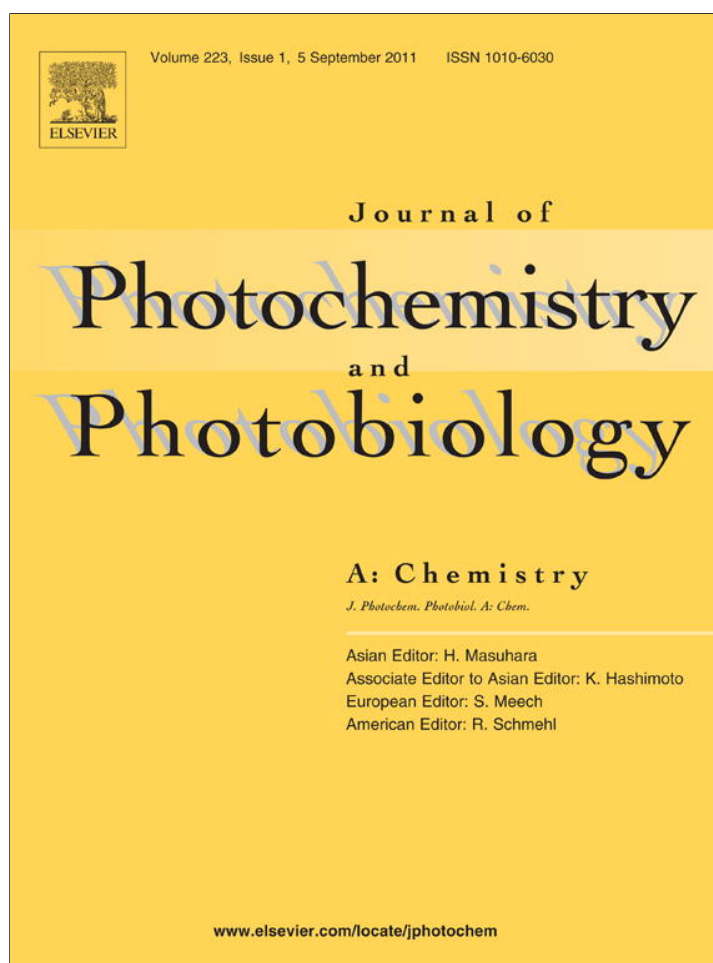


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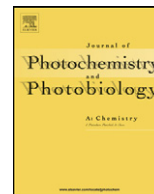
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Efficiency determination of the laser-induced reaction of NO($A^2\Sigma^+$) with CO₂

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ABSTRACT

The reaction of NO excited in the electronic state $A^2\Sigma^+$, $v' = 2$ with CO₂ has been studied. This has been carried on by irradiating NO samples in excess of CO₂ 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 CO₂. A reaction rate constant value of $(1.30 \pm 0.12) \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ 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 CO₂.

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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 ¹⁵N 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 CO₂.

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, CO₂. At 3000 K, an upper limit $\leq 5 \times 10^{-15} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ 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 CO₂, the products NO₂ and carbon monoxide, CO, are formed [4,5]. Additionally, electronic quenching rate constants of NO($A^2\Sigma^+$, $v' = 0-2$) of 4.05×10^{-10} , 3.80×10^{-10} , $5.18 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, respectively, have been recently reported for CO₂ [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 CO₂. 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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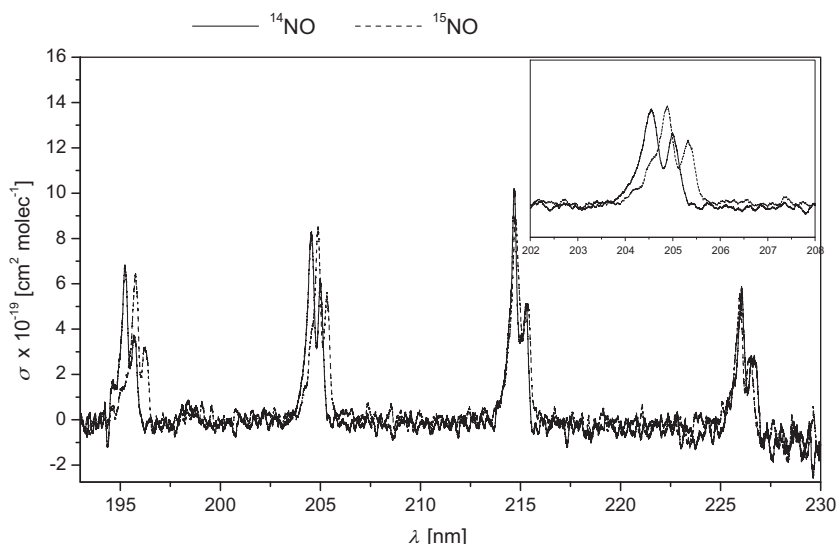


Fig. 1. Low-resolution UV spectra of samples of 3.5 Torr of nitric oxide and 150 Torr of CO₂. Natural abundance NO (solid); pure ¹⁵NO (dash).

The samples were prepared in a high vacuum system (10⁻⁸ Torr) and were purified through freeze–thaw cycles using liquid N₂ to eliminate non-condensable gases, particularly O₂. 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 ¹⁵NO, 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 ¹⁵NO, were synthesized and provided by INVAP S.E. Villa Golf laboratory [7] and used in mixtures with CO₂ (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 ¹⁴NO₂, pure ¹⁵NO and ¹⁵NO₂ and CO in mixtures with either 150 or 760 Torr of CO₂ 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 CaF₂ 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 CaF₂ 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 ¹⁵NO 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 ¹⁵NO 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 CO₂. Therefore, measurements have been carried on in excess of CO₂. The UV spectra of both natural abundance NO and ¹⁵NO and of mixtures of both species in mixtures with 150 Torr of CO₂ were registered.

Fig. 1 shows the low-resolution absorption cross-section measured for natural abundance NO and ¹⁵NO. 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 ¹⁵NO) and 150 Torr of CO₂ 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:

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

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

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

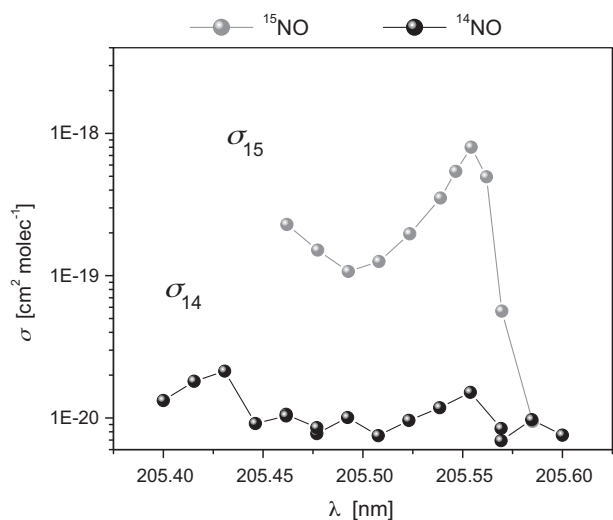


Fig. 2. Laser absorption cross-sections of pure ^{15}NO and 150 Torr of CO_2 (gray) and pure ^{14}NO and 150 Torr of CO_2 (black).

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 ($r_i = 0.0037$) 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

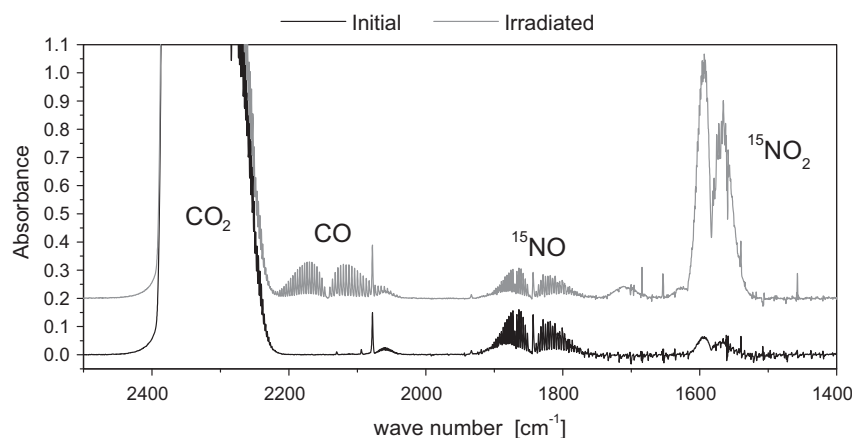


Fig. 3. FTIR spectra of a sample of 10 Torr of pure ^{15}NO and 150 Torr CO_2 before and after irradiation with 84,900 pulses ($\lambda = 205.55$ nm).

Table 1
Experimental conditions.

	Sample composition [^{15}NO , natural abundance NO, CO_2]	Pulse energy [$\mu\text{J pulse}^{-1}$]	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

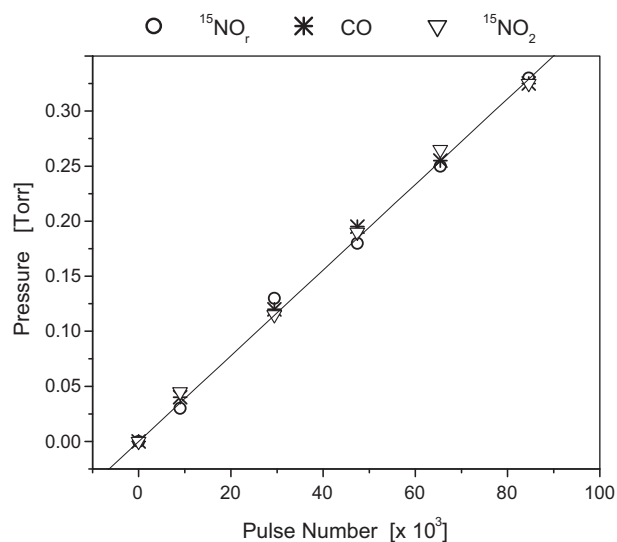


Fig. 4. Pulse-to-pulse evolution of the pressures of ^{15}NO reacted, $^{15}\text{NO}_r$, and of CO and $^{15}\text{NO}_2$ generated during the irradiation of the sample of experiment 4.

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 $^{15}\text{NO}_2$ 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 $^{15}\text{NO}_2$ and the CO band head are observed at 1583 cm^{-1} and 2142 cm^{-1} , respectively.

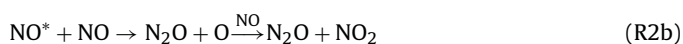
Fig. 4 shows the pulse-to-pulse evolution of the pressures of ^{15}NO reacted, NO_r , and of CO and $^{15}\text{NO}_2$ generated. An excellent correlation between the reactant consumed and the products

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 CO₂, the NO molecules excited in the A(2Σ⁺) state, NO*, react according to:



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



and the second as



In the presence of CO₂, the following reactions will take place as well:



Cohen and Hecklen [5] have measured the ratio of CO to N₂ production as an estimator of the relative importance of the channels R3 and R2, respectively, for different CO₂ 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 CO₂ (R3):

$$\frac{k_2}{k_3} = 0.34 \quad (3)$$

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 CO₂ 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 (CO₂:NO) ≥ (100:1), the production of NO₂ through reaction (R2) would be negligible. Thus, for this particular condition the net result of the photochemical reaction of NO(A²Σ⁺) shown in Fig. 4 would be the production of CO and NO₂ 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(2Σ⁺). 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

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

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.

	$f[\text{NO}]_0$ [$\mu\text{Torr pulse}^{-1}$]	$\Delta[\text{NO}]$ [$\mu\text{Torr pulse}^{-1}$]
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

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

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:

$$\sigma = \frac{ri}{1+ri}\sigma_{15} + \frac{1}{1+ri}\sigma_{14} \quad (6)$$

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 CO₂ to give CO and NO₂.

On the other hand, the vibrational dependence of the quenching rates of NO(A²Σ⁺, ν') for $\nu' = 0-2$ levels has been recently investigated for He, Ar, Xe, N₂, O₂, N₂O, CO₂ and SF₆ by Nee et al. [6]. The authors have used synchrotron radiation in the 200–230 nm wavelength range to excite the $\nu' = 0-2$ bands of NO(A²Σ⁺) 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 CO₂, the determined global quenching rates constants of NO(A²Σ⁺, ν') for

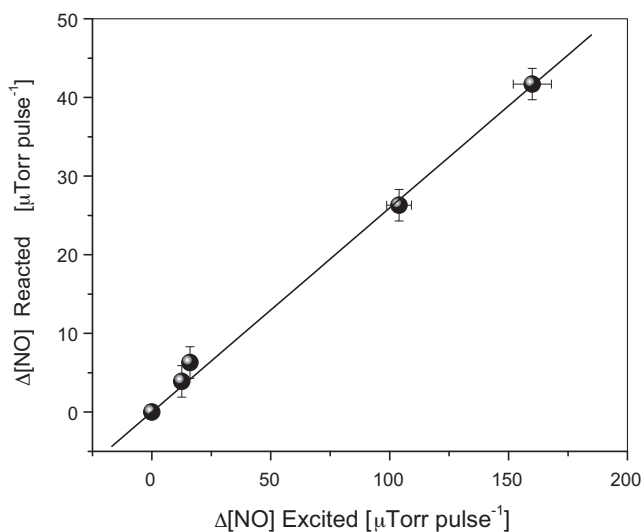


Fig. 5. Concentration of NO consumed in reaction per pulse vs. concentration of NO excited per pulse.

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

We have thus determined the rate constant value for the reaction of NO with CO₂ from the value of the quenching rate constant of NO(A²Σ⁺, ν' = 2) by CO₂ [6] and the efficiency value derived from the data shown in Fig. 5. This value resulted in $(1.30 \pm 0.12) \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$.

5. Conclusions

We have studied the reaction of NO excited in the electronic state A(²Σ⁺, ν' = 2) with CO₂.

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 CO₂ to give CO and NO₂.

From this efficiency value and the global quenching rate of NO(A²Σ⁺, ν') for ν' = 2 level for CO₂ determined by Nee et al. [6] a value of $(1.30 \pm 0.12) \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ was determined for the reaction rate constant of NO excited in the A(²Σ⁺, ν' = 2) electronic state with CO₂.

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