Millimeter- and Submillimeter-wave Kinetic Spectroscopy of Reaction Intermediates

YASUKI ENDO, HIDETO KANAMORI, and EIZI HIROTA

Institute for Molecular Science, Okazaki 444, Japan

A spectroscopic method has been developed to study chemical reaction processes through *in situ* observation of the time profile of molecular absorptions in the millimeter- and submillimeter-wave regions. The method has been applied to oxidation reactions of unsaturated hydrocarbons initiated by mercury photosensitization. It has also been combined with the excimer laser photolysis to examine photodecomposition processes of SO₂, CS₂, and Cl₂SO, where nascent distributions of photofragments such as SO and CS were measured. Advantages and disadvantages of the method have been discussed in some detail.

KEY WORDS: millimeter-wave and submillimeter-wave kinetic spectroscopy; O + ethylene reaction; O + acetylene reaction; excimer laser photolysis of CS₂; excimer laser photolysis of SO₂; excimer laser photolysis of Cl₂SO.

INTRODUCTION

Optical spectroscopy, in particular laser-induced fluorescence (LIF), has been extensively employed to investigate chemical reaction processes through real-time monitoring of reaction intermediate species. In contrast, spectroscopy in the infrared and microwave regions has rarely been used as a monitoring tool, because its sensitivity has been insufficient to detect short-lived species present in the reaction system. However, recent progress in spectroscopic techniques has been making infrared and microwave spectroscopy of great use for the study of chemical reactions. In fact, Kanamori *et al.*¹ have demonstrated that

infrared diode laser spectroscopy unveiled interesting features of the 193-nm photolysis of SO_2 through observation of vibration-rotation spectra of a photofragment SO.

Optical spectroscopy has obviously an advantage of being highly sensitive. However, quite a large number of molecules do not show any electronic spectra in the wavelength regions easily accessible with conventional techniques. Some molecules do not fluoresce, presumably because of predissociation, preventing the highly sensitive method of LIF from being applied. In contrast, vibration-rotation spectra and rotational spectra are quite abundant for most molecules in the infrared through microwave regions, and may be readily used to monitor molecular species. It should be pointed out that the permanent dipole moment, which governs the intensity of a pure rotational transition, can be measured by observing Stark effects or may be estimated by *ab initio* molecular orbital (MO) calculations. The transition dipole moment, either vibrational or electronic, is much harder to determine both experimentally and theoretically, making it difficult to convert the observed spectral intensity to the abundance of molecules.

There are few limitations on rotational spectroscopy. In the microwave region the pressure broadening is dominant in linewidth, and several hundred millitorr are a practical upper limit on the sample pressure. When the pressure exceeds this limit, the absorption signal would become too broad to be discriminated against the background. Attention should also be paid to the rotational temperature; it can often differ from that of the sample cell. In such cases molecules must be relaxed in rotational freedom by adding some appropriate buffer gases, in order to derive the vibronic population from the intensity of a rotational transition. In spite of these drawbacks, millimeter-(mm-) and submillimeter-(submm-) wave spectroscopy provides information on chemical reaction mechanism which is often complementary to those derived from other methods, as described in the present paper.

In the present study, we initiated chemical reactions by either mercury photosensitization or excimer laser photolysis and monitored photofragments by mm- and submm-wave spectroscopy. We refer to this technique as mm- and submm-wave kinetic spectroscopy. Only a few studies have exploited the photolysis to investigate transient molecules by microwave spectroscopy. Pickett and Boyd² reported an observation of the $N = 1-0$ transition of HCO generated by mercury-

sensitized decomposition of CH_3CHO . They found that this method of HCO generation was more efficient than the $\text{F} + \text{H}_2\text{CO}$ reaction. More recently, Kolbe and Leskovar³ observed transient microwave absorptions of SO and CS produced by the excimer laser photolysis of SO_2 and CS_2 , respectively.

EXPERIMENTAL

Figure 1 shows the experimental setup employed in the present study. The system consists of a frequency-stabilized mm- or submm-wave source, an absorption cell, a detector, and electronic circuitry. A series of klystrons are used as sources of mm-wave in the frequency region below 200 GHz, while submm-wave is generated by multiplying the 80–100 GHz output of a klystron with a Millitech MU4-2T quadrupler.

The mm-wave klystron is stabilized by a Microwave Systems PLS-60 together with a home-made harmonic mixer against an X-band oscillator in the region of 8.2–12.4 GHz, which is either a Varian X-13 klystron or a Watkins Johnson YIG tuned transistor oscillator and acts as an intermediate frequency standard; a modification is made for the phase detector of the stabilizer⁴. The X-band oscillator is stabilized by a Microwave Systems MOS-5 to the 15-MHz output from a YHP 3335A frequency synthesizer used as a primary frequency standard. A YHP 5342A frequency counter monitors the frequency of the X-band

Figure 1 Block diagram of the experimental setup.

oscillator. Both the synthesizer and the counter are controlled by a 16-bit desk-top personal computer NEC 9801E through a GP-IB interface.

The mm- or submm-wave radiation is transmitted through the absorption cell and is detected by a liquid helium-cooled InSb bolometer QMC QFI/2. The response time of the detector is shorter than $1\ \mu\text{s}$, which is short enough for the present study. Strong signals are video-detected, i.e. the detector output is amplified by a low-noise video amplifier with the band-width extending from 0.5 Hz to 500 kHz, and is then fed to a transient digitizer Kawasaki Electronica TMR-80, which consists of an 8-bit 50-ns A/D converter and a 4 kilobyte memory. The digitized data are transferred to the personal computer through a home-made parallel interface and are accumulated in the computer memory. The data transfer rate and the data accumulation routine are optimized so that the repetition rate for data acquisition can be increased up to 30 Hz. For the present study, noise reduction is more crucial than time resolution. Hence eight successive data points are summed up, reducing 4096 data to 512 and degrading the time resolution from 50 ns to 400 ns. The trigger pulse often masks weak signals, but, because this type of interference is reproducible, it is easily eliminated by taking the difference between the signal at the line center and that ± 1.5 or ± 2.5 MHz from the center.

The video-detection is affected quite a lot by low-frequency vibration, especially when the data are integrated for a time interval as long as 100 ms—it is best to place the whole apparatus on a vibration-free desk. In spite of these provisions, the video-detection is often insufficient in sensitivity to observe weak signals, and is replaced in such cases by source frequency modulation. A tone burst signal of 1 MHz chopped at 50 kHz is applied to the repeller of a source klystron, and the signal is demodulated by a phase-sensitive detector (PSD) operated at 100 kHz. The output of the PSD is fed to the transient digitizer. The frequency modulation combined with stray capacity of the PSD increases the response time of the system to about 0.3 ms, but the sensitivity is much improved.

The video-detection, although much less sensitive than source frequency modulation, yields the absorbance of a line in an absolute scale, because it allows us to measure the total output of the detector and the transient absorption signal in the same scale. On the other hand, the source modulation signal intensity depends upon the modu-

lation depth, and care must be taken in converting the PSD output to the signal intensity. A comparison of the signal intensities obtained by the two detection schemes shows that the source modulation signal is about 0.3 times as intense as that by video-detection, a factor being very close to the theoretical value $1/(2\sqrt{2})$ expected when the modulation signal is large enough.

In order to observe the spectrum of a transient species, the signal is integrated for two identical intervals of time, one before and the other after a trigger pulse to initiate the reaction, and the difference between the two resulted signals is recorded, as shown in Figure 2, while the frequency of the microwave source is scanned stepwise. This method, which is referred to as the spectroscopy mode, is used to measure the center frequency and the width of a line, which are required to calculate the abundance of the species responsible for this line.

Two types of absorption cells have been used, as described below. They are pumped by a turbomolecular pump, with a speed of either

Figure 2 Recording of the signal by a two-gated-integrator system: the signals (b) and (a) derived from the transient digitizer are fed into the personal computer to calculate their difference.

200 l/s or 250 l/s, followed by liquid nitrogen traps and a rotary pump. A butterfly valve is placed between the cell and the turbomolecular pump, to adjust the pumping speed. The linear pumping speed in the cell is typically 4–5 m/s, making it necessary to reduce the repetition rate of the experiment as low as 2 Hz. The flow rates of gases are adjusted by mass flow controllers, and their pressures are measured by a capacitance manometer to a precision of 0.1 mtorr.

MERCURY PHOTSENSITIZED REACTION

The mercury sensitized reaction was induced in a quartz cell 1 m in length and 9 cm in inner diameter, as shown in Figure 3. A short pyrex glass tube was attached to each end of the quartz tube in order to install a gas inlet port, a pressure gauge port, and a pumping port. The diameter of the pumping port was made as large as 5.5 cm to maintain a high pumping speed. Both ends of the cell were sealed with Teflon lenses with focal length of about 25 cm. The quartz tube was surrounded by 15 germicidal lamps, 30 W each, which are commercially available. The cell and the germicidal lamps were inserted in an aluminum pipe of 25 cm diameter, in order to reflect all the ultraviolet light back to the cell. A Zeeman coil was wound around the aluminum pipe to generate a magnetic field of 20–30 gauss for picking out

Figure 3 Absorption cell used for mercury-sensitized reactions.

paramagnetic lines from among diamagnetic lines. The coil was also useful for compensating for the Earth's magnetic field. The Hg lamps were lighted on and off by a home-made power supply, with rise and fall times of less than 0.2 ms. The pulse duration was chosen typically to be about 4 ms long. The sample gases were passed over a mercury reservoir prior to introducing into the cell, to saturate with mercury vapor. If the pumping speed was too fast, the amount of mercury in the sample gas was too small to initiate the reaction, and thus the linear pumping speed had to be maintained lower than 4–5 m/s.

Photolysis of $\text{CH}_2\text{CHOCH}_3$, CH_3CHO , and N_2O

The present method has been tested on the following reactions:

where the species underlined were monitored by observing their rotational spectra. Endo *et al.*⁵ have observed the mm-wave spectrum of the vinoxy radical CH_2CHO , and the molecular parameters reported therein were employed to predict the frequencies of transitions in the submm-wave region used for monitoring. An example of the observed signal is shown in Figure 4. By using the ordinary expression for the intensity of a pure rotational transition (see, for example, Eq. (5) of Ref. 11), the observed intensity has been converted to the abundance, as indicated in the ordinate of Figure 4, by assuming an *ab initio* value⁶ of the dipole moment. We have also shown that reaction (2) really generates HCO: its submm-wave spectrum⁷ was observed with a good *S/N* ratio.

It has already been well established that N_2O is efficiently decomposed to $\text{N}_2 + \text{O}$ by mercury sensitized reaction, i.e. reaction (3). This reaction was used in the present study to initiate oxidation reactions. The rate of N_2O decomposition was measured by observing the $J = 14-13$ transition of N_2O at 351 667.8 MHz. A typical value thus obtained was 3.5×10^{14} molecules $\text{cm}^{-3} \text{s}^{-1}$ at 20 mTorr. The rate constant of this reaction is consistent with that of reaction (1) when one takes into account the quantum yield close to 1 for both of the reactions and the quenching cross sections reported for the precursors.

Figure 4 Time profile of the $17_{0,17}$ – $16_{0,16}$ transition of the vinoxy radical generated by mercury sensitized decomposition of methyl vinyl ether. The ordinate represents the abundance of the radical converted from the observed intensity. The lower trace shows the shape of the Hg light pulse.

Oxidation reaction of acetylene

Two channels have been proposed for the oxidation reaction of acetylene:

but the branching ratio has not been settled. Almost no spectroscopic studies have been reported on the HCCO radical until quite recently.^{8,9} Endo and Hirota¹⁰ have observed its pure rotational spectrum for the first time in the submm-wave region, which was employed in the present study to monitor the HCCO radical.

Figure 5 shows examples of the time profiles of the spectra of HCCO and CO generated, respectively, by reactions (4a) and (4b), which were observed by source frequency modulation, since both spectra were quite weak. It is clearly seen that the HCCO signal increases in intensity almost linearly with time while the Hg lamps are on, but starts to decrease as soon as the lamps are switched off. It is thus concluded that HCCO is really a primary product, as reaction (4a) indicates. In contrast, the CO absorption grows much slower than that of HCCO; at the end of each light pulse, the intensity reaches only one-third of the

Figure 5 Time profiles of absorptions of HCCO and CO generated by the reaction of acetylene with atomic oxygen. The transitions employed are $16_{0,16}-15_{0,15} F_1$ and $J = 3-2$ for HCCO and CO, respectively. The intensities have been converted to the abundances, as shown in the ordinate. The lower trace shows the Hg light pulse.

steady-state value. It must also be noted that CO is much more abundant than HCCO; its steady-state concentration is 9.5×10^{11} molecules cm^{-3} . There must be secondary processes which yield CO. They need to be scrutinized more carefully, in order to establish participation of reaction (4b).

The present method has also been applied to a similar system, the $\text{O} + \text{C}_2\text{H}_4$ reaction, and has yielded the branching ratio for the three possible channels, $\text{CH}_2\text{CHO} + \text{H}$, $\text{CH}_3 + \text{CHO}$ and $\text{H}_2\text{CCO} + \text{H}_2$.¹¹

EXCIMER LASER PHOTOLYSIS

For this experiment the quartz cell was replaced by either a 100-cm long or a 50-cm long Pyrex glass tube 10 cm in diameter. One of the Teflon lenses which was on the input side of the cell was exchanged by one of similar design, except that a hole 20 mm in diameter was drilled at a place slightly off from the center, as shown in Figure 6. Either a flat plate or a concave lens with the 10-cm focal length, either being made of fused silica, was fitted to the hole as a window. A fused silica prism was placed just above the input microwave horn to introduce the

Figure 6 Absorption cell used for excimer laser photolysis experiments.

ultraviolet light from an excimer laser Lumonics TE-861T-4 into the cell almost coaxially with the microwave beam. At an initial stage, the 1-m long cell was used with the flat window, but it was later found that the shorter cell equipped with the concave lens window produced transient species more efficiently. The absorption cell was pumped through 2.54 mm diameter bellows 50 cm in length by turbomolecular pump, which limited the effective pumping speed so that the repetition rate of excimer laser shot had to be chosen as less than 2 Hz.

Photolysis of CS₂

Kanamori and Hirota¹² have investigated the same reaction by infrared (IR) diode laser kinetic spectroscopy and have found that CS molecules generated were initially spread over a wide range of vibrational and rotational levels compatible with available energy. As this investigation has demonstrated, infrared spectroscopy allows us to observe vibration–rotation spectra with quite different vibrational and rotational quantum numbers, but it is rather difficult to determine the nascent distribution in each vibrational state quantitatively. It is primarily because experimental conditions, such as overlapping of the excimer and IR laser beams, are quite difficult to reproduce, making it extremely hard to compare the intensities of two lines far apart in wavelength. The intensity measurement is more reliable, although not very accurate, for microwave spectroscopy than for diode laser spectroscopy. This holds particularly for cases where one wishes to derive the vibrational distribution from the intensity of rotational transitions; one needs to compare two rotational transitions of the same rotational

quantum number, but in different vibrational states, which normally appear quite close in frequency. One drawback of rotational spectroscopy is that it covers only a limited range of rotational transitions.

Bogey *et al.*¹³ have reported the mm- and submm-wave spectra of CS up to $\nu = 20$, but no frequency measurements have been performed for the lines in excited vibrational states in the regions of 300–400 GHz. Therefore, such lines were measured in the present study using the spectroscopy mode described above.

Figure 7 illustrates the time profiles of the $J = 3-2$ transition of CS in $\nu = 1$ generated by the 193 nm photolysis of CS₂; trace (b) was obtained for CS₂ of 5 mTorr, whereas trace (a) with 80 mTorr of argon added. It clearly shows that there was no nascent population of CS in $\nu = 1, J = 2$ in the case of pure CS₂. Addition of argon accelerated rotational relaxation, as indicated by a sharper rise of the signal than in the case without argon. The decay of the signal was slower when argon was added. This is perhaps due to the diffusion of CS being decelerated by argon, without affecting vibrational relaxation much. A close examination of Figure 7 indicates that the vibrational population may be estimated from the intensity of the rotational spectrum after the rotational relaxation is completed, provided that other processes

Figure 7 Time profiles of the $J = 3-2$ transition of CS in $\nu = 1$ generated by the 193-nm photolysis of CS₂: (a) 5 mTorr of CS₂ with 80 mTorr of argon added and (b) 5 mTorr of CS₂ only. The ordinate corresponds to absorption intensity in an arbitrary scale.

including chemical reactions are much slower than rotational relaxation.

Figure 8 compares the time profiles of the $J = 7-6$ transitions of CS in $\nu = 0$ up to $\nu = 5$, with 400 mTorr of argon added. At this pressure, the rotational relaxation is completed within $10 \mu\text{s}$. By extrapolating the signals after $10 \mu\text{s}$ to $t = 0$, the nascent vibrational distribution was derived, as shown in Figure 9. It may be decomposed into two components, one being dominant in lower vibrational states, but decreasing rapidly with the vibrational quantum number and the other being widely spread up to very high vibrational states. The former corresponds to the singlet channel, i.e. the channel yielding 1D sulfur atoms and the latter to the triplet channel with sulfur atoms prepared in the 3P ground states. The available energy allows CS molecules to occupy vibrational states of ν up to 5 or 6 in the singlet channel, whereas ν may be as large as, or even greater than, 12 in the triplet channel. Figure 8 shows that the ground-state intensity keeps increasing fairly rapidly with time, notwithstanding that high- ν state intensities do not start to decrease. The reason is not clear at present.

Figure 8 Time profiles of the $J = 7-6$ transitions of CS in $\nu = 0$ up to $\nu = 5$, generated by the 193-nm photolysis of CS_2 . The sample pressures were 10 and 400 mTorr for CS_2 and argon, respectively. The ordinate corresponds to absorption intensity in an arbitrary scale.

Figure 9 Nascent vibrational distribution of CS generated by the 193-nm photolysis of CS_2 .

Photolysis of SO_2

Kanamori *et al.*¹ have reported that $X^3\Sigma^-$ SO generated by the 193-nm photolysis of SO_2 is prepared mainly in $\nu = 2$ (about 70%) and some in $\nu = 1$, through observation of the vibration-rotation spectra of nascent SO. In the present study, an attempt was made to determine the same nascent distribution from the rotational spectrum of SO. Figure 10 reproduces examples of the observed signals, the $J, N = 8, 8-7, 7$ transitions of SO in $\nu = 0$ to $\nu = 3$. The transition frequencies were determined based upon the data of Bogey *et al.*¹⁴ It is seen that SO is mainly prepared in states with $\nu < 3$, although the available energy is large enough to encompass states up to $\nu = 6$. The populations are shown in Figure 11, which were obtained by summing the intensities of all the three spin components. The present results may look to be incompatible with those of Kanamori *et al.*¹, but, if one notes that the latter is derived from vibration-rotation spectra, the discrepancy is not

Figure 10 Time profiles of the $N = 8-7 F_2$ transitions of $X^3\Sigma^-$ SO in $\nu = 0$ to $\nu = 3$, generated by the 193-nm photolysis of SO_2 . The ordinate corresponds to absorption intensity on an arbitrary scale.

Figure 11 Nascent vibrational populations of SO in $X^3\Sigma^-$ generated by the 193-nm photolysis of SO_2 .

Figure 12 Time profiles of the $X^3\Sigma^-$ SO signals for a longer period of time than in Figure 10. The ordinate corresponds to absorption intensity on an arbitrary scale.

so serious, and in fact the two results are consistent. The details will be discussed elsewhere.

Figure 12 reproduces the time profiles for a long period of time. It clearly shows the effect of the vibrational relaxation from excited states. It is interesting to note that the sum of the populations in the $\nu = 0$ to $\nu = 3$ states is almost constant after the rotational relaxation is completed. The population decrease after 5 ms is ascribed to SO being pumped out from the cell and also to SO being eliminated by reactions with other species. Because the decay rate is much faster for SO than for CS, SO is probably eliminated mainly by chemical processes.

Photolysis of Cl_2SO

Three channels have been proposed for the 193-nm photolysis of Cl_2SO ¹⁵

The excess energy is much larger than that of the SO_2 photolysis, and thus $^1\Delta$ SO may also be detected. The rotational spectrum^{16,17} and CO_2 laser magnetic resonance spectrum¹⁸ have already been reported for

Figure 13 The $J = 8-7$ transition of SO in the $a^1\Delta v = 2$ state, generated by the 193-nm photolysis of Cl_2SO . The absorption is given on an arbitrary scale.

$^1\Delta$ SO. In the present study of the Cl_2SO photolysis, $^1\Delta$ SO was in fact detected for the vibrational states of v up to 5. Figure 13 shows an example of the observed spectrum, the $J = 8-7$ transition of SO in the $a^1\Delta v = 2$ state.

CONCLUSION

The present study has demonstrated the potentiality and usefulness of mm- and submm-wave spectroscopy in investigating initial processes of photochemical reactions. The sensitivity of the method has been found to be sufficient to monitor short-lived photofragments and to follow the time profiles of their spectral intensities. Mercury-sensitized reaction and excimer laser photolysis have been employed as a means of initiating chemical reactions. Other methods, such as flash photolysis, may well be exploited without much difficulties. The present system will also be useful for spectroscopic studies of transient molecules which have escaped observations by other methods.

Acknowledgements

The authors thank Professors S. Tsuchiya and S. Koda of the University of Tokyo for helpful discussions and suggestions, especially on mercury photosensitized reactions.

References

1. H. Kanamori, J. E. Butler, K. Kawaguchi, C. Yamada and E. Hirota, *J. Chem. Phys.* **83**, 611 (1985).
2. H. M. Pickett and T. L. Boyd, *Chem. Phys. Lett.* **58**, 446 (1978).
3. W. F. Kolbe and B. Leskovar, *Rev. Sci. Instrum.* **56**, 1577 (1985).
4. H. M. Pickett, *Rev. Sci. Instrum.* **48**, 706 (1977).
5. Y. Endo, S. Saito and E. Hirota, *J. Chem. Phys.* **83**, 2026 (1985).
6. E. S. Huyser, D. Feller, W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.* **104**, 2956 (1982).
7. G. A. Blake, K. V. L. N. Sastry and F. C. DeLucia, *J. Chem. Phys.* **80**, 95 (1984).
8. S. L. N. G. Krishnamachari and R. Venkatasubramanian, *Pramana*, **23**, 321 (1984).
9. G. Inoue and M. Suzuki, *J. Chem. Phys.* **84**, 3709 (1986).
10. Y. Endo and E. Hirota, unpublished results.
11. Y. Endo, S. Tsuchiya, C. Yamada, E. Hirota and S. Koda, *J. Chem. Phys.* **85**, 4446 (1986).
12. H. Kanamori and E. Hirota, unpublished results.
13. M. Bogey, C. Demuynck and J. L. Destombes, *J. Mol. Spectrosc.* **95**, 35 (1982).
14. M. Bogey, C. Demuynck and J. L. Destombes, *Chem. Phys.* **66**, 99 (1982).
15. M. Kawasaki, K. Kasatani, H. Sato, H. Shinohara, N. Nishi, H. Ohtoshi and I. Tanaka, *Chem. Phys.* **91**, 285 (1984).
16. S. Saito, *J. Chem. Phys.* **53**, 2544 (1970).
17. W. W. Clark and F. C. DeLucia, *J. Mol. Spectrosc.* **60**, 332 (1976).
18. C. Yamada, K. Kawaguchi and E. Hirota, *J. Chem. Phys.* **69**, 1942 (1978).