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Rate constants of the O(¹D) reactions with N_2 , O_2 , N_2O , and H_2O at 295 K

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Abstract

Using a technique of laser flash photolysis coupled with vacuum ultraviolet laser-induced fluorescence spectroscopy, the rate coefficients of $O(^{1}D)$ reactions with N₂, O₂, N₂O, and H₂O at 295 ± 2 K have been determined to be $k_{N_2} = (3.29 \pm 0.27) \times 10^{-11}$, $k_{O_2} = (4.06 \pm 0.24) \times 10^{-11}$, $k_{N_2O} = (1.35 \pm 0.08) \times 10^{-10}$ and $k_{H_2O} = (2.07 \pm 0.18) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. The quoted uncertainties include estimated errors and are the 95% confidence level. The k_{N_2} and k_{N_2O} values obtained are larger than the current NASA/JPL recommendations by 26% and 16%, respectively, although they are still within the error limits associated with the recommendations.

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1. Introduction

In the terrestrial atmosphere, $O(^{1}D)$ atom is mainly produced from the photolysis of O_{3} in the ultraviolet region [1–4]. Although the abundance is very low, a small fraction of $O(^{1}D)$ reactions create highly reactive species from highly unreactive species; this minor pathway for $O(^{1}D)$ loss is often the major pathway for the generation of the reactive species. Specifically, OH radical in the stratosphere and troposphere and NO (and eventually all nitrogen oxides) in the stratosphere are produced mostly from the reactions of $O(^{1}D)$ with inert H₂O and N₂O.

$$O(^{1}D) + H_{2}O \rightarrow 2OH \tag{1}$$

$$O(^{1}D) + N_{2}O \rightarrow 2NO$$
⁽²⁾

The reactive species OH and NO are immensely important in the atmosphere [1-4].

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Therefore, there are now large kinetic databases concerning chemical reactions involving $O(^{1}D)$ at ambient temperatures [3,4]. A variety of experimental techniques have been utilized to investigate the kinetics of the atmospheric $O(^{1}D)$ reactions [5–18]. The $O(^{1}D)$ concentration can be monitored by emission spectroscopy (ES) at 630 nm associated with $O(^{1}D-^{3}P)$ transition [8,9]. It is also possible to measure the $O(^{1}D)$ concentration by resonance absorption (RA) via the $3s^{1}D-2p^{1}D$ transition at 115.2 nm [7]. When the branching ratio for $O(^{3}P)$ production is significant in O(¹D) reactions, the total reaction rate constants of $O(^{1}D)$ can be determined from the temporal evolution rate of the $O(^{3}P)$ products. The $O(^{3}P)$ atoms can be monitored by RA spectroscopy and resonance fluorescence (RF) spectroscopy via the $3s^{3}S^{0}-2p^{3}P_{i}$ transition at 130 nm [12,15–17]. A microwave-powered oxygen atom lamp has been utilized to obtain VUV radiation at 130 nm in those experiments. Recently, we have demonstrated that laser-induced fluorescence (LIF) spectroscopy via the 3s¹D-2p¹D transition at 115.2 nm is a powerful technique to study the chemical processes in the atmosphere [19–28]. For instance, photodissociation processes of atmospheric O₃

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in the UV region have extensively been studied by the LIF detection of $O(^{1}D)$ atoms [21–24,26–28]. The kinetic measurements for $O(^{1}D)$ reactions have also been performed through the LIF detection of $O(^{1}D)$ [18,25].

Based on critical reviews of those experimental studies, both NASA/JPL [5] and IUPAC [6] databases include the recommendation values of the kinetic data for use in atmospheric studies. Very recently, some experimental studies which have revisited the $O(^{1}D)$ reactions with atmospheric molecules have suggested that there are discrepancies in the rate constants between the currently recommended values and newly measured values [15–18]. For instance, three different groups at National Oceanic and Atmospheric Administration (NOAA), Georgia Institute of Technology, and University of Leeds, have independently conducted the kinetic studies to measure the rate constant of $O(^{1}D) + N_{2}$ reaction $(k_{N_{2}})$ at 295 K [15]. They determined the $k_{N_{2}}$ value to be 3.1×10^{-11} cm³ mole $cule^{-1} s^{-1}$, which is larger than the latest NASA/JPL recommendation by 19%. The difference strongly affects modeling studies of the production rates of OH radical in the atmosphere, because the OH radical is formed mainly through reaction (1) and the steady-state concentration of atmospheric O(¹D) is predominantly dependent on k_{N_2} and k_{O_2} . Therefore, it is obvious that further kinetic studies are required to investigate the discrepancies revealed by the recent studies.

In this Letter, we report the experimental determinations of the rate constants for $O(^{1}D)$ reactions with N₂, O₂, N₂O and H₂O at 295 ± 2 K. Time-resolved experiments to measure the decay profiles of $O(^{1}D)$ in the presence of reactants reveal the rate constants, in which the relative concentration of $O(^{1}D)$ has been monitored by LIF spectroscopy at 115.2 nm. Results are compared with the recent kinetic measurements by other groups and the NASA/JPL and IUPAC recommendations.

2. Experimental

The experimental apparatus used in the present study is almost the same as in our previous studies on the photochemical processes involving $O(^1D)$ [19–28]. Pulsed laser-flash photolysis combined with time-resolved LIF was used in all experiments to investigate the reaction kinetics of $O(^1D)$. Reactant mixtures of N₂O and collision partners (N₂, O₂, N₂O, and H₂O) and a large excess of Helium are slowly introduced into a reaction chamber through calibrated mass flow meters (STEC, SEC-400). Photolysis of N₂O at 193 nm was used to generate the $O(^1D)$ atoms, in which the 193 nm laser light was obtained by an Excimer laser (Lambda Physik, Optex). The initial concentration of $O(^1D)$, $[O(^1D)]_{t=0}$, was about 2×10^{11} atoms cm⁻³, which was estimated from the reported absorption cross section of N₂O $(8.95 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1})$ [5], the photolysis laser fluence $(1.4 \times 10^{14} \text{ photons cm}^{-2})$, and the O(¹D) quantum yield from N₂O photolysis at 193 nm (\approx 1) [5,6].

Tunable VUV radiation around 115.22 nm was generated by frequency tripling of UV laser light in Ar phase-matched Xe [29]. The 345.6 nm laser light $(\approx 7 \text{ mJ/pulse})$ was focused into the cell containing the Xe/Ar mixture with a fused silica lens (f = 170). The typical partial pressures of Xe and Ar were 30 and 60 Torr, respectively. Photolysis and probe laser beams crossed at right angles in the reaction chamber. The distance between the probe beam entrance window and the crossing point of the two lasers was 70 mm. The distance between the crossing point of the two lasers and the window where the fluorescence exits the cell was 60 mm. The O(¹D) LIF was detected by a solar-blind photomultiplier tube (EMR, 541J-08-17), in which the direction of the LIF observation was orthogonal to the propagation direction of both VUV probe and photolysis laser beams. Output from the PMT was pre-amplified and fed into a gated integrator (Stanford Research, SR-250). Temporal decay profiles of $O(^{1}D)$ as a function of the delay time between the photolysis and probe laser pulses were thus measured in the experiments. The delay time was controlled by a digital pulse generator (Stanford Research, DG535).

The reaction chamber was evacuated continuously using a rotary pump through a liquid nitrogen trap. Pressure in the chamber was monitored by a capacitance manometer (MKS, Baratron622). Total pressure in the chamber was maintained at 5 Torr with an excess of He which was added to thermalize the velocity distribution of $O(^{1}D)$ generated from the photolysis of $N_{2}O$ within 500 ns [19]. Physical quenching of $O(^{1}D)$ by He was negligible under our experimental conditions, because the room-temperature rate constant for $O(^{1}D)$ + He was reported to be 7×10^{-16} cm³ molecules⁻¹ s⁻¹ [30]. The reactant concentrations in the chamber were estimated using the mass flow rates and pressures. All the mass flow meters were calibrated using a primary mass flow calibrator (STEC, SF-1). The uncertainties in the mass flow rate and pressure measurements were estimated to be $\pm 2\%$ for N₂O, N₂, O₂, and He. For H₂O experiments, a stable flow of water vapor was produced by bubbling a flow of He through a liquid sample of distilled H₂O maintained at 290 K. The absolute concentration of H₂O was determined using a thermo-hygrometer (Shinyei Co., TRH-CA). The uncertainty in the H₂O concentration measurements was estimated to be $\pm 4\%$. Purities of N₂, O₂, N₂O and He were 99.99995% (Japan Fine Products Co.), 99.9% (Nihon Sanso Co.), 99.9% (Air Liquid Japan Co.), and 99.9999% (Air Liquid Japan Co.), respectively. They were used in the experiments without further purification. All experiments have been performed at 295 ± 2 K.

3. Results and discussion

Fig. 1 shows a trace of the observed temporal profile of $O(^1D)$ LIF signal at 115.2 nm following the 193 nm pulsed laser irradiation of a mixture of 25 mTorr of N₂O and 200 mTorr of O₂ in 5 Torr of He diluent. The time-resolved VUV–LIF signal of $O(^1D)$ atoms produced by the photolysis of N₂O exhibits an initial jump followed by a slower decay. The subsequent decay follows pseudo-first-order kinetics and provides information on the kinetics of $O(^1D) + O_2$ reaction at 295 K. We have estimated an uncertainty of ±2% in the pseudo-first-order decay rates for $O(^1D)$ decay attributable to the non-linear least squares fitting method and the choice of the range of data used here.

Fig. 2 shows a plot of the observed pseudo-first-order decay of $O(^{1}D)$ in the presence of N_{2} , O_{2} , $N_{2}O$, and $H_{2}O$ reactants. Straight lines drawn in Fig. 2 are the results of linear least squares fit analysis. The slopes of the straight lines give the bimolecular rate constants of $(3.29 \pm$ $0.27) \times 10^{-11}$, $(4.06 \pm 0.24) \times 10^{-11}$, $(1.35 \pm 0.08) \times 10^{-10}$ and $(2.07 \pm 0.18) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for O(¹D) reactions with N2, O2, N2O, and H2O, respectively. Quoted uncertainty in the bimolecular rate constants is two standard deviations, which includes the uncertainty in the slope of a plot of the pseudo-first-order decay rates versus the reactant concentration (Fig. 2) and the estimated systematic uncertainties in the measurements. The systematic uncertainties are due to the uncertainties in the concentration of the excess reagents and the statistical uncertainties in the values of the pseudo-first-order rate constants derived from the exponential fitting.



Fig. 1. A typical trace of the LIF signal of $O(^1D)$ as a function of the delay time between the N₂O photolysis and $O(^1D)$ probe laser pulses. The inset shows a plot of ln(LIF intensity) versus the delay time. The $O(^1D)$ atoms are detected using a technique of vacuum UV laser-induced fluorescence (VUV–LIF) at 115.22 nm corresponding to the $3s^1D^0$ – $2p^1D$ transition. Reactant pressures are 25 mTorr, 200 mTorr, and 5 Torr for N₂O, O₂ and He, respectively. Experiments were performed at 295 ± 2 K.



Fig. 2. Plot of pseudo-first-order loss of $O(^1D)$ atoms versus the concentration of N_2 (rectangular), O_2 (triangle), H_2O (rhombus), and N_2O (circle). Slopes are the results of linear weighted fit analysis of the experimental data and indicate the bimolecular rate constants for those $O(^1D)$ reactions at 295 ± 2 K.

Table 1 lists the room-temperature bimolecular rate constants of the O(¹D) reactions, in which both the results from the present study and previous studies are included for comparison. For $O(^{1}D) + N_{2}$ reaction, the presently determined k_{N_2} value is in agreement with the recent reports by Ravishankara et al. [15], Strekowski et al. [16], Dunlea and Ravishankara [17], Blitz et al. [18], within the uncertainties. Although the five recent results are still within the error limits of the current NASA/JPL recommendation, they are larger than the recommendation systematically. For $O(^{1}D) + O_{2}$ reaction, the presently determined k_{O_2} value is in good agreement with the available literature values within the quoted uncertainties, as listed in Table 1. For $O(^{1}D)$ + H₂O reaction, our value is in good agreement with the values reported by Amimoto et al. [10], Gericke and Comes [13], Wine and Ravishankara [12], and Dunlea and Ravishankara [17], within the quoted uncertainties. Those five data agree with the current NASA/JPL and IUPAC recommendations within the quoted uncertainties, but are slightly smaller than the recommendations systematically.

OH radicals in the lower and middle atmosphere are predominantly produced by the reaction of H₂O with O(¹D) which is generated by O₃ photolysis. Due to its pivotal role in the atmosphere, accurate estimation of the atmospheric OH production rate is an important issue [2–4]. The atmospheric OH production rate, P(OH), is expressed as follows:

$$P(OH) = \frac{2 k_{H_2O}[H_2O]}{k_{H_2O}[H_2O] + k_{N_2}[N_2] + k_{O_2}[O_2]} \times J(O^1D) \times [O_3]$$
(3)

In Eq. (3), k_X are the rate constants for O(¹D) reactions with X, and $J(O^1D)$ is the rate of O(¹D) production

Table 1 Summary of the room-temperature rate constants of $O(^{1}D)$ reactions with N₂, O₂, N₂O, and H₂O

Reactant	Rate constant ^a	Detected species ^b	Experimental technique ^c	Reference
N ₂	3.29 ± 0.27	$O(^{1}D)$	LIF	This work
	3.24 ± 0.3	$O(^{3}P)$	RF	Strekowski et al. [16]
	3.00 ± 0.24	$O(^{3}P)$	RF	Dunlea and Ravishankara [17]
	3.06 ± 0.25	$O(^{1}D)$	LIF	Blitz et al. [18]
	3.1 ± 0.2	O(¹ D),	LIF	Ravishankara et al. [15]
		$O(^{3}P)$	RF	
	2.8 ± 0.6	$O(^{1}D)$	ES	Streit et al. [8]
	2.4 ± 0.1	$O(^{3}P)$	RA	Amimoto et al. [10]
	2.52 ± 0.25	O(³ P)	RF	Wine and Ravishankara [12]
	2.6 ± 0.3	$O_2(b^1\Sigma_{\sigma}^+)$	ES	Shi and Barker [14]
	2.6 ± 1.0			Sander et al. [5]
	2.6 ± 0.4			Atkinson et al. [6]
O ₂	4.06 ± 0.24	$O(^{1}D)$	LIF	This work
	4.2 ± 0.4	$O(^{3}P)$	RF	Strekowski et al. [16]
	3.89 ± 0.25	$O(^{3}P)$	RF	Dunlea and Ravishankara [17]
	3.8 ± 0.4	$O(^{1}D)$	LIF	Blitz et al. [18]
	4.1 ± 0.5	$O(^{1}D)$	ES	Streit et al. [8]
	4.2 ± 0.2	$O(^{3}P)$	RA	Amimoto et al. [10]
	4.0 ± 0.8			Sander et al. [5]
	4.0 ± 0.5			Atkinson et al. [6]
N ₂ O	1.35 ± 0.08	$O(^{1}D)$	LIF	This work
	1.27 ± 0.08	$O(^{3}P)$	RF	Dunlea and Ravishankara [17]
	1.07 ± 0.10	$O(^{1}D)$	LIF	Blitz et al. [18]
	1.1 ± 0.2	$O(^{1}D)$	ES	Davidson et al. [9]
	1.2 ± 0.1	$O(^{3}P)$	RA	Amimoto et al. [10]
	1.17 ± 0.12	$O(^{3}P)$	RF	Wine and Ravishankara [12]
	1.16 ± 0.35			Sander et al. [5]
	1.16 ± 0.2			Atkinson et al. [6]
H ₂ O	2.07 ± 0.18	$O(^{1}D)$	LIF	This work
	1.96 ± 0.18	$O(^{3}P)$	RF	Dunlea and Ravishankara [17]
	2.3 ± 0.5	$O(^{1}D)$	ES	Streit et al. [8]
	1.95 ± 0.3	$O(^{3}P)$	RA	Amimoto et al. [10]
	2.6 ± 0.5	$O(^{3}P)$	RA	Lee and Slanger [11]
	2.02 ± 0.41	OH	RA	Gericke and Comes [13]
	1.95 ± 0.2	$O(^{3}P)$	RF	Wine and Ravishankara [12]
	2.2 ± 0.4	~ /		Sander et al. [5]
	2.2 ± 0.5			Atkinson et al. [6]

^a In units of 10^{-11} cm³ molecule⁻¹ s⁻¹ for N₂ and O₂ reactions, and 10^{-10} cm³ molecule⁻¹ s⁻¹ for N₂O and H₂O reactions. Quoted uncertainties associated with this work are two standard deviations including the uncertainty in the slope of a plot of the pseudo-first-order decay rates versus the reactant concentration and the estimated systematic uncertainties in the measurements.

^b Species detected for kinetic measurements.

^c LIF, laser-induced fluorescence spectroscopy; RF, resonance fluorescence spectroscopy using an oxygen atom lamp; RA, resonance absorption spectroscopy; ES, emission spectroscopy.

from O₃ photolysis. The *P*(OH) value is very sensitive to k_x values. Using the rate constants determined in the present study, we have estimated the fractional change in the calculated OH production rate relative to that calculated from the current recommendations. Although the uncertainty in the OH production rate calculated from the recommendations is relatively large (~35% at the 67% confidence level) due to propagation of the uncertainties in the rate constants, the OH production rate calculated from the rate constants, the OH production rate calculated from our new rate constants is roughly 15% smaller than that from the recommendations. Recent studies have suggested that the calculated OH production rates become smaller throughout the lower and middle atmosphere by taking the newly measured rate

constants into account [17,18]. Our estimation is consistent with those suggestions.

In this study, the room-temperature rate constant for $O({}^{1}D) + N_{2}O$ reaction has also been determined to be $k_{N_{2}O} = (1.35 \pm 0.08) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, as listed in Table 1. Our $k_{N_{2}O}$ value is roughly 20% larger than the NASA/JPL and IUPAC recommended values, although our value is still within the error limits of the recommendations. The largest value among the previously determined values for $O({}^{1}D) + N_{2}O$ reaction was reported to be $(1.27 \pm 0.08) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ by Dunlea and Ravishankara [17], which is close to our value. They measured the $k_{N_{2}O}$ value in the temperature range between 220 and 370 K, and observed no significant temperature dependence as identified in some previous studies. Their k_{N_2O} values are systematically higher than the current NASA/JPL recommendations between 220 and 370 K.

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