

# Cavity-enhanced velocity modulation spectroscopy

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The spectroscopic study of molecular ions is of great importance to a variety of fields, but is challenging as ions are typically produced in plasmas containing many orders of magnitude more neutral molecules than ions. The successful technique of velocity modulation permits discrimination between ion and neutral absorption signals and has allowed the study of scores of molecular ions in the past quarter century. However, this technique has long been considered to be inappropriate for use with cavity-enhanced techniques, owing to the directional nature of the velocity modulation. Here we report what we believe to be the first demonstration of cavity-enhanced velocity modulation spectroscopy, utilizing a  $2f$  phase-sensitive demodulation scheme. This approach offers the promise of combining very high-sensitivity spectroscopic techniques with ion-neutral discrimination, which could extend the applicability of velocity modulation to intrinsically weak transitions and to ions that cannot be produced in high abundance. The use of a cavity also permits Lamb dip spectroscopy, which offers higher resolution and precision in frequency measurements and may be useful in measuring collisional rate coefficients. © 2010 Optical Society of America

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Molecular ions play important roles in many fields, ranging from chemistry to propulsion to astrophysics, but they pose significant challenges to the laboratory spectroscopist. Two of the greatest challenges are preparing ions in sufficient quantities in the gas phase and detecting absorption lines of ions in the presence of interfering transitions of neutral molecules, which are typically several orders of magnitude more abundant. The production of large quantities of ions has been most successfully addressed by exploiting the positive column of a glow discharge, as first demonstrated by Claude Woods' group in the microwave [1] and later by Oka in the IR [2]. But it was not until the development of the velocity modulation technique by Saykally's group [3] that absorptions owing to neutral molecules could be avoided, so that these discharges could be fully exploited for ion spectroscopy. In the past quarter century, nearly 50 molecular ions have been studied by using velocity modulation, as reviewed in [4].

Much of the recent development work on velocity modulation has focused on improving the signal-to-noise ratio (S/N), to permit the study of trace ions or intrinsically weak transitions. The combination of optical heterodyne modulation with velocity modulation [5,6] has pushed the noise level close to the shot-noise limit with moderately intense lasers. Further improvement in the S/N therefore will require an extension of the optical path length through the plasma. The typical state of the art in this respect is a modified White cell [5,6] that affords a total path length of  $\sim 8$  m. This path length could, in principle, be increased dramatically by enclosing the positive column in a high-finesse optical cavity, as has been employed for the NICE-OHMS technique [7]. However, traditional velocity modulation spectroscopy re-

lies on the difference in the ion drift velocity between the two half-cycles of an AC discharge, so the  $1f$  signal vanishes in a cavity (or any bidirectional multipass cell). In this work, we demonstrate that ion-neutral discrimination can be preserved in cavity-enhanced velocity modulation spectroscopy by using a  $2f$  demodulation scheme.

Our experimental setup is illustrated in Fig. 1. Molecular ions ( $N_2^+$ ) are produced in an uncooled positive column discharge cell in a continuous flow of nitrogen at a pressure of  $\sim 3.4$  Torr. The cell used is identical to that described in [8], with the exception that the

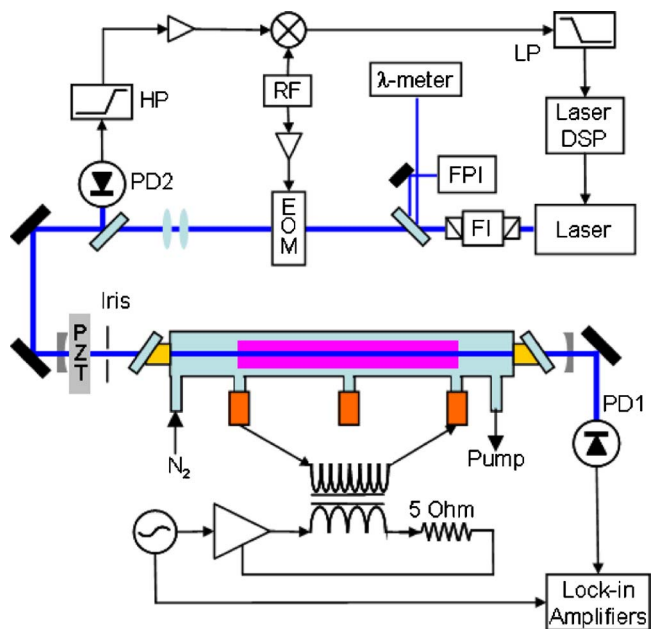


Fig. 1. (Color online) Experimental setup.

cavity ringdown mirrors in that reference have been replaced by BK7 Brewster windows to allow the insertion of an intracavity iris. The plasma is produced by an AC sine wave (3.8 kV<sub>pp</sub>, 40 kHz) delivered to two water-cooled electrodes spaced by ~40 cm, and generated by a step-up transformer, the primary loop of which is driven by an audio amplifier (AE Techron 5050) in series with a 5 Ω resistive load for plasma stabilization. The cell is placed inside an optical cavity that consists of two fused silica dielectric mirrors with 1 m radii of curvature and reflectivity 99.7%, separated by ~1.3 m. One of the mirrors is mounted to a cylindrical piezoelectric transducer (Piezomechanik), which controls the length of the cavity. The finesse of the cavity is reduced to ~100 by using the intracavity iris, to facilitate locking.

A ring Ti:sapphire laser (Sirah Matisse-TS) is locked to the cavity by using the Pound–Drever–Hall (PDH) method [9]. The backreflection from the cavity is sampled by using an ordinary beam splitter, and a Faraday isolator is placed at the output of the laser to prevent mode hops owing to optical feedback. Sidebands are generated by using an electro-optic modulator (at 8.1 MHz), and the output of the photodiode monitoring the backreflection is sent through a high-pass (1.6 kHz) filter, amplified (24 dB), and then mixed with the RF modulation frequency and low-pass filtered (1.9 MHz) to produce an error signal that can be fed into the laser’s control circuitry to keep the laser on resonance with the cavity. The laser is scanned by applying a DC voltage to the cavity piezo; a continuous tuning range of ~3.5 GHz has been routinely achieved. The laser frequency is measured by using both a Fabry–Perot interferometer (Toptica FPI-100) and a wavemeter (Bristol 621A-IR) with an accuracy of 70 MHz, and multiple contiguous ~3.5 GHz scans can then be stitched together.

The transmitted light from the cavity is sent through bandpass filters to reduce plasma emission and then focused onto a photodiode, which is placed ~2 m away from the plasma to further reduce the plasma emission. The output of this photodiode is sent to two lock-in amplifiers, both referenced to the plasma frequency, but with different sensitivities and different phases to optimize the discrimination between ion and neutral signals.

A representative spectrum is shown in Fig. 2. One lock-in amplifier is primarily sensitive to molecular ion signals, in this case a close blend of the  $Q_{11}(14)$  and  $Q_{12}(6)$  transitions of the  $v=1\leftarrow 0$  band of the Meinel system ( $A^2\Pi_u-X^2\Sigma_g^+$ ) of  $N_2^+$ . The observed frequency of this blend is in excellent agreement with that reported in a previous Fourier transform spectroscopy study of this band [10] and is illustrated by the vertical line in Fig. 2. The other lock-in is sensitive to neutral signals, in this case an unassigned transition that is likely part of the  $v=4\leftarrow 4$  band of the first positive ( $B^3\Pi_g-A^3\Sigma_u^+$ ) system of  $N_2$  [11]. In contrast to direct absorption studies [8,10,11], in which neutrals and ions can be separated only by quantum mechanical assignment or by their differing response to plasma conditions such as pressure, they

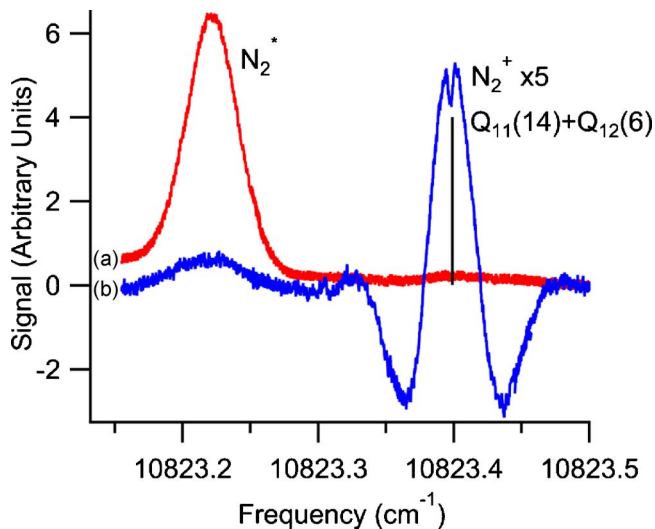


Fig. 2. (Color online) Spectral lines of, a,  $N_2^*$  and, b,  $N_2^+$ , recorded simultaneously by using two lock-in amplifiers with different phase settings.

are clearly separable by their different line shapes and phases in the present experiment.

The  $N_2^+$  transitions show a line shape that is well described as a second derivative of a Gaussian (with a Lamb dip, discussed below). The velocity modulation of the ions could be viewed as a wavelength modulation of the two counterpropagating laser beams in the cavity (in the ions’ rest frame), thus yielding a familiar  $2f$  line shape. The lock-in signal from the velocity modulation can also be simulated by assuming that the ions have a Gaussian (thermal) distribution of velocities, but that the center velocity oscillates in time, in phase with the discharge voltage. Trace a in Figure 3 shows the time-dependent absorption of  $N_2^+$  at line center, owing to ions with zero velocity along the cavity axis; such ions are most abundant at the zero crossing of the discharge voltage, as there is no electric field to cause a net drift velocity. Trace c shows the  $N_2^+$  absorption far from the line center, owing to ions with a large velocity along the cavity axis; such ions are most abundant at the maxima of the discharge voltage, and thus appear  $180^\circ$  out of phase from the ions in trace a. This qualitatively explains why the wings of the  $N_2^+$  line show

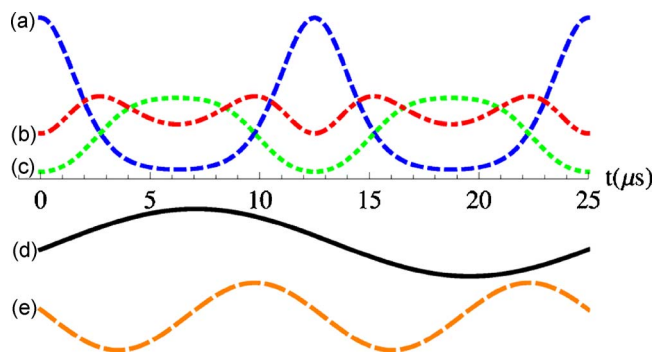


Fig. 3. (Color online) Simulated time-dependence of the  $N_2^+$  absorption, a, at line center; b, at the zero-crossing; and, c, at the minimum, compared with, d, the electric field. Trace e, time-dependent concentration of  $N_2^*$ .

up with the opposite sign from the line center in the lock-in signal shown in Fig. 2. The  $N_2^+$  transitions do not show significant concentration or amplitude modulation, which would appear as an ordinary Gaussian line shape.

In contrast, the  $N_2^*$  lines do appear with ordinary Gaussian line shapes, approximately  $78^\circ$  out of phase from the  $N_2^+$  lines. These electronically excited nitrogen molecules are produced by impact with energetic electrons ( $\geq 6.2$  eV) in the plasma, and their concentration is modulated by the discharge, but their velocity is unaffected. The observed value of the phase difference between  $N_2^*$  and  $N_2^+$  is not understood at present, but is likely to be pressure dependent.

Because of the high-intensity laser field inside the cavity, many of the observed transitions exhibit Lamb dips, as evident in the  $N_2^+$  line in Fig. 2. To our knowledge, this is the first time Lamb dips have been observed in molecular ion spectra by using tunable laser absorption spectroscopy. The only previous report of a Lamb dip in a molecular ion ( $D\text{Br}^+$  [12]) involved a laser magnetic resonance approach, which may be less generally applicable than the present approach. With improved frequency calibration (e.g., with an optical frequency comb), it will be possible to measure the transition frequencies of molecular ions with greatly enhanced resolution and precision, relative to Doppler-limited spectroscopy. Accurate measurements of the width of the Lamb dips as a function of laser power and discharge pressure may also allow measurement of the pressure broadening coefficients, and thereby the ion-neutral collisional rate coefficients. At present, the observed linewidth of the Lamb dips ( $\sim 130$  MHz) appears to be dominated by the frequency jitter of the cavity, as it is independent of the pressure of the discharge and it is considerably larger than is expected from unresolved hyperfine structure.

The present work demonstrates the feasibility of cavity-enhanced velocity modulation spectroscopy, but several improvements to the current system will be needed before this technique can exceed the sensitivity of other established velocity modulation experiments (e.g., [6]). First, the noise level must be substantially reduced from the present value of an equivalent fractional absorption of  $\sim 10^{-5}$ . When measurements are taken with the plasma off, the noise level is  $\sim 10^{-7}$ , which indicates that our biggest source of noise is either electrical pickup or optical emission from the plasma. It should be possible to mitigate this noise by a combination of better shielding and/or a wavelength modulation scheme. The use of heterodyne spectroscopy with a sideband frequency equal to the free spectral range of the cavity, as in [7], may be especially useful in improving the noise level.

Second, the finesse of the cavity must be increased, to extend the effective absorption path length. The maximum finesse of our cavity is currently limited by the quality of our laser lock, which can be significantly improved by adding an acousto-optic modulator for high-frequency corrections. Additionally, we can improve the frequency stability of the system by

locking the cavity to the laser instead of the reverse. The laser itself can then be locked either to its internal reference cavity or to an optical frequency comb. Another limit to our finesse is the presence of the Brewster windows, which could be avoided by mounting the cavity mirrors directly to the plasma cell, as in [8]. Ultimately, our current mirrors can be replaced by supermirrors to further increase the finesse. Finally, the signal can also be enhanced by using a longer discharge cell and by employing liquid nitrogen cooling to reduce the partition function of the molecular ions and the Doppler linewidth.

In this Letter we have demonstrated, for the first time to our knowledge, the use of cavity-enhanced spectroscopy together with velocity modulation. This combination offers the promise of substantially increasing the effective path length in velocity modulation experiments and permitting the study of extremely weak transitions of ions that can be produced in abundance, as well as the study of ions that are difficult to produce in quantity. In the limit of a high-finesse cavity combined with heterodyne spectroscopy [7], the S/N of the most sensitive velocity modulation experiments [5,6] could be improved by a factor of  $10^3$  or more. Furthermore, the presence of Lamb dips in the cavity-enhanced spectra opens the door to high-precision molecular ion spectroscopy as well as measurements of ion-neutral collisional rate coefficients.

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## References

1. T. A. Dixon and R. C. Woods, *Phys. Rev. Lett.* **34**, 61 (1975).
2. T. Oka, *Phys. Rev. Lett.* **45**, 531 (1980).
3. C. S. Gudeman, M. H. Begemann, J. Pfaff, and R. J. Saykally, *Phys. Rev. Lett.* **50**, 727 (1983).
4. S. K. Stephenson and R. J. Saykally, *Chem. Rev.* **105**, 3220 (2005).
5. J. L. Gottfried, B. J. McCall, and T. Oka, *J. Chem. Phys.* **118**, 10890 (2003).
6. C. P. Morong, J. L. Gottfried, and T. Oka, *J. Mol. Spectrosc.* **255**, 13 (2009).
7. J. Ye, L. S. Ma, and J. L. Hall, *J. Opt. Soc. Am. B* **15**, 6 (1998).
8. S. L. Widicus Weaver, M. B. Wiczer, B. Negru, J. P. DiGangi, B. A. Tom, and B. J. McCall, *J. Mol. Spectrosc.* **249**, 14 (2008).
9. R. W. P. Drever, J. L. Hall, F. V. Kowalski, J. Hough, G. M. Ford, A. J. Munley, and H. Ward, *Appl. Phys. B* **31**, 97 (1983).
10. D. W. Ferguson, K. N. Rao, P. A. Martin, and G. Guelachvili, *J. Mol. Spectrosc.* **153**, 599 (1992).
11. F. Roux, F. Michaud, and J. Verges, *J. Mol. Spectrosc.* **97**, 253 (1983).
12. M. Havenith, M. Schneider, W. Bohle, and W. Urban, *Mol. Phys.* **72**, 1149 (1991).