AIP | Review of Scientific Instruments

Mid-infrared concentration-modulated noise-immune cavity-enhanced optical heterodyne molecular spectroscopy of a continuous supersonic expansion discharge source

Courtney N. Talicska, Michael W. Porambo, Adam J. Perry, and Benjamin J. McCall

Citation: Review of Scientific Instruments **87**, 063111 (2016); doi: 10.1063/1.4953652
View online: http://dx.doi.org/10.1063/1.4953652
View Table of Contents: http://scitation.aip.org/content/aip/journal/rsi/87/6?ver=pdfcov
Published by the AIP Publishing

Mid-infrared concentration-modulated noise-immune cavity-enhanced optical heterodyne molecular spectroscopy of a continuous supersonic expansion discharge source

Courtney N. Talicska,[1] Michael W. Porambo,[1] Adam J. Perry,[1] and Benjamin J. McCall[1,2]
[1]*Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA*
[2]*Departments of Astronomy and Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA*

(Received 6 November 2015; accepted 27 May 2016; published online 14 June 2016)

Concentration-modulated noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS) is implemented for the first time on a continuous gas-flow pinhole supersonic expansion discharge source for the study of cooled molecular ions. The instrument utilizes a continuous-wave optical parametric oscillator easily tunable from 2.5 to 3.9 μm and demonstrates a noise equivalent absorption of $\sim 1 \times 10^{-9}$ cm^{-1}. The effectiveness of concentration-modulated NICE-OHMS is tested through the acquisition of transitions in the ν_1 fundamental band of HN_2^+ centered near 3234 cm^{-1}, with a signal-to-noise of ~40 obtained for the strongest transitions. The technique is used to characterize the cooling abilities of the supersonic expansion discharge source itself, and a Boltzmann analysis determines a rotational temperature of ~29 K for low rotational states of HN_2^+. Further improvements are discussed that will enable concentration-modulated NICE-OHMS to reach its full potential for the detection of molecular ions formed in supersonic expansion discharges. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4953652]

INTRODUCTION

Molecular ions play key roles in the chemistry and physics of combustion,[1,2] atmospheric chemistry,[3] and interstellar processes,[4] making the study of molecular ions an active area of research. Laboratory spectroscopy remains a leading tool for investigating molecular ions, but many challenges arise when spectroscopically investigating these highly reactive species. These challenges include weak spectral signals that result from the low abundance of ions formed in laboratory plasmas and high plasma temperatures which lead to dilute, complex spectra due to the population of many quantum states.

Over the past few decades many techniques have been developed to overcome these challenges. Effective isolation of ion signals from those of considerably more abundant neutral molecules has been achieved through velocity modulation spectroscopy.[5] The problem of low number densities has been mitigated by the use of sensitive spectroscopic techniques including cavity ring-down spectroscopy (CRDS)[6,7] and frequency modulation spectroscopy (FMS).[8] Cavity-enhanced techniques such as CRDS effectively increase the optical path length of the sample by placing the ion source in an optical cavity, resulting in a larger signal than conventional single-pass absorption methods. FMS achieves high spectroscopic sensitivity by decreasing the technical noise in the detected signal, theoretically down to the shot noise limit. While both cavity-enhanced and frequency modulation methods result in improved detection sensitivities, even greater spectroscopic sensitivity can be achieved by combining the strengths of each of these methods. This method, known as noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS) has demonstrated sensitivities down to 1×10^{-14} cm^{-1} Hz$^{-1/2}$ for neutrals in the near-IR.[9] The NICE-OHMS technique has been extended into the mid-IR with broad tunability[10] and has also been successfully combined with velocity modulation spectroscopy for ion-neutral discrimination.[11]

Hollow cathode cells[12,13] and positive column discharge sources[14] have long been recognized for their ability to produce high densities of ions in the laboratory. However, even when cryogenically cooled, the lowest temperatures achieved by these sources are on the order of 100 K. At these temperatures there are still significant populations of ions in high-energy states, thus the problem of population dilution has not fully been addressed by these sources. Cryogenic ion traps have demonstrated the ability to cool molecular ions to very low temperatures.[15] Cooled molecular ions have also been produced by coupling electric discharges to supersonic expansions, achieving rotational temperatures on the order of 10 K.[16–22] In addition to producing cold molecular ions, these sources have the unique ability to efficiently produce ions that other ion sources cannot, including primary and cluster ions.

The sensitivity of spectroscopic techniques used to probe molecular ions in an expansion discharge source can be improved through electrical modulation of the source, which provides a degree of concentration modulation of the ion signal. Improved detection of molecular ions has been demonstrated using this method.[21] However, modulation of an expansion discharge has not yet been applied to the NICE-OHMS technique. In this work we introduce concentration-modulated NICE-OHMS as a technique capable of improving the sensitivity with which ions formed in an expansion discharge source can be detected. This method is used to record transitions in the ν_1 fundamental band of the HN_2^+ ion, and a Boltzmann analysis is performed to characterize the rotational cooling of ions formed in the source. The determined rotational

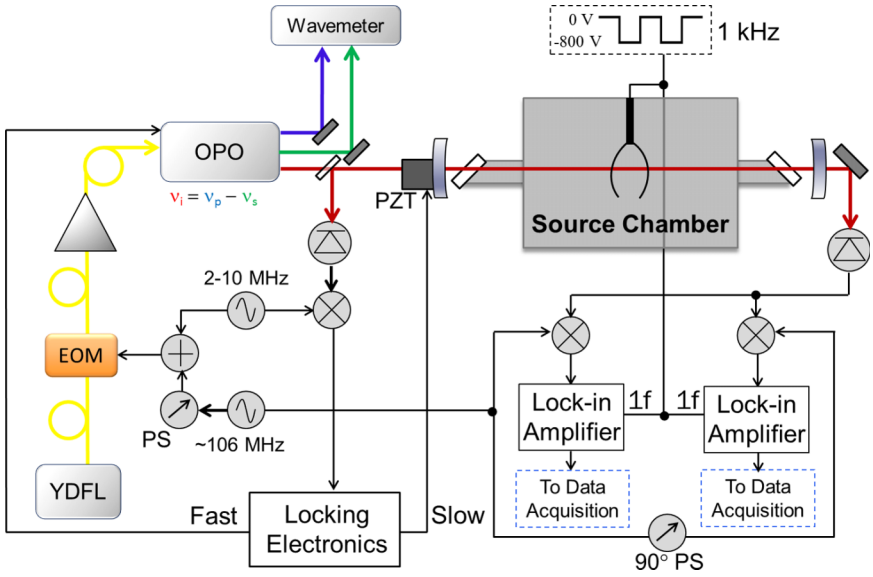

FIG. 1. Block diagram of the concentration-modulated NICE-OHMS instrument. OPO: optical parametric oscillator shown with pump (P), signal (S), and idler (I) beams; YDFL: Ytterbium-doped fiber laser; EOM: electro-optic modulator; PZT: piezoelectric transducer; PS: phase shifter.

temperature is found to be comparable to that recorded in similar discharge sources that have been probed by different spectroscopic methods.

EXPERIMENTAL

The concentration-modulated (cm) NICE-OHMS instrument developed for this work is shown in Figure 1. The optical parametric oscillator (OPO) used in this work has previously been used in spectroscopy of molecular ions in a positive-column glow discharge.[14] A ytterbium-doped fiber laser is phase modulated by a fiber electro-optic modulator (EOM) to produce RF sidebands for heterodyne detection and Pound-Drever-Hall (PDH) locking. The modulated light is amplified before being used to pump a singly-resonant OPO (Aculight Argos 2400 SF). As a result, the heterodyne (~106 MHz) and PDH locking (2–10 MHz) sidebands are imprinted onto the idler beam (2.5–3.9 μm). The idler beam of the OPO is coupled into a ~1.4 m cavity (finesse of ~130) placed symmetrically about the source chamber such that the idler passes perpendicularly through the axis of the expansion. A CaF_2 window is used to pick off the light reflected from the cavity, which is then focused onto a fast InSb detector (Kolmar KISDP-0.5-J1/DC, 30 MHz bandwidth) and demodulated at the locking frequency. Slow corrections (<70 Hz) are made to the cavity length by a piezoelectric transducer (PZT) attached to one of the cavity mirrors, and fast corrections (0.07–10 kHz) are sent to a PZT attached to one of the signal cavity mirrors within the OPO head.

Light transmitted through the cavity is focused onto a fast photodiode (Vigo PVM-10.6-1, ~125 MHz bandwidth) before being demodulated at ~106 MHz by a pair of electronic mixers set to be 90° out of phase with each other. In this variation of the NICE-OHMS technique, we add an additional layer of modulation by electrically modulating the discharge via a square wave sent to a high-voltage modulation circuit. As described below, this circuit provides an on-off switch to the DC voltage sent to the source and results in a periodically varied concentration of ions. The outputs of the electronic mixers are then sent to a pair of lock-in amplifiers where they are further demodulated at the modulation frequency of the source before being recorded by a custom-made data acquisition program.

The design of the continuous gas-flow supersonic expansion source has been described in detail in an earlier publication.[22] While the cathode used in this work retains the dimensions and shape described there (a trumpet-flared pinhole with 1.0 mm starting and 2.4 mm ending inner diameters), it has been replaced by one machined from tungsten (previously stainless steel) in the hope of further improving the lifetime of the source. It has been found previously that the density of H_3^+ ions produced varies with current supplied to the source (10^{10}–10^{12} cm^{-3} for 30–120 mA), and HN_2^+ is expected to be formed in similar quantities in a predominantly hydrogen expansion.[22] Scans in this study were obtained while running the source at a 1 kHz modulation frequency and a current of 110 mA, which required approximately −800 V be supplied from the power source to the cathode through a 1 kΩ 100 W ballast resistor.

Key to this study is the integration of a custom high-voltage modulation circuit, shown in Figure 2. The circuit uses an optoisolator (Avago Technologies ACNV2601-000E) to separate the low-voltage input of a function generator from the high-voltage supplied by the power supply. The output of this optoisolator is fed into a gate-driver (ON Semiconductor MC33153PG) for an insulated-gate bipolar transistor (IGBT) (Infineon IHW30N160R2) before being output through the ballast resistor to the cathode of the source. The performance of the modulation circuit was assessed for modulation frequencies ranging from ~25 Hz–85 kHz, with the circuit breaking down in the low frequency regime due to high transient voltage spikes.

HN_2^+ was formed in a Campargue-type expansion from a mixture of hydrogen and nitrogen gas each regulated to

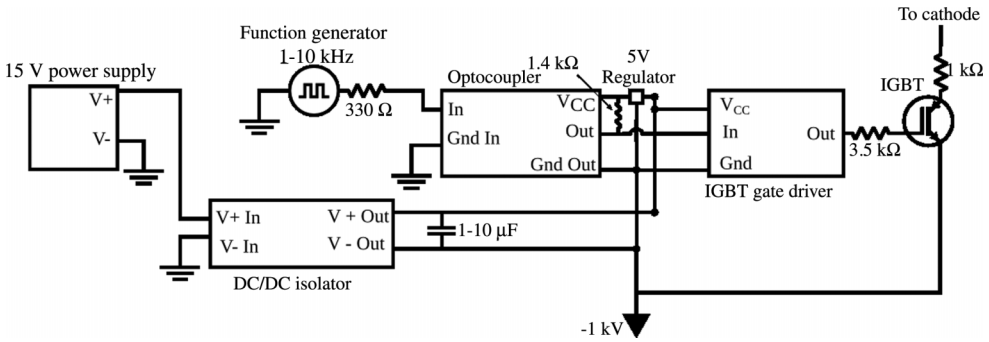

FIG. 2. Schematic of the custom high-voltage circuit used to modulate the discharge.

control their respective gas flow rates and combined before being flowed into the source. Equal backing pressures (34 psig H_2, 34 psig N_2) gave the strongest signal and all scans were performed with these conditions. The pumping speed delivered to the vacuum chamber was adjusted by partially closing a gate valve to give a background chamber pressure of approximately 750 mTorr (as recorded by a Varian 531 thermocouple gauge tube sensor), chosen for its ability to produce a pronounced barrel-shock structure and the strongest observed ion signal.

RESULTS AND DISCUSSION

Previous characterization of the unmodulated supersonic expansion discharge source using CRDS revealed a rotational temperature for H_3^+ of 80–110 K.[22] With its larger rotational constants (B = 43.5605 cm^{-1}, C = 20.6158 cm^{-1} [23]) and thus lower density of rotational states, H_3^+ does not cool as efficiently in a supersonic expansion as HN_2^+ (B = 1.5539 cm^{-1} [24]). Due to its capacity to cool more efficiently, HN_2^+ is used in this work to investigate the cooling abilities of the source using concentration-modulated NICE-OHMS.

To assess the rotational cooling of HN_2^+ in the source, transitions in the ν_1 fundamental band of HN_2^+, centered near 3234 cm^{-1}, were recorded. All scans used in the analysis were obtained at just over 2 cm downstream of the source nozzle. At distances closer to the expansion nozzle a peculiar lineshape was observed, which is discussed in detail in the thesis work of Porambo.[25] An unprocessed scan of each transition (each of which took approximately 1 min to acquire) is given in Figure 3. These scans were taken at a detection phase of ~160° as fit by a lineshape model taken from Equations (1)–(3) in the work of Foltynowicz *et al.*[26] The acquired scans given in Figure 3 were then smoothed using a 10-point boxcar averaging algorithm. The average of peak-to-peak intensities from at least three boxcar-smoothed scans of each line was normalized to their respective transition dipole moments as calculated in Townes and Schawlow.[27] Due to a dead spot in the frequency coverage of the OPO, the R(1) transition was not recorded.

Figure 4 shows the Boltzmann analysis of these normalized intensities, plotted against lower state energies calculated using the rotational constants reported by Kabbadj *et al.*[24] The two distinct slopes shown in Figure 4 are representative of the non-equilibrium nature of the expansion as has been reported in similar analyses by Xu *et al.*[19] and Louviot *et al.*[28] Analyzing the slope of the low J transitions ($J \leq 3$) gives a rotational temperature of ~29 K. This temperature is similar to the 33 K rotational temperature determined for low J transitions of HN_2^+ in a corona slit nozzle discharge expansion reported by Xu *et al.*[19] and also agrees well with the 25 K rotational temperature reported by Anderson *et al.* for low J transitions of this ion in a pulsed slit expansion discharge.[20]

Utilizing equations detailed in the work of Ma *et al.* the NICE-OHMS saturation parameter associated with the work presented here has an upper bound of ~6.[29] At this degree of saturation the effect on the peak-to-peak intensity of the absorption Doppler profile is demonstrated to be <5%, and is not large enough to alter the temperature calculated by the Boltzmann analysis. To further support the determined temperature this analysis was repeated with the intensities of the predominantly dispersion-phase channel, which

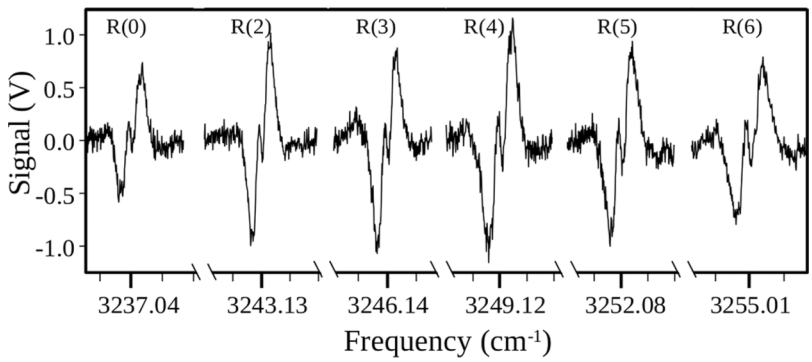

FIG. 3. Scans of the R(0), and R(2–6) transitions of the ν_1 fundamental band of HN_2^+. Each tick on the frequency axis represents 0.01 cm^{-1}.

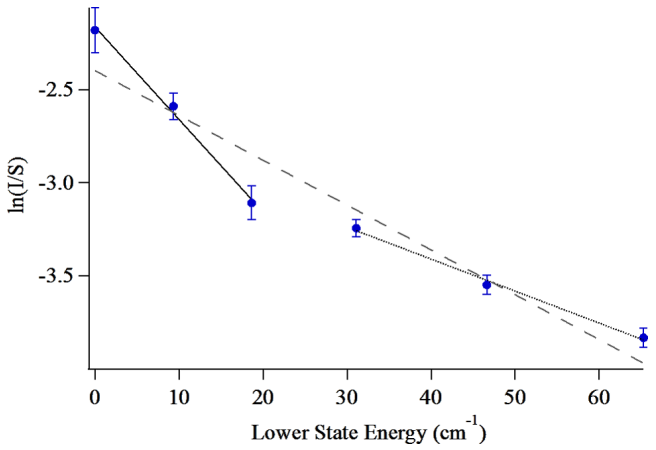

FIG. 4. A Boltzmann diagram of the rotational distribution of HN_2^+ shown with 2σ error bars. The fit to the low J (R(0), R(2), and R(3), solid line) gives a temperature of ~29 K, while the fit to the high J values (R(4)– R(6), dotted line) gives a temperature of ~84 K. The dashed line corresponds to a fit to all J values.

demonstrate peak-to-peak intensities unaffected by this level of saturation. The temperatures calculated from the absorption and dispersion-phase channels agree, substantiating the rotational temperature of ~29 K calculated for HN_2^+ formed in the expansion.

The lower temperature obtained for HN_2^+ (~29 K) compared to H_3^+ (80–110 K[22]) in the same continuous gas-flow supersonic expansion discharge source was anticipated due to the higher density of rotational states associated with low J values of HN_2^+. The low temperature achieved for HN_2^+ in this work also agrees well with those achieved for comparable ions in studies of a concentration-modulated pulsed-gas slit expansion discharge by Dong *et al.* where HD_2O^+ and H_2DO^+ were cooled to 34 K and 40 K, respectively.[30,31] The cooling abilities of the source as verified by the concentration-modulated NICE-OHMS technique are thus in accordance with the cooling achieved in expansion discharges probed by other spectroscopic methods.

The high J transitions ($J \geq 4$) indicate a warmer temperature of ~84 K, similar to the phenomenon reported by Xu *et al.* where higher J transitions of HN_2^+ gave warmer temperatures.[19] The observed increase in temperature for high J levels is an expected result of larger energy spacings among these levels which results in less efficient cooling through rotation-to-translation energy transfer. As shown by the dashed line in Figure 4, a fit to all J values does not encapsulate the normalized intensities of all J levels, even when including 2σ errors in the measurements. This is indicative of the non-equilibrium nature of supersonic expansions and highlights the need for separate fits to the low and high J values in the Boltzmann analysis.

The FWHM of HN_2^+ scans acquired in this work is ~100–110 MHz as supported by the Doppler-broadened lineshape model of Foltynowicz *et al.*[26] As the FWHM of HN_2^+ is already on the order of the heterodyne sideband spacing, further optimizing the sideband spacing is not expected to yield a significant increase in the acquired signal.[32] For ions with larger FWHMs (such as H_3^+) the heterodyne modulation frequency may be adjusted to optimize the obtained signal, but is limited by the fact that this frequency must be an integer multiple of the free-spectral-range of the cavity and must be within the bandwidth of the mid-infrared detector used to recover the transmitted signal.

Improved detection of ions formed by the source may be achieved by increasing the source modulation frequency, further reducing noise in the system. Throughout the course of this study scans were obtained at a source modulation frequency of ~1 kHz. At higher frequencies the source current was found to take time to stabilize during the plasma "on"-cycle as evidenced by monitoring the source current using a Hall-effect sensor placed just before the source. Resolving this current instability would allow the source modulation frequency to be limited only by the expansion of ions through the laser probe region. The theoretical upper limit to this modulation will vary based on the expansion velocity of the ion under study, but is expected to be on the order of 100 kHz barring any limits due to the modulation circuit and lock-in amplifier bandwidth.[21]

The main advantage of this instrument over previously designed FMS, CRDS, and multi-pass setups is the potential for achieving a higher sensitivity through the combination of cavity-enhancement, heterodyne detection, and lock-in detection. Here, the performance of the concentration-modulated NICE-OHMS spectrometer is characterized by the noise equivalent absorption sensitivity.[9] This value is derived from the rms of the baseline noise present in the scans which, for cm-NICE-OHMS, is flat (uninfluenced by drift) and free of etalons. After correction for amplification in the detection train the noise equivalent absorption sensitivity of the cm-NICE-OHMS instrument is found to be $\sim 1 \times 10^{-9}$ cm^{-1}, which demonstrates the low noise level that can be achieved with the cm-NICE-OHMS technique. It should be noted that further reduction of noise may be achieved through an increased source modulation frequency.

CONCLUSIONS

This work demonstrates the first implementation of concentration-modulated NICE-OHMS for the investigation of molecular ions formed in a supersonic expansion discharge source. In addition, this technique has been used to successfully characterize the cooling abilities of the source itself. Analysis of low J transitions of HN_2^+ formed in the expansion indicates a rotational temperature of ~29 K, similar to the cooling observed for this ion in a continuous gas-flow corona and a pulsed gas-flow slit expansion discharge.[19,20] The low rotational temperature of ions formed by the source tailors this setup toward the investigation of large molecular ions which typically exhibit dilute, congested spectra in higher-temperature ion sources.

To fully realize the potential of concentration-modulated NICE-OHMS of a supersonic expansion discharge source for the investigation of ions formed in less abundance than HN_2^+, it will be necessary to continue to improve the instrument. Increasing the sample path length through the use of a slit geometry could easily improve the obtainable signal strength by a factor of 3 or 4, as slits with lengths of 3–4 cm have previously been used in expansion discharges.[21] In addition,

the cavity finesse is currently limited by the presence of Brewster's windows on the expansion chamber. If a method of directly mounting the cavity mirrors to the chamber can be realized, the finesse could be improved to the limit of the reflectivity of obtainable mirrors and the locking bandwidth of the system. However, this improvement is made difficult by the mechanical vibrations of the Roots blower pump.

While the aforementioned methods would likely be the most influential in increasing the strength of the signal obtained by cm-NICE-OHMS, there are several additional measures which may serve to improve the effectiveness of this and future cm-NICE-OHMS instruments. In this work the baseline is observed to be flat and free of etalons. However, future implementations may find the use of a proton-exchange electro-optic modulator and etalon-immune distances useful to eliminate background signals, especially in the case of large scanning windows.[33,34] Additionally, increasing the heterodyne modulation index such that more than one pair of sidebands is produced has been proposed as a method by which to further strengthen the NICE-OHMS signal.[35] Overall, the instrument described here makes important steps towards the more sensitive detection of molecular ions formed in supersonic expansion discharges, and can be further improved upon to take full advantage of the concentration-modulated NICE-OHMS technique.

ACKNOWLEDGMENTS

The authors would like to thank James N. Hodges for insightful discussions regarding the effects of saturation on the NICE-OHMS lineshape, and G. Stephen Kocheril for his help in acquiring spectra for this study. We also wish to acknowledge Thomas J. Houlahan for designing the electrical diagram given in Figure 2, and Jessica M. Pearson for help implementing the modulation circuit used in this work. This work has been supported by the NASA Earth and Space Science Fellowship program (No. NNX12AL60H) and the National Science Foundation (Grant No. CHE 12-13811).

[1]R. D. Thomas, Mass Spectrom. Rev. **27**, 485 (2008).
[2]A. Kiendler, S. Aberle, and F. Arnold, Atmos. Environ. **34**, 2623 (2000).
[3]F. Cacace and G. de Petris, Int. J. Mass Spectrom. **194**, 1 (2000).
[4]W. D. Geppert and M. Larsson, Chem. Rev. **113**, 8872 (2013).
[5]C. S. Gudeman, M. H. Begemann, J. Pfaff, and R. J. Saykally, Phys. Rev. Lett. **50**, 727 (1983).
[6]G. Berden, R. Peeters, and G. Meijer, Int. Rev. Phys. Chem. **19**, 565 (2000).
[7]A. O'Keefe and D. A. G. Deacon, Rev. Sci. Instrum. **59**, 2544 (1988).
[8]G. C. Bjorklund, M. D. Levenson, W. Lenth, and C. Ortiz, Appl. Phys. B: Photophys. Laser Chem. **32**, 145 (1983).
[9]J. Ye, L. Ma, and J. L. Hall, J. Opt. Soc. Am. B **15**, 6 (1998).
[10]M. W. Porambo, B. M. Siller, J. M. Pearson, and B. J. McCall, Opt. Lett. **37**, 4422 (2012).
[11]B. M. Siller, M. W. Porambo, A. A. Mills, and B. J. McCall, Opt. Express **19**, 24822 (2011).
[12]T. Amano, J. Opt. Soc. Am. B **2**, 790 (1985).
[13]K. N. Crabtree, C. A. Kauffman, B. A. Tom, E. Beçka, B. A. McGuire, and B. J. McCall, J. Chem. Phys. **134**, 194311 (2011).
[14]K. N. Crabtree, J. N. Hodges, B. M. Siller, A. J. Perry, J. E. Kelly, P. A. Jenkins II, and B. J. McCall, Chem. Phys. Lett. **551**, 1 (2012).
[15]O. Asvany, F. Bielau, D. Moratschke, J. Krause, and S. Schlemmer, Rev. Sci. Instrum. **81**, 76102 (2010).
[16]T. A. Miller, B. R. Zegarski, T. J. Sears, and V. E. Bondybey, J. Phys. Chem. **84**, 3154 (1980).
[17]P. C. Engelking, Rev. Sci. Instrum. **57**, 2274 (1986).
[18]L. I. Yeh, M. Okumura, J. D. Myers, J. M. Price, and Y. T. Lee, J. Chem. Phys. **91**, 7319 (1989).
[19]Y. Xu, M. Fukushima, T. Amano, and A. R. W. McKellar, Chem. Phys. Lett. **242**, 126 (1995).
[20]D. T. Anderson, S. Davis, T. S. Zwier, and D. J. Nesbitt, Chem. Phys. Lett. **258**, 207 (1996).
[21]S. Davis, M. Fárník, D. Uy, and D. J. Nesbitt, Chem. Phys. Lett. **344**, 23 (2001).
[22]K. N. Crabtree, C. A. Kauffman, and B. J. McCall, Rev. Sci. Instrum. **81**, 86103 (2010).
[23]C. M. Lindsay and B. J. McCall, J. Mol. Spectrosc. **210**, 60 (2001).
[24]Y. Kabbadj, T. R. Huet, B. D. Rehfuss, C. M. Gabrys, and T. Oka, J. Mol. Spectrosc. **163**, 180 (1994).
[25]M. W. Porambo, "Development of a sensitive mid-infrared spectrometer for the study of cooled molecular ions," Ph.D. thesis, The University of Illinois, 2015.
[26]A. Foltynowicz, F. Schmidt, W. Ma, and O. Axner, Appl. Phys. B: Lasers Opt. **92**, 313 (2008).
[27]C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, 1955).
[28]M. Louviot, N. Suas-David, V. Boudon, R. Georges, M. Rey, and S. Kassi, J. Chem. Phys. **142**, 214305 (2015).
[29]W. Ma, A. Foltynowicz, and O. Axner, J. Opt. Soc. Am. B **25**, 1144 (2008).
[30]F. Dong, D. Uy, S. Davis, M. Child, and D. J. Nesbitt, J. Chem. Phys. **122**, 224301 (2005).
[31]F. Dong and D. J. Nesbitt, J. Chem. Phys. **125**, 144311 (2006).
[32]P. Ehlers, I. Silander, and O. Axner, J. Opt. Soc. Am. B **31**, 2051 (2014).
[33]I. Silander, T. Hausmaninger, and O. Axner, J. Opt. Soc. Am. B **32**, 2104 (2015).
[34]P. Ehlers, A. C. Johansson, I. Silander, A. Foltynowicz, and O. Axner, J. Opt. Soc. Am. B **31**, 2938 (2014).
[35]P. Ehlers, J. Wang, I. Silander, and O. Axner, J. Opt. Soc. Am. B **31**, 1499 (2014).