Laboratory studies on the product quantum yields in the photolysis of ozone and model calculations for the stratosphere

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O3 plays several extremely important roles in the Earth's atmosphere. Production of atomic oxygen from the photodissociation of O3 has been a subject of interest to atmospheric scientists. Many experimental and theoretical studies have shown that there are two primal pathways in the Hartley band photolysis of O3 at 220 - 300 nm;

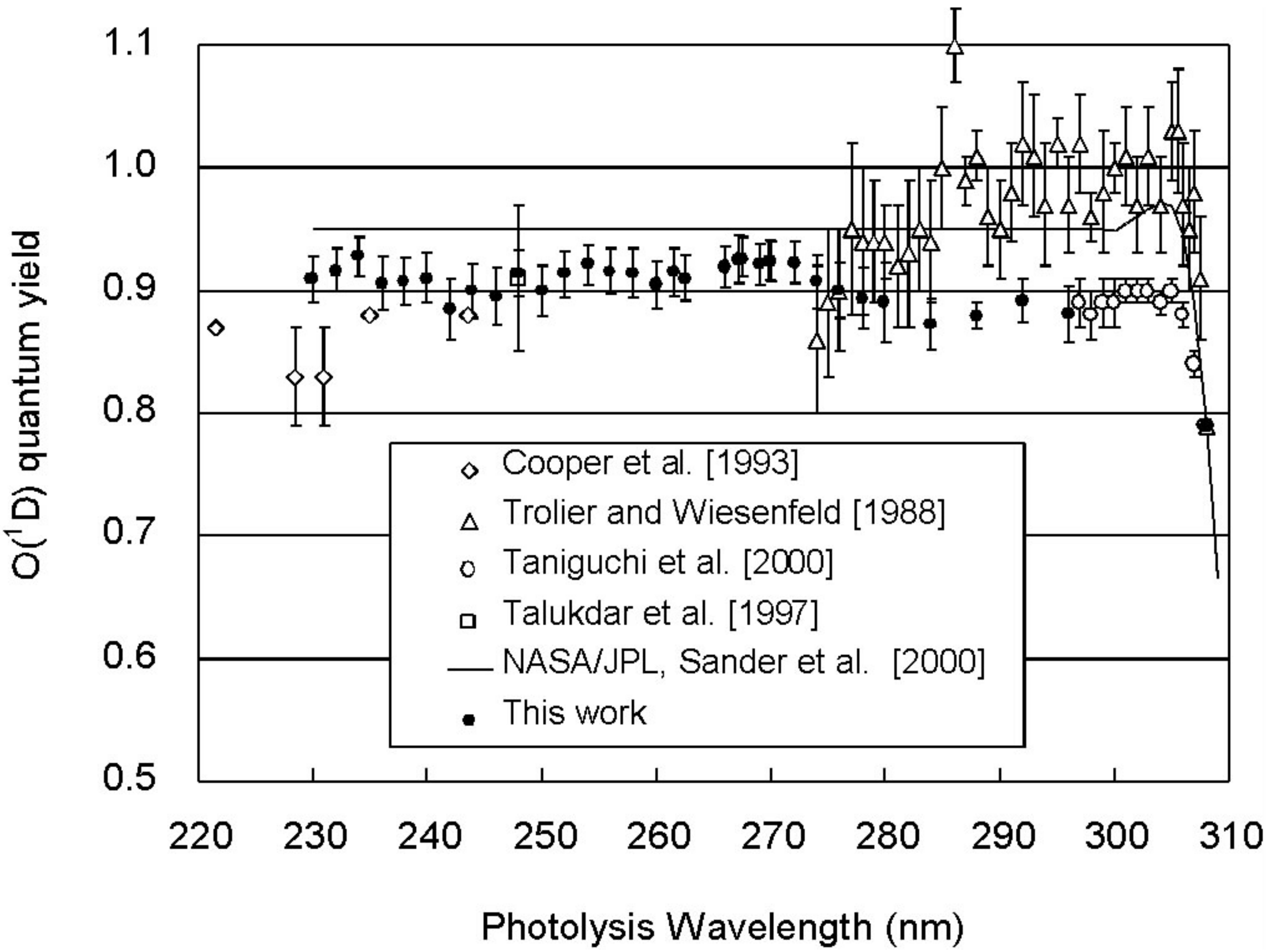
O3 + hv -- O(1D) + O2 (1)

-- O(3P) + O2. (2)

Both processes are spin-allowed from the singlet state of ozone. The NASA/JPL panel has recommended the quantum yield value of 0.95 over the Hartley band between 240 and 300 nm for use in the stratospheric modeling. The IUPAC subcommittee have recommended the formula of (1.98 - 301 / lambda) for the photolysis wavelength (lambda) between 271 and 300 nm and a constant value of 0.87 for 222 - 271 nm.

In the present study the O(3Pj) atoms produced in the Hartley band photolysis of O3 between 230 - 308 nm are directly detected by laser-induced fluorescence in the vacuum UV region (VUV-LIF). Using the VUV-LIF technique, the relative quantum yields of O(1D) and O(3P) formation from O3 photolysis between 297 - 329 nm have been measured previously by our group. This is the first report on the systematic measurements of the O(1D) quantum yields from ozone photolysis in the wide range of wavelength in the UV region. As a photolysis light source in this study an optical parametric oscillator (OPO) with a second harmonic generator was used, which allowed us to generate tunable UV light in the wide wavelength range in the UV region. The quantum yield values for O(1D) formation in the photolysis of ozone at 297 K are determined as a function of the photolysis wavelength, using the O(1D) quantum yield value of 0.79 at 308 nm as a reference. The measured quantum yield was almost independent of the photolysis wavelength between 230 and 305 nm, with the almost constant value of 0.88 - 0.93 over the Hartley band. Figure shows the quantum yield for O(1D) formation in the Hartley band photolysis of O3 obtained at 297K as a function of photolysis wavelength. For comparison, the yield values reported by other groups are also shown. A broken line indicates the yield values recommended by NASA/JPL panel, which are constant (0.95) between 240 and 300 nm.

Using the O(1D) quantum yield values obatined experimentally in this study, one-demensional photochemical model calculations for the stratosphere were performed. The model was originaly developed by Dr. S. Solomon (NOAA/AL), which includes about 120 chemical reactions. The annual mean profiles for chemical species were calculated assuming a latitude of 40 degree, with the chemical kinetics and photochemical data presented by the latest NASA/JPL recommendations other than the ozone photolysis data. The results of the runs with our new ozone photolysis data are compared with those of the runs with the ozone photolysis data recommended by NASA/JPL. The concentrations of OH calculated with our new values of O(1D) quantum yields were lower than the predicted with the NASA/JPL(2000) by up to 6 %, while the O3 concentrations were higher by up to 3%.



1.1
1.0
0.9
0.8
0.7
0.6
0.5
O(1D) quantum yield
220
230
240
250
260
270
280
290
300
310
Photolysis Wavelength (nm)
Cooper et al. [1993]
Trolier and Wiesenfeld [1988]
Taniguchi et al. [2000]
Talukdar et al. [1997]
NASA/JPL, Sander et al. [2000]
This work