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Efficiency determination of the laser-induced reaction of $NO(A(^2\Sigma^+))$ with CO_2

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ABSTRACT

The reaction of NO excited in the electronic state $A(^2\Sigma^+, v'=2)$ with CO_2 has been studied. This has been carried on by irradiating NO samples in excess of CO_2 with a home-made dye laser pumped by a commercial frequency tripled Nd:YAG laser. The samples have been analyzed by FTIR spectrometry before and after irradiation to obtain the fraction of molecules reacted per pulse. The NO excitation efficiency was determined from the measurement of the absorption cross-section, the sample transmittance and the energy of the laser pulse. A value of (0.26 ± 0.01) was obtained for the reaction efficiency, indicating that about 25% of the excited NO molecules reacted with CO_2. A reaction rate constant value of $(1.30 \pm 0.12) \times 10^{-10}\ \mathrm{cm^3\ molecules^{-1}\ s^{-1}}$ was determined from the value of the reaction efficiency obtained in this work and the global electronic quenching rate constant of $NO(A^2\Sigma^+, v'=2)$ reported by Nee et al. [6] for CO_2.

1. Introduction

Nitric oxide, NO, is a highly reactive gas that participates in many chemical reactions. It controls many physiological functions and, as a minor constituent, plays a major role in the chemistry of the atmosphere [1].

NO is released into Earth's atmosphere by both natural and human-generated sources. Natural sources include volcanoes, oceans, biological decay and lightning strikes. Nitric oxide is a common byproduct of combustion, and cars and fossil-fuel burning power plants are two main sources of the molecule. Once released, it reacts with oxygen to produce nitrogen dioxide contributing to the problem of air pollution, playing roles in the formation of both smog and acid rain. Moreover, the selective reaction of excited nitric oxide with carbon dioxide has been proposed as a method for separating ^{15}N isotopes [2]. It is therefore desirable to understand as completely as possible the kinetics of nitric oxide in the presence of different gases and, particularly, of CO_2.

Nitric Oxide absorbs UV radiation in the 150–230 nm wavelength range [3]. In the ground electronic state it does not react with carbon dioxide, CO_2. At 3000 K, an upper limit $\leq 5 \times 10^{-15}\ \mathrm{cm^3\ molecules^{-1}\ s^{-1}}$ has been estimated for the rate constant of this reaction [4]. However, it has been demonstrated that the reactivity of nitric oxide increases considerably in the excited state, $A(^2\Sigma^+)$, and that, in the presence of CO_2, the products NO_2 and carbon monoxide, CO, are formed [4,5]. Additionally, electronic quenching rate constants of $NO(A^2\Sigma^+, v'=0\text{–}2)$ of 4.05×10^{-10}, 3.80×10^{-10}, $5.18 \times 10^{-10}\ \mathrm{cm^3\ molecules^{-1}\ s^{-1}}$, respectively, have been recently reported for CO_2 [6]. However, the authors did not discriminate between chemical and physical quenching.

In this work we have studied the reaction of NO excited in the electronic state $A(^2\Sigma^+, v'=2)$ with CO_2. Different experimental arrangements and sample composition have been used to elucidate the reaction kinetics. This allowed us to discriminate between chemical and physical quenching and to determine the efficiency and rate constant value of the reaction.

2. Experimental

A homemade dye-laser was used as radiation source in the UV high-resolution absorption and reaction experiments. It consists of a grazing incidence optical resonator followed by an amplifying stage, both using a solution 40 μM of EXALITE 411 (Exciton) in dioxane. The emission of this dye is in the 386–396 nm and 402–419 nm bands. Both stages were excited with pulses from a frequency tripled Nd:YAG laser (355 nm), Continuum Surelite I. The amplifier output was frequency doubled with a type I BBO crystal and a prism was used to separate the emergent collinear beams. The generated pulses, with energies between 30 and 130 μJ, 5 ns (FWHM) length and 10 Hz repetition rate, were tuned in the 205–210 nm wavelength range. Irradiation was performed with a collimated beam 2 mm diameter with a quasi-homogeneous *top hat* type transverse energy distribution profile.

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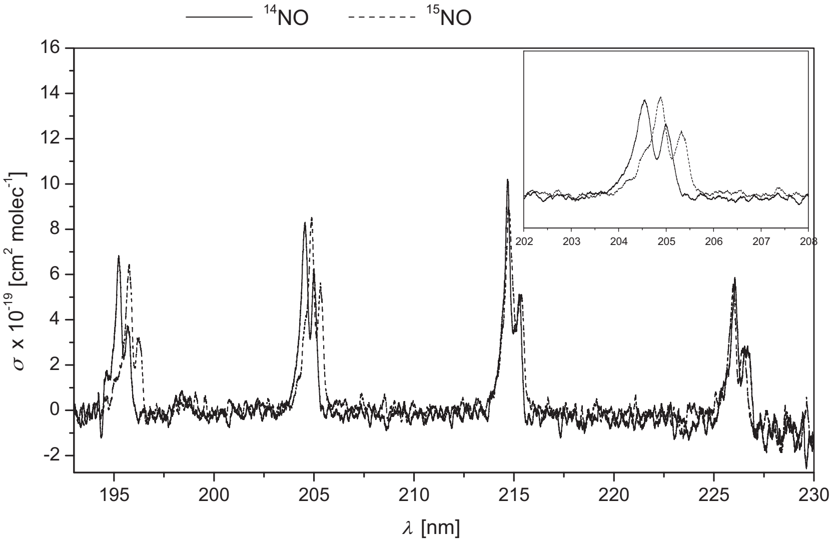

Fig. 1. Low-resolution UV spectra of samples of 3.5 Torr of nitric oxide and 150 Torr of CO_2. Natural abundance NO (solid); pure ^{15}NO (dash).

The samples were prepared in a high vacuum system (10^{-8} Torr) and were purified through freeze–thaw cycles using liquid N_2 to eliminate non-condensable gases, particularly O_2. Initially, natural abundance nitric oxide, NO, was used, but the cutoff wavelength of the BBO crystal did not allow us to reach the absorption maximum wavelength. As a result, the fraction of molecules excited per pulse was too low and many hours of irradiation were needed to obtain an appreciable amount of reaction so as to be able to quantify the reactant disappearance and products generation in an accurate manner. Therefore, we decided to work with pure ^{15}NO, since the maximum absorption wavelength of this species could be reached with our dye laser. This enabled a larger fraction of molecules to be excited per pulse and, in consequence, the irradiation periods were considerably reduced. Isotopic mixtures of the reactants were also used in order to check the reproducibility of the results and the absence of isotopic effect.

The reactants, natural abundance nitric oxide, NO, and pure ^{15}NO, were synthesized and provided by INVAP S.E. Villa Golf laboratory [7] and used in mixtures with CO_2 (AGA 99.996%).

The reactants and products analysis was performed by infrared spectrometry with a FTIR spectrometer Perkin-Elmer, System 2000. Usually, 40 scans with a resolution of 1 cm^{-1} were used to obtain each spectrum. Calibrated standards of natural abundance NO and $^{14}NO_2$, pure ^{15}NO and $^{15}NO_2$ and CO in mixtures with either 150 or 760 Torr of CO_2 were used to determine the samples' composition.

The absorption experiments were performed at room temperature using cylindrical Pyrex glass cells of different diameters (1.55 and 3 cm) and lengths (10, 15 and 84 cm) sealed with CaF_2 windows.

The reaction experiments were performed using two cells: A and B. Cell A was a cylindrical Pyrex glass cell 15.1 cm long and 1.1 cm internal diameter sealed with CaF_2 windows. Cell B was a cross shaped Pyrex glass cell, each arm 10 cm long and 3 cm internal diameter, sealed with quartz windows in one arm and KCl in the other.

The natural abundance nitric oxide, NO, and pure isotopic ^{15}NO low-resolution UV spectra in the wavelength range 190–232 nm were registered in an experimental set-up consisting of a Deuterium lamp, a 0.5 m Ebert type Jarrel Ash monochromator and a Thorn-Emi 9817 QB photomultiplier.

3. Results

3.1. Absorption experiments

The low-resolution UV spectra of natural abundance NO and ^{15}NO were registered at two different pressures, 3.5 and 10 Torr, to find the absorption maxima of each isotopic species in order to choose the laser wavelengths range to be used for excitation. The discrete vibrational bands reported by Okabe [3] have been initially surveyed and a pressure dependence of the integrated absorption cross-section was observed induced by CO_2. Therefore, measurements have been carried on in excess of CO_2. The UV spectra of both natural abundance NO and ^{15}NO and of mixtures of both species in mixtures with 150 Torr of CO_2 were registered.

Fig. 1 shows the low-resolution absorption cross-section measured for natural abundance NO and ^{15}NO. Four rovibrational bands with different degrees of isotopic shift are observed. The insert shows an enlargement of the 205 nm band chosen to perform the experiments.

These experiments allowed us to define the laser wavelength range, 205.4–205.6 nm, to be swept in high-resolution absorption experiments in order to obtain the local absorption maxima.

The fraction of NO molecules excited by the laser used to determine the reaction efficiency is calculated from the laser absorption cross-sections values integrated in the laser line width. The high-resolution laser absorption experiments were carried on in the reduced region of interest. The high-resolution laser absorption cross-sections were determined for samples of 10 Torr of NO (natural abundance and pure ^{15}NO) and 150 Torr of CO_2 from the sample transmittance calculated from the measured incident and transmitted energies averaged over 300 pulses using Beer-Lambert law. The laser absorption cross-sections of both samples are shown in Fig. 2.

The expressions used to calculate them were:

$$\sigma_{15} = -\frac{1}{PL}\ln\left(\frac{\tau_1}{\tau_{\text{cell}}}\right) \tag{1}$$

$$\sigma_{14} = -ri\sigma_{15} - \frac{1+ri}{PL}\ln\left(\frac{\tau_2}{\tau_{\text{cell}}}\right) \tag{2}$$

where ri is the isotopic relation given by the ^{15}NO to ^{14}NO partial pressures ratio, P is the total sample pressure, L is the cell length and τ_{cell} the cell transmittance. The pure ^{15}NO and natural

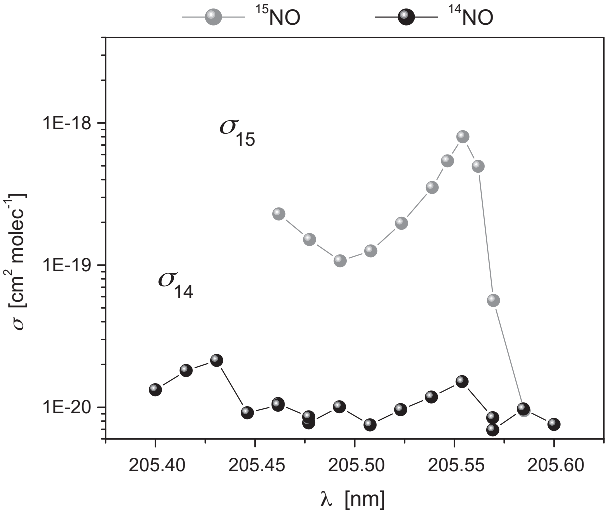

Fig. 2. Laser absorption cross-sections of pure ^{15}NO and 150 Torr of CO_2 (gray) and pure ^{14}NO and 150 Torr of CO_2 (black).

abundance NO transmittances corresponding to the isotopic ratio of the sample are τ_1 and τ_2, respectively. The spectrum of the pure ^{14}NO species has been obtained by subtracting the contribution of the ^{15}NO ($ri = 0.0037$) to the natural abundance NO spectrum.

It can be observed in the figure that in the 205.4–205.6 nm wavelength range the isotopic species ^{15}NO has a quite narrow absorption maximum while the ^{14}NO species absorption feature has no structure and is nearly two orders of magnitude lower.

3.2. Reaction experiments

Once the optimum laser irradiation wavelength and the absorption cross-sections for each isotopic species at that wavelength were determined, we proceeded to study the reaction efficiency. This was performed by exciting the $A(^2\Sigma^+)$–$X(^2\Pi)$ transition in natural abundance NO and pure ^{15}NO as well as in mixtures of both isotopic species in excess of CO_2 and determining the pulse-to-pulse evolution of the NO reactant disappearance and CO and NO_2 products generation by infrared spectrometry.

Several experiments were performed under the four experimental conditions summarized in Table 1. The irradiation wavelength was $\lambda = 205.55$ nm corresponding to the maximum absorption of the ^{15}NO species.

Fig. 3 shows the FTIR spectra of a typical experiment performed under the experimental condition 4, before and after irradiation with 84,900 laser pulses. In the spectrum before irradiation the band corresponding to the anti-symmetric stretch of CO_2 is evidenced at 2349 cm^{-1} and, at 1843 cm^{-1}, the band head of ^{15}NO is observed. Small amounts of $^{15}NO_2$ formed during the gas handling in process of filling the cell are also present in this spectrum. Undoubtedly, NO reacts since, as it can be appreciated in the spectrum after irradiation, its concentration has fallen down and both NO_2 and CO appear as products. The amounts of NO_2 generated by reaction are much greater than those produced during gas handling as can be seen in the figure. The bands corresponding to the anti-symmetric stretch of $^{15}NO_2$ and the CO band head are observed at 1583 cm^{-1} and 2142 cm^{-1}, respectively.

Fig. 4 shows the pulse-to-pulse evolution of the pressures of ^{15}NO reacted, NO_r, and of CO and $^{15}NO_2$ generated. An excellent correlation between the reactant consumed and the products

Table 1
Experimental conditions.

	Sample composition [^{15}NO, natural abundance NO, CO_2]	Pulse energy [μJ pulse^{-1}]	Cell
1	[9.4, 8.2, 722]	110 ± 10	A
2	[10.1, 0.0, 130]	100 ± 10	A
3	[10.0, 0.6, 730]	130 ± 10	A
4	[10.0, 0.0, 150]	53 ± 5	B

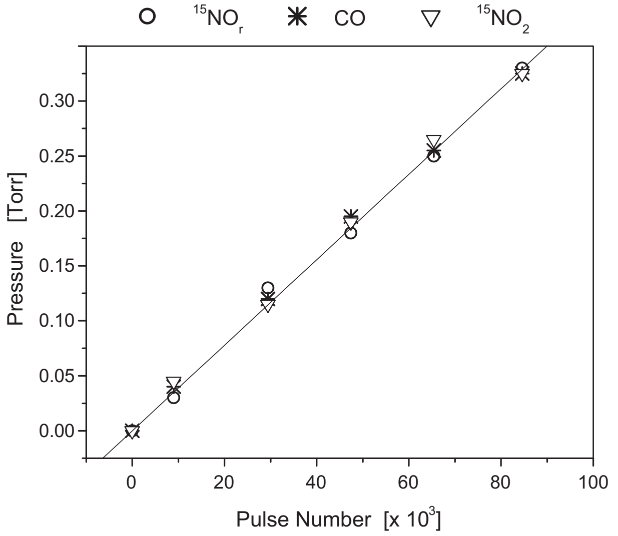

Fig. 4. Pulse-to-pulse evolution of the pressures of ^{15}NO reacted, $^{15}NO_r$, and of CO and $^{15}NO_2$ generated during the irradiation of the sample of experiment 4.

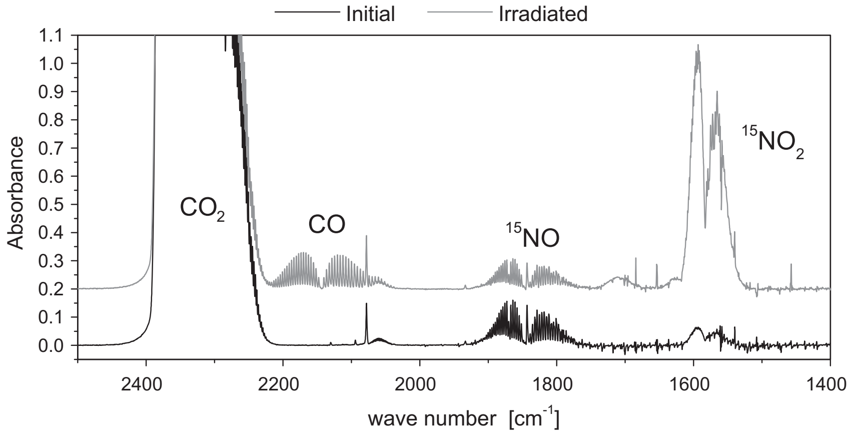

Fig. 3. FTIR spectra of a sample of 10 Torr of pure ^{15}NO and 150 Torr CO_2 before and after irradiation with 84,900 pulses ($\lambda = 205.55$ nm).

formed is observed evidencing the occurrence of the kinetic mechanism proposed, described by equations R1 and R3.

Similar results were obtained in all the experiments performed under the four experimental conditions previously described.

4. Discussion

The results obtained are consistent with the mechanism proposed in Ref. [5]. In the absence of CO_2, the NO molecules excited in the $A(^2\Sigma^+)$ state, NO*, react according to:

$$NO + h\nu \rightarrow NO^* \tag{R1}$$

$$NO^* + NO \xrightarrow{2NO} N_2 + 2NO_2 \tag{R2a}$$

$$NO^* + NO \rightarrow N_2O + O \xrightarrow{NO} N_2O + NO_2 \tag{R2b}$$

$$NO^* + NO \rightarrow 2NO \tag{R2c}$$

Reaction (R2a) can occur through two kinetically indistinguishable channels, the first of which can be schematized as

$$\begin{array}{l} NO^* + NO \rightarrow N_2 + O_2 \\ NO + NO + O_2 \rightarrow 2NO_2 \end{array} \tag{R2a1}$$

and the second as

$$\begin{array}{l} NO^* + NO \rightarrow NO_2 + N \\ N + NO \rightarrow N_2 + O \\ O + NO \rightarrow NO_2 \end{array} \tag{R2a2}$$

In the presence of CO_2, the following reactions will take place as well:

$$NO^* + CO_2 \rightarrow NO + CO_2 \tag{R3a}$$

$$NO^* + CO_2 \rightarrow NO_2 + CO \tag{R3b}$$

Cohen and Heicklen [5] have measured the ratio of CO to N_2 production as an estimator of the relative importance of the channels R3 and R2, respectively, for different CO_2 and NO ratios. From the results obtained, the authors have determined the ratio of the rate constants of the reactions of NO* with NO (R2) and with CO_2 (R3):

$$\frac{k_2}{k_3} = 0.34 \tag{3}$$

where $k_2 = k_{2a} + k_{2b} + k_{2c}$ and $k_3 = k_{3a} + k_{3b}$. They have additionally concluded that the rate constant of the physical quenching reaction (R3a), k_{3a}, is negligible related to that of the chemical reaction (R3b), k_{3b}, and thus $k_3 \approx k_{3b}$.

In excess of CO_2 pressure the rate of reaction (R2) will be much lower than that of reaction (R3) and will effectively not compete. Even though the product of reaction (R2) is the same as that of reaction (R3), for molar ratios (CO_2:NO) ≥ (100:1), the production of NO_2 through reaction (R2) would be negligible. Thus, for this particular condition the net result of the photochemical reaction of $NO(A^2\Sigma^+)$ shown in Fig. 4 would be the production of CO and NO_2 through reaction (R3).

As a result of the irradiation, the laser pulse excites a fraction *f* of the NO molecules in the electronic excited state $A(^2\Sigma^+)$. This fraction is related to the number of photons absorbed per molecule.

In low absorption conditions and at a moderate degree of excitation so that the transition is not saturated, it can be written as

$$f \approx \frac{4\sigma}{\pi D^2}\frac{E}{h\nu} \tag{4}$$

where σ is the absorption cross-section, *E* the laser pulse energy, *D* the cell diameter and $h\nu$ the photon energy.

Table 2
Concentrations of NO excited and reacted per pulse.

	$f\,[NO]_0$ [μTorr pulse^{-1}]	Δ [NO] [μTorr pulse^{-1}]
1	104 ± 5.2	26.3 ± 2
2	16 ± 0.8	6.3 ± 2
3	160 ± 8	41.7 ± 2
4	12.6 ± 5.2	3.9 ± 2

In strong absorption conditions, the laser attenuation along the optical path length must be taken into account and the resultant expression is

$$f \approx \frac{4\sigma}{\pi D^2}\frac{E}{h\nu}\frac{\tau - 1}{\ln(\tau)} \tag{5}$$

where τ is the sample transmittance. This expression indicates that the excitation degree can be calculated from the laser parameters, *E* and ν, the cell diameter, *D*, the molecular parameter, σ, the sample pressure and the measurement of the transmittance, τ.

When the sample is composed of a mixture of absorbing molecules, the absorption cross-section, σ, corresponds to the weighted average of the absorption cross-sections of the individual components:

$$\sigma = \frac{ri}{1+ri}\sigma_{15} + \frac{1}{1+ri}\sigma_{14} \tag{6}$$

where *ri* is the isotopic ratio.

The number of NO molecules excited per pulse is estimated as *f* times the number of the initial NO molecules. Table 2 shows the values obtained in the experiments performed under the four experimental conditions described.

A linear correlation is obtained between the concentration of NO reacted and excited per pulse as shown in Fig. 5. The slope is 0.26 ± 0.01 indicating that 26% of the NO excited molecules react with CO_2 to give CO and NO_2.

On the other hand, the vibrational dependence of the quenching rates of $NO(A^2\Sigma^+, v')$ for $v' = 0$–2 levels has been recently investigated for He, Ar, Xe, N_2, O_2, N_2O, CO_2 and SF_6 by Nee et al. [6]. The authors have used synchrotron radiation in the 200–230 nm wavelength range to excite the $v' = 0$–2 bands of $NO(A^2\Sigma^+)$ at 226, 215, and 205 nm. They have determined the quenching rates by measuring the variation of the fluorescence intensity as a function of pressure in the presence of foreign gases. For CO_2, the determined global quenching rates constants of $NO(A^2\Sigma^+, v')$ for

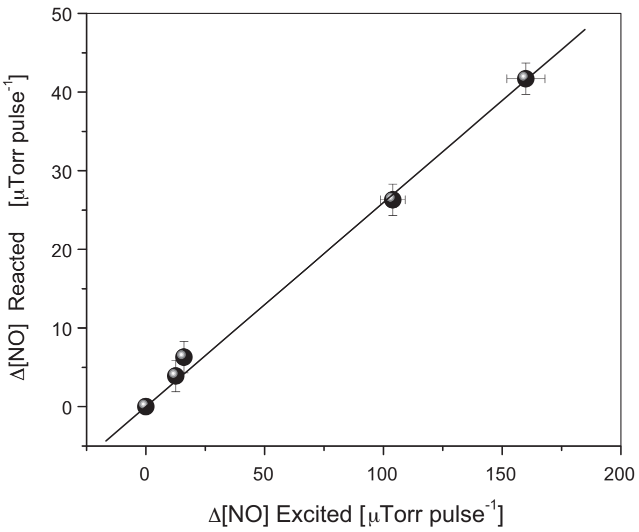

Fig. 5. Concentration of NO consumed in reaction per pulse vs. concentration of NO excited per pulse.

$v' = 0–2$ levels were $(4.05 \pm 0.20) \times 10^{-10}$, $(3.80 \pm 0.16) \times 10^{-10}$ and $(5.18 \pm 0.24) \times 10^{-10}$ cm^3 molecules^{-1} s^{-1}, respectively.

We have thus determined the rate constant value for the reaction of NO with CO_2 from the value of the quenching rate constant of NO($A^2\Sigma^+$, $v' = 2$) by CO_2 [6] and the efficiency value derived from the data shown in Fig. 5. This value resulted in $(1.30 \pm 0.12) \times 10^{-10}$ cm^3 molecules^{-1} s^{-1}.

5. Conclusions

We have studied the reaction of NO excited in the electronic state A($^2\Sigma^+$, $v' = 2$) with CO_2.

High-resolution laser absorption cross-sections values integrated in the laser line width have been obtained in a reduced wavelength range around 205 nm. These cross-sections values enabled us to calculate the fraction of NO molecules excited per pulse.

The excellent agreement between the reactant consumed and the products formed in the experiments performed using different experimental conditions evidenced the occurrence of the reaction through the kinetic mechanism proposed. Moreover, it has been found that 26% of NO excited molecules react with CO_2 to give CO and NO_2.

From this efficiency value and the global quenching rate of NO($A^2\Sigma^+$, v') for $v' = 2$ level for CO_2 determined by Nee et al. [6] a value of $(1.30 \pm 0.12) \times 10^{-10}$ cm^3 molecules^{-1} s^{-1} was determined for the reaction rate constant of NO excited in the A($^2\Sigma^+$, $v' = 2$) electronic state with CO_2.

Acknowledgements

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