CO (P<sub>2</sub>).

The reaction mechanism for the channel (3) is proposed here for the first time.



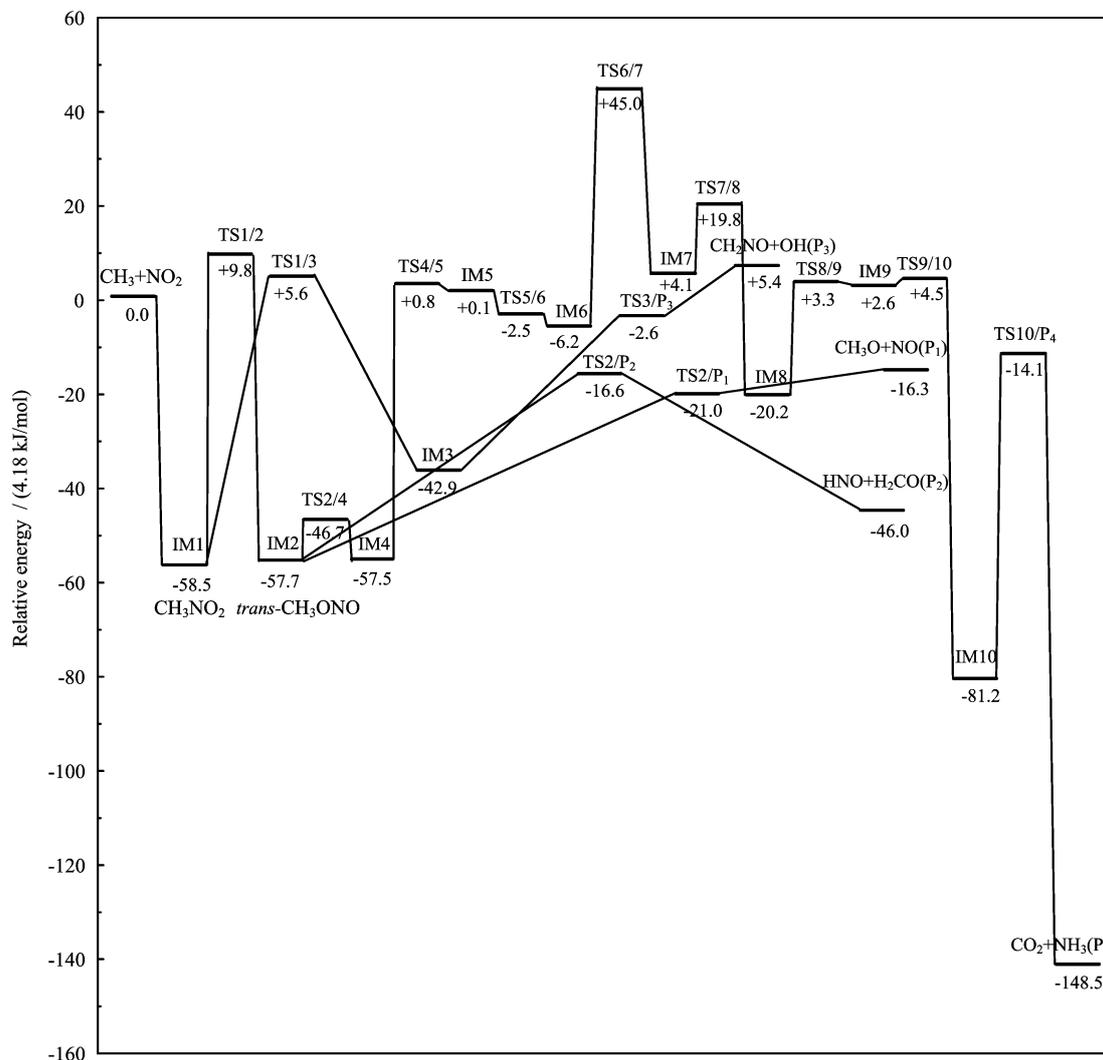
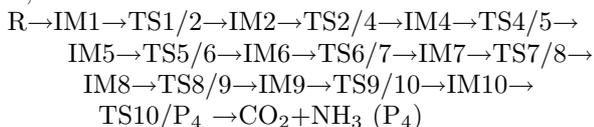


FIG. 3 Scheme of the PES for the  $\text{CH}_3+\text{NO}_2$  reaction. The energies of all the species are calculated at the CCSD(T)/6-311++G(df,p)//MP2/6-311G(d,p) levels.

In IM1 ( $\text{CH}_3\text{NO}_2$ ), one of the H atoms transfers from the carbon atom to the O atom at the same side of the molecule skeleton, and form an intermediate IM3 ( $\text{H}_2\text{N}(\text{O})\text{OH}$ ,  $\text{C}_s$ ). The rupture of N–O (at the side of N–OH) in IM3 leads to the final products  $\text{CH}_2\text{NO}+\text{OH}$  ( $\text{P}_3$ ). The fact that Zabarnic *et al.* found the product OH in the photolysis of  $\text{CH}_3\text{NO}_2$  supports this mechanism [23].

It is interesting that  $\text{CO}_2$  is found as a reaction product in the experiment. For the reactions leading to  $\text{CO}_2$ , we have only calculated the pathways leading to  $\text{CO}_2+\text{NH}_3$ . The results of calculations suggest that the reaction could possibly undergo a very complicated process, as follows:



In the reaction, the two oxygen atoms in the reactant

$\text{NO}_2$  and the three hydrogen atoms in  $\text{CH}_3$  exchange their positions completely. The enormous change of the molecular framework happens in IM8, a four-membered ring of the heavy atoms C, O, O, N. It is noticed that there is a high barrier between IM6 and IM7. The related process is a hydrogen atom shifting from an oxygen atom to the nitrogen atom.

#### IV. CONCLUSION

The elementary reaction of  $\text{CH}_3$  radical with  $\text{NO}_2$  was initiated by laser photolysis of  $\text{CH}_3\text{Br}$  or  $\text{CH}_3\text{I}$  at 248 nm, and the reaction products were detected by TR-FTIR emission spectroscopy. The vibrationally excited species OH, HNO and  $\text{CO}_2$  were found for the first time. The product channels of  $\text{CH}_2\text{NO}+\text{OH}$  and  $\text{HNO}+\text{H}_2\text{CO}$  were identified. A strong NO emission was also found, indicating that the channel

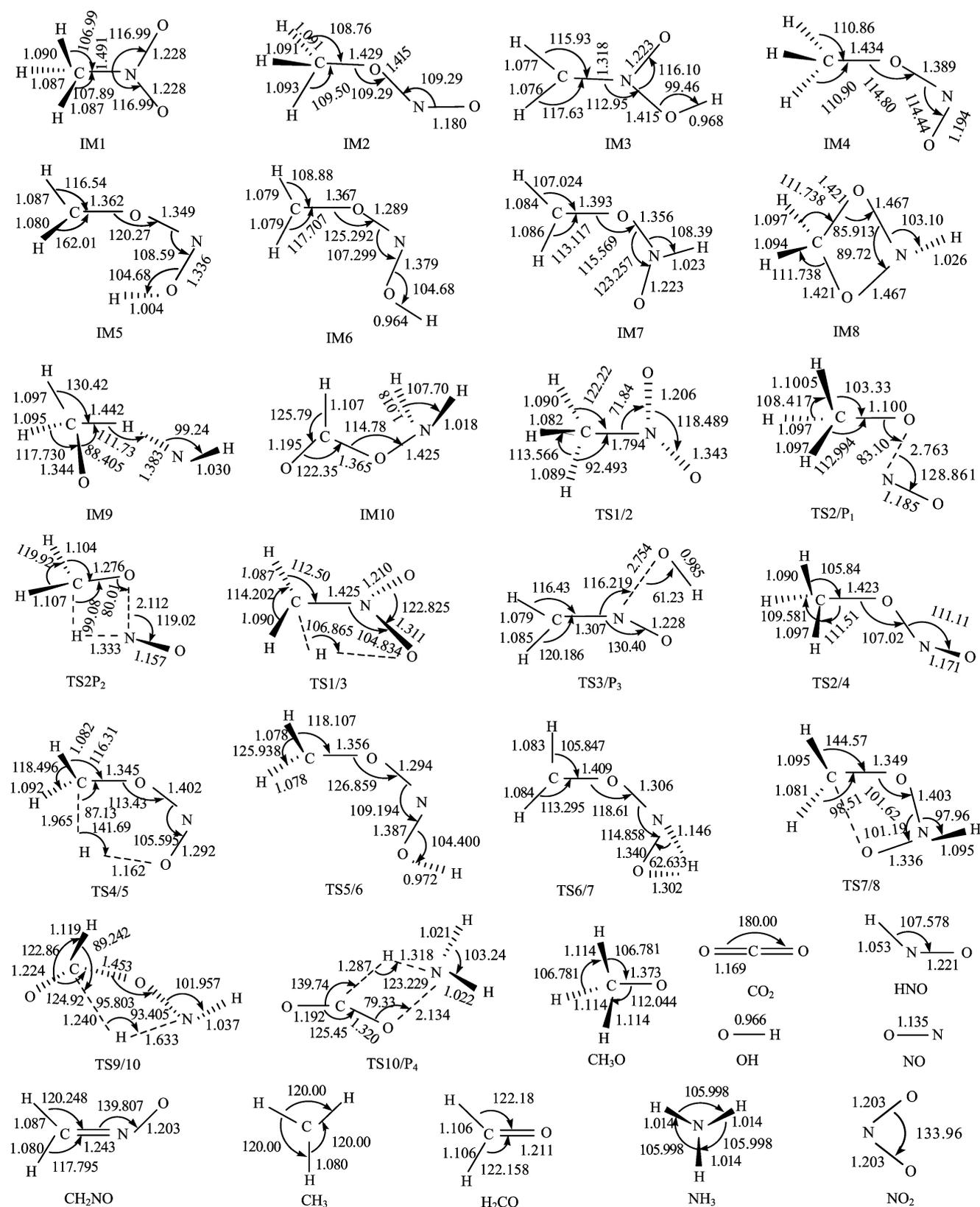


FIG. 4 Optimized structures of reactants, transition states, intermediates and products (bond length in Å and angle in (°)).

CH<sub>3</sub>O+NO reported in the previous literature is the major channel. The reaction mechanisms were also studied by the *ab initio* calculations at the CCSD(T)/6-311++G(df,p)//MP2/6-311G(d,p) level. The calculated results are in agreement with the experimental studies. The mechanisms of the three product channels have been clarified. For the channels leading to CH<sub>3</sub>O+NO and to HNO+H<sub>2</sub>CO, our calculated results are in agreement with Zhang's. In the present work we suggest a mechanism for producing CH<sub>2</sub>NO+OH for the first time.

## V. ACKNOWLEDGMENTS

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