

FT-IR Spectroscopy of CO Produced by the Photodissociation of Hexafluoroacetylacetone

Mitsuhiro KUSABA and Yoshiaki TSUNAWAKI

Abstract

Photochemistry of Hexafluoroacetylacetone has been studied by photoproduct analysis using infrared spectroscopy. Hexafluoroacetylacetone was irradiated by KrF excimer laser with the oscillation wavelength of 248 nm during 100 seconds and the photoproducts were analyzed by transmittance measurement of FT-IR in the spectral region between 3500 cm^{-1} and 1300 cm^{-1} . One of the photoproducts was CO. It was estimated that the formation efficiency of CO was approximately 0.6.

1. Introduction

Vacuum-ultraviolet (VUV) and ultraviolet (UV) laser have been used to investigate material processing and photochemistry. In particular, the photodissociation reaction from higher excited states has been studied using the laser which has the high photon energy. There is not, however, any detector measuring absolute energy in the VUV region. We have started to develop a chemical actinometer between VUV and UV region using the photoreaction of organic molecule such as acetylacetone in the gas phase.

Acetylacetone has been widely used as a chelating reagent for the preparation of many useful organometallic compounds. It can exist as two different structural isomers such as

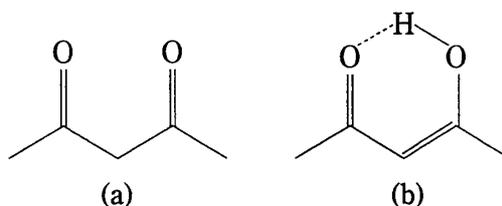


Fig.1 Structure of acetylacetone. (a) Diketo form, (b) Enol form

Received December 2, 2003

Department of Electrical Engineering and Electronics, Osaka Sangyo University

diketo and enol shown in Fig. 1, and it is well known from much spectroscopic evidence that the relative population of these two structural isomers varies depending on the characteristics of the environment. In the gas phase at room temperature, acetylacetone is known to exist predominantly as the enol form^{1,2}). The preference of the enol form in the gas phase is due to the formation of a relatively strong intramolecular hydrogen bonding in the enolic acetylacetone. The molecular structure of the enolic acetylacetone in the ground electronic state has been debated for a long time and seems to remain controversial in terms of whether the hydrogen-bonded hydrogen atom is positioned at the center between two adjacent oxygen atoms or not^{3,4,5}). According to UV spectroscopic study, the enolic acetylacetone in the gas phase has a broad structureless absorption band peaked at around 270 nm, which is attributed to the electronically allowed $\pi \rightarrow \pi$ transition^{2,6}). Photochemistry of acetylacetone^{7,8}) and hexafluoroacetylacetone⁹) have been studied using jet spectroscopy method and the photoproduct of OH radical was observed⁹).

In this work, after the Hexafluoroacetylacetone in the gas phase was irradiated by UV laser, the photoproducts were analyzed by infrared spectroscopy. The absorption due to CO was observed in the spectral region between 2250 and 2025 cm^{-1} and the absorbance of the produced CO increases linearly with increasing the laser fluence. The formation efficiency of CO was estimated to be approximately 0.6.

2. Experimental

The sample cell is made of glass with the windows of MgF_2 . The cell shows the characteristic of transmittance of 70 to 95 percent for the middle infrared region above 1300 cm^{-1} . The path length of the light in the cell is 10 cm. Hexafluoroacetylacetone (1,1,1,5,5,5-Hexafluoro-2,4-pentanedione, HFA) (Aldrich, 98%) is used without further purification and it is enclosed in the sample cell with the pressure of 667 Pa. The absorption spectrum in the UV region was measured by spectrophotometer (Hitachi, U-3500). The absorbance at 248 nm of the sample measured by the spectrophotometer was used for calculating the absorbed laser photons. The excitation light source was KrF excimer laser (Lambda Physik, COMPex 102) with the oscillation wavelength of 248 nm and the laser pulse width of 25 ns (full width at half maximum). The sample was irradiated by the laser during 100 seconds under the conditions of the repetition frequency of 1 Hz and the typical laser fluence of 40 mJ/cm^2 . Photoproducts were analyzed by fourier transform infrared spectroscopy. The transmittance spectra of the products were measured in the region between 3500 cm^{-1} and 1300 cm^{-1} using a FT-IR spectrometer (Bruker, IFS-113V) at a 0.5 cm^{-1} resolution.

The formation efficiency of CO, η_{CO} , is defined as follows;

$$\eta_{\text{CO}} = \frac{\text{the number of formed CO}}{\text{the number of absorbed photons by HFA}} \quad (1)$$

3. Results and discussion

The absorption spectrum of HFA in the region between 200 nm and 340 nm shows in Fig. 2. The near and vacuum UV absorption spectra of HFA have been discussed in detail⁶. The absorption peak at 267 nm is assigned to spin-allowed $\pi\text{-}\pi^*$ transition of the enolic HFA, with a molar extinction coefficient of 8×10^3 . This absorption spectrum suggests that a KrF excimer laser can be employed as the light source to excite the $\pi\text{-}\pi^*$ transition band of HFA.

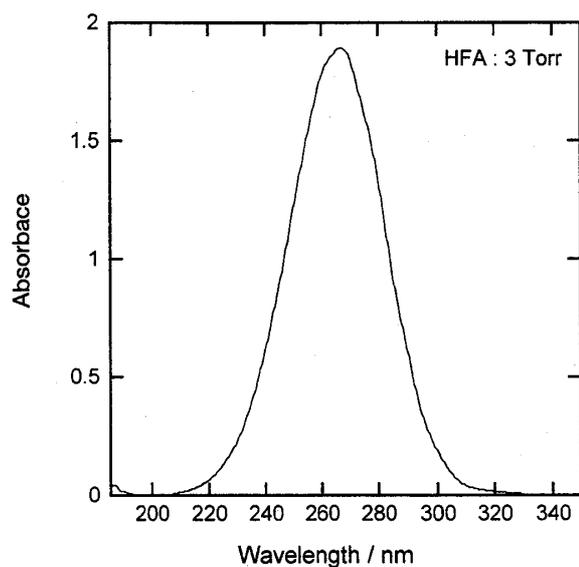


Fig. 2 UV spectrum of HFA

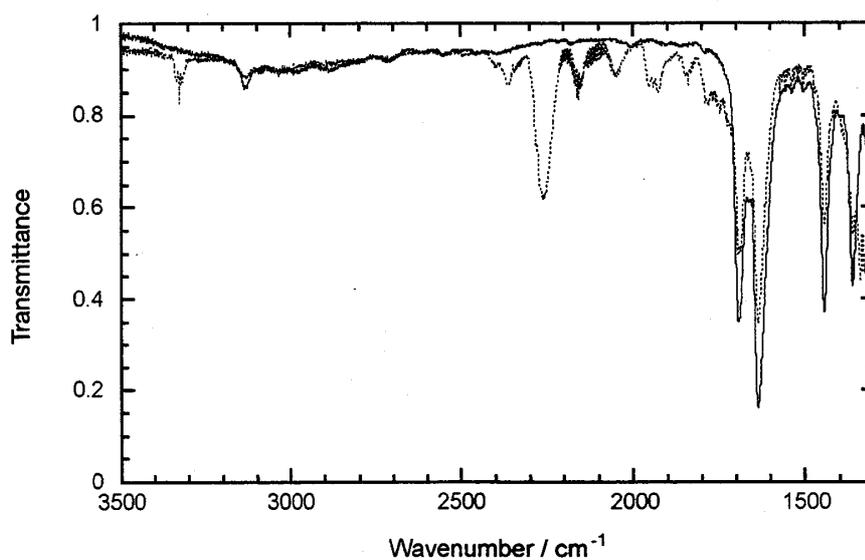


Fig. 3 IR spectra of HFA before(solids line) and after(dots line) KrF excimer laser irradiation.

The transmittance spectra between 3500 cm^{-1} and 1300 cm^{-1} region before the irradiation with KrF laser (solids line) and after that (dots line) are shown in Fig. 3. The IR spectra of HFA have been studied in detail^{3,10c} and some peaks of absorption bands appears at 3140 cm^{-1} and in the region between 1800 cm^{-1} and 1300 cm^{-1} . The absorption band at 3140 cm^{-1} is due to the C-H stretching mode. The sharp strong bands at 1690 cm^{-1} and 1636 cm^{-1} are assigned to the C=O stretching and the C=C stretching coupled with the C-H in-plane bending mode, respectively. The band at 1448 cm^{-1} is due to a super position of the C-O stretching and the O-H...O in-plane bending modes and the band at 1368 cm^{-1} is the stretching vibrations of the CF_3 . After the laser irradiation, the intensities of these absorption peaks decreased and the absorption peaks of the photoproducts appeared in the region between 2500 cm^{-1} and 1750 cm^{-1} . The absorption lines in the region between 2250 cm^{-1} and 2000 cm^{-1} were in quite agreement with the vibrational lines of CO. The formation of OH radical was not observed in this work, because it will be active and easily react with other species.

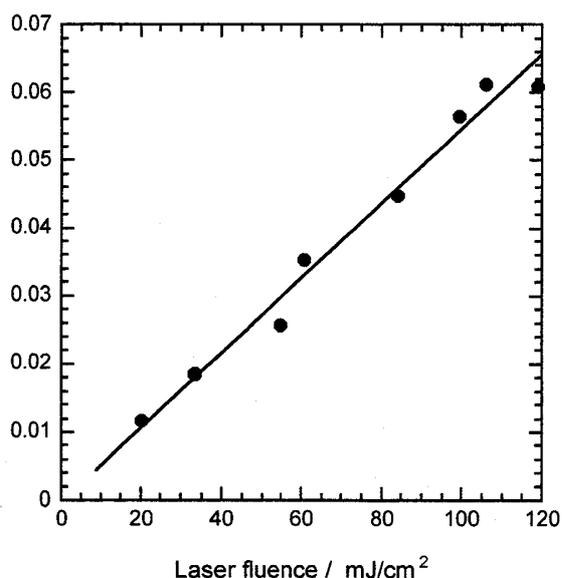


Fig. 4 Laser fluence dependence of absorbance of the produced CO

Figure 4 shows the relationship between the absorbance of the produced CO and the KrF laser fluence. The absorbance of CO increases linearly with increasing the laser fluence. Therefore, it is found that CO is produced by one-photon process. The following reaction of CO can not be induced by KrF laser because the produced CO has the absorption spectrum below 200 nm . Once CO is produced, the CO is not reacted with other species. The concentration of the produced CO was determined by the calibration curve between the concentration and the absorbance of CO. It was estimated that the formation efficiency of CO was approximately 0.6.

4. Conclusions

It was found that the photodissociation of HFA is induced by UV laser irradiation. One of the photoproducts was CO. The absorbance of the CO increases linearly with increasing the laser fluence. The formation efficiency of CO was estimated to be approximately 0.6. The photodissociation mechanisms will be clarified by the experiment using laser flash photolysis. This experiment suggests that HFA will be used as a chemical actinometer in the UV region.

References

- 1). J. Powling, H. J. Bernstein, *J. Am. Chem. Soc.*, **73**, (1951)4553.
- 2). H. Nakanishi, H. Morita, S. Nagakura, *Bull. Chem. Soc. Jpn.*, **50**, (1977)2255.
- 3). H. Ogoshi, K. Nakamoto, *J. Chem. Phys.*, **45**, (1966)3113.
- 4). K. Iijima, A. Ohnogi, S. Shibata, *J. Mol. Struct.*, **156**, (1987)111.
- 5). N. S. Hush, M. K. Livett, J. B. Peel, G. D. Willett, *Aust. J. Chem.*, **40**, (1987)599.
- 6). H. Nakanishi, H. Morita, S. Nagakura, *Bull. Chem. Soc. Jpn.*, **51**, (1978)1723.
- 7). M. C. Yoon, Y. S. Choi, S. K. Kim, *Chem. Phys. Lett.*, **300**, (1999)207.
- 8). M. C. Yoon, Y. S. Choi, S. K. Kim, *J. Chem. Phys.*, **110**, (1999)11850.
- 9). M. C. Yoon, Y. S. Choi, S. K. Kim, *J. Phys. Chem. A*, **104**, (2000)4352.
- 10). S. F. Tayyari, Th. Zeegers-Huyskens, J. L. Wood, *Spectrochimica Acta*, **35A**, (1979)1265.