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SUPPORTING INFORMATION

Formation of H_3O^+ and OH by CO_2 and N_2O trace gases in the atmospheric environment

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1. Average Internal Energy Distribution upon Photoionization

The procedure to get the internal energy of N_2O upon photoionization, can be found in paragraph 2.1 of SI of [1]. We use measured Mass-Analyzed Threshold Ionization Spectroscopy (MATI) cross-sections [2] to obtain the average internal (E_{INTER}) and kinetic (E^{el}_{Kin}) energy distribution upon photoionization of N_2O shown in Figure S1 :

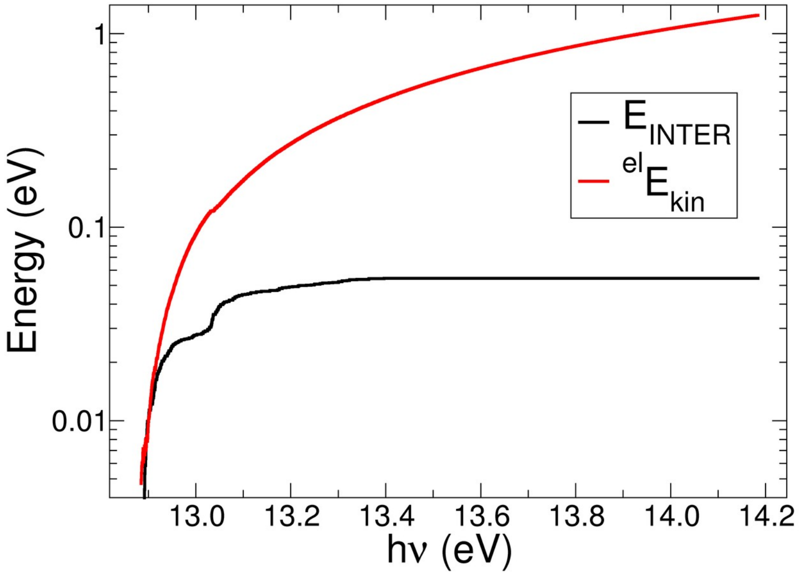

Figure S1: Average internal energy of the N_2O^+ ion (black line) and average kinetic energy of the photoelectron (red line) as a function of the photoionization energy hν.

2. Rate Coefficients from mass spectra

The experimental measurement of mass intensities recorded as a function of photoionization energy of X (X=CO_2, N_2O) ion which reacts with the neutral H_2O allows the determination of the rate coefficients of the reaction steps leading to the final products.

The network of exothermic reactions involving the X ion and H_2O neutral molecules is the following:

$$X^+ + H_2O \xrightarrow{k_{HT}} H\,X^+ + O\,H \qquad (1)$$

$$X^+ + H_2O \xrightarrow{k_{CT}} H_2O^+ + X \qquad (2)$$

$$H\,X^+ + H_2O \xrightarrow{k_{PT}} H_3O^+ + X \qquad (3)$$

$$H_2O^+ + H_2O \xrightarrow{k_{WW}} H_3O^+ + OH \qquad (4)$$

The values of the different rate coefficients (k) at room temperature has been taken from [3], and are reported in table S1

	N_2O	**CO_2**
k_{HT}	$2.10\cdot10^{-10}\pm0.31\cdot10^{-10}$	$6.00\cdot10^{-10}\pm0.90\cdot10^{-10}$
k_{CT}	$1.89\cdot10^{-9}\pm0.28\cdot10^{-9}$	$1.80\cdot10^{-9}\pm0.27\cdot10^{-9}$
k_{PT}	$2.83\cdot10^{-9}\pm0.70\cdot10^{-9}$	$2.65\cdot10^{-9}\pm0.53\cdot10^{-9}$
k_{WW}	$2.05\cdot10^{-9}\pm0.20\cdot10^{-9}$	$2.05\cdot10^{-9}\pm0.20\cdot10^{-9}$

Table S1: Rate coefficients ($cm^3s^{-1}molecule^{-1}$) for the reaction networks at T=300K

In order to obtain the rate coefficients at photoionization energies grater than the IE, a kinetic model is developed based on the equations related to the network of reactions 1-4:

$$\frac{da_{X^+}}{dt} = -k_{HT}\,a_{X^+}\cdot a_{H_2O} - k_{CT}\,a_{X^+}\cdot a_{H_2O} \qquad (5)$$

$$\frac{da_{HX^+}}{dt} = k_{HT}\,a_{X^+}\cdot a_{H_2O} - k_{PT}\,a_{HX^+}\cdot a_{H_2O} \qquad (6)$$

$$\frac{da_{H_2O^+}}{dt} = k_{CT}\,a_{X^+}\cdot a_{H_2O} - k_{WW}\,a_{H_2O^+}\cdot a_{H_2O} \qquad (7)$$

$$\frac{da_{H_3O^+}}{dt} = k_{PT}\,a_{H\,X^+}\cdot a_{H_2O} + k_{WW}\,a_{H_2O^+}\cdot a_{H_2O} \qquad (8)$$

, where the activities (*a*) of the different molecular species are the number densities present in the experimental apparatus derived from measured pressures.

The analytical solution of the above system of differential equations is solved under the hypothesis that the activity of the neutral water is constant during the reactions, being the number density of X^+ ion negligible with respect to the neutral species. The activities of the ionic species are proportional to the mass intensities recorded at times t_F. The pseudo rate coefficient γ is defined as: $\gamma=k_{HT}+k_{CT}$.

$$a_{X^+}(t_F)=a_0 e^{-\gamma a_{H_2O} t_F} \tag{9}$$

$$a_{HX^+}(t_F)=\frac{a_0(\gamma-k_{CT})}{\gamma-k_{PT}}\left(e^{-k_{PT} a_{H_2O} t_F}-e^{-\gamma a_{H_2O} t_F}\right) \tag{10}$$

$$a_{H_2O^+}(t_F)=\frac{k_{CT} a_0}{\gamma-k_{WW}}\left(e^{-k_{WW} a_{H_2O} t_F}-e^{-\gamma a_{H_2O} t_F}\right) \tag{11}$$

$$a_{H_3O^+}(t_F)=a_0\left(\frac{-(\gamma-k_{CT})}{\gamma-k_{PT}} e^{-k_{PT} a_{H_2O} t_F}+\frac{(\gamma-k_{CT})}{(\gamma-k_{PT})} e^{-\gamma a_{H_2O} t_F}-\frac{k_{CT}}{\gamma-k_{WW}} e^{-k_{WW} a_{H_2O} t_F}+\frac{k_{CT}}{(\gamma-k_{WW})} e^{-\gamma a_{H_2O} t_F}-e^{-\gamma a_{H_2O} t_F}+1\right)$$
(12)

The a_0 coefficient is the sum of the number density of all the ions at time t_F : $a_0=a_{X^+}(t_F)+a_{HX^+}(t_F)+a_{H_2O^+}(t_F)+a_{H_3O^+}(t_F)$, and it is a time constant because of the charge conservation during the reactions, and it is equal to the initial number density of the X^+ ion.

The evaluation of the rate coefficients for the reactions of X^+ with water at each photon energies is based on the hypothesis that the reaction 3) and 4) are not affected by the internal energy of the initial photoexcited ion X^+, and that both H_2O and H_2O^+ are at room temperature in the present experimental conditions. The rate coefficient k_{PT} and k_{WW} are considered constant with hν. This assumption is based on the fact that the fast charge exchange between X^+ and water will produce a H_2O^+ ion with an internal energy which is not much affected by the thermal content of the X^+. Instead, for reaction 3), this is considered to be in the collision regime: the Su-Chu Langevin rates [4] (see fig. S2) are $K_L^{N_2O/CO_2}(300\,K)=2.490\cdot 10^{-9}$ $cm^3 s^{-1} molecule^{-1}$ which are within the error of the rate coefficient at room temperature (See tab S1).

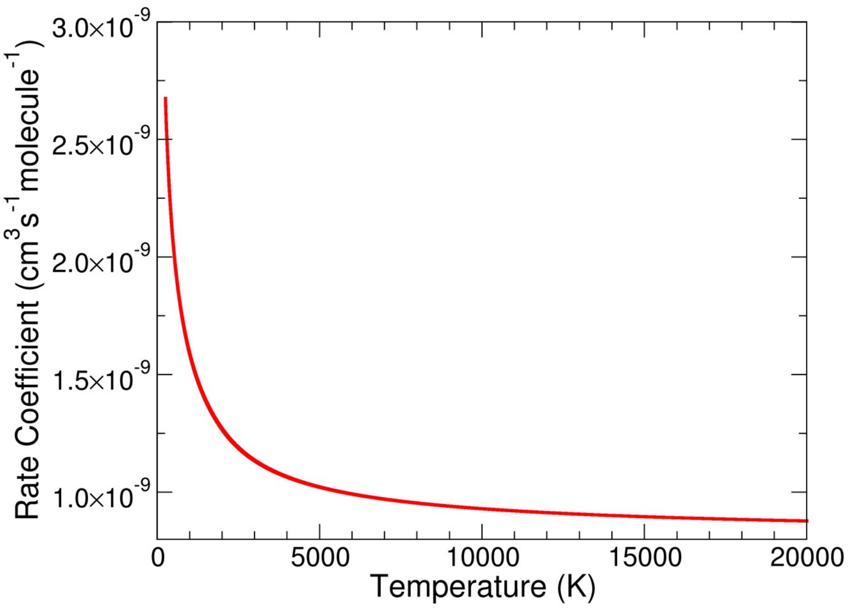

Figure S2: Collision rate coefficient for reaction 3) in the Su-Chu Langevin approximation

We have fixed the value of k_{PT} at its value at room temperature, and we have verified that lower values of k_{PT}, which occurs when the temperature increases, affect the rate coefficients of equations 1) and 2) within $0.2\cdot 10^{-9}$ $cm^3 s^{-1} molecule^{-1}$, which is close to their errors.

This assumption will allow, by using of eqs. 9 and 10, the evaluation of $k_{HT}(h\nu)$, $k_{CT}(h\nu)$ at each photon energies hν by using the experimental mass of X^+ and HX^+.

The t_F is evaluated by the solving the ratio of equation 9 and 10 and the experimental mass ratio $m_X^+(t_F)/m_{HX^+}(t_F)$, where γ is a known quantity at T=300K (see tab. 1), and a_{H_2O} is given by the partial pressure of H_2O and is reported in tab S2.

	P_{H_2O} (mbar)	a_{H_2O} (molecule/cm^3)	t_F (s)	$a_o(h\nu=IE)$
CO_2	$4.3\cdot 10^{-5}\pm 1.3\cdot 10^{-5}$	$1.0\cdot 10^{12}\pm 0.3\cdot 10^{12}$	$1.25\cdot 10^{-4}\pm 0.68\cdot 10^{-4}$	23332.52963
N_2O	$8.2\cdot 10^{-5}\pm 2.5\cdot 10^{-5}$	$2.0\cdot 10^{12}\pm 0.6\cdot 10^{12}$	$7.78\cdot 10^{-4}\pm 7.64\cdot 10^{-4}$	1535.75705

Table S2: Final times of reaction for reaction of N_2O^+ and CO_2^+ with water. The error on the pressure is estimated as 30%.

The final times t_F allow to compute the total ions a_o: from eq. 9 we have calculated the total ions yields at hν=IE, as reported in tab. S2. The values of total ion yields at different photon energies are calculated by scaling with the CO_2 (fig. S3) and N_2O (fig. S4) PES cross sections $(\phi(h\nu))$ $a_o(h\nu)=a_o(IE)\cdot\phi(h\nu)/\phi(IE)$

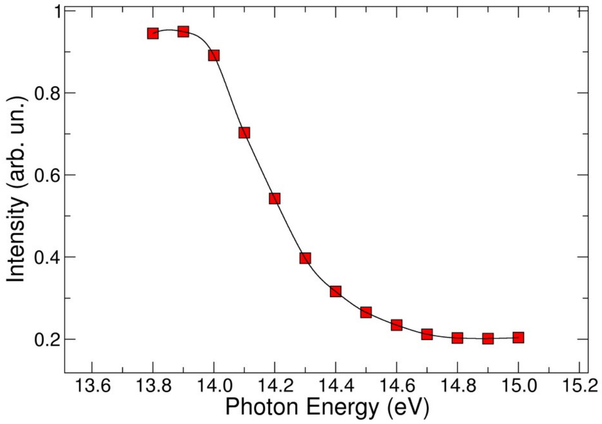

Figure S3: Photon-electron spectrum of CO_2 shown from ionization energies up to 15 eV.

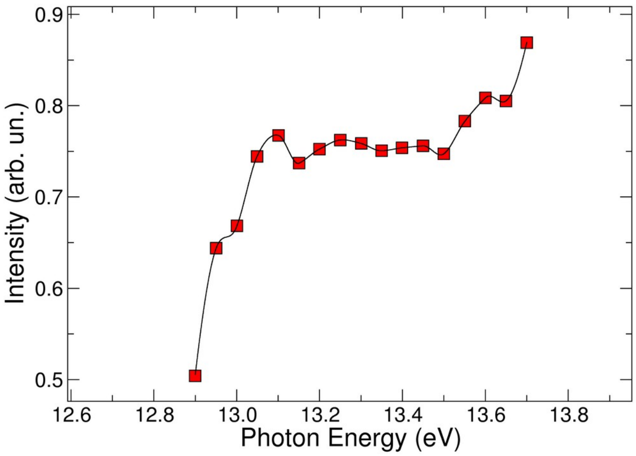

Figure S4: Photon-electron spectrum of N_2O shown from ionization energies up to 13.7 eV.

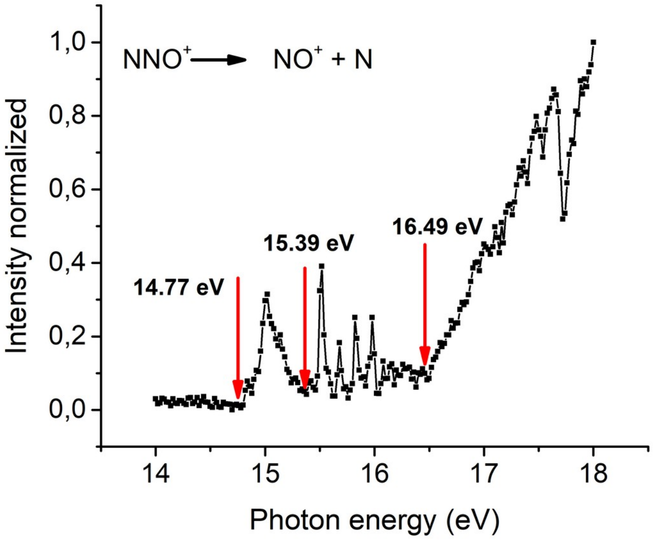

Figure S5: PIEC of NO$^+$ from N_2O^+

Table S3: Frequencies (cm^{-1}) of the products of HT and CT reactions:

	N_2OH^+	**Vibrational Mode**
ν_1	437	NNO in plane bending
ν_2	488	NNO out of plane bending
ν_3	1063	NO stretching
ν_4	1377	HON in plane bending
ν_5	2325	NN stretching
ν_6	3472	OH stretching
	N_2O	
ν_1	599	Bending
ν_2	599	Bending
ν_3	1297	Symm. stretching
ν_4	2260	Asymm. stretching
	H_2O^+	
ν_1	1457	Bending
ν_2	3358	Symm. stretching
ν_3	3411	Asymm. stretching
	OH	
ν_1	3737	OH stretching
	CO_2H^+	
ν_1	540	OCO in plane bending
ν_2	590	OCO out of plane bending
ν_3	1036	HOC in plane bending
ν_4	1252	Symm. OCO stretching
ν_5	2427	Asymm. OCO stretching
ν_6	3524	OH stretching
	CO_2	
ν_1	666	Bending
ν_2	666	Bending
ν_3	1341	Symm. stretching
ν_4	2384	Asymm. stretching

Table S4. Energy distribution of the products for HT channel: $CO_2^+ + H_2O \rightarrow HCO_2^+ + OH$

hν (eV)	**HCO_2^+**			**OH**
	Vibrational Energy (cm^{-1})	**Mode excitation**	**Kinetic Energy (cm^{-1})**	**Kinetic Energy (cm^{-1})**
13.8	2850	$2\nu_1+3\nu_2$	850	2250
13.9	2382	$\nu_1+\nu_2+\nu_4$	1024	2712
14.0	2756	$\nu_1+2\nu_2+\nu_3$	1016	2690
14.1	2662	$\nu_2+2\nu_3$	1075	2846
14.2	2967	$\nu_1+\nu_5$	1020	2701
14.3	3412	$4\nu_1+\nu_4$	907	2400
14.4	3152	$2\nu_1+2\nu_3$	992	2626
14.5	3108	$3\nu_3$	1015	2686
14.6	3108	$3\nu_3$	1031	2729
14.7	3412	$4\nu_1+\nu_4$	955	2527
14.8	2872	$3\nu_1+\nu_4$	1117	2955
14.9	3240	$6\nu_1$	1030	2726
15.0	3390	$3\nu_1+3\nu_2$	1009	2670

Table S5. Energy distribution of the products for CT channel: $CO_2^+ + H_2O \rightarrow CO_2 + H_2O^+$

hν (eV)	**CO_2**			**H_2O^+**		
	Vibrational Energy (cm^{-1})	**Mode excitation**	**Kinetic Energy (cm^{-1})**	**Vibrational Energy (cm^{-1})**	**Mode excitation**	**Kinetic Energy (cm^{-1})**
13.8	8010	$8\nu_1+2\nu_3$	646	0		1578
13.9	8658	$13\nu_1$	506	0		1238
14.0	8405	$3\nu_1+3\nu_3+\nu_4$	257	1457	ν_1	627
14.1	4391	$\nu_1+\nu_3+\nu_4$	467	4868	$\nu_1+\nu_3$	1141
14.2	8387	$7\nu_1+\nu_3+\nu_4$	327	1457	ν_1	801
14.3	8387	$7\nu_1+\nu_3+\nu_4$	336	1457	ν_1	823
14.4	7450	$2\nu_3+2\nu_4$	623	1457	ν_1	1524
14.5	10132	$4\nu_3+2\nu_4$	279	0		682
14.6	9737	$5\nu_1+3\nu_3+\nu_4$	411	0		1004
14.7	9430	$7\nu_1+2\nu_4$	507	0		1241
14.8	7073	$\nu_1+3\nu_3+\nu_4$	360	2914	$2\nu_1$	881
14.9	4671	$5\nu_1+\nu_3$	505	4868	$\nu_1+\nu_3$	1236
15.0	6389	$4\nu_1+\nu_3+\nu_4$	451	3411	ν_3	1102

Table S6. Energy distribution of the products for HT channel: $N_2O^+ + H_2O \rightarrow N_2OH^+ + OH$

hν (eV)	**N_2OH^+**			**OH**
	Vibrational Energy (cm^{-1})	**Mode excitation**	**Kinetic Energy (cm^{-1})**	**Kinetic Energy (cm^{-1})**
12.90	437	ν_1	468	1238
12.95	0		619	1638
13.00	0		627	1658
13.05	437	ν_1	532	1407
13.10	437	ν_1	545	1441
13.15	0		668	1770
13.20	437	ν_1	554	1468
13.25	437	ν_1	558	1477
13.30	437	ν_1	560	1483
13.35	437	ν_1	564	1494
13.40	0		686	1815
13.45	0		686	1815
13.50	437	ν_1	566	1498
13.55	437	ν_1	566	1498
13.60	0		686	1815
13.65	437	ν_1	566	1498
13.70	437	ν_1	566	1498

Table S7. Energy distribution of the products for CT channel: $N_2O^+ + H_2O \rightarrow N_2O + H_2O^+$

hν (eV)	**N_2O**			**H_2O^+**
	Vibrational Energy (cm^{-1})	**Mode excitation**	**Kinetic Energy (cm^{-1})**	**Kinetic Energy (cm^{-1})**
12.90	1896	$\nu_1+\nu_3$	445	1087
12.95	2495	$2\nu_1+\nu_3$	304	744
13.00	2495	$2\nu_1+\nu_3$	312	764
13.05	2260	ν_4	407	995
13.10	1896	$\nu_1+\nu_3$	526	1287
13.15	2260	ν_4	425	1039
13.20	1797	$3\nu_1$	566	1382
13.25	2260	ν_4	435	1063
13.30	2260	ν_4	437	1069
13.35	2396	$4\nu_1$	402	983
13.40	2260	ν_4	443	1084
13.45	2260	ν_4	443	1084
13.50	1896	$\nu_1+\nu_3$	549	1342
13.55	1896	$\nu_1+\nu_3$	549	1342
13.60	1797	$3\nu_1$	578	1412
13.65	1797	$3\nu_1$	578	1412
13.70	1896	$\nu_1+\nu_3$	549	1342

3. Radiative Power

The vibrational radiative power emission has been evaluated by using the HITEMP database [5]. In particular the most abundant isotope composition has been selected for both CO_2 and N_2O molecules. The cutoff of the intensity of the lines has been put at 10^{-32} cm^{-1}/(molecule cm^{-2}) after proper verification of convergence. The radiative power for each vibrational excited state defined by the triplet ν_1, ν_2, ν_3 has been evaluated with the following equation:

$$RP(\nu_1,\nu_2,\nu_3)=\frac{\sum_i A_i S_i \nu_i e^{-E_i^{rot}/KT^{rot}}}{\sum_i A_i S_i g_i e^{-E_i^{rot}/KT^{rot}}} \tag{13}$$

where for each energy transition *i* whose upper vibrational state belongs to the ν_1, ν_2, ν_3 triplet, A_i is the Einstein spontaneous emission coefficient in s^{-1}, S_i is the intensity in cm^{-1}/(molecule cm^{-2}), ν_i is the emission frequency in cm^{-1}, g_i is the statistical weight of the upper state, T^{rot} is the rotational temperature, E_i^{rot} is the upper state rotational energy, and is given by the difference between the upper state energy and the vibrational energy of the upper state. On the other hand, the thermal vibrational radiative power is defined as:

$$TRP(T)=\frac{\sum_i A_i S_i \nu_i e^{-E_i/KT}}{\sum_i A_i S_i g_i e^{-E_i/KT}} \tag{14}$$

where E_i is the ro-vibrational energy of the *i* transition, and the sum is over all the transitions. The state selected radiative lifetimes are calculated with the following equation:

$$\tau(\nu_1,\nu_2,\nu_3)=\frac{\sum_i A_i S_i e^{-E_i^{rot}/KT^{rot}}}{\sum_i A_i S_i g_i e^{-E_i^{rot}/KT^{rot}}} \tag{15}$$

The thermal radiative lifetimes are given by following equation:

$$\tau_{TH}(T)=\frac{\sum_i A_i S_i e^{-E_i/KT}}{\sum_i A_i S_i g_i e^{-E_i/KT}} \tag{16}$$

Table S8: Vibrational energies and temperature at different photon energies for CO_2.

hν (eV)	**Vibrational Energy (cm^{-1})**	**Vibrational Temperature (K)**	**Radiative Power (W/molecule)**	**Radiative Lifetime (s)**
13.8	8010	3694	$3.62 \cdot 10^{-19}$	1402.73
13.9	8658	3933	0.00	//
14.0	8405	3840	$1.05 \cdot 10^{-17}$	42.19
14.1	4391	2339	$3.52 \cdot 10^{-16}$	1.02
14.2	8387	3833	$2.68 \cdot 10^{-16}$	1.27
14.3	8387	3833	$2.68 \cdot 10^{-16}$	1.27
14.4	7450	3487	$1.08 \cdot 10^{-16}$	3.75
14.5	10132	4474	$2.87 \cdot 10^{-18}$	206.47
14.6	9737	4329	$6.23 \cdot 10^{-18}$	86.30
14.7	9430	4217	$1.09 \cdot 10^{-16}$	2.88
14.8	7073	3347	$1.11 \cdot 10^{-17}$	41.14
14.9	4671	2446	$8.76 \cdot 10^{-18}$	10.59
15.0	6389	3093	$3.03 \cdot 10^{-16}$	1.15

Data from HITEMP database: Thermal distribution at T=250K radiative power (TRP) $5.67 \cdot 10^{-18}$ W/molecule, lifetime (τ_{TH})= 21.19 s. The rotational temperature is fixed at 250K

Table S9: Vibrational energies and temperature at different photon energies for N_2O

hν (eV)	**Vibrational Energy (cm^{-1})**	**Vibrational Temperature (K)**	**Radiative Power (W/molecule)**	**Radiative Lifetime (s)**
12.90	1896	1307	$4.46{\cdot}10^{-18}$	40.19
12.95	2495	1555	$1.83{\cdot}10^{-18}$	122.03
13.00	2495	1555	$1.83{\cdot}10^{-18}$	122.03
13.05	2260	1459	$1.33{\cdot}10^{-16}$	2.31
13.10	1896	1307	$4.46{\cdot}10^{-18}$	40.19
13.15	2260	1459	$1.33{\cdot}10^{-16}$	2.31
13.20	1797	1264	$1.37{\cdot}10^{-19}$	1079.8
13.25	2260	1459	$1.33{\cdot}10^{-16}$	2.31
13.30	2260	1459	$1.33{\cdot}10^{-16}$	2.31
13.35	2396	1515	$9.57{\cdot}10^{-20}$	2276.67
13.40	2260	1459	$1.33{\cdot}10^{-16}$	2.31
13.45	2260	1459	$1.33{\cdot}10^{-16}$	2.31
13.50	1896	1307	$4.46{\cdot}10^{-18}$	40.19
13.55	1896	1307	$4.46{\cdot}10^{-18}$	40.19
13.60	1797	1264	$1.37{\cdot}10^{-19}$	1079.8
13.65	1797	1264	$1.37{\cdot}10^{-19}$	1079.8
13.70	1896	1307	$4.46{\cdot}10^{-18}$	40.19

Data from HITEMP [ref] database: at T=250K radiative power (TRP) $9.64{\cdot}10^{-19}$ W/molecule, lifetime (τ_{TH}) 216.51 s. The rotational temperature is fixed at 250K

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