氏名 荒木 光典

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論文審査委員 主査 教授 中村 宏樹
　教授 齊藤 修二
　教授 加藤 立久
　教授 見附 孝一郎
　教授 高木 光司郎（富山大学）
Introduction

Over one hundred molecular species have been detected in interstellar space by radio astronomical observations. It is generally accepted that the most abundant molecules in dark clouds have been already detected. These interstellar molecules are mainly produced by ion-molecule reactions, which are uniquely efficient in the interstellar physical conditions of low temperature and low density. This makes molecular ions extremely important intermediates in the interstellar chemistry even at very small abundances. Since detection of ions in interstellar space has been extremely limited, it is thought that they have not accumulated sufficient observational information to explain the reaction scheme. Physical and chemical processes in the interstellar space can be studied by using spectral lines of the molecular ions, and laboratory microwave spectroscopy is a powerful tool for supplying precise transition frequencies of the ions to radio astronomy. However, laboratory measurements are not easy because of the difficulty in producing sufficient concentrations of ions. Development of efficient production methods for molecular ions will make it possible to observe many more of them by microwave spectroscopy.

Several interstellar molecules have been found to have large D/H ratios enhanced by factors of $10^3 - 10^4$ over the primordial cosmic D/H ratio of $\sim 1.5 \times 10^{-5}$. For example, the abundance ratio of the deuterated species to HCN, [DCN]/[HCN], is found to be 0.023 in the dark cloud, Taurus Molecular Cloud (TMC-1). This enhancement is called "deuterium enrichment." The degree of the deuterium enrichment is determined by physical conditions and related reactions in interstellar clouds. In other words the deuterium enrichment is generally a good probe to study the reaction scheme in space. As a result laboratory microwave spectroscopic studies of deuterated species are important in astronomy as well as in molecular spectroscopy. He has studied several deuterated molecular ions related to interstellar phenomena.

Microwave spectra of $\text{D}_3\text{O}^+$ and $\text{D}_3\text{S}^+$

The hydronium ion $\text{H}_3\text{O}^+$ is a precursor to fundamental hydroxy interstellar molecules. For example, OH and $\text{H}_2\text{O}$ are generated by an exothermic recombination of electrons with $\text{H}_3\text{O}^+$. Similarly $\text{H}_2\text{DO}^+$ is a precursor to OD and HDO and is
generated by a series of ion-molecule reactions starting from a reaction of O with H₂D⁺. H₂D⁺ is a key molecule in the interstellar deuterium fractionation processes. Therefore, the interstellar [H₂DO⁺]/[H₃O⁺] ratios are very important information for an understanding of the fractional reaction scheme in molecular clouds. Although the inversion-rotation spectrum of H₃O⁺ is well known, prediction of H₂DO⁺ is not easy because it requires a precise molecular structure of H₃O⁺ and a precise potential for inversion motion of H₃O⁺. So, to obtain an improved molecular structure and potential of H₃O⁺, he studied the inversion-rotation spectrum of its fully deuterated species D₃O⁺.

Microwave spectra of the ions were observed using a microwave spectrometer at the Institute for Molecular Science. The spectrometer was a 100 kHz source-modulated system. Microwave radiation was generated with a combination of frequency multipliers and klystrons. An InSb photoconductive detector cooled by liquid helium was used to measure the power of microwave radiation. A free space discharge cell was cooled by circulating liquid nitrogen through a copper tube soldered on a copper sheet covering the glass cell.

After several trials he found that deuterated species of H₃O⁺ were efficiently produced by a hollow-cathode dc-glow discharge in a mixture of D₂ and D₂O in a 2 m length and 10 cm diameter free-space absorption cell. The length of the hollow cathode was 1.3 m. The production of the ions in the cell is increased by the hollow cathode effect.

Fifty three P- and Q-branch transitions between the lowest pair of levels of the inversion motion were precisely measured in the frequency region of 220 to 565 GHz. An analysis of the observed spectral lines yielded molecular constants for the upper (0') and lower (0") levels in the inversion motion. The inversion splitting was accurately determined to be 15.35550086(147) cm⁻¹, where the number in parentheses denotes one standard deviation of the fit. Combined with IR data, the inversion splitting of D₃O⁺ for the ν₂ inversion state was determined to be 191.38874(98) cm⁻¹. As a total, two inversion splittings were precisely determined by microwave spectroscopy and are important information for a proper understanding of the inversion potential of H₃O⁺. Potential function parameters can be revised using the two inversion splittings. Furthermore, a reliable inversion splitting of H₂DO⁺ can now be estimated from the new potential function parameters and used to predict transition frequencies of
H$_2$DO$^+$.  

The average structures ($r_*$ structure) of H$_3$O$^+$ and D$_3$O$^+$, that is, averaged for zero point motion in the ground vibrational state, were derived from their averaged rotational constants.  The results are as follows: for D$_3$O$^+$ (0" ; $r_* = 0.98392(152)$ Å, $\theta_* = 113.62(65)\,^\circ$, and for D$_3$O$^+$ (0" ; $r_* = 0.98510(152)$ Å, $\theta_* = 112.94(65)\,^\circ$ where $r$ is O-D bond length and $\theta$ D-O-D bond angle.  The equilibrium structure ($r_s$ structure) of H$_3$O$^+$, a hypothetical structure of the potential, was determined from the $r_s$ structures of H$_3$O$^+$ and D$_3$O$^+$ by extrapolations.  The $r_s$ structure was obtained to be $r_s = 0.9780(59)$ Å and $\theta_s = 112.8(25)\,^\circ$.  As a result, he was able to estimate the rotational constants of H$_2$DO$^+$ from the structures of H$_3$O$^+$ and D$_3$O$^+$, which were used to predict a spectral pattern of H$_2$DO$^+$.  

In addition, he succeeded in observing the D$_3$S$^+$ ion generated by the hollow-cathode discharge.  The $J = 1-0$ to 4-3 spectral lines of D$_3$S$^+$ were measured in the 152 - 610 GHz region.  The molecular constants were determined from the measured frequencies.  The precise molecular structure of H$_3$S$^+$ and D$_3$S$^+$ was derived from their rotational constants.

**Microwave spectra of HCNH$^+$ and its deuterated species**

The method of a magnetically confined dc-glow discharge was employed to efficiently produce a protonated ion HCNH$^+$, whose concentration was enhanced due to a lengthening of ion-rich negative glow and an increase of ionizing electron density.  Around the absorption cell is wound a solenoid coil of enameled wire.  The magnetic field was generated to confine the discharge plasma.  The HCNH$^+$ and its isotopic species were produced by the discharge in HCN and/or DCN at around -120 °C.  The optimum magnetic field was about one hundred Gauss.

The interstellar protonated hydrogen cyanide ion, HCNH$^+$, is mainly produced by reactions of HNC and HCN with H$_3^+$, HCN$^+$ or H$_3$O$^+$, and is also considered to be a precursor of HNC, HCN and CN in dark molecular clouds.  Detection of HCND$^+$ may give information about the deuterium fractionation in molecular clouds.  The pure rotational transitions of HCNH$^+$, and its isotopic species, HCND$^+$ and DCND$^+$, were measured in the 107 - 482 GHz region.  The rotational constant $B_0$ and the centrifugal distortion constant $D_0$ for each ion were precisely determined by a least-squares fitting to the observed spectral lines.  The observed rotational transition...
frequencies and the predicted ones are accurate within about 30 to 40 kHz and are useful for astronomical searches of HCNH$^+$ and HCND$^+$. 
論文の審査結果の要旨

本研究は宇宙空間に存在するいわゆる星間分子の生成とその組成の理解にとって分子イオンが重要な役割を果しているという観点から、3種類の分子イオンH₂O⁺、SH⁺及びHCNH⁺についてマイクロ波スペクトルを正確に測定し、これらの分子構造を決定している。特に、星間分子中における重水素の存在比が高い事から、これら分子イオンの重水素化物（D₃O⁺、SD₃⁺、HCND⁺、DCND⁺）に着目し、その分子構造を高い精度で決定することに成功している。

先ず、OHやH₂O等の基本的なヒドロキシ化合物を電子との再結合過程で生成する重要な先駆体としてのH₃O⁺イオンに着目した。重水素化物H₂DO⁺の構造の推定をも目指して、D₃O⁺の反転回転遷移スペクトルの測定と解析を行っている（H₂DO⁺自身の実験は大変難しく、現在まだ成功していない）。十分な量の分子イオンを生成する事自体大変難しいことであるが、何回もの試みの後、ホーキーソード直流グロー放電を用いてD₂とD₂Oの混合気体からD₃O⁺を十分な濃度生成する事に成功している。その上で、最低の反転準位間のP及びQ-枝の遷移を220〜565GHzの範囲で根気よく高精度で測定し、それらを詳細に解析する事によって、反転分裂に対する最も信頼に値する数値を導出する事に成功している。ν₂反転準位の分裂値をも正確に決定している。更に、これらの正確なデータを基に、D₃O⁺のr₂構造等の分子構造をも詳細に確定している。これらに基づき、H₂DO⁺のスペクトルをも予測している。これは、今後の電波天文学にとって大いに役立つものと期待される。

同様な実験手段を用いて、SD₃⁺のスペクトルを152〜610GHz領域で詳細に測定し、分子構造をも決定している。

更に、星間分子雲におけるHCN、HNC、及びCN等の先駆体と考えられているHCNH⁺とその重水素置換体（HCND⁺及びDCND⁺）の反転遷移を107〜482GHz領域で詳細に測定し回転定数等の分子構造定数を決定している。スペクトルの同定は、将来これら分子イオンを宇宙空間で探索する時に大いに役立つと思われる。

以上、電波天文学にとって非常に重要なもの、しかも研究室実験の大変難しい分子イオンの重水素化物についてマイクロ波スペクトルを測定すると同時に同定し、分子構造を精度高く決定した事は高く評価される。学位論文としての水準に十分達しているものと判断された。また、本研究の内容は権威ある英文の学術雑誌3報に既に報告されている（いずれも出願者が第一著者である）。

また、口述試験は1月18日午後半時間に亘って実施された。D₃O⁺の実験を取り研究の全貌の発表を行うとともに、研究所研究内容及び基礎学力に関する質疑応答が実施された。研究内容とその背景に関する説明を行い、質問にも適確に答えており、博士の学位を得るのに十分であると判断された。

また、語学力については、論文が英語で書かれており、その能力は水準に達していると判断された。公開発表会でも研究内容の発表を要領良く行うとともに質問にも適確に答えており、最終的に審査委員全員一致で合格と判定した。