Ultraviolet Absorption Spectrum of CF_3I

Askar Fahr, Akshaya K. Nayak. and Robert E. Huie

***Chemical Kinetics & Thermodynamics** Division*
National Institute of Standards & Technology
Gaithersburg, MD 20899

Abstract.

The ultraviolet absorption spectrum of CF_3I has been measured in the gas phase over the wavelength range 160-350 nm at 295 K and over the wavelength range 240-350 nm **for** temperatures ranging from 218 to 333 K. Two absorption bands centered at 171 nm and 267.5 nm were observed. At wavelengths greater than about 280 nm. the absorption cross section decreased with decreasing temperature. At the maximum at 267.5 nm, the absorption mainly increased with decreasing temperature.

Background

The most important chemical fire extinguisher presently in use is CF_3Br. This compound is quite stable in the troposphere and diffuses to the stratosphere, where it is broken down by photolysis. The recent discovery that a chemical cycle involving bromine could be responsible for a considerable fraction of the halogen-induced ozone loss in the lower stratosphere[1,2,3] has resulted in an impending ban on the use of CF_3Br.[4] Bromine is important in stratospheric chemistry even though its concentration is exceeded by chlorine by more than a factor of one hundred. This is due to the greater efficiency of the bromine cycle and to coupling reactions which allow bromine to act synergistically on the chlorine cycle.

CF_3I has been identified as a possible replacement for CF_3Br.[5,6] In addition, CF_3I shows promise in blends for use as refrigerant fluids.' Unlike CF_3Br, CF_3I can be removed in the troposphere by photolysis'

$$CF_3I + h\nu \rightarrow CF_3 + I$$

or reaction with OH[9]

$$CF_3I + OH \rightarrow CF_3 + HOI$$

The former process is probably the more important channel.

Because the lifetime of CF_3I in the atmosphere depends on the rate of its photolysis, accurate absorption cross sections are needed. In addition, a fire extinguishing agent such as this is likely to be released not only at ground level but also at high altitude where the temperature is quite low. Therefore, the determination of the temperature dependence of the absorption cross section is essential for more accurate assessment of the atmospheric impact of CF_3I.

Experimental Procedure:

Ultraviolet absorption spectrum and the temperature dependencies of the absorption cross sections were determined employing a one meter, single beam, vacuum monochromator provided with interchangeable vacuum uv and uv photomultipliers, a deuterium light source. analog to digital circuitry, a computer controlled wavelength stepping motor drive, and computerized data acquisition.'' A band-pass optical filter with maximum transmission between 320 and 350 nm was used to eliminate the scattered light for more accurate measurement of low absorptions. The variable temperature cell($\ell = 18$ cm) is jacketed and is housed in a vacuum chamber. Temperature regulation from about 220 to 330 K is achieved through circulation of cooled or heated propanol. Thermal equilibrium is usually obtained after about one hour or less with a typical temperature gradient of 1°K. Adherence to Beer-Lambert absorption law was assured through variation of the sample pressure. The reported absorption cross sections at each temperature were obtained by combining and averaging independent measurements each at a different pressure. The sample pressure for each measurements depended on the wavelength range and the magnitude of the absorption. Pressure measurements were made using capacitance manometers operating in the range 0 to **1.3** KPa and **0** to **1.3 MPa.** Sample pressures were chosen such that appreciable absorption (more than 15% and less than 85%) was observed **so** that the absorption cross sections can be determined with good accuracy and with a typical precision of 2%.

Results and Discussion:

The ultraviolet absorption spectrum of CF_3I was measured between 160 and **350** nm at **295** K and between 240 and **350** nm for temperatures of **218, 233, 253, 273,** and **333 K.** The absorption spectrum (Figure 1) exhibits two bands, one centered about **171** nm and a weaker, broad, band centered about 267 nm.

The absorption spectra for CF_3I at the various temperatures, over the wavelength range 240 nm to **350** nm, are compared in Figure 2. The cross section decreases by decreasing temperature at longer wavelengths (about 280 nm to **350** nm). At about 280 nm, absorption cross sections do not significantly change with changing temperature. In the region of the absorption maximum, the **cross** section increases with decreasing temperature, reaching a maximum at **253 K,** and decreases slightly at lower temperatures.

There have been several recent determinations of the absorption cross section for CF_3I at room temperature. Values of λ^{max} are all within **1.5** nm of the value of 267.5 nm found in the present work: Brouwer and Troe[11] and Dvorkin. et al.[12] both reported 266 nm; Molina. et *al.*[8] reported 266.1 nm; Walters, et *al.*[13] reported 266.5; and Solomon, et *al.*[14] reported 267 nm. Values of the maximum cross section, σ^m, show about a 15% variation. Our value of 7.05×10^{-19} cm^2 is the greatest, followed by values of 6.92,[12] 6.45,[14] 6.25,'' 6.20,'' and 6.05[13] (all $\times 10^{-19}$ cm^2).

The band center is observed to shift sqmewhat to higher wavelengths with increasing temperature. The shift. from room temperature to temperatures in excess of 1000 K. was found to be represented well by a linear equation.[11,12] Over the temperature range of the present work, the correction would be predicted to amount to about 1 nm, in agreement with the present observations.

For $\lambda > 280$ nm, all of the results show decreasing cross sections with decreasing temperature. The present data are fit well by the semi-logarithmic expressions, $\sigma_\lambda = \sigma_o^\lambda \exp(-L/\lambda)$, for $\lambda > 320$ nm. and $\sigma_T = \sigma_o^T \exp(-\theta/T)$. Values of these parameters are given in Table I for σ_o^λ and L, and Table II for σ_o^T and 8. Figure 3 illustrates the plot log σ vs. 1/T for six wavelengths.

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Figure Captions

Figure 1. Ultraviolet absorption spectrum of CF_3I at 295 K.

Figure 2. Absorption spectra for CF_3I at different temperatures from 218 to 333 K. Insert: spectrum over the range 260 - 280 nm.

Figure 3. Plot of the uv absorption cross section against 1/T at selected wavelengths.

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Table I. Parameters of the semi-logarithmic expressions for the wavelength dependence of the absorption cross section for 1 > 320 nm.

T, K	σ_o^{λ}	1
218	93.4581	14964
253	92.3076	14693
273	92.2627	14729
295	92.0366	14744
333	89.5043	14009

λ, nm	σ_o^{T}	θ
300	34.4	72.17
310	19.5	102.5
320	7.56	113.1
350	0.207	130.6

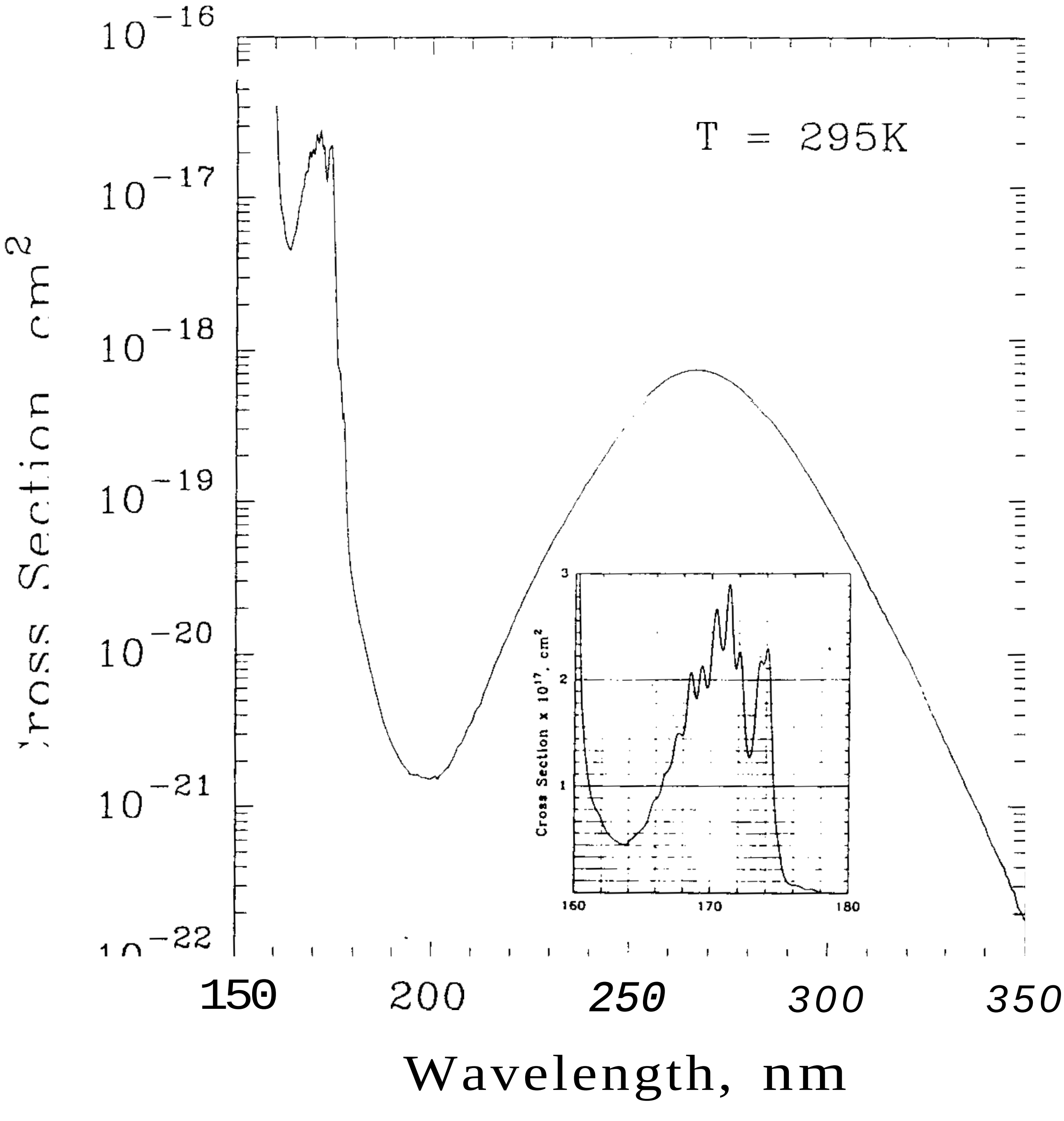

Figure 1. **Ultraviolet absorption spectrum of CF_3I at 295 K.**

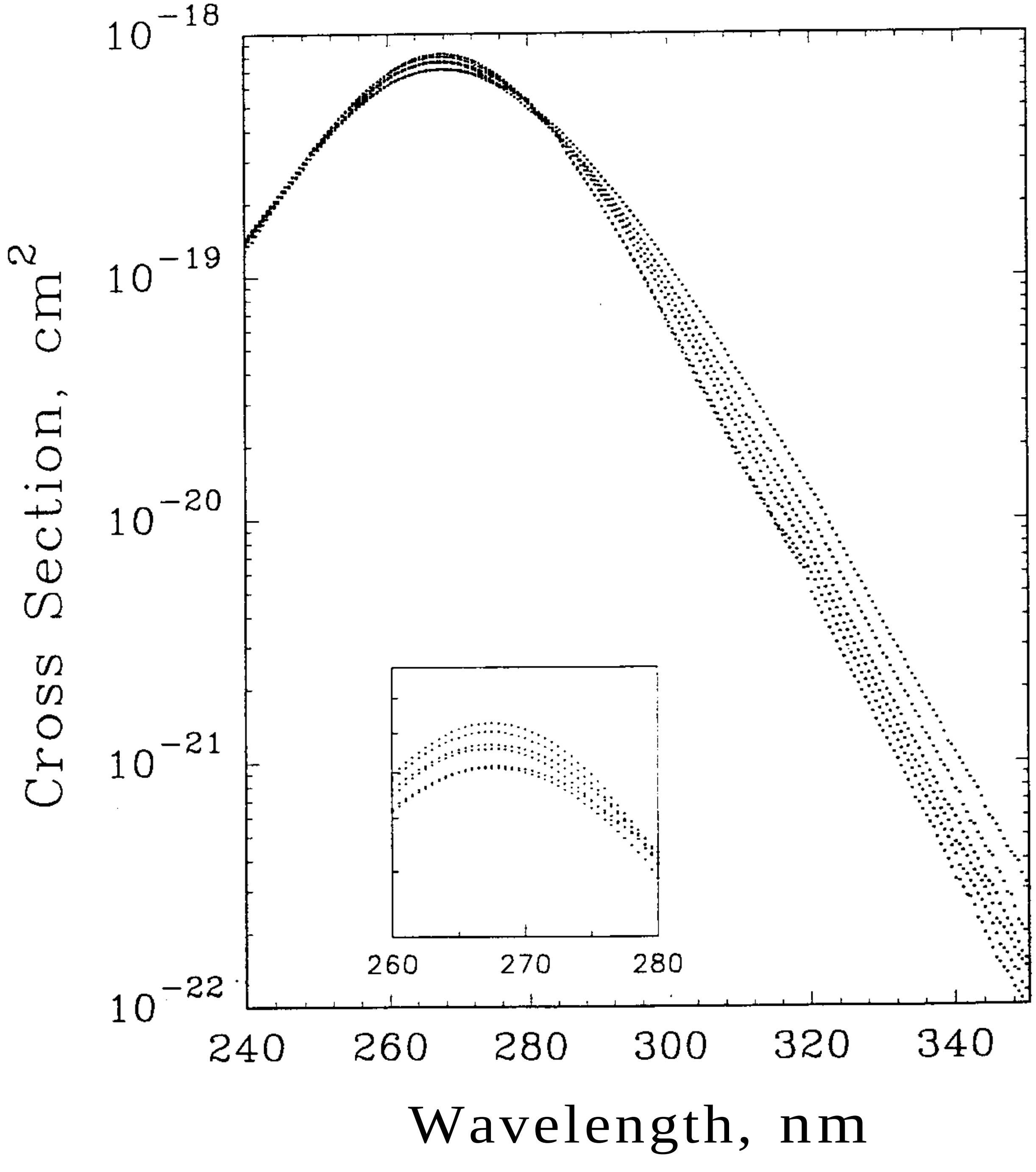

Figure 2. **Absorption spectra for CF_3I at different temperatures from 218 to 333 K. Insert: spectrum over the range *260* - 280 nm.**

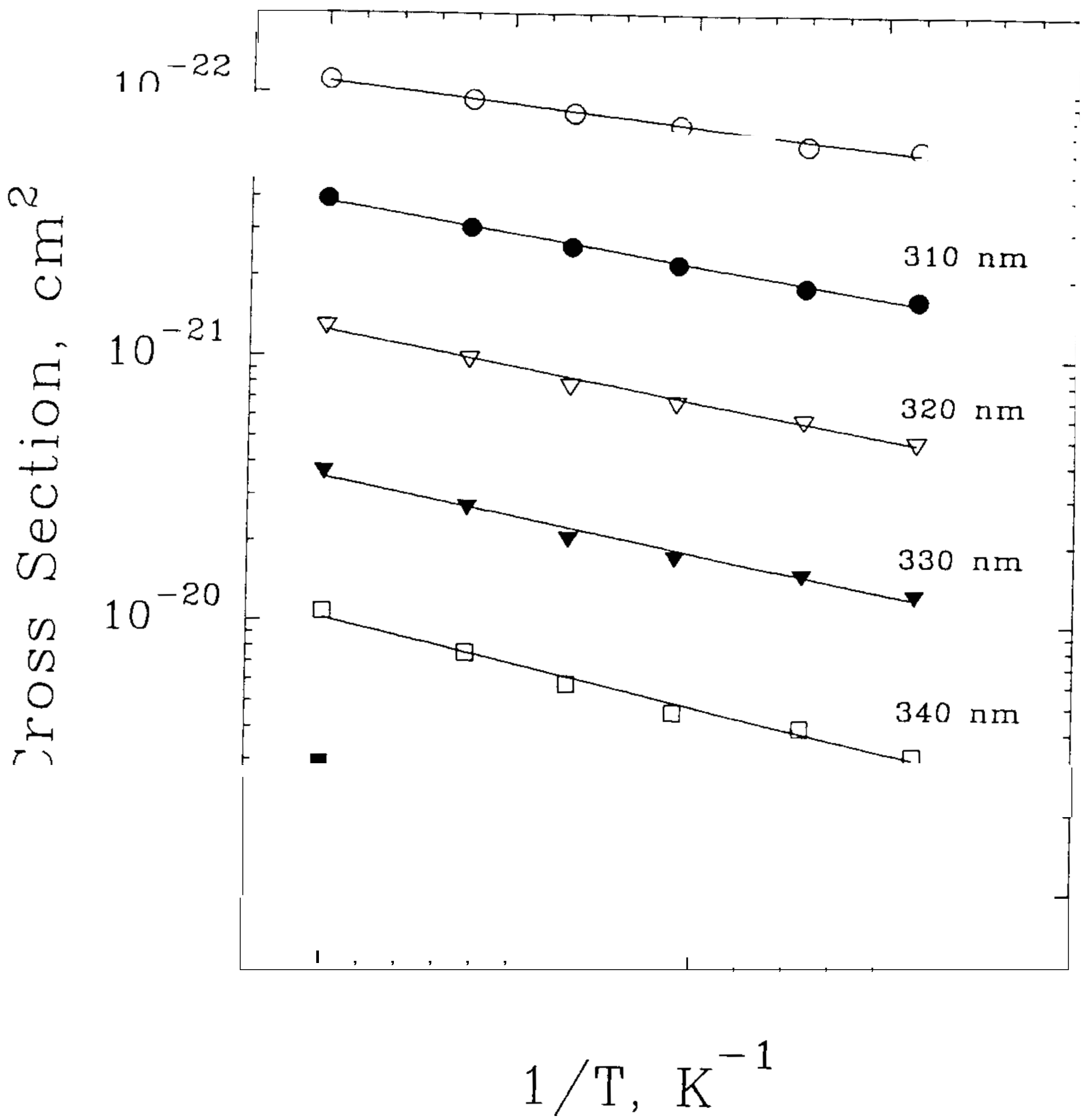
10⁻²²
10⁻²¹
10⁻²⁰
310 nm
320 nm
330 nm
340 nm
Cross Section, cm²
1/T, K⁻¹

Figure 3.