

Fourier Transform 분광기를 이용한 불안정한 분자의 방출분광학

李相國* · 金恩植

釜山大學校 自然科學大學 化學科

(1992. 6. 19 접수)

Emission Spectroscopy of Unstable Molecules using a Fourier Transform Spectrometer

Sang Kuk Lee* and Un Sik Kim

Department of Chemistry, Pusan National University, Pusan 609-735, Korea

(Received June 19, 1992)

요 약. 불안정한 분자의 방출분광학에 사용이 가능하도록 Fourier Transform 분광기를 변형시켰다. 불안정한 분자 라디칼 CH_3S 는 고전압 직류 방전에 의한 supersonic expansion 속에서 jet 형태의 흐름으로 생성되었다. Supersonic expansion에 의하여 냉각된 라디칼의 형광 스펙트럼은 Fourier Transform UV/VIS 분광기에 의해서 얻어졌다. 스펙트럼의 signal/noise 비율은 증가하였으며, 분자 라디칼 CH_3S 의 회전구조도 명확하게 볼 수 있었다.

ABSTRACT. Fourier Transform UV/VIS spectrometer has been modified for emission spectroscopy with the technique of supersonic expansion, in which the unstable molecular radical CH_3S has been generated in a jet by a high voltage DC discharge. The fluorescence spectra of the supersonically cooled radical have been recorded on a Fourier Transform UV/VIS spectrometer. The ratio of signal to noise of the spectra has been improved substantially. Also the rotational structure has been clearly resolved for CH_3S molecular radical.

INTRODUCTION

One of the most important instruments in experimental chemistry is a Fourier Transform (FT) spectrometer. Since 1970's, a Fourier Transform spectrometer has been rapidly developed with a personal computer and its rate processor, extending its spectral range into from millimeter wave to UV. However, most of the commercially available FT spectrometers have been designed to analyze stable organic compounds for absorption spectroscopy in the infrared frequency range.

In modern molecular spectroscopy, one of the most interesting subjects is to identify the structure of unstable species by using a tunable laser such as a dye laser, by which the molecular population at the ground state is being pumped to the

upper state. The fluorescence from the relaxation process at the upper state is monitored to produce a laser induced fluorescence (LIF) spectrum. The advantages of LIF are high sensitivity and easy selection of the transitions to be pumped compared to the old style of dispersive method.

On the other hand, since the Doppler effect of emission is so broad in the visible and UV range, a supersonic expansion technique developed by Smalley *et al.*^{1,2} has been widely employed to reduce the linewidth of transition peaks. The linewidth of the peaks depends on the peak frequency, the molecular weight, and the temperature of the molecules³. The only factor which can be varied is the temperature of the molecules. And the rotational temperature of the molecules can

be controlled by the difference in pressure between the orifice of the nozzle in a supersonic expansion system. In some cases, the rotational temperature of the molecules has been lowered to within 10 K by using a pulsed nozzle and a powerful boost pump⁴.

A FT spectrometer has advantages over a conventional dispersive method in a few ways; accuracy of the frequency, quick scanning over the wide frequency region, and high resolution. Recently, the resolution of commercially available FT spectrometer has been greatly improved with the technique of stabilizing the motion of the moving mirror. The absorption spectra of many molecules have been obtained with a FT infrared spectrometer and White cell⁵⁻⁷. And a few of FT UV/VIS spectrometer have been already applied with a supersonic expansion system to the emission spectroscopy of unstable species such as CN without further modification of its system⁸. In this case they obtained a good emission spectrum of CN because it emits very strong fluorescence in the visible and UV range. However, it was fairly difficult for the above system to apply to molecules with very weak emission such as CH₃S⁹. Thus, further developments have been done to improve the availability of FT spectrometer in the emission spectroscopy.

IDEA FOR MODIFICATION OF FT SPECTROMETER

Since the emission spectroscopy with a FT UV/VIS spectrometer is mainly different from the absorption spectroscopy in the strength of the radiation source, we have, at first, to understand the process of how to obtain the data in FT spectroscopy. In absorption spectroscopy, the scanner (moving mirror) initially makes a round trip over the whole range to find the most intensive point, which is called 'center burst point', in the interferogram. In this process, the system easily finds the right moving distance of the scanner from the initial trip due to the strong intensity of a blackbody radiation source. Then the scanner only moves back and forth the region which has been

already determined from the initial round trip.

However, in emission spectroscopy, the intensity of a radiation source is so weak that the probability for the system of finding the right traveling distance of scanner decreases with decreasing intensity of the radiation. Thus it eventually becomes nearly zero when the value of S/N of the radiation approaches to 1. Therefore, we have tried to modify the spectrometer in a two ways.

The first one is to determine the right traveling distance of the scanner which has been applied to the FT UV/VIS spectrometer for the first time. It can be done manually with help of a strong blackbody radiation source and a proper optical filter.

The second one, which has been already applied by other groups⁸ to an emission spectroscopy is to improve the sensitivity of the detector because the intensity of a radiation is extremely weak in emission spectroscopy of the unstable species. For this object, a highly sensitive photomultiplier tube (PMT) has been employed with a preamplifier. Also, a proper range of an optical filter has been employed to discard strong emission from the discharge of a carrier gas (mostly, He, Ar) and to prevent the folding (aliasing) effect of the spectrum during the process of the Fourier Transform.

EXPERIMENTAL

Commercially available chemical, dimethyl sulfide (CH₃)₂S was purchased from Aldrich and used as a precursor without further purification. The vapors of the compound were fed to the discharging cell with a carrier gas, usually helium. The concentration of the precursor compound in a carrier gas could be controlled by immersing the container in a constant temperature bath or by adjusting the opening of the by-pass valve of the sample cell. The concentration of the sample in the mixture is believed to be less than 1%.

The experimental apparatus¹⁰ used is shown in Fig. 1. The gaseous mixture was expanded through 0.3 mm diameter of nozzle into a vacuum chamber made by 2 inches diameter of 4-way glass cross, in which the chamber has been eva-

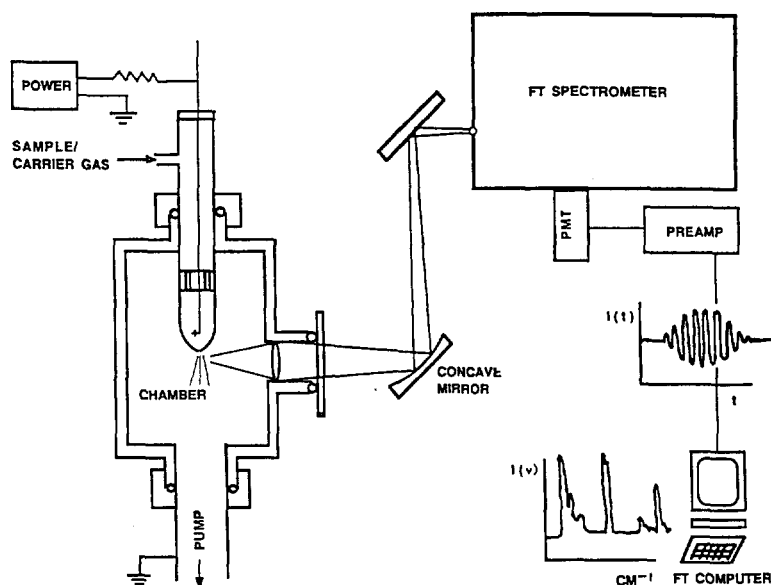


Fig. 1. Schematic diagram of experimental apparatus showing the details of the supersonic jet, high voltage discharge, and a Fourier Transform UV/VIS spectrometer.

cuated by a 800 l/min roots blower pump, Edwards Model E2M80. With 2~3 atm pressure of a carrier gas, the chamber pressure has been maintained at about 50~100 mtorr during the operation. However, the use of a mechanical vacuum pump without a boost pump has only increased the rotational temperature of the compound by about 20 K.

The nozzle has been made from a thick glass tube of 0.5 cm inside diameter and 30 cm long, narrowed at one end to a capillary to produce the desired size of opening. The anode, formed by a 1.5 mm diameter of stainless steel wire, was inserted via an O-ring seal into the glass tube to within 1~3 mm from the orifice. The anode was biased by a 3000 V with a DC power supply, and the discharge was stabilized using a 500 K Ω current limiting balast resistor. The power supply has been operated at the maximum voltage. Under these operating conditions the discharge current was about 4~5 mA. The cathode has been used with 7.6 cm diameter of copper tube connecting the chamber and the vacuum pump. The distance between two electrodes is about 30 cm. The optimum condition could be obtained by adjusting the

position of anode from the orifice. The light emanating from the discharge was collimated using a two quartz lenses, where the first lens was located at only 5 cm away from the flame to increase the solid angle and focussed using a concave mirror into the emission port of the spectrometer.

The FT spectrometer used for this work is Bruker IFS-120HR installed at the Laser Spectroscopy Facility in the Ohio State University. The maximum resolution obtainable with this spectrometer is 0.00167 cm^{-1} , but it is degraded to $1/10^6$ of the wavelength in the optical frequency region. The relative accuracy of the frequency is believed to be better than 10^{-7} of the frequency from the calibration with iodine lines. The optical alignment has been optimized by adjusting the position of a fixed mirror with a quartz beam splitter. The ordinary Si diode detector has been replaced by a Hamamatsu R106UH photomultiplier tube (PMT) to increase the sensitivity of the detector. The output of the detector was connected to the electronics of the spectrometer through an EG&G 113 preamplifier. The entire optical system was maintained under vacuum during the experiment. Since the emission of He lines from the discharge

are much stronger than that of the molecular transitions of the unstable species, a narrow band (100 Å) interference optical filter has been used in front of the detector to get rid of the unwanted emission and avoid the folding effect of the spectrum.

The ratio of signal to noise was mainly limited by the source noise, i.e. the fluctuations in the discharge intensity. But it turned out from a considerable amount of experimentation that a proper design of the nozzle has played a very important role in stabilizing the discharge. The emission was taken from the flame just below the nozzle.

With the software and hardware provided by Bruker, the scanning mode can be switched to either automatic or manual without difficulty. But we have to count the position of the center burst point with a suitable blackbody radiation source and an optical filter for manual mode, and let the scanner travel the region defined by the count.

For the count of the position of the center burst point, the spectrometer has been set at manual mode. A tungsten lamp as a radiation source and a narrow band interference filter (10 nm) at the peak wavelength of 410 nm have been used. The position of the center burst point was counted from this continuous radiation source. With this count, the travelling range of the scanner was determined and the software parameters for scanner movement was changed. Then, the radiation source was switched to the emission of the discharge.

Initially, survey scans have been obtained at low, 2 cm^{-1} resolution. Subsequently, after the experimental conditions were optimized, higher resolution scans were obtained at the resolution of 0.05 cm^{-1} which was narrower than the Doppler width of the carrier gas at that rotational temperature. Typically 100 scans have been averaged to obtain a good quality of survey spectrum.

RESULTS AND DISCUSSIONS

Suppose that the radiation beam of the single frequency exists in a FT spectrometer, then we have an interferogram of exactly sine wave whose

frequency depends on the wavelength of the beam and the velocity of the moving mirror (scanner). For the situation when a sample emits radiation at more than one frequency, i.e., more than one spectral peak, the overall result is the summation of the individual peaks, and beat patterns of varying complexity are built up. The beat pattern becomes more distinctive if more than three spectral lines are involved, and rather complex when several randomly spaced lines of different intensities exist. The breadth of the package generated by the scanner decreases with increasing number of different frequency of the radiation.

However, if there is absolutely no noise in the interferogram, every portion of the interferogram has exactly same amount of information on the molecule. However, in fact, random noise exists in every part of the spectrum and the ratio of signal to noise is very important factor in deciding the quality of the spectrum. Thus, the wave package which has the better S/N ratio compared to other parts should be included to get a better quality of final spectrum after the Fourier transform.

Fig. 2 shows a portion of interferogram and spectrum of CH_3S radical obtained with automatic mode. Since the weak emission from CH_3S made its ratio of signal to noise equal to nearly 1, it was very difficult for the system to determine the right position of the center burst point and the travelling range of the scanner. However, the operation at manual mode generated the right interferogram and spectrum shown in *Fig. 3*, even though the same experimental conditions were applied to the discharging system. From the comparison of *Figs. 2* with *3*, it has turned out that the intensity of the interferograms in *Fig. 2* is corresponding not to that of the center burst point but to that of the edges of the interferogram in *Fig. 3*. In the automatic mode, the system has failed to find the position of the center burst point and produced a wrong interferogram and spectrum for this unstable molecule. The center burst point of the interferogram shown in *Fig. 2* is corresponding to the edge of the interferogram in

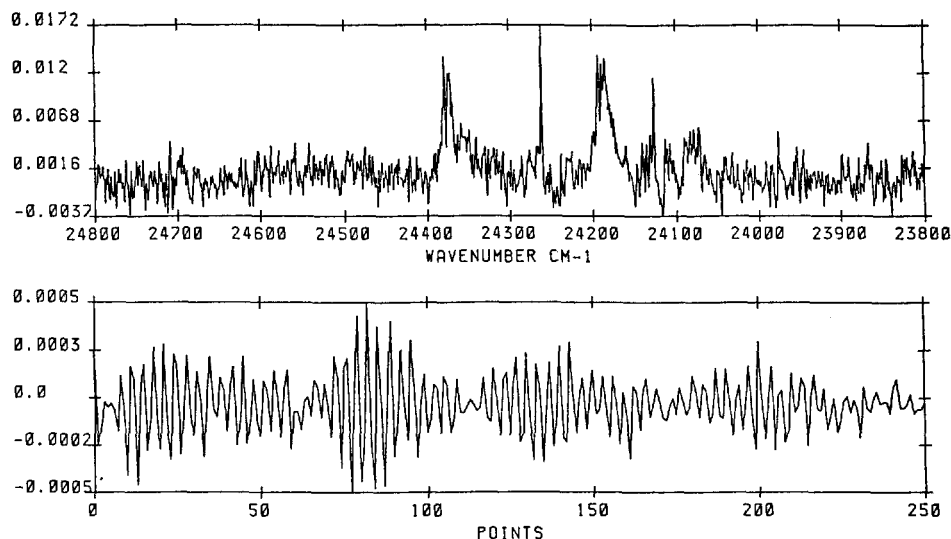


Fig. 2. CH_3S emission interferogram and its spectrum obtained with automatic mode from the discharge of the mixture of $\text{He}-(\text{CH}_3)_2\text{S}$. The spectrum shows large fluctuation in the baseline due to the weak emission of the CH_3S .

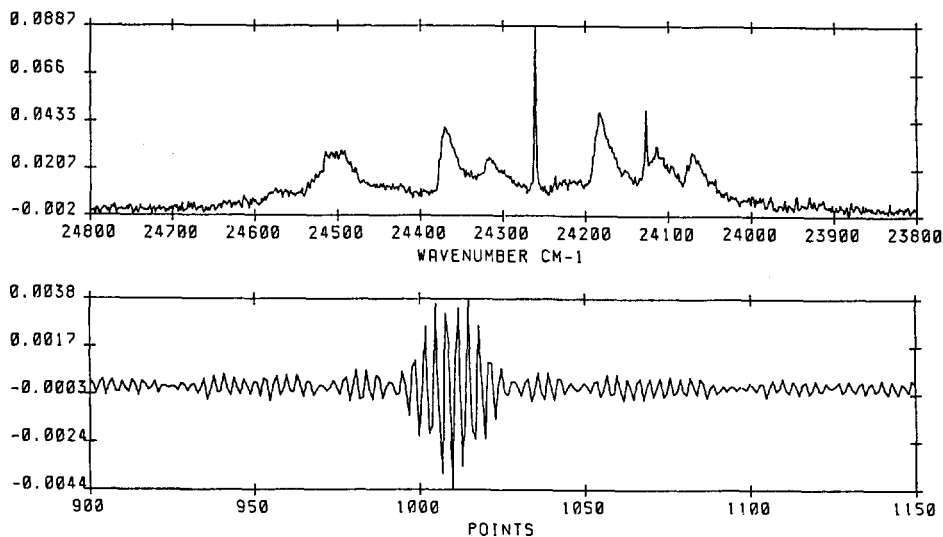


Fig. 3. CH_3S emission interferogram and its spectrum obtained with manual mode under the exactly same condition of the discharge as those given in Fig. 2. The peaks at 24372 and 24183 cm^{-1} are corresponding to the transitions of $A^2A_1 \rightarrow X^2E_{3/2} 3_3^0$ and $2_1^0 3_2^1$, respectively according to Ref. 11. Also the sharp peaks at 24126 and 24260 cm^{-1} are of the He-lines from the carrier gas.

Fig. 3. The package of the interferogram in Fig. 3 is not shown in Fig. 2 because the travelling range determined by automatic mode was not correct. Thus, the system has lost much of the information about the molecule. From the survey spec-

tra shown in Figs. 2 and 3, it has been turned out that, with new method, the ratio of signal to noise has been improved by a factor of more than 10. Also, the new method presents much better spectrum from the comparison with the previous

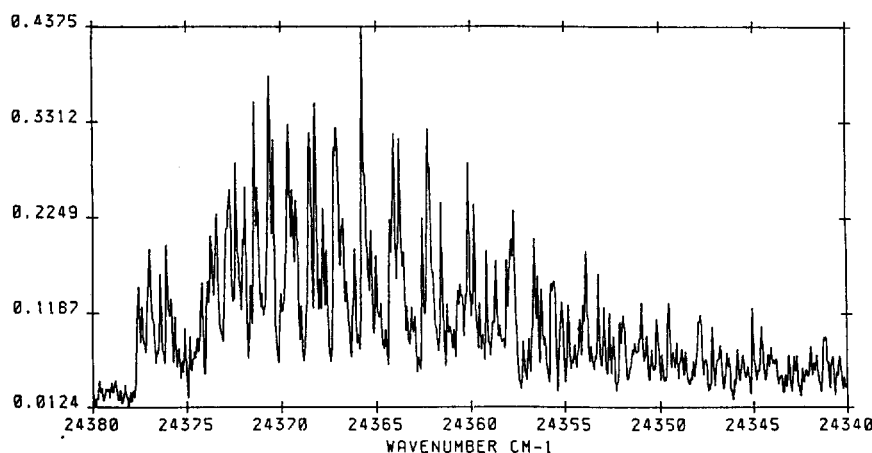


Fig. 4. High resolution emission spectrum of CH_3S at the resolution of 0.05 cm^{-1} . This spectrum corresponds to the transition of $A\ ^2A_1 \rightarrow X\ ^2E_{3/2}\ 3_2^0$. For this spectrum, emission has been integrated for 8 hrs with an interference optical filter of window range of 10 nm.

emission spectra⁹. The vibrational peaks of CH_3S shown in Fig. 3 can be easily assigned according to the previous paper¹¹ using the LIF method. With confidence obtained from the survey spectrum, we have tried to obtain higher resolution spectrum of CH_3S at resolution = 0.05 cm^{-1} shown in Fig. 4. For this spectrum, 1000 scans over 8 hrs have been averaged. From this spectrum, we can see the clearly resolved rotational structure whose analysis is in progress. The rotational temperature of the molecule produced in this method is believed to be about 60 K from the fitting to the observed spectra¹².

CONCLUSION

From the above results, it has been shown with FT UV/VIS spectrometer that the ordinary method used for absorption spectroscopy is not very helpful for emission spectroscopy of the unstable species which emit very weak radiation. However, the modification of the scanning mode has improved the quality of the spectra of unstable species. In addition, the use of the very sensitive detector such as a PMT with a proper optical filter increases the ratio of signal to noise of the spectra dramatically. Even though we have improved the ability of FT UV/VIS spectrometer for emission spe-

ctroscopy, the sensitivity of the spectra is limited by the population of the molecules at the upper state. However, the advantages of FT spectrometer such as accuracy of the frequency, high resolution, and scanning speed can be fully used for this purpose over the laser induced fluorescence (LIF) method.

ACKNOWLEDGEMENT

This work was supported by the Korea Science and Engineering Foundation (Grant No. 923-0300-007-2). The author (SKL) thanks The Ohio State University for allowance in taking the experimental data.

REFERENCES

1. R. E. Smalley, B. L. Ramakrishna, D. H. Levy, and L. Wharton, *J. Chem. Phys.* **61**, 4363 (1974).
2. R. E. Smalley, L. Wharton, and D. H. Wharton, *J. Chem. Phys.* **63**, 4977 (1975).
3. W. Gordy and R. L. Cook, "Microwave molecular Spectra", p. 45, John Wiley & Sons, New York, 1984.
4. L. Yu, S. C. Foster, J. M. Williamson, and T. A. Miller, *Chem. Phys. Lett.* **162**, 431 (1989).
5. S. Urban, R. D'Cunha, J. Manheim, and K. N.

- Rao, *J. Mol. Spectrosc.* **118**, 298 (1986).
6. L. Lechuga-Fossat, J. M. Flaud, C. Camy-Peyret, and J. W. C. Johns, *Can. J. Phys.* **62**, 1889 (1984).
7. J. I. Choe, T. Tipton, and S. G. Kukolich, *J. Mol. Spectrosc.* **117**, 292 (1986).
8. E. C. Richard, D. J. Donaldson, and V. Vaida, *Chem. Phys. Lett.* **157**, 295 (1989).
9. K. Ohbayashi, H. Akimoto, and I. Tanaka, *Chem. Phys. Lett.* **52**, 47 (1977).
10. M. H. Suh, S. K. Lee, B. D. Rehfuss, T. A. Miller, and V. E. Bondybey, *J. Phys. Chem.* **95**, 2727 (1991).
11. M. Suzuki, G. Inoue, and H. Akimoto, *J. Chem. Phys.* **81**, 5405 (1984).
12. S. K. Lee, unpublished data.