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Direct measurements of NO_2 photolysis rates for México City

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RESUMEN

Se reportan medidas de las constantes de fotólisis del NO_2 a NO y $O(^3P)$ como frecuencias de fotólisis $J_{(NO2)}$ para la Ciudad de México. Estas frecuencias se midieron usando un reactor, en donde una concentración conocida de NO_2 se fotodisocia para diferentes tiempos de exposición. La radiación UV se midió con un radiómetro Eppley. Se muestra una comparación con valores calculados usando un modelo de transferencia de radiación y la fórmula de Madronich.

ABSTRACT

Direct measurements of the rate of NO_2 photolysis to NO and $O(^3P)$ are reported as photolysis frequencies $J_{(NO2)}$ for México City. These frequencies were measured using a flow reactor, where a known concentration of NO_2 was photolysed for different experimental exposure times. UV radiation was measured with an Eppley UV radiometer. Comparisons with calculated values using a radiation transfer model, and Madronich's formula are shown.

1. Introduction

Air quality models require accurate, reliable photolysis rate constants of photolabile species. These values are often unavailable from calculations using default values for typical conditions. This paper reports measurements of photolysis frequencies of nitrogen dioxide

$$NO_2 + h\nu \xrightarrow[\lambda<420nm]{} NO + O$$

in Mexico City downtown. Comparisons with modeled values and with calculated values from empiric and semi-empiric procedures are shown.

The presence of cloud, particles and aerosols increases uncertainty in computations, that is why frequent measures of photolysis are needed when the chemistry of the atmosphere is investigated *in situ* (Brauers and Hofzumahaus, 1992). However, the experimental measurement of the NO_2 photolysis rate constant presents some difficulties even when the atmosphere is free of clouds and aerosols. One has to take special care measuring the usually very low gas concentration, flow, reaction temperatures and other variables. Moreover, one should be able to minimize experimental errors arising from absorption, reflection and refraction at the walls of the tube, and shadowing by nearby instrumentation and structures. A more practical way to continuously estimate NO_2 photolysis rate values is through establishing a semi-empirical correlation between discrete experimental values of these rates and solar actinic fluxes. (Jackson *et al.*, 1975, Zafonte *et al.*, 1977 and Madronich, 1987). However these correlations are locally dependent.

Using reported values of the photolysis rate constant $J_{(NO2)}$ and solar fluxes from the literature, Madronich (1987) evaluated the quality of the available experimental data on $J_{(NO2)}$. This evaluation was carried out by intercomparing $J_{(NO2)}$ measurements and simultaneous measurements of downward UV irradiance. He used a simplified treatment of diffuse and direct sunlight to correlate the UV irradiance E and J, through $J = C[f^{-1} + 2A_L]E$, where f is a function of diffuse and direct sunlight, and of the solar zenith angle. He applied his model to the full set of available data and proposed an empirical correlation introducing altitude as an independent variable in addition to the customary UV Eppley irradiance. However, the data used by Madronich were obtained at 0.0, 0.3, 1.8 and only one up to 3.0 km above sea level and latitudes above 33° North. Therefore it was considered necessary to see if the database used was wide enough to reproduce observations under Mexico City conditions (2240 masl and 19°20' North).

2. Experimental technique

To measure $J_{(NO2)}$, a dilute mixture of NO_2 is photolysed for different exposure times. Steady state conditions are considered for the reaction mechanism of NO_2. Thus,

$$\frac{d(NO_2)}{dt} = -J[NO_2]$$

where J is the photolysis constant and k' the wall constant. If the initial concentration of nitrogen dioxide is $[NO_2]_0$ for $t = 0$,

$$\ln\left(\frac{NO_2}{[NO_2]_0}\right) = -Jt$$

The photolysis frequency of nitrogen dioxide was determined using a quartz flow reactor, where for different exposure times, a known concentration of NO_2 (50 ppm) in nitrogen (ALPHAGAZ) was photolysed. Figure 1 shows schematically the experimental configuration to measure the NO2 photolysis rates and solar fluxes. A flow of diluted NO_2 is passed through a flow meter (AALBORG, Model GFM-1700, Range 0-5 l), constant flow is maintained with a flow regulator (VICI, CONDYNE, Model SA202-3(3)1). A solenoid valve (ALLTECH, ATKOMATIC, Model K38G16VN), diverts the flow either to the quartz reactor (1", o.d., 1 m long) or to the nitrogen oxides chemiluminicent analyzer (Columbia Sc. In. Co., Model NA510-2). All gas tubing was made of Teflon (1/4", o.d., ALLTECH) covered with black tape. Connections were made with stainless steel (SWAGELOK). In the reactor mode, the reactor output is sent to the analyzer in which concentrations of NO, NO_2 and NO_x are measured. Voltage outputs for each one of the channels is connected to a PCL812 data acquisition board (PC-LabDas, 1991). A thermocouple J type, an Eppley radiometer, a pressure transducer (the pressure inside reactor was constant) are connected to an amplifier PCL789 board (PC-LabDas, 1991) and then to the PCL812 data acquisition board. This is mounted in a PCLAB 80386 computer. The nitrogen oxides analyzer was calibrated *in situ*. In order to have different exposure times, sections of the reactor were covered from sunlight. One length was used one day long. 4 different lengths were used. This design requires stable clear sky conditions usually met during the dry season. The Eppley radiometer (THE EPPLEY LAB., Model 27992) has a UV filter and a photocell placed behind a diffusing plate made of quartz. The spectral window is from 295 to 385nm.

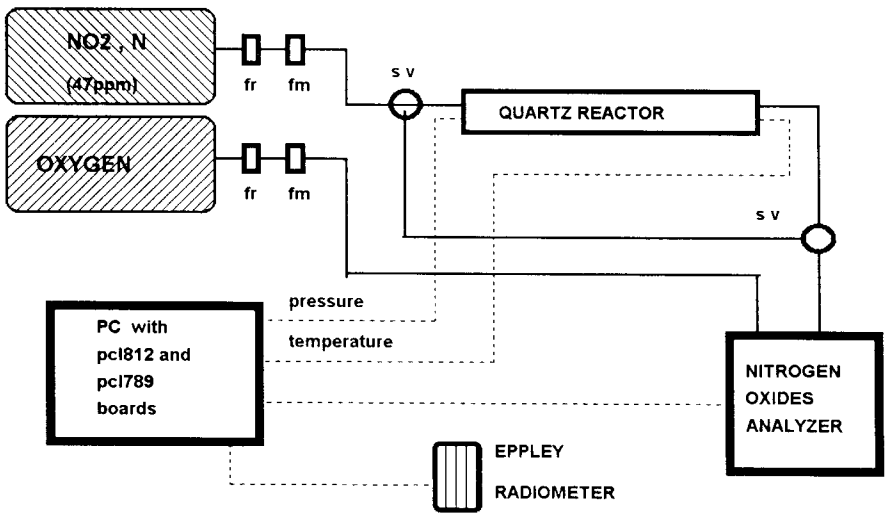

Fig. 1. Experimental diagram.

3. Results and conclusions

The experiment was carried out in the roof of Palacio de Minería (19°25' 59" N, 99°07' 58" W, 2233 m above sea level) in downtown Mexico City, the days February 9-13, 1994. Measurements of temperature, pressure, UV radiation and NO, NO_2 and NO_x concentrations were obtained every minute. Four different reactor lengths (94, 74, 64 and 54cm) were used, these add to a total of 2000 measurements. Figure 2 shows the photolysis rate constants and the averaged UV fluxes, measured by the above procedure. The times for minima and maxima observed with both instruments correlate well. Measured values of $J_{(NO2)}$ for five days in February are shown by solid triangles and irradiance UV with a continuous curve.

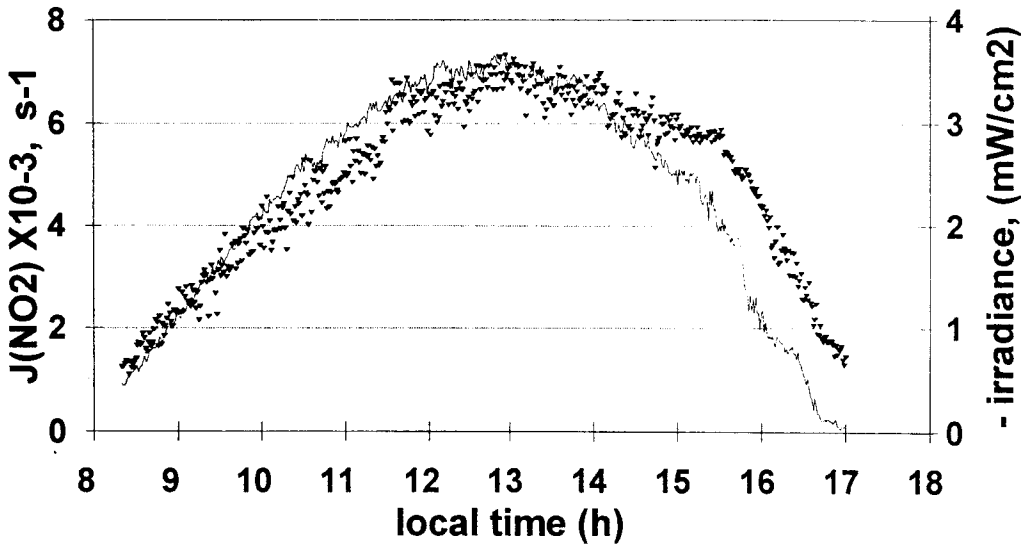

Fig. 2. Photolysis rates of NO_2 (solid triangles) and the averages UV fluxes (continuous curve) for Mexico City.

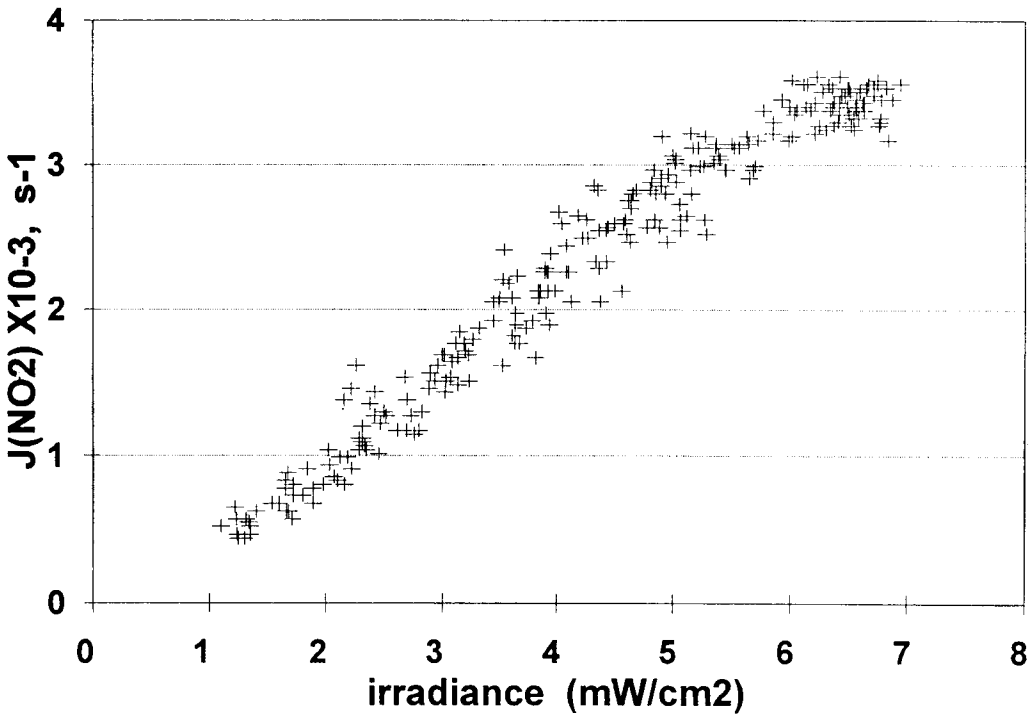

Fig. 3. Photolysis rates NO_2 vs. UV irradiance obtained in polluted air conditions, in Mexico City.

Figure 3 shows a plot of the NO_2 rates vs. irradiances obtained in clear sky conditions. Figure 4 presents values of photolysis rate constant obtained by different methods. Solid triangles represent the experimental $J_{(NO2)}$ values. Solid squares show estimated values using our delta Eddington model for clear sky conditions at an assumed regional albedo of 10% for λ <410 nm, refraction index of 1.4 $\pm$ 0.05i and ozone column of 290 UD. Contributions to $J_{(NO2)}$ are

calculated from the direct beam of the sun (J_0), the downward (J_d) and the upward scattered light (J_u). For comparison reasons the upward scattered light at botton layer was assumed to be zero for the base case. Empty squares correspond to Torijano's *et al.*, model (1992), which is based on the results for actinic flux of Demerjian *et al.* (1980), which a height, absorption and dispersion of particles corrections. Values of J obtained using $J = C(f^{-1} + 2A_L)E$, eq. 9 in Madronich (1987), with f obtained using output from the theoretical calculations and the experimental value of UV irradiances (solid circles), and the ones calculated by means of $J = 1.35E/[(0.56 + 0.03z)\cos\theta + 0.21]$, eq. 12 in Madronich (1987), as it is, and considering 2233 masl (empty circles).

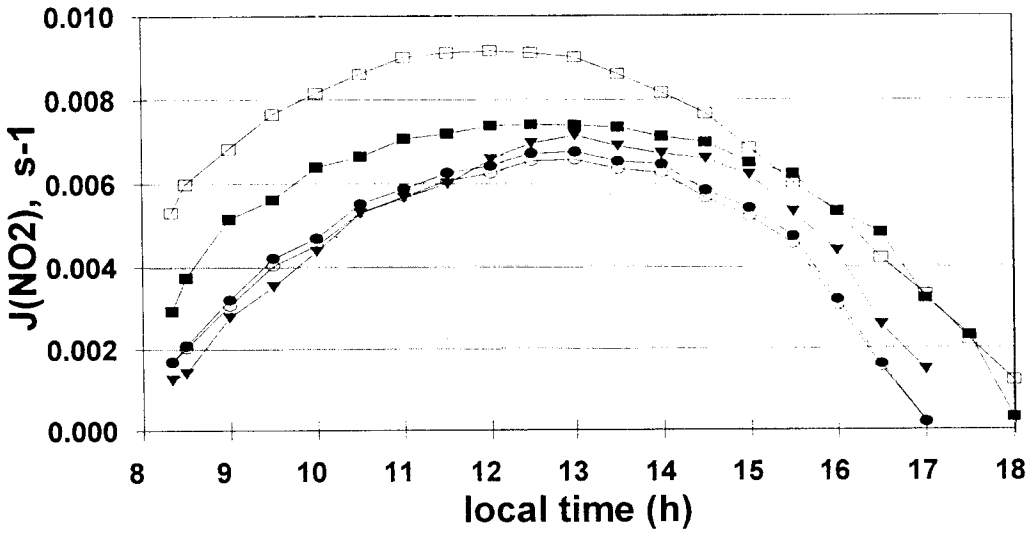

Fig. 4. Comparison of phohtolysis rates of NO_2. Solid triangles are experimental values, solid squares are theoretical values (Ruiz-Suárez *et al.*, 1993), empty squares are theoretical values (Torijano *et al.*, 1992), solid and empty circles are values obtained with eqs. 9 and 12 in Madronich, 1987, respectively.

It is clear that at large zenith angles the theoretical calculations, over predict the photolysis rate constant. However, it should be pointed out that currently, the model assumes a city in a flat terrain and length obstruction and reflection from nearby buildings is not taken into account. The ready use the equation as it is, falls short of the experimental values of J, most likely because of local and geographic effects not present in the data set used to obtain the fitted constants. It seems logical to consider that the semiempirical model may be better suitted for routine work provided *ad hoc* local values of constants f and A_L (albedo) can be obtained. The former require a better characterization of aerosol properties such as refractive index and particle distributions. Also a big family of field observations may be used for calibration of radiation transfer models.

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