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# Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: [www.elsevier.com/locate/jqsrt](http://www.elsevier.com/locate/jqsrt)

## Notes

# Revised ultraviolet absorption cross sections of H<sub>2</sub>CO for the HITRAN database

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## ARTICLE INFO

### Article history:

Received 14 January 2011

Received in revised form

1 February 2011

Accepted 3 February 2011

Available online 18 February 2011

### Keywords:

Ultraviolet spectroscopy

Atmospheric spectroscopy

Atmospheric measurements

## ABSTRACT

A revised set of temperature-dependent absorption cross sections for ultraviolet (UV) measurements of formaldehyde (H<sub>2</sub>CO) has been derived from two existing sets of laboratory cross sections, one using a Fourier transform spectrometer (FTS), and one using a grating instrument. This is conducted to satisfy the recommendation of the HITRAN Advisory Committee to provide a dataset with the spectral resolution and wavelength calibration of Fourier transform spectrometer measurements with the better intensity calibration that the grating measurements obtained. The re-scaled cross sections are now in the HITRAN database, and are recommended for use in atmospheric measurements and modeling, including photolysis calculations.

Published by Elsevier Ltd.

## 1. Introduction

Formaldehyde serves as the major proxy for measurements of volatile organic compounds (VOCs) using UV spectroscopy. UV measurement of H<sub>2</sub>CO from satellites was first investigated for the Global Ozone Monitoring Experiment (GOME) and the SCanning Imaging Absorption spectroMeter for Atmospheric ChartographY (SCIAMACHY) instruments [1]. It was first demonstrated for GOME [2,3], and is now measured using the GOME, SCIAMACHY, and Ozone Monitoring Instrument (OMI) instruments (cf. Chance [4]). H<sub>2</sub>CO is additionally measured in ground-based spectroscopy to investigate lower atmospheric pollution, and in laboratory studies related to tropospheric chemistry (cf. Gratien et al. [5]). Measurement accuracy is directly limited by the accuracy of the reference absorption cross sections. Ideally, these would be measured: (1) At a number of temperatures, spanning the appropriate atmospheric range; (2) using an FTS at sufficiently high spectral resolution to provide a reference

for the various atmospheric spectrometers (usually operating at medium spectral resolution); (3) in units of wavenumbers (cm<sup>-1</sup>), which directly give vacuum wavelengths (since most atmospheric measurements are made using dispersive instruments); and (4) at absolute accuracy of several percent or better.

There are several excellent candidate reference absorption cross sections of H<sub>2</sub>CO for use in atmospheric measurements. However, none of them meet all of the criteria above. Therefore, a composite temperature-dependent set of cross sections is derived here from two selected data sets, for use in quantitative atmospheric measurements until improved FTS laboratory measurements have been performed.

## 2. Current data sets

Cantrell et al. [6] (hereafter CC) performed FTS measurements from 25,920 to 33,299 at 1.00 cm<sup>-1</sup> (apodized) resolution, corresponding to ~0.011 nm resolution, which is sufficient for atmospheric measurements using dispersive instruments. Measurements were made at 223, 233, 243, 253, 263, 273, 283, and 293 K. Cross sections with linear temperature dependence are provided on a grid of ~0.5 cm<sup>-1</sup>. Cross section uncertainties are estimated to be < 10%.

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Previous UV cross sections for formaldehyde in the HITRAN database [7,8] are calculated using this linear temperature dependence at three temperatures (280, 290, and 300 K) and then cubic-spline interpolated to an even wavenumber increment of  $0.244 \text{ cm}^{-1}$ , corresponding to more than twice the sampling of the original data.

Meller and Moortgat [9] (hereafter MM) performed measurements with a grating spectrometer at 0.021–0.028 (average 0.025) nm spectral resolution. 298 K measurements were made from 225 to 375 nm. Additional measurements were made at 223, 253, and 323 K, to give temperature dependence from 250 to 356 nm, covering most of the range of common atmospheric fitting windows [2,3,11]. Cross sections with linear temperature dependence are given at 0.04 nm resolution, with air wavelengths. Uncertainties are reported as 5%, but at least  $3 \times 10^{-22} \text{ cm}^2$ . The authors note that the CC cross sections are  $\sim 10\%$  lower than theirs. The original MM absorption cross sections are available at [www.atmosphere.mpg.de/spectral-atlas-mainz](http://www.atmosphere.mpg.de/spectral-atlas-mainz) [10].

Gratien et al. [5] performed simultaneous measurements in the ultraviolet and infrared, in order to determine the overall quality of current reference spectra. While they did not measure the UV comprehensively and provide a new set of reference cross sections, they were able to demonstrate that the CC cross sections are biased systematically low, meaning that atmospheric measurements analyzed using them will obtain systematically high values of  $\text{H}_2\text{CO}$ .

### 3. Revised cross sections

The HITRAN Advisory Committee recommended in its 2010 meeting that the CC cross sections be re-scaled in intensity to the MM cross sections, to become the new HITRAN database cross sections for  $\text{H}_2\text{CO}$ . This provides a dataset with the advantages of both the CC and the MM measurements, in that the FTS resolution and wavelength calibration is maintained, while the better intensity calibration is retained.

The re-scaling is accomplished by performing non-linear least-squares fitting of the 298 K CC cross sections to the 298 K MM cross sections over the wavelength range 301.01–360.00 nm. The MM cross sections are first converted to vacuum wavelengths using the Edlén formula [12]. The fitting includes intensity, intensity offset, Gaussian width (convolving CC to the coarser resolution of MM) and a residual spectral shift. The fitted parameters, with  $1\sigma$  fitting uncertainties are as follows: A scaling factor of 1.1096(15); an offset of  $9.71(3.67) \times 10^{-23} \text{ cm}^2$ ; a Gaussian width (half-width at  $1/e$  intensity) of 0.02369(16) nm; and a spectral shift of 0.00427(13) nm. The fitted shift between CC and MM is almost consistent with the stated MM wavelength accuracy of 0.003 nm [9]. An additional

fitting test was performed over 337.01–356.00 nm (the atmospheric fitting window in [3]). The difference in scaling was 3% (a 1.078 scaling factor).

Ultraviolet cross sections, including the linear temperature dependence are recalculated over the full range supplied by CC using the scaling (1.1096) and offset ( $9.71 \times 10^{-23} \text{ cm}^2$ ) determined here. Uncertainties are estimated as in [9] as the larger of 5% and  $3 \times 10^{-22} \text{ cm}^2$ . The re-scaled cross sections are now in the HITRAN database, sampled as before, and are recommended for use in atmospheric measurements and modeling, including photolysis calculations. Caution should be used when the cross sections are extrapolated in temperature significantly beyond the range of laboratory measurements.

### Acknowledgment

This work was supported by NASA and the Smithsonian Institution.

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