The rotational spectra of the $HCCCNH^+$, $NCCNH^+$, and CH_3CNH^+ ions

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The rotational spectra of the $HCCCNH^+$, $NCCNH^+$, and CH_3CNH^+ ions have been observed in a supersonic molecular beam by Fourier transform microwave (FTM) spectroscopy. The rotational and centrifugal distortion constants were determined for all three, and the nitrogen quadrupole hyperfine coupling constants for $HCCCNH^+$ and $NCCNH^+$. From the respective Doppler shifts, it is found that the velocities of the ions are 3% larger than those of the parent unprotonated molecules, and the linewidths are greater by about 50%. The concentration of the ions near the nozzle is approximately 10^{11} cm^{-3}, which is sufficiently high to be detectable in the visible and the IR by present laser techniques. © *2000 American Institute of Physics.* [S0021-9606(00)01829-8]

I. INTRODUCTION

In addition to a number of rare gas ionic complexes, more than 30 polyatomic ions have been observed by high-resolution spectroscopy, mainly at IR wavelengths in conventional discharge cells.[1] Five of these have been observed in supersonic jets: three by direct IR laser absorption spectroscopy[2,3] (H_3^+, N_2H^+, and H_3O^+), and two at cm wavelengths by Fourier transform microwave (FTM) spectroscopy[4] ($HOCO^+$ and $HOCS^+$), a technique that has been used with considerable success to study radicals and reactive isomers in supersonic molecular beams.[5] With recent improvements in the sensitivity of FTM spectroscopy and increased yields of reactive molecules in our molecular beam, we have now succeeded in detecting the rotational spectra of three more polyatomic ions: $HCCCNH^+$, $NCCNH^+$, and CH_3CNH^+. The narrow linewidths in our rotationally cold molecular beam ($T_{rot} \sim 3-10$ K) allow the determination of both nitrogen hyperfine structure (hfs) when present, and the drift velocities of the ions relative to the neutral molecules in the beam; from the line intensities it has been possible to determine the number densities of the ions as well.

II. EXPERIMENT

The FTM spectrometer used for the work here currently operates from 5 to 43 GHz.[6] The ions were produced in a dc discharge in the throat of a supersonic discharge nozzle similar to that used to observe neutral reactive species such as the C_nH radicals.[7] We began by optimizing the production of $HOCO^+$ and $HOCS^+$, two ions that Ohshima and Endo[4] had detected with a spectrometer similar to ours. They diluted the organic precursors (0.1%–0.2%) in equal molar mixtures of H_2 and Ar, but we found that the line intensity of $HOCS^+$ increased by a factor of about 8 when Ar was omitted (and similarly when Ne was used with H_2). The strongest lines of $HCCCNH^+$, $NCCNH^+$, and CH_3CNH^+ were then observed with HCCCN, NCCN, or CH_3CN diluted in H_2 to <0.1%.

With a stagnation pressure behind the valve of 2.5 kTorr and a 6 Hz pulse rate of the gas, the total flow rate was about 20 cm^3 s^{-1}. The discharge potential (1000 V) and the gas pulse duration (~ 100 μs) were nearly the same for each ion.

Owing to the high sensitivity and narrow linewidths in our FTM spectrometer when using an axial expansion, we were able to precisely compare the spectra of ions and neutral molecules. From the Doppler splitting one can determine the relative velocities of ions and neutrals and from the linewidths one can determine whether there is a source of excess line broadening for ions over neutrals. As Fig. 1 illustrates, the $J = 2 \rightarrow 1$ transition of ^{18}OCS has well-resolved Doppler components corresponding to a velocity of 2049 ± 4 m s^{-1} in a beam of 95% H_2 and 5% Ne, where the velocities (and linewidths) were determined from least-squares fits of Lorentzian profiles to approximately 10 spectra, and the quoted uncertainties are the 1σ standard deviations of the mean. Also shown in Fig. 1 is a spectrum of the same transition of $HOCS^+$ in the same discharge where the Doppler splittings correspond to a velocity of 2116 ± 3 m s^{-1}. The ions are evidently moving faster than the neutrals by 67 ± 5 m s^{-1}. The linewidth of $HOCS^+$, 23 ± 3 kHz, is also greater than that of ^{18}OCS, 16.1 ± 0.6 kHz, possibly an indication of pressure broadening (see Sec. IV).

III. OBSERVED SPECTRA

There is little question of the present identifications, owing to the close agreement of the rotational and centrifugal distortion constants with those observed in the IR, and to the quadrupole hfs which confirms the presence of nitrogen in two of the ions. Without further discussion the IR identifications are assumed here.

A. $HCCCNH^+$

Lee and Amano undertook the first high-resolution spectroscopy of $HCCCNH^+$ in the infrared, detecting the ν_1 fundamental (N–H stretch), and obtaining fairly accurate rotational and centrifugal distortion constants for the ground vibrational state.[8] Using these, Kawaguchi *et al.*[9] identified
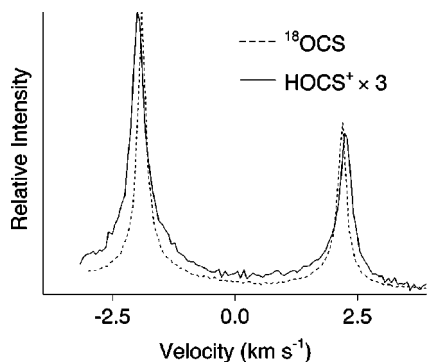
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FIG. 1. The FTM spectra of the $2{\to}1$ transition of HOCS$^+$ at 22 906.607 MHz and ^{18}OCS at 22 819.396 MHz observed in the same discharge. The double-peaked profiles are instrumental in origin, the Doppler splitting that results when the molecular beam interacts with the two traveling waves that compose the confocal mode of the Fabry–Perot cavity. The line profiles, which are plotted vs. velocity, are the averages of 9 spectra with total integration times of 75 min for HOCS$^+$ and 20 min for ^{18}OCS.

two rotational transitions of this ion towards the cold dense astronomical source TMC–1: $J=5{\to}4$ at 43.3 GHz and $4{\to}3$ at 34.6 GHz. Guided by the astronomical frequencies, we then detected the four lowest rotational transitions listed in Table I. As Fig. 2(a) shows, nitrogen quadrupole hyperfine structure (hfs) is barely resolved in the $2{\to}1$ transition, but is fairly well resolved in the $1{\to}0$ transition [Fig. 2(b)], and the quadrupole coupling constant eQq is well determined. Quadrupole hfs collapses as $1/J^2$, and is unresolved in the next two transitions: $3{\to}2$ at 26.0 GHz and $4{\to}3$ at 34.6 GHz.

The standard expression for the rotational transitions of a closed-shell linear molecule with quadrupole hfs was fit to the measured frequencies in Table I. Only three constants are required to reproduce the four lowest rotational transitions to an rms uncertainty of 3 kHz: the rotational constant B, the centrifugal distortion constant D, and the quadrupole coupling constant eQq. The best fit B and D constants are compared in Table II with those derived from the IR measurements,[8] the astronomical observations,[9] and *ab initio* calculations,[10] with excellent agreement overall. Frequencies calculated from the IR measurement[8] agree to better than 1 MHz with those in Table I. The rotational constant calculated from theory is almost identical to the value in Table II when B_e is converted to B_0 using vibration–rotation cou-

FIG. 2. Spectra of HCCCNH$^+$. (a) The $J=2{\to}1$ line showing the resolved $F=1{\to}0$ hyperfine component, and the strongly blended hyperfine components within the central linewidth. (b) The $J=1{\to}0$ line showing the two strongest hyperfine components: $F=2{\to}1$ and $1{\to}1$. Integration times were 14 m for (a) and 68 m for (b). Shown beneath the observed spectra are stick diagrams derived from the constants in Table II with Doppler doubling; the synthetic spectra were calculated from the stick diagrams with linewidths equal to the measured widths.

pling constants calculated *ab initio*;[10] the astronomical, IR, and theoretical centrifugal distortion constant agrees with the empirical determination here to within 5%.

B. NCCNH$^+$

The rotationally resolved spectrum of protonated cyanogen, NCCNH$^+$, was also first observed in the laboratory at IR wavelengths.[11] It was subsequently detected in the millimeter-wave band in a hollow cathode discharge, but the spectrum was very weak, attributed by the authors to the possible occurrence of many reactions that lead to products

TABLE I. Measured microwave frequencies of HCCCNH$^+$.

Transition $J'-J$	$F'-F$	Frequency[a] (MHz)	$O-C$[b] (kHz)
$1{\to}0$	$2{\to}1$	8657.987(3)	3
	$1{\to}1$	8658.030(3)	-4
$2{\to}1$	$1{\to}1$	17 315.888(3)	-2
	$2{\to}1$	17 315.974(3)	0
	$3{\to}2$	17 315.974(3)	4
$3{\to}2$		25 973.931(5)	-2
$4{\to}3$		34 631.861(5)	0

[a]Estimated uncertainties (in parentheses) are 1σ experimental errors in units of the last significant digit.
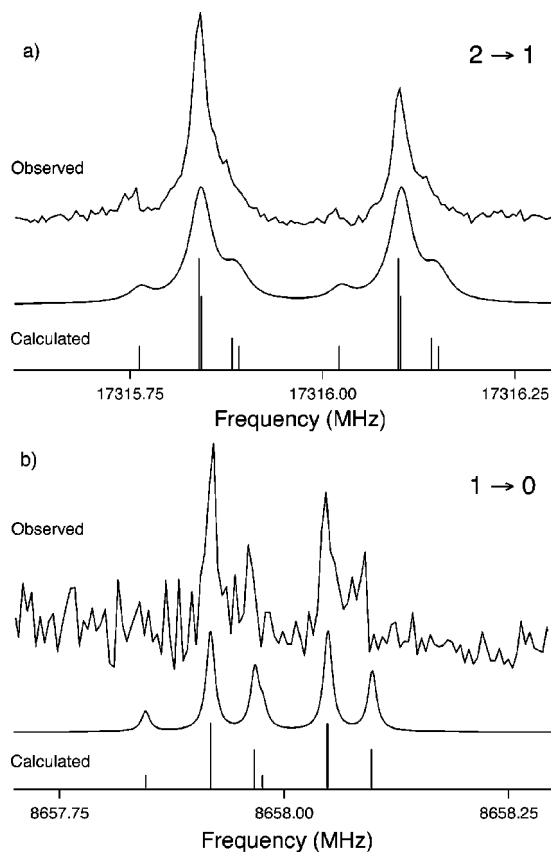[b]Frequencies calculated from the constants in Table II.

TABLE II. Spectroscopic constants of HCCCNH$^+$ (in MHz).

Constant[a]	This work	Astronomical[b]	IR[c]	Theory[d]
B	4328.9970(5)	4329.0010(10)	4328.892(71)	4328.99
$D\times10^3$	0.448(24)	0.478(11)	0.445(23)	0.413
eQq	0.167(6)	$\cdots$	$\cdots$	$\cdots$

[a]Here, and in Tables IV–VI, the estimated uncertainties (in parentheses) are 1σ in units of the last significant digit.
[b]Reference 9.
[c]Reference 8.
[d]Reference 10.

TABLE III. Measured microwave frequencies of $NCCNH^+$.

Transition [a]			Frequency [b]	$O - C$ [c]
$J' - J$	$F_1' - F_1$	$F' - F$	(MHz)	(kHz)
$1 \rightarrow 0$	$2 \rightarrow 1$	$2 \rightarrow 2$	8874.648	4
	$1 \rightarrow 1$	$1 \rightarrow 2$	8874.677	-2
	$1 \rightarrow 1$	$2 \rightarrow 1$	8876.250	-2
	$2 \rightarrow 1$	$3 \rightarrow 2$	8876.313	5
	$0 \rightarrow 1$	$1 \rightarrow 0$	8876.335	-6
	$2 \rightarrow 1$	$1 \rightarrow 2$	8878.763	0
$2 \rightarrow 1$	$3 \rightarrow 2$	$3 \rightarrow 3$	17 750.377	-4
	$2 \rightarrow 2$	$1 \rightarrow 1$	17 750.632	4
	$3 \rightarrow 2$	$2 \rightarrow 1$	17 750.666	1
	$1 \rightarrow 2$	$0 \rightarrow 1$	17 750.718	-2
	$2 \rightarrow 1$	$2 \rightarrow 1$	17 751.963	-6
	$3 \rightarrow 2$	$3 \rightarrow 2$	17 752.048	3
	$2 \rightarrow 1$	$3 \rightarrow 2$	17 752.134	-3
	$3 \rightarrow 2$	$4 \rightarrow 3$	17 752.158	6
	$2 \rightarrow 2$	$1 \rightarrow 2$	17 754.749	3
	$3 \rightarrow 2$	$2 \rightarrow 2$	17 754.778	-5
	$2 \rightarrow 1$	$1 \rightarrow 0$	17 754.806	4
	$1 \rightarrow 0$	$0 \rightarrow 0$	17 754.806	2

[a]The transitions are labeled according to the coupling scheme $\mathbf{F}_1 = \mathbf{J} + \mathbf{I}_1$ and $\mathbf{F} = \mathbf{F}_1 + \mathbf{I}_2$, where $\mathbf{I}_1$ refers to the outer nitrogen and $\mathbf{I}_2$ to the inner nitrogen.
[b]Estimated measurement uncertainties are 2 kHz.
[c]Frequencies calculated from the constants in Table IV (this work).

other than $NCCNH^+$.[12] Our estimate of the abundance of $NCCNH^+$, however, indicates that $NCCNH^+$ is formed with nearly the same efficiency as other protonated ions we have studied; there is no evidence for significant branching reactions involving NCCN.

Six hyperfine-split components of the $J = 1 \rightarrow 0$ transition and 11 components of the $2 \rightarrow 1$ transition of $NCCNH^+$ were measured (Table III). As Fig. 3 shows, lines of $NCCNH^+$ have been observed with high resolution and sensitivity. Hfs from the inner nitrogen is 22 times smaller than that of the outer nitrogen and is resolved in the $1 \rightarrow 0$ transition, but as Fig. 3 shows is only partially resolved in the $2 \rightarrow 1$ transition. The four best-fit spectroscopic constants in Table IV reproduce the 17 frequencies in Table III to an rms uncertainty (4 kHz) that is comparable to the measurement uncertainties.

As for $HCCCNH^+$, the rotational and centrifugal distortion constants of $NCCNH^+$ derived from the IR and the millimeter-wave measurements are in excellent agreement with those we find. The theoretical value[13] of B agrees to 0.14% and that of D to 3%.[14] The $NCCNH^+$ ion has not

been identified in space, but it is a good candidate for astronomical detection because its dipole moment is large:[13] 6.45 D.

C. CH_3CNH^+

Protonated methyl cyanide, CH_3CNH^+, also had only been observed at high resolution in the IR (Ref. 15) prior to the present work. Although some of the K levels in the ν_1 IR band (N–H stretch) are perturbed,[16] the two lowest rotational transitions calculated from the IR constants are within 0.6 MHz of those measured here. Of the five protonated ions, lines of CH_3CNH^+ are the weakest and have the largest widths [full width at half maximum (FWHM) ~ 55 kHz at 17 GHz]. The same transitions of $CH_3C^{15}N$, devoid of nitrogen quadrupole hfs, exhibit partially resolved nuclear spin–rotation magnetic hfs from the methyl hydrogens that is comparable to the nitrogen–14 quadrupole hfs expected in CH_3CNH^+. Owing to complex structure of the line profiles, we were unable to assign the nitrogen quadrupole hfs of this ion.

Turner *et al.*[17] undertook an inconclusive search for CH_3CNH^+ in the 3 mm wave band toward several dense astronomical clouds. Possible evidence was claimed for the $6 \rightarrow 5$ transition in three of these at approximately the right frequency, but near 100 GHz, line frequencies calculated from the spectroscopic constants in Table V are more than 2 MHz higher than those which they used. With accurate line frequencies in hand, a significantly better astronomical search could now be done for this ion with the very sensitive radio telescopes at hand.

D. Abundances

From a comparison of the intensities of the ionic lines with those of stable neutral molecules in our supersonic beam, it has been possible to determine the approximate number densities of the ions. This was done in the following steps. First, the ratio of the line intensities of the $J = 2 \rightarrow 1$ rotational transition of the ion and the parent neutral was measured in the same discharge. Then the number of neutral molecules per gas pulse (abundance) was determined by comparing the parent neutral with the same transition of ^{18}OCS in a calibrated sample of 1% OCS in Ne. The abundances obtained by this method are fairly accurate provided the dipole moments are known: those of $HCCCNH^+$

TABLE IV. Spectroscopic constants of $NCCNH^+$ (in MHz).

Constant	FTM (this work)	FTM plus mm-wave (recommended)	Millimeter-wave [a]	IR [b]	Theory [c]
B	4438.0116(11)	4438.011 54(27)	4438.010 64(45)	4438.23(8)	4432
$D \times 10^3$	0.533(15)	0.530 63(21)	0.530 13(16)	0.602(25)	0.517(5)
eQq(outer)	$-5.480(3)$	$-5.480(3)$	$\cdots$	$\cdots$	$\cdots$
eQq(inner)	$-0.250(8)$	$-0.250(8)$	$\cdots$	$\cdots$	$\cdots$

[a]Reference 31.
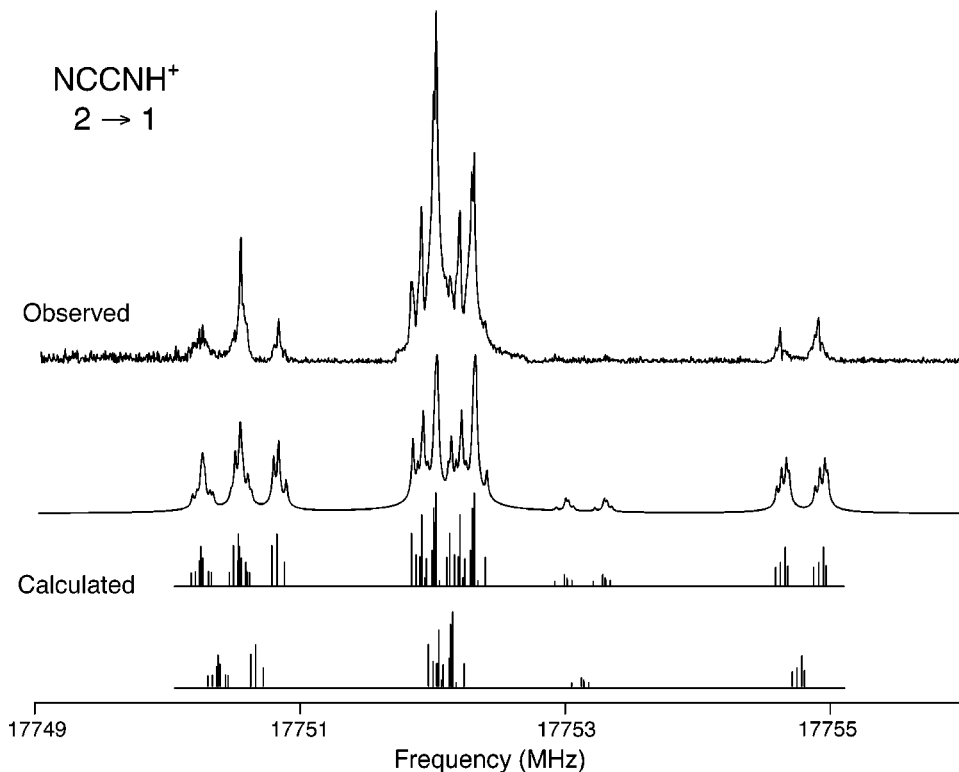[b]Reference 11.
[c]Reference 13.

FIG. 3. The $J=2\rightarrow1$ transition of NCCNH$^+$. The observed spectrum is a composite of 70 spectra, each 100 kHz wide, with a total integration time of 1 h. Shown beneath the observed spectrum are stick diagrams derived from the constants in Table IV with Doppler doubling (upper) and without Doppler doubling (lower); the synthetic spectrum (second from top) was calculated from the upper stick diagram for an assumed linewidth of 30 kHz.

(1.61 D), NCCNH$^+$ (6.45 D), and CH$_3$CNH$^+$ (1.01 D) have been calculated *ab initio*;[10,13,18] that of HOCS$^+$ (1.2 D) has been estimated.[17]

We find that the ratio HOCS$^+$/OCS is approximately 3×10^{-4}, and the ratios HCCCNH$^+$/HCCCN and CH$_3$CNH$^+$/CH$_3$CN are 5×10^{-4} and 2×10^{-3}, respectively. Because of the nonpolarity of NCCN, the ratio NCCNH$^+$/NCCN could not be determined by this method. The number of ions per gas pulse is then derived to be 2×10^{12} for HOCS$^+$ and HCCCNH$^+$, 6×10^{11} for NCCNH$^+$, and 1×10^{12} for CH$_3$CNH$^+$. These estimates of the abundances assume that the spatial distributions of the ions and the neutral molecules are the same in our beam; the ratio of ions to neutrals may depend somewhat on the position within the jet, but the present experiment is unable to determine this dependence with any sensitivity.

The concentrations of the ions probably approach 10^{11} cm^{-3} near the throat of the expansion, on the assumption that the density of the gas is approximately 10 times smaller than at the orifice of the pulsed valve. These concentrations are only about an order-of-magnitude less than that of N$_2$H$^+$, one of the most stable polyatomic ions whose con-

centration near the orifice of slit-jet discharge nozzles of $\sim10^{12}$ cm^{-3} has been estimated by IR laser[19] and millimeter-wave absorption spectroscopy.[20]

IV. DISCUSSION

The quadrupole coupling constant (eQq) is a sensitive measure of the electric field gradient in a molecule. That of the outer nitrogen in NNH$^+$ and NCCNH$^+$ is roughly comparable to that of other molecules with a terminal nitrogen, such as HCN (-4.7 MHz; Ref. 21) and HCCCN (-4.3 MHz; Ref. 22), but, as Table VI shows, eQq for the inner nitrogen is very small. There is a simple qualitative explanation for this effect: in the prototypical ion HCNH$^+$, an SCF calculation indicates that there is a large negative net charge on the nitrogen atom.[23] It is well known from the theory of quadrupole coupling in molecules,[24] that a negative charge on the coupling atom screens the nucleus from the fields of the electrons in the $2p$ valence shell. Consequently, eQq(inner) is predicted to be significantly smaller than that of the terminal nitrogen. Although the charge distribution in HCCCNH$^+$ and NCCNH$^+$ seems not to have been calculated, there is indirect evidence from their calculated geometrical structures that the charge distributions are similar to that of HCNH$^+$. *Ab initio* calculations[13] establish that the

TABLE V. Spectroscopic constants of CH$_3$CNH$^+$ (in MHz).

Constant	This work [a]	IR [b]	Theory [c]
B	8590.556 75	8590.40(19)	8600.1
$D\times10^3$	3.125	2.99(18)	$\cdots$
$D_{JK}\times10^3$	156.75	156.2(38)	$\cdots$

[a]Derived from the measured frequencies for $J_K=1_0\rightarrow0_0$ (17 181.101 MHz), $2_0\rightarrow1_0$ (34 362.127 MHz), and $2_1\rightarrow1_1$ (34 361.500 MHz).
[b]Reference 16.
[c]Reference 18.

TABLE VI. Quadrupole coupling constants (in MHz).

Ion	eQq(inner)	eQq(outer)	Reference
NNH$^+$	$-1.3586(38)$	$-5.6902(21)$	32
HCNH$^+$	$-0.49(7)$	$\cdots$	33
NCCNH$^+$	$-0.250(8)$	$-5.480(3)$	This work
HCCCNH$^+$	$0.167(6)$	$\cdots$	This work

C–N bond is significantly shortened upon protonation of the terminal nitrogen in the parent molecules HCN, HCCCN, and NCCN. Shortening of the C–N bond in these ions is consistent with a large negative charge on the inner nitrogen as the measurements of eQq in Table VI appear to confirm.

There are several possible sources of line broadening in our experiment. If the main source of broadening were the result of the time-of-flight (TOF) of the molecules through the long Fabry–Perot cavity, then the width (hereafter FWHM) of the $J = 2 \rightarrow 1$ transition of ^{18}OCS at 22.8 GHz would be more than 10 times smaller than what we observe (16 kHz). For example, in a beam of 95% H_2 and 5% Ne, the TOF linewidth is $v/(\pi d) \sim 0.9$ kHz, where $v = 2.1 \times 10^5$ cm s^{-1} and $d = 70$ cm, the approximate mirror separation of our Fabry–Perot cavity. The actual linewidth in our experiment is much greater than that because the supersonic beam is poorly collimated and there is a significant component of the velocity parallel to the direction of propagation.

The linewidth of the $J = 2 \rightarrow 1$ transition of $HOCS^+$ is 1.44 ± 0.18 times that of ^{18}OCS in the same discharge. The increased width of the ion with respect to the neutral is considerably larger than the ratio of the velocities (1.032 ± 0.002) in the 95% H_2 and 5% Ne beam, implying that there is an additional source of broadening of about 10 kHz for the ions. One possible cause for the greater linewidth of $HOCS^+$ is collisional broadening. Owing to the long range ion–dipole interaction, collisional cross-sections of ions with neutrals are several times larger than those of neutral molecules.[25] Recently, Pearson *et al.*[26] measured the pressure broadening coefficient of HCO^+ with H_2 near 10 K, and showed that it is very large (500 MHz/Torr). We estimate that the pressure in the center of the cavity is $\sim 1 \times 10^{-5}$ Torr during the gas pulse, so the increased linewidth of the ion may be attributable to pressure broadening, if the pressure broadening coefficient for collisions of $HOCS^+$ with H_2 is comparable to that of HCO^+.

The production of the protonated ions in the present discharge is plausibly given by the reactions

$$H_2 + H_2^+ \rightarrow H_3^+ + H, \tag{1}$$

$$H_3^+ + X \rightarrow XH^+ + H_2, \tag{2}$$

$$XH^+ + e^- \rightarrow X + H, \tag{3}$$

where X is a neutral polyatomic molecule such as HCCCN, etc. From this simple chemical scheme, it follows that the ratios of the concentration of the protonated ion to parent neutral is $[XH^+]/[X] \sim ([H_3^+]k_2)/([e^-]k_3)$. Reaction (2) has been measured for all of the species discussed here. For most, reaction (2) occurs close to the Langevin rate of $(1 - 2) \times 10^{-9}$ cm^3 s^{-1}, but those involving HCCCN and CH_3CN occur at rates that are $5 - 10$ times higher.[27] Because the molecular beam must be electrically neutral (i.e., $[H_3^+] \sim [e^-]$) and on the assumption that the electron recombination rate is $10^{-6} - 10^{-7}$ cm^3 s^{-1},[28] then $[XH^+]/[X] \sim (10^{-3} - 10^{-4})$, which is very close to the ratios that are observed in our beam (Sec. III D).

It should now be feasible to detect other protonated ions, such as $HSCS^+$, CH_3CCCNH^+, and HC_5NH^+ with the present technique. In addition to these ions which have not

been studied by high-resolution spectroscopy, there are several ions that are particularly important in the formation of interstellar molecules, most notably $C_3H_3^+$ (Ref. 29) and $SiCCH^+$ (Ref. 30). Although $C_3H_3^+$ does not possess a permanent electric dipole moment, $C_3H_2D^+$ is estimated to have a fairly large dipole moment (0.4 D) owing to the large separation of the center-of-mass and charge. The rotational spectra of c-C_3H_2 and SiCC in our spectrometer are very intense, so if the ratio of the protonated ion to neutral parent is 10^{-3} as observed here, it may be also be possible to observe $C_3H_2D^+$ and $SiCCH^+$.

[1] E. Hirota, Chem. Rev. **92**, 141 (1992).
[2] M. Fukushima, M.-C. Chan, Y. Xu, A. Taleb-Bendiab, and T. Amano, Chem. Phys. Lett. **230**, 561 (1994).
[3] Y. Xu, M. Fukushima, T. Amano, and A. R. W. McKellar, Chem. Phys. Lett. **242**, 126 (1995).
[4] Y. Ohshima and Y. Endo, Chem. Phys. Lett. **256**, 635 (1996).
[5] P. Thaddeus, M. C. McCarthy, M. J. Travers, C. A. Gottlieb, and W. Chen, Faraday Discuss. **109**, 121 (1998).
[6] M. C. McCarthy, M. J. Travers, A. Kovács, C. A. Gottlieb, and P. Thaddeus, Astrophys. J., Suppl. Ser. **113**, 105 (1997); M. C. McCarthy, A. J. Apponi, V. D. Gordon, C. A. Gottlieb, P. Thaddeus, T. D. Crawford, and J. F. Stanton, J. Chem. Phys. **111**, 6750 (1999).
[7] C. A. Gottlieb, M. C. McCarthy, M. J. Travers, J.-U. Grabow, and P. Thaddeus, J. Chem. Phys. **109**, 5433 (1998).
[8] S. K. Lee and T. Amano, Astrophys. J. Lett. **323**, L145 (1987).
[9] K. Kawaguchi, Y. Kasai, S.-I. Ishikawa, M. Ohishi, N. Kaifu, and T. Amano, Astrophys. J. Lett. **420**, L95 (1994).
[10] P. Botschwina and Ä. Heyl, Mol. Phys. **97**, 209 (1999).
[11] H. E. Warner and T. Amano, J. Mol. Spectrosc. **145**, 66 (1991).
[12] T. Amano and F. Scappini, J. Chem. Phys. **95**, 2280 (1991).
[13] P. Botschwina and P. Sebald, Chem. Phys. **141**, 311 (1990).
[14] P. Botschwina, J. Flügge, and S. Seeger, J. Mol. Spectrosc. **157**, 494 (1993).
[15] T. Amano, Astrophys. J. Lett. **330**, L137 (1988).
[16] T. Amano, J. Mol. Spectrosc. **153**, 654 (1992).
[17] B. E. Turner, T. Amano, and P. A. Feldman, Astrophys. J. **349**, 376 (1990).
[18] P. Botschwina, J. Mol. Spectrosc. (in press).
[19] D. T. Anderson, S. Davis, T. S. Zwier, and D. J. Nesbitt, Chem. Phys. Lett. **258**, 207 (1996).
[20] H. Linnartz, T. Motylewski, F. Maiwald, D. A. Roth, F. Lewen, I. Pak, and G. Winnewisser, Chem. Phys. Lett. **292**, 188 (1998).
[21] A. G. Maki, J. Phys. Chem. Ref. Data **3**, 221 (1974).
[22] W. J. Lafferty and F. J. Lovas, J. Phys. Chem. Ref. Data **7**, 441 (1978).
[23] T.-K. Ha and M. T. Nguyen, Chem. Phys. Lett. **97**, 503 (1983).
[24] W. Gordy and R. L. Cook, *Microwave Molecular Spectra* (Wiley, New York, 1984).
[25] T. G. Anderson, C. S. Gudeman, T. A. Dixon, and R. C. Woods, J. Chem. Phys. **72**, 1332 (1980).
[26] J. C. Pearson, L. C. Oesterling, E. Herbst, and F. C. De Lucia, Phys. Rev. Lett. **75**, 2940 (1995).
[27] V. G. Anicich and W. T. Huntress, Jr., Astrophys. J., Suppl. Ser. **62**, 553 (1986).
[28] J. B. A. Mitchell, Phys. Rep. **186**, 217 (1990).
[29] Y. Xie and J. E. Boggs, J. Chem. Phys. **90**, 4320 (1989); T. J. Lee, A. Willets, J. F. Gaw, and N. C. Handy, *ibid.* **90**, 4330 (1989).

[30] J. R. Flores, A. Largo-Cabrerizo, and J. Largo-Cabrerizo, J. Mol. Struct.: THEOCHEM **148**, 33 (1986).

[31] G. Cazzoli, C. D. Esposti, and F. Scappini, J. Chem. Phys. **97**, 6187 (1992).

[32] P. Caselli, P. C. Myers, and P. Thaddeus, Astrophys. J. Lett. **455**, L77 (1995).

[33] L. M. Ziurys, A. J. Apponi, and J. T. Yoder, Astrophys. J. Lett. **397**, L123 (1992).