

UV ABSORPTION CROSS SECTION OF ACETONE AT DIFFERENT PRESSURES IN 298- 837 TEMPRATURE RANGE

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ABSTRACT

Gas phase absorption cross section of acetone have been measured in flow reactor at wavelength 193nm (the $n-\pi^*$ system) at temperatures between 298 and 837 K at 193nm. Absorption measurements were performed by using a ArF laser source and dependence of absorption cross section with temperature has been derived. The absorption cross sections of actone increase with increase in pressure. Generally it also increase with increase in temperature. The spectra are fitted to a parameterized curve to allow for calculations of the cross sections as a function of temperature and pressure. Our measurements are in agreement with recent acetone cross section study.

Keywords: Acetone, Laser photolysis, UV absorption, Temperature dependence.

INTRODUCTION

Among volatile organic compounds present in atmosphere, acetone is considered as a model system for understanding the photochemistry of carbonyl compounds due to its simplest carbonyl form.¹⁻⁶ The reaction of acetone in the presence of sun light in atmosphere has cascade effects. In the presence of sunlight, the excited photons from the acetone break bonds and generate free radicals, which in turn react with many molecules present in the atmosphere like HNO_3 , NO_2 , OH etc. and contribute in the NO_x formation in the environment. Their photochemical behavior ultimately affects the ozone formation in troposphere⁴⁻⁷.

Other than the environmental implication of acetone, its thermochemistry is of interest to the scientific community. Determination of the quantum yield and photolysis yield of acetone in UV radiation provide useful information about the fate of chemical reactions in atmosphere. This information will help to determine how the photolysis proceeding via α -bond cleavage from UV light. The photolysis of acetone is the most studied of the photochemical processes. When

acetone absorbs photons which can provide sufficiently high energy for excitation, acetone represents a prototypical three-body dissociation process involving the breaking of two similar chemical bonds. Of dynamical interest, is the coupling of two bond breaking steps and extent of coupling¹²⁻¹⁶.

The existence of different spectroscopic methods for probing the photo products of acetone fragments has resulted in the extraction of considerable information concerning the energy distributions of the photolytic products. Despite various recent studies on the photodissociation chemistry of acetone, the sequence of events leading to the photolytic scattered fragments is still largely unresolved and in dispute. In the present experiments, tried to measure absorption cross section of acetone in order to pursue further and explore the gas phase UV photodissociation dynamics of acetone. The first absorption band in acetone appeared at 260 nm which corresponds to an $n \leftarrow \pi^*$ ($S_1 \leftarrow S_0$) transition. The mechanism is postulated to involve the promotion of a nonbonding electron on the oxygen to an

antibonding orbital localized on the carbonyl moiety.

The dissociation of acetyl radical is possible if its internal energy exceeds the barrier to dissociation which is provided by sunlight or another excitation source



The kinetics studies of addition of CH_3 to CO resulted a CH_3CO barrier to dissociation of 17.260.5 kcal/mole as reported by various theoretical studies⁹.

EXPERIMENTAL

The absorption cross section of acetone was measured as a function of temperature and pressure 1, 3 and 10 bar. The experimental set up is given in Figure 1. The technique is based on UV absorption spectroscopy. The stainless steel cell with 45 cm length was used to study the absorption of acetone. The temperature range covered in this study was 298 – 837 K. The high resistance was wrapped around the cell to achieve the temperature. Temperature was recorded by K type thermocouple. The 0.02 – 0.04 mole fraction of acetone in acetone -water solutions were used as described by Sangwan et al.^{2,7,9,12} The cell was equipped with fused silica windows to allow entry of laser beam. The reflectivity of the windows was determined to be 87 %. Before use, the solutions were degassed

by using freeze – pump - thaw cycles. The solution of acetone - water was injected to the cell by flowing through flow of helium. The vacuum pump was connected to the cell and the pressure of reactant inside the cell was monitored by baraton monometer. The flow rate of helium was 100 – 300 sccm. Light from an ArF excimer laser (Lambda Physik) entered in the cell by employing various objective elements along the path of laser beam. The intensity of the laser light passed through the cell was measured with and without the acetone/water mixture entering the cell using a energy meter as well as the pyroelectric detector. Various concentration of acetone was used to The reference intensity was provided by measuring the intensity of blue fluorescence from a quartz plate installed before the entrance of the reactor. The fluorescence light was passed through the spectrograph and measured by a PMT. This allowed significant reduction of the measurement errors associated with the fluctuation of the laser pulse energy. The cross-sections measured using laser light were confirmed by measuring the UV absorption spectra using xenon arc lamp in combination with the spectrograph and the ICCD camera (Figure 1). The cross-sections were calculated from the spectra measured in the presence and in the absence of acetone in the reactor.

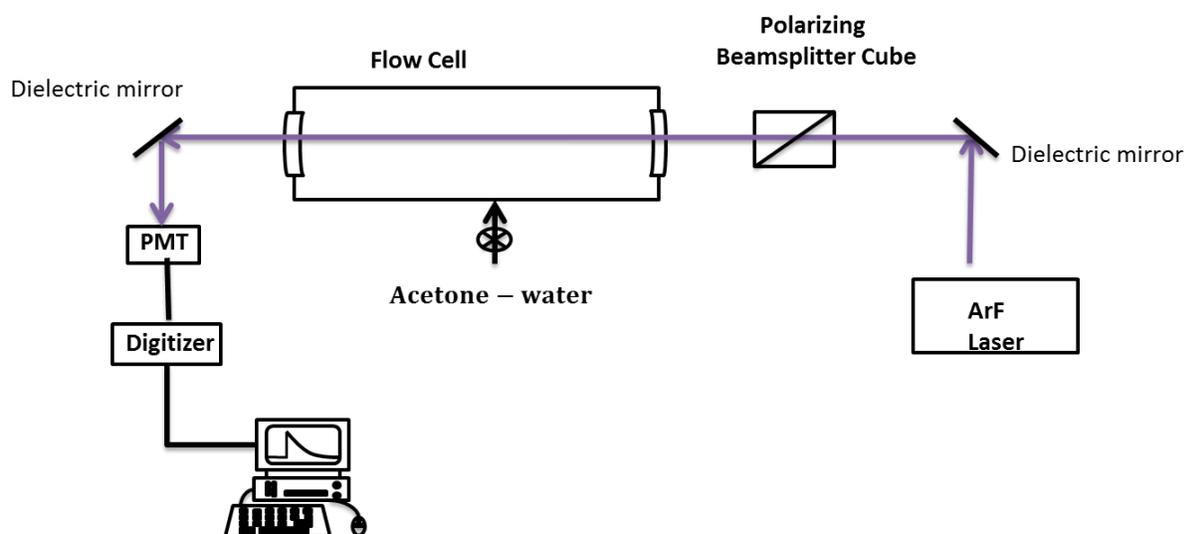


Fig. 1: Experimental set up

RESULT AND DISCUSSION

The acetone absorption cross section was calculated by applying Lambert Beer law

$$-\ln(I/I_0) = \sigma n l$$

Where I is the intensity of light after passing through the adsorbent, I_0 is the incident light, n is the concentration of acetone, σ is the absorption cross section, l is the length of the cell which is 45 cm.

The acetone cross section was obtained by applying the Lambert Beer law

The dependences on temperature are almost linear, and the linear fits with two fitting parameters are almost indistinguishable from the linear fits forced through zero at zero temperature (Figure 2). In addition, assuming linear pressure dependence of the slope, the fit results in the following expression

$$\sigma_{\text{Acetone}}/10^{-18} \text{ cm}^2/\text{molecule}^{-1} = a_0 + a_1(T/K - 298) + a_2(T/K - 298)^2 \quad (2)$$

Due to the comparable widths of the emission and absorption lines as well as to the multitude of lines with different oscillator strengths the Lambert Beer law has its own limitation. At high absorption, the Beer-Lambert law is, in general, not applicable, and the apparent cross-sections can be used only for small absorptions that do not exceed about 20%. To evaluate the deviations from the Beer-Lambert law at larger absorptions, the spectroscopic model described in the paper by Sangwan et al.¹² was used. In case of the Lambert-Beer law applicability, these curves would be constant (unity) independent of the apparent absorption. This representation allows simple correction of the observed absorbance profiles (Fig. 2).

As can be seen from Figure 2 the absorption cross section increases with pressure. However, the temperature dependence of the absorption cross section is not linear. After 500 K temperature it no longer increases with increase in temperature. The values of absorption cross sections were obtained and presented in Table 1.

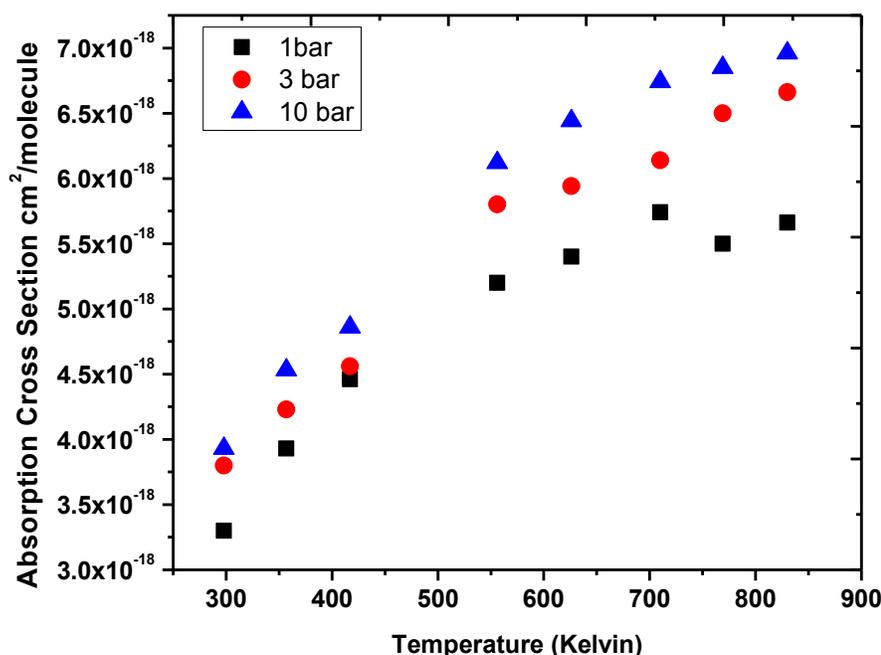


Fig. 2: The plot of absorption cross section of acetone at different pressure and temperature

Table 1: Absorption cross-sections of acetone (σ_{193} (acetone) / 1×10^{-18} cm²molecule⁻¹) at 193 nm at different temperatures and pressures, measured using laser light at 193 nm

Temperature	Absorption cross section cm ² /molecule 1 bar	Absorption cross section cm ² /molecule 1 bar	Absorption cross section cm ² /molecule 1 bar
298	3.3×10^{-18}	3.8×10^{-18}	3.93×10^{-18}
357	3.93×10^{-18}	4.23×10^{-18}	4.53×10^{-18}
417	4.46×10^{-18}	4.56×10^{-18}	4.86×10^{-18}
558	5.2×10^{-18}	5.8×10^{-18}	6.12×10^{-18}
629	5.44×10^{-18}	5.94×10^{-18}	6.44×10^{-18}
718	5.74×10^{-18}	6.14×10^{-18}	6.74×10^{-18}
773	5.5×10^{-18}	6.5×10^{-18}	6.85×10^{-18}
837	5.66×10^{-18}	6.66×10^{-18}	6.96×10^{-18}

CONCLUSION

The absorption cross measurements were performed for acetone which is atmospherically and chemically important species. The absorption cross section of acetone increases with the pressure, at 298 K, the absorption cross section of acetone at 193 nm was 3.3×10^{-18} cm² molecule⁻¹ and 3.93×10^{-18} cm² molecule⁻¹. The temperature dependence of acetone was also measured although it behaves linearly, but after 500 K it does not increase.

Our measurements are in line with the absorption cross section reported by Sangwan et al.^{7,12,14}

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