

Rotational spectroscopy of molecular ions using diode lasers

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We report here the first application of tunable diode lasers to study the pure rotational spectroscopy of molecular ions. High J rotational transitions of molecular cations ArH^+ , NeH^+ , HeH^+ , OH^+ , H_2O^+ , and anion OH^- have been observed.

I. INTRODUCTION

With the rapid development of semiconductor technology in recent years, the tunable diode lasers (TDL) have become increasingly important for high resolution spectroscopy. The unique feature of the infrared TDL includes the narrow linewidth (3–10 MHz) and the wide tunability, which makes it possible to perform high resolution and high sensitivity spectroscopy in any infrared region between 30–3 μm . Because of this, TDL have been successfully applied to study the vibration–rotation spectra of molecular ions.¹ We report here the first application of TDL for rotational spectroscopy of molecular ions. The two diode lasers used in this experiment oscillate in the 25–27 μm region which corresponds to nearly the long wavelength limit of the commercially available diodes. We studied diatomic cations ArH^+ , NeH^+ , HeH^+ , OH^+ , and anion OH^- and the asymmetric top molecular ion H_2O^+ in high rotational levels. The high J rotational transitions give higher order vibration–rotation constants and also crucial information of the kinetics of molecular ions in discharges.

II. EXPERIMENTAL

The apparatus used for this experiment is similar to that reported earlier.² Briefly, the infrared radiation generated in a LS-3 IR spectrometer was passed through an air cooled discharge tube (12 mm i.d. 80 cm long) and focused onto a liquid He cooled Cu:Ge detector which is located at the exit of 0.5 m monochromator. Different ions were generated in ac glow discharges with a variety of gas mixtures at the discharge frequency of 3 kHz. The velocity modulation technique developed by Gudeman and Saykally was employed.³ While the discharge current was kept at 150 mA, the discharge voltage varied from 2 kV to 5 kV, depending on the gas mixture.

Two Laser Analytics mesa-stripe geometry TDL were used as infrared sources. One mainly oscillated around 27 μm and the other around 25 μm . The 25 μm diode has a spectral coverage of $\sim 60 \text{ cm}^{-1}$ with many gaps. The typical tuning range of each single mode was about one wave number and the attainable power on the detector was 3–5 μW on the average. Optimum adjustment of the diode temperature and current were especially important for the low frequency diodes because the laser linewidth is often affected by the off-axis modes, multiple filaments and other factors leading to a drastic decrease of sensitivity. Our detection limit at this frequency was $\sim 10^{-5}$ which corresponded to an absorption

coefficient of 10^{-7} cm^{-1} with a single pass of 80 cm. The 27 μm diode has not allowed us to achieve the same sensitivity and coverage as the 25 μm diode.

Frequencies of the lines were measured using the FTIR spectra of CS_2 , $^{13}\text{CS}_2$,⁴ and N_2H_4 ,⁵ as calibration. The accuracy of our measurement is typically $\pm 0.003 \text{ cm}^{-1}$.

III. OBSERVED SPECTRA

All the molecular ions studied are light ions with large rotational constants ($B = 10\sim 30 \text{ cm}^{-1}$) and large permanent dipole moments ($> 1 \text{ D}$). The observed transitions are high J transitions with $J \geq 9$ for all ions except for HeH^+ . Because of the high rotational energy levels an air-cooled discharge tube was employed. Compared with the usual vibration–rotation spectroscopy where lower J levels are often studied, this rotational spectroscopic study deals with lower molecular populations but with higher dipole moments. The absorption cross sections at these temperatures are calculated to be in the range of 10 \AA^2 , which are comparable to that of vibration–rotation spectroscopy. For most ions, the ion density is estimated to be on the order of $10^9/\text{cm}^3$ which makes the absorption coefficients of 10^{-6} cm^{-1} , considerably above our detection limit.

A. ArH^+

The vibration–rotation emission spectrum of this ion was first observed by Brault and Davis in a carbon hollow cathode lamp with a Fourier transform infrared spectrometer.⁶ They observed the fundamental as well as hot bands emission spectrum up to $v = 5 \rightarrow 4$ and determined the vibration–rotation constants very accurately. Based on their rotational constants, we measured seven high J ($J \geq 20$) rotational transitions of different vibrational levels from $V = 0$ to $V = 4$, and their frequencies are listed in Table I. Figure 1 shows the transition of $V = 0$ $J = 22 \leftarrow 21$ and $V = 1$ $J = 23 \leftarrow 22$ with 1f velocity modulation. Since all the measured transitions agree very well with the values calculated from the constants of Brault and Davis, no attempt has been made to improve the molecular constants.

ArH^+ rotational transitions were first observed in the discharge of Ar with a trace of H_2 , but we found that the signal increased up to ten fold with the presence of a large amount of He. Adding He increases the discharge temperature since the electronic temperature is approximately proportional to ionization potential of the main discharge gas. Both vibrational and rotational relaxation processes will be

TABLE I. Rotational transition frequencies of molecular ions.

Molecular ion	Permanent dipole moment (D)	Transitions	Measured frequency (cm ⁻¹)	Predicted frequency (cm ⁻¹)	Relative intensity ^a		
ArH ⁺	1.4 ^b	$V=0 J=21 \leftarrow 20$	408.899	408.899	...		
		$J=22 \leftarrow 21$	426.107	426.107	...		
		$J=23 \leftarrow 22$	443.013	443.009	...		
		$V=1 J=23 \leftarrow 22$	426.246	426.244	...		
		$V=2 J=23 \leftarrow 22$	409.750	409.748	...		
		$V=3 J=25 \leftarrow 24$	422.232	422.227	...		
NeH ⁺	3.004 ^c	$V=0 J=13 \leftarrow 12$	427.413	427.471	...		
		$V=4 J=25 \leftarrow 24$	404.871	404.876	...		
HeH ⁺	1.66 ^d	$V=0 J=7 \leftarrow 6$	448.160	448.167	...		
		$V=0 J=12 \leftarrow 11$	410.553	410.561	1		
OH ⁺	2.32 ^e	$J=13 \leftarrow 12$	410.405	410.407	1		
		$J=14 \leftarrow 13$	410.265	410.254	1		
		...	427.327	...	0.14		
		...	427.472	...	0.14		
		...	428.199	...	0.14		
		...	433.172	...	0.57		
		...	433.157	...	0.71		
		...	434.480	...	0.14		
		...	435.154	...	0.14		
		...	437.076	...	0.07		
H ₂ O ⁺	437.141	...	1		
		...	438.627	...	0.14		
		...	438.658	...	0.29		
		...	438.712	...	0.14		
		...	438.681	...	0.07		
		OH ⁻	1.04 ^f	$V=0 J=10 \leftarrow 9$	366.863	366.871	1
				$J=11 \leftarrow 10$	401.760	401.776	0.74

^aRelative intensities were assigned to be unity for the strongest transitions for each ion.

^bThe permanent dipole moment of ArH⁺ has been experimentally determined by K. B. Laughlin *et al.* (Ref. 35) recently. For frequency prediction, see Ref. 6.

^cFor permanent dipole moment, see Ref. 9. For frequency prediction, see Ref. 7.

^dFor permanent dipole moment, see Ref. 36. For frequency prediction, see Ref. 12.

^eFor permanent dipole moment, see Ref. 21. For frequency prediction, see Ref. 15.

^fFor permanent dipole moment, see Ref. 28. For frequency prediction, see Ref. 26.

slower in collisions with He than with Ar. These two factors are probably the main contributions to the increase of the ArH⁺ signal. The absorption signal was maximized in the mixture of H₂:Ar:He = 1:4:12, and ArH⁺ density was estimated to be 10¹¹/cm³.

The most interesting part of this experiment is the observation of the rotational transitions of individual vibrational states from $V=0$ to $V=4$ which has enabled us to monitor ArH⁺ concentration in each vibrational state. We have found that vibrational temperature varied significantly with the ratio of H₂/Ar/He, and it is also significantly different from the rotational temperature. The detail of the above phenomena will be discussed in a separate paper.

B. NeH⁺

The first high resolution vibration-rotation spectra of the fundamental band of ²⁰NeH⁺ and ²²NeH⁺ were studied by Wong, Bernath, and Amano⁷ with a difference frequency laser system. The more complete vibration-rotation spectra of fundamental as well as hot bands were later studied in emission in the hollow-cathode lamp discharge of Ne and H₂ mixture by Ram, Bernath, and Brault.⁸ The molecular con-

stants of NeH⁺ have been very well determined.

In our experiment, we have observed the pure rotational transition of $J=13 \leftarrow 12$ in glow discharge of Ne with trace H₂, similar to what Wong *et al.* used. The transition frequency is listed in Table I which agrees very well with the calculated frequency by using the molecular constants derived by Ram *et al.*⁸ The signal-to-noise ratio was about 20. Assum-

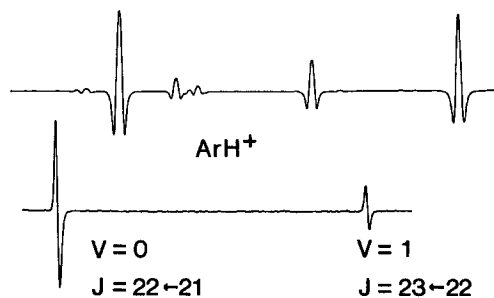


FIG. 1. The rotational transitions of ArH⁺ at ground and first excited vibrational states. The time constant of the detection is 1 s. The upper trace is CS₂ reference spectrum.

ing the discharge temperature of 600 K and using the permanent dipole moment of 3.0 D calculated by Rosmus and Reinsch,⁹ we estimate the ion density to be $\sim 4 \times 10^{10}/\text{cm}^3$. Due to the narrow coverage of TDL, other ground state rotational transitions were not observed.

As in the experiment of ArH^+ , we also tried to detect the rotational transition of the vibrationally excited NeH^+ in the ac glow discharge. Although the prediction is quite accurate and our diode laser was operated very well at the predicted frequency, no line was found. The preliminary explanation on this will be presented in a separate paper on the kinetics study of the formation of protonated inert gas molecular ions.

C. HeH^+

HeH^+ is isoelectronic with H_2 and is the simplest closed-shell heteronuclear molecule. Since it is a fundamental, important molecular ion, HeH^+ has been subjected to intensive study both in theory and experiment. Aided by the theoretical prediction by Bishop and Cheung,¹⁰ the first vibration-rotation spectrum was studied by Tolliver, Kyrala, and Wing¹¹ by using Doppler-tuned ion beam resonance in which they observed high J P -branch lines. More complete coverage of the fundamental band as well as hot band and isotope species were subsequently studied by Bernath and Amano,¹² and by Crofton and Oka,¹³ both using difference frequency systems and a glow discharge. The observed spectroscopic constants agreed excellently with the theoretical predictions.

We observed only one transition $J = 7 \leftarrow 6$ because of the widely spaced spectrum ($B = 33.56 \text{ cm}^{-1}$), and limited coverage of our diode. The frequency of this line is listed in Table I and agrees very well with the value calculated from the molecular constants of Bernath and Amano. The discharge mixture was 1% of H_2 in 1 Torr He, and HeH^+ concentration was estimated to be $\sim 5 \times 10^8/\text{cm}^3$.

D. OH^+

The OH^+ ion has the ground state electronic configuration $X^3\Sigma^-$, and it belongs to the typical Hund's case (b). OH^+ has been subject to extensive spectroscopic study in ultraviolet,¹⁴ infrared,¹⁵ and submillimeter wave regions.¹⁷ Its occurrence in comet tail has been identified,¹⁸ and its existence in interstellar space still remains to be established. We observed the rotational transition $N = 13 \leftarrow 12$ at 410 cm^{-1} (Fig. 2). While the triplet spin-rotation fine structure have been observed, the hyperfine structure was not resolved because of the Doppler-limited resolution. The frequencies of these transitions are listed in Table I, together with the calculated frequencies obtained by using the molecular constants of Merer *et al.* from optical emission experiments. Although the transition frequency of the central component $J = 13 \leftarrow 12$ agrees excellently with the calculation, the other two fine structure frequencies show significant deviation beyond the experimental uncertainty ($\pm 0.003 \text{ cm}^{-1}$), from the calculated value using Miller-Townes formula for the rotational levels of $^3\Sigma$ molecules.¹⁹ The slight reduction of spacing between the spin multiplets suggests that the inclu-



FIG. 2. The rotational transitions $N = 13 \leftarrow 12$, $F_3 \leftarrow F_3$ of OH^+ . The time constant of lock-in detection is 1 s. The upper trace is CS_2 reference spectrum.

sion of the rotational dependence of spin-rotation coupling is necessary at this level, hence the Hamiltonian derived by Tinkham and Strandberg was employed.²⁰ Although it is difficult to obtain an accurate constant from just three transitions observed here, a rough estimate for the centrifugal distortion constant of spin-rotation coupling γ_D is $5 \times 10^{-5} \text{ cm}^{-1}$ which agrees quite well with the result from low J rotational transition measurements.¹⁶

OH^+ was observed in the discharge of 5% H_2 and O_2 in He with total pressure of 4 Torr. We estimate the density of OH^+ to be $\sim 10^9/\text{cm}^3$ from the predicted dipole moment of 2.32 D,²¹ assuming a rotational temperature of 800 K.

E. H_2O^+

Like OH^+ , H_2O^+ has been studied in various spectroscopic regions²²⁻²⁴ and identified to exist in the tail of Comet Kohoutek.²⁵ In our experiment we concentrated on the investigation of the rotational spectrum around $425\text{--}440 \text{ cm}^{-1}$ and found 13 lines which presumably belong to the group of $N = 10 \leftarrow 9$ and $11 \leftarrow 10$. The frequencies of these lines as well as their relative intensities are listed in Table I. These transitions have been distinguished from the transitions due to hot band of H_3O^+ by their different chemical behavior in the discharge. The molecular constants provided by earlier work are limited to the low J , low K transitions, and predictions for high J rotational transition are inaccurate. We have attempted to assign these transitions based on the newly improved molecular constants of H_2O^+ by B. Dinelli *et al.*²⁴ Due to the complicated band structure and large uncertainty for the centrifugal distortion constants, we have not yet been able to assign these transitions. Further study on this ion will be reported later.

F. OH⁻

OH⁻ is one of the few negative ions studied by high resolution spectroscopy,²⁶ and it was also the first object of our experiment on ion rotational spectroscopy.²⁷ We have observed the transitions $J = 10 \leftarrow 9$ and $J = 11 \leftarrow 10$, and their frequencies are listed in Table I. (See Ref. 27 for more details). These frequencies have been combined with those of vibration-rotation transitions to determine accurate molecular constants.²⁶

OH⁻ was generated in an ac glow discharge of a gas mixture H₂/O₂, NH₃/O₂ and H₂O/O₂ in a platinum-coated discharge tube. Figure 3 shows the variation of the absorption signal intensity as a function of the fraction of H₂, NH₃, or H₂O in the total pressure.

As we have already reported in our previous paper,²⁷ the most interesting aspect of this experiment was the discovery of the great enhancement of the concentration of the negative ion OH⁻ by using the metal-coated discharge tubes. We observed this phenomena when the discharge tube was coated thinly by Cu vapor which was generated by the discharge sputtering on Cu electrodes. It was later proved that a chemically coated platinum discharge tube is more effective. In the platinum coated discharge tube with H₂/O₂ or NH₃/O₂ mixture, we have estimated OH⁻ density to be $\sim 10^{10}/\text{cm}^3$ using the predicted permanent dipole moment of 1.04 D²⁸ and the assumed rotational temperature of ~ 800 K. This phenomenon certainly indicated the importance of the surface chemistry to the negative ion formation in gas phase glow discharge.

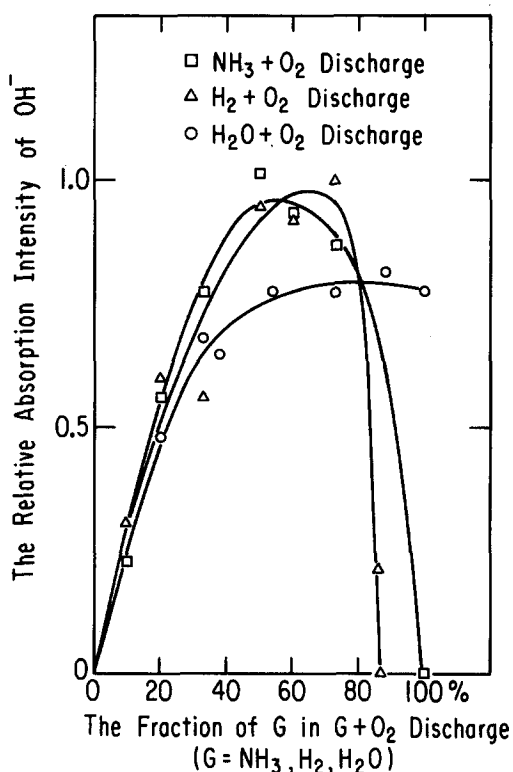
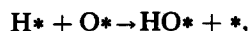


FIG. 3. The variation of OH⁻ absorption signal intensity in the gas mixture of G + O₂ (G = H₂, NH₃, and H₂O) discharge.

One possible explanation for the enhancement of OH⁻ production by a metal coated tube is due to the catalytic surface reaction. Lin and co-workers^{29,30} have shown that OH radical can be produced very efficiently on a hot polycrystalline platinum surface with the gas mixture of H₂/O₂ or H₂O/O₂, etc. They also indicated that OH radical was formed through the thermal desorption process



where * indicates the active site on Pt surface. In the discharge tube, electrons are absorbed on the inner wall of the discharge tube with high density. The tunneling energy of an electron to chemically absorbed molecules on the metal surface is very low, hence OH radicals on the surface will catch an electron easily and form OH⁻. OH⁻ thus formed will be expelled to the gas phase by the radial electric field which is created by the ambipolar diffusion and will be destroyed by collisional dissociation or recombination. We believe that OH⁻ production is facilitated through the above process. The catalyzed decomposition of ammonia on hot Pt surface was studied by Melton and Emmett.³¹

Very recently, Sanche³² has reported the experimental study of the formation of O⁻ ions via dissociative attachment in electron scattering from O₂ condensed on a polycrystalline platinum surface. In his experiment, a very low energy electron beam (0.4–15 eV) has been accelerated to an electrically isolated polycrystalline platinum ribbon on which O₂ is physisorbed. He observed that O⁻ was formed and peak intensity occurred at 6.6 eV which was very close to the gas phase value (4.6 eV). He suggested that the capture of the low energy electron at a particular molecular site leads to the formation of transient anions which will decay into the accessible channels including dissociative attachment to form O⁻. In our glow discharge condition, the mean electronic energy is low (~ 2 eV), and the electrons will constantly bombard the platinum coated discharge wall through ambipolar diffusion. One can assume that O₂ adsorbed on the surface will undergo electronically stimulated dissociative process and thus O⁻ is formed. O⁻ has been known to react with H₂ and NH₃ to form OH⁻ efficiently.^{33,34}

Another possible explanation of this phenomenon is that the electric properties of the glow discharge are changed after the tube is coated with metal. The evidence is the observation of a paler discharge with less degree of striation and the current dependence of the negative ion concentration. The metal coating of the wall probably reduces the inhomogeneity of the axial electric field gradient and therefore change the electric properties, reducing the electronic temperature so that more radicals will form negative ions via slow electron attachment processes instead of being ionized by fast electrons. The fact that both Pt and Cu coating, which have different surface catalytic properties, enhance the formation of negative ions supports this argument.

IV. SUMMARY

We have demonstrated the application of IR diode laser to study the high J rotational transitions of light molecular ions. This will not only help to study the higher order centri-

fugal distortion effect in molecular Hamiltonians, but also provide interesting information for the study of rotational dynamics of the transient molecular ions inside of the glow discharge.

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