Color Center Laser Spectroscopy of Primary Ions in a Slit Jet Discharge

C. Michael Lindsay

Oka Ion Factory[TM]

October 20, 1997

9:30am, Kent Hall, Room 114

Candidacy Committee: Levy, Scherer, Sibener

Critical Review: Resonant x-ray scattering beyond the Born-Oppenheimer approximation: Symmetry breaking in the oxygen resonant x-ray emission spectrum of carbon dioxide. *J. Chem. Phys.*, <u>106</u>, 3439 (1997).

1   Introduction

The primary ions X^+, produced by simple ionization of a stable molecule X, are some of the simplest molecular systems yet to be spectroscopically studied in the infrared region under high resolution. In addition, they have important implications in interstellar chemistry and in theoretical quantum mechanics. These radical cations have for the most part gone uninvestigated due to their high reactivity and therefore the difficulty in generating sufficient concentrations using conventional steady state plasmas.

In this prospectus, I propose the first high-resolution spectroscopic investigations of several primary ions via infrared absorption spectroscopy of ions in supersonic jets.

2   A Brief Discussion of Ion Spectroscopy

In order to discuss the apparatus and species of interest, it is important to define the primary ions, discuss the problems associated with their generation in the laboratory and present their interstellar importance.

2.1   Ions

Starting with an ordinary neutral molecule, ions can be generated by adding or removing an electron or proton. These processes, along with dissociation and associations, lead to families of ions (see Fig.1).[1] Nearly all of the species in this figure have been spectroscopically studied. A series of species that are particularly difficult to generate in large concentration are the radical cations. In a plasma discharge, the initial reaction that occurs is the removal of an electron from a neutral in an electron bombardment or Penning ionization. Those ions that are created in this process are frequently referred as *primary ions*. These ions then undergo subsequent reactions with other neutrals to produce different species.
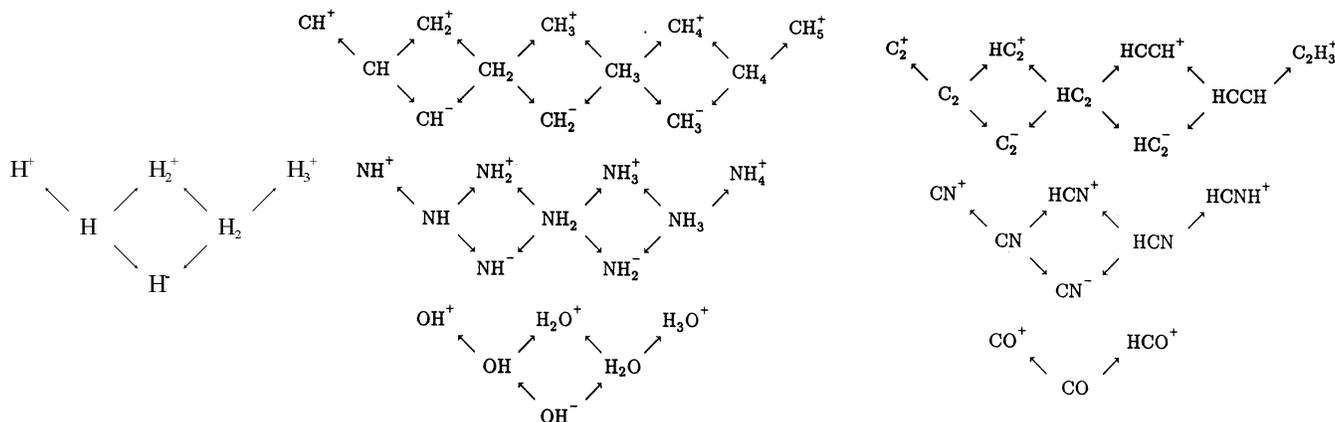

Fig. 1. 'Families' of ions and radicals based on H_2, CH_4, NH_3, H_2O, HCCH, HCN and CO molecules.

2.2   Laboratory Work

Investigations into the spectroscopy of polyatomic ions have traditionally focused on the protonated ions (i.e. $C_2H_3^+$, NH_4^+, CH_5^+, etc…)[2] because protonation of neutrals is exothermic via collision

with H_3^+. The anions of these families have also been studied extensively. Except for a few isolated cases [3-6] the infrared spectra of polyatomic primary ions are unknown.

Spectroscopically investigated ions are generally produced in plasmas, where electron bombardment and Penning ionization create the first ions. Since they are open shell systems, the primary ions are very reactive. With the many surrounding neutrals, these ions undergo further reactions with Langevin cross sections. Once a steady state is reached, the plasma composition can no longer be characterized by the initial EB or PI reactions but by a complex network of chemistry.

Under steady state conditions, there are many species present. The experimentalist's role, then, is to vary the plasma conditions such as the relative concentrations of the initial gases, total pressure, discharge current, and temperature, to optimize the formation of the species of interest. As it turns out, this results in a method suitable to probe many protonated and fragmented species. Several primary ions were also successfully observed in this fashion due to alternate reactions that reproduce the original ion. In general, however, this method fails for most primary ions and an alternative method must be developed.

2.3   Interstellar Observation

Previously thought to be composed only of atoms and dust particles, diffuse and dense interstellar clouds are now known to be mainly composed of molecules. The study of these molecules existence has combined the efforts of chemists, spectroscopists and astronomers. It is now widely believed that the majority of molecular species are synthesized via gas phase, ion-neutral reactions similar to those in laboratory plasmas, though at much at lower temperatures and densities.

Dense interstellar clouds are nearly perfect vacuums by laboratory standards. These clouds contain gases at densities of 10^4-10^6 cm^{-3}, mostly H_2 and He. Since the interiors of these clouds are shielded from the destructive ultraviolet radiation, the ionization is effected by the ubiquitous cosmic rays. Many complicated large molecules result from the subsequent ion-neutral reactions, the largest observed being $HC_{11}N$.[7] Diffuse clouds, on the other hand, contain much lower densities ($\sim 10^2$ cm^{-3}) and are composed primarily of H and H_2, although detection of other diatomics containing N and C have been identified.

While the main scenario of the ion chemistry within interstellar clouds is reasonably established, there remain many questions. Although the majority of emission and absorption spectra of dense clouds have been assigned, many of the absorption bands in diffuse clouds defy identification. These unidentified bands are known as the diffuse interstellar bands. In diffuse clouds, molecules are no longer protected from interstellar ultraviolet radiation and are ionized and dissociated.[8] One theory of the diffuse interstellar bands suggests that the carriers are ionized forms of large molecules originally produced in dense clouds.[8-10] In order to identify these bands, it would be useful to have spectra of the primary ions generated from neutrals known to exist within the dense clouds including, CH_4, HCN, HC_nN (n=3-11).

3   Proposed Studies

The species that I propose to study are only a few of the many primary ions yet to be observed. The following discussion looks into the importance of each and the interesting features that I expect to encounter.

3.1 HD^+

HD^+ has been extensively studied spectroscopically since 1976[11] and most recently by Carrington in 1993.[12] As a single electron system, very accurate rotation-vibration non-adiabatic energy levels have been calculated up to $v = 9$.[13] Because this ion is so well understood, it will be useful as a test species to study the efficiency and sensitivity of the newly designed ion slit jet/color center laser system.

The fundamental vibration band center is located at 1912.14 cm^{-1} and is far outside of the color center tuning range. We will therefore be observing the overtones of HD^+. Hunter *et al.* [13] has calculated the band origins to be at 3728.37cm^{-1}, 3538.80 cm^{-1} and 3354.55 cm^{-1} for the $2v\leftarrow0$, $3v\leftarrow1$ and $4v\leftarrow2$ first overtone transitions, respectively. Higher overtones are predicted in this region but are unlikely to be observed due to the relatively low vibrational temperature of the molecules in the free expansion.

3.2 CH_4^+

Being one of the simplest cases where a Jahn-Teller distorted structure is predicted, CH_4^+ is a fundamentally important species. Considered by theorists to be a simple model, it has been studied under numerous theoretical treatments (see Frey *et al.* for a list [14]). Astronomically, CH_4^+ is important in dense cloud chemistry and has been proposed by Herzberg as the carrier of the diffuse interstellar bands in his Nobel Prize lecture![10]

Previous experimental work has been limited, due to the difficulty in producing this radical cation. Experiments have remained limited to low resolution work, beginning with photoelectron spectroscopy 1960's.[15,16] To provide insight into the structure, Coulomb-explosion experiments were performed at Argonne National Labs in the first half of the 1980's.[17,18] Most recently, (early 1990's) electron spin resonance of CH_4^+ and its various isotopes was performed in solid neon matrices at 2.5-11K.[19,20] Still, direct high-resolution spectroscopy has never been performed in any spectral region.

There are several Jahn-Teller distorted structures for the T_d group that are possible: C_{2v}, D_{2d}, C_{3v}, and C_s. The most recent theoretical calculations predict the following vibrations within the color center laser tuning range (Table 1).[14] High-resolution infrared absorption studies will provide insight into the structure and behavior of this interesting system.

C_{2v}	D_{2d}	C_{3v}	C_s
A_1 = 2890 cm^{-1}	E = 2870 cm^{-1}	E = 2900 cm^{-1}	A' = 2880 cm^{-1}
= 3230 cm^{-1}	A_1 = 2980 cm^{-1}	A_1 = 2730 cm^{-1}	A'' = 2890 cm^{-1}
B_2 = 3010 cm^{-1}		= 3120 cm^{-1}	= 3030 cm^{-1}

3.3   **HCN^+ and Beyond ($HC_{2n+1}N^+$)**

       HCN^+ is also fundamentally interesting. The ground and first excited electronic transitions are only separated by ~3200 cm^{-1} which is approximately the energy of the fundamental ν_1 stretch, resulting in a breakdown of the Born-Oppenheimer approximation. When considering this plus the strong Renner-Teller coupling between ν_2 bending vibration and electronic energy, we expect the spectrum to yield complicated patterns.

       The majority of experiments studying this species have been photoelectron spectroscopy.[21-23] Despite the recent resolution improvements in photoelectron experiments, the technique still cannot satisfactorily resolve rotational transitions for most primary ions. The infrared absorption spectrum has also been observed, but in a cold (~5K) neon matrix where rotations are completely halted.[24] The results from this experiment do not agree with those of PES, even when taking matrix shifts into consideration. We expect to see many transitions in our region of the infrared including both the ν_1 symmetric stretch and the electronic excitation from the $X^2\Sigma^+$ to the $A^2\Pi$ state.

       Although the nature of HCN^+ in the interstellar medium is reasonably understood, its related family of cyanopolyacetylene primary ions is not. As mentioned above, the parent neutral molecules have long been known to exist in dense clouds. As suggested by Watson,[8] these compounds may provide insight into diffuse cloud chemistry and perhaps the carriers of the diffuse interstellar bands. Studying the chemistry of HCN in the plasma expansion discharge will help us understand the conditions that promote the formation of these cyanopolyacetylenes, which can then be used in the future to study these large, linear molecules.

4   Experimental Setup

       One reason that the primary ions have been studied very little is because they are transient and do not exist in measurable spectroscopic concentrations under steady state conditions. These molecules are highly reactive intermediates and are the stepping stones to other stable, well-studied ions. It is, therefore, first necessary to design an apparatus that will generate appropriate conditions that increase the lifetime of these species long enough to be spectroscopically studied. In addition, we need an infrared source that will supply tunable high power radiation sufficient to study the species of interest. What follows is a description of the setup that I am currently developing that will accomplish these goals.

4.1   **Ion Slit Jet Expansion Apparatus**

       Expanding gases in slit jets is a common tool that spectroscopists use to study molecules and clusters at sub-Doppler resolutions. When combined with an electric discharge, a supersonic jet becomes a powerful tool to used create and control molecular ions in ways that are not possible in traditional plasma discharges.

4.1.1   What Is It? Why Does It Work?

A free-jet expansion is formed when a gas under high pressure is allowed to escape out through a small aperture into a region of low pressure. Cooling occurs when the random motion of the molecules is converted to the directed mass flow. To illustrate this, we begin with the total energy of the system, which must be conserved during this process. Total energy is then the sum of the internal energy, U (U = U_{trans} + U_{vib} + U_{rot}), the potential energy pV and the kinetic energy $\frac{1}{2}Mu^2$. We have then:

$$U_o + p_oV_o + 1/2Mu_o^2 = U + pV + \frac{1}{2} Mu^2$$

Assuming thermal equilibrium in the high-pressure chamber (which is reasonable assuming that the mass flow through the aperture is small), motion follows a Maxwellian distribution, and therefore u_o = 0. In order to create this expansion, we experimentally make $p_o \gg p$, and therefore we can approximate p = 0. The resulting energy relationship becomes:

$$U_o + p_oV_o = U + \frac{1}{2} Mu^2$$

This equation demonstrates that if most of the initial energy is converted directly to the mass flow kinetic energy, the internal energy (U) must decrease. In the supersonic jet, this is exactly what occurs (Fig 2).[25] Initially, there is large relative motion within the gas with zero mass flow. However, after the aperture, the mass flow is increased to supersonic velocities and the relative motion between molecules is very small, thus "cooling" the system's internal energy. This condition produces a number of characteristics that are favorable to spectroscopic analysis.
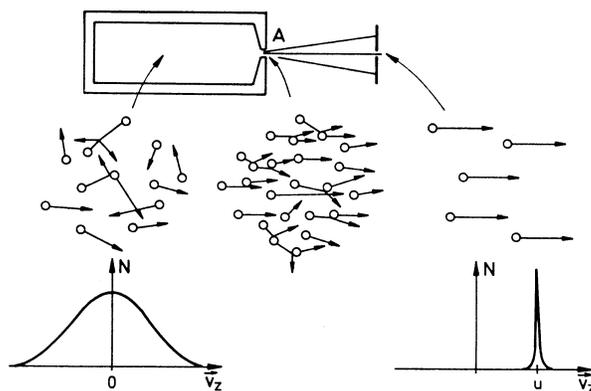

Fig. 2. Molecular model of adiabatic cooling by collisions during the expansion from a reservoir with a Maxwellian velocity distribution into the directed molecular flow with a narrow distribution around the flow velocity *u*.

The primary benefit that a free expansion provides is the decreased Doppler width. Doppler broadening is nearly eliminated when the laser probes the expanding gas perpendicular to the mass flow vector. We define z as the direction of flow and x as the direction of the slit. Because nearly all motion is in the v_z direction, there is very little motion in the v_x and v_y. The resulting spectra provide narrow

transition peaks by eliminating much of the broadening and blurring associated with normal, warm gas spectra.

Another benefit of a free jet is the effective cooling of the internal motions. Only translational motion is cooled directly by the expansion. However, translational-rotational energy transfer occurs very quickly: on the order of $\sim 10^{-9}$ sec. Translational-vibrational energy transfer occurs $\sim 10^{-5} sec^{26}$. As a result of the internal motion being coupled, one would expect a dramatic rotational followed by a less efficient vibrational cooling. This is demonstrated, and typical experimental values are $T_{trans} \sim 0.001 - 1K$, $T_{rot} \sim 1-50$ K and $T_{vib} = \sim 10-300$ K. Not only does this simplify a complicated spectrum by reducing the number of populated energy levels, but it also concentrates the population of lower energy levels so that normally weak signals can be observed.

Finally, using the free expansion provides us with a (nearly) collisionless environment. This will be useful to generate the primary ions because the ions do not have as likely a chance to collide into another molecule with sufficient energy to cause reaction. The most convincing evidence of this was observed in Amano's lab[27] in a hollow cathode discharge. In a typical discharge, the ratio of H_2^+ to H_3^+ is $\sim 10^{-2}$-10^{-3} and in the interstellar medium, 10^{-3}-10^{-4}.[28] The relationship between these species is governed by the following reaction:

$$H_2 + H_2^+ \rightarrow H + H_3^+ \qquad \text{(exothermic by } \sim 1.7 \text{ eV)}$$

H_2^+ is initially formed by electron bombardment, and quickly reacts to H_3^+ as explained above with a Langevin cross section.[29] In Amano's discharge, the concentration of H_2^+ was 10 times *greater* than that of H_3^+, overcoming the enormous tendency to generate H_3^+. The above reaction is a benchmark of nearly all ions studied spectroscopically to date, and these results provide compelling evidence that the primary ions can be created in this fashion.

4.1.2   Free Expansion Chamber

The pumping requirements that are necessary to achieve adequate pressure differences with reasonable mass throughput are quite demanding. Traditionally, many spectroscopists revert to a pulsed source, where the gas is added into the vacuum chamber in short bursts. Pulsing the output allows a smaller (cheaper) pump to be used due to the decreased mass flow. This has the drawback of having the total signal modulated. By the recommendation of Levy and Sibener,[30] we decided to use the "brute force" approach and have purchased an Edwards vapor booster pump backed by a mechanical rotary pump. Having a large pump allows us to continuously flow gas through the slit and frees us to modulate the electric discharge. The result is a signal where the ion transitions are modulated and the neutral species are generally not. Sending this signal to a lock-in amplifier allows us to observe the ion absorption and remove the noise and neutral absorption.

A stainless steel chamber will be set atop the pump and has three "arms". Brewster windows will be mounted to the two oppositely facing flanges (See Fig.5) where I will multi-pass the gas expansion parallel the slit.

4.1.3   Ion Sources

Many different ion sources have been designed and used throughout the years.[27,31-35] I will be constructing two different sources, each of which will provide different environments for ion formation (Fig.3).

The first source will be based on Nesbitt's setup.[32] This source is composed of a simple slit with a discharge occurring from two steel cathode jaws that also act as the narrowest aperture. There are two reasons for this sort of system. First, The electrons flow against the motion of the gas, therefore dramatically increasing electron-neutral collisions. Secondly, the discharge occurs before the aperture, where are many collisions. This, therefore, provides an environment where controllable number of ion-neutral reactions can occur, a condition necessary for Penning ionization.

The other source will be based on a hollow cathode type arrangement.[27] Here, the discharge occurs during the expansion of the gas, and provides a nearly collisionless environment for the ions. This is useful as discussed above in section 5.1.1.
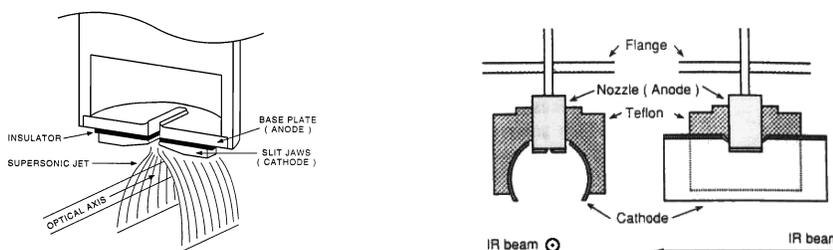

Fig. 3. Slit jet discharge sources. (left) Nesbitt-type discharge where the cathode is a set of stainless steel jaws, discharging electrons upstream through the slit. (right) Example of a 'hollow-cathode' type discharge. The discharge occurs after the slit where the cathode is an arc discharging to the base of the slit.

4.2   Development of a High Resolution Infrared Spectrometer

In order to study the primary ions' rotation-vibration states, we need a high-resolution tunable infrared source. For this, we have chosen to use our color center laser due to its broad tuning range (~2940 cm^{-1}-4350 cm^{-1}) and high power output power (~20mW). Although other laser sources do cover this region, (difference frequency systems, for example) none can match its power output. The commercially available color center lasers, however, have inherent problems with respect to their tuning processes, and in order to be suitable for long-range studies, a new setup is required. A discussion follows, explaining how I plan to overcome these hindrances by computer controlling the color center laser resulting in a convenient and efficient high-resolution spectrometer.
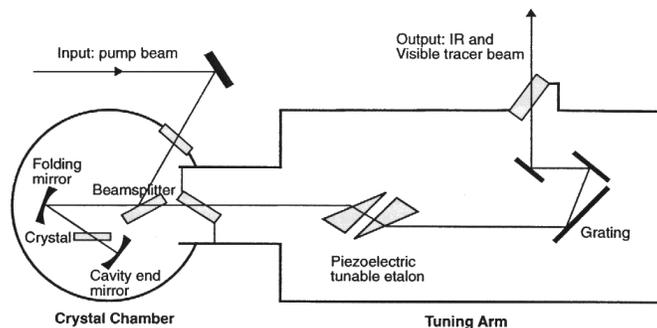
Fig. 4. Burleigh FCL-20 Color Center Laser. Single frequency selection is performed by simultaneously tuning the cavity folding mirror, the piezoelectric tunable etalon and the Littrow mounted grating.

4.2.1   Color Center Lasers

Color or 'F' centers are electrons trapped in some sort of insulating crystal, usually an alkali halide. Due to various nearest neighbor combinations (holes, doped atoms, and multiple F-centers) a wide variety of lasing tuning bands are available, ranging from 0.8 - 4 μm, spanning ultraviolet, visible and most near-infrared radiation.[36] By the end of the 1970's, color center lasers became commercially available primarily due to the demand for a simple, yet powerful infrared source. The result was the popular Burleigh FCL.

Figure 4 shows the schematic of our Burleigh FCL-20. Frequency scanning is obtained by simultaneously coordinating the three tuning elements within the laser cavity: the cavity length, intracavity etalon and Littrow mounted diffraction grating. The end cavity mirror and one of the etalon's prisms are mounted to piezoelectric transducers (PZT). Turning the screw bar externally changes the grating orientation. The standard arrangement calls for the grating to be hand turned and the etalon and cavity mirror to be ramped via a ramp generator/amplifier. In order to achieve continuous single-mode output, the etalon must precisely track the cavity mode. This is accomplished operating the cavity and etalon controllers in a feed-forward master-slave arrangement and is the method in which our laser has been scanned in the past.

If we lived in an ideal world, the setup would work. However, due to non-idealities in the PZT's, voltage drifting within the PZT controllers and the inability to rotate the grating element effectively, problems arise when one scans in this fashion. Common consequences include "mode hopping" (the switching from one cavity mode to its neighbors, resulting in ~300MHz of spectrum being rescanned or skipped) and multi-mode operation (output of more than one frequency of light). In order to overcome these problems, one must scan slowly paying careful attention to these problems and constantly adjust the controls, manually. When also considering that a continuous scan is limited by a single etalon ramp (~1 cm^{-1}) and must be realigned and adjusted between scans, scanning long ranges becomes very tedious and time consuming.

4.2.2 Continuous Scanning and Control

Users of the Burleigh FCL's have dealt with these problems as well as those whom have built similar systems. For some groups, this inconvenience became a matter of life, and others were not inconvenienced (our group previously) because they required only a few short-range scans. In 1982, Curl and coworkers developed an elaborate setup which computer controlled the entire scanning process, and piecewise continuously scanned the entire range of the FCL.[37] The original procedure was slow and quite involved but was simplified and improved over the years.[35,38-42]

By looking at the setup, you may notice several independent components that cause this setup to operate (Fig. 5, green dashed box). The first and most important section of this setup is the locked scanning of the etalon and cavity modes. One of the primary problems of this setup is that the etalon fails to properly track the cavity mode. The solution to this problem can be solved by adding a ~5Hz, 2V dither to the etalon PZT via a Lock-In Stabilizer.[38] A detector signal is sent back into the stabilizer's lock-in amplifier and an error signal is sent to the folding mirror's ramp generator. This closed loop "locks" the two modes together. The Lock-In Stabilizer is programmed to ramp the cavity PZT back to the next cavity automatically. Therefore, the computer controls the etalon and grating motion for continuous, piecewise scanning.
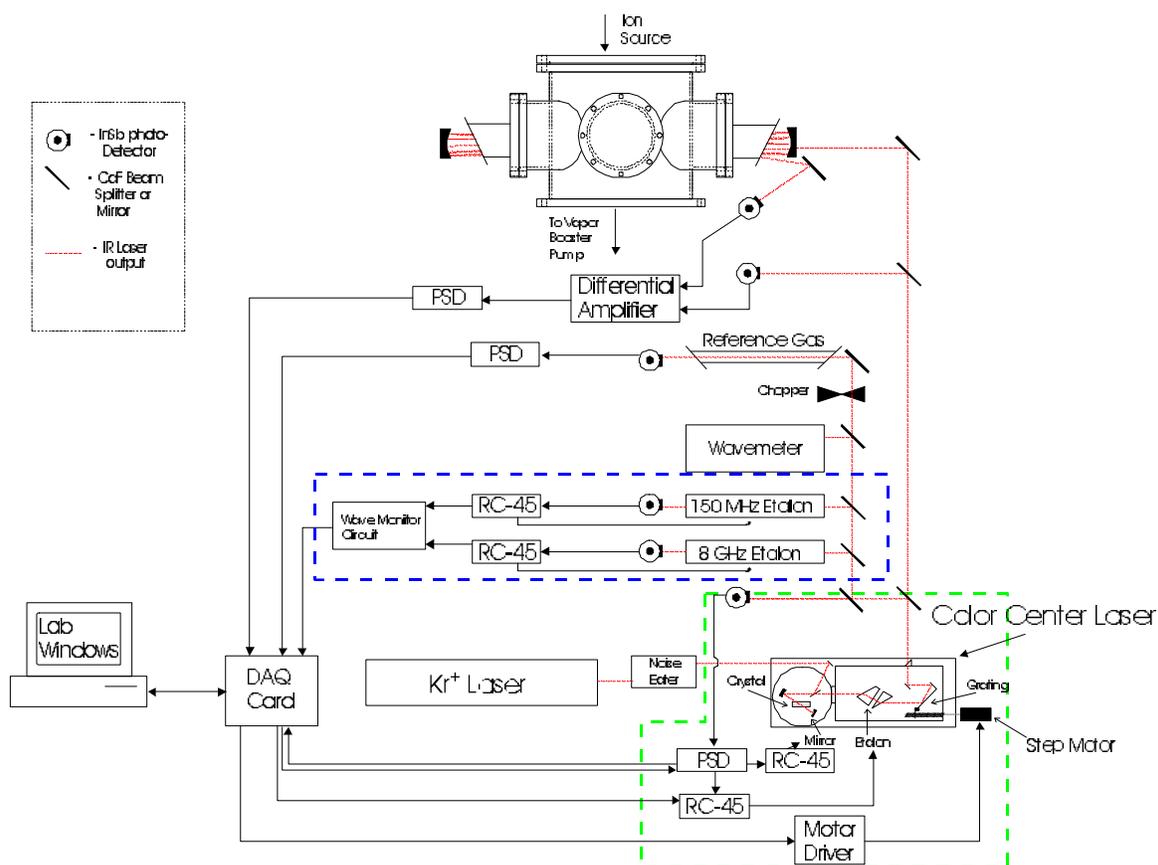
Fig. 5. Schematic of the proposed laser and slit jet absorption setup.

4.2.3   Linearization

Although the above scanning procedure decreases the likelihood of mode hoping and the problems previously discussed, there will always be uncontrollable gaps in our scanning procedure due to laser fluctuations, temperature drifts, etc.   In order to assess and account for these nonlinear behaviors, I will use what some groups call a wave monitor circuit (see Fig. 5, blue dashed box). I have two external etalons (150MHz and 8GHz) that are ramped, and at some point in their ramp, the laser is allowed to go through the etalon cavity. The wave monitor circuit outputs the ramp voltage for which the detector detects a signal. As the laser is tuned, the ramp voltage for which light transmits through the etalon changes, and so does the output signal. As a result, we have a voltage that is proportional to frequency. Because we do not know which etalon mode the laser is propagating through, we need two etalons: one for course diagnostics, and another, temperature stabilized etalon outputs the precise signal and has a resolving power on the order of several hundred kHz.

This circuit is extremely useful in that it very precisely depicts the scanning behavior of the laser at every data point. Most setups must assume some sort of linearity, whether it is between two reference lines, or two etalon fringes. With the wave monitor, we can "see" when the laser hops a mode, or varies in any way other than expected. This data in turn is calibrated to several gas reference lines and is used as the frequency measurement.

Due to the computer control, sensitive diagnostics, and powerful qualities of the color center crystal themselves, this laser setup will provide reliable, high-resolution infrared monochromatic radiation. Through the last 15 years of improvements in techniques, scanning times have accelerated tremendously. Due to the improvements and simplifications to the original setups from the early eighties, one group with a similar setup claims scanning speeds of 10 cm^{-1}/hr.[39] When compared with scanning rates of the Oka group's previous apparatus of ~1 cm^{-1}/hr, (on a good day) the scanning rate will be 10 fold improvement and will tremendously increase the ability to study the vibrational spectra of ions more quickly, more accurately, and more efficiently than in the past.

5   Conclusion

The spectroscopy of these fundamental ion systems have failed to be explored, primarily because the traditional approach to performing ion spectroscopy in steady state plasmas promotes multiple reactions that favor the generation of secondary species and the elimination of the primary ions. A slit-jet expansion coupled with an electric discharge promises to overcome this problem and open a window to probe previously unseen systems. Due to the theoretical nature of these models and the potential insight into the chemistry of interstellar diffuse clouds, the spectroscopy of the primary ions poses to be an exciting and challenging endeavor.

References

1 T. Oka, in *Frontiers of Laser Spectroscopy of Gases*, Vol. 234, edited by A. C. P. Alves, J. M. Brown, and J. M. Hollas (Kluwer Academic Publishers, Dordrecht, 1988), pp. 353-377.

2 E. Hirota, *Chem. Rev.* 92, 141-173 (1992).

3 M. G. Bawendi, B. D. Rehfuss, B. M. Dinelli, M. Okumura, and T. Oka, *J. Chem. Phys.* 90, 5910-5917 (1989).

4 J. M. Frye and T. J. Sears, *Mol. Phys.* 62, 919-37 (1987).

5 T. R. Huet, Y. Kabbadj, C. M. Gabrys, and T. Oka, *J. Mol. Spectrosc.* 163, 206-13 (1994).

6 M. F. Jagod, M. Rosslein, C. M. Gabrys, B. D. Rehfuss, F. Scappini, M. W. Crofton, and T. Oka, *J. Chem. Phys* 97, 7111-23 (1992).

7 D. Smith, *Chem. Rev.* 92, 1473-1485 (1992).

8 J. K. G. Watson, *Astrophys. J.* (in press).

9 G. H. Herbig, *Annu. Rev. Astrophys.* 33, 19-73 (1995).

10 G. Herzberg, in *Nobel Lecture* (The Nobel Foundation, 1971).

11 W. H. Wing, G. A. Ruff, W. E. Lamb, Jr., and J. J. Spezeski, *Phys. Rev. Lett.* 36, 1488-91 (1976).

12 A. Carrington, C. A. Leach, A. J. Marr, R. E. Moss, C. H. Pyne, and T. C. Steimle, *J. Chem. Phys.* 98, 5290-301 (1993).

13 G. Hunter, A. W. Yau, and H. O. Pritchard, *At. Data & Nucl. Data Tables* 14, 11-20 (1974).

14 R. F. Frey and E. R. Davidson, *J. Chem. Phys.* 88, 1775-1785 (1988).

15 C. R. Brundle and M. B. Robin, *J. Chem. Phys.* 53, 2196-2213 (1970).

16 B. P. Pullen, T. A. Carlson, W. E. Moddeman, G. K. Schweitzer, W. E. Bull, and F. A. Grimm, *J. Chem. Phys.* 53, 768-82 (1970).

17 Z. Vager, E. P. Kanter, G. Both, P. J. Cooney, A. Faibis, W. Koenig, B. J. Zabransky, and D. Zajfman, *Phys. Rev. Lett.* 57, 2793-5 (1986).

18 D. S. Gemmell, E. P. Kanter, and W. J. Pietsch, *J. Chem. Phys.* 72, 1402-4 (1980).

19 L. B. Knight, Jr., G. M. King, J. T. Petty, M. Matsushita, T. Momose, and T. Shida, *J. Chem. Phys* 103, 3377-85 (1995).

20 M. Matsushita, T. Momose, T. Shida, and L. B. Knight, Jr., *J. Chem. Phys.* 103, 3367-76 (1995).

21 C. Fridh and L. Asbrink, *J. Electron. Spectrosc. & Relat. Phenom.* 7, 119-38 (1975).

22 D. C. Frost, S. T. Lee, and C. A. McDowell, *Chem. Phys. Lett.* 23, 472-5 (1973).

23 R. T. Wiedmann and M. G. White, *J. Chem. Phys.* 102, 5141-5151 (1995).

24 D. Forney, W. E. Thompson, and M. E. Jacox, *J. Chem. Phys.* 97, 1664-74 (1992).

25 W. Demtröder, *Laser Spectroscopy: Basic Concepts and Instrumentation*, 2nd ed. (Springer, Berlin, 1996).

26 W. H. Flygare, *Acc. Chem. Rev.* 1, 121-127 (1968).

27 M. Fukushima, M. C. Chan, Y. J. Xu, A. Talebbendiab, and T. Amano, *Chem. Phys. Lett.* 230, 561-566 (1994).

28 H. H. Lee, R. P. A. Bettens, and E. Herbst, *Astron. Astrophys. Suppl. Ser.* 119, 111-14 (1996).

29 T. Oka and M. F. Jagod, *J. Chem. Soc. Faraday Trans.* 89, 2147-2154 (1993).

30 D. Levy and S. Sibener, Private Communication.

31 G. Hilpert, H. Linnartz, M. Havenith, M. J. J. ter, and W. L. Meerts, *Chem. Phys. Lett.* 219, 5-6 (1994).

32 C. M. Lovejoy and D. J. Nesbitt, *J. Chem. Phys.* 86, 3151-3165 (1987).

33 Y. Xu, M. Fukushima, T. Amano, and A. R. W. McKellar, *Chem. Phys. Lett.* 242, 125 (1995).

34 K. R. Comer and S. C. Foster, *Chem. Phys. Lett.* 202, 216-20 (1993).

35   M. Ishiguro, T. Imajo, K. Harada, M. Matsubara, K. Tanaka, and T. Tanaka, *Chem. Phys. Lett.* 263, 629-634 (1996).

36   L. F. Mollenauer, in *Tunable laser*, Vol. 59, edited by L. F. Mollenauer and J. C. White (Springer-Verlag, Berlin, 1987), pp. 225-277.

37   J. V. V. Kasper, C. R. Pollock, R. F. Curl, Jr., and F. K. Tittel, *Appl. Opt.* 21, 236-47 (1982).

38   D. Reinert, H. Solka, W. Zimmermann, A. Stahn, and W. Urban, *J. Phys. E: Sci. Instrum.* 22, 30-38 (1989).

39   E. R. T. Kerstel, K. K. Lehmann, T. F. Mental, B. H. Pate, and G. Scoles, *J. Phys. Chem.* 95, 8282-8293 (1991).

40   H. Adams, R. Bruggemann, P. Dietrich, D. Kirsten, H. Solka, and W. Urban, *J. Opt. Soc. Am.* 2, 815-827 (1985).

41   Z. S. Huang, K. W. Jucks, and R. E. Miller, *J. Chem. Phys.* 85, 3338-3341 (1986).

42   B. H. Pate, K. K. Lehmann, and G. Scoles, *J. Chem. Phys* 95, 3891-3916 (1991).