

Plasma diagnosis by high-resolution spectroscopy of transient molecules

Eizi Hirota

The Graduate University for Advanced Studies, Hayama, Kanagawa 240-01, Japan

Abstract: Seven transient molecules, of which four are expected to play important roles primarily in deposition processes in plasma and three mainly in etching processes, were discussed on a basis of high-resolution vibration-rotation infrared spectra. A simple modification of infrared diode laser spectroscopy as referred to as *kinetic spectroscopy* allowed us to observe such spectra as functions of time. Applications of this spectroscopy to the diagnosis of three plasma processes were described to illustrate the potentiality as well as the versatility of the method: silane RF discharge plasma, methane RF and methanol ECR plasmas, and ECR etching plasma.

INTRODUCTION

In most plasmas very complicated chemical reactions take place, and, if we wish to control the plasma, we should know the details of these chemical processes. During chemical reactions there are a few intermediate species, and some of them play important roles in the processes. Most of them are free radicals, *i.e.* species with unpaired electrons, and some others are ionic species. All of these intermediate species are obviously very reactive and thus of short lifetime. So it is quite difficult to detect them and to examine their properties in detail. We should apply methods of high sensitivity and of high selectivity. However, plasmas prevent many sophisticated methods from being applied, because plasmas contain many charged particles and are full of strong light. We have successfully applied infrared diode laser spectroscopy.

In the present paper I will focus attention to seven intermediate key species: CH₃, SiH₃, SiH₂, SiH, CF₃, CF₂, and CF. The first four contribute mainly to deposition processes and the last three to etching processes.

HIGH-RESOLUTION SPECTROSCOPY OF TRANSIENT MOLECULES

The spectra of free radicals differ from those of ordinary molecules because of the contributions of the angular momenta associated with the spin and/or orbital motions of the unpaired electrons. So I will briefly explain the characteristic feature of the vibration-rotation spectra of the seven molecules.

Methyl radical CH₃

The methyl radical is one of the most fundamental organic free radicals, but its high-resolution infrared spectra in the gas phase were observed for the first time in 1981 (ref.1). My group succeeded in observing the ν_2 band, *i.e.* the out-of-plane bending mode by infrared diode laser spectroscopy. We observed not only the fundamental band, but also hot bands $\nu = 2 \leftarrow 1$ up to $4 \leftarrow 3$ and derived the potential function for the out-of-plane bending vibration. The function does not show any potential hump at the origin, namely the methyl radical is a completely planar molecule. I should, however, call attention to the fact that the potential function has a large quartic term, namely it is rather flat at the bottom with sharp rise at the both sides. Because the molecule is of regular triangle shape, the totally symmetric C-H stretching ν_1 band is infrared-inactive. However, two groups (ref.2) have applied Raman spectroscopy to observe the vibration-rotation spectra at high resolution.

We have extended the infrared observation to another mode, ν_3 , which is a degenerate C-H stretching mode and appears at the 3 μm region (ref.3). For a quantitative monitoring of methyl radicals, the ν_2 band may be a little more convenient than the ν_3 band, because ν_2 is a parallel band and its Q branch lines are more easily employed than any other lines. For the quantitative analysis we must convert the observed spectral intensity to the abundance or density of the molecule under study. For this conversion we need to know the transition dipole moment, which is unfortunately quite difficult to determine for transient molecules like free radicals experimentally. In the case of methyl, the intensities of both the ν_2 and ν_3 bands were measured by several groups (ref.4), but for other transient molecules we borrow the values which are calculated by *ab initio* methods and are well calibrated against known data on related molecules.

Because of importance of the methyl radical, its fully deuterated species was also subjected to infrared and Raman spectroscopic investigations (ref.5), and the vibration-rotation spectra are ready used for a quantitative analysis.

There is one more fundamental band, ν_4 , the in-plane bending mode, for which no observations of the spectra have been reported for both of the isotopic species.

Silyl radical SiH₃

This molecule is a silicon analogue of methyl, but its molecular structure is quite different from that of methyl. We observed the ν_2 band by infrared diode laser spectroscopy (ref.6). Most R branch transitions were observed split into two components. This is one of the complications typical of free radicals, namely the splittings are caused by the interaction of the unpaired electron spin with the overall rotation, referred to as the spin-rotation interaction. Furthermore, each vibrational state is split by the tunneling motion into a symmetric and an antisymmetric state, as in a classical example of ammonia, namely the potential function for the ν_2 mode is not of single minimum, but of double minima. The tunneling splitting is one tenth of cm^{-1} in the ground state and about 6.7 cm^{-1} in the first excited state. For a quantitative analysis we must pay attention to this unique potential function.

Recently Sumiyoshi *et al.* (ref.7) extended the infrared diode laser observation to ν_3 , the degenerate Si-H stretching band. This band may also be used for the chemical analysis after properly corrected for the effects of the Coriolis interaction with the ν_1 band.

Silylene SiH₂

This molecule is not a free radical, namely it does not contain any unpaired electrons in the ground electronic state, but it is quite reactive and we regard it as an intermediate species in many chemical reactions.

We observed and analyzed the ν_2 H-Si-H bending band (ref.8). The signal-to-noise ratio of the spectral lines observed for this band was not high, primarily because the lifetime of this molecule is short, and we found this ν_2 band was not strong enough to determine the abundance of SiH₂ in plasma quantitatively. So we decided to extend our measurements to the 5 μm region, where we expect to detect three bands, ν_1 , $2\nu_2$, and ν_3 , of which ν_3 would be the strongest, stronger than ν_2 by a factor of 3 or more, and would thus be most suitable for the quantitative analysis. In this experiment we employed the 193 nm photolysis of phenylsilane, which was found to produce both SiH₂ and SiH; the ν_3 absorption lines of SiH₂ were observed as strong as those of SiH. I have assigned many absorption lines to the three bands and have almost completed the analysis.

Silyldyne radical SiH

The vibration-rotation spectra of this radical have been extensively recorded by Fourier transform spectroscopy (ref.9) and also by laser magnetic resonance spectroscopy (ref.10). Although it is a simple diatomic molecule, the presence of an unpaired electron complicates the energy level structure. It is a Π radical, namely the unpaired electron occupies a π orbital. Because the field is axially symmetric about

the molecular axis, the electron in a π orbital may be regarded to acquire the orbital angular momentum component of one unit along the molecular axis. Then the electron spin angular momentum has also a well-defined component along the molecular axis, its magnitude being $1/2$. These two types of angular momentum components add or subtract each other to result in the total component of $3/2$ and $1/2$ and accordingly the ${}^2\Pi$ state is split into two spin states referred to as ${}^2\Pi_{3/2}$ and ${}^2\Pi_{1/2}$; the splitting is caused by the spin-orbit interaction, its magnitude being equal to the spin-orbit interaction constant. The components of the total angular momentum along the molecular axis are of half-integer because the electron spin participates in the coupling. As a result each rotational state is given the half-integer rotational quantum number. In ${}^2\Pi_{3/2}$ the rotational state starts with $J = 3/2$ and then those with $J = 5/2$, $7/2$, and so on follow, whereas the rotational ladder begins with $J = 1/2$ in the ${}^2\Pi_{1/2}$ state.

There are two equivalent π orbitals, π_x and π_y . When the unpaired electron occupies π_x , the molecular rotations about the x and y axes are no more equivalent. Thus each rotational state is split into two. This phenomenon is called Λ -type doubling. This doubling has been observed in many P and R branch transitions.

Trifluoromethyl radical CF_3

In sharp contrast with methyl, this radical is pyramidal. The fluorine substitution tends to make the molecule nonplanar. The radical with one F atom CH_2F is a quasi-planar molecule, the non-planarity becomes more prominent in the difluorinated species, and finally the trifluoromethyl radical becomes a rigid pyramidal molecule. We then anticipate to observe all four fundamental bands by infrared spectroscopy, but so far only the degenerate C-F stretching band ν_3 was observed and analyzed (ref.11).

Carbon difluoride CF_2

This molecule has been known for some time, because it is quite stable, *i.e.* chemically inert. Now all of the three fundamental bands have been observed and analyzed in detail mainly by Davies' group (ref.12).

Carbon monofluoride radical CF

This is also a ${}^2\Pi$ radical, and the vibration-rotation spectra were observed for both of the spin states (ref.13).

Besides seven species I discussed, there are several other species which might be of considerable importance for plasma studies. The following are such species for which high-resolution spectra have been reported: CCl , SiF , SiF_2 , GeH , GeF , GeF_2 , SiN , Si_2H_2 , $HNSi$, H_2SiO , NCl , C_4Si , Si_2C_3 , C_2Si , H_3^+ , RgH^+ (Rg denoting a rare gas atom), $SiCl^+$, $HOSi^+$, CH_3^+ , SiH_3^+ , and Si_2^- .

INFRARED LASER KINETIC SPECTROSCOPY

In order to observe high-resolution vibration-rotation spectra of transient species that play key roles in processes in plasma, we normally generate them by electric discharge directly in a cell attached to an infrared diode laser spectrometer (ref.14). We need a quite large amount of transient molecules for such studies, and a most common method of generating such species is plasma. Therefore, we may say that the relation between transient molecule and plasma is similar to that between chicken and egg.

The infrared laser beam emitted from a diode laser is split into three parts, one for observing reference spectra, the second for recording fringes generated by an étalon, which are used as scales, and the main part for spectroscopy of transient molecules. The infrared diode laser consists of $PbSnSe$, $PbSe$ or $PbEuSe$ and is available over the nearly entire infrared region. It works at temperatures below the liquid nitrogen temperature. One diode covers a region about 100 cm^{-1} wide, but one mode extends only for 1 cm^{-1} or less. The output typically ranges from 0.1 to 1 mW .

We have modified the infrared diode laser spectroscopic system in order to observe time-dependent

phenomena while keeping the wavelength resolution high (ref.15). We call this method *kinetic spectroscopy*. The modification we made is quite simple; we inserted a transient recorder in the signal detection circuitry and operated it synchronously with, for example, an excimer laser. We may replace the excimer laser by a pulsed discharge source. The output of the transient recorder is fed to a personal computer for processing the signal. Our infrared diode laser spectrometer is sensitive enough to record the signal of molecules as small in number as 10^{11} , whereas one excimer laser pulse contains about 10^{17} photons. So we have a good chance to detect transient species by this device. The response time of this system is about $0.3 \mu\text{s}$, which is determined mainly by the infrared detector; we may use a high-speed detector, but at the expense of sensitivity. I should like to call attention to the fact that it takes about $0.1 \mu\text{s}$ to pass the infrared beam through the cell. I am thus afraid that it would be quite difficult to improve the time resolution of the spectrometer, but even this time resolution provides us with many interesting results.

We have used this system either as a gated integrator or as a signal averager. In the former mode of operation, we set several pairs of time gates of equal length, one before and the other after the experiment starts, integrate the signals collected by the gates while repeating the experiment, and take the differences in signals from the pair gates, while we scan the source diode laser slowly. We thus record time-resolved spectra as many as the number of the pairs of gates. Once we detect signals of a transient species by this mode, we may switch to the second mode, which allows us to follow the time variation of the signal intensity.

APPLICATIONS TO THE DIAGNOSIS OF PLASMAS: THREE EXAMPLES

Silane discharge plasma

The first example is the RF silane discharge plasma resulting in amorphous silicon. We would expect at least three intermediate species SiH_3 , SiH_2 and SiH and wished to clarify their roles in the process. We may achieve this goal by monitoring their vibration-rotation spectra mentioned above.

When we switched on the discharge for 0.45 ms , the signal of SiH_3 grew rapidly and fell off after the discharge was switched off. We repeated the experiment every 28.6 ms and thus found the effective lifetime of SiH_3 to be 10 to 15 ms (ref.16). We could reproduce the decay curve of the SiH_3 signal intensity neither by an exponential curve nor by a second-order reaction model; we needed both a linear and a second-order term. We confirmed that the first-order term was mainly caused by diffusion of radicals and the second-order term by a binary recombination reaction (ref.17).

Our results on SiH_3 may be compared with those on SiH and SiH_2 . We found that the signal of SiH decayed within 1 ms or so, an order of magnitude shorter than the lifetime of SiH_3 (ref.18). It was not possible to determine the abundance and the effective lifetime of SiH_2 quantitatively. The life in the photolysis system mentioned earlier was of the order of $10 \mu\text{s}$.

We have concluded that the most dominant intermediate in silane RF discharge plasma is the silyl radical SiH_3 among the three species. Namely its abundance $8 \times 10^{11} \text{ cm}^{-3}$ is an order of magnitude or more larger than that of SiH (refs.16 and 18). Although we could not determine the density of SiH_2 quantitatively, it certainly does not exceed that of SiH . From the analysis of the decay curve of the SiH_3 signal, we determined the binary recombination rate constant to be $1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is now supported by a few other groups. We also determined the diffusion constants of SiH_3 in hydrogen and in silane (ref.17).

We then proceeded to measure the spatial distribution of SiH_3 in the cell. Although the spatial resolution of infrared laser spectroscopy is not high, we got the population of radicals as a function of distance from the electrodes. From this distribution we estimated the flux of radicals incident to the ground electrode, and, by assuming an appropriate sticking coefficient, we calculated the growth rate of the amorphous silicon film, which agreed quite well with the observed value. We thus conclude that in RF plasma of silane the SiH_3 radical plays the most important roles and the deposition of amorphous silicon takes place mainly by the reaction of SiH_3 radicals with the surface of the substrate (refs.19 and 20).

CH₃ radical density in RF methane plasma and in electron cyclotron resonance CH₃OH and CH₃OH/H₂ plasmas

Goto and his collaborators applied infrared diode laser spectroscopy to monitor methyl radicals in RF methane plasma. They found that the density of methyl radicals was of the order of 10^{12} cm^{-3} and the diamond film formation was highly correlated with the methyl radical density (ref.21).

Goto *et al.* have recently examined an ECR (electron cyclotron resonance) methane plasma. In this case the methyl radical was as small in number as 10^{10} cm^{-3} , compared with 10^{12} cm^{-3} in RF plasma. They got, however, an order of magnitude more methyl radicals from methanol and methanol/hydrogen plasmas, suggesting that these materials are better suited than methane for diamond film formation by ECR plasma (ref.22).

CF_x (x = 1-3) radical densities in ECR etching plasmas

Goto and his coworkers focussed attention to etching processes by monitoring carbon fluoride molecules as intermediates. The precursors used include perfluorocyclobutane C₄F₈, fluoroform CHF₃, carbon tetrafluoride CF₄, and hexafluoroethane C₂F₆. Because most C-F stretching bands appear in a narrow wavelength region, the spectra of intermediates are often overlapped by those of precursors and/or products. However, by taking the difference between the spectra with discharge on and discharge off, Goto *et al.* could measure the spectral intensities of carbon fluoride intermediates accurately.

Goto *et al.* examined the microwave power dependence of the spectral intensities of three intermediate species CF, CF₂ and CF₃ and found that the three species behaved quite differently. This fact provides us with a means of preferring one species to another (ref.23). Goto also observed another type of differential dependencies on the amount of hydrogen added.

One of the most remarkable results of these studies is that preferential injection of CF₂ combined with a few other parameters adjusted allows us to selectively etch SiO₂ on the silicon surface (ref.24).

CONCLUSION AND FUTURE PROSPECTS

My group has shown in collaboration with Professor Goto's group at Nagoya University that infrared diode laser spectroscopy provides us with detailed information on chemical processes taking place in plasmas which is difficult or almost impossible to obtain by other methods. A most serious limitation of infrared spectroscopy is the low sensitivity. This is primarily ascribed to the low output power of the source diode. The infrared diode is often difficult to operate and is of short lifetime. These difficulties will be eliminated by introducing more powerful infrared sources. One of the most promising sources would be the difference-frequency laser system; its working region has recently been extended down to 10 μm , although the conversion efficiency of the mixing element is still quite low (ref.25). Another candidate would be the quantum-well laser (ref.26). We may also anticipate that remarkable progress in the pulsed laser technology will revolutionize the spectroscopy in the infrared region. It would become possible for us in near future to cover the entire infrared region with tunable pulsed lasers of high output power and also of high spectral resolution.

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