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PREFACE

This year's *Annual Review of Physical Chemistry* presents articles that represent the wide range of topics that comprise physical chemistry. Although the systems studies vary from proteins to small gas phase ions, a similar approach characteristic of physical chemists may be found in many of the articles; for example, the chapter "Stimulated Annealing in Crystallography." The nominal topic is the analysis of x-ray data for very large molecules. The analysis is by computer fitting of model structure to the data and, thus, the discussion concerns numerical methods. The analysis mimics the physical process of annealing, and so the numerical methods are similar to those developed in studying that process. The article thus touches on the structure of biopolymers, crystallography, numerical methods, simulation, and modeling of structure and relaxation. We expect the chapter to be relevant to the work of a large fraction of physical chemists.

We welcome Stephen R. Leone to the Editorial Committee as Associate Editor. We thank C. Bradley Moore, who is retiring from this position to attend the press of other duties. Brad Moore provided perspective on a particularly wide range of topics in modern physical chemistry. Steve Leone has already applied his own expertise to reading the manuscripts of this volume.

Bonnie R. Meyers took over in Summer 1990 as Production Editor. She shepherded last year's volume through its last stages on an extremely short deadline and has guided this volume through its complete production cycle. The Committee looks forward to benefiting from her expertise for many years to come.

THE EDITORIAL COMMITTEE

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FROM HIGH-RESOLUTION SPECTROSCOPY TO CHEMICAL REACTIONS

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INTRODUCTION

One can learn a lot from history, and from the history of science. However, history itself is not science. In other words, we cannot carry out an experiment to prove a statement made about history; history depends on who has described the past. Many people have probably learned that history taught at school differs depending on the teacher; some teachers are very interesting, but others are boring.

The Prefatory Chapters of the *Annual Review of Physical Chemistry* have been prepared by distinguished scientists. Many of them summarize what they contributed to science; their articles are a history of science based upon their personal experience. This reflection made me hesitant to prepare this Prefatory Chapter; I am afraid that my personal experience may not invoke any interest of the readers. However, I have convinced myself that a description of the achievements of my research coworkers must be of some interest and some value at least to a few people, and finally I accepted the invitation of the Editor.

HISTORICAL BACKGROUND

In 1952, I joined Professor Morino's group as an undergraduate student of the University of Tokyo. One day, I found a short article in a Japanese

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journal. I forget the details, but the author was probably Masataka Mizushima. He reported structural studies of simple molecules by using a spectroscopic method. I was very surprised by the enormous number of digits he quoted for the structural parameters. At that time, we had to be content with three digits, e.g. 1.76 ± 0.02 Å for the C–Cl bond length. So I brought this journal to the laboratory and naively asked Professor Morino how they could achieve such extraordinarily high accuracy. It was already 1952, but I had only very limited information on the new development of science. Professor Morino replied that it must be done with microwave spectroscopy. At that time, Townes & Dailey (1–3) published their famous method of interpreting the nuclear quadrupole coupling data; many chemists were already engaged with this new method of microwave spectroscopy, but I did not know anything about it. The next year, I started my graduate study by using electron diffraction; rotational isomerism was the central theme of my graduate work. However, I kept the memory that microwave spectroscopy was a fascinating technique, and I wished I could use it.

In the fifth, and last, year of my graduate course, Professor Morino allowed me to change my method from electron diffraction to microwave. Fortunately, in the Physics Department, which was and still is next to the Chemistry Department, Professor Shimoda had already started microwave spectroscopy, and I could learn the necessary techniques from his collaborators. Takeshi Oka was a chemistry student, but he spent most of his graduate course in the Physics Department under the guidance of Professor Shimoda. Thus he was already an expert in microwave when I started construction of a microwave spectrometer in the Chemistry Department. He was of great help when I started research in microwave spectroscopy.

I enjoyed studying a few molecules with my newly constructed spectrometer (4, 5), but soon I began to seek directions of research that other microwave researchers had not been taking. One problem we young people in Professor Morino's group thought of was vibration-rotation interactions. This problem had mainly been attacked by vibrational spectroscopists, and microwave researchers had no intention of applying their method to this problem. One of our results on this project was obtained with sulfur dioxide (6). I planned to detect rotational spectra in the excited states of all three normal modes and hoped to determine the equilibrium structure, as well as all six third-order anharmonic potential constants. It took us a long time to observe all the vibrational satellites we needed, but finally Kikuchi, Saito, and I arrived at the goal. In this connection, I am pleased to add that Professor Morino has recently extended this study and has concluded that our earlier results are quite satisfactory.

The second direction I thought of was large-amplitude motions. In the

Chemistry Department, the late Professor San-ichiro Mizushima, Professor Morino, and their coworkers had carried out systematic studies on rotational isomerism (7). As is well known, the term "gauche" was coined by Professor Mizushima. The main theme of my graduate study constituted a small part of this project. I thought, however, that rotational isomers meant nothing but the presence of minima in the internal-rotation potential function. In other words, they merely represented some static concepts, and we should try to get a more global view of internal rotation. Specifically, we should determine the potential function itself experimentally. For this purpose, microwave spectroscopy should be extremely useful; I suspected it would provide us with various types of detailed data. To me, dynamic phenomena were and are much more interesting than static ones.

Fortunately I could start the study at Harvard University in Professor E. Bright Wilson's laboratory; I stayed at Harvard from 1960 to 1962, and amply enjoyed the pertinent instruction of Professor Wilson. There, I started on a program to determine, or "estimate," the internal-rotation potential function by using data supplied by microwave spectroscopy. The first compound I studied was n-propyl fluoride (8). The internal-rotation potential parameters I determined are poor in precision, as reproduced in Table 1. Later, Durig et al (9) and Caminati et al (10) revised my result. Although I could study only a few molecules in this way (11–13), other people, in particular Professor Durig and coworkers, have been supplying

Table 1   Internal rotation potential function of n-propyl fluoride[a]

Fourier coefficient (kcal/mol)	Hirota (8)	Durig et al (9)	Caminati et al (10)[b]
V_1	3.22(202)	0.22(10)	—
V_2	−3.05(172)	−0.683(31)	—
V_3	6.48(215)	3.660(11)	2.776(43)
V_4	−1.25(117)	—	—
V_5	0.37(34)	—	—
V_6	−0.76(54)	0.034(6)	−0.079(20)
V_7	−0.002(290)	—	—
V_{max1}[c]	10.4(44)	4.246	4.186
V_{max2}[d]	4.7(15)	3.560	3.465

[a] Values in parentheses represent estimated uncertainties and apply to the last digits of the constants.
[b] Structural relaxation has been considered.
[c] V_{max1} denotes the barrier height between the two gauche forms, namely the *cis* barrier.
[d] V_{max2} denotes the barrier height between the gauche and *trans* forms, measured from the gauche bottom.

a large amount of beautiful data; the number of molecules for which the potential function was derived surely exceeds 50, and probably is now approaching 100.

I was and am very interested in not only internal rotation and rotational isomerism, but also in large-amplitude motions in general. One recent example is $NaBH_4$, which Yoshiyuki Kawashima and I have been studying (Y. Kawashima et al 1990, submitted for publication). The molecule shows a very interesting spectrum, which we think is at least partly due to the internal motion of the BH_4 group.

FREE RADICAL STUDIES AT THE UNIVERSITY OF TOKYO AND KYUSHU UNIVERSITY

Chemical reactions are certainly more dynamical topics and more central to chemistry than large-amplitude motions. During my two-year stay in the US, I began to think of ways to find an access to this important problem and what I could contribute with my chosen tool, microwave spectroscopy. Finally, I arrived at a conclusion: We should try to detect reactive intermediate species by microwave spectroscopy.

I admit that we were quite influenced by Herzberg and coworkers at the National Research Council (NRC) Canada. They had already accumulated a large amount of extensive, important, and beautiful data on such transient molecules by using a combination of flash photolysis and high-resolution electronic spectroscopy in the ultraviolet to near infrared (IR) regions (14). I thought that if we could apply microwave spectroscopy to this problem, we would get more detailed information on transient molecules than we would by using electronic spectroscopy. Up to 1960, only two transient molecules were detected by microwave spectroscopy: OH by Townes and coworkers (15) and CS by Mockler & Bird (16). In the US and Canada, I visited three microwave laboratories, which had been involved in similar projects: those of Rollie Myers at Berkeley, David Lide at the National Bureau of Standards Washington, and C. C. Costain at NRC Canada. But, by the time of my visit, they had apparently given up; they told me that it was too difficult to detect transient molecules by microwave spectroscopy.

In spite of this pessimistic situation, I returned to Tokyo in 1962 hoping that we would be able to detect transient species by microwave spectroscopy and open a new field. It was fortunate for us that Takayoshi Amano joined our group when I returned; he was interested in some dynamical problems, rather than in static structure determinations. Thus, we started free radical studies by microwave spectroscopy. At first, we did not know anything about free radicals; we did not know how to generate

them, we did not know how reactive they were, etc. So, we spent a few years without any positive results. However, from 1967 to 1975, we made slow but steady steps and detected SO (17), ClO (18, 19), NS (20), BrO (21), NCO (22, 23), and SF (24). I certainly admit that our progress was very slow, but I must also say that the detection of free radicals was extremely difficult at that time. We needed some breakthrough in spectroscopic techniques.

FREE RADICAL STUDIES AT THE INSTITUTE FOR MOLECULAR SCIENCE, AND SPECTROSCOPY OF THE METHYL AND SILYL RADICALS

In 1975, I was invited to join a new research institute, the Institute for Molecular Science in Okazaki. At a research institute, we could concentrate on difficult problems. As a supervisor of students, however, I would not give these problems to students, who could stay with us for only a limited period of time. When I accepted the invitation of Professor Akamatu, the first Director-General of the Institute, I immediately chose the spectroscopic study of free radicals as the main theme of my group. First, I selected good people, otherwise we would lose the game. Fortunately, I succeeded in getting able collaborators, including Shuji Saito, Chikashi Yamada, Yasuki Endo, and Kentarou Kawaguchi. We also introduced IR laser spectroscopy in addition to microwave spectroscopy as our main tools. We have successfully detected and studied about 100 transient species (25). I concentrate here on two examples, the methyl and silyl radicals.

The Methyl Radical

Herzberg (26) was the first to determine the structure of this radical in the gaseous phase experimentally. He photographed ultraviolet transitions to Rydberg states and he could resolve rotational structures for a CD_3 band at 2140 Å and bands of CH_3 and CD_3 at 1500 Å. As shown in Figure 1 (27), Herzberg took the missing R(0) line in the CD_3 $\tilde{B}-\tilde{X}$ band as an evidence that the methyl radical was planar or nearly planar in the ground electronic state. The absence of any strong hot bands led Herzberg to conclude that any potential hump should be lower than 200 cm^{-1}. Numerous other studies were also carried out on this important free radical, including the fine work by Milligan and Jacox (28, 29), but information obtained on the structure was more or less indirect. I should also mention a pioneer work of Pimentel and coworkers (30), who used a rapid scan IR spectrometer. This work and Herzberg's results indicated that the v_2 band, i.e. the out-of-plane bending mode, will appear around 600 cm^{-1}.

Figure 1 Spectrogram showing the parallel band of CD_3 at 2144 Å, taken by G. Herzberg (supplied by the courtesy of Dr. G. Herzberg).

Because of the fundamental importance of this radical, I decided to apply our IR diode laser spectrometer to it. Fortunately, Hiizu Iwamura, who is now in the Department of Chemistry of the University of Tokyo, was Professor at the Institute when I planned to investigate methyl. He suggested that we use di-*tert*-butyl peroxide as a precursor. Our problem was the diode laser, as was often the case; at that time, i.e. 1980, the American Government prohibited the export of IR diodes around 16 μm, because the IR spectrum of UF_6 in that region was classified. Fortunately, Fujitsu, a Japanese electric company, supplied us with several diodes of good quality, and thus Yamada and I (31) could observe the $CH_3 \nu_2$ band. As shown in Figure 2, the spectrum was very strong, and it was easy to identify CH_3 lines even on a scope; CH_3 lines appeared as broad lines because of large Doppler widths. We made assignments for $v_2 = 1-0$, 2–1, and 3–2 and derived the potential function, as shown in Figure 3.

In 1953, Walsh (32) published a series of papers, in which he predicted the geometry of simple molecules based on a simple molecular-orbital consideration. However, the methyl radical was a case for which his theory could not make any definite conclusion as to its planarity. As Figure 3 shows, there is no potential hump at the center, although this function has an unusually large quartic term. We suspected that this large quartic term was caused by a vibronic interaction with an excited electronic state of a_2'' symmetry. When I spoke on this result at Texas Tech University, G. Wilse Robinson questioned our conclusion. He said that he could not believe the planarity of the molecule until we got data on CD_3 consistent with our data on CH_3. Sears and coworkers (33, 33a) subsequently observed the v_2 band of CD_3 in support of our interpretation. So, I believe that now Robinson is also satisfied. We have extended the observation and have assigned the $v_2 = 4-3$ band. As I discuss below, Hermann & Leone (34) observed emission spectra of higher hot bands of CH_3, which, although of much lower resolution, are also consistent with our results.

We then observed the v_3 band, the degenerate C–H stretching band in the 3-μm region, by using a difference-frequency laser system, in collaboration with Amano, Bernath, and coworkers (35) at NRC. Because the methyl radical is planar and of D_{3h} symmetry, the v_1 band is IR inactive. Engel and coworkers (36, 36a) thus employed coherent anti-Stokes Raman spectroscopy to observe this totally symmetric band. Although their data are of lower resolution than the IR data, they could determine the vibration-rotation interaction constants. I started an analysis of the anharmonic potential function of methyl in 1979, well before our observation of the v_2 band. After we successfully detected this band, I slightly adjusted the potential constants (37). Figure 4 compares the α constants thus calculated with the observed values. The agreement is good not only for CH_3, but
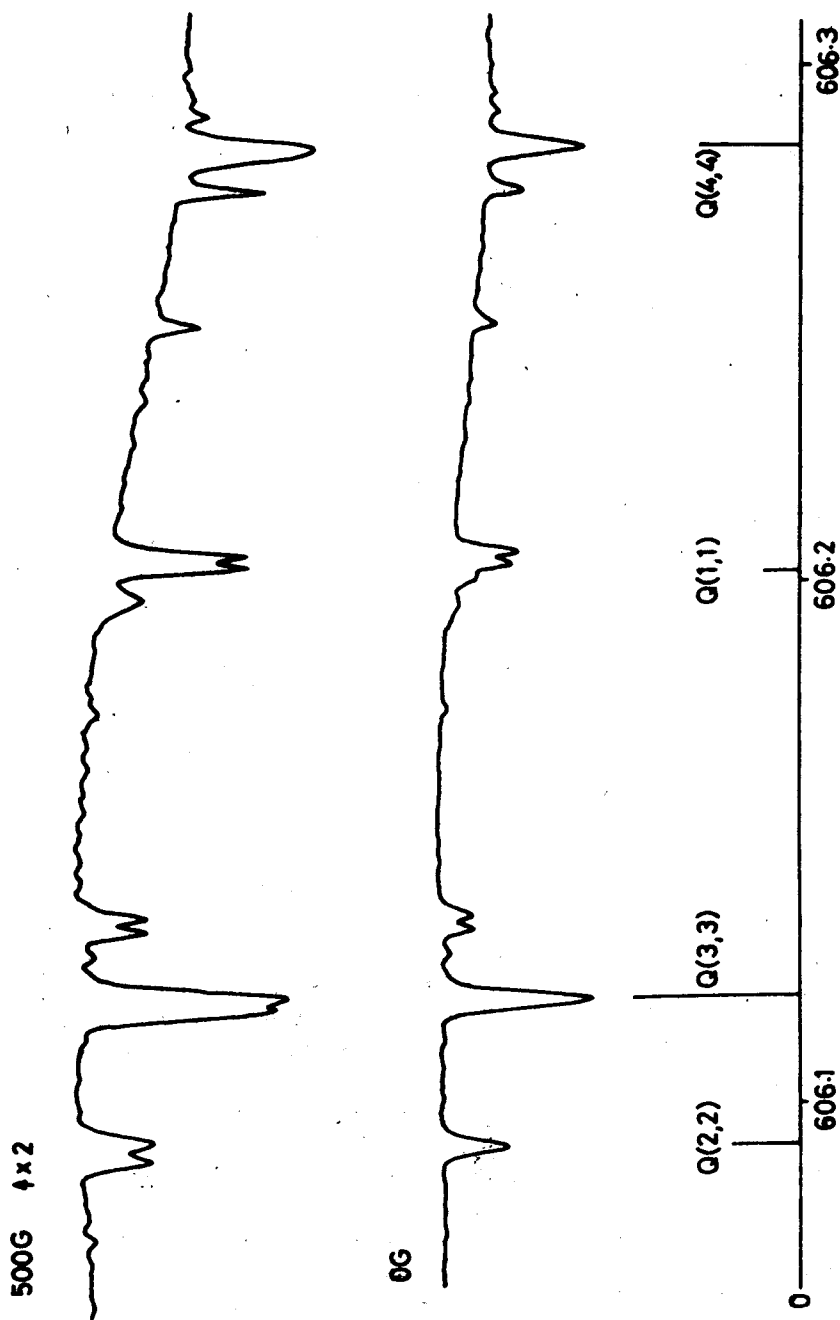
Figure 2 $^{Q}Q_K(N)$ lines with $N = K = 1-4$ of the $CH_3\nu_2$ fundamental band. The lower trace represents zero-field spectra, whereas the upper trace is obtained with a magnetic field of 500 G (reproduced with permission from Ref. 31).
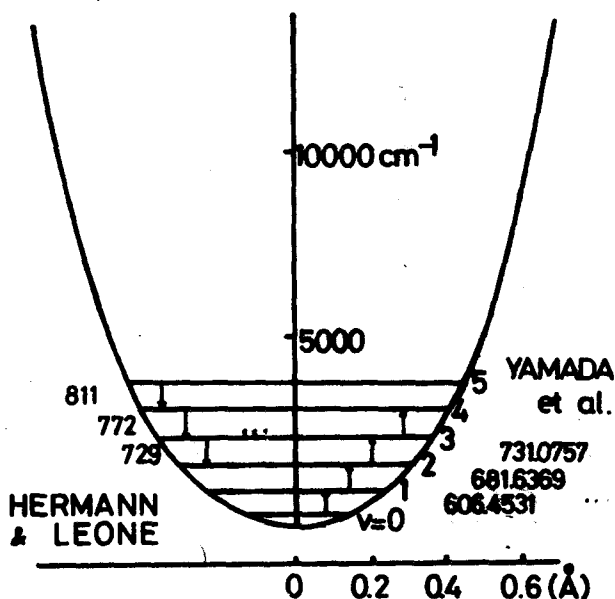
Figure 3   Potential function for the CH$_3 \nu_2$ out-of-plane bending mode.

also for CD$_3$. There is one normal mode left unobserved, namely the ν_4 band. We have some data on this band, and I hope to analyze this band in the near future.

The methyl radical is of fundamental importance in many fields, which also holds for the analysis of vibration-rotation interactions. We can give explicit expressions for many of the vibration-rotation interaction constants. Recently, a beautiful paper was published by Oka's group (38); they have been applying their results mainly to CH$_3^+$. This ion is a more ideal D$_{3h}$ molecule; its ν_2 potential function is closer to a harmonic potential than that of CH$_3$. Interestingly, there is a simple rule for vibration-rotation interaction constants (E. Hirota 1988, unpublished): When n normal modes belong to one symmetry species, all vibration-rotation parameters, like the expansion coefficients of the moment of inertia in terms of normal coordinates, are fixed by $n(n-1)/2$ pieces of information in the harmonic potential function together with the atomic masses and the geometry of the molecule. The methyl radical has two one-dimensional symmetry species, a$_1'$ and a$_2''$, and one two-dimensional symmetry species, e'. Therefore, only one piece of information may be derived from vibration-rotation constants of this radical, or in other words, all the vibration-rotation
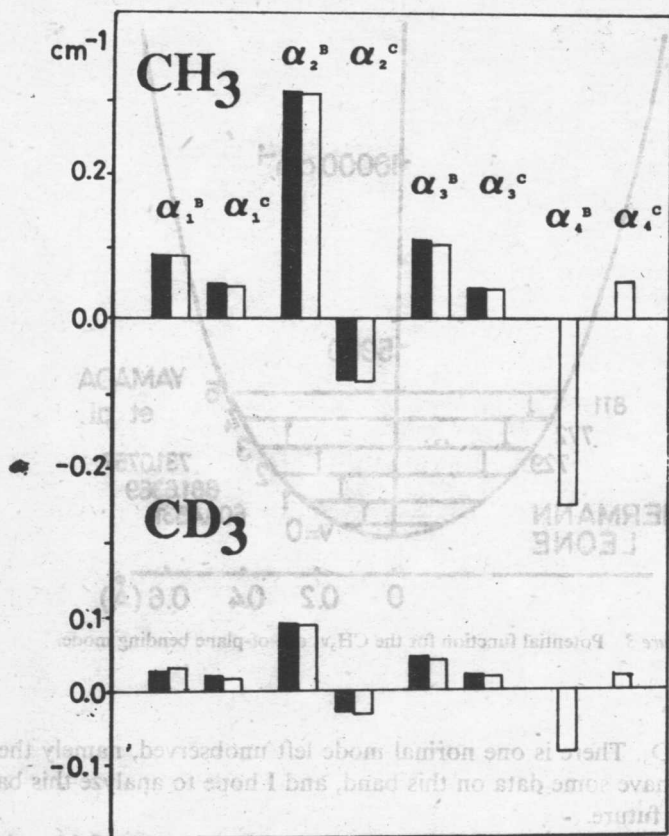
Figure 4 Vibration-rotation interaction constants of the CH_3 and CD_3 radicals. Black and white poles represent the observed and calculated values, respectively. The third-order anharmonic potential constants employed are $F_{rrr} = -33 \pm 6$ md/Å^2, $F_{aaa}/\sqrt{6} = -0.57 \pm 0.20$ mdÅ, and $F_{144} = -0.4$ md (1 and 4 stand for the totally symmetric and the degenerate bending internal coordinates, respectively).

interaction constants of this molecule are determined by one parameter related to the harmonic potential force field. Oka chose the first-order Coriolis coupling constant and expressed the inertial defects in terms of this parameter.

I have left one important constant unanalyzed, i.e. the ℓ-type doubling constant q, which has been determined for the v_3 band of both CH_3 and CD_3 (39). This constant should supply us with information on the anharmonic force field; it yields a linear relation between k_{333} and k_{334}

and thus should be useful in refining my potential function. The force field I employed to predict the α constants gives a value for q_3 an order of magnitude larger than the observed value. But, the two k constants are of opposite sign and the ℓ-type doubling constant corresponds to a difference between two large terms. The ℓ-type doubling constant in the $v_4 = 1$ state yields a similar relation between k_{344} and k_{444}.

The Silyl Radical

It is a natural extension of our research to go down the periodic table. This tendency surely explains why we studied the silyl radical. Yamada and I obtained such nice results on the methyl radical that we thought we could enjoy spectroscopy of silyl, as well. I also suspected that the silyl radical would afford us more than that. Although my knowledge of the fabrication of electronic devices was very limited, I thought this species might play an important role in many processes of practical importance. So we decided to try to detect this radical by IR diode laser spectroscopy.

Before we started, we knew that electron spin resonance (ESR) studies (40, 41) had already established the nonplanarity of the molecule; they estimated the HSiH angle to be about $112.7°$. Molecular orbital calculations also predicted the molecule to be nonplanar (42–44), which contrasts sharply with CH_3. Why are the two molecules so different? When I presented our IR spectroscopic results on SiH_3 at the 1986 Austin Symposium, someone asked me this question, but I could not answer. I thought it was too involved to give a simple answer, and I still think so. But, at the symposium a kind gentleman did reply to the question. He said that the energy separation between s and p orbitals is larger in Si than in C, thus sp^2 or sp^3 hybridization would become less important in SiH_3 than in CH_3, making the bonding orbitals of Si closer to a pure p orbital than those of C. This answer is probably right, and will be understandable to those who like this sort of explanation.

Yamada and I (45) started searching for the spectrum of the v_2 band of SiH_3, because the corresponding band of CH_3 was so strong. However, we found it quite difficult to observe the IR spectrum of SiH_3; the molecule is too light for IR diode laser spectroscopy and the absorption was not as strong as the v_2 band of CH_3. Furthermore, ab initio calculations predicted vibrational frequencies that were too high; we often lost our way. After a long search, we finally got the spectrum and its assignment.

We found the v_2 band to be split into two components, which were probably caused by inversion, as in the case of ammonia. The splitting of about 6.9 cm^{-1} was thus ascribed mainly to the splitting in the upper state $v_2 = 1$. Although our data were limited, we could estimate the barrier height to the inversion to be about 1900 cm^{-1}, and the splitting in the

ground state to be about 0.1 cm^{-1}. The band origin we determined is 727.9438 and 721.0486 cm^{-1} for $v_2 = 1^- \leftarrow 0^+$ and $1^+ \leftarrow 0^-$, respectively, which are 50–60 cm^{-1} lower than ab initio estimates. We also obtained approximate values for the Si–H length and the H–Si–H angle to be 1.456–1.468 Å and 108.5–110.5°, respectively.

DEVELOPMENT OF HIGH-RESOLUTION KINETIC SPECTROSCOPY AND ITS APPLICATIONS TO CHEMICAL REACTIONS

As we accumulated the spectroscopic data on transient molecules, I started to dream of using these data in related fields. For example, I wished we could provide more dynamical information on chemical reactions by using our own spectroscopic data and our own high-resolution spectroscopic methods. I thought we should maintain the high resolution of our methods, otherwise we would lose our identity.

Figure 5 illustrates what I dreamed of: I hoped to record two-dimensional spectra, one axis being the ordinary frequency or wavelength scale at high resolution and the other representing the time axis. The uncertainty principle of Heisenberg prohibited us from getting very detailed data beyond a certain limit in this two-dimensional area, but our method is still far from this limit. For example, a frequency resolution of 1 MHz can be achieved only when the time resolution is worse than 0.17 μs. Our signal detection circuitry had a time response of about 0.3 μs. Thus, it was still quite far from the Fourier limit imposed by the uncertainty principle, in
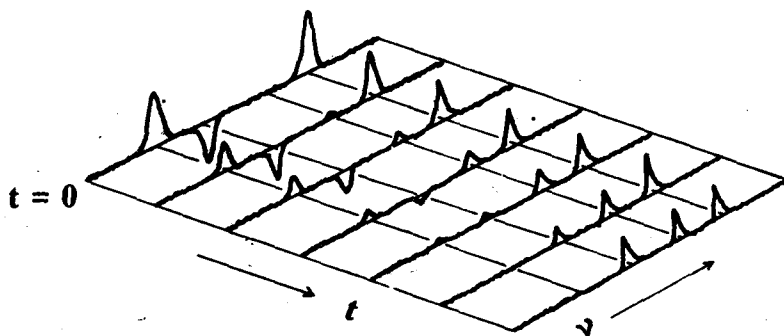
Time-resolved high-resolution spectrum

Figure 5 Observation of time-resolved high-resolution spectra.