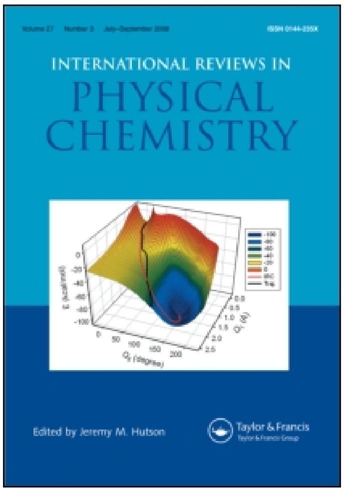

International Reviews in Physical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

Transient molecules, free radicals and molecular ions, investigated by high-resolution spectroscopy

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To cite this Article Hirota, Eizi(1989) 'Transient molecules, free radicals and molecular ions, investigated by high-resolution spectroscopy', International Reviews in Physical Chemistry, 8: 2, 171 — 205

To link to this Article: DOI: 10.1080/01442358909353228

URL: http://dx.doi.org/10.1080/01442358909353228

INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1989, VOL. 8, NOS. 2/3, 171–205

Transient molecules, free radicals and molecular ions, investigated by high-resolution spectroscopy

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High-resolution spectroscopic techniques, in particular microwave and infrared diode laser spectroscopy, have been applied to detect, identify and characterize transient molecules such as free radicals and molecular ions in the gas phase through the observation of their rotational, rovibrational and/or rovibronic spectra. Some recent results are discussed in detail. Kinetic spectroscopy has been developed in the infrared and microwave regions to clarify chemical and physical processes involving transient molecules; photochemical and photo-induced reactions are investigated by recording the spectra of intermediate species with this technique in real time. Two applications of spectroscopy of transient molecules are mentioned; one is detection and identification of interstellar molecules and the other is development of a means for diagnosing discharge plasmas such as those employed for making thin films of amorphous silicon.

1. Historical background

The present article reports spectroscopic studies of transient molecules of small size in the gas phase carried out in Japan using high-resolution techniques mainly in the microwave and infrared regions. Transient molecules, in particular free radicals with unquenched electron spin and/or orbital angular momenta, play important and unique roles in the field of molecular structure; their high-resolution spectra exhibit fine and hyperfine structure, which provides us with detailed information on the electronic structure of the molecules. Transient species also act as intermediates in chemical reactions, and thus the confirmation of their presence in chemical systems is a prerequisite for clarifying the reaction mechanism. High-resolution spectroscopy will allow us not only to identify intermediate species, but also to determine their populations in each rovibronic level in real time. We find high-resolution spectra of transient molecules to be significant in many fields: astrophysics, environmental science and processes in factories.

When the present author started, together with Takayoshi Amano, a study of transient molecules with microwave spectroscopy in 1962, Herzberg's group in Ottawa had already achieved outstanding results on free-radical studies by combining the technique of flash photolysis with high-resolution electronic spectroscopy (Herzberg 1966). In the infrared, matrix-isolation techniques have been developed successfully to record the vibrational spectra of free radicals. However, because of the inherently low sensitivity of infrared spectroscopy, almost no gas-phase spectra had been reported on transient molecules, except for the pioneer studies of Pimentel and his co-workers (Herr and Pimentel 1965), who developed the so-called rapid-scan infrared spectrometer.

The first observation of the microwave spectrum of a free radical was accomplished by Townes and his co-workers (Dousmanis *et al.* 1955), who succeeded in observing a number of Λ-doublet transitions of the OH radical. To the knowledge of the present author, Costain, Lide, Myers and others also tried to observe the microwave spectra of

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free radicals, but did not succeed until around 1963; most microwave spectroscopists were rather pessimistic in applying their techniques to the study of free radicals.

Amano and Hirota spent a few years without obtaining any results. After several trials, they arrived at the conclusion that sulphur monoxide would be one of the free radicals to be studied first and electric discharge in some sulphur- and oxygen-containing molecules would be the most efficient method of producing SO. This was the case: they succeeded in observing the microwave spectrum of SO. Soon after this success, two papers were published in *J. chem. Phys.* reporting detection of SO by microwave spectroscopy (Powell and Lide 1964, Winnewisser *et al.* 1964). Amano *et al.* (1967, 1968a) went on to the observation of the spectra of $^{32}S^{16}O$ in the first excited vibrational state and also of the $^{33}S^{16}O$ and $^{34}S^{16}O$ species; the former gave the equilibrium molecular constants and the latter provided us with information on the electronic structure through the ^{33}S hyperfine parameters.

Amano and his co-workers then extended the microwave study to ClO (Amano *et al.* 1968b, 1969a, Amano and Hirota 1977), NS (Amano *et al.* 1969b), NCO (Saito and Amano 1970, Amano and Hirota 1972b), SF (Amano and Hirota 1973) and BrO (Amano *et al.* 1972a). S. Saito also entered this field, and succeeded in detecting SO in $X^3\Sigma^-$ (Saito 1969) and in $a^1\Delta$ (Saito 1970), HCO (Saito 1972), IO (Saito 1973), HO_2 (Saito 1977, Saito and Matsumura 1980) and HNO (Saito and Takagi 1972, 1973, Takagi and Saito 1972). Progress was rather slow, until a new research institute, the Institute for Molecular Science (IMS), was founded in 1975 in Okazaki, where the present author's group advanced the study by developing several new spectroscopic techniques such as infrared diode laser spectroscopy. Microwave spectroscopy was extended to shorter-wavelength regions to increase the effective sensitivity. The results obtained by this group are summarized in review articles (Hirota 1980, 1983, 1985b, Kawaguchi *et al.* 1983c, Saito *et al.* 1984b, Hirota and Kawaguchi 1985, Hirota and Saito 1987, Endo *et al.* 1987a) and in a book (Hirota 1985a). Table 1 summarises the transient molecules investigated at the Institute for Molecular Science.

2. Experimental methods

The spectroscopic methods used for studying transient molecules must be of a high sensitivity, so electronic spectroscopy would be a reasonable choice. Recent advances in tunable lasers in the visible, ultraviolet, and even vacuum-ultraviolet regions give further credit to this choice. However, the author's group chose spectroscopy in longer-wavelength regions (i.e. microwave and infrared). They thought that one could achieve much higher resolution and thus obtain detailed results on transient molecules, although limited mainly to the ground electronic state.

The author's group overcame the difficulties inherent in millimetre- and submillimetre-wave spectroscopy, namely generation, transmission and detection of the radiation, by employing a free-space cell made of a Pyrex glass tube, typically 12 cm in diameter and 1 m in length, sealed at each end with a Teflon lens. A glass tube is particularly suitable for studying chemically active species. They found that an InSb detector designed for far-infrared radiation worked very well for mm- and submm-waves. Fortunately, extremely efficient frequency multipliers have recently become available commercially and have allowed us to reach nearly 400 GHz, or 0·75 mm. The use of a free-space cell necessitated us to give up Stark modulation and replace it with an old technique of microwave spectroscopy, source frequency modulation. The latter technique suffers seriously from reflection of microwaves, but in our arrangement the absorption cell was not fixed to the microwave source or the detector, so that we could

Table 1. Transient species investigated at the Institute for Molecular Science. References without year denote results to be published or published at the time of writing.

Species	Transition	Reference
Diatomic		
LiH, LiD	Vibrational $X^1\Sigma^+$	Yamada and Hirota (1988)
PH, PD	Rotational $X^3\Sigma^-$	Ohashi *et al.* (1984)
AsH	Rotational $X^3\Sigma^-$	Kawaguchi and Hirota (1984)
LiO	Rotational $X^2\Pi$	Yamada *et al.* (1989b)
	Vibrational $X^2\Pi$	Yamada and Hirota
NaO	Rotational $X^2\Pi$	Yamada *et al.* (1989a)
KO	Rotational $X^2\Pi$	Yamada *et al.*
RbO	Rotational $X^2\Sigma^+$	Yamada *et al.*
BO	Rotational $X^2\Sigma^+$	Tanimoto *et al.* (1986a)
AlO	Rotational $X^2\Sigma^+$	Yamada *et al.*
BCl	Rotational $X^1\Sigma^+$	Endo *et al.* (1983d)
SiN	Rotational $X^2\Sigma^+$	Saito *et al.* (1983c)
	Electronic $A^2\Pi$–$X^2\Sigma^+$	Yamada and Hirota (1985) Yamada *et al.* (1988)
C_2	Electronic $d^3\Pi_g$–$a^3\Pi_u$	Suzuki *et al.* (1985c)
CS	Vibrational $X^1\Sigma^+$	Yamada and Hirota (1979) Kanamori and Hirota (1987)
CF	Rotational $X^2\Pi$	Saito *et al.* (1983a)
	Vibrational $X^2\Pi$	Kawaguchi *et al.* (1981a)
CCl	Rotational $X^2\Pi$	Endo *et al.* (1982b)
	Vibrational $X^2\Pi$	Yamada *et al.* (1981a)
SiF	Rotational $X^2\Pi$	Tanimoto *et al.* (1983)
SiCl	Rotational $X^2\Pi$	Tanimoto *et al.* (1984)
GeF	Rotational $X^2\Pi$	Tanimoto *et al.* (1986b)
N_2	Electronic $a^1\Pi_g$–$a'^1\Sigma_u^-$	Yamada and Hirota (1987)
NS	Vibrational $X^2\Pi$	Matsumura *et al.* (1980)
PO	Rotational $X^2\Pi$	Kawaguchi *et al.* (1983a)
	Vibrational $X^2\Pi$	Butler *et al.* (1983)
PS	Vibrational $X^2\Pi$	Kawaguchi *et al.* (1988b)
NCl	Rotational $X^3\Sigma^-$	Yamada *et al.* (1983d, 1986d)
	Vibrational $X^3\Sigma^-$	Yamada *et al.* (1986a)
PF	Rotational $X^3\Sigma^-$	Saito *et al.* (1985b)
	Vibrational $X^3\Sigma^-$	Yamada *et al.* (1987)
PCl	Rotational $X^3\Sigma^-$	Minowa *et al.* (1985)
	Vibrational $X^3\Sigma^-$	Kanamori *et al.* (1985d)
SO	Rotational $a^1\Delta$	Endo *et al.* (1987b)
	Vibrational $X^3\Sigma^-$	Kawaguchi *et al.* (1979) Kanamori *et al.* (1985a, b, c)
	Vibrational $a^1\Delta$	Yamada *et al.* (1978) Kanamori *et al.* (1988)
OF	Vibrational $X^2\Pi$	McKellar *et al.* (1983a)
OBr	Vibrational $X^2\Pi$	Butler *et al.* (1984)
SF	Rotational $X^2\Pi$	Endo *et al.* (1982a)
	Vibrational $X^2\Pi$	Endo *et al.* (1983b)
SCl	Vibrational $X^2\Pi$	Yamada *et al.* (1986c) Tiemann *et al.*
FeO	Rotational $X^5\Delta$	Endo *et al.* (1984a)
Linear		
HBO	Rotational $\tilde{X}^1\Sigma^+$	Kawashima *et al.* (1987a, 1989a)
	Vibrational $\tilde{X}^1\Sigma^+$	Kawashima *et al.* (1986a)
FBO	$\left.\begin{array}{l}\text{Rotational}\\ \text{Vibrational}\end{array}\right\}\tilde{X}^1\Sigma^+$	Kawashima *et al.* (1987b)

Table 1 (*continued*).

Species	Transition	Reference
ClBO	$\left.\begin{array}{l}\text{Rotational}\\ \text{Vibrational}\end{array}\right\}\tilde{X}^1\Sigma^+$	Kawaguchi *et al.* (1982)
HBNH	Vibrational $\tilde{X}^1\Sigma^+$	Kawashima *et al.* (1987c)
C_3 (quasi-linear)	Vibrational $\tilde{X}^1\Sigma^+$	Matsumura *et al.* (1988)
		Kawaguchi *et al.*
CCH, CCD	Rotational $\tilde{X}^2\Sigma^+$	Endo *et al.* (1989)
	Vibrational $\tilde{X}^2\Sigma^+$	Kanamori *et al.* (1987)
		Kanamori and Hirota (1988a, b)
		Kawaguchi *et al.* (1988c)
CCO	Rotational $\tilde{X}^3\Sigma^-$	Yamada *et al.* (1985a)
	Vibrational $\tilde{X}^3\Sigma^-$	Yamada *et al.* (1986b)
BO_2	Vibrational $\tilde{X}^2\Pi$	Kawaguchi *et al.* (1981b)
		Kawaguchi and Hirota (1986c)
NCO	Rotational $\tilde{X}^2\Pi$	Kawaguchi *et al.* (1983b, 1985d)
	Rotational $\tilde{A}^2\Sigma^+$	Suzuki *et al.* (1986)
CCN	Electronic $\tilde{A}^2\Delta$–$\tilde{X}^2\Pi$	Kawaguchi *et al.* (1984)
	Rotational $\tilde{A}^2\Delta$	Suzuki *et al.* (1985d)
CCCO	Rotational $\tilde{X}^1\Sigma^+$	Tang *et al.* (1985)
HCCN	Rotational $\tilde{X}^3\Sigma^-$	Saito *et al.* (1984a)
Bent triatomic		
CH_2, CD_2	Vibrational $\tilde{X}^3B_1$	McKellar *et al.* (1983b)
CCl_2	Rotational $\tilde{X}^1A_1$	Fujitake and Hirota
SiH_2	Vibrational $\tilde{X}^1A_1$	Nishiwaki *et al.*
SiFCl	Rotational $\tilde{X}^1A'$	Fujitake and Hirota
$SiCl_2$	Rotational $\tilde{X}^1A_1$	Tanimoto *et al.*
		Fujitake and Hirota
HCF, DCF	Electronic $\tilde{A}^1A''$–$\tilde{X}^1A'$	Kakimoto *et al.* (1981)
		Suzuki *et al.* (1981, 1984)
		Butcher *et al.* (1984)
		Suzuki and Hirota (1986)
	Vibrational $\tilde{X}^1A'$	Suzuki and Hirota (1988)
HCCl	Electronic $\tilde{A}^1A''$–$\tilde{X}^1A'$	Hirota (1981)
		Kakimoto *et al.* (1983)
HSiF	Electronic $\tilde{A}^1A''$–$\tilde{X}^1A''$	Suzuki *et al.* (1985a)
		Suzuki and Hirota (1986)
HNO	Rotational $\tilde{A}^1A''$	Takagi *et al.* (1980, 1985, 1986)
		Hirota (1986b)
		Takagi *et al.*
HPO	Rotational $\tilde{X}^1A'$	Saito *et al.* (1986a)
NH_2	Vibrational $\tilde{X}^2B_1$	Kawaguchi *et al.* (1980)
	Vibrational $\tilde{A}^2A_1$	Amano *et al.* (1982a)
		Kawaguchi *et al.* (1987a)
PH_2	Rotational $\tilde{X}^2B_1$	Endo *et al.* (1983a)
		Kajita *et al.* (1987)
	Electronic $\tilde{A}^2A_1$–$\tilde{X}^2B_1$	Curl *et al.* (1978)
		Kakimoto and Hirota (1982)
PF_2	Rotational $\tilde{X}^2B_1$	Saito *et al.* (1986b)
PO_2	Rotational $\tilde{X}^2A_1$	Kawaguchi *et al.* (1985c)
SF_2	Rotational $\tilde{X}^1A_1$	Endo *et al.* (1979)
HCO(DCO)	Rotational $\tilde{X}^2A'$	Hirota (1986a)
		Endo and Hirota (1988b)
FCO	Vibrational $\tilde{X}^2A'$	Nagai *et al.* (1981b)
HO_2, DO_2	Rotational $\tilde{X}^2A''$	Saito and Matsumura (1980)
		Saito *et al.* (1983b)

Table 1 (*continued*).

Species	Transition	Reference
	Vibrational $\tilde{X}^2A''$	Nagai *et al.* (1981a)
		Yamada *et al.* (1983c)
		Lubic *et al.* (1984)
		Uehara *et al.* (1985)
		Hirota (1986a)
FO_2	Vibrational $\tilde{X}^2A''$	Yamada and Hirota (1984)
HSO, DSO	Rotational $\tilde{X}^2A''$	Endo *et al.* (1981b)
	Electronic $\tilde{A}^2A'$–$\tilde{X}^2A''$	Kakimoto *et al.* (1980)
		Ohashi *et al.* (1980, 1988)
FSO	Rotational $\tilde{X}^2A''$	Endo *et al.* (1981a)
	Vibrational $\tilde{X}^2A''$	Endo *et al.*
ClSO	Rotational $\tilde{X}^2A''$	Saito *et al.*
ClS_2	Rotational $\tilde{X}^2A''$	Fujitake *et al.*
Symmetric top		
BH_3	Vibrational $\tilde{X}^1A'_1$	Kawaguchi *et al.* (1987b)
CH_3	Vibrational $\tilde{X}^2A''_2$	Yamada *et al.* (1981b)
		Amano *et al.* (1982b)
		Hirota and Yamada (1982)
		Yamada and Hirota (1983a)
SiH_3	Vibrational $\tilde{X}^2A_1$	Yamada and Hirota (1986b)
CF_3	Rotational $\tilde{X}^2A_1$	Endo *et al.* (1982c)
	Vibrational $\tilde{X}^2A_1$	Yamada and Hirota (1983b)
SiF_3	Rotational $\tilde{X}^2A_1$	Tanimoto *et al.*
CH_3O	Rotational $\tilde{X}^2E$	Endo *et al.* (1984b)
		Momose *et al.* (1988)
		Momose *et al.*
CH_3S	Rotational $\tilde{X}^2E$	Endo *et al.* (1986a)
NO_3	Vibrational $\tilde{X}^2A'_2$	Ishiwata *et al.* (1985)
Asymmetric top consisting of more than three atoms		
H_2CS	Rotational $\tilde{a}^3A_2$	
	$\tilde{A}^1A_2$	Suzuki *et al.* (1983, 1985b)
CH_2F	Rotational $\tilde{X}^2B_1$	Endo *et al.* (1983c)
	Vibrational $\tilde{X}^2B_1$	Yamada and Hirota (1986a)
CH_2Cl	Rotational $\tilde{X}^2B_1$	Endo *et al.* (1984c)
CH_2CHO,	Rotational $\tilde{X}^2A''$	Endo *et al.* (1985)
CD_2CDO		Endo and Hirota (1988a)
HCCO, DCCO	Rotational $\tilde{X}^2A''$	Endo and Hirota (1987)
CH_3CO	Rotational $\tilde{X}^2A'$	Endo and Hirota
C_2H_3	Vibrational $\tilde{X}^2B_2$	Kanamori *et al.*
Molecular ion		
HCO^+, DCO^+	Rotational $\tilde{X}^1\Sigma^+$	Hirota and Endo (1988)
	Vibrational $\tilde{X}^1\Sigma^+$	Kawaguchi *et al.* (1985b, 1986b)
HBF^+	Vibrational $\tilde{X}^1\Sigma^+$	Kawaguchi and Hirota (1986a)
CO_2^+	Vibrational $\tilde{X}^2\Pi_g$	Kawaguchi *et al.* (1985a)
$HCNH^+$	Vibrational $\tilde{X}^1\Sigma^+$	Tanaka *et al.* (1986)
		Kajita *et al.* (1988)
$HCCCNH^+$	Vibrational $\tilde{X}^1\Sigma^+$	Kawaguchi *et al.*
H_3S^+	Vibrational $\tilde{X}^1A_1$	Amano *et al.* (1987)
H_2F^+	Vibrational $\tilde{X}^1A_1$	Kawaguchi *et al.*
H_2Cl^+	Vibrational $\tilde{X}^1A_1$	Kawaguchi and Hirota (1986d)
H_2Br^+	Vibrational $\tilde{X}^1A_1$	Kawaguchi *et al.*
CF^+	Vibrational $X^1\Sigma^+$	Kawaguchi and Hirota (1985)

Table 1 (*continued*).

Species	Transition	Reference
FHF^-	Vibrational $\tilde{X}^1\Sigma_g^+$	Kawaguchi and Hirota (1986b, 1987)
$ClHCl^-$	Vibrational $\tilde{X}^1\Sigma_g^+$	Kawaguchi (1988a)
$H_3^+(H_2D^+)$	Rotational $\tilde{X}^1A'$	Saito *et al.* (1985a)
N_2^+	Electronic $A^2\Pi_u$–$X^2\Sigma_g^+$	Miller *et al.* (1984)
Atomic		
He*, Ar*		Nagai *et al.* (1982)
Cl*		Kajita *et al.*
He^+, Ar^+		Yamada *et al.* (1985b)

adjust their relative positions to reduce the effect of reflection to some extent. A personal computer compensates for the background distortion by fitting the baseline to a polynomial function, provided that the distortion is much smoother in frequency than the absorption signal. The computer accumulates the signals obtained by repetitive scanning of the microwave source, averages and smoothes the resulted spectrum, and reads out the centre frequencies of absorption lines. Figure 1 reproduces the block diagram of the spectrometer the author's group has been using (Endo and Hirota 1987).

When the author's group started a study of transient molecules at the IMS in 1976, it was difficult to generate tunable laser light in the infrared. Therefore, the author's group started with a laser-magnetic-resonance (LMR) spectrometer using a CO_2, N_2O, or CO laser as a source (Yamada *et al.* 1978). Although the high performance of LMR is well recognized, the limitation in wavelength coverage makes this method much less attractive than would be expected from its high potentiality. Fortunately, shortly after the author's group started, infrared diode lasers became commercially available over nearly the entire infrared region. Infrared diodes are still at a primitive stage; they are much inferior to the near-infrared diodes such as distributed feedback (DFB) lasers. Nevertheless, they have brought about a new epoch in infrared spectroscopy; both the sensitivity and resolution have been much improved.

Figure 2 illustrates an infrared diode laser spectroscopic system the author's group employs to study paramagnetic molecules (Hirota 1985b). The laser beam is divided into three parts, the first part for recording the fringes of an etalon acting as wavelength markers, the second for observing the spectra of a reference sample used as a wavelength standard, and the last, main part for detecting transient molecules. The absorption cell is of White-type multiple reflection and is also equipped with electrodes to induce discharge within it. A coil winds around the cell to apply a Zeeman field: an a.c. field is superimposed on a d.c. bias to modulate absorption lines. We may also modulate the discharge (Endo *et al.* 1983b). This method is suited to detecting diamagnetic lines of a transient species, because otherwise we must resort to source frequency modulation, which suffers from fringes caused by reflection of the infrared beam and allows us to achieve only moderate sensitivity. The overall performance of the spectrometer is still highly dependent on the quality of the source diode.

There are a number of ways of producing transient molecules. We have three main means of generating short-lived molecules or to initiate reactions leading to them. The one most frequently employed is electrical discharge. We may induce discharge directly in our cell or we may generate some active species in a side arm placed upstream and

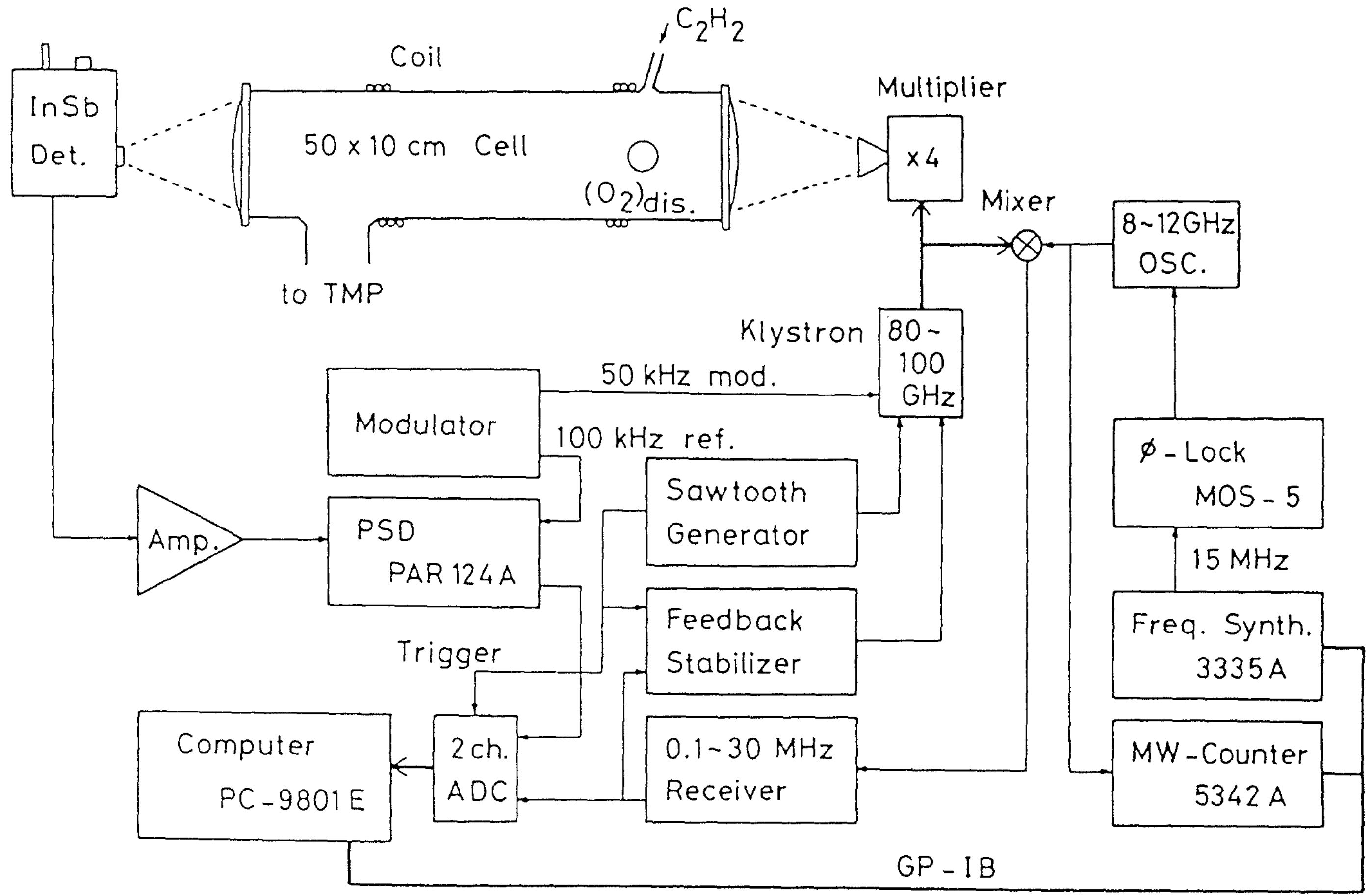

Figure 1. **Block diagram of a submillimetre-wave spectrometer (reproduced from Endo and Hirota (1987) with permission of *J. Chem. Phys.*).**

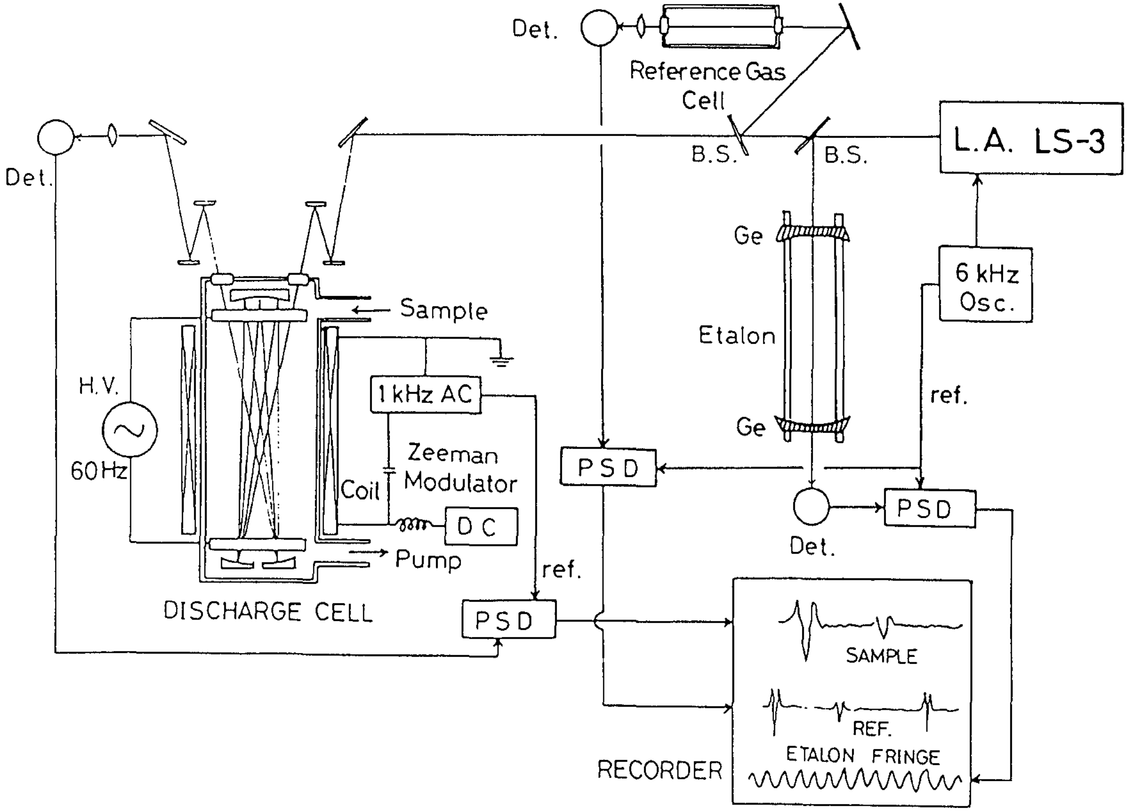

Figure 2. Infrared diode laser spectrometer. Source frequency modulation is employed to record the reference spectrum and the etalon fringes, whereas Zeeman modulation is used to detect the spectra of transient species generated in the discharge cell (reproduced from Hirota (1985b) with permission of Elsevier).

mix them with a second species to create transients of interest in the cell. The intracell discharge can be either d.c. or a.c. (low frequency, e.g. 60 Hz) glow discharge in most cases, whereas microwave discharge is most common in external cases. The discharge is efficient and versatile when generating transient molecules, but suffers from the drawback of making by-products. The second method relies on thermal decomposition or reaction. Because thermal reaction proceeds through contact of precursors with the hot wall of the reaction vessel, it is quite difficult to produce molecules of lifetime shorter than 100 ms or so by this technique. However, we may induce thermal reactions directly in the cell to shorten the time scale of detection. The third technique uses photochemical decomposition of molecules. This method has long remained impractical for absorption spectroscopy in the infrared and microwave regions, simply because ordinary lamps emit an insufficient number of photons. High-power lasers such as excimer or carbon dioxide have recently become available which generate fragment molecules with enough concentration for spectroscopic detection. The photochemical process is in general much cleaner than the discharge, and fragments generated by this process often exhibit interesting quantum-state distributions in a nascent stage. The author's group has combined this technique with time-resolved observation of spectra to develop so-called kinetic spectroscopy (section 4).

3. Examples of structures of free radicals and molecular ions

3.1. *Diatomic free radicals: electronic structure inferred from hyperfine coupling constants*

As listed in table 1, a number of diatomic radicals have been investigated. Microwave studies provide us with a clue to elucidate electronic structure from the observed hyperfine coupling constants. Table 2 lists some $^2\Pi$ radicals, for which we determined the *a*, *b*, *c* and *d* hyperfine constants. Frosch and Foley (1952) defined these constants as

$$a = 2g_N\beta\beta_N\langle r^{-3}\rangle_O, \tag{1}$$

$$b = b_\eta - c/3, \tag{2}$$

$$b_\eta = (8\pi/3)g_S g_N\beta\beta_N\langle\delta(0)\rangle_S, \tag{3}$$

$$c = (3/2)g_S g_N\beta\beta_N\langle(3\cos^2\theta - 1)/r^3\rangle_S, \tag{4}$$

$$d = (3/2)g_S g_N\beta\beta_N\langle\sin^2\theta/r^3\rangle_S, \tag{5}$$

Table 2. Hyperfine coupling constants of $^2\Pi$ radicals.

Constant (MHz)	CF	CCl	SiF	SiCl
$2g_N\beta\beta_N\langle r^{-3}\rangle_O$	705·82	80·199	312·35	43·67
$g_S g_N\beta\beta_N\langle r^{-3}\rangle_S$	674·59	69·06	300·7	39·4
	(1·00)	(1·00)	(1·00)	(1·00)
$g_S g_N\beta\beta_N\langle(3\cos^2\theta - 1)/r^3\rangle_S$	−235·15	−26·3	−117	−14·0
	(−0·35)	(−0·38)	(−0·39)	(−0·36)
$g_S g_N\beta\beta_N\langle\sin^2\theta/r^3\rangle_S$	528·11	54·808	239·3	30·93
	(0·78)	(0·79)	(0·80)	(0·78)
$g_S g_N\beta\beta_N\langle\delta(0)\rangle_S$	151·64	−1·2	68	2
s-character (%)	0·29	−0·02	0·13	0·03
spin density (%)	15·3	15·7	6·8	9·0

where g_S and g_N denote the electron spin and the nuclear g factors respectively, β and β_N the Bohr and nuclear magneton respectively, and r and θ stand for the distance of the unpaired electron from the nucleus involved in the hyperfine interaction and the angle between the $\mathbf{r}$ vector and the molecular axis respectively. The averages $\langle \ldots \rangle_O$ and $\langle \ldots \rangle_S$ are taken over the spatial and spin coordinates of the unpaired electron respectively. The b_π term is referred to as the Fermi contact term and is proportional to the probability of finding the unpaired electron at the nucleus (i.e. $\delta(0)$). The a term is caused by the magnetic interaction of the unpaired electron orbital motion with the nuclear moment, whereas the rest are ascribed to the electron spin and nuclear spin–magnetic dipole interaction. We may calculate $g_S g_N \beta \beta_N \langle r^{-3} \rangle_S$ from $d+c/3$ and compare it with a. The two values are quite close for the four radicals listed in table 2. According to equations (4) and (5), c and d are equal to $-(2/5)$ and $(4/5)$ times $g_S g_N \beta \beta_N \langle r^{-3} \rangle_S$ respectively, if the unpaired electron occupies a pure p_π orbital. The observed constants satisfy these relations closely, as the ratios given in parentheses indicate. The Fermi term gives an estimate for the s character of the unpaired electron orbital, because it involves $\langle \delta(0) \rangle_S$, whereas $g_S g_N \beta \beta_N \langle r^{-3} \rangle_S$ may be converted to the spin density, by comparing both values with corresponding data on a free atom, either F or Cl in the present case. The s character is negligibly small, confirming that the unpaired electron orbital is essentially a p_π orbital. The spin density at the halogen atom is much less than 50%, indicating that the unpaired electron is more localized on the carbon or silicon atom. The unpaired electron orbital 3π in CCl, for example, may be regarded as consisting of a carbon $2p_\pi$ and a chlorine $3p_\pi$ orbital,

$$(3\pi) = (0{\cdot}843)^{1/2} 2p_\pi(\mathrm{C}) - (0{\cdot}157)^{1/2} 3p_\pi(\mathrm{Cl}).$$

The next highest π orbital, 2π, will be approximately given by

$$(2\pi) = (0{\cdot}157)^{1/2} 2p_\pi(\mathrm{C}) + (0{\cdot}843)^{1/2} 3p_\pi(\mathrm{Cl}).$$

Because (3π) and (2π) are occupied by one and four electrons respectively, the total number of π electrons in Cl is $0{\cdot}157 + 4 \times 0{\cdot}843 = 3{\cdot}529$ (i.e. 0·471 electrons are transferred from Cl to C).

Similar analysis can be applied to other free radicals. If both nuclei have finite spin, the spectra will be very complicated, but by analysing them we can get more detailed information on the electronic structure. Examples include NCl (Yamada *et al.* 1983d, Yamada *et al.* 1986a, d), PF (Saito *et al.* 1985b) and PCl (Minowa *et al.* 1985).

Yamada *et al.* have recently investigated a series of metal monoxides, LiO (Yamada *et al.* 1989b), NaO (Yamada *et al.* 1989a), KO, RbO and AlO. The hyperfine constants obtained for the former four radicals are almost completely understood by the ionic form M^+O^-. The unpaired electron occupies a p_π orbital in LiO, NaO and KO in the ground electronic state, whereas the electron goes in a p_σ orbital in RbO. In other words, the ground electronic state is Π for the former three radicals, but the lowest Σ state passes the Π state somewhere between KO and RbO and becomes the lowest electronic state for RbO. The hyperfine structure of AlO requires three electron configurations, AlO, Al^+O^- and $Al^{2+}O^{2-}$; Al, Al^+ and A^{2+} will then have the configurations $(3s)^2(3p)^1$, $(3s)^2$ and $(3s)^1$ respectively, and thus Al and Al^{2+} contribute to the $\langle (3\cos^2\theta - 1)/r^3 \rangle_S$ and $\langle \delta(0) \rangle_S$ terms respectively, whereas Al^+ has nothing to do with hyperfine interactions. The proportions of the three configurations are estimated to be 67·8, 13·1 and 19·1% respectively.

3.2. *Planarity of MH_3 molecules*

Walsh has developed a molecular-orbital approach to predict the geometries of simple molecules. In one of his series of papers (Walsh 1953) he discussed the planarity of MH_3-type molecules. Because both the $2a_1$ and 1e orbitals favour a planar configuration, there is almost no doubt that BH_3 will be planar; the ground-state electron configuration of BH_3 is $(1a_1)^2(2a_1)^2(1e)^4$. The next lowest molecular orbital is $3a_1$ which, according to Walsh, gets lower as the HMH angle decreases, as electrons in this orbital tend to make the molecule pyramidal. Ammonia (with $(1a_1)^2(2a_1)^2(1e)^4(3a_1)^2$) is pyramidal in accordance with this expectation, although the barrier height is not high, so that the inversion splitting is appreciable, even in the ground state. Walsh's theory cannot predict the geometry of the methyl radical. Although he favoured a nonplanar structure, Herzberg (1961) concluded from the electronic spectra of CD_3 that the molecule was planar or almost planar.

The author's group succeeded in observing the ν_2 band of the methyl radical in the 600 cm^{-1} region using an infrared diode laser spectrometer with Zeeman modulation (Yamada *et al.* 1981b). We found that CH_3 radicals could be produced by passing many CH_3-containing molecules through discharge: examples were CH_3I, $(CH_3)_2CO$, CH_3SH, CH_3OH, and CH_4. The best source was di-*tert*-butylperoxide, $(CH_3)_3COOC(CH_3)_3$, which Professor H. Iwamura suggested we use; the molecule could be decomposed thermally at 350 to 400°C, but 60 Hz discharge in it was found to be much more efficient.

We could have observed not only the fundamental band, but also two hot bands, $v_2 = 2 \leftarrow 1$ and $3 \leftarrow 2$, and have derived the potential function for the ν_2 out-of-plane bending mode. The function does not show any hump at the planar configuration, establishing the planarity of the molecule conclusively. The quartic term of the potential function is, however, anomalously large.

It has been predicted theoretically that, when hydrogen atoms of the methyl radical are replaced by electronegative atoms or groups, the molecule tends to become nonplanar. Yamada and Hirota (1983b) have shown that the CF_3 radical takes a fairly rigid pyramidal structure. Then questions arise as to the structures of two intermediate molecules, CH_2F and CHF_2. Unfortunately it has been quite difficult to find an appropriate precursor for the latter molecule. The author's group investigated the former and found that the molecule is almost, but not completely, planar; the inertial defect was found to be negative, $-0{\cdot}0090$ uÅ^2 even in the ground state and a low-lying vibrational state was detected at about 300 cm^{-1} above the ground state (Endo *et al.* 1983c). These data may be compared with those on a molecule with a less electronegative substituent, CH_2Cl: $0{\cdot}0333$ uÅ^2 (Endo *et al.* 1984c) and 400 cm^{-1} (Jacox and Milligan 1970, Andrews and Smith 1970). The latter molecule behaves normally; nothing has been observed to indicate nonplanarity.

It is well known that atoms in the third row of the periodic table have valence angles much smaller than those of the corresponding second-row elements; the valence angles are close to 90° in most cases. This tendency may be explained by the larger energy difference between the p and s orbitals in a third-row element than in a second-row element. In other words, sp^3 hydridization is less important in the former than in the latter. Therefore we may expect that the silyl radical is nonplanar, in contrast with the methyl radical. Yamada and Hirota (1986b) have shown that this is the case, but the molecule also executes inversion, as in the case of ammonia. They observed the ν_2 band to be split into two components, one at 727·9438 (11) and the other at 721·0486 (9) cm^{-1}, which were assigned to $v_2 = 1^- \leftarrow 0^+$ and $1^+ \leftarrow 0^-$ respectively. They fitted these two origins by assuming two types of inversion potential function, one being based upon a vibronic interaction model and the other an ordinary quartic–quadratic type:

$$V(z)=(k/2)z^2+(\Delta E/2)-\tfrac{1}{2}(\Delta E^2+4a^2z^2)^{1/2}, \tag{6}$$

$$V(z)=az^4-bz^2, \tag{7}$$

where z denotes the inversion coordinate and k, ΔE, a and b are parameters. For equation (6), ΔE was rather arbitrarily fixed at $5\times 10^4\,\mathrm{cm}^{-1}$. Two parameters, k and a in equation (6) and a and b in equation (7), were then varied to reproduce the two band origins. The height of the potential barrier and the splittings in $v_2=0$ and $v_2=1$ thus calculated are listed in table 3. The equilibrium inversion coordinate z_0 was combined with the B_0 rotational constant to calculate two structure parameters r_0(Si–H) and θ_0(HSiH), which are also included in table 3. Johnson *et al.* (1989) have recently observed multiphoton ionization spectra of SiH_3 and SiD_3, and derived the vibrational term values in the ground electronic state up to $v_2=3$. Although the precision of their data is three to four orders of magnitude lower than that of Yamada and Hirota's experiment, they may have obtained more realistic potential barriers; 1935 and $1925\,\mathrm{cm}^{-1}$ for SiH_3 and SiD_3 respectively. The infrared spectra of SiH_3 are extremely useful in diagnosing silane discharge plasmas, as are discussed in the last section.

The present author's group observed the ν_2 band of BH_3 generated by the photolysis of B_2H_6 or BH_3CO at 193 nm and by a discharge in a B_2H_6/He mixture (Kawaguchi *et al.* 1987b). They succeeded in recording the Q branch series with $J=K$, but did not observe other branches. The Q series observed was also found to be perturbed, probably by a Coriolis interaction with the ν_4 state. Thus Kawaguchi *et al.* could not have established the planarity of the BH_3 molecule.

3.3. *HBO, FBO, ClBO and HBNH*

No spectroscopic data have been reported on XBO in the gas phase, where X is either hydrogen or a halogen. This is in sharp contrast with XBS and XBSe, for which extensive studies have been carried out using microwave or infrared spectroscopy.

Kawashima *et al.* (1986a) have recently succeeded in detecting HBO by infrared diode laser spectroscopy; they generated the molecules by an a.c. discharge in a mixture of B_2H_6, O_2 and He with the partial pressures of 100, 100 and 230 mTorr respectively, and detected the absorption signals in synchronization with the discharge. Subsequently Kawashima *et al.* (1987a) observed the pure rotational spectra of HBO and its isotopic species, in the ground vibrational state and in excited vibrational states. They employed all the rotational and vibrational–rotational data to calculate the

Table 3. Inversion potential barrier and molecular structure of the SiH_3 radical.

	Equation (6)	Equation (7)
$V_{\max}$ (cm^{-1})	1868	1728
ΔE_0 (cm^{-1})	0·144	0·079
ΔE_{1_0} (cm^{-1})	6·75	6·82
z_0 (Å)	0·465	0·509
r_0(Si–H) (Å)	1·468	1·456
θ_0(HSiH) (degrees)	110·5	108·5

Table 4. Molecular structures of XBO, XBS and XBSe.

		r(X–B) (Å)	r(B–M)† (Å)
XBO	X = H	1·16667 (41)‡	1·20068 (10)‡
	F	12833 (7)§	1·2072 (7)§
	Cl	1·68200 (28)¶	1·20563 (35)¶
XBS	X = H	1·1698 (4)‡	1·5978 (1)‡
	Cl	1·681 (1)§	1·606 (1)§
XBSe	X = Cl	1·664 (2)§	1·751 (2)§

† M = O, S, or Se.

‡ r_e.

§ r_s.

¶ r_m (r_m is a good approximation for r_e).

equilibrium structure and the second- (i.e. harmonic) and third-order potential constants (Kawashima *et al.* 1989a). The equilibrium bond lengths thus derived are r_e(H–B) = 1·166 67 (41) Å and r_e(B–O) = 1·200 68 (10) Å. They also noticed that the ν_1 state of $D^{11}BO$ is in Coriolis resonance with the $\nu_2 + \nu_3$ state.

In searching for the ν_2 band of BO_2 in a 60 Hz discharge system of a BCl_3/O_2 mixture, Kawaguchi *et al.* (1982) found the ν_3 B–Cl stretching band of ClBO. They also applied microwave spectroscopy to derive detailed information on the structure of the molecule. Kawashima *et al.* (1987b) extended a similar study to a BF_3, O_2 and He system and observed the rotational and the vibrational and rotational spectra of FBO. Table 4 compares the structure parameters of XBO with those of XBS and XBSe.

Kawashima *et al.* (1989b) thought that the NH group is isoelectronic with the O atom and may replace the latter. In fact, HBO is easily trimerized to form boroxane, a six-membered molecule

HB–O–BH–O–BH–O,

and O atoms in this ring may be substituted with NH until we arrive at borazane, a trimer of HBNH, namely

HB–NH–BH–NH–BH–NH.

Kawashima *et al.* (1987c) then tried to observe the spectra of the monomer HBNH and succeeded; HBNH was produced by an a.c. discharge in a mixture of diborane and ammonia. The ν_3 (i.e. mainly B–N stretching) band was observed at 1786·193 02 (72) and 1823·401 07 (86) cm^{-1} for $H^{11}BNH$ and $H^{10}BNH$ respectively, but no pure rotational spectra were detected, presumably because the permanent dipole moment is too small.

3.4. *Free radicals of interest for chemical reactions*

3.4.1. *Vinoxy (formyl methyl) radical*

The vinoxy radical is known to play important roles in many organic reactions including oxidation reactions of olefins. Two electronic bands have been reported, one at 347·7 and the other at 1249 nm, which were assigned to $\tilde{B}^2A'' - \tilde{X}^2A''$ and $\tilde{A}^2A' - \tilde{X}^2A''$ respectively. Heaven *et al.* (1983) and DiMauro *et al.* (1984) resolved the rotational structure of the former band. Endo *et al.* (1985) employed millimetre-wave spectroscopy to derive very detailed information on the molecular structure of the radical, in particular on the hyperfine structure.

Endo *et al.* employed two reactions to generate vinoxy radicals: $C_2H_4+O_2$ (microwave discharge) and $CH_3CHO+CF_4$ (microwave discharge). The latter was found to be several times more efficient than the former, but the former was a much cleaner system. Some low-N, and high-K transitions showed well resolved quartet structure, indicating that two protons among the three were involved in hyperfine interactions. A few lines were found to be further split by up to 0·5 MHz by the coupling with the third proton. Endo *et al.* derived molecular constants from the observed spectra, as listed in table 5.

The spin–rotation interaction constant $\epsilon_{aa} = -898{\cdot}98\,(35)$ MHz is well explained if one takes into account the interaction with the $\tilde{A}\,^2A'$ state located at about 8000 cm^{-1} above the ground state. The negative sign of ϵ_{aa} is consistent with the vinoxy radical in the ground electronic state being a π radical. As shown in table 5, the off-diagonal term T_{ab} of the dipolar hyperfine coupling tensor is determined for the two protons making dominant contributions to the hyperfine interaction and thus allows us to calculate the principal values and the angle between the principal axis and the inertial axis. The results summarized in table 5 clearly indicate that protons 1 and 2 are assigned to those in the CH_2 group, *trans* and *cis* to the oxygen atom respectively. The vinoxy radical in the ground electronic state is mainly of the $\cdot CH_2{-}CH{=}O$ form rather than the $CH_2{=}CH{-}O\cdot$ form, and thus the radical should be called formyl methyl rather than vinoxy.

In order to get more information on the structure of the radical, Endo and Hirota (1988a) investigated the fully deuterated vinoxy radical. The inertial defect shown in table 5 assures the planarity of the radical. By assuming *ab initio* values (Dupuis *et al.* 1982) for the parameters involving hydrogens, after making a simple, but reasonable correction of +0·01 Å for all C–H bond lengths, Endo and Hirota calculated the C–C

Table 5. Molecular constants of the vinoxy (formyl methyl) radical in the ground electronic state.

	CH_2CHO	CD_2CDO
A (MHz)	66676·87 (113)	43228·726 (170)
B (MHz)	11 447·0489 (146)	10064·7201 (70)
C (MHz)	9758·9160 (140)	8155·9795 (65)
Δ (uÅ^2)	0·0576	0·0605

	proton 1	proton 2 (in CH_2CHO)
T_{xx} (MHz)	28·76	28·64
T_{yy} (MHz)	−31·05	−28·73
T_{zz} (MHz)	2·29	0·09
θ (degrees)	31·8	84·9

(x and y are in the molecular plane, x being nearly parallel to C–H. θ denotes the angle between x and a)

$r(C_1{-}C_2)$ (Å)	1·408 (10)	$\theta(C_1C_2O)$ (degrees)	122·4 (1)
$r(C_2{-}O)$ (Å)	1·261 (11)	$\theta(H_1C_1C_2)$ (degrees)	[120·5]
$r(C_1{-}H_1)$ (Å)	[1·080]	$\theta(H_2C_1C_2)$ (degrees)	[120·2]
$r(C_1{-}H_2)$ (Å)	[1·081]	$\theta(H_3C_2C_1)$ (degrees)	[117·8]
$r(C_2{-}H_3)$ (Å)	[1·088]		

(Values in square brackets are assumed)

and C–O bond lengths and the CCO angle, as listed in table 5, which are in fair agreement with *ab initio* results.

The microwave spectrum of vinoxy has been employed to study some oxidation reactions of olefins (Endo *et al.* 1986b); vinoxy is one of the important intermediates in these reactions and its rotational spectrum has proved useful in monitoring its abundance in real time, as discussed in section 4.

3.4.2. *HCCO radical*

It has been argued that oxidation of acetylene by oxygen atoms proceeds in two channels: $C_2H_2 + O \rightarrow CH_2 + CO$ or $HCCO + H$. However, lack of spectroscopic data on HCCO has prohibited any definite conclusion. A few attempts have been reported to observe electronic spectra of the HCCO radical, but the results are not conclusive and some of them have been shown to be erroneous.

The HCCO radical is interesting also from the view point of molecular structure. If the molecule is completely linear, it will have a $^2\Pi$ ground electronic state, like an isoelectronic molecule NCO. As the molecule is bent, the orbital degeneracy is lifted, resulting in two electronic states, one of A′ and the other of A″ symmetry, a phenomena referred to as the Renner–Teller effect. The linearity and energy-level structure of the molecule in the ground electronic state will thus reflect the effect of the Renner–Teller interaction with the other component state.

Endo and Hirota (1987) have succeeded in observing the millimetre-wave spectra of HCCO. They generated HCCO radicals by using two reactions: microwave discharge products of CF_4 with ketene and discharged oxygen with acetylene. The latter was found to be about twice as efficient as the former. An anomalous feature soon became evident for the K_a dependence of the spin splitting; a Padé-type expression was required to reproduce effective $\epsilon_{aa}(K)$ constants, namely

$$\epsilon_{aa}(K) = \epsilon_{aa}/(1 + tK_a). \qquad (8)$$

Table 6. Molecular constants of the HCCO and DCCO radicals.

	HCCO	DCCO
A (GHz)	1243 (45)	652·1 (36)
B (MHz)	10896·788 (41)	9926·8008 (104)
C (MHz)	10766·466 (39)	9755·2316 (126)
Δ_0 (uÅ^2)	0·155 (15)	0·120 (4)
ϵ_{aa} (MHz)	−247 827 (74)	−112 201 (34)
ϵ_{bb} (MHz)	−43·1 (27)	−30·62 (85)
ϵ_{cc} (MHz)	13·8 (27)	10·20 (69)
$\lvert\epsilon_{ab}+\epsilon_{ba}\rvert/2$ (MHz)	1619 (53)	275 (31)
t	0·56493 (97)	0·247246 (171)
	Endo and Hirota (1987)	Harding (1981)
r(C–H) (Å)	1·056 (4)	1·090
r(C–C) (Å)	1·314 (25)	1·320
r(C–O) (Å)	[1·150]	1·150
θ(HCC) (degrees)	138·7 (14)	132·0
θ(CCO) (degrees)	[180]	166·0

(Values in square brackets are assumed)

Table 6 reproduces molecular parameters of primary importance derived for HCCO and DCCO. The inertial defect was calculated from the observed rotational constants to be 0·155 (15) and 0·120 (4) uÅ^2 for the two isotopic species. The molecule is essentially planar. Although only four pieces of information were available, Endo and Hirota found it difficult to reconcile the observed data with a bent CCO structure; a linear chain was much preferred. The structure parameters estimated by Endo and Hirota are included in table 6, where they are compared with those by an *ab initio* calculation (Harding 1981). The apparently short C–H length may be ascribed to a large-amplitude C–H bending motion.

The negative sign of ϵ_{aa} indicates the ground electronic state of HCCO to be of A″ symmetry. When a simplified expression for ϵ_{aa}:

$$\epsilon_{aa} = -4AA_{SO}/\Delta E \tag{9}$$

is used with a spin–orbit interaction constant of 27·1 cm^{-1} (carbon atom) or 158·5 cm^{-1} (oxygen atom), the separation between the excited A′ state and the ground state is calculated to be 540 or 3200 cm^{-1}. Because the unpaired electron spin density is more localized on carbon than on oxygen, the former values $A_{SO} = 27{\cdot}1$ and $\Delta E = 540\,\text{cm}^{-1}$ will be more realistic.

The excited state split from the ground state by Renner–Teller interaction is likely to take a linear structure with levels approximately linear in K_a. The separation between the levels of the excited and ground states specified by the same K_a will thus be approximated by $\Delta E_0 + \omega' K_a$, where ΔE_0 and ω' denote the electronic energy and the bending frequency of the excited state respectively. Therefore t in equation (8) corresponds to $\omega'/\Delta E_0$. As table 6 shows, the t value of DCCO is about one-half that of HCCO, in support for the above interpretation.

The microwave spectrum of HCCO has been applied by Endo and Hirota to explore the oxidation mechanism of acetylene, as discussed in section 4.

3.5. *Carbenes and silylenes*

It has been widely accepted that carbenes CXY play unique roles in the reactions of organic molecules; singlet and triplet carbenes exhibit quite different chemical behaviours in many respects, for instance stereospecificity. However, spectroscopic studies on simple carbenes have been incomplete, only the parent carbene CH_2 being an exception. The study of simple silylenes has been even more behind, in spite of their important roles in organosilicon chemistry.

The present author's group applied high-resolution c.w. dye-laser spectroscopy to HCF (Kakimoto *et al.* 1981, Suzuki *et al.* 1981, Suzuki *et al.* 1984), HCCl (Hirota 1981, Kakimoto *et al.* 1983), and HSiF (Suzuki *et al.* 1985a). These molecules had already been shown to have singlet ground states, and the $\tilde{A}^1A''$–$\tilde{X}^1A'$ transitions of HCF and HCCl had been known to be perturbed extensively. The two states $\tilde{A}^1A''$ and $\tilde{X}^1A'$ may be thought to be derived from a Δ state in a limit of linearity, which is split by Renner–Teller interaction, and thus the interaction between $\tilde{A}$ and $\tilde{X}$ may cause serious perturbations and even some magnetic activities, which are ascribed to the electron orbital and rotation interaction. Many perturbed lines of the $\tilde{A}$–$\tilde{X}$ transition show large Zeeman effects, but in practice the observed Zeeman effects exceed those expected from Renner–Teller interaction in many cases, and have been ascribed to mixing of the $\tilde{A}$ state with the low-lying $\tilde{a}^3A''$ state. Unfortunately it is still difficult to get an overview for the triplet state; *ab initio* calculations gave triplet–singlet separations scattered over several thousand reciprocal centimetres. The $\tilde{A}^1A''$–$\tilde{X}^1A'$ transition of HSiF is, in

Table 7. ^{35}Cl nuclear quadrupole coupling tensors of dichlorocarbene, dichlorosilylene, and related molecules.

	CCl_2	H_2CCl_2	$SiCl_2$	H_2SiCl_2
χ_{zz} (MHz)	−63·40	−76·2	−35·86	−42·0
χ_{xx} (MHz)	58·19	36·2	33·32	21·0
χ_{yy} (MHz)	5·21	39·8	2·54	21·0
(z is parallel to M–Cl and y is perpendicular to the MCl_2 plane)				
i_σ	0·26	0·32	0·59	0·62
π_c	0·32	−0·02	0·18	0·00
$i_c = i_\sigma - \pi_c$	−0·06	0·34	0·41	0·62

contrast, virtually free of any perturbations, and no clue has been available to detect the $\tilde{a}^3A''$ state. In this respect, it might be interesting to note that most simple carbenes have singlet ground states; an exception is methylene. Saito *et al.* (1984a) reported another exception, HCCN; this molecule is unique in that it is linear in the ground triplet state $\tilde{X}^3\Sigma^-$.

Fujitake and Hirota and Tanimoto *et al.* have recently investigated CCl_2 and $SiCl_2$ by microwave spectroscopy; microwave studies allow us to derive electron distribution in the molecules through analysis of the nuclear electric-quadrupole hyperfine structure. The results are shown in table 7, which lists the principal values of the ^{35}Cl nuclear quadrupole coupling tensor calculated from the observed values in the inertial axis system by assuming the z principal axis to be coincident with the M–Cl bond (M = C or Si). It is striking that the tensors of both CCl_2 and $SiCl_2$ deviate much from cylindrical symmetry, which is preserved for most M–Cl single bonds, as is the case for H_2CCl_2 and H_2SiCl_2, included in table 7 for comparison. This non-axial symmetry is caused by π electron backdonation from Cl to M. A simple treatment, of Townes–Dailey type, was applied to the quadrupole coupling tensors to derive the σ-bond ionicity i_σ, the π character π_c, and the total ionicity $i_c = i_\sigma - \pi_c$. As expected, both CCl_2 and $SiCl_2$ have large π characters, 0·32 and 0·18 respectively, and the silylene is further characterized by a large ionicity $i_\sigma = 0·59$.

3.6. *Molecular ions*

Because of the large cross-sections, referred to as the Langevin cross-section, for reactions of ionic species with neutrals, many people thought that high-resolution spectroscopy of ions was impractical. However, this was not the case. Dixon and Woods (1975) succeeded in observing the rotational spectrum of CO^+ generated in a d.c. glow-discharge plasma. In the infrared, Oka (1980) reported the observation of the ν_2 band of H_3^+. Since then Saykally, Amano, and a few other groups have contributed to spectroscopic studies of molecular ions in the infrared and microwave regions (Carrington and Thrush 1988, Maier 1989). Spectroscopy of ions has obviously been motivated by interest in interstellar molecules. Current understanding is that ion–molecule reactions are most crucial in forming these molecules, and thus much effort has been expended to detect key ionic species both in the laboratory and in interstellar space.

Special techniques have been devised to observe the spectra of ions sensitively and selectively. Velocity modulation, developed by Saykally and his co-workers (Gudeman *et al.* 1983) is a good example, and has been widely employed; it is based upon Doppler shifts of ion spectra caused by discharge electric field and allows us to discriminate between positive and negative ions by using phase-sensitive detection of the signals. Kawaguchi *et al.* (1985b) paid attention to the finding of De Lucia *et al.* (1983) that the rotational spectra of HCO^+ and HN_2^+ were enhanced in intensity by a factor of 18 to 20 by applying a magnetic field of 200 G. Although this type of intensity change depends critically upon the sample pressure, Kawaguchi *et al.* thought this effect could be incorporated into a modulation method for detecting ions. They called it magnetic field modulation; the field needed was of the order of 100 G, much smaller than that normally employed for Zeeman modulation.

A large fraction of the molecular ions so far detected are protonated ions MH^+, namely the species formed by attaching a proton to a stable molecule M. These species always have stable molecules as counterparts (an exception would be H_3^+). For example, H_3S^+ is very similar to PH_3 and H_2Cl^+ to H_2S. There are a series of isoelectronic linear molecules of HXY or HXY^+, namely HBF^+, HBO, HCO^+, HCN, HNN^+, HNC and HOC^+. Hirota (1988), by using the Hellmann–Feynman theorem, found that the electrostatic forces acting on H and the end atom are 'larger' in ionic species than in neutral species.

Kawaguchi *et al.* (1985a) succeeded in detecting the ν_3 band of CO_2^+. The most interesting feature of this band is that its origin 1423·0821 (8) cm^{-1} is almost 1000 cm^{-1} smaller than that of the neutral CO_2 and, when combined with $(2\nu_3) = 2938\ cm^{-1}$, derived from electronic spectroscopy (Johns 1964), the hot band $2\nu_3 - \nu_3$ would have the origin at 1515 cm^{-1}, much larger than the fundamental origin. Kawaguchi *et al.* explained these observations by a vibronic interaction between $\tilde{A}\,^2\Pi_u$ and $\tilde{X}\Pi_g$ states through the ν_3 mode. They also thought that the large intensity of the ν_3 band resulted from intensity borrowing from the $\tilde{A}$–$\tilde{X}$ electronic transition.

Kawaguchi and Hirota (1986b) detected a unique ion, FHF^-. The generation of this species required fluorocarbon compounds like CF_4, C_2F_4 and CHF_3 and

Table 8. Molecular constants of FHF^- and FDF^-.

	E_v (cm^{-1})	B (cm^{-1})	D ($10^{-6} cm^{-1}$)	η (cm^{-1})†
FHF^-				
(000)	0·0	0·334183 (10)	0·4305 (44)	
(100)	583·0539 (13)	0·331850 (11)	0·4431 (49)	
(010)	1286·0284 (22)	0·336069 (12)	0·4635 (61)	0·531339 (38)
(001)	1331·1502 (7)	0·316973 (11)	0·4608 (44)	
(101)	1848·6989 (14)	0·314132 (27)	0·4755 (54)	0·3443 (54)
(110)	1858·48 (35)	0·33327 (87)	[0·4643]‡	
FDF^-				
(000)	0·0	0·335787 (13)	0·4240 (18)	
(100)	—	0·333331 (31)	0·427 (28)	
(010)	928·7303 (17)	0·337106 (15)	0·4447 (98)	0·591532 (18)
(001)	934·1933 (7)	0·322944 (14)	0·4565 (69)	
(101)	1469·1852 (8)	0·319687 (43)	[0·464]‡	0·4704 (49)
(110)	1509·55 (53)	[0·3346]‡	[0·464]‡	
(201)	1397·2363 (13)§	0·316151 (29)	0·472 (25)	

† Coriolis interaction matrix element.
‡ Fixed.
§ $E_v(201) - E_v(100)$.

hydrogen. The strong C–F bond would be essential in stabilizing the FHF^- ion generated. Initial observations were made by magnetic field modulation, and later the negative charge was established by velocity modulation. Intensity alternation and the magnitude of the B rotational constant pinned down the species to be FHF^-. Because the 1849 cm^{-1} band was so strong, Kawaguchi and Hirota initially assigned it to the ν_3 fundamental band. The corresponding band of FDF^- was observed at 1397·2363 (13) cm^{-1}.

These ν_3 frequencies are 400 to 500 cm^{-1} higher than the values observed in solid state or predicted by *ab initio* results. Kawaguchi and Hirota carefully examined anharmonicities and other factors to trace the origins of the discrepancies without success. They also repeated searching for the spectra and finally detected the true ν_3 band at 1331·1502 (7) cm^{-1} (Kawaguchi and Hirota 1987). The ν_2 band was found to be very close to the ν_3 band, namely appearing at 1286·0284 (22) cm^{-1} and was in strong Coriolis interaction with ν_3; the ν_2 band was observed only through intensity borrowing from ν_3. No Q branch lines were observed for ν_2. The 1849 cm^{-1} band was reassigned to $\nu_1+\nu_3$. The Coriolis matrix elements which were derived for the ν_3/ν_2 and $(\nu_1+\nu_3)/(\nu_1+\nu_2)$ pairs differ much from those calculated by ordinary second-order vibration–rotation theory, namely they are only 78% and 50% of the calculated values respectively. These observations suggest that the vibrational motions of FHF^- deviate considerably from harmonic.

The band observed for FDF^- at 1397 cm^{-1} needs to be reassigned. Kawaguchi and Hirota found that it was not $\nu_1+\nu_3$, but $2\nu_1+\nu_3-\nu_1$. They observed the ν_3/ν_2 pair at 934·1933 (7)/928·7303 (17) and $(\nu_1+\nu_3)/(\nu_1+\nu_2)$ at 1469·1852 (8)/1509·55 (53) cm^{-1}. The equilibrium rotational constant was calculated to be 0·342 069 (21) and 0·342 119 (31) cm^{-1} for FHF^- and FDF^- respectively; the two values agree within experimental errors. The former value leads to the r_e(F–F) distance of 2·277 71 (7) Å. Table 8 summarizes molecular constants obtained for FHF^- and FDF^-.

4. Kinetic spectroscopy: development and applications to chemical reactions

The experiments described above were carried out in steady state conditions and do not provide us with any dynamical information on chemical processes except for rough estimates of the lifetimes of the species in the reaction cell. It is a natural extension of the research to develop a method which allows us to explore the chemical and physical processes in real time. Such a time-resolved spectroscopic method is referred to as kinetic spectroscopy.

The most serious problem of kinetic spectroscopy is its sensitivity; the major spectroscopic methods that the author's group has been using are absorption spectroscopy, in the infrared and microwave regions, and are inherently low in sensitivity. This drawback may be remedied to some extent, if one can generate transient species in high concentrations, even for a short period of time. Flash photolysis has been widely employed since the success of Norrish and Porter and Herzberg and his co-workers. Recent advances in laser science have produced high-power lasers such as excimer lasers. A feasible approach to kinetic spectroscopy would thus combine either infrared or microwave spectroscopy with excimer laser photolysis. The absorption spectroscopic methods described in section 2 require at least 10^{10} to 10^{12} molecules to record their spectra. An ArF excimer laser typically delivers a pulse of 100 mJ in 10 nm width with the repetition rate of 10 to 50 Hz. One pulse thus contains 10^{17} photons at 193 nm. Even if the quantum yield is as small as 10^{-4}, we may expect to observe the spectra of photofragments.

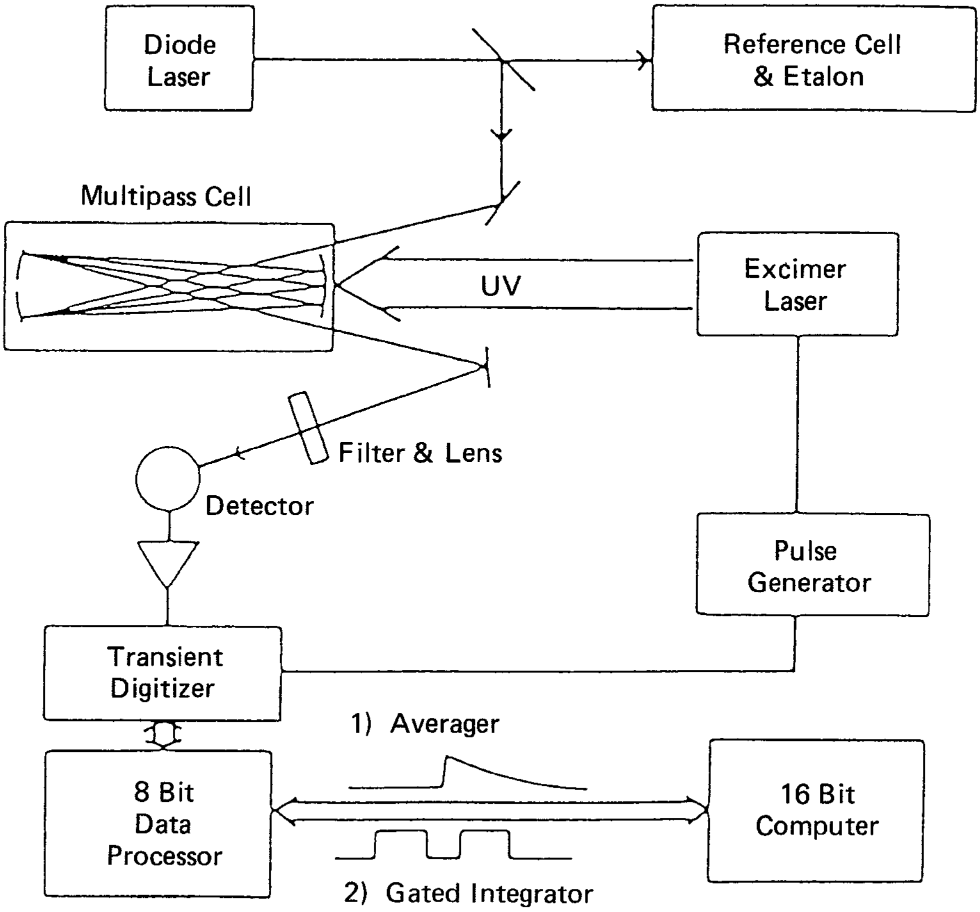

Figure 3. Schematic diagram of an infrared diode laser kinetic spectrometer (reproduced from Kanamori *et al.* (1985b) with permission of *J. Molec. Spectrosc.*).

Figure 3 illustrates a typical arrangement for infrared-diode-laser kinetic spectroscopy (Kanamori *et al.* 1985b, 1985c). A multiple-reflection White-type cell is modified so that the excimer laser beam is introduced to overlap with the infrared beam as closely as possible. The infrared beam, after being detected by an ordinary photovoltaic or photoconductive detector, is fed to a transient recorder, which has a maximum sampling speed of 50 ns per channel for 1024 eight-bit channels. The transient recorder is triggered by the excimer laser pulse. The output is transferred to a 16-bit computer. The repetition rate of data acquisition can be increased up to 50 Hz. This system is capable of two functions, gated integrator and signal averager. The former is used to record time-resolved spectra. We normally set up three pairs of time gates, one before and the other after the excimer laser pulse, and take the differences, while we scan the infrared diode laser slowly. This function eliminates slowly varying signals of precursors or products, unless they are very strong. Once we observe time-dependent signals in this way, we fix the diode laser frequency at the centre or wing of a line and change the function of the detection system to signal averager, which records the time variation of the signal line. The response time of the system is about 0·3 μs, which is mainly determined by the infrared detector and the associated pre-amplifier. This response time is by no means short, but in most cases the nascent distribution can be measured by adjusting the sample pressure.

A similar modification was applied to the microwave spectrometer described in section 2 (Endo *et al.* 1987a). In order to increase the sensitivity the time resolution was degraded from 50 ns to 400 ns. The InSb bolometer detector has a response time shorter than 1 μs. Video detection is affected by low-frequency vibrations, and, if higher sensitivity is required, replaced by source-frequency modulation at the expense of time resolution to 0·3 ms. An excimer laser was used as a photolysis source. An old technique of mercury-sensitized reaction was also employed, although time resolution was as long as a few milliseconds. A typical arrangement is shown in figure 4 (Endo *et al.* 1987a).

When applied to photochemical reactions, infrared-laser kinetic spectroscopy primarily provides us with the nascent distributions of photofragments over vibrational and rotational levels. Because the excimer-laser photon energy, the dissociation energy of the bond in a precursor and the vibrational and rotational energies of the fragment we are looking at are all specified in infrared kinetic spectroscopy, the width of the observed vibration–rotation spectra of photofragments must match exactly the remaining translational energy allocated to the fragment we are observing. The only uncertainties in energy are due to the thermal energy of the precursor and the energy spread of the excimer laser. Kanamori and Hirota (1987) investigated the photolysis of CS_2 at 193 nm by monitoring vibration–rotation spectra of CS. They found that CS fragments are spread over all the vibration–rotation levels that are compatible with the energy balance. Furthermore, the Doppler profile of the CS spectra is well accounted for by taking into account the two channels resulting in sulphur atoms in the ^3P and ^1D states. The contributions of the two channels are nearly equal.

If the upper vibrational state is more populated than the lower state, the transition is expected to appear as an emission, or the infrared laser beam will be amplified. This was in fact the case for SO generated by the photolysis of sulphur dioxide at 193 nm (Kanamori *et al.* 1985a); the $v=2$ state was found to be most populated, the $v=1$ state followed it, and the $v=0$ state least populated among the three. So, both the $v=2$–1 and 1–0 transitions appeared as emissions at least for a few microseconds after the photolysis. Kanamori *et al.* also reported another interesting observation that the F_1 and F_3 spin components of SO were more populated than the F_2 component. These findings are useful information in unveiling the mechanism of the photodissociation of SO_2 from the $\tilde{C}$ state.

An interesting relaxation process was reported by Kanamori *et al.* (1987), who intended to generate CCH radicals by photolyzing acetylene at 193 nm. Although they observed a number of lines in the region where the C–C stretching band of CCH appeared, they could not assign them. When they mixed acetylene with some appropriate gases such as hydrogen, methane, and carbon monoxide, new lines with a different time profile appeared and were readily assigned to the C–C stretching band of the CCH radical in the ground $\tilde{X}^2\Sigma^+$ electronic state. This fact indicates that CCH radicals are prepared in highly excited vibronic states, although no emission lines have been observed. As Curl and his co-workers (Carrick *et al.* 1982, 1983, Curl *et al.* 1985, Yan *et al.* 1987a, b, Stephens *et al.* 1988) have shown, the $\tilde{A}^2\Pi$ excited state of CCH is located about 3600 cm^{-1} above the ground state. Because CCH has a bending

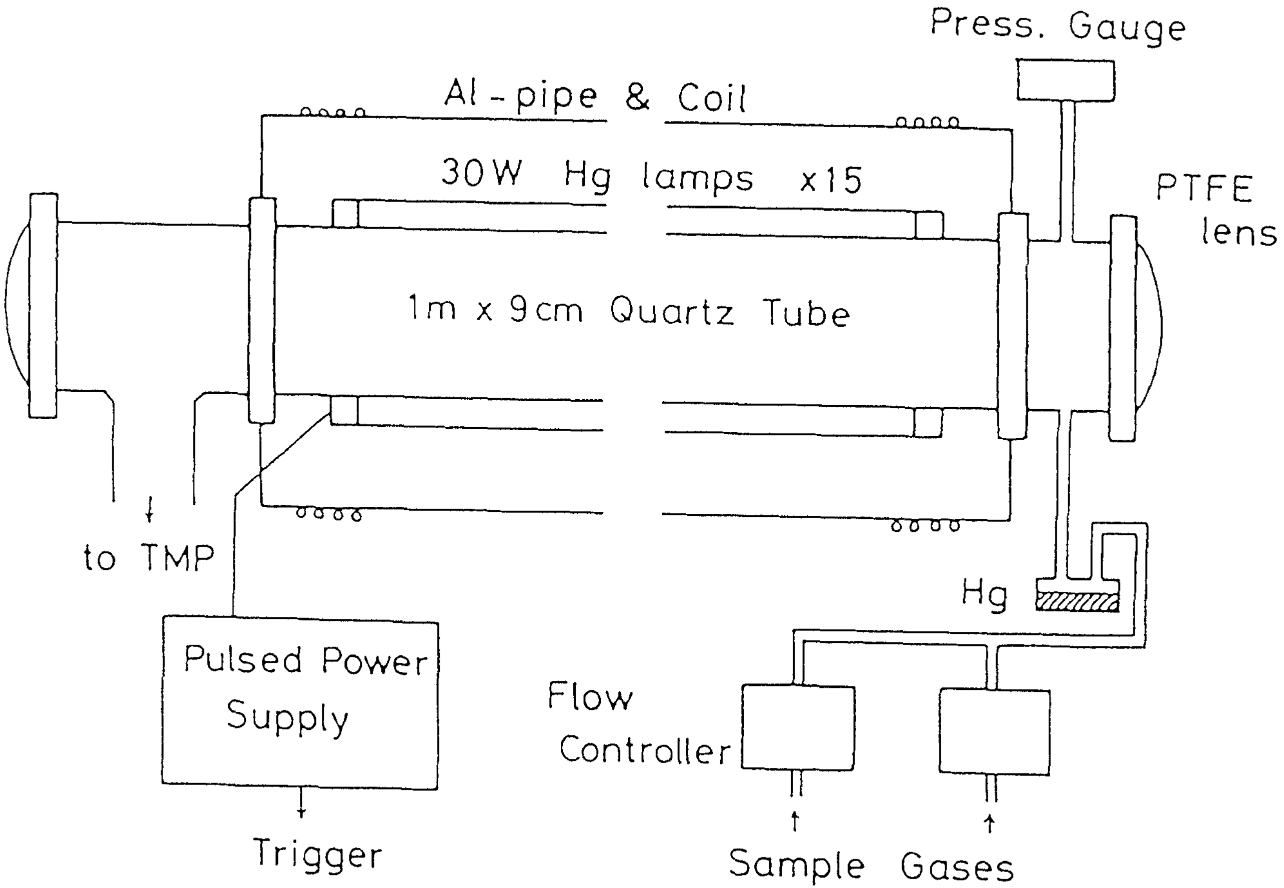

Figure 4. Absorption cell of a microwave kinetic spectrometer employed for mercury-sensitized reactions (reproduced from Endo *et al.* (1987a) with permission of *Laser Chem.*).

vibration of Π symmetry, quite a large fraction of vibrational states associated with the ground $\tilde{X}^2\Sigma^+$ state are vibronically mixed with the vibrational levels of $\tilde{A}^2\Pi$. Curl *et al.* reported a number of vibronic states present in the 3 μm region. The lines which Kanamori *et al.* observed initially, without using any buffer gases, were later assigned to the transition from the ν_3 (i.e. the C–C stretching state to a vibronic state which Curl *et al.* reported to be at 3693 cm^{-1} above the ground vibronic state (Kanamori and Hirota 1988b)). The author's group tried to generate CCH radicals by the reaction of F atoms with acetylene, but without success. The kinetic experiment described above led Kawaguchi *et al.* (1988c) to produce CCH by a discharge method; they obtained CCH by a discharge in a mixture of C_2H_2 and H_2 with partial pressures of 100 and 600 mTorr.

Another, more important example of transient molecules generated by kinetic spectroscopy is the vinyl radical investigated by Kanamori *et al.* This radical has been known to act as an important intermediate in many organic reactions such as additions to an acetylenic bond and decompositions of ethenoid compounds. Organic chemists inferred the vinyl radical to be a σ radical, based mainly upon product analyses and reaction rate determinations. Electron spin resonance studies also led to the same conclusion, and gave an estimate for the barrier height to the in-plane C–H_α tunnelling motion of about 2 kcal mol^{-1}. However, no high-resolution spectroscopic studies have been carried out, leaving the molecular structure uncertain. Kanamori *et al.* generated vinyl radicals by the photolysis of vinyl halides at 193 nm and succeeded in observing an out-of-plane band around 900 cm^{-1}, which was mainly CH_2 wagging in character. The band was found to consist of two component bands, each showing spin statistical weight either 1 : 3 or 3 : 1 in alternative way for the two component bands for even : odd K_a levels. These observations were well accounted for by the in-plane C–H_α tunnelling motion making the molecule of C_{2v} effective symmetry. The difference between the origins of the two component bands was determined to be 0·0541 (11) cm^{-1}, but the tunnelling splitting in each state and thus the barrier height remain undetermined. There is evidence to favour a tunnelling barrier which is considerably smaller than the *ab initio* calculated values of 3200 cm^{-1} (Dupuis and Wendoloski 1984) and 2200 cm^{-1} (Paddon-Row and Pople 1985).

A number of reactions involving halogen atoms have been investigated by observing the fine structure transition $^2P_{1/2}$–$^2P_{3/2}$ of halogens detached from the reactant. This method has been applied to iodine, the fine structure transition of which appears in the near infrared. However, it has been difficult to use for chlorine atoms, because their fine structure splitting is only 882 cm^{-1} or 0·1 eV. Tiemann *et al.* (1988) have shown that this fine structure transition can be monitored with infrared-diode-laser kinetic spectroscopy and they have investigated the photolysis processes of five chlorine-containing molecules, HCl, CH_3Cl, CH_2Cl_2, C_6H_5Cl and PCl_3.

Kinetic spectroscopy meets the requirements for studies of various types of chemical reactions. Endo *et al.* (1986b) have examined the mechanism of the O + ethylene reaction using microwave kinetic spectroscopy. Four channels had been taken into account by previous investigators:

$$O(^3P) + C_2H_4 \rightarrow \text{vinoxy} + H \qquad \text{(a)}$$

$$\rightarrow CH_3 + HCO \qquad \text{(b)}$$

$$\rightarrow CH_2 + H_2CO \qquad \text{(c)}$$

$$\rightarrow CH_2CO + H_2 \qquad \text{(d)}$$

Endo *et al.* generated O(^{3}P) by mercury-sensitized decomposition of N_2O and observed the microwave spectra of vinoxy, HCO and H_2CO as functions of time. They also recorded the CH_3 absorption by infrared kinetic spectroscopy to check the microwave results. The branching ratios they derived are $0{\cdot}4 \pm 0{\cdot}1$, $0{\cdot}5 \pm 0{\cdot}1$ and $0{\cdot}1 \pm 0{\cdot}05$ for (a), (b) and (c) respectively, at the sample pressure of 0·03 Torr. Koda *et al.* (1987) subsequently extended the measurements to the fully deuterated systems and obtained a remarkably large deuterium effect: the ratio (b)/(a) is $1{\cdot}2 \pm 0{\cdot}2$ for C_2H_4, whereas it is as large as $6 \pm 1{\cdot}5$ for C_2D_4. They explained this large isotope effect qualitatively by competition between unimolecular dissociation on the triplet surface and intersystem crossing leading to a singlet surface followed by 1,2–hydrogen migration and C–C cleavage. More recently, Endo *et al.* repeated the measurement while replacing mercury sensitization with excimer-laser photolysis thereby improving the time resolution. They have confirmed their previous results.

Endo *et al.* (1987a) also investigated the O + acetylene reaction, for which they focused attention on two channels: $O + HCCH \rightarrow HCCO + H$ and $CH_2 + CO$. Oxygen atoms were again produced by mercury-sensitized decomposition of N_2O and the rotational spectra of HCCO and CO were monitored with microwave kinetic spectroscopy. A preliminary result suggests that the former channel is dominant at an initial stage of the reaction, although quite a large amount of CO is produced subsequently, probably through secondary processes.

Other systems like $O + SiH_4 \rightarrow OH + SiH_3$ and $O + CH_4 \rightarrow OH + CH_3$ are being investigated by monitoring SiH_3 and CH_3 radicals respectively, by infrared-diode-laser kinetic spectroscopy.

5. Applications to astrophysics: detection and identification of interstellar molecules

Since the detection of the OH radical in 1963, remarkable progress has been brought about on radioastronomical studies of interstellar molecules; about 80 molecules have been identified in space. It should be stressed that about 40% of these molecules are transient species in laboratory conditions. Astrophysical observation of interstellar molecules has thus prompted laboratory studies of short-lived molecules. Molecular ions serve as good examples: they play important roles in forming many other interstellar molecules through efficient ion–molecule reactions.

The present author's group has collaborated with radio-astronomers at Nobeyama Radio Observatory, and has suggested searching for some of the transient species listed in table 1. There are a number of candidates; SiN, PO, PO_2, FeO, CCO, HPO, HSO, HCCO and NaO, but none of them have been identified in interstellar space with ultimate certainty. The only exception is C_3; the infrared spectrum of this molecule was clearly identified by Hinkle *et al.* (1988) in the atmosphere of IRC + 10216.

On the other hand, Saito, Yamamoto and their co-workers have been very successful in collaboration with radio astronomers. This group started setting up a new microwave laboratory at Nagoya University in 1985 and has already detected a large number of transient molecules, as listed in table 9.

In 1986 radio-astronomers (H. Suzuki *et al.* 1986) at Nobeyama detected a pair of doublets at 23 566 MHz in TMC–1, and they soon found another pair of lines which satisfied with the first one the frequency relations expected for a $^2\Pi$ molecule; the larger splitting was ascribed to Λ-doubling and the smaller ones to hyperfine interaction. The rotational constant derived from the spectrum was close to that expected for C_6H, although linear even-carbon chain monohydrides, $C_{2n}H$, had been known to have the

$\tilde{X}^2\Sigma^+$ ground state. However, soon they realized that, as the number of carbon atoms in the chain is increased, the lowest $^2\Pi$ state becomes lower and passes the $^2\Sigma^+$ state between C_4H and C_6H. The observed lines were thus assigned to C_6H in $\tilde{X}^2\Pi_{3/2}$. Later Saito *et al.* (1987a) observed lines of C_6H in the higher spin state $\tilde{X}^2\Pi_{1/2}$ in IRC+10216.

A quite strong line was observed at 45 379 MHz from Sgr B2, TMC–1 and TMC–2 with the radio-telescope at Nobeyama and was referred to as U45379. It took laboratory spectroscopists several years to identify the chemical species responsible for this line, because it was not accompanied by any satellites and did not satisfy any integer relations with other lines expected for linear molecules. When Saito *et al.* (1987d) were trying to observe the rotational spectrum of the CS^+ ion using a discharge in a carbon disulphide and He mixture, they detected three paramagnetic lines at 258·274, 259·055, and 259·701 GHz, which they realized were reasonably assigned to F_3, F_2, and F_1 components of a triplet species. Finally they concluded that the molecule they were observing was CCS in $\tilde{X}^3\Sigma^-$, and U45379 was assigned to $J, N = 4, 3 \leftarrow 3, 2$ (i.e. F_1 component of CCS). The F_1 and F_3 components of a $^3\Sigma^-$ molecule do not satisfy

Table 9. Transient species investigated at Nagoya University.

	Species	State	Reference†
Diatomic	NF	$a^1\Delta$	Yamamoto and Saito (1987)
	CO	$a^3\Pi_\sigma, a'^3\Sigma^+$	Yamamoto and Saito (1988)
	PO (dipole moment)		Kanata *et al.* (1988)
	PS	$X^2\Pi$	Ohishi *et al.* (1988)
	CP	$X^2\Sigma^+$	Saito *et al.* (1989)
	BS	$X^2\Sigma^+$	Tanimoto *et al.* (1988)
	AlS		
	CaS	$X^1\Sigma^+$	Takano *et al.* (1989)
	MgS	$X^1\Sigma^+$	Takano *et al.* (1989)
Linear	C_3H	$\tilde{X}^2\Pi\ v$	Yamamoto *et al.*
	C_4H	$\tilde{X}^2\Sigma^+\ v_7, 2v_7$	Yamamoto *et al.* (1987a)
	C_6H	$\tilde{X}^2\Pi$	Suzuki *et al.* (1986)
			Saito *et al.* (1987a)
	CCS	$\tilde{X}^3\Sigma^-$	Saito *et al.* (1987d)
	CCCS	$\tilde{X}^1\Sigma^+$	Yamamoto *et al.* (1987b)
	C_3N	$\tilde{X}^2\Sigma^+\ v_5$	Mikami *et al.* (1989)
	CCCCSi	$\tilde{X}^1\Sigma^+$	Ohishi *et al.*
Asymmetric top	C_3H_2 (dipole moment)		Kanata *et al.* (1987)
	cyclic–C_3H	$\tilde{X}^2B_2$	Yamamoto *et al.* (1987c)
	CH_2CN	$\tilde{X}^2B_1$	Saito *et al.* (1988b)
			Irvine *et al.* (1988)
	CH_2N		
	HS_2		
	HNCN		
	H_2NO		
	H_2NS		
	$NH_2(ND_2)$		
Molecular ion	HBF^+	$\tilde{X}^1\Sigma^+$	Saito *et al.* (1987b)
	H_2Cl^+	$\tilde{X}^1A_1$	Saito *et al.* (1988a)
	H_3S^+	$\tilde{X}^1A_1$	Saito *et al.* (1987c)

† References without year denote results either in press or unpublished.

integer relations, and this had prohibited this line from being identified. Yamamoto *et al.* (1987b) realized that another species was also present in the same discharge system, namely CCCS in $\tilde{X}^1\Sigma^+$. These two molecules account for many U lines (i.e. lines left unassigned). Although the astro-chemical significance of these findings has not been much appreciated, it should be noted that CCO, the oxygen analogue of CCS, detected by Yamada *et al.* (1985a) in the laboratory has not been identified definitely in interstellar space; CCS and CCCS may give us a clue to unveiling characteristic features of sulphur chemistry in space.

Another remarkable finding of the Nagoya group is cyclic C_3H. When Yamamoto *et al.* (1987c) were exploring low-lying vibrational satellites of linear C_3H using a discharge in a C_2H_2, CO and He mixture, they observed additional paramagnetic lines which were not ascribable to linear C_3H. The optimum conditions were also different for the two species; the new species required CO. Finally they concluded that the molecule was a planar near-oblate symmetric top with K_a = even levels lacking; cyclic C_3H was one of the molecules compatible with these observations. Later they observed the spectra of a deuterated species, which was also consistent with the above interpretation. They detected this molecule in TMC–1; the abundance was almost the same for linear and cyclic C_3H, but was an order of magnitude lower than that of C_3H_2.

Saito *et al.* (1984a) had previously observed the rotational spectrum of an interesting carbene HCCN and suspected that this molecule played an important role in forming long carbon chain cyanides in space. However, the molecule has not been detected in space. This molecule was produced in the laboratory by the reaction of fluorine atoms with acetonitrile. Because theoreticians were interested in the linearity of this molecule, Saito *et al.* (1988b) continued to search for other spectral lines using the reaction system mentioned above, and detected groups of lines at every 20 GHz. They assigned these to the CH_2CN radical, which was previously expected to be present in the reaction system as one of the transient species. Searches for this molecule in space soon resulted in identification of it in TMC–1 and Sgr B2.

A most recent success of laboratory and interstellar space collaboration was achieved on the C_4Si molecule. In this connection one should pay attention to the detection of the CSi molecule in $X^2\Pi$ both in space and in the laboratory (Cernicharo *et al.* 1989). These two results may stimulate the opening of a new field in silicon chemistry.

6. Applications to plasma science: diagnosis of silane discharge plasma

Once the spectra of transient species are observed and unambiguously assigned, they can be of great use for many purposes. Applications to chemical reactions described in section 4 are an example. This section illustrates a recent development of a method for diagnosing molecular processes taking place in discharge plasma.

The discharge plasma has already been employed to produce useful materials; for example a thin film of amorphous silicon can be used as a solar cell. Efforts have been made to find discharge conditions that lead to high-quality films, but molecular processes from the starting material, silane, to amorphous silicon have not been well explored; some groups have been insisting SiH_2 to be a most important intermediate, whereas others have been focusing attention on SiH_3. Controversy is caused by insufficient information having been available on the intermediate processes. In particular, no reliable spectroscopic data had been reported on SiH_3 until Yamada and Hirota (1986b) succeeded in observing its ν_2 band using infrared-diode laser spectroscopy.

In the autumn of 1987, the present author's group started a collaborative study, with T. Goto and his associates at Nagoya University, to develop a method for diagnosing molecular processes in discharge plasma. Our main tool has been infrared-diode-laser spectroscopy combined with time-resolved detection software developed for kinetic spectroscopy, as described in section 4. We have focused attention on SiH, SiH_2 and SiH_3 and have aimed at establishing a routine procedure which allows us to determine absolute concentrations of these species in the silane discharge plasma in real time (Itabashi *et al.* 1988). One could measure the concentrations of SiH and SiH_2 using laser-induced fluorescence, but this method is difficult to apply to SiH_3. This is very unfortunate, since SiH_3 is a most crucial species in silane discharge plasma. Infrared-laser spectroscopy, although suffering from many drawbacks, is versatile and allows us to monitor the three important species at the same time.

Infrared spectra in the gas phase are available for SiH and SiH_3, whereas such data are lacking for SiH_2; only matrix infrared spectra of SiH_2 have been published. Therefore we have initiated infrared-diode-laser spectroscopy of SiH_2. We have found that kinetic spectroscopy combined with the 193 nm photolysis of phenylsilane yields the vibration–rotation spectra of SiH_2 with good signal-to-noise ratio. It also readily discriminates spectral lines of other species from those of SiH_2, based on the time profiles of the spectra. Nishiwaki *et al.* have thus completed analysis of the ν_2 band of SiH_2, however we found that this band was too weak to use for quantitative analysis. We proceeded to observe spectral lines in the 5 μm region, where we expect to detect the ν_1, ν_3 and $2\nu_2$ bands. We have already observed nearly 200 lines; most of them are an order of magnitude stronger than the ν_2 lines and, when properly assigned, are readily used for determination of the SiH_2 abundance. Analysis is being advanced by taking into consideration Coriolis interactions between ν_1 and ν_3 and also between $2\nu_2$ and ν_3 and Fermi resonance between ν_1 and $2\nu_2$.

We have examined silane plasmas prepared by d.c. glow discharge. For ease of detection, we switched the discharge on and off and detected absorption signals synchronously. Figure 5 shows the absorption cell employed; the central part is made of a stainless steel tube 117 cm long and 10 cm in inner diameter, which is grounded, and two anodes, 1·5 mm diameter tungsten pins, are placed at either end of the stainless tube. To align the infrared beam, a glass tube about 40 cm in length is attached at either end. The pulse duration is about 0·5 ms, and the repetition rate is typically 670 Hz and 35 Hz, for SiH and SiH_3 respectively. Figure 6 shows a typical spectrum of the SiH $v=1\leftarrow 0$ $R_1(1\cdot 5)$ line, which is split into two components by Λ-type doubling (Kato *et al.* 1988).

We have found that SiH radicals decay in silane discharge plasma through their reaction with SiH_4. This process is fairly complicated; SiH and SiH_4 seem to form a metastable complex, which, when stabilized by collisions with other molecules, leads to end products, but otherwise dissociates into SiH and SiH_4. The decay rate constant of SiH is greatly dependent on the pressure of a buffer gas. We have also found that we must allow for a long time (10 h or more) until precursor and buffer gas are well mixed. In any case SiH seems to be eliminated from the discharge system within 100 μs. Although our study on SiH_2 is still at a preliminary stage, this radical's lifetime is even shorter.

These properties of SiH and SiH_2 are in sharp contrast with that of SiH_3. This radical is eliminated by a binary recombination or disproportionation reaction. Although the rate constant is as large as 10^{-10} cm^3 mol^{-1} s^{-1}, the frequency of binary encounter is low, making the overall elimination rate of SiH_3 radicals quite slow, the

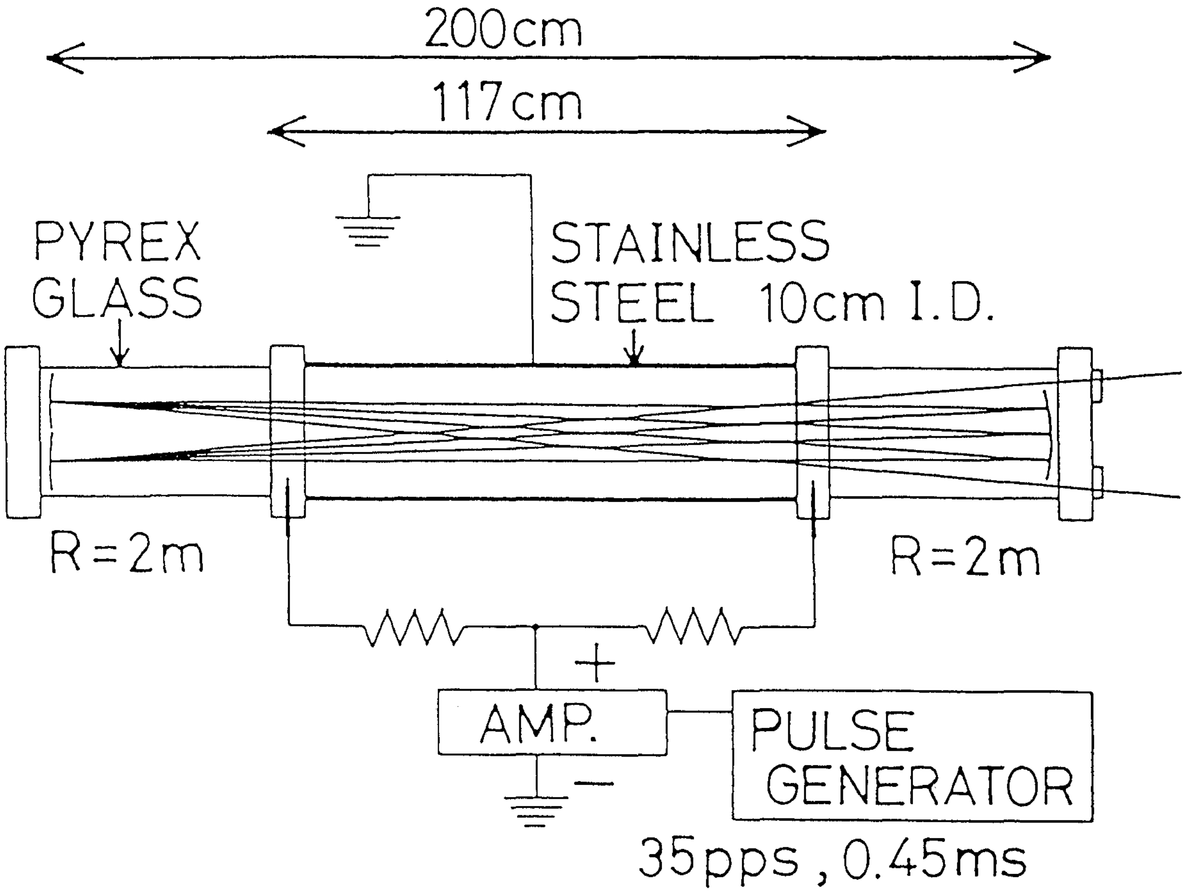

Figure 5. Discharge cell for infrared absorption spectroscopy. Two anodes are made of tungsten pins of 1·5 mm diameter and a cylindrical cathode is made of stainless steal (reproduced from Itabashi *et al.* (1988) with permission of *Jap. J. appl. Phys.*).

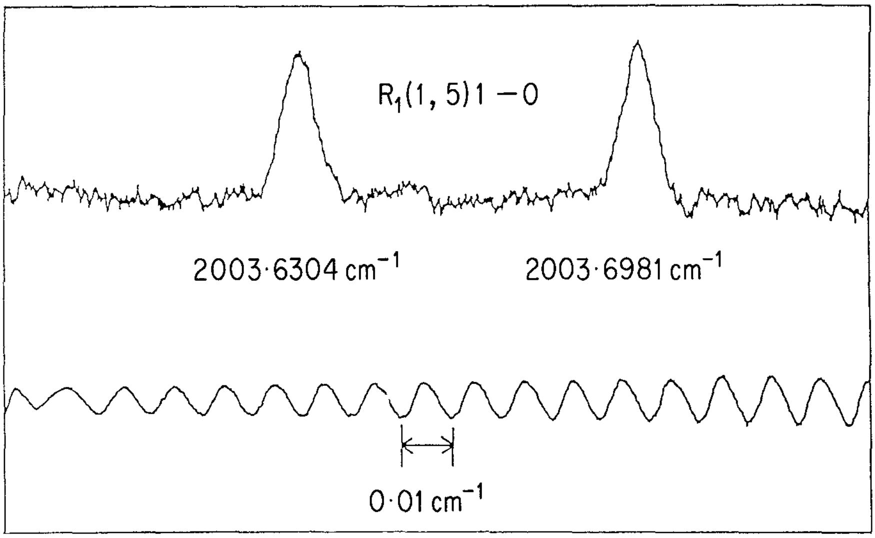

Figure 6. $R_1(1{\cdot}5)$ transition of the SiH $v=1$–0 band recorded by discharge modulation (reproduced from Kato *et al.* (1988)).

mean lifetime being of the order of 10 ms. As a result, the decay curve of SiH_3 clearly exhibits the contribution of diffusion processes (Itabashi *et al.* 1989). Our qualitative conclusion on the molecular processes in the silane discharge plasma is that the discharge may produce all three intermediates, in considerable amounts at an initial stage, but that SiH and, in particular, SiH_2 react rapidly with the precursor SiH_4 and are removed from the system. SiH_3 is of relatively long life in the plasma, and a considerable fraction of this radical drifts to the wall of the reactor.

We have employed the transition dipole moments calculated by Allen and Schaefer (1986) using an *ab initio* method in converting the absorption intensities to the abundances. There is no obvious experimental way to measure the vibrational transition dipole moment for a transient species like SiH_n. We are planning to compare the infrared results on SiH and SiH_2 with those by laser-induced fluorescence. Another drawback of the infrared method is that it measures absorptions and, because the vibrational transition intensity is one or two orders of magnitude smaller than the electronic transition intensity, we have to make the path length as long as possible, often at the expense of the spatial resolution. In spite of these shortcomings, the infrared method is versatile and is at present the only method of determining the concentration of the SiH_3 radical. Recently a resonance-enhanced multiphoton ionization method was proposed (Johnson *et al.* 1989), but any technique based on detection of charged particles resulting from ionization will be difficult, or almost impossible to apply to the discharge plasma where other charged species are abundant. The infrared method described above will be readily applied to the discharge plasma of hydrocarbons; the CH_3 radical will be one of the key species and its spectra have already been explored in detail (Yamada *et al.* 1981b), as mentioned in section 3.2.

7. Concluding remarks

The present article reports high-resolution spectroscopic results obtained mainly at the Institute for Molecular Science (i.e. by the present author's group), and also by Shuji Saito and Satoshi Yamamoto's group at Nagoya University. Many other groups have also been contributing to the study of transient molecules from different view points. Among them four groups should be mentioned here; they have been working in the fields quite close to ours. Takehiko Tanaka, Keiichi Tanaka and their co-workers at Kyushu University have recently started an infrared-diode-laser spectroscopic study of transient species, and have observed the vibration–rotation spectra of SiF, SiF^+ (Akiyama *et al.* 1989) and GeF^+. Yoshiaki Hamada of the University of Tokyo and Harutoshi Takeo and Chi Matsumura's group at the National Chemical Laboratory for Industry have performed a complementary study, using Fourier transform infrared and microwave spectroscopy respectively, on transient molecules generated mainly by pyrolysis. The species they detected have lifetimes much longer than those of most species discussed in the present article, but many of them were previously unknown as listed in table 10. Hiromichi Uehara and his associates at Josai University have been focusing attention on high-temperature molecules (i.e. molecules that vaporize at high temperature), and have observed the vibration–rotation spectra of NaCl (Horiai *et al.* 1988, Uehara *et al.* 1989a), GeS (Uehara *et al.* 1989b), LiCl, InF, NaOH and PbO using a diode laser and a Fourier transform spectrometer.

High-resolution spectroscopy of transient molecules is prosperous and will, no doubt, flourish more in the future. Needless to say, we must always try to improve our facilities and to invent new methods based on new principles. With these pre-requisites

Table 10. New transient molecules generated by pyrolysis at the University of Tokyo and National Chemical Laboratory for Industry.

Molecule	Reference
$CH{\equiv}CCH{=}NH$ (propargylimine)	Hamada *et al.* (1984) Sugie *et al.* (1985a)
$CH_3CH{=}CHNH_2$ (1-aminopropene)	Hamada *et al.* (1985)
$CH_2{=}CHNH{-}CH_3$ (N-methylvinylamine)	Sugie *et al.* (1985b)
$NH{=}CHCN$ (C-cyanomethanimine)	Takeo *et al.* (1986) Hamada *et al.* (1986)
$CH_3{-}N{=}C{=}CH_2$ (N-methylketenimine)	Amatatsu *et al.* (1987c)
$CH_2{=}N{-}CH{=}CH_2$ (2-azabutadiene)	Amatatsu *et al.* (1987b) Sugie *et al.* (1989)
$\underline{HC{=}N{-}CH_2{-}CH_2}$ (1-azetine)	Amatatsu *et al.* (1987a) Sugie *et al.* (1989)
$CH_2{=}NCl$ (N-chloromethylenimine)	Sugie *et al.* (1989)
$BH(OH)_2$	Kawashima *et al.* (1978)
BFHOH	Kawashima *et al.* (1978)
$BF(OH)_2$	Kawashima *et al.* (1979)
BH_2NH_2 (aminoborane)	Sugie *et al.* (1979, 1987)
BH_2OH (Hydroxyborane)	Kawashima *et al.* (1981)
B_2H_5Cl (chlorodiborane)	Sugie *et al.* (1985c)
CH_3OBH_2 (methoxyborane)	Kawashima *et al.* (1986b)
$\underline{HB{-}O{-}BH{-}NH{-}BH{-}O}$ (3-H-3-azacyclotriboroxine)	Kawashima *et al.* (1989b)
$\underline{HB{-}NH{-}BH{-}O{-}BH{-}NH}$ (3-oxacyclotriborazane)	Kawashima *et al.* (1989b)

fulfilled, many important and interesting species that have eluded our observation will be detected and will bring us new developments in molecular science. There remain many unknown factors on the behaviour of molecules in highly excited states including metastable states of high spin multiplicity and also in states where molecules execute very large amplitude motions like isomerization and even dissociation. Weakly bound complexes of transient species may disclose new chemistry, and for such studies high-resolution spectroscopy will remain indispensable.

Acknowledgments

The author is grateful to Professor Saburo Nagakura, the former Director General of IMS, for giving him a chance to summarize the results obtained by his group at IMS. He also thanks Shuji Saito, Chi Matsumura, and Yoshiaki Hamada for informing him of their recent results.

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