UV Absorption Cross Sections of Nitrous Oxide (N_2O) and Carbon Tetrachloride (CCl_4) between 210 and 350 K and the Atmospheric Implications

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Atmos. Chem. Phys.

Abstract. Absorption cross sections of nitrous oxide (N_2O) and carbon tetrachloride (CCl_4) are reported at five atomic UV lines (184.95, 202.548, 206.200, 213.857, and 228.8 nm) at temperatures in the range 210 – 350 K. In addition, UV absorption spectra of CCl_4 are reported between 200 – 235 nm as a function of temperature (225 – 350 K). The results from this work are critically compared with results from earlier studies. For N_2O, the present results are in good agreement with the current JPL recommendation enabling a reduction in the estimated uncertainty in the N_2O atmospheric photolysis rate. For CCl_4, the present cross section results are systematically greater than the current recommendation at the reduced temperatures most relevant to stratospheric photolysis. The new cross sections result in a 5 – 7% increase in the modeled CCl_4 photolysis loss, and a slight decrease in the stratospheric lifetime, from 51 to 50 years, for present day conditions. The corresponding changes in modeled inorganic chlorine and ozone in the stratosphere are quite small. A CCl_4 cross section parameterization for use in atmospheric model calculations is presented.

1. Introduction

The long-lived atmospheric species nitrous oxide (N_2O) and carbon tetrachloride (CCl_4) are ozone depleting substances (ODSs) and potent radiative forcing agents (Forster, 2007; WMO, 2007). The abundance and atmospheric lifetimes of N_2O and CCl_4 are, therefore, important to understanding stratospheric ozone recovery and climate change as well as the linkage between these issues; an accurate model representation of stratospheric ozone recovery is needed for climate projections. N_2O is included under the Kyoto Protocol, which has the goal of lowering the overall emission of greenhouse gases. The atmospheric abundance of CCl_4 has decreased steadily since the 1990s following the regulation of its production and consumption under the Montreal Protocol (2007).

N_2O and CCl_4 are removed in the stratosphere primarily via UV photolysis with some loss due to $O(^1D)$ reaction (e.g., Johnston et al., 1979; WMO, 1990). The overall atmospheric lifetimes of N_2O (115 years) and CCl_4 (~26 years) (WMO, 2007) also include loss due to soil uptake (Freney et al., 1978; Happell and Roche, 2003), thought to be a minor removal process, and for CCl_4 uptake by the ocean (Lovelock and Maggs, 1973; Yvon-Lewis and Butler, 2002). The atmospheric budget (sources and sinks) of CCl_4 is presently not well understood.

The atmospheric photolysis rate coefficient, J, is given by

$$J = \int J(\lambda) = \int \sigma(\lambda,\mathrm{T})\,\Phi(\lambda)\,F(\lambda,Z,\chi)\,d\lambda \qquad (1)$$

where $\sigma(\lambda,T)$ is the absorption cross section at wavelength λ and temperature T, $\Phi(\lambda)$ is the photolysis quantum yield and $F(\lambda,Z,\chi)$ represents the solar flux that is a function of wavelength, altitude (Z), and solar zenith angle (χ). An accurate determination of the atmospheric photolysis lifetime requires precise knowledge of the absorption cross sections of N_2O and CCl_4 as a function of wavelength and temperature. Figure 1 shows the room temperature UV absorption spectra of N_2O and CCl_4 currently recommended by Sander et al. (2006). The absorption spectrum of N_2O is continuous with diffuse band structure around a peak at ~182 nm with monotonically decreasing cross sections at wavelengths >195 nm. The CCl_4 UV absorption spectrum is also continuous with a broad peak near 176 nm and a weaker peak (shoulder) near 202 nm. The most critical wavelength region for the atmospheric photolysis of N_2O and CCl_4 is between 200 and 230 nm.

There are numerous studies of the room temperature UV absorption spectra of N_2O and CCl_4 currently available in the literature that are reviewed in Sander et al. (2006) and Atkinson et al. (2004). Fewer studies are available for the temperature dependence of the absorption spectra. The estimated uncertainty in the recommended absorption cross sections is, however, significant for the purposes of atmospheric model calculations. The JPL06-2 evaluation (Sander et al., 2006) reports 15% and 10% levels of uncertainty (1σ) for the combination of absorption cross sections and photolysis quantum yields of N_2O and CCl_4, respectively; the majority of the estimated uncertainty being most likely in the absorption cross section.

The overarching goal of this work was to reduce the overall uncertainty in the UV absorption cross sections of N_2O and CCl_4 that are used as input to atmospheric models. This was accomplished through a series of laboratory measurements and a critical review of previously published studies. An emphasis in this study was placed on the characterization of the temperature dependence of the absorption cross sections for which more limited data sets are currently available. Absorption cross sections were measured at the atomic lines 184.95, 202.548, 206.200, 213.857, and 228.8 nm between 210 and 350 K. Absorption cross sections at 184.95 nm are not critical for atmospheric photolysis rate calculations due to low solar fluxes at this wavelength, however, it is commonly used in laboratory studies and instrument calibration schemes. Our single wavelength measurements revealed systematic discrepancies in the CCl_4 UV absorption cross section data at reduced temperatures with the currently recommended values at the wavelengths most critical to atmospheric photolysis rate calculations. Therefore, absorption spectra of CCl_4 were also measured between 200 and 235 nm as a function of temperature using a diode array spectrometer to provide more complete wavelength coverage and enable the determination of a wavelength and temperature dependent absorption cross section parameterization for use in atmospheric models.

2. Experimental Details

Absorption cross sections were determined using the Beer-Lambert law

$$A(\lambda) = -\ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = \sigma(\lambda)\, L\, [X] \qquad (2)$$

where A is the measured absorbance at wavelength λ, $I(\lambda)$ and $I_0(\lambda)$ are the measured light intensity with and without the sample present in the absorption cell, respectively, L is the optical absorption pathlength, and [X] is the concentration of species X. The concentrations of N_2O and CCl_4 were determined using absolute pressure measurements of the pure compound or dilute mixtures of the compound in He and the ideal gas law. Absorption was measured for a range of concentrations and the cross section determined from a linear least-squares fit of A versus L[X] for each wavelength and temperature. Cross sections were measured at the atomic lines 184.95, 202.548, 206.200, 213.857, and 228.802 nm (hereafter referred to as 185, 203, 206, 214, and 229 nm, respectively) at seven temperatures (210 – 350 K). In addition, absorption spectra of CCl_4 were measured between 200 and 235 nm as a function of temperature (225 – 350 K) using a diode array spectrometer.

The experimental apparatus consisted of a light source, optical cut-off and band-pass filters, a jacketed cylindrical Pyrex absorption cell, and a detector. The light sources for the single wavelength measurements were atomic resonance lamps: a Hg Pen-Ray lamp for 185 nm, a Zn lamp for 203, 206, and 214 nm, and a Cd lamp for 229 nm. The Zn and Cd lamps had outputs stable to 0.1%. The Hg lamp was driven by a 20 kHz 50% duty cycle alternating current square wave to improve its output stability. Constant current was approximated by inserting a ballast resistor in series with the lamp. The Hg lamp intensity was stable to better than 0.5% over the course of an absorption measurement.

The lamp output passed through an optical band-pass filter and adjustable iris before passing through the absorption cell. Band-pass filters (FWHM ~10 nm) served to isolate the atomic transition of interest and reduce light intensity from unwanted lines within the absorption cell. In addition, neutral density filters between the light source and absorption cell were used to attenuate the light intensity, minimize photolysis of the sample in the absorption cell, and enable measurements to be made over a greater range of lamp intensities.

The temperature of the absorption cell was maintained by circulating a temperature-regulated fluid through the cell jacket. The absorption path length was completely within the temperature-regulated region of the absorption cell. Changing the window mount configuration was used to change the path length between 90.45 and 55.8 cm. Variations in the temperature of the room led to small but measureable differences in the measured N_2O absorption cross sections. Therefore, the temperature of the absorption cell was regulated above ambient temperature for our N_2O room temperature (298 K) measurements. This was not an issue for the CCl_4 measurements due to the weak temperature dependence of the absorption cross sections.

Thermocouples in direct contact with the gas at each end of the cell were used to measure the gas temperature. The temperature gradient along the length of the cell was ~0.5 K for temperatures ≥263 K and ~1 K for temperatures ≤243 K. The average temperature was used in the data analysis.

The light exiting the absorption cell was monitored using either a photodiode or a 0.25 m monochromator with a photomultiplier tube (PMT). The monochromator was tuned to the peak of the atomic lines and had a spectral resolution of ~0.3 nm. Signals were recorded continuously at a sampling rate of 1 KHz. Due to the lower stability of the Hg lamp output a dual solar-blind photodiode detector setup was used where one detector monitored the lamp output and the second detector monitored the signal through the absorption cell. The ratio of the signals was used in the data analysis. Measurements collected at 214 and 229 nm used both photodiode and monochromator detection systems whereas measurements at 203 and 206 nm used the monochromator setup.

A diode array spectrometer was used to measure the absorption spectrum of CCl_4 between 200 and 235 nm with a resolution of ~1 nm. The diode array spectrometer is described in more detail elsewhere (Papanastasiou et al., 2009). The wavelength scale was calibrated to within 0.2 nm using the emission lines from the Hg, Zn, and Cd lamps. A 30 W broadband D_2 lamp, intensity stability of better than ≤0.3%, was used for the light source.

Absorption signals and spectra were recorded by first flushing the absorption cell with a flow of He, evacuating the cell, and then recording an initial $I_0(\lambda)$. For the single wavelength measurements, approximately 100 one second averages were used to obtain $I_0(\lambda)$. The cell was then flushed several times with the sample, filled, and an $I(\lambda)$ recorded. Gas temperature equilibration was rapid as monitored by the thermocouple reading of the gas temperature. Finally, the cell was evacuated, flushed with He, and a final value of $I_0(\lambda)$ recorded. In all cases, the initial and final $I_0(\lambda)$ values agreed to better than 0.3%. At least six measurements were performed for each wavelength with sample concentrations in a range to yield absorption signals between 0.05 and 0.9.

2.1 Materials

Two different N_2O (UHP, 99.999%) samples were used without purification. N_2O was used either pure or in mixtures prepared off-line with a He (UHP, 99.99%) bath gas. Mixtures were prepared manometrically in darkened 12 L Pyrex bulbs. Different mixing ratios (~1 to 10%) were used during the course of the study to optimize the pressure and absorption measurements at the different wavelengths.

CCl_4 (99.9%, CHROMASOLV grade) was degassed using several freeze-pump-thaw cycles prior to use. Dilute gas mixtures of CCl_4 in He (~0.2 to 2%) were prepared manometrically in darkened 12 L Pyrex bulbs. A bulb mixture was stable over the period of the measurements, several days, as verified by replicate UV absorption measurements. Gas chromatography/mass spectrometry, GC/MS, and infrared absorption measurements of the CCl_4/He mixtures were used to evaluate the sample purity. The GC/MS analysis showed no detectable impurities. Infrared absorption measurements were performed using a Fourier transform spectrometer (FTIR) at 1 cm^{-1} resolution using a small volume multi-pass absorption cell (pathlength of 485 cm). The infrared spectrum of a CCl_4/He mixture that was used in the UV absorption measurements yielded a band strength (integrated between 725 and 825 cm^{-1}) of 6.7×10^{-17} cm^2 $molecule^{-1}$ cm^{-1} in good agreement, within 5%, with available literature values (Nemtchinov and Varanasi, 2003; Sharp et al., 2009). There were no impurities detected in the infrared spectrum.

The vapor pressures of N_2O and CCl_4 established some limitations for the concentration and range of absorbance available for the measurements, particularly for the reduced temperature measurements. For N_2O, this was only an issue in the measurements at 229 nm, where the cross section is small, limiting our measurements to temperatures $\geq$225 K. For CCl_4, the maximum CCl_4 pressure was kept well below its vapor pressure, which is ~ 0.3 Torr at 210 K, ~ 1 Torr at 225 K, and ~5 Torr at 243 K (Yaws, 1999).

Absolute pressures were measured using calibrated 100 and 1000 Torr capacitance manometers. Total pressures in the absorption cell ranged from 10 to 700 Torr during the course of the measurements.

3. Results and Discussions

The UV absorption cross section results for N_2O and CCl_4 over the temperature range 210 – 350 K are presented separately below. The temperatures included in this study were chosen to cover the range most relevant to the atmosphere and enable direct comparison with previously reported measurements. A comparison of the present work with existing literature values and the current

JPL06-2 recommendation (Sander et al., 2006) is presented and a new recommendation for CCl_4 is given. The uncertainty limits throughout the paper are at the 2σ (95% confidence level) unless stated otherwise.

3.1 Nitrous oxide (N_2O)

3.1.1 UV Absorption cross sections

The gas-phase UV absorption cross sections of N_2O measured at 185, 203, 206, 214, and 229 nm at 210, 225, 243, 263, 298, 324, and 350 K are summarized in Table 1. The precision of the measurements was high and a temperature dependence of the N_2O absorption cross section was observed at each wavelength. The absorption cross sections decreased with decreasing temperature at each wavelength with the change in cross section being greater at longer wavelengths. For example, decreases in the N_2O cross section of ~46% at 203 nm and ~70% at 214 nm were measured between 350 and 210 K.

The measured absorbance behaved linearly over a wide range of values, $0.05 \leq A \leq 0.95$. A summary of Beer-Lambert plots at each wavelength is given in the Supplementary Information. The data obtained at the various wavelengths were of similar quality. The consistency and reliability of the measurements was extensively tested by variation of the experimental measurement parameters such as sample mixing ratios, optical pathlengths, probe light intensity (optical filtering), and detection methods (photodiode and monochromator/PMT). The final absorption cross section values, Table 1, were obtained by including all data obtained at a specific wavelength and temperature in a weighted linear least-squares fit of the data using Eq. 2. The precision of the fits of the data to Eq. 2 was typically better than 1%. The final N_2O cross section values obtained at each wavelength are shown in Fig. 2.

The N_2O absorption cross section at 185 nm, which is commonly used in laboratory studies and instrument calibration, is given by the expression

$$\sigma_{184.95\ \mathrm{nm}}(\mathrm{T}) = 1.0033 \times 10^{-19} + 6.1561 \times 10^{-23} \times \mathrm{T} + 2.6583 \times 10^{-25} \times \mathrm{T}^2 \quad (3)$$

with $\sigma_{185\ \mathrm{nm}}(298\ \mathrm{K}) = 1.4 \times 10^{-19}\ \mathrm{cm}^2\ \mathrm{molecule}^{-1}$ and an absolute uncertainty of 2%.

3.1.2 Error Analysis

The measurement precision and estimated absolute uncertainties are given in Table 1. The uncertainties for the different wavelengths are comparable, although there is a slight increase in uncertainty at the lower temperatures. The accuracy of the present work enables a critical evaluation of previous studies and an overall reduction of the estimated uncertainty in the cross section values as discussed in Section 3.1.3.

Uncertainties associated with temperature, pressure, optical pathlength, sample mixing ratio, and the absorbance measurements contribute to the overall uncertainty of the absorption cross sections. The uncertainty in temperature was 0.5 K for temperatures ≥263 K and ~1 K at lower temperatures. The uncertainty in the measured cell pressure and calibration of the pressure gauges is estimated to be ~0.2%. The optical pathlength and sample mixing ratios have uncertainties of <0.5%. The random noise in the absorbance measurements and drift in the light source output, I_0, were ≤0.5%. Typically, the uncertainty in the measurements was ≤0.001 absorbance units yielding a measurement precision of ~0.5% for temperatures between 298 and 350 K and ~1% at reduced temperatures.

Variations in experimental parameters such as sample mixing ratio and optical pathlength yielded results that agreed to within 0.5%. In a few cases, the same sample mixture was used for absorption measurements at two different wavelengths and the self-consistency of the cross section values obtained was excellent. Variations of the optical setup including different combinations of optical filters and lamp intensity yielded negligibly different absorption cross sections, values agreed to within 0.1%. In addition, the use of the two detection methods, photodiode and monochromator/PMT setups, at 214 and 229 nm yielded cross sections that agreed to within 0.5%. The uncertainties quoted in Table 1 were obtained from the root mean square of the measurement precision and estimated systematic uncertainties given above.

3.1.3 Comparison with Previous Studies

There are numerous measurements of N_2O UV absorption cross sections reported in the literature (Bates and Hays, 1967; Cantrell et al., 1997; Creasey et al., 2000; Hubrich and Stuhl, 1980; Mérienne et al., 1990; Selwyn et al., 1977; Thompson et al., 1963; von Hessberg et al., 2004; Yoshino et al., 1984; Zelikoff et al., 1953). The majority of the previous studies were performed at room temperature, nominally 298 K. Few of these studies report cross sections at the specific wavelengths (atomic lines) used in our study. Therefore, for the purpose of comparison only, the data from the previous studies were interpolated to the wavelengths of this work. For the Merienne et al. (1990) and Selwyn et al. (1977) studies, the reported cross section parameterizations were used to obtain cross section values at the appropriate wavelengths. Uncertainty estimates are reported in a limited number of the earlier studies. For clarity, the uncertainties from only a few of the most relevant studies are included in Fig. 2.

At 185 nm the level of agreement among the various studies is ~4% as shown in Fig. 2. The data from Zelikoff et al. (1953), Romand and Mayence (1949), Bates and Hayes (1967), and Thompson et al. (1963) have not been included as their cross sections are significantly different from the other works and are most likely in error. The data from Johnston and Selwyn (1975) was superseded by Selwyn and Johnston (1977) and is therefore not included. At room temperature, our 185 nm results are in excellent agreement with the values reported by Creasey et al. (2000) and slightly greater, but within our estimated uncertainty, than the values reported by Selwyn et al. (1977) and Cantrell et al. (1997). Note, that the Selwyn et al. parameterization is currently recommended in JPL06-2 (Sander et al., 2006). The values reported by Yoshino et al. (1984) and Hubrich and Stuhl (1980) are less than our value and fall outside our estimated uncertainty.

The absorption cross section of N_2O at 185 nm decreases by ~14% between 350 and 210 K. The studies of Selwyn et al. (1977) (194, 225, 243, 263, and 302 K), Hubrich and Stuhl (1980) (208 and 298 K), Cantrell et al. (1997) (298 and 353 K), and von Hessberg et al. (2004) (233 and 283 K) have reported cross section values at the temperatures given in parenthesis. Our work is in good agreement with the values reported by Selywn et al. (1977) and Cantrell et al. (1997). The difference in the cross sections between Hubrich and Stuhl (1980) and von Hessberg et al. (2004) and our work is in the absolute value of the cross section rather than its temperature dependence.

At 203, 206, 214, and 229 nm the agreement between the room temperature cross sections from the present work and previously published studies is very good, agreement to within 2.5%. The agreement of our cross section data with those from Mérienne et al. (1990) and Selwyn et al. (1977) is ~2%. The values from Hubrich and Stuhl (1980) show larger scatter at the various wavelengths with the largest deviations at 203 and 206 nm but still they only differ by 4 and 3%, respectively, from our work.

Selwyn et al. (1977) (194 – 302 K), Mérienne et al. (1990) (220 – 296 K), von Hessberg et al. (2004) (233 and 283 K), and Hubrich and Stuhl (1980) (208 and 298 K) have reported temperature dependent cross section values at longer wavelengths. Our results at 203 and 206 nm are smaller than the values reported by Selwyn et al. (1977) and Mérienne et al. (1990) by 3 to 4%. At 214 and 229 nm, our cross section values are ~3% higher than those reported by Selwyn et al. (1977) and ~2% lower than reported by Mérienne et al. (1990). Our estimated absolute cross section uncertainty is ~2% which is shown in Fig. 2. The estimated uncertainties reported by Selwyn et al. (1977) and Mérienne et al. (1990) are also ~2%.

In summary, the high precision and accuracy of the present cross section measurements are consistent, within our estimated uncertainty limits, with the current JPL06-2 (Sander et al., 2006) recommended N_2O cross section parameterization for use in atmospheric modeling, which was based on the study of Selwyn et al. (1977). On the basis of the present work and a critical evaluation of literature data, we estimate the overall uncertainty in the N_2O absorption cross sections most relevant to atmospheric photolysis to be 4%.

3.2 Carbon tetrachloride (CCl_4)

3.2.1 UV Absorption cross sections

Single wavelength UV absorption cross sections of CCl_4 were measured at 210, 225, 243, 263, 298, 324, and 350 K. The results are summarized in Table 2 and shown in Fig. 3. The precision of the measurements was high and a temperature dependence of the CCl_4 absorption cross section was observed at all wavelengths. The CCl_4 absorption cross section decreased with decreasing temperature at 185, 213, and 229 nm but showed an increase at 203 nm and a nearly temperature independent behavior at 206 nm. The different behavior of the cross section temperature dependence is most likely a result of the diffuse structure in the CCl_4 UV absorption spectrum, Fig. 1, which has a weak peak (shoulder) near 202 nm.

Over the range of concentrations and temperatures (210 – 350 K) included in this study, the absorbance data were well represented by the Beer-Lambert law, Eq. 2. A summary of Beer-Lambert plots at each wavelength is given in the Supplementary Information. Excellent agreement among the data was obtained for all variations of the experimental parameters including using different sample mixing ratios, optical path length, probe light intensity (optical filtering), and measurement detection methods. The Beer-Lambert plots for all the wavelengths were of comparable quality. The precision of the fits of the data to Eq. 2 was typically better than 1%. The cross section uncertainty increased slightly at the lower temperatures, primarily due to limitations in the range of measurements imposed by the vapor pressure of CCl_4. The final cross section results were determined by including all data obtained at a specific wavelength and temperature in a weighted linear least-squares fit using Eq. 2.

The CCl_4 absorption spectrum was measured over the wavelength range 200 – 235 nm at 225, 243, 263, 295, 324, and 350 K. The CCl_4 spectra reported here are an average of at least 4 individual spectra recorded at different CCl_4 concentrations. The CCl_4 absorbance scaled linearly with concentration at all wavelengths and temperatures investigated in accordance with the Beer-Lambert law. The use of samples with different mixing ratios produced identical results within the precision of the measurement. Photolysis of the sample was found to be negligible, <0.5%, during the course of an absorption measurement.

The shape and temperature dependence of the CCl_4 absorption spectra in the 200 – 235 nm wavelength region is consistent with the behavior observed in the single wavelength measurements. The diode array and single wavelength cross section results agreed to within 3% at 203 and 206 nm. The diode array spectra were scaled to the more accurate single wavelength cross section values. There is a small but systematic increase in the CCl_4 absorption cross section around 202 nm with decreasing temperature. At wavelengths >210 nm, the absorption cross section decreases with decreasing temperature, e.g. ~30% decrease at 230 nm between 295 and 225 K.

3.2.2 Error Analysis

The uncertainties associated with the measurements and experimental parameters discussed in Section 3.1.2 for N_2O also apply to the measurements with CCl_4. For CCl_4, the precision of the cross section measurements was between 0.2 and 0.5% for temperatures ≥295 K. At lower temperatures, the precision of the measurements was ~1%. The cross sections obtained using samples with different mixing ratios agreed to within the precision of the measurement, ~0.5%. Changing the optical pathlength yielded cross sections that agreed to within 0.4% at all temperatures suggesting that condensation in the absorption cell or on the cell windows did not affect the measurement. The estimated absolute uncertainty of our measurements was ~2% at temperatures ≥295 K, see Table 2. The uncertainty at lower temperatures was higher with a maximum uncertainty of ~6% at 229 nm and 225 K.

For the diode array spectrum measurements the overall stability of the optical system was a key determinant of the measurement precision. The precision in the measured absorbance values was better than 1% between 200 – 220 nm but increased to ~9% at 235 nm due to the weak absorption signals. At wavelengths greater than 220 nm, the uncertainty in the measurement increased with decreasing temperature due to the weaker CCl_4 absorption.

3.2.3 Comparison with Previous Studies

In general, the precision and accuracy of the present measurements was better than obtained in previous CCl_4 cross section studies. A comparison of the present results at each wavelength with the previously reported values (Burton et al., 1994; Causley and Russell, 1977; Gillotay and Simon, 1990; Gordus and Bernstein, 1954; Ho, 1998; Hubrich and Stuhl, 1980; Ibuki et al., 1986; Prahlad and Kumar, 1995; Rowland and Molina, 1975; Roxlo and Mandl, 1980; Seccombe et al., 1999; Simon et al., 1988; Vanlaethem-Meuree et al., 1978) is shown in Fig. 3. First, we will discuss the room temperature, nominally 298 K, cross section data. At 185 nm, the data from Causley and Russell (1977), Ho (1998), Roxlo and Mandl (1980), and Seccombe et al. (1999) are significantly different from the other data sets and are thought to be in error. Our measurement is in excellent agreement with the current JPL06-2 recommended value, to within 0.3%, which is based on an average of data from Hubrich and Stuhl (1980) and Simon et al. (1988). The agreement with the individual studies is, however, poor with a ~20% spread in cross section values. For 203 and 206 nm the works of Rowland and Molina (1975), Vanlaethem et al. (1978), Hubrich and Stuhl (1980), Simon et al. (1988), and Prahlad and Kumar (1995) fall within our estimated uncertainty. At 214 nm, there is excellent agreement between our measurement and the JPL06-2 recommendation, within 0.5%, and good agreement between our data and that of Prahlad and Kumar (1995) and Simon et al. (1988), within 2%. Our measurement at 229 nm is ~5% smaller than the JPL recommended value. Overall, there is good agreement between the present room temperature measurements and those from Prahlad and Kumar (1995) and Simon et al. (1988).

There are two previous studies that have examined the temperature dependence of the CCl_4 UV absorption spectrum. Simon et al. (1988) and Prahlad and Kumar (1995) report temperature independent cross sections at wavelengths <204 nm and <206.5 nm, respectively, and a systematic decrease in cross section with decreasing temperature at longer wavelengths. Unlike the works of Prahlad and Kumar (1995) and Simon et al. (1988), both our single wavelength and diode array measurements resolve a weak cross section temperature dependence for wavelengths <204 nm. The inability to resolve the temperature dependent behavior in the earlier studies leads to an increased uncertainty in their cross section parameterizations at short wavelengths.

At wavelengths >206 nm, we observed a decrease in absorption cross section with decreasing temperature, see Figs. 3 and 4, similar to that of Prahlad and Kumar (1995) and Simon et al. (1988), although the magnitude of the dependence was statistically different. The largest difference between the data sets is at 214 nm where our measurements are approximately 10% larger at 225 K than the data from Simon et al. (1988) and Prahlad and Kumar (1995). The reason for the differences is unknown but may be a result of the improved precision of the present measurements. Measurements made in the previous studies at CCl_4 pressures near the compound's vapor pressure (1999), especially at reduced temperatures, may have also influenced the earlier measurements. For example, Simon et al. (1988) report using a maximum CCl_4 pressure of 4 Torr at 225 K. In our measurements at 225 K the maximum CCl_4 pressure used was ~1 Torr.

The systematic differences found in the CCl_4 absorption cross section temperature dependence led us to develop a revised parameterization of the UV absorption cross sections that is based on our single wavelength and diode array spectrum measurements. For consistency, the same polynomial parameterization used by Simon et al. (1988)

$$\log_{10}(\sigma(\lambda,\mathrm{T})) = \sum_i \mathrm{A}_i\lambda^i + (\mathrm{T} - 273)\sum_i \mathrm{B}_i\lambda^i \qquad (4)$$

was used here where the A_i and B_i parameters were determined from a least squares fit of our experimental data. Measurements at temperatures greater than room temperature are not directly relevant to the atmosphere but increase the reliability of the cross section parameterizations. The A_i and B_i values are listed in Table 3. It should be noted that in the fitting procedure, the single wavelength results were included and weighed more heavily than the diode array measurements since the former were more certain, especially at wavelengths greater than 220 nm. The CCl_4 absorption cross sections calculated using the parameters in Table 3 are shown in Fig. 4. The cross sections obtained from the parameterization agree to within 3% with our experimental values. The parameters in Table 3 can be used to calculate the cross sections over the wavelength range 200 – 235 nm and temperatures between 210 and 350 K.

3.3 Atmospheric Implications

On the basis of the present work no revision to the currently recommended N_2O cross sections are called for. However, the combination of the precise measurements presented here and a critical evaluation of results from previous studies leads to an estimated 2σ uncertainty in the cross section values between 185 – 230 nm of 4%.

The work presented here suggests that the current recommended cross sections of CCl_4 should be revised. We now examine the atmospheric impacts of our new CCl_4 UV absorption cross sections and their temperature dependence using the NASA/Goddard 2D model (Fleming et al., 2007; Newman et al., 2009). This model has fully interactive chemistry, dynamics, and radiation, and has frequently been used in scientific studies and assessments of the middle atmosphere (e.g., WMO, 2007). The results presented here are from simulations for 1950 – 2100 utilizing specified time dependent surface mixing ratio boundary conditions from scenario A1 of WMO (2007) for ozone depleting substances, and IPCC SRES scenario A1B for the greenhouse gases (Nakicenovic et al., 2000). We will show model results using CCl_4 cross sections from this work compared with those from JPL06-2.

Figures 5 and 6 show the latitude-height distributions of CCl_4 and related quantities for year 2000 annually averaged conditions. The CCl_4 mixing ratio distribution (Fig. 5, top) reflects emissions at the surface from various industrial uses (WMO, 2007), and the very large photochemical loss in the lower stratosphere. The modeled loss rate due to UV photolysis is shown in Fig. 6 (top), using the absorption cross sections obtained in this work. Maximum loss rates of 60 – 80 ppt/year occur in the tropical lower stratosphere, and quickly taper off to much smaller values (<1 pptv/year) away from this region. This is significantly larger than the loss rate due to reaction with $O(^1D)$ (Fig. 6, middle), which has a maximum of 0.5 – 0.7 ppt/year. The photolysis loss is as much as 100 – 200 times greater than the $O(^1D)$ loss in the tropical lower stratosphere (Fig. 6, bottom). This ratio is generally consistent to that reported previously, showing that photolysis is the dominant atmospheric loss process for CCl_4.

Figure 5 (middle) shows the ratio of the modeled CCl_4 photolysis rate using the cross sections obtained in this work to that obtained using the JPL06-2 cross sections. The new cross sections result in a 5 – 7% increase in the CCl_4 photolysis rate throughout most of the stratosphere. This difference decreases with decreasing height into the troposphere, and is ~0.5 – 1% at the lowest model level (942 hPa, 0.5 km). The impact of the new CCl_4 cross sections on the CCl_4 mixing ratio depends on both the mixing ratio distribution and the photolysis frequency, both of which vary strongly with altitude. Compared with JPL06-2, the new cross sections result in smaller CCl_4 mixing ratios throughout the lower stratosphere (Fig. 5, bottom). The maximum difference of -1.9 ppt (~5%) occurs in the tropics at 20 – 25 km, coincident with the largest photolysis loss rate (Fig. 6, top). The corresponding increase in total inorganic chlorine (Cl_y) is four times the magnitude of the values in Figure 5 (bottom), with a maximum of +7.5 ppt in the tropical lower stratosphere. This increase is <1% of the background Cl_y, so that the resulting decreases in profile and total column ozone are very small: <0.1% and <0.05 DU, respectively. As reflected in Figure 5 (bottom), there is no change in Cl_y (or ozone) above ~30 km since the larger cross sections of the present work are just converting CCl_4 to Cl_y at a lower altitude compared with the JPL06-2 cross sections.

Changes in these modeled loss rates will impact the computed stratospheric lifetime of CCl_4. The lifetime is computed as the atmospheric burden (total number of molecules) divided by the loss rate, both of which are vertically integrated and globally/annually averaged. The lifetime is controlled mainly by the loss rate and the rate of transport of a species through the stratospheric loss region. The lifetime is important in determining the length of time over which a molecule of CCl_4 will have a significant impact on ozone depletion or global warming, and in deriving surface mixing ratio boundary conditions from emissions estimates for use in atmospheric models (e.g., Kaye et al., 1994).

Figure 7 shows the time series for 1950 – 2100 of our model-computed CCl_4 stratospheric lifetime using the cross sections obtained in this work (red curve) and from the JPL06-2 recommendations (black curve). These simulations use specified mixing ratio boundary conditions with no explicitly imposed soil or ocean loss. Therefore, the present day stratospheric lifetime of 50 – 52 years in Fig. 7 is significantly older than the value of 26 years cited in WMO (2007) which accounts for the surface loss processes of CCl_4. We note also that the values in Fig. 7 are older than the stratospheric lifetime range of 28 – 46 years cited in WMO (2003; 2007). This range was based, in part, on older models which had circulations that were too fast, as seen in comparisons of model age-of-air simulations with observations (Hall et al., 1999). Models with faster circulations and younger age-of-air transport chemicals more rapidly through the stratospheric loss region, and result in younger lifetimes for ODSs such as CFC-11 and CFC-12 (Douglass et al., 2008). Since our current model age-of-air compares well with observations, the 50 – 52 year stratospheric lifetime for CCl_4 for present day conditions appears to be reasonable.

Figure 7 shows a general decrease in lifetime from ~60 years in 1950 to ~48 years by 2100. As discussed in Douglass et al. (2008), this is an expected result of the acceleration of the Brewer-Dobson circulation throughout the 21st century due to climate change, which is a robust feature of most chemistry-climate models (e.g., Eyring et al. (2007)). The circulation enhancement and decrease in lifetime is somewhat larger for 1950-2000 due to a combination of ozone depletion and climate change. Figure 7 shows that the larger absorption cross sections and increased CCl_4 photolysis loss rate obtained in this work (compared with JPL06-2) yield slightly younger lifetimes throughout the time period. The increase in stratospheric photolysis loss of 5 – 7% (Fig. 5, middle) leads to lifetimes that are younger by 1 – 1.5 years (~2%) for 1950 – 2100 in Fig. 7. However, this change is significantly smaller than the range of uncertainty in the CCl_4 lifetime due to soil loss (50 – 418 years) and ocean loss (82 – 191 years) processes cited in WMO (2007).

4. Conclusions

The UV absorption cross sections of N_2O and CCl_4 have been measured at 185, 203, 206, 214, and 229 nm between 210 and 350 K. This work aimed to reduce the overall uncertainties in the atmospheric photolysis lifetimes of these compounds through reduction in the uncertainties in the absorption cross section values. In the case of N_2O, our cross section measurements were in excellent agreement with the earlier works of Selwyn et al. (1977) and Mérienne et al. (1990) at all wavelengths and temperatures investigated in this work. Based on the high accuracy and precision of our measurements, and the agreement with earlier studies we estimate the 2σ uncertainty in the cross section data to be 4% or less between 185 and 228 nm. In the stratosphere N_2O is removed by UV photolysis and reaction with $O(^1D)$. Therefore, a reduction of the N_2O photolysis lifetime uncertainty directly impacts the uncertainty in model calculated stratospheric NO_x production from the reaction of $O(^1D)$ with N_2O. For CCl_4, a systematically weaker temperature dependence of the absorption cross sections in the most critical wavelength region for atmospheric photolysis than currently recommended in JPL06-2 (Sander, 2006) was found in this study. A new recommendation for the parameterization of CCl_4 absorption cross sections, including temperature dependence, between 200 – 235 nm is given here. We estimate the uncertainty in the CCl_4 absorption cross sections in this region to be 4%. Model calculations show that the new cross sections result in a 5 – 7% increase in the photolysis loss of CCl_4 throughout the lower stratosphere. The resulting stratospheric lifetime of CCl_4 decreases slightly, from 51 to 50 years (~2%), for present day conditions. The corresponding changes in modeled inorganic chlorine and ozone in the stratosphere are quite small. The reduced uncertainties in the N_2O and CCl_4 absorption cross section data, and in photolysis lifetimes, will provide for improved model calculations of ozone recovery.

Acknowledgements: This work was supported in part by NOAA's Climate Goal and in part by NASA's Atmospheric Composition Program. We thank S. Ciciora for technical assistance, M. Baasandorj for assistance with the FTIR measurements, J. Gilman for the GC/MS sample analyses, and A.R. Ravishankara for helpful discussions.

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Table 1. UV Absorption Cross Sections for N_2O (10^{-20} cm^2 molecule^{-1})

Wavelength (nm)	Cross Section (10^{-20} cm^2 molecule^{-1})						
	210 K	**225 K**	**243 K**	**263 K**	**298 K**	**324 K**	**350**
184.95	13.06 ± 0.03[a]	13.29 ± 0.02	13.43 ± 0.04	13.72 ± 0.03	14.29 ± 0.06	14.74 ± 0.01	15.21 ± 0.02
	(± 0.27)[b]	(± 0.28)	(± 0.28)	(± 0.28)	(± 0.29)	(± 0.31)	(± 0.32)
202.548	1.903 ± 0.007	2.017 ± 0.008	2.161 ± 0.008	2.36 ± 0.01	2.753 ± 0.009	3.12 ± 0.01	3.540 ± 0.008
	(± 0.043)	(± 0.072)	(± 0.081)	(± 0.082)	(± 0.092)	(± 0.095)	(± 0.11)
206.200	0.958 ± 0.005	1.027 ± 0.001	1.133 ± 0.005	1.258 ± 0.004	1.541 ± 0.007	1.802 ± 0.006	2.090 ± 0.007
	(± 0.028)	(± 0.029)	(± 0.032)	(± 0.037)	(± 0.035)	(± 0.041)	(± 0.047)
213.857	0.181 ± 0.001	0.199 ± 0.001	0.227 ± 0.001	0.269 ± 0.002	0.364 ± 0.001	0.461 ± 0.003	0.576 ± 0.002
	(± 0.0041)	(± 0.0045)	(± 0.0051)	(± 0.0061)	(± 0.0053)	(± 0.0067)	(± 0.0084)
228.802	–	0.00478 ± 0.00007	0.00592 ± 0.00003	0.00773± 0.00007	0.01286 ± 0.00004	0.01920 ± 0.00007	0.02812 ± 0.00008
	–	(± 0.00032)	(± 0.00035)	(± 0.00017)	(± 0.00038)	(± 0.00052)	(± 0.00068)

[a] Precision of the measurements at the 2σ (95% confidence) level.

[b] Absolute uncertainty of the measurements at the 2σ level are given in parenthesis.

Table 2. UV absorption cross sections for CCl_4 obtained in this work

Wavelength (nm)	Cross Section (10^{-20} cm^2 molecule^{-1})						
	210 K	**225 K**	**243 K**	**263 K**	**295 K**	**324 K**	**350 K**
184.95	355 ± 1[a]	377 ± 1	395 ± 1	405 ± 0.6	418 ± 0.8	430 ± 1	440 ± 1
	(± 9.6)[b]	(± 10.2)	(± 10.6)	(± 10.9)	(± 8.5)	(± 8.8)	(± 9.1)
202.548	68.9 ± 0.5	67.5 ± 0.3	67.4 ± 0.3	66.2 ± 0.2	64.9 ± 0.1	63.8 ± 0.2	62.5 ± 0.3
	(± 7.1)	(± 2.5)	(± 2.4)	(± 2.4)	(± 1.6)	(± 2.2)	(± 1.8)
206.200	57.3 ± 0.5	58.8 ± 0.6	59.3 ± 0.2	59.1 ± 0.1	58.7 ± 0.2	57.8 ± 0.2	57.3 ± 0.4
	(± 3.3)	(± 1.8)	(± 1.9)	(± 1.9)	(± 1.6)	(± 1.5)	(± 1.6)
213.857	31.1 ± 0.2	32.0 ± 0.1	33.0 ± 0.1	33.6 ± 0.1	35.2 ± 0.1	35.7 ± 0.1	36.2 ± 0.1
	(± 1.8)	(± 0.89)	(± 0.91)	(±0.95)	(± 0.72)	(± 0.86)	(± 0.87)
228.802	–	3.39± 0.04	3.67 ± 0.02	4.10 ± 0.01	4.85 ± 0.01	5.66 ± 0.01	6.44 ± 0.02
	–	(± 0.21)	(± 0.12)	(± 0.12)	(± 0.11)	(± 0.13)	(± 0.15)

[a] Precision of the measurements at the 2σ (95% confidence) level.

[b] Absolute uncertainty of the measurements at the 2σ level are given in parenthesis.

Table 3. CCl_4 absorption cross section parameterization for 200 – 235 nm and 210 – 350 K obtained in this work

$$\log_{10}(\sigma(\lambda,\mathrm{T})) = \sum_i A_i\lambda^i + (\mathrm{T} - 273)\sum_i B_i\lambda^i$$

i	A_i	B_i
0	1112.736208	-1.116511649
1	-22.02146808	0.02447268904
2	0.1596666745	-0.0001954842393
3	-0.0005104078676	6.775547148e-07
4	6.062440506e-07	-8.621070147e-10

Figure Captions

Figure 1: The JPL06-2 (Sander et al., 2006) recommended UV absorption cross section spectra of N_2O and CCl_4 at 298 K. The shaded area highlights the wavelength region most important for atmospheric photolysis. The vertical lines correspond to the wavelengths of the atomic lines used in this work.

Figure 2: Temperature dependent N_2O absorption cross sections obtained in this work (●). The shaded region represents the estimated absolute 2σ (95% confidence level) uncertainty from our work including estimated systematic errors. Included for comparison are results from previous studies as indicated in the legend. The data from Merienne et al. (1990) and Selwyn et al. (1977) are plotted using the cross section and temperature dependence parameterizations reported in their work. Data from Zelikoff et al. (1953) are not included due to their large deviation from the other studies. The results from Selwyn et al. (1977) supercedes the results from Johnston and Selwyn (1975), which are not shown.

Figure 3: Temperature dependent CCl_4 absorption cross sections obtained in this work (●). The shaded region represents the estimated absolute 2σ (95% confidence level) uncertainty from our work including estimated systematic errors. Included for comparison are results from previous studies as indicated in the legend. The data from Simon et al. (1988), the data set currently recommended by JPL06-2 (Sander et al., 2006) for use in atmospheric modeling, are plotted using the cross section and temperature dependence parameterization reported in their work. Data from Causley and Russell (1977), Seccombe et al. (1999), Ho (1998), and Roxlo and Mandl (1980) are not included due to the large deviation from the other studies.

Figure 4: Absorption spectra of CCl_4 obtained using a diode array spectrometer (solid lines) at temperatures given in the legend. The shaded region represents the estimated absolute 2σ (95% confidence level) uncertainty at 295 K including estimated systematic errors. Also included for comparison are the absorption cross sections obtained from the single wavelength measurements in this work (●). The deviation of the measured spectra from the cross section parameterization given in Table 3 is given in the lower frame.

Figure 5: (Top) Modeled distribution of CCl_4 mixing ratio (ppt); (middle) ratio of the photolysis loss of CCl_4 using UV absorption cross sections obtained in this work to that using absorption cross sections from JPL06-2 (Sander et al., 2006); (bottom) modeled CCl_4 mixing ratio difference (ppt) using absorption cross sections obtained in this work and that using absorption cross sections from JPL06-2. All values are annual averages for year 2000. The contours plotted in the bottom panel are -.1, -,4, -.8, -1.2, and -1.6 ppt.

Figure 6: (Top) Modeled photochemical loss rate of CCl_4 due to photolysis (in parts per trillion per year) using the UV absorption cross sections obtained in this work. Also shown are the CCl_4 loss rate due to reaction with $O(^1D)$ (middle), and the ratio of the photolysis loss to the $O(^1D)$

loss (bottom). All values are annual averages for year 2000. The contours plotted in the top panel are 1, 3, 10, 20, 40, 60, and 80 ppt/year.

Figure 7: Time series for 1950 – 2100 of the modeled photochemical lifetime of CCl_4 (years) using the UV absorption cross sections obtained in this work (red), and absorption cross sections from JPL06-2 (Sander et al., 2006) (black). Note that the calculation of lifetime does not include any surface land or ocean loss of CCl_4.