

# My 45 Years of Astrochemistry: Memoirs of Takeshi Oka

## 1. NH<sub>3</sub>: CHARLIE TOWNES, KOICHI SHIMODA, JIM WATSON

I decided to devote my research career to studies of interstellar molecules on December 17, 1968. On that day I read in the Sussex Library of the National Research Council of Canada (NRC) in Ottawa the December 16 issue of *Physical Review Letters*, in which the discovery of interstellar NH<sub>3</sub> through radio emission between inversion levels of the  $J = K$  metastable NH<sub>3</sub> was reported by the group of Charlie Townes.<sup>1</sup> Totally unaware that such work had been underway, I was thunderstruck. The discovery revealed rich chemistry in interstellar space and initiated the concept of “Molecular Clouds” with unexpected high density, which was to affect astronomy in a profound way. I also had my personal reason to get excited. My paper on the  $\Delta k = 3n$  selection rule on collisions of NH<sub>3</sub> with He had just appeared in the October 1 issue of *The Journal of Chemical Physics* (JCP).<sup>2</sup> Applying the powerful technique of microwave double resonance that I inherited from my thesis supervisor, Koichi Shimoda, at the University of Tokyo, I was studying selection rules of spectroscopy and collisions. In spectroscopy, I worked as an anarchist, demonstrating that the selection rules in the textbooks are by no means sacred and many “forbidden” transitions are allowed. In studying collisions, I worked as a lawmaker, revealing experimentally that the changes of rotational levels, which appear random, follow approximate but simple selection rules. Such subtleties of selection rules in spectroscopy and collisions, however, are washed out in the laboratory due to high pressure and result in thermal distributions according to the maximum entropy principle. In the low densities of interstellar space, however, the two processes may be competitive, and the intricacy of the selection rules is manifest in their raw forms! On that day I was to give my progress report at Herzberg’s group meeting, but I scrapped my prepared report and talked about the discovery of interstellar NH<sub>3</sub>.

I sent my JCP paper to Townes. I sent it without an accompanying letter since I was sure he would understand it right away. Sure enough, in the May 1, 1969 issue of *The Astrophysical Journal* (ApJ), the authors (including Townes) used the collisional  $\Delta k = 3n$  rule for the analysis of interstellar NH<sub>3</sub>.<sup>3</sup> In this paper they stated that the  $\Delta k = \pm 3$  radiative transition (spontaneous emission) occurs via the electric octopole moment of NH<sub>3</sub> and takes longer than the age of the Universe. I immediately thought that this could not be right. The spontaneous breakdown of symmetry must produce a small dipole moment to cause the forbidden transitions. Jim Watson completed the theory. We found that the forbidden  $(J, K) = (2, \pm 2) \rightarrow (1, \mp 1)$  spontaneous emission has a lifetime of 300 years, 8 orders of magnitude less than the age of the Universe.<sup>4</sup> Thirty years later, when H<sub>3</sub><sup>+</sup> was discovered in the Galactic center, this spontaneous emission, which was somewhat academic for NH<sub>3</sub>, became essential since its lifetime is only 27.6 days and competitive with collisions in diffuse clouds.<sup>5</sup> Jim Watson is a supreme theorist, and his work greatly inspired me and influenced my experimental research. The

theory of vibration–rotation interactions was originated by Edward Teller, founded by Bright Wilson, and completed by Jim. His 1968 paper on the simplification of the Wilson–Howard Hamiltonian is the most beautiful paper on theoretical spectroscopy by any of my contemporaries.<sup>6</sup>

Following NH<sub>3</sub>, H<sub>2</sub>O and H<sub>2</sub>CO were discovered in interstellar clouds. They each appeared in a most dramatic way in the centimeter region – NH<sub>3</sub> in emission from metastable levels, H<sub>2</sub>O as an intense maser with a spectacular velocity profile, and H<sub>2</sub>CO in strong absorption of the 2.73 K cosmic background radiation. All of those manifestations of extraordinary molecular distributions added fuel to my fascination with interstellar molecules since each of them is the result of the subtle interplay of collisional and radiative selection rules. My first paper in ApJ 1970 was on the cooling of H<sub>2</sub>CO due to radiative selection rules analogous to adiabatic demagnetization.<sup>7</sup> Although Townes and Cheung’s<sup>8</sup> analysis using collisional selection rules became the orthodoxy, I still think my explanation is alive. Spectroscopists fall in love with molecules; my first love was H<sub>2</sub>CO. I obtained my Ph.D. at the University of Tokyo in 1960 by performing microwave spectroscopy of H<sub>2</sub>CO in Shimoda’s lab. Koichi Shimoda is a genius experimentalist and did first-class experiments with very limited budgets in impoverished post-World War II Japan. It was tremendous luck for me that Charlie Townes stayed in Shimoda’s lab for half a year while on sabbatical leave in 1956 when I was a freshman graduate student in Shimoda’s lab. I learned greatly from listening to discussions between the two physicists. Following Shimoda’s design, Eizi Hirota and I constructed a microwave spectrometer in Yonezo Morino’s lab in Chemistry; that was the beginning of Hirota’s great work on free radicals, which was to blossom from 1975 to 1990 at the Institute of Molecular Sciences in Okazaki.

The subtle interplay between the radiative and collisional effects has become my bread and butter and was later applied to H<sub>3</sub><sup>+</sup> in the Galactic Center<sup>5</sup> (Section 7) and the anomalous diffuse interstellar bands toward Herschel 36.<sup>9</sup>

## 2. CYANO-POLYACETYLENE: HARRY KROTO

I wanted to discover new interstellar molecules. I joined NRC radio astronomers in using the 46 m radio telescope in the Algonquin Provincial Park, 200 km west of Ottawa. Although the microwave dish was there, the detection system took a long time to come. When it was usable in 1973, centimeter spectra had been exhausted and the frontier of radio astronomy had moved to the millimeter wave region. Particularly significant were the 1970 discoveries of CO by Wilson, Jefferts, and Penzias and of “X-ogen” by Buhl and Snyder, which was correctly conjectured to be HCO<sup>+</sup> by Klemperer; they were to become the cornerstones of astrochemistry. We tried several

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molecules without success. I was exhausted and miserable on the train rides from the Observatory back to Ottawa after each week of overnight observations with Lorne Avery, Norm Broten, and John MacLeod. I badly needed novel heavy molecules with strong lines in the centimeter region. Therefore, when Harry Kroto of the Sussex University wrote to me in early March 1975 about his new laboratory spectrum of  $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$  and asked me whether I was interested in searching for it in interstellar space, I jumped on it – I was like a drowning man clutching for a straw. I wrote back to him, “Yes!! I am very very very very very much interested.” To our great surprise and delight, we detected a strong  $J = 4 \rightarrow 3$  emission line from Sgr B2, the treasure house of molecules near the Galactic center some 25,000 light years away.<sup>10</sup> I was amazed by the estimated total mass of the molecule,  $\sim 1000$  earth masses, needed to make such a strong signal. Upon writing the discovery paper, I looked in Chemical Abstracts and was further surprised to find that  $\text{HC}_5\text{N}$  was not listed. It was a new molecule in the literature then available! This was the beginning of the investigations of long carbon chain molecules.

Kroto's laboratory attempt to vaporize the next member,  $\text{HC}_7\text{N}$ , was met with difficulty, and we went to the Observatory without the laboratory frequency. As eloquently written by Kroto,<sup>11</sup> the heroic effort of his student Colin Kirby made the crucial frequency available just in time for the start of our observation on March 26, 1977. In those days of no e-mail, Colin called Margaret, Harry's wife, who in turn called Fokke Kreutzberg at NRC, and he called the Observatory; at least three people jotted down the rotational constant and centrifugal distortion constant, each with seven effective figures, correctly. Shortly after 1:00 a.m., we clearly saw the  $J = 9 \rightarrow 8$  line toward the Taurus Molecular Cloud (TMC-1).<sup>12</sup> Harry calls it “the most exciting and memorable scientific day of my life”. The laboratory spectrum could not be obtained for the next chain,  $\text{HC}_9\text{N}$ , and I used a very simple extrapolation using the known series  $\text{H}(\text{C}\equiv\text{C})_n\text{CN}$  ( $n = 0-3$ ).<sup>13</sup> Surprisingly, the predicted frequency was good to five significant figures, accurate enough for detecting the  $J = 18 \rightarrow 17$  line.<sup>14</sup> The frequency range of our heterodyne detector was very limited, and it was lucky that all three molecules happened to have a transition within the range of 0.7 GHz. Each time the acetylene chain got longer from  $\text{HC}_3\text{N}$  to  $\text{HC}_7\text{N}$  to  $\text{HC}_9\text{N}$ , the column density decreased by a factor of  $\sim 4$ . This made the detection of the next chain  $\text{HC}_{11}\text{N}$  impractical, and I stopped the project there. When this molecule was discovered 20 years later by the Thaddeus group,<sup>15</sup> it appeared at a frequency that agreed with my prediction to seven digits. Considering the fact that the moment of inertia nearly doubles upon inserting one acetylene chain, this was amazing. Those molecules behave well!

Kroto's desire to show that the long carbon chain molecules we had seen in space could be produced in the atmospheres of red giant carbon stars such as IRC+10216 led to beautiful serendipitous discovery of  $\text{C}_{60}$  using Rick Smalley's beam machine. Thus, radio astronomy has led to a major discovery in chemistry.

### 3. LABORATORY SPECTRUM OF $\text{H}_3^+$ : GERHARD HERZBERG, ALEX DOUGLAS, JIM WATSON

I was mystified by the discovery that the molecules unknown to chemists exist so abundantly in the hostile environment of low-temperature and low-density interstellar space. The explanation for this had been given in 1973 by Herbst and Klemperer and by W. D. Watson, who showed that ion-neutral reactions are

the key and  $\text{H}_3^+$  plays the central role in it as the universal proton donor (acid). According to Watson, “Due to the widespread abundance of  $\text{H}_2$ , ion-molecule reactions with  $\text{H}_2$  and  $\text{H}_3^+$  can be the chief formation process for small interstellar molecules in a large fraction of the interstellar gas.” It looked like observing  $\text{H}_3^+$  in interstellar space was the most fundamental thing to do in astrochemistry. But its spectrum was unknown. The spectrum of  $\text{H}_3^+$  had been a Holy Grail for spectroscopists since the first attempt by J. J. Thomson. Herzberg's persistent attempts to find it in emission since 1941 were well known. In 1975, I decided to try to find the spectrum in absorption. There were two papers in 1971 saying that detection of the spectrum in absorption was impossible, but when I checked the orders of magnitude of essential parameters, a technique I had learned from Shimoda, I was convinced that the detection was feasible. I went to Alex Douglas, head of our group, and asked for the budget to assemble a difference frequency system developed by Alan Pine at the MIT Lincoln Lab in 1974 and a positive column discharge system used by Claude Woods in Wisconsin. Alex's answer on that day was a flat “no”, and I left asking him to reconsider. When I went to see him the next week, he approved the budget. I was surprised. Not only was our section budget tight and my proposal would consume much of it, but it was evident that I was ignorant on the subject of molecular ions. I was outside the main stream of Herzberg's group and did not participate in the spectroscopy of unstable species. Moreover, Herzberg himself was looking for the  $\text{H}_3^+$  spectrum in emission. It was courageous and generous of them to let me try. Anyhow, this decision by them has finalized my subsequent research up until today, and I am forever grateful to their trust in me. Alex Douglas was an extremely bright spectroscopist who identified interstellar  $\text{CH}^+$ , the first interstellar molecular ion, when he was a Master's student of Herzberg. He identified William Huggins's comet spectrum as due to  $\text{C}_3$  and discovered many spectra of novel radicals. He proposed carbon chains as carriers of diffuse interstellar bands based on the Douglas effect, the internal conversion of energy in polyatomic molecules, and our discovery of long carbon chain molecules.

My wife Keiko and I had four children, and my evenings and Sundays were for them, but otherwise I concentrated on the search of the  $\text{H}_3^+$  spectrum. I kept away from all conferences except the biannual laser spectroscopy meeting, where I learned the rapidly developing laser techniques. A slow worker, I needed 4 1/2 years to assemble the apparatus and find the first line of  $\text{H}_3^+$  on April 24, 1980. By May 9, 10 lines were measured, and their frequency pattern and response to plasma conditions convinced me that I had the right spectrum, but I did not have the firm line assignments. On the evening of May 9, Jim Watson came into my lab and, with his usual candor, advised me to stop this quixotic attempt to find the Holy Grail. Upon looking at the 10 lines, however, he got interested. When I went to the lab the next morning, I saw on my desk 10 lines all assigned to the  $\nu_2$  fundamental band of  $\text{H}_3^+$ , except one line, which was hydrogen Brackett- $\alpha$ . By the beginning of June, 15  $\text{H}_3^+$  lines were observed, and I drafted a manuscript and sent it to *Physical Review Letters* on June 6.<sup>16</sup> As soon as I sent the paper I started preparation for the detection of interstellar  $\text{H}_3^+$ .

### 4. SPECTROSCOPY OF MOLECULAR IONS: STUDENTS, RICH SAYKALLY, TAKAYOSHI AMANO

My observation of the  $\text{H}_3^+$  spectra did not make a big splash, but I received responses in the form of job offers from a few

well-known universities. I had long wanted to work with students, and I accepted the offer from the University of Chicago since its offer via Steve Berry on February 26, 1979 was the first and predated the successful detection of the  $\text{H}_3^+$  spectrum. Chandrasekhar and Yoichiro Nambu there were big magnets also. I moved to Chicago on July 15, 1981 as a 49 year old professor jointly affiliated with the Department of Chemistry and the Department of Astronomy and Astrophysics. I started from completely empty rooms, some of which were once used by Thorfin Hogness, who first wrote down the celebrated  $\text{H}_3^+$  production reaction  $\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}$ , and later by Robert Mulliken.

It took me a while to start up the lab, and my next new spectrum of  $\text{NH}_4^+$  did not arrive until early May 1983. By then, several other groups had jumped in the field of infrared ion spectroscopy using tunable laser sources, the field opened up by the discovery of the  $\text{H}_3^+$  spectrum, and gotten ahead of me. Rich Saykally, who did great work on ion rotational spectra at Wisconsin as a graduate student of Claude Woods and at NBS (now NIST) in JILA as a postdoc of Ken Evenson, started a large ion spectroscopy group in Berkeley in 1979 based on color center lasers and diode lasers. On January 18, 1983, we heard shocking news that Saykally's group had successfully demonstrated the method of velocity modulation, a major invention in molecular ion spectroscopy that became indispensable in my work using positive column plasmas. The audacious young professor with brilliant students and postdocs became our fiercest competitor. They squarely beat us in the field of anion spectroscopy. Takayoshi Amano, who took over my spectrometer in Ottawa and replaced my clumsy standing-wave dye laser with a ring laser, observed spectra of  $\text{HeH}^+$  and  $\text{NeH}^+$ . He also discovered many novel spectra of free radicals more along the line of Herzberg's group. Using liquid-nitrogen-cooled hollow cathode discharges, he was to lead the field of protonated ions. He is now *the* leader in submillimeter spectroscopy of molecular ions. Davies in Cambridge, Kawaguchi and Hirota in Okazaki, and Sears of Brookhaven National Laboratories also joined in. The rotational constants, accurately determined from infrared spectra, led to searches for rotational spectra in the millimeter and submillimeter regions, and the groups of Woods in Wisconsin, De Lucia at The Ohio State University, Bogey, Demynek, and Destombes in Lille, and Meerts and Dymanus in Nijmegen joined in, and the field flourished for two decades.

My Chicago group concentrated on  $\text{H}_3^+$  and the most fundamental ions containing one heavy atom like  $\text{OH}^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{NH}_2^+$ ,  $\text{NH}_3^+$ ,  $\text{NH}_4^+$ ,  $\text{CH}_2^+$ ,  $\text{CH}_3^+$ , and  $\text{CH}_5^+$ . Each ion had its own idiosyncrasy in its plasma chemistry and as a vibrator, and each spectrum was different.<sup>17</sup> I have vivid memories of studying each ion; each resulted in approximately one thesis. Mitchio Okumura, now at Caltech, found the spectrum of  $\text{NH}_2^+$ , a quasi-linear molecule. He also initiated the ultra-high-resolution solid hydrogen spectroscopy with Man-Chor Chan, now at the Chinese University of Hong Kong, which was later developed by Takamasa Momose, now at the University of British Columbia. This project, greatly contributed by David Weliky now at Michigan State and Rob Dickson now at Georgia Tech, is outside the scope of this article. Mounji Bawendi, now at MIT studied  $\text{NH}_3^+$ , although his thesis work was on hot-bands of  $\text{H}_3^+$ , which played a critical role in deciphering Jupiter emission spectrum observed in 1989. Mark Crofton, now at Aerospace, and others spent enormous amount

of time on carbo-ions such as  $\text{CH}_3^+$ ,  $\text{C}_2\text{H}_2^+$ ,  $\text{C}_2\text{H}_3^+$ ,  $\text{C}_2^-$ , etc., which play pivotal roles in interstellar carbon chemistry.

The case of  $\text{H}_3\text{O}^+$  is memorable because of acrobatics needed to decipher the spectrum. This ion has the inversion motion like its isoelectronic  $\text{NH}_3$ , but because the central charge attracts hydrogen atoms inward, it is more planar and has a higher inversion frequency. To use  $\text{H}_3\text{O}^+$  as an astronomical probe, determination of this frequency was imperative. For this purpose, we needed to observe the  $1^- \leftarrow 1^+$  inversion  $\nu_2$  hot band with a band origin at  $373\text{ cm}^{-1}$ . Diode lasers were the only tunable sources at this frequency, but the spectrum was at the lowest edge of the tunability (both may still be true today, nearly 30 years later). Also the frequency coverage of the diode was very patchy – about one-third. Di-Jia Liu, now at the Argonne National Laboratories, and I had to struggle with a spectrum devoid of P-branch lines and patchily covered Q and R branch lines. It was like a jigsaw puzzle with 80% of the pieces missing. But somehow we got lucky and determined the inversion splitting to be  $55.3462\text{ cm}^{-1}$ , sufficiently accurate<sup>18</sup> for the submillimeter group in Nijmegen to observe many inversion lines systematically.<sup>19</sup>

I understood all spectra of molecular ions studied except the spectrum of protonated methane,  $\text{CH}_5^+$ . We observed 900 lines of C–H stretch bands, and I was convinced that they are lines of  $\text{CH}_5^+$  from their plasma chemical behaviors, but I could not decipher the spectrum. I did not even know where to begin. Unlike  $\text{CH}_4$ , where the four hydrogen atoms are semirigidly attached to the central carbon in the tetrahedral structure, the five hydrogen atoms in  $\text{CH}_5^+$  are swarming around the central  $\text{C}^+$ , creating a complicated spectrum. I have surrendered and published my only unassigned spectrum in 1999.<sup>20</sup> In conferences, I predicted that it would take at least two decades to understand the spectrum. Although David Nesbitt greatly simplified the spectrum by using a jet plasma, the solution is still far to come. I now think two decades was a gross underestimate.

Those laboratory ion spectra obtained in my lab and other laboratories lay somewhat dormant for about two decades, but when the Herschel Observatory with its powerful HIFI spectrograph was launched there was an avalanche of observations of  $\text{OH}^+$ ,  $\text{H}_2\text{O}^+$ , and  $\text{H}_3\text{O}^+$ , which have been reported since 2010. These ions have emerged as powerful probes of the oxygen chemistry and of cosmic rays. In the future, all molecular ions discussed in this section will be discovered either through their rotational spectra or vibrational spectra and will play important roles as astrophysical probes.

## 5. DETECTION OF INTERSTELLAR $\text{H}_3^+$ IN DENSE CLOUDS: TOM GEBALLE

My first search for interstellar  $\text{H}_3^+$  on the nights of March 23 and 24, 1981 at the Mayall Telescope on Kitt Peak using the Fourier transform spectrometer of Don Hall and Steve Ridgeway was a miserable failure.<sup>21</sup> I realized that the technology of astronomical infrared spectroscopy was far behind the radio astronomy and much developmental work was needed. Charlie Townes, who initiated the avalanche of radio astronomical discoveries, had moved out of radio and was pioneering astronomical infrared spectroscopy; I asked his advice for a possible collaborator. He immediately mentioned Tom Geballe, his former student in Berkeley, then moving to the United Kingdom Infrared Telescope (UKIRT) on Mauna Kea Hawaii. I called him and observed with him and Eric Persson on the nights of December 4 and 5, 1982 at NASA

Infrared Telescope Facility (IRTF). Since then, Tom and I have been working together on  $\text{H}_3^+$  for over 30 years. Tom's prescient choice of infrared stars has been the biggest factor in the great development of the astronomical  $\text{H}_3^+$  spectroscopy. I am forever grateful to Charlie for this crucial advice. Even with Tom's expertise, however, it took many years of gradually improving the sensitivity of spectrometer before interstellar  $\text{H}_3^+$  was finally detected 14 years later.

In the meantime, the first natural  $\text{H}_3^+$  spectrum outside of laboratories arrived in 1989 as a serendipitous discovery of strong emission at  $2.1 \mu\text{m}$  from Jupiter, which Jim Watson assigned to the  $2\nu_2^2 \rightarrow 0$  first overtone band. Because of the strong coupling of vibration and rotation, the analysis was not straightforward; he used Bawendi's laboratory spectrum of the  $2\nu_2^2 \leftarrow \nu_2^1$  hot band to assign low  $J$  lines and the result of the variational calculations by Miller and Tennyson to assign high  $J$  lines. Soon afterward, Tom and I observed the stronger fundamental  $\nu_2^1 \rightarrow 0$  Jupiter emission on the mornings of September 14–19, 1989.<sup>22</sup> We found that the intense  $\text{H}_3^+$  spectrum from the colossal plasmas in the polar regions of Jupiter ionospheres<sup>23</sup> is extremely pure and free of background. The spectrum is so pure that planetary scientists do not need to use a spectrometer but simply use a camera with a proper filter to take images of Jupiter and measure the intensity of the  $\text{H}_3^+$  emission and study morphology and temporal variations of Jovian plasmas. It was a shame that we were looking for a weak  $\text{H}_3^+$  spectrum in objects 1000 light years away while the strong emission was waiting to be discovered in Jupiter, which is only 40 light minutes away. We are nitwits up against nature. The  $\nu_2^1 \rightarrow 0$  emission was observed also in Uranus and Saturn and became a powerful tool for planetary scientists for studying planetary ionospheres. We had an exciting 5 years observing  $\text{H}_3^+$  in planetary ionospheres, including the spectroscopic observations of the impact of the Shoemaker-Levy 9 comet on Jupiter from July 14 to 26, 1994 with Steven Miller. Someday the  $\text{H}_3^+ \nu_2^1 \rightarrow 0$  emission will be found in extra-solar Jupiters.

In 1994, big news arrived that John Lacy and others including Tom observed weak infrared absorption of  $\text{H}_2$  toward NGC 2024. This observation became possible because of the recently installed high-resolution CSHELL spectrometer of the IRTF with its sensitive  $256 \times 256$  InSb array, which made the operation of the infrared astronomical spectroscopy somewhat close to that of radio astronomy 30 years previous. I then knew that the detection of  $\text{H}_3^+$  was imminent since the dipole spectrum of  $\text{H}_3^+$  is stronger than the quadrupole spectrum of  $\text{H}_2$  by nine orders of magnitude, and this would override the small abundance of  $\text{H}_3^+$ . Tom and I submitted proposals to the IRTF in 1994 and 1995, but they were rejected three semesters in a row. In the meantime, a similar  $256 \times 256$  array was also installed on the UKIRT CGS4 spectrometer. We asked for service (quick response) time at UKIRT, and Tom, now Head of Operations there, scheduled a service night on April 29, 1996. Within one hour he detected  $\text{H}_3^+$  in two dense clouds, GL 2136 and W33A.<sup>24</sup> We waited for a long 2 1/2 months until July 15 to verify that the lines shifted by the right amount due to the earth's motion and then submitted a paper to *Nature*.<sup>25</sup> Since 1972, the presence of  $\text{H}_3^+$  had been assumed in chemical model calculations in astrochemistry for 24 years, but this was now validated. Thus started the observational investigations of interstellar  $\text{H}_3^+$ .

## 6. $\text{H}_3^+$ IN DIFFUSE CLOUDS AND COSMIC RAYS: BEN MCCALL, TOM GEBALLE

Although it took a long 15 years to find the first signal, once detected,  $\text{H}_3^+$  was found everywhere and kept bringing us big surprises. On the night of July 10, 1997, a year after the discovery, Tom and I were at the UKIRT along with Ben McCall, who joined my group as a new graduate student at this crucial time, and the night turned out to be the most surprising night in our lives.<sup>26</sup> We pointed the telescope to the Galactic Center (GC), a complex and active region Tom was very familiar with from his earlier studies. To our surprise and delight, we found huge signals of  $\text{H}_3^+$  toward two infrared stars GCIRS 3 and GCS 3-2.<sup>27</sup> Its absorptions were at least 10 times stronger than the first signals observed a year earlier and had an intricate velocity profile extending over  $200 \text{ km s}^{-1}$ . We had been happy to have finally pinned down interstellar  $\text{H}_3^+$  in dense clouds, but that was simply a confirmation of a prediction. Instead, we now had completely unexpected spectra which will take us many years to understand. The surprise did not end there on that night. Past midnight, Tom pointed the telescope to Cygnus OB2 No. 12, the very faint visible star discovered by Bill Morgan of the Yerkes Observatory in 1952, and  $\text{H}_3^+$  was clearly detected. This was surprising since the gas toward that visible star must be diffuse and contain many electrons which would rapidly destroy  $\text{H}_3^+$  through the very fast dissociative recombination.<sup>28</sup> The surprising results obtained in that one night have opened up new fields and would keep us busy for decades.

Ben took a double Ph.D. in chemistry and astronomy, and his systematic studies of  $\text{H}_3^+$  in dense and diffuse clouds constituted the astronomy part of his thesis.  $\text{H}_3^+$  in dense clouds is seemingly well-behaved, just as theory predicted, but  $\text{H}_3^+$  in diffuse clouds was unexpected. The observed  $\text{H}_3^+$  column densities in diffuse clouds are comparable with those in dense clouds in spite of the fact that the reddening and therefore the amount of hydrogen are 10 times less.<sup>29</sup> It was clear that the  $\text{H}_3^+$  to hydrogen ratio  $n(\text{H}_3^+)/n_{\text{H}}$  is 10 times higher in diffuse clouds than in dense clouds.<sup>30</sup> While Ben was a postdoc in Rich Saykally's lab as a Miller fellow, he measured the rate constant of the dissociative recombination of  $\text{H}_3^+$ , the most crucial laboratory parameter for  $\text{H}_3^+$  in diffuse clouds, using the CRYRING ion storage ring at the Manne Siegbahn Laboratory in Stockholm with the group of Mats Larsson, who is *the* leader in the field of the dissociative recombination, especially of  $\text{H}_3^+$ . Combining the laboratory results with astronomical observations, Ben reached the conclusion that the cosmic-ray ionization rate  $\zeta$  in diffuse clouds is an order of magnitude greater than that in dense clouds.<sup>31</sup> Thus the value of  $\zeta \approx 10^{-17} \text{ s}^{-1}$  that had been held as the canonical value for over 30 years both theoretically and observationally was shown to be more than an order of magnitude too small in diffuse clouds.

Through further systematic observation by Ben and his student Nick Indriolo at University of Illinois at Urbana–Champaign, the use of  $\text{H}_3^+$  has emerged as the most direct manner to determine the intensities of low-energy (1–100 MeV) cosmic rays.<sup>32</sup> Together with observation of  $\gamma$ -rays, which probe high-energy ( $\geq 1 \text{ GeV}$ ) cosmic rays,  $\text{H}_3^+$  may lead us to a better understandings of the cosmic rays, one of the most important and least understood subjects in astrophysics.

## 7. H<sub>3</sub><sup>+</sup> IN THE CENTRAL MOLECULAR ZONE OF THE GC: TOM GEBALLE, MIWA GOTO

As noted in Section 5, the first surprise of our H<sub>3</sub><sup>+</sup> observations in the Galactic center was the strong absorptions with complex velocity profiles. We were further surprised to find the ubiquity of H<sub>3</sub><sup>+</sup> in gas columns from the central Sgr A\* to the supermassive Quintuplet Cluster 30 pc to the East. High H<sub>3</sub><sup>+</sup> column densities on the order of  $3 \times 10^{15} \text{ cm}^{-2}$  were found toward each of a dozen or so stars without exception, indicating the H<sub>3</sub><sup>+</sup> surface filling factor of 100%.<sup>33</sup> The Central Molecular Zone (CMZ) of the GC, a region with radius of  $\sim 150$  pc, is known to be very rich in molecules, accommodating  $\sim 10\%$  of all molecules in the Galaxy in the small volume of  $\sim 10^{-5}$  of the Galaxy, but H<sub>3</sub><sup>+</sup> is even more concentrated in that region!

It was timely that large-diameter telescopes equipped with high-resolution infrared spectrometers became available around the turn of the century. Our second surprising observation of the GC H<sub>3</sub><sup>+</sup> arrived when we used the 8 m Subaru Telescope with the IRCS spectrometer and found strong absorption by H<sub>3</sub><sup>+</sup> in the (J, K) = (3, 3) metastable rotational level 361 K above the (1, 1) ground level.<sup>34</sup> Until then, our observations had been limited to *para*-H<sub>3</sub><sup>+</sup> in the ground (1, 1) level and *ortho*-H<sub>3</sub><sup>+</sup> in the (1, 0) level 32.86 K above, reflecting the cold environment for H<sub>3</sub><sup>+</sup>. The high population in the (3, 3) level clearly indicated high temperatures in the CMZ. Moreover, the spectrum of H<sub>3</sub><sup>+</sup> in the (3, 3) level showed a wide velocity profile extending nearly 200 km s<sup>-1</sup>. These characteristics made metastable H<sub>3</sub><sup>+</sup> a useful fingerprint, discriminating between gas in the CMZ and gas in the foreground.

In 2003, Tom and I started to use the 8 m telescope of the Gemini South Observatory equipped with the Phoenix Spectrometer assembled by Ken Hinkle in Cerro Pachon, Chile. Located in the southern hemisphere, ideal for observations of the GC, the spectrometer was to be our work horse for 7 years. Our third surprise was the observed lack of H<sub>3</sub><sup>+</sup> in the (2, 2) level, which is 210 K below the well-populated (3, 3) level.<sup>35</sup> The nonthermal negative excitation temperature is due to the forbidden (2,  $\pm 2$ )  $\rightarrow$  (1,  $\mp 1$ ) spontaneous emission mentioned in Section 1. The lack of H<sub>3</sub><sup>+</sup> in the (2, 2) level clearly demonstrated the low density of the GC environment. The ab initio theory of H<sub>3</sub><sup>+</sup> has been developed to the extent that the theoretical emission life of 27.6 days is very accurate. Therefore, the environments where H<sub>3</sub><sup>+</sup> resides must have densities well below the critical density of  $\sim 200 \text{ cm}^{-3}$ . A model calculation for thermalization of H<sub>3</sub><sup>+</sup> using accurate spontaneous emission rates and a very approximate collision theory based on Boltzmann's principle of detailed balancing has been developed.<sup>5</sup> Applications of these model calculations to observed column densities have quantified the presence of warm ( $\sim 250$  K) and diffuse ( $< 100 \text{ cm}^{-2}$ ) gas from Sgr A\* to 30 pc to the East.<sup>35,33</sup>

The fourth surprise was the high ionization rate and large cloud dimensions required to account for the observed strong absorptions and hence high H<sub>3</sub><sup>+</sup> total column densities. Since the advent of H<sub>3</sub><sup>+</sup> as a probe, the cosmic ray ionization rate has been shown to be on the order of  $3 \times 10^{-17} \text{ s}^{-1}$  for dense clouds and  $3 \times 10^{-16} \text{ s}^{-1}$  for diffuse clouds in the Galactic disk, but the rate in the CMZ was found to be another factor of 10 higher, on the order of  $3 \times 10^{-15} \text{ s}^{-1}$ . The high H<sub>3</sub><sup>+</sup> column densities also require long path lengths, indicating very significant volume filling factor of warm and diffuse gas in the CMZ. Thus both a hitherto unsuspected vast amount of gas in

a new category of environment and an unusually high ionization rate have been revealed in the CMZ by H<sub>3</sub><sup>+</sup> spectroscopy.

In those findings, we used bright infrared stars in the GC that had been found by previous investigators. In 2009, Tom and I launched a new project to find many more stars suitable for H<sub>3</sub><sup>+</sup> spectroscopy, covering wider regions of the CMZ. This is a time-consuming project and will take several more years to complete, but it is already bearing rich fruit. H<sub>3</sub><sup>+</sup> spectroscopy toward the first groups of such stars, located from 140 pc West of Sgr A\* to 85 pc East, have brought big surprises. The spectra toward new stars also show vast amounts of the warm and diffuse gas and the high ionization rate, but their velocity profiles are wildly different from previous spectra toward stars near the center.<sup>36,37</sup> We could also observe dense clouds in hotbeds of recent star formation near the center, not only in Sgr A but also in Sgr B, C, and E. Our observations also appear to be revealing the Expanding Molecular Ring in the outskirts of the CMZ, whose dimensions and velocities are comparable to those previously reported but are qualitatively different in that they imply pure expansion without rotation. These are ongoing projects, and I look forward to many more surprises.

Readers who are interested in more details of the recent development of chemistry, astronomy, and physics of H<sub>3</sub><sup>+</sup> are referred to the three special H<sub>3</sub><sup>+</sup> issues of the *Philosophical Transaction of the Royal Society* in 2000, 2006, and 2012.<sup>38</sup>

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