

CHAPTER IX

An intense slit discharge source of jet cooled molecular ions and radicals
($T_{\text{rot}} < 30 \text{ K}$)

9.1 Introduction

Radicals and molecular ions are among the most chemically reactive species known and play a key role in chemistry ranging from the upper atmosphere¹⁻³ to molecular synthesis in the interstellar medium.⁴⁻⁶ This high reactivity comes at a considerable cost to experimentalists: such transient species are often very difficult to maintain at sufficient concentrations to probe experimentally. Of particular interest, therefore, has been the development of direct absorption laser techniques for high resolution spectroscopy of radicals/molecular ions present in electrical discharges, where these reactive molecules can be maintained at relatively high steady state concentrations⁷⁻¹⁰ However, as a result of the electron impact ionization and/or dissociation event leading to formation of the radical/molecular ion, the rovibrational temperatures in conventional discharge cells can be inconveniently high. Even with cryogenically cooled discharge walls, rovibrational temperatures are typically >300-500 K, which can result in substantially complicated spectra as well as significant dilution of population in any given quantum state sampled by a high resolution probe laser.

One powerful alternative has been to situate the discharge in the throat of a supersonic expansion. This method was initially pioneered by Engelking and coworkers,¹¹ who developed a sharp tungsten tip “Corona” discharge ionization source behind the pinhole of a continuous wave (cw) expansion nozzle. These Corona sources yield appreciable densities of rotationally cold radicals (with $T_{\text{rot}} \leq 15$ K) at the expansion orifice, and have proved quite useful for a variety of emission and laser induced fluorescence studies.¹² However, as these pinhole sources offer short path lengths and have densities that drop off *quadratically* with distance downstream, they are generally insufficient to use with direct absorption techniques. Furthermore, the spectral widths observed in a *pinhole* expansion are typically limited by angular spread of the uncollimated free jet, which when viewed with high resolution methods adds significantly to the experimental Doppler profile.

In recent years, there has been progress toward building *shaped* discharge expansions for matching the ion or radical density appropriately to a long pass direct absorption geometry. Foster *et al.*¹³ have used cw discharges across metal knife edges defining a slit expansion, and succeeded in detecting radicals such as NH_2 with direct diode laser absorption. A multiple pin extension of the original Engelking method has been used by Meerts *et al.*¹⁴ to generate a cw Corona slit discharge, which was able to detect the NO^+ and N_2H^+ molecular ions with modest signal to noise (S/N) ratios. Efforts by Amano and coworkers¹⁵ with a combined hollow cathode/cw slit discharge have succeeded in detecting several ions such as H_3^+ , N_2H^+ , and H_3O^+ in the near-IR. A dramatic improvement in

sensitivity has been reported by Amano, McKellar and coworkers¹⁶ for a cw expansion excited by a single 1.5 kV Corona pin behind a slit nozzle. This work demonstrated S/N greater than 200:1 on single rovibrational lines in H_3^+ , though with rotational temperatures varying between 33K and 93K and spectral linewidths of order 300 MHz.

Our group has recently been developing discharge methods for use with *pulsed* slit supersonic expansions, in an effort to achieve lower rotational temperatures, narrower velocity collimation linewidths and greater radical/ion densities. Our goal is an intense source for high resolution IR laser absorption spectroscopy of jet cooled molecular ions, radicals, radical clusters and ion clusters. This paper describes such an approach which achieves high densities (10^{10} - $10^{12}/\text{cm}^3$), long absorption paths (80 cm), and sub-Doppler linewidths (75-100 MHz) for both radicals and molecular ions, supersonically cooled to rotational temperatures of 30 K or lower. In this work, we demonstrate the performance of this jet cooled source with sample near-IR difference frequency spectra of the OH radical, as well as simple protonated molecular ion species such as N_2H^+ and H_3O^+ .

9.2 Experiment

The present studies have been implemented on the Boulder near-IR slit jet cluster spectrometer,^{17,18} for which the pulsed valve has been recently modified (see Figure. 9.1) to accommodate the new discharge capabilities. The high

SLIT DISCHARGE SOURCE

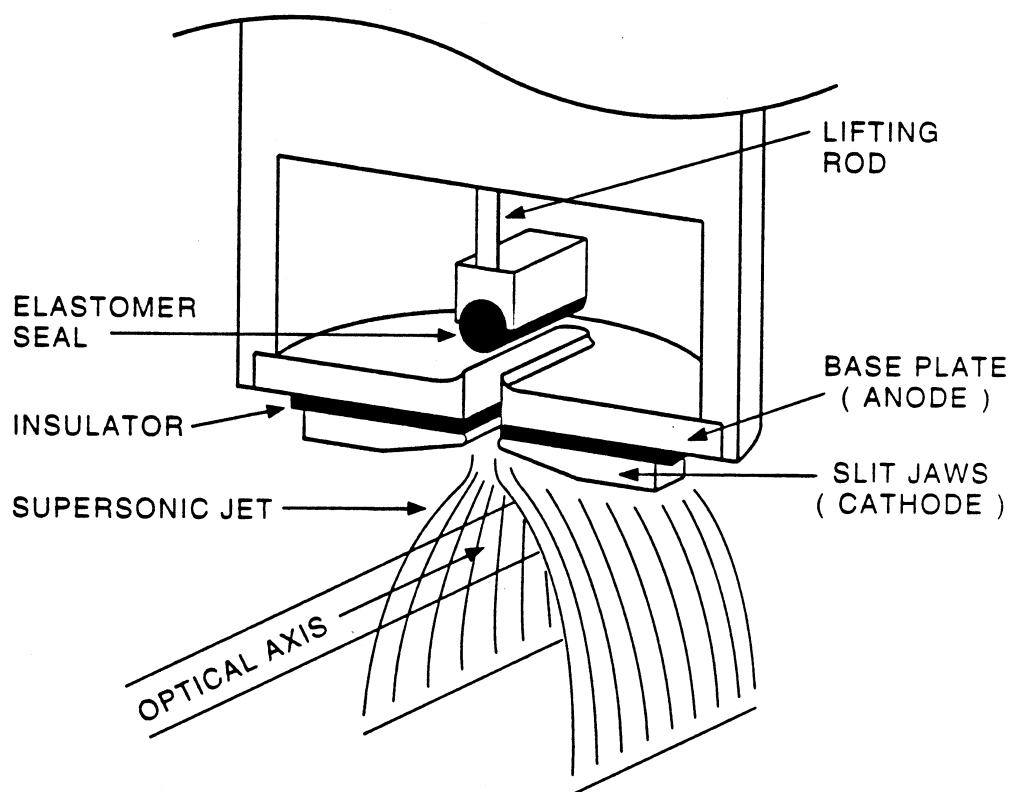


Figure 9.1 Schematic of the discharge slit source for jet cooled molecular ions and radicals. The electrons flow from the negatively biased jaws (cathode) to the pulsed valve body (anode). This leads to a more stable uniform discharge, whereby the heavier and much lower mobility cations travel *downstream* with the pulsed supersonic flow.

resolution light source is obtained by subtracting single mode Ar⁺ and ring dye lasers in a temperature phase matched LiNbO₃ crystal. The difference frequency light is split into signal and reference beams and balanced to near shot noise limited levels by dual beam subtraction electronics. The IR signal beam is multipassed with White cell optics 20 times through the long axis of the slit expansion roughly 1 cm downstream of the slit orifice. The absorbance sensitivity is typically 10⁻⁶/√Hz, but since detection is in a 1000 μsec pulse with a roughly 10 KHz bandwidth, this translates into a 10⁻⁴ minimum absorbance per pulse with only a 2% duty cycle. Though the sensitivity can be further enhanced by signal averaging and/or higher duty cycle phase sensitive detection methods, this is already sufficient to see intense absorption signals on jet cooled molecular ions and radicals.

The basic discharge design is shown in Figure 9.1. Two electrically isolated stainless steel jaws form the limiting aperture (300 μm) for the 4 cm slit expansion, separated from the pulsed valve body by a thin (1 mm) Vespel insulator. A *negative* bias voltage is applied to both jaws; the electron current therefore flows across the insulator *against* the supersonic gas stream, and terminates on the inside (ground) of the pulsed valve. Operation with *positive* polarity jaws leads to an unstable discharge with less efficient total radical/molecular ion generation due to localized filamentary breakdown. This asymmetry in the discharge polarity is most likely due to the large difference in electron and a buffer gas cation mobilities, which is much less favorable for flux of the much heavier cations *upstream* against the supersonic gas flow. The

discharge strikes and ceases automatically with gas flow in the slit region. However, in order to eliminate any sporadic arcing to the grounded vacuum chamber walls, gating circuits are used to switch the discharge voltage to the jaws on and off 50 μ sec before and after the gas pulse arrival. Typically the discharge operates with a 300 V potential difference between the jaws and ground, corresponding to a peak current density of 1.5 A across 500 Ω ballast resistors. The discharge is essentially completely confined inside the 300 μ m wide slit width, and visually uniform along the full 4 cm dimension of the slit length. Qualitatively similar ion/radical densities are obtained in He, Ne and Ar discharge expansions, though with differences in experimentally observed Doppler widths due to the dependence of expansion velocity on the diluent gas mass.

9.3 Results

9.3.1 Jet cooled radicals in the slit discharge

As a demonstration of the slit discharge capability to produce large densities of jet cooled radicals, a sample high resolution scan over the $v = 1 \leftarrow 0$, Q(1.5) transition out of the lower spin orbit state ($^2\Pi_{3/2}$) of OH is shown in Figure 9.2. The direct absorption OH radical signals are optimized for 0.1% of H₂O in “first run Ne” (70%Ne/30%He), at a total pressure of 450 Torr. Peak absorbances are >2%, with a signal to noise ratio better than 200:1. The Λ -type doubling, i.e., the lifting of the Π electronic degeneracy due to overall rotation of the molecule, is clearly resolved. Due to the low rotational temperatures in the slit jet, these are essentially the *only* two lower states appreciably populated in the $v = 1 \leftarrow 0$

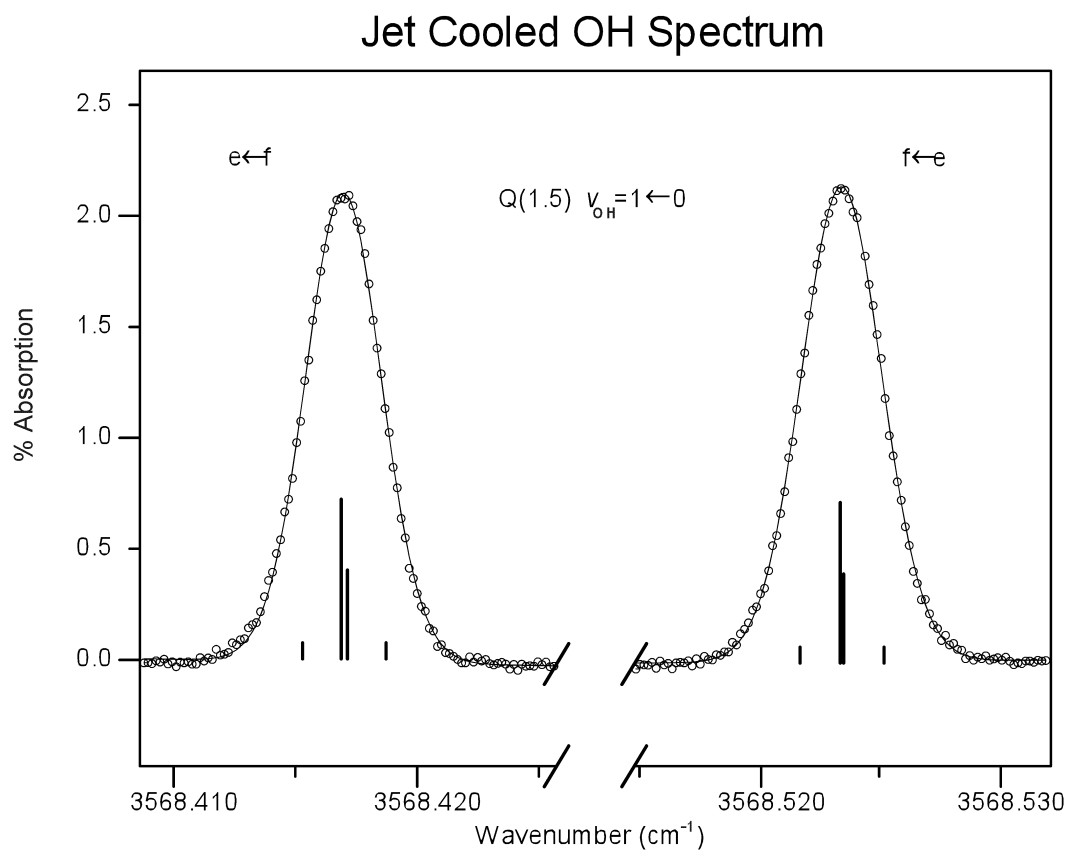


Figure 9.2 A sample scan over a single rovibrational transition of OH radicals, demonstrating the high S/N attainable in the slit discharge via direct IR laser absorption methods. The high resolution line shapes reflect a combination of Λ -type doubling and broadening due to residual Doppler (0.003 cm^{-1}) as well as OH hyperfine structure (0.0003 cm^{-1}).

spectrum. Due to supersonic cooling under these discharge conditions, transitions out of the upper spin orbit state ($E_{\text{spin orbit}} = 126.3 \text{ cm}^{-1}$) could not be detected and the Q(2.5) transition out of the next higher ($J = 2.5$) Λ -doubled rotational level ($\Delta E = 83.7 \text{ cm}^{-1}$) is >50-fold weaker in intensity. Based on the experimentally known OH line strengths¹⁹, this corresponds to an upper limit on rotational/spin orbit temperature of <34 K.

The widths of the two Λ -doublet features ($\Delta v_{\text{FWHM}} = 117 \text{ MHz}$) are 2-3 fold narrower than anticipated for OH Doppler widths at room temperature ($\Delta v_{\text{Doppler}} = 320 \text{ MHz}$). This is because the expansion geometry narrows the transverse velocity distribution along the slit axis to values consistent with Doppler profiles at the supersonic rotational temperature. Interestingly, however, the experimentally observed OH linewidths are still significantly (10%) broader than anticipated for the 34 K upper limit on rotational temperature, which can be easily verified by comparison with Doppler profiles for stable closed shell species in the jet. As indicated by the stick spectrum in Figure 9.2, this additional broadening is real and arises from underlying magnetic hyperfine structure, due to the interaction of nuclear spin ($I_{\text{H}} = 1/2$) on the H atom with unquenched spin and/or electronic orbital angular momenta of the OH radical. These hyperfine energy level splittings are known from previous studies,²⁰ with the relative intensities of each hyperfine component calculated from Clebsch Gordon algebra. Thus, the Doppler width for each component (constrained to all be the same) can be obtained by least squares analysis of the high resolution line profiles. The results indicate $\Delta v_{\text{Doppler}} = 106(5) \text{ MHz}$; this corresponds to a 33(3) K translational

temperature, which is consistent with the rotational temperatures determined above. Though the OH hyperfine structure is too closely spaced to resolve completely, the ~70-100 MHz Doppler widths typically observed in the slit jet discharge are sufficient to resolve fine and hyperfine structure in other open shell species. For example, we have recently succeeded in obtaining rovibrational spectra of CH₃ radical in the ν_3 asymmetric CH stretching band ($\Delta v_{\text{Doppler}} = 75$ MHz), which reveal rich spin-rotation structure and partial resolution of Fermi contact hyperfine structure. To our knowledge, this represents the first resolution of hyperfine structure for CH₃ radical in the gas phase, and provides a direct measure of electron spin polarization across a CH bond. A complete discussion of this spectroscopic analysis will be presented elsewhere.²¹

One advantage of high resolution direct absorption methods is that *absolute* absorbances can be simply related to *absolute* molecular concentrations via Beer's law. Based on a integrated absorbance of $3.0 \times 10^{-4} \text{ cm}^{-1}$ (shown in Figure 9.2), the total number density of OH radicals in the slit discharge can be inferred from i) the integrated cross section¹⁹ for the Q(1.5) OH($v = 1 \leftarrow 0$) transition ($9.5(12) \times 10^{-19} \text{ cm/molecule}$) and ii) an 80 cm path length to be $3.9 \times 10^{12} \text{ OH radicals/cm}^3$ at a distance 1 cm downstream of the slit. For a 300 μm slit width and a $1/r$ drop off in density, this translates into an OH number density at the discharge orifice of approximately $1 \times 10^{14} \text{ radicals/cm}^3$. From other spectroscopic studies in our lab, the slit discharge source generates peak concentrations of other jet cooled species such as CH₃ radical at nearly comparable levels.

9.3.2 Jet cooled molecular ions in the slit discharge

In addition to open shell jet cooled radicals, the pulsed slit jet discharge source also generates jet cooled molecular ions, produced in surprisingly high concentrations in the discharge prior to the expansion region. Indeed, there is sufficient molecular ion density to see intense direct absorption signals on the $v_3 = 1 \leftarrow 0$ bands of H_3O^+ and H_3^+ , as well as partially deuterated isotopomers of these species. By way of example, typical data over an isolated rovibrational transition ($J, K = 1, 1 \leftarrow 1, 0$) in H_3O^+ is shown in Figure 9.3, demonstrating the high S/N ratios for molecular ions that can be obtained via direct absorption methods in the pulsed slit expansion. Peak molecular ion absorptions on the order of 2% (S/N approx. 200:1) are relatively routine, which is entirely adequate for spectroscopic searches. For example, we have recently scanned over the 3500-3600 cm^{-1} (OH stretch) region in Ne/ $\text{H}_2/\text{D}_2\text{O}$ mixtures, and obtained jet cooled spectra of partially deuterated hydronium ion, H_2DO^+ and HD_2O^+ . A detailed analysis of these mono- and dideutero-ion species is currently in progress.²²

It would be useful to characterize the rotational temperatures for these molecular ions. For this we turn to protonated nitrogen, N_2H^+ , which has a rotational constant (1.553971(20) cm^{-1}) low enough to act as a reliable “thermometer” in the discharge and has been well studied via velocity

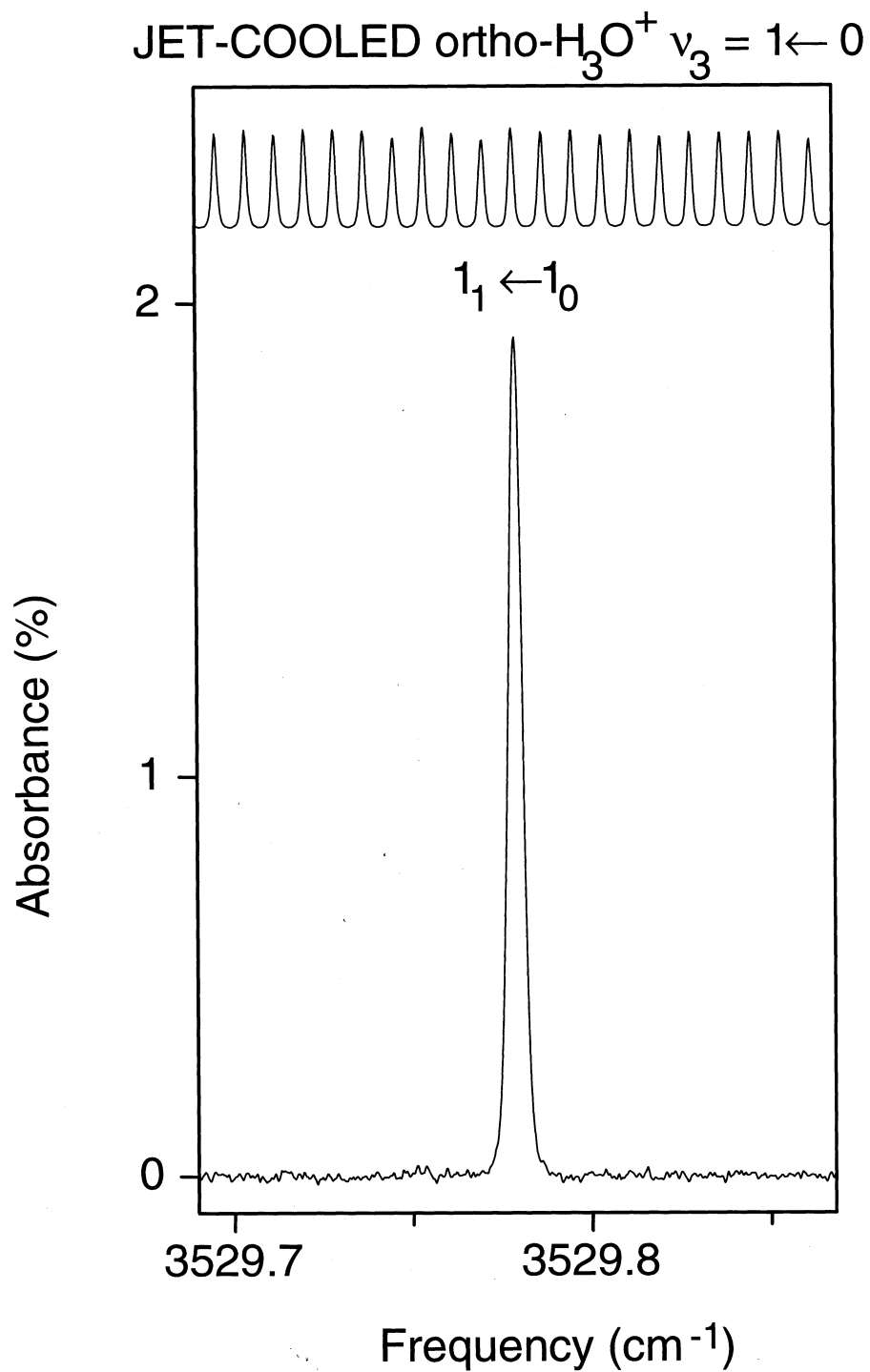


Figure 9.3 Sample data scan over the $(J,K) = (1,1) \leftarrow (1,0)$ ν_3 transition in H_3O^+ , demonstrating the 1-2% absorption strengths on individual rovibrational transitions of molecular ions

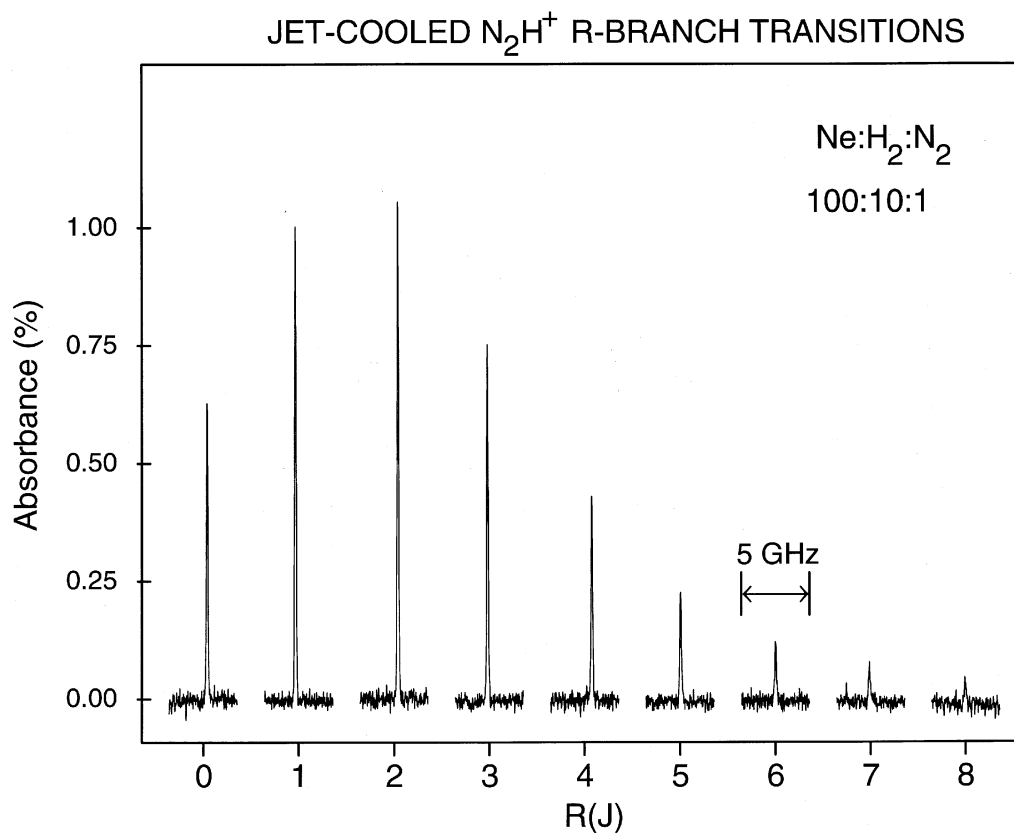


Figure 9.4 Scans over a series of R-branch transitions in N_2H^+ ($\nu_1 = 1 \leftarrow 0$), demonstrating the limited number of rotational levels populated in the slit discharge expansion.

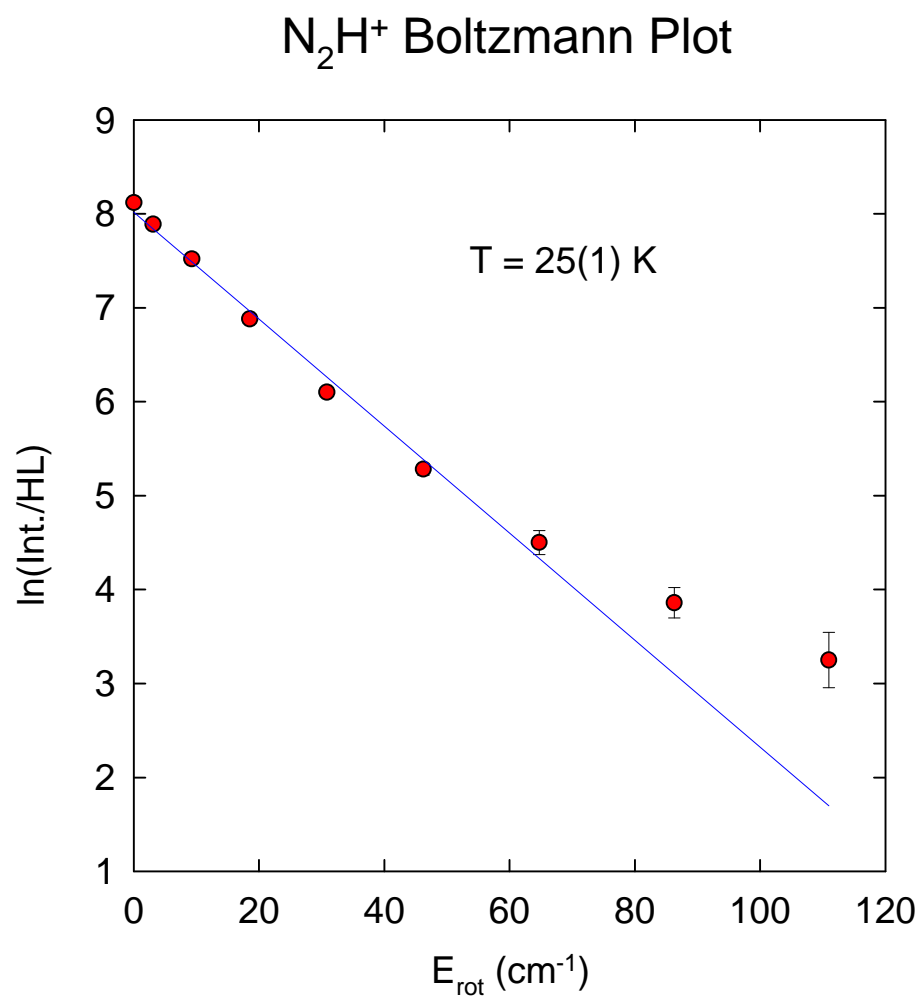


Figure 9.5 Boltzmann plot for the N_2H^+ ($v_1=1\leftarrow 0$) spectra in Figure 9.4, indicating the 25(1) K rotational temperatures typical of the slit discharge expansion environment.

modulation spectroscopy.²³ Direct absorption signals on these species are indicated in Figure 9.4, which shows a progression of rovibrational transitions out of $J'' = 0, 1, 2, \dots, 7$. Peak absorbances in this figure are of order 1%, which is roughly a factor of 2 lower than can be typically obtained. The direct absorption data are integrated and plotted versus lower rotational energy as in a standard Boltzmann analysis in Figure 9.5. The Boltzmann plot is quite linear and well characterized by a rotational temperature of 25(1)K. There also are deviations for $J > 6$, indicative of slightly non-Boltzmann behavior for the more widely spaced rotational levels.

As demonstrated in Section 9.3.1, the absolute number densities of molecular ions in the slit discharge viewing region can be inferred from Beer's Law. Specifically, the integrated absorbance of the N_2H^+ band in the slit discharge can be readily estimated from Figure 9.5 to be $3.0 \times 10^{-4} \text{ cm}^{-1}$. The integrated band strength for the ν_1 NH stretch in N_2H^+ has been measured by Keim *et al.* with fast ion beam methods to be $7.6 \times 10^{-17} \text{ cm/ion}$.²⁴ For an 80 cm path length, this translates into a mean density of N_2H^+ of $4.9 \times 10^{10} \text{ ions/cm}^3$ in the IR laser region. Based on a $1/r$ drop off in concentration with distance downstream, this implies ion densities on the order of $1.5 \times 10^{12} \text{ ions/cm}^3$ at the slit orifice. This is comparable to estimates of ion densities used for velocity modulation experiments with conventional discharge positive column and hollow cathode geometries, but with the additional advantage of a 10-fold reduction both in rotational temperature and Doppler broadening.

9.4 Summary

An intense slit jet discharge source for generating radical and molecular ion densities at the 10^{10} - 10^{12} molecules/cm³ level is described, with sufficient path length and rotational cooling for high resolution, direct absorption spectroscopy under supersonic cooled conditions of $T_{\text{rot}} < 30$ K. We have exploited this source in a number of spectroscopy studies of molecular ions and radicals, as will be described in the subsequent chapters..

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