

# High-Resolution Infrared Spectroscopy of Molecular Ions

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*Phil. Trans. R. Soc. Lond. A* 1988 **324**, 163-178

doi: 10.1098/rsta.1988.0009

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## High-resolution infrared spectroscopy of molecular ions

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Experimental techniques of high-resolution infrared absorption spectroscopy are described with an emphasis on the modulated hollow-cathode discharge techniques. Among the recent results, the  $\nu_1$  fundamental band of  $\text{HOCS}^+$  ( $\nu_0 = 3435.16 \text{ cm}^{-1}$ ) and the  $X^2\Pi$  and  $a^4\Sigma^-$  system of  $\text{NH}^+$  ( $\nu_0 = 2903.17 \text{ cm}^{-1}$  in  $X^2\Pi$  state,  $\nu_0 = 2544.30 \text{ cm}^{-1}$  in  $a^4\Sigma^-$  state, and  $\Delta E(a^4\Sigma^- - X^2\Pi) = 323.90 \text{ cm}^{-1}$ ) are presented to illustrate the quality and type of information that the high-resolution ion spectroscopy can provide. Another topic discussed is the abundance ratio  $[\text{HCO}^+]/[\text{HO}^+]$  as measured in the laboratory and its astrophysical implications. The measurement has been made possible by our recent detection of the  $\nu_1$  fundamental band of  $\text{HOC}^+$  ( $\nu_0 = 3268.03 \text{ cm}^{-1}$ ). A rate-equation analysis was performed by assuming a reaction scheme to derive the rate constants of several key reactions.

## 1. INTRODUCTION

High-resolution infrared spectroscopy of molecular ions has been one of the most dynamic fields in molecular spectroscopy since the detection of the  $\nu_2$  fundamental band of  $\text{H}_3^+$  by Oka (1980). Almost all recent observations of ions in the gas phase have been achieved by using tunable infrared laser sources such as difference-frequency lasers, colour-centre lasers, and diode lasers. A breakthrough was brought about by the advent of the velocity-modulation technique (Gudeman *et al.* 1983) and the modulated hollow-cathode discharge (Foster *et al.* 1984). Without these techniques, progress would have been very much slower, because ionic species are of very small concentration and are buried among much more stable and more abundant neutral species. The quality of data obtained with those tunable laser sources is very high and the amount of information is plentiful, because of their high resolution and precision. Rotational constants determined by the infrared analyses are often accurate enough to predict the rotational transition frequencies within a few megahertz to assist microwave spectroscopists to search for the lines in the laboratory.

A few review papers appeared in the past several years. Gudeman & Saykally listed 14 ions including  $\text{HD}^+$ ,  $\text{CH}^+$ , and  $\text{KrH}^+$  in their review article (1984). Kawaguchi & Hirota's review paper (1985) included 22 ions with some deuterated species counted separately. A more recent review by Sears (1987) cited 41 ions (excluding  $\text{HD}^+$ ,  $\text{CH}^+$ , and  $\text{KrH}^+$ ). Now 12 more positive and negative ions and several more new bands are to be added to Sears's compilation as of February, 1987. Table 1 is a supplement to the table provided by Sears. This growing list of the ions studied with tunable infrared laser techniques is an indication of how rapid the progress has been.

It is not possible to discuss here all the results obtained so far, even though they are limited to the newest ones in the past year. In this article, experimental techniques of difference-frequency laser spectroscopy with a hollow-cathode discharge as an ion source and several new results obtained with this technique are presented.

TABLE 1. MOLECULAR IONS STUDIED BY TUNABLE INFRARED LASER SPECTROSCOPY

(Additional to the table compiled by Sears (1987).)

<i>diatomics</i>			
molecule		comments <sup>a</sup>	references
NH <sup>+</sup>		(1-0) bands in a and X states (DF)	Kawaguchi & Amano (1987a)
SH <sup>+</sup>		(1-0) band (DL)	Brown <i>et al.</i> (1986)
SH <sup>-</sup>		(1-0) band (DL)	Greubele <i>et al.</i> (1987a)
<i>triatomic</i>			
molecule	vibrational mode	comments	references
HOC <sup>+</sup>	$\nu_1$ $\nu_1 + \nu_2 - \nu_2$	DF	Nakanaga & Amano (1987b) Amano (1987)
HF <sup>+</sup>	$\nu_1; \nu_3$	DF; DL	Kawaguchi & Amano (1987b); Kawaguchi & Hirota (1986a)
H <sub>2</sub> Cl <sup>+</sup>	$\nu_1, \nu_3; \nu_2$	DF; DL	Lee <i>et al.</i> (1987); Kawaguchi & Hirota (1986b)
NH <sub>2</sub> <sup>+</sup>	$\nu_3$	DF	Rehfuss <i>et al.</i> , personal communication <sup>b</sup>
N <sub>3</sub> <sup>-</sup>	$\nu_3$	DL	Polak <i>et al.</i> (1987)
NCO <sup>-</sup>	$\nu_3$	DL	Greubele <i>et al.</i> (1987b)
NCS <sup>-</sup>	$\nu_1$	DL	Greubele <i>et al.</i> , personal communication <sup>c</sup>
<i>tetra-atomic</i>			
molecule	vibrational mode	comments	references
HOCS <sup>+</sup>	$\nu_1$	DF	Nakanaga & Amano (1987c)
C <sub>2</sub> H <sub>2</sub> <sup>+</sup>	$\nu_3$	DF	Crofton <i>et al.</i> (1987)
HCNH <sup>+</sup>	$\nu_1, \nu_2; \nu_3$ $\nu_4; \nu_5$ $\nu_1 + \nu_4 - \nu_4, \nu_1 + \nu_5 - \nu_5$	DF DL	Attman <i>et al.</i> (1984a, b); K. Kawaguchi, personal communication; Tanaka <i>et al.</i> (1986); Ho <i>et al.</i> (1987); Amano & Tanaka (1986)
NH <sub>3</sub> <sup>+</sup>	$\nu_3$	DF	
SH <sub>3</sub> <sup>+</sup>	$\nu_1, \nu_3; \nu_2$	DF; DL	Nakanaga & Amano (1987a, d); Amano <i>et al.</i> (1987)
<i>more than four atoms</i>			
molecule	vibrational mode	comments	reference
HC <sub>3</sub> NH <sup>+</sup>	$\nu_1$	DF	Lee & Amano (1987)

<sup>a</sup> Abbreviations: DF, difference frequency laser; DL, diode laser.<sup>b</sup> B. D. Rehfuss, B. M. Dinelli, M. Okumura, M. G. Bawendi & T. Oka.<sup>c</sup> M. Greubele, M. Polak & R. J. Saykally.<sup>d</sup> M. G. Bawendi, B. D. Rehfuss, B. M. Dinelli, M. Okumura & T. Oka.

## 2. EXPERIMENTAL TECHNIQUES

The first high-resolution continuous-wave-difference-frequency spectrometer system was developed by Pine. Details of the system are described in his papers (see, for example, Pine 1974, 1976). Figure 1 shows a schematic diagram of a spectrometer system at National Research Council of Canada. Frequency-tunable infrared radiation is generated by mixing single-mode Ar<sup>+</sup> laser (Coherent INNOVA 90-5) radiation with tunable dye laser (Coherent 699-21) radiation in a LiNbO<sub>3</sub> crystal contained in a temperature-controlled oven. A typical power of the resulting infrared radiation was estimated to be about 30  $\mu$ W at around 3  $\mu$ m, with an input power of 400 mW of tunable dye laser radiation and 200 mW of single-mode Ar<sup>+</sup> laser radiation, by using the short circuit current responsivity of an InSb detector provided by the manufacturer. The linewidth of the difference-frequency radiation is a few megahertz. A combination of the two typical Ar<sup>+</sup> laser lines and a Rh-6G dye laser generates difference-frequency radiation in the range of *ca.* 2400–4400  $\text{cm}^{-1}$ .

Figure 2 shows tuning characteristics of the difference frequency laser. This range covers most C–H, N–H, O–H, and S–H stretching vibrational bands. The wide frequency coverage

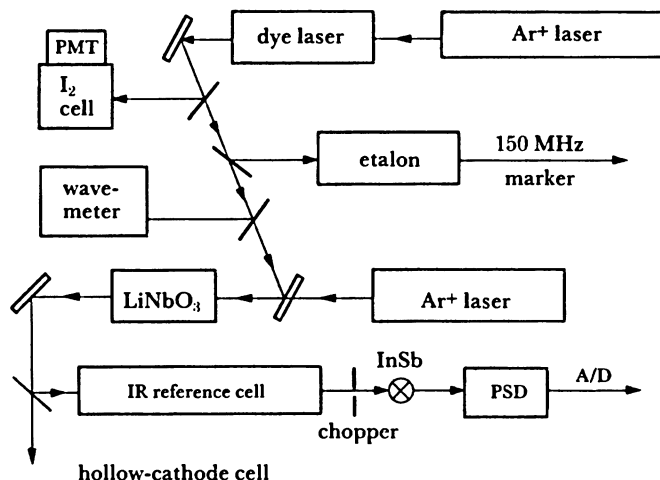
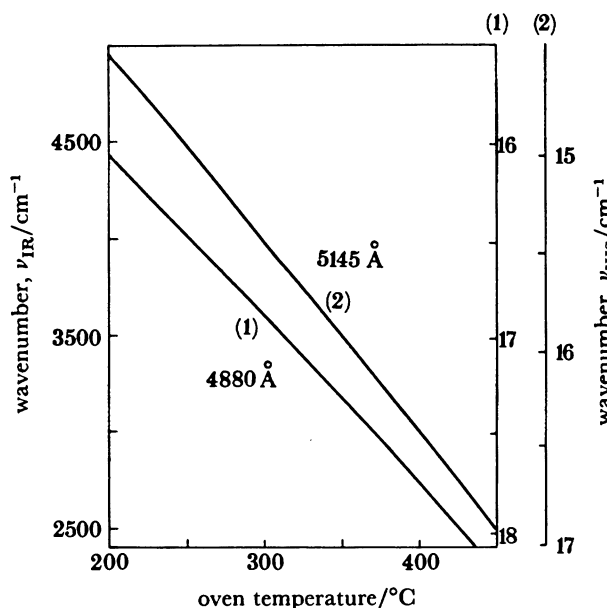


FIGURE 1. Schematic diagram of the difference-frequency laser system.

FIGURE 2. Tuning characteristics of  $\text{LiNbO}_3$  crystal for (1) 488.0 nm and (2) 514.5 nm  $\text{Ar}^+$  laser lines (Amano 1983).

and easy tunability of difference frequency lasers are of great advantage in searching for lines of unknown species. However, usually one encounters a severe overlapping problem from much stronger lines, mostly because of parent molecules and stable reaction products, because most of these stable species also have vibrational bands near the bands of interesting ions we want to observe. So velocity modulation or amplitude-discharge modulation are essential to extract the lines due to ions and moreover to enhance the detection sensitivity because the laser source is very noisy. A hollow-cathode discharge, which is known to be an excellent source of ions, has been successfully employed to observe ions in absorption with tunable laser sources first in the far-infrared region (van den Heuvel & Dymanus 1982) and later in the 3–5  $\mu\text{m}$  region

(Foster *et al.* 1984; Amano 1985). In particular, the hollow-cathode discharge combined with magnetic-field modulation (Kawaguchi *et al.* 1985) has proved to be a powerful technique.

Figure 3 is a schematic diagram of a hollow-cathode discharge cell and the signal detection system. The design of the cell is similar to that used by Foster *et al.* (1984). A cathode is made of copper or stainless steel pipe of 38 mm inner diameter and 80 cm in length. A set of multireflection mirrors is placed inside the vacuum enclosure. The discharge can be cooled by flowing liquid nitrogen, cooled methanol or water through copper tubing wound around the cathode. A sine-wave signal is amplified by an audio amplifier (Bryston model 4B, maximum output of 800 W), and is applied to the water-cooled stainless-steel anode through a step-up transformer (Hammond 737 X). Because of the electrode arrangements, the breakdown voltage is much higher when the anode is negative to the cathode. Therefore this type of cell works as a rectifier so that the discharge turns on only when the anode is positive, and the concentration of short-lived species produced in the discharge is modulated with almost 100% efficiency. On the other hand, the modulation efficiency of stable species and the parent molecules is much less, depending on the modulation frequency and the lifetime of the species. It was found that the signal:noise ratio is optimum at a modulation frequency of around 5–20 kHz for ions. Modulation faster than 20 kHz resulted in decrease in the signal intensity. At a modulation frequency of 5 kHz, the maximum peak discharge current was about 1 A. After phase-sensitive detection, the line shape appears as the 'true line shape' rather than the first derivative.

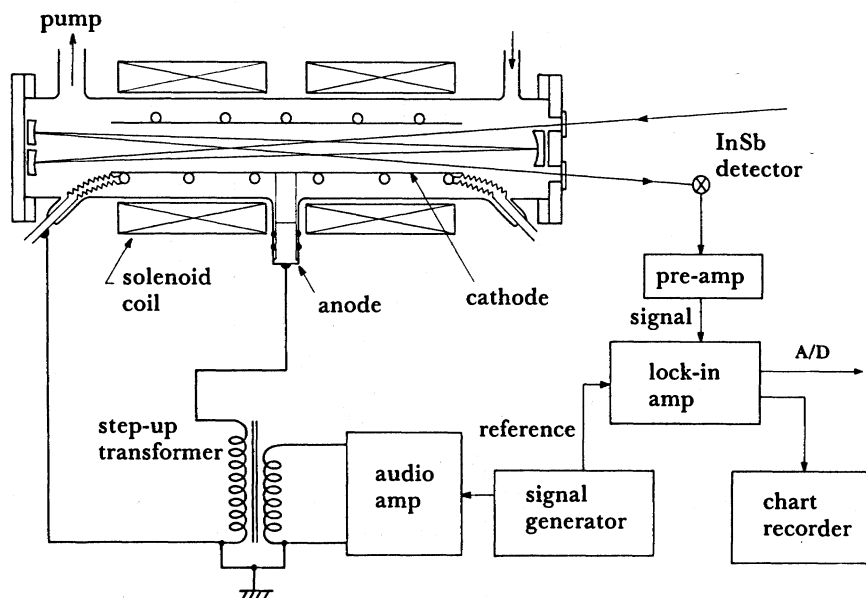


FIGURE 3. Schematic diagram of the hollow-cathode discharge cell. The cathode, which is made of either copper or stainless steel tubing, is 80 cm long and 38 mm in inner diameter. The typical optical pathlength is 24–32 m. The solenoid generates an axial magnetic field for examination of the field dependence of absorption lines.

The difference-frequency laser system is controlled by a microcomputer system (HP-9816). The scan of the ring dye laser is made in steps having increments of about 20 MHz. The infrared radiation passes through the multipass discharge cell and is detected by an InSb photovoltaic detector. The signal is sent to a lock-in amplifier, and the resulting DC signal is fed to an A-D

converter. At the same time, the absorption signals of a suitable reference gas are recorded and sent to the computer memory through another A-D converter. A temperature-stabilized etalon (Burleigh CFT-500) in the dye laser beam with a free spectral range of 150 MHz is used to provide the frequency markers for interpolation of the frequency measurements. The marker signal is shaped and fed to a timer and pacer interface card. The signals are displayed on the screen with absorption lines of reference gas and with optional frequency markers. The frequency scale is calculated by using the markers and the frequencies of the reference lines, which are input by moving a cursor on the screen onto the line peaks and by typing their wave numbers. Then, a peak-finding routine is activated to obtain the wave numbers of the absorption lines of the sample of interest. The minimum detectable absorption of our system reaches about 0.002% or the minimum detectable peak absorption coefficient of  $10^{-8} \text{ cm}^{-1}$  with a 20 m pathlength with a time constant of 400 ms. More discussion on the sensitivity and the detectable abundance of ions is given by Nakanaga & Amano (1987c).

The amplitude-discharge modulation method does not always uniquely identify signals due to ions, but also detects lines due to short-lived neutral species. A hollow-cathode discharge, which is a good source of ions, is very attractive in spite of this shortcoming. Saito *et al.* (1985) demonstrated that an axial magnetic field of 100 G† applied to a hollow-cathode discharge resulted in almost 100% loss of the signal intensity in their detection of a millimetre-wave line of  $\text{H}_2\text{D}^+$ . It was found that, when the magnetic-field strength is increased, the intensity of the ion signals decreases rapidly, whereas the decrease of the signal intensity of neutral species is not so dramatic. This is contrary to the enhanced ion concentration in the extended negative glow in magnetic field found by DeLucia & co-workers (1983). An example of such magnetic field effect in a hollow-cathode discharge is given in figure 4. The different behaviour of ions under the axial magnetic field is used to discriminate signals due to ions from those of neutral species. This technique offsets the shortcomings to great extent, and it has been applied to the

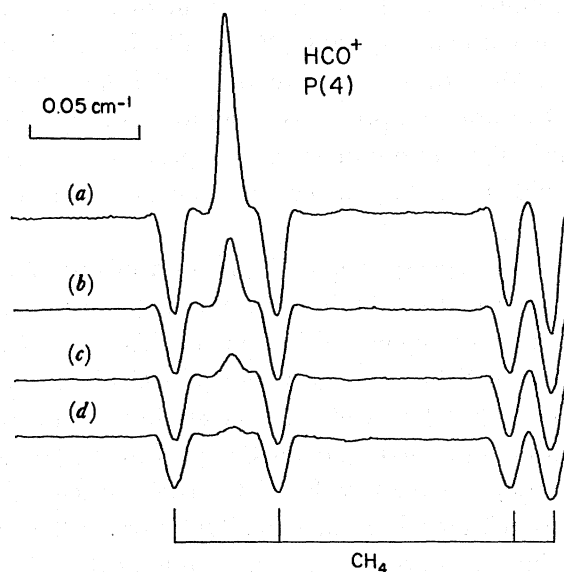


FIGURE 4. The P(4) line of the  $\nu_1$  fundamental band of  $\text{HCO}^+$  together with the  $\text{CH}_4$  lines recorded in a hollow-cathode discharge under several different axial magnetic fields: (a) 0 G; (b) 75 G; (c) 120 G; and (d) 150 G. The phase of the lock-in amplifier was set optimum for the  $\text{HCO}^+$  line (Amano 1985).

$$\dagger 1 \text{ G} = 10^{-4} \text{ T.}$$

detection of ions more or less as a standard technique with hollow-cathode discharges. In this context, it should be emphasized that the velocity modulation has an even greater advantage, because it can distinguish not only ions from neutrals but also negative ions from positively charged species (see, for example, Rosenbaum *et al.* 1986; Liu & Oka 1986).

As mentioned above, the frequency measurements rely greatly on known infrared lines of stable molecules measured with Fourier-transform spectrometers (a few typical examples are  $N_2O$  (Amiot & Guelachvili 1976; Amiot 1976),  $D_2O$  (Papineau *et al.* 1981) and  $H_2S$  (Lechuga-Fossat *et al.* 1984)) and with a difference-frequency laser system by Pine (1980*a,b*) (a few examples include  $H_2CO$ ,  $C_2H_2$  and  $H_2O$ ). It is rather common that we are forced to use the spectra from different sources as references to measure a single band, and we have found that the internal consistency among the measured frequencies from different sources is very satisfactory.

### 3. RESULTS

#### (a) *The $\nu_1$ fundamental band of $HOCS^+$*

$HOCS^+$  is isovalent with the ions  $HOCO^+$  and  $HONN^+$  studied recently in the submillimetre-wave and infrared regions.  $HOCO^+$  was first (tentatively) identified in interstellar space through the observation of its millimetre-wave emission lines (Thaddeus *et al.* 1981). A definite confirmation was provided by Bogey *et al.* (1984) by detecting the submillimetre-wave lines in the laboratory. Shortly after, the  $\nu_1$  fundamental band of this ion was observed in a hollow-cathode discharge in the 3  $\mu m$  region (Amano & Tanaka 1985*a,b*).

On the other hand, protonated  $N_2O$  was unknown spectroscopically when a search for the  $\nu_1$  band was undertaken. Vibration-rotation absorption lines were detected in a hollow-cathode discharge through a mixture of  $N_2O$  and  $H_2$ , and the lines were assigned as the  $\nu_1$  band of protonated  $N_2O$  (Amano 1986). However, it was not conclusive if the species detected was the O-protonated or N-protonated form from the experiment alone, although it was concluded that it was a bent molecule with an angle of HON or of HNN of about  $117^\circ$ . Two groups (Rice *et al.* 1986; Yamashita & Morokuma 1986) reported *ab initio* calculations immediately after and indicated that the O-protonated isomer is likely to be the species detected in the infrared experiment. Quite recently the submillimetre-wave spectrum was detected in the laboratory (Bogey *et al.* 1986*c*) guided by the molecular constants determined from the infrared analysis.

There has been no previous spectroscopic observation of protonated OCS. A few *ab initio* calculations have been performed to obtain the rotational constants, the proton affinity, and the relative stability of the three conceivable isomers (Taylor & Scarlett 1985; Scarlett & Taylor 1986). Protonated OCS has also been the subject of astrophysical interest (Fock & McAllister 1982; Taylor & Scarlett 1985). A possibility of the presence of  $HOCS^+$  and  $HSCO^+$  and the relative abundance to that of OCS in the interstellar clouds have been discussed by Fock & McAllister (1982). Taylor & Scarlett (1985) discussed possible assignments of unidentified lines observed in interstellar space to  $HOCS^+$  or  $HSCO^+$ . However, no conclusions could be made because there was no spectroscopic study of these ions at the time.

Although an *ab initio* molecular-orbital (MO) calculation suggested that the S-protonated form,  $HSCO^+$ , may be more stable than the O-protonated,  $HOCS^+$ , we started the search for  $HOCS^+$  in view of the fact that HSCN, an isomer of HNCS, is not known in the gas phase. Protonated OCS was generated in a hollow-cathode discharge in a gas mixture of  $H_2$  (*ca.*

400 mTorr†) and OCS (*ca.* 15 mTorr) (Nakanaga & Amano 1987*c*). We found a series of absorption lines that were regularly spaced and could be assigned as the P- and R-branch lines of a-type transitions. Subsequently we found the b-type Q-branch lines,  ${}^{\text{P}}\text{Q}_1(J)$  and  ${}^{\text{T}}\text{Q}_0(J)$ . Figure 5 shows these Q-branch lines.

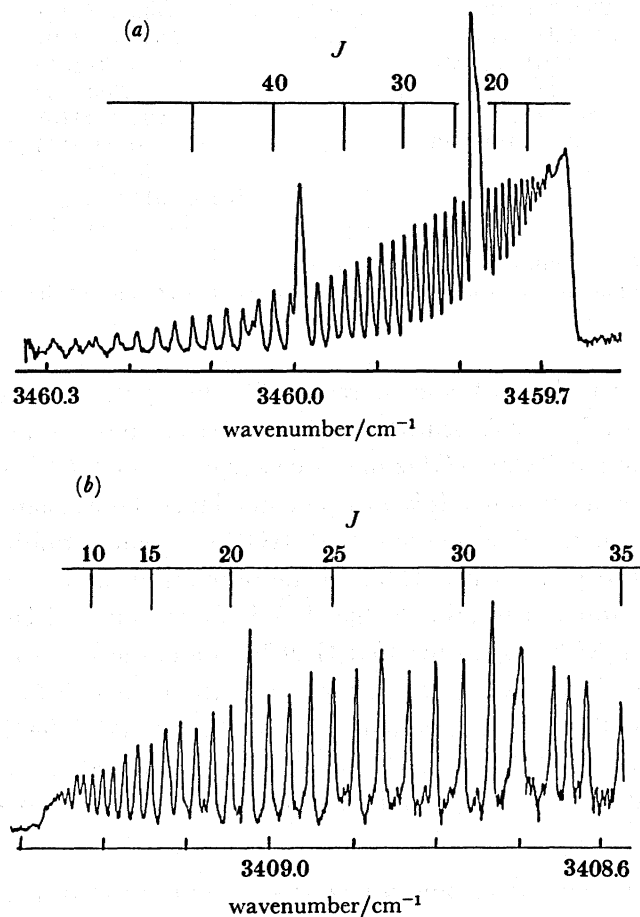


FIGURE 5. Examples of the Q-branch lines of HOCS<sup>+</sup> recorded with a detection time constant of 0.4 s. (Nakanaga & Amano 1987*c*). (a) The  ${}^{\text{T}}\text{Q}_0(J)$  transitions. The strong features around  $J = 23$  and  $J = 38$  are the lines of unidentified species. (b) The  ${}^{\text{P}}\text{Q}_1(J)$  transitions. The  $J = 21$ ,  $J = 31$ , and  $J = 32$  lines are overlapped with unassigned lines. An unassigned line is also evident between the  $J = 33$  and  $J = 34$  lines.

We have assigned about 550 lines (Nakanaga & Amano 1987*c*) and the molecular constants were determined by a least-squares fit with an effective hamiltonian in the *A*-reduced representation (Watson 1977). Table 2 lists the molecular constants determined from the fit. The mean deviation of the fit was 0.0007 cm<sup>-1</sup>. From the present infrared measurements, we can conclude that the species detected is an O-protonated isomer, because the vibrational frequency (3435 cm<sup>-1</sup>) is very unlikely to be an S-H or C-H stretching vibrational frequency. Also the rotational constants obtained here are consistent with those calculated for HOCS<sup>+</sup> (Taylor & Scarlett 1985). The rotational constants are determined precisely to give predictions of the rotational transition frequencies with an accuracy of about several hundreds of kilohertz for the low-*J* lines and about a few megahertz for the lines in the 200–300 GHz region. These

† 1 mTorr  $\approx 133.3 \times 10^{-3}$  Pa.



TABLE 2. MOLECULAR CONSTANTS (IN MEGAHERTZ) OF HOCS<sup>+</sup>

	ground state		$\nu_1 = 1$ state experiment
	experiment	theory <sup>a</sup>	
$A$	782695.7 (38) <sup>b</sup>	746 156	740356.5 (40)
$B$	5750.551 (49)	5 803	5746.278 (47)
$C$	5703.030 (50)	5 758	5696.792 (49)
$\Delta_J$	0.001 104 (20)		0.001 101 (19)
$\Delta_{JK}$	0.2819 (15)		0.263 1 (14)
$\Delta_K$	993.68 (77)		233.30 (110)
$\Sigma_J$	0.0000198 (43)		0.0000127 (40)
$\Phi_K$	0.0 <sup>c</sup>		-46.823 (97)
$\nu_0$			102983614.2 (27)
			[3435.163 611 (88) cm <sup>-1</sup> ]

<sup>a</sup> scf calculation with (Taylor & Scarlett 1985).

<sup>b</sup> Values in parentheses are one standard error to the last digits of the constants.

<sup>c</sup> Fixed.

frequencies may prove to be useful in searching for this species in interstellar space or in laboratory experiments. Taylor & Scarlett (1985) suggested that two unidentified interstellar lines at 92.353 GHz and at 103.915 GHz might be assigned to HOCS<sup>+</sup> on the basis of their *ab initio* calculated rotational constants. It is now concluded that those assignments are not correct.

It was expected from a naive analogy that HOCS<sup>+</sup> would exhibit quasilinearity more conspicuously than HOCO<sup>+</sup>, because HNCS is more quasilinear than HNCO (Winnewisser 1985). However, as compared in table 3, the  $A$  and  $\Delta_K$  constants of HOCS<sup>+</sup> are very much smaller than those of HNCS, indicating that HOCS<sup>+</sup> is an almost normal bent molecule. An *ab initio* calculation by Taylor & Scarlett (1985) correctly predicted the  $A$  rotational constant for HOCS<sup>+</sup> to be 778 GHz at self-consistent field (scf) level and 746 GHz with a correction. This difference between HOCS<sup>+</sup> and HNCS may be explained by considering resonance structures as discussed in a previous publication (Nakanaga & Amano 1987c).

TABLE 3. SUMMARY OF THE BAND ORIGIN FOR THE  $\nu_1$  FUNDAMENTAL BANDS AND THE MAJOR MOLECULAR CONSTANTS IN THE GROUND STATES OF HOCS<sup>+</sup> AND THE RELATED MOLECULES

	HOCS <sup>+</sup>	HNCS <sup>a,b</sup>	HOCO <sup>c,d</sup>	HNCO <sup>e,f</sup>	HONN <sup>g,h</sup>	HNNN <sup>i,j</sup>
$\nu_0$ /cm <sup>-1</sup>	3435.16	3538.6	3375.37	3537.7	3330.91	3336
$A$ /MHz	782696	1361530	789939	918504	625954	610996
$B$ /MHz	5750.55	5883.46	10773.72	11071.01	11301.56	12034.15
$C$ /MHz	5703.03	5845.61	10609.44	10910.58	11084.28	11781.45
$\Delta_K$ /MHz	993.7	57520	1123.6	6066	242.8	259.0

References: <sup>a</sup> Draper & Werner (1974). <sup>b</sup> Yamada *et al.* (1979). <sup>c</sup> Amano & Tanaka (1985b). <sup>d</sup> Bogey *et al.* (1986a, b). <sup>e</sup> Yamada (1972). <sup>f</sup> Yamada (1980). <sup>g</sup> Amano (1986). <sup>h</sup> Bogey *et al.* (1986c). <sup>i</sup> Dows & Pimentel (1955). <sup>j</sup> Bendtsen & Winnewisser (1975).

According to an *ab initio* calculation at scf level (Scarlett & Taylor 1986), HSCO<sup>+</sup> is more stable than HOCS<sup>+</sup> by 34 kJ mol<sup>-1</sup> (17 kJ mol<sup>-1</sup> with inclusion of electron correlation effect). Although which is more stable seems to be a rather subtle problem, HSCO<sup>+</sup> may be detectable in the same discharge where HOCS<sup>+</sup> is found. So we searched for HSCO<sup>+</sup> in the range of 2450–2600 cm<sup>-1</sup> by employing the same reaction conditions for HOCS<sup>+</sup>. The search, however, revealed no evidence of HSCO<sup>+</sup>.

*(b) Infrared spectra of NH<sup>+</sup>*

NH<sup>+</sup> is a unique molecule in the sense that it has a low-lying electronic excited state a<sup>4</sup>Σ<sup>-</sup>. Optical emission spectra of NH<sup>+</sup> were first recorded by Lunt *et al.* (1935) more than 50 years ago. However, NH<sup>+</sup> has not been investigated so extensively as an isoelectronic diatomic molecule CH. Since the first high-resolution ultraviolet (uv) emission observation by Feast (1951), it has been known that the energy difference between the X<sup>2</sup>Π and a<sup>4</sup>Σ<sup>-</sup> states is only 500 cm<sup>-1</sup> (*T<sub>e</sub>*), and the two states interact each other strongly. However, no quantitative analyses have been made to unravel the complicated perturbation.

The present high-resolution infrared investigation casts light directly on the perturbation. NH<sup>+</sup> was generated through a hollow-cathode discharge either in a mixture of N<sub>2</sub> (*ca.* 10 mTorr), H<sub>2</sub> (*ca.* 10 mTorr), and He (*ca.* 1.4 Torr) or in a mixture of NH<sub>3</sub> (*ca.* 10 mTorr) and He (*ca.* 1.4 Torr). Most measurements were done with dry-ice cooling, but ice or water cooling was equally effective with some change in the rotational temperature.

Because the perturbation is so severe, it is essential to treat the X<sup>2</sup>Π and a<sup>4</sup>Σ<sup>-</sup> states simultaneously. The existing formulas for the rotation and fine-structure energy levels for <sup>4</sup>Σ electronic states (Budo 1937; Albritton *et al.* 1977) are extended to include the higher-order centrifugal distortion terms of the spin–spin and the spin–rotation interactions. The spin–orbit interaction between the two states that is a major cause of the perturbation is taken into account explicitly. The hamiltonian matrix was set up in terms of the case (*a*) basis. The details about the theory are given by Kawaguchi & Amano (1987*a*).

The search problem usually associated with unknown widely spaced vibration–rotation bands was greatly alleviated by using the term values given by Colin & Douglas (1968) to predict the transition frequencies. The assignments of the <sup>2</sup>Π–<sup>2</sup>Π transitions were rather straightforward, because most lines were found near the predicted frequencies. A preliminary least-squares fit was made with the term values for extra levels observed by Colin & Douglas (1968) to predict the transitions within a<sup>4</sup>Σ<sup>-</sup> and the ones between the X<sup>2</sup>Π and a<sup>4</sup>Σ<sup>-</sup> states. The final least-squares fit was made with the measured infrared transitions, the combination differences, the term values obtained by Colin & Douglas (1968) corrected for systematic deviations (Kawaguchi & Amano 1987*a*), and the two far-infrared rotational transitions measured by Verhoeve *et al.* (1986) with appropriate relative weights.

Table 4 lists some major molecular constants for comparison with the previous experimental and theoretical values. Because Colin & Douglas (1968) did not fully analyse the perturbation quantitatively, the vibrational frequencies, the spin–orbit coupling constants, and *T<sub>0</sub>* value for the a<sup>4</sup>Σ<sup>-</sup> state were not determined very well previously. It is not straightforward to derive *B<sub>e</sub>* from *B<sub>0</sub>* and *B<sub>1</sub>*, especially in a light hydride like NH<sup>+</sup>. The equilibrium rotational constant for the ground state is estimated to be 470450 MHz after the corrections described by Kawaguchi & Amano (1987*a*), and the equilibrium bond length is calculated to be 1.069 Å†. As compared in table 4, the agreement between the experimental and theoretical values is very good except for an earlier scf calculation. The equilibrium bond length *r<sub>e</sub>* in the a<sup>4</sup>Σ<sup>-</sup> state was calculated without making the second-order correction, as it was expected to be small. Comparisons with several *ab initio* calculated values are also made in table 4.

† 1 Å = 10<sup>-10</sup> m = 10<sup>-1</sup> nm.

TABLE 4. MAJOR MOLECULAR CONSTANTS (RECIPROCAL CENTIMETRES UNLESS OTHERWISE STATED) OF NH<sup>+</sup>

	X <sup>2</sup> Π state		
	experimental		calculated
$B_0$	15.331 128 (46) <sup>a</sup>	15.35 <sup>b</sup> 15.587 <sup>d</sup>	15.41 (PNO-CI) <sup>c</sup> 15.30 (CEPA) <sup>c</sup>
$B_1$	14.725 118 (69)	—	14.80 (PNO-CI) <sup>c</sup> 14.68 (CEPA) <sup>c</sup>
$B_e$	15.6925 <sup>c</sup>	—	15.71 (PNO-CI) <sup>c</sup> 15.61 (CEPA) <sup>c</sup>
$D_0$	0.001 6313 (15)	0.001 7 <sup>b</sup>	—
$A_0$	81.6568 (21)	77.8 <sup>b</sup>	77.895 <sup>f</sup>
$\nu_0$	2903.1718 (21)	2922 <sup>b</sup> 2980.65 <sup>d</sup>	2938.6 (PNO-CI) <sup>c</sup> 2893.0 (CEPA) <sup>c</sup>
$r_e$	1.069 Å	—	1.068 Å (PNO-CI) <sup>c</sup> 1.071 Å (CEPA) <sup>c</sup> 1.069 Å (SCF-CI) <sup>g</sup> 1.070 Å (MRSDCI) <sup>h</sup> 1.047 Å (SCF) <sup>i</sup>
		a <sup>4</sup> Σ <sup>-</sup> state	
$B_0$	14.66001 (14)	14.69 <sup>b</sup> 14.984 <sup>d</sup>	— —
$B_1$	13.93295 (10)	—	—
$B_e$	15.0523	—	—
$D_0$	0.001 8270 (33)	(0.001 8) <sup>b</sup>	—
$\nu_0$	2544.3004 (40)	2520 <sup>b</sup> 2652.29 <sup>d</sup>	—
$T_0$	323.8976 (45)	354 <sup>b</sup> 189.9 <sup>d</sup>	—
$r_e$	1.092 Å	—	1.093 Å (SCF-CI) <sup>g</sup> 1.079 Å (SCF) <sup>i</sup>

Notes: <sup>a</sup> One standard error to the last digits of the constants. <sup>b</sup> Colin & Douglas (1968). <sup>c</sup> Rosmus & Meyer (1977). <sup>d</sup> Experimental value of Colin & Douglas (1968) analysed by Wilson (1978). <sup>e</sup> Corrected, (see Kawaguchi & Amano (1987a)). <sup>f</sup> Wilson (1978). <sup>g</sup> Guest & Hirst (1977). <sup>h</sup> Kusunoki *et al.* (1986). <sup>i</sup> Liu & Verhaegen (1970).

(c) *Laboratory measurements of the abundance ratio [HCO<sup>+</sup>]/[HOC<sup>+</sup>] and their astrophysical implications*

The formation and depletion mechanism of HOC<sup>+</sup> and the abundance ratio [HCO<sup>+</sup>]/[HOC<sup>+</sup>] in interstellar space have attracted a great deal of interest theoretically and experimentally (see, for example, Dixon *et al.* 1984; Jarrold *et al.* 1986). Woods *et al.* (1983) attempted to detect this ion in interstellar space on the basis of a laboratory measurement by Gudeman & Woods (1982), and they tentatively assigned a line observed at the predicted frequency towards Sgr-B2 to HOC<sup>+</sup>. Woods *et al.* (1983) estimated the abundance ratio [HCO<sup>+</sup>]/[HOC<sup>+</sup>] to be about 330, assuming the identification was correct, and discussed that it might be even more than 500 if the identification was incorrect.

There are two points that should be solved: (i) What is the branching ratio of the reactions



and (ii) What are the rate constants of depletion reactions of HOC<sup>+</sup>? Illies *et al.* (1982, 1983) investigated the reaction system with the ion cyclotron resonance (ICR) mass-spectrometric

technique. They concluded that  $6 \pm 5\%$  of the initial products from the reaction between  $\text{H}_3^+$  and CO leads to formation of  $\text{HOC}^+$ , assuming the catalytic isomerization of  $\text{HOC}^+$  by  $\text{H}_2$ ,



is negligible. Later Wagner-Redeker *et al.* (1985) reinvestigated the system, and concluded that the 6% should be interpreted to be the lower limit, because the  $\text{H}_2$  catalytic isomerization will occur to a substantial degree according to a phase-space calculation, which is contrary to another phase-space calculation by DeFrees *et al.* (1984) who concluded that the catalytic isomerization process (3) is too slow to explain the large depletion of  $\text{HOC}^+$ . Green (1984) also indicated that the isomerization was inefficient. More recently Jarrold *et al.* (1986) reinvestigated the reaction theoretically and experimentally. Their new conclusion was that the catalytic isomerization reaction (3) does not have a large activation energy contrary to the previous calculations (Green 1984; DeFrees *et al.* 1984), and that it is efficient process in depletion of  $\text{HOC}^+$ . Because  $\text{H}_2$  is very abundant in dense interstellar clouds, the abundance ratio,  $[\text{HCO}^+]/[\text{HOC}^+]$ , tentatively given by Woods *et al.* (1983) may be too low, suggesting that the tentative identification of the line observed in Sgr-B2 might be in error.

Recently the infrared absorption of the  $\nu_1$  band of  $\text{HOC}^+$  ( $\nu_0 = 3268 \text{ cm}^{-1}$ ) was observed in a hollow-cathode discharge through a mixture of CO and  $\text{H}_2$  (Nakanaga & Amano 1987*b*). The reaction conditions were quite different from those used in previous microwave observations (Gudeman & Woods 1982; Blake *et al.* 1983; Bogey *et al.* 1986*b*) in which a large amount of Ar is needed as a buffer gas. The relative intensity of the infrared absorption lines of  $\text{HCO}^+$  and  $\text{HOC}^+$  was measured as a function of the pressures of  $\text{H}_2$  and CO. All the measurements were done with a fast-flow system and the pressure was measured at the exit of the cell. This method is direct and much more reliable than indirect and somewhat ambiguous mass-spectrometric measurements. From a rate-equation analysis, the rate constants of the key reactions were estimated with a reasonable accuracy.

First we found that the rotational temperature of  $\text{HCO}^+$  and  $\text{HOC}^+$  was approximately equal to the cell temperature ( $-50^\circ\text{C}$ ) from relative-intensity measurements of several vibration-rotation lines. All the measurements were done with a peak discharge current of 500 mA, unless stated otherwise. Details of the measurements and analysis are presented in a paper by Amano & Nakanaga (1987) and only a brief summary is given here.

The optimum CO pressure for the production of  $\text{HOC}^+$  was found to be about 25 mTorr and it seems to shift towards higher pressure as the pressure of  $\text{H}_2$  increases from 200 mTorr to 600 mTorr. The signal intensity of  $\text{HOC}^+$  is less dependent on the pressure of  $\text{H}_2$ . In 1981, Nobes & Radom (1981) pointed out that the isomerization reaction



might be very efficient to deplete  $\text{HOC}^+$ . The pressure dependence measured here, indeed, suggests that CO plays a primary role in depletion of  $\text{HOC}^+$  whereas  $\text{H}_2$  has only a secondary effect.

Figure 6 shows an example of the absorption lines of  $\text{HCO}^+$  and  $\text{HOC}^+$  at a CO pressure of 15 mTorr and  $\text{H}_2$  pressure of 420 mTorr. We obtained the intensity ratio  $I(\text{HCO}^+)/I(\text{HOC}^+) = 88 \pm 3$  at this condition. The abundance ratio was calculated to be  $382 \pm 12$  by using the transition dipole moments for the bands of  $\text{HCO}^+$  ( $\mu = 0.168 \text{ D}^\dagger$ ) and  $\text{HOC}^+$

$^\dagger 1 \text{ D} = 3.33 \times 10^{-30} \text{ C m.}$

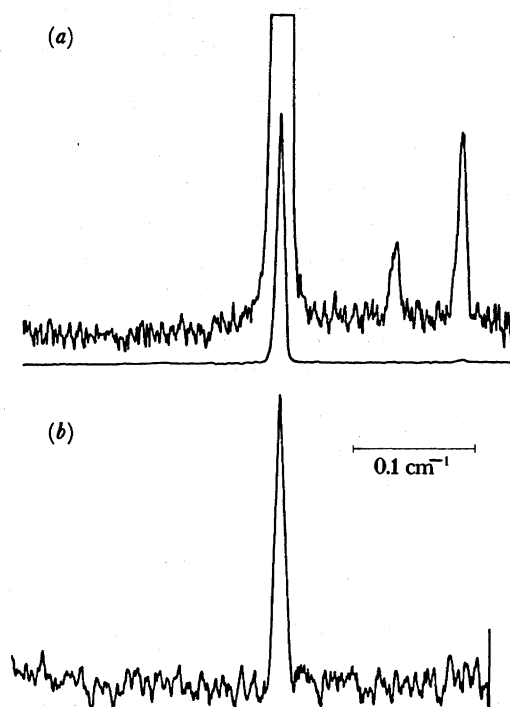


FIGURE 6. The R(8) lines of (a) HCO<sup>+</sup> and (b) HOC<sup>+</sup> recorded at the same gain settings with normalized infrared power. The middle trace was recorded with a hundredth of the gain of the top trace (Amano & Nakanaga 1987).

TABLE 5. REACTIONS CONSIDERED IN THE RATE-EQUATION ANALYSIS

reaction	rate constant
$\text{H}_2 + \text{H}_3^+ \rightarrow \text{H}_3 + \text{H}$	$k_1$
$\text{H}_3^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{H}_2$	$k_2$
$\text{H}_3^+ + \text{CO} \rightarrow \text{HOC}^+ + \text{H}_2$	$k_3$
$\text{HOC}^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{CO}$	$k_4$
$\text{HOC}^+ + \text{H}_2 \rightarrow \text{HCO}^+ + \text{H}_2$	$k_5$
$\text{HA}^+ + e \rightarrow \text{products}$	$K_r$

( $\mu = 0.350$  D) recently calculated by P. Botschwina (personal communication). Because the rotational temperatures of HCO<sup>+</sup> and HOC<sup>+</sup> are found to be almost the same and the rotational constants of the two ions are similar, no further corrections have been made to derive the abundance ratio from the intensity ratio.

We have considered the reactions listed in table 5 to analyse the observed pressure dependence. A set of rate equations was set up, and the stationary concentrations of HOC<sup>+</sup> and HCO<sup>+</sup> were calculated to be

$$[\text{HOC}^+] = \frac{k_3[\text{H}_3^+][\text{CO}]}{k_4[\text{CO}] + k_5[\text{H}_2] + K_r[\text{M}]}, \quad (5)$$

$$[\text{HCO}^+] = \frac{[\text{H}_3^+][\text{CO}]}{K_r[\text{M}]} \left\{ k_2 + \frac{k_3(k_4[\text{CO}] + k_5[\text{H}_2])}{k_4[\text{CO}] + k_5[\text{H}_2] + K_r[\text{M}]} \right\}, \quad (6)$$

where

$$[\text{H}_3^+] = \frac{k_1[\text{H}_2][\text{H}_2^+]}{(k_2 + k_3)[\text{CO}] + K_r[\text{M}]} \quad (7)$$

and the abundance ratio  $[\text{HCO}^+]/[\text{HOC}^+]$  is given as

$$\frac{[\text{HCO}^+]}{[\text{HOC}^+]} = \frac{k_2}{k_3} + \left(\frac{k_2}{k_3} + 1\right) \frac{k_4[\text{CO}] + k_5[\text{H}_2]}{K_r[\text{M}]} \quad (8)$$

In the derivations, the dissociative recombination rate  $K_r$  was assumed to be equal for  $\text{H}_3^+$ ,  $\text{HCO}^+$ , and  $\text{HOC}^+$ . From (5) and (7), the optimum concentration of CO for formation of  $\text{HOC}^+$  is given by

$$[\text{CO}]_m = \sqrt{\left\{ \frac{K_r[\text{M}](K_r[\text{M}] + k_2[\text{H}_2])}{k_4(k_2 + k_3)} \right\}} \quad (9)$$

where  $[\text{M}]$  denotes the concentration of free electrons and all other possible impurities including the cell wall that lead to the depletion of the ions. It was found that the abundance ratio depended on both the CO and  $\text{H}_2$  concentrations linearly. The abundance ratio  $[\text{HCO}^+]/[\text{HOC}^+]$  extrapolated to the 'zero CO pressure' shows a linear dependence on the  $\text{H}_2$  pressure. From the intercept and the slope,  $k_2/k_3$  is found to be about 46 and  $k_5/K_r[\text{M}]$  is approximately equal to  $4.1 \times 10^{-16} \text{ cm}^3$ . The rate constant  $k_3$  is obtained to be  $3.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , if  $k_2$  is  $1.8 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  (Jarrold *et al.* 1986). The slope of the plot of the abundance ratio  $[\text{HCO}^+]/[\text{HOC}^+]$  against the CO pressure gives  $k_4/K_r[\text{M}]$ . However, we found that the plot is not completely linear, showing a systematic deviation from the model. So there is some ambiguity in determination of the slope. Thus we obtained

$$k_4/K_r[\text{M}] = (3.3 \pm 1.7) \times 10^{-15} \text{ cm}^3 \quad (10)$$

by taking the ambiguity into account. The optimum CO pressure for the formation of  $\text{HOC}^+$  was found to be 25 mTorr when the  $\text{H}_2$  pressure was 200 mTorr. Therefore from (9) we obtain

$$\sqrt{(k_2 k_4)/K_4[\text{M}]} = 2.2 \times 10^{-15} \text{ cm}^3 \quad (11)$$

by neglecting  $k_3$ . Equations (10) and (11) give  $k_4 = (4.0 \pm 1.8) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  and  $K_r[\text{M}] = (1.2 \pm 0.3) \times 10^6 \text{ s}^{-1}$ . Because the ratio  $k_5/K_r[\text{M}]$  was already known above,  $k_5$  is now determined as  $(4.8 \pm 1.2) \times 10^{-1} \text{ cm}^3 \text{ s}^{-1}$ .

In the model stated above, the reverse reaction of (2) was neglected. However, it may not be negligible at least at the temperature range at which this experiment was done. The phase shift observed for the  $\text{H}_3^+$  line as the CO pressure was increased may be an indication of the reverse reaction (Amano & Nakanaga 1987). The model used here may be over simplified. The most important species not incorporated in the model is probably  $\text{CO}^+$ . The reaction between  $\text{CO}^+$  and  $\text{H}_2$  is also thought to proceed rapidly (Jarrold *et al.* 1986).

The isomerization of  $\text{HOC}^+$  by CO is a very fast process, and the rate constant  $k_4$  is about an order of magnitude larger than that obtained by Wagner-Redeker *et al.* (1985). On the other hand, the catalytic isomerization process of  $\text{HOC}^+$  to  $\text{HCO}^+$  by  $\text{H}_2$  is slower than that obtained by Jarrold *et al.* (1986). In the laboratory, CO plays a dominant role in isomerization of  $\text{HOC}^+$ . The rate constant of the formation reaction of  $\text{HOC}^+$ ,  $k_3$ , was found to be approximately equal to that obtained by Jarrold *et al.* (1986).

In the laboratory, the abundance ratio  $[\text{HCO}^+]/[\text{HOC}^+]$  was found to be 210 at the optimum reaction condition for production of  $\text{HOC}^+$ . This ratio, however, cannot be transferred to the astrophysical observations. In typical dense dark clouds,  $\text{H}_2$  is much more abundant relative to CO. Therefore the rate of the catalytic isomerization is much faster than the isomerization by CO.

Let us assume some typical fractional abundances in dense molecular clouds to be  $[\text{CO}]/[\text{H}_2] = 5.8 \times 10^{-5}$  and  $[e]/[\text{H}_2] = 3.5 \times 10^{-8}$  (see, for example, Freeman & Millar 1983). Then  $[\text{HCO}^+]/[\text{HOC}^+]$  is calculated to be of the order of  $10^7$  from (8). On the other hand, if a line of  $\text{HOC}^+$  is detected, the abundance ratio may serve as a measure to determine the relative abundance of CO and free electrons. As stated above, all the measurements were done at about  $-50^\circ\text{C}$ . Some preliminary measurements at a lower temperature, with liquid nitrogen for cooling the discharge, indicate no drastic change in abundance ratio  $[\text{HCO}^+]/[\text{HOC}^+]$ . However, the rate constants may be very different at the interstellar cloud temperature (see, for example, Adams & Smith 1987). If the isomerization of  $\text{HOC}^+$  by CO proceeds via the complex as suggested by Nobes & Radom (1981), the process may be more efficient at lower temperature.

#### 4. CONCLUDING REMARKS

The detection limit of ions has been pushed forward in recent years by about a factor of  $10^3$ , which has been realized by the modulated hollow-cathode discharge or the velocity-modulation technique as well as by improvements in laser sources. Further improvement may be attained by employing the ratio technique, because the sensitivity is limited by the source noise in the current system. The infrared-spectroscopic techniques have proved to be powerful to allow the detection of such species as  $\text{C}_2\text{H}_2^+$ ,  $\text{C}_2\text{H}_3^+$ ,  $\text{HC}_3\text{NH}^+$  and a number of negative ions that were regarded as a very remote goal only a few years ago.

In this article, a few examples were chosen from among the most recent results to illustrate several aspects of the high-resolution spectroscopy of ions. Although the accuracy of the frequency measurements is limited by the Doppler width, the molecular constants can be determined precisely to predict the pure rotational lines within a few megahertz uncertainty, because the number of lines obtainable from the analysis of the band spectrum is plentiful and fairly high- $J$  transitions can be observed. This accuracy is good enough as a starting point to search for the microwave lines in the laboratories, and the observation of the microwave lines are essential to determine the rotational transition frequencies that lead to definite identification of the interstellar lines.

The high-resolution infrared absorption spectroscopy can be utilized for plasma diagnosis, as demonstrated by Pan & Oka (1987). In relatively simple reaction systems, the technique may be useful to identify the reaction intermediates, and more direct information on the reaction mechanism and the rate constants can be derived. Interactions with other fields such as gas-phase ion-molecule reaction kinetics, *ab initio* MO calculations, and molecular astrophysics will continue to be vital and productive.

I thank A. R. W. McKellar for reading the manuscript and for his comments.

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