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Efforts focused on four activities related to the central objective of studying metal-containing clusters, HEDM molecules, and clusters of ceramic materials. Nineteen AFOSR supported papers were published on the following topics (including five journal cover articles): 1) Development of high resolution (100 MHz), high sensitivity pulsed infrared cavity ringdown spectroscopy as a general tool for trace species characterization. 2) Infrared cavity ringdown system with medium (900 MHz) resolution constructed and operational. 3) IR studies of hydrogen bonding in water, methanol, ethanol, and butanol clusters carried out. 4) More difficult IR experiments on laser vaporized carbon and silicon carbide initiated.

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FINAL TECHNICAL REPORT

AFOSR GRANT #F49620-96-1-0411

"Infrared Cavity Ringdown Laser Absorption Spectroscopy: Metal-containing Clusters and HEDM Molecules"

(Period Covered: 08/05/96 - 02/04/00)

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Efforts focused on four activities related to the central objective of studying metal-containing clusters, HEDM molecules, and clusters of ceramic materials. Nineteen AFOSR-supported papers were published on the following topics (including five journal cover articles): 1) Development of high resolution (100 MHz), high sensitivity pulsed infrared cavity ringdown spectroscopy as a general tool for trace species characterization. 2) Infrared cavity ringdown system with medium (900 MHz) resolution constructed and operational. 3) IR studies of hydrogen bonding in water, methanol, ethanol, and butanol clusters carried out. 4) More difficult IR experiments on laser vaporized carbon and silicon carbide initiated.

Ph.D. Degrees awarded to:

Dr. Joshua B. Paul (Fall, 1998)
Dr. Robert A. Provencal (Fall, 1999)

M.S. Degree awarded to Chris Chapo (Spring, 1999)

Technical Summary

Infrared spectroscopy is a powerful and time-honored technique for characterizing chemical materials. State-of-the-art technology for IR spectroscopy employs Fourier transform spectrometers, color center, diode, and difference frequency lasers, and pulsed optical parametric amplifier (OPO/OPA) systems. These widely used approaches all suffer from either complexity, restricted tuning range, or relatively low sensitivity. IR cavity ringdown laser absorption spectroscopy (CRLAS) with pulsed laser sources promises an impressive combination of convenience, high sensitivity, and very broad tuning range. The major focus of our work during this grant period has been to advance the technique of IR-CRLAS, and to apply it to a variety of trace species produced in pulsed supersonic beams, including metal-containing molecules, hydrogen bonded clusters, and covalent carbon and silicon carbide clusters.

A medium (ca. 900 MHz) resolution pulsed IR CRLAS spectrometer employing Stimulated Raman Scattering (SRS) of a pulsed dye laser with a continuous tuning range from visible to 10 μm, was constructed and used in detailed studies of water methanol, ethanol, and butanol clusters. These studies were extended to the more difficult class of laser-vaporized carbon and silicon carbide clusters, with the goal of applying these to ceramic materials and HEDM species. The HEDM molecule Al NH was also studied.

A high resolution (100 MHz) version of this experiment was designed built, and tested. It features an external cavity diode laser seeded Alexandrite laser to produce 40 MHz pulses in the 700-800 nm region and SRS to downconvert into the IR, and has tunability from far IR to the visible. Numerous invited cover articles were published on these systems and their initial applications. Initial studies of metal-containing molecules (WO ad Cr_2) were carried out collaboratively with the Bondybey group at the Technical University in Munich in the visible region of the spectrum.

A Medium-Resolution (900 MHz) IR CRLAS Spectrometer

The design of this system is shown in Figure 1, and has been described in numerous feature articles [155, 181, 190, 191, 204, 220]. It employs a commercial YAG-pumped dye laser at visible wavelengths and a long multi-pass high pressure hydrogen cell for stimulated Stokes scattering downconversion into the IR. This system produces ca. 5 ns pulses with 100-500 μJ of energy over the range 10 μm – 2 μm. With available "supermirrors," we achieve fractional absorption sensitivity of ~ 1×10^{-6} throughout most of this region.

We have first exploited this system for the study of water and alcohol clusters in pulsed planar supersonic expansion. After perfecting the technology, we were able to make the first direct absorption measurements of H_2O and D_2O dimers, trimer, tetramer, pentamer, and hexamers.

This allowed us to exact absolute number densities for the clusters in the expansion and to assess the capability of this method as an *in situ* probe of water clusters and other species in equilibrium environments. We were also able to carry out the first systematic study of alcohol (methanol, ethanol, and butanol) clusters in the mid-IR as a result of combining the H_2 SRS source with our CRLAS detection scheme (Figure 2).

The next step was to perform the much more difficult IR-CRLAS studies of clusters generated by laser vaporization in supersonic beams. In order to develop this capability, we carried out studies of the pure carbon clusters C_3, C_5, and C_9 previously studied by our diode laser experiments in order to perfect the combination of these laser plasma sources with ringdown detection. We seek to exploit the ultra-high sensitivity and rapid scan capability of CRLAS, which will be indispensable for the proposed work with ceramic clusters. The ν_3 band of C_5 is shown in Figure 3 for comparison.

We are presently nearing the ability to begin study of metal carbide clusters and HEDM species. As an initial step we initiated a study of Al NH, itself of possible HEDM interest and previously observed by IR spectroscopy in a cryogenic matrix. Representative spectra, measured in a plasma of laser vaporized aluminum with NH_3 in the He buffer gas, are shown in Figure 4. Analysis is still in progress.

Over the last 1 1/2 years, we have devoted much effort to the design, construction, and testing of a high resolution IR-CRLAS experiment. We decided to base the design on a tunable Alexandrite laser (Light Age Inc.) which provides >150 mJ/pulse with a 50 MHz transform limited bandwidth. This high spectral brightness is converted into the IR by SRS in a combination of H_2 and D_2 Raman cells. This scheme will allow us to cover the entire mid-IR with narrowband pulsed tunable radiation, permitting us to measure infrared spectra of virtually all molecules with Doppler-limited resolution (a 10x improvement over the present system). This new CRLAS system is currently operational with narrow linewidths over a limited wavelength range. We are working to extend the range of this high resolution system.

A High Resolution (100 MHz) IR CRLAS Spectrometer

Most of our efforts over the last two years have been devoted to the design, construction, and testing of a high resolution IR-CRLAS experiment. This would achieve a 10-30 fold increase in sensitivity and provide Doppler-limited spectra, like diode lasers. We decided to base the design on a tunable injection-seeded Alexandrite laser (Light Age Inc.), rather than on the OPO/OPA system originally requested in this proposal. We chose this route because the combination of the Alexandrite laser and SRS I H_2 and D_2 cells promised continuous spectral coverage from far IR (ca. 500 cm^{-1}) to the UV, with narrow linewidths – probably limited by the SRS downconversion process. Both the tuning range and the spectral resolution can thus greatly surpass those available with commercial OPO/OPA systems. However, this approach required great care in the optical design and the detailed exploration of the SRS process with regard to linewidth limitations. The design of the system is shown in Figure 5.

We have now demonstrated (Figure 6) that this system does indeed produce tunable IR pulses with linewidths less than 250 MHz. Moreover, it appears that ca. 500 μJ pulses can be produced over much of the IR (measured for 1900-2000 cm^{-1} but currently limited by the availability of the diode seed lasers). We are just now beginning experiments on laser vaporized species with this system to test the synchronization of the laser pulses with the pulsed production of the sample, which has also proven to be a difficult modification of the Alexandrite system, achieved by Light Age Inc. We have worked closely with them in the design of this spectrometer, which should be producing spectra of new species very soon.

Molecules Studied

A. *Metal-Containing Species*

A major object of the technical development described above is the study of metal-containing species, particularly clusters comprising ceramic materials. We have collaborated with the Bondybey group in Munich in the study of simple high temperature metal oxides (e.g. tungsten oxide) [218], by CRLAS in the visible, as they have developed sophisticated technology for producing such refractory species in pulsed supersonic jets. Chromium dimers were also studied, but attempts to extend this approach to titanium have not yet worked [222]. The plan is to adapt these sources for use in our IR cavity ringdown spectrometers.

B. *HEDM Species*

The molecule Al NH has been proposed as a possible HEDM molecule, being observed previously in a cryogenic matrix. We have measured rotationally resolved spectra near 1890 cm^{-1}, as shown in Figure 4, by laser vaporizing aluminum with NH_3 in the helium buffer gas. Carbon clusters and silicon carbide clusters have also been studied by IR CRLAS at "medium resolution" (Figure 3).

C. *Hydrogen Bonded Clusters*

As discussed above, a series of studies of water clusters and alcohol clusters, were carried out with the goal of characterizing the differences in hydrogen bonding that are effected as the H in a molecule is replaced by sequentially larger hydrophobic groups. We decided to carry out this study largely to gain experience in the difficult technology of the IR CRLAS system before undertaking the much more demanding laser vaporization experiments.

Publications Supported by This Grant
(numbers correspond to complete publication list)

155.* J.J. Scherer, J.B. Paul, A. O'Keefe, and R.J. Saykally, "Cavity Ringdown Laser Absorption Spectroscopy: History, Development, and Application to Pulsed Molecular Beams," *Chemical Reviews* 97, 1, 25-51 (**1997**).

***Cover Article.**

189. J.B. Paul, C.P. Collier, J.J. Scherer, A. O'Keefe, and R.J. Saykally, "Direct Measurement of Water Cluster Concentrations by Infrared Cavity Ringdown Laser Absorption Spectroscopy," *J. Phys. Chem. A* **101**, 5211 (**1997**).

190.* J.B. Paul and R.J. Saykally, "Cavity Ringdown Laser Absorption Spectroscopy," *Analytical Chemistry A* 69, 287 (**1997**).

***Cover Article.**

191.* J.B. Paul, J.J. Scherer, A. O'Keefe, and R.J. Saykally, "Cavity Ringdown Laser Absorption Spectroscopy," *Laser Focus World* 33, 71-80 (**1997**).

***Cover Article.**

196. A.I. Boldyrev, J. Simons, J.J. Scherer, J.B. Paul, C.P. Collier, and R.J. Saykally, "On The Ground Electronic States Of Copper Silicide and Its Ions," *J. Chem. Phys.* 108, 5728 (**1998**).

204.* J.B. Paul, R.A. Provencal, C. Chapo, E. Michael, A. Pettersson, and R.J. Saykally, "Infrared Cavity Ringdown Laser Absorption Spectroscopy of Transient Species in Pulsed Supersonic Expansions," *1997 ACS Symposium Series 720 on Cavity-ringdown spectroscopy: an ultratrace-absorption measurement technique*, Kenneth W. and Marianna A. Busch, editor, pp. 162-173 (**1999**).

***Cover Article.**

206. J.B. Paul, R.A. Provencal, and R.J. Saykally, "Characterization of the $(D_2O)_2$ Hydrogen-Bond-Acceptor Antisymmetric Stretch by IR-Cavity Ringdown Laser Absorption Spectroscopy," *J. Phys. Chem. A* **102**, 3279 (**1998**).

208. R.A. Provencal, J.B. Paul, E. Michael, and R.J. Saykally, "Cavity Ringdown Laser Absorption Spectroscopy," *Photonics Spectra* **32**, 159-166 (**1998**).

209. J.B. Paul, R.A. Provencal, C. Chapo, A. Pettersson, and R.J. Saykally, "Infrared Cavity Ringdown Spectroscopy of Water Clusters: O-D Stretching Bands," *J. Chem. Phys.* **109**, 10201 (**1998**).

213. J.B. Paul, R.A. Provencal, C. Chapo, K. Roth, R. Casaes, and R.J. Saykally, "Infrared Cavity Ringdown Spectroscopy of the Water Cluster Bending Vibrations," *J. Phys. Chem. A* **103**, 2972 (**1999**).

214. C.J. Chapo, J.B. Paul, R.A. Provencal, K. Roth, and R.J. Saykally, "Is Arginine Zwitterionic or Neutral in the Gas-Phase? Results from IR Cavity Ringdown Spectroscopy," *J. Am. Chem. Soc.* **120**, 12956-12957 (**1998**).

217. R.A. Provencal, J.B. Paul, K. Roth, C. Chapo, R.N. Casaes, R.J. Saykally, G.S. Tschumper, and H.F. Schaefer, III, "Infrared cavity ringdown spectroscopy of methanol clusters: Single donor hydrogen bonding," *J. Chem. Phys.* **110**, 4258 (**1999**).

218. D. Kraus, R.J. Saykally, and V.E. Bondybey, "Cavity Ringdown Laser Absorption Spectra of Tungsten Oxide," *Chem. Phys. Lett.* 295, 285-288 (**1998**).

220.* R.A. Provencal, J.B. Paul, C.N. Chapo, and R.J. Saykally, "Cavity Ringdown Laser Absorption Spectroscopy," *Spectroscopy* 14, 24 (**1999**).

***Cover Article.**

221. A. O'Keefe, J.J. Scherer, J.B. Paul, and R.J. Saykally, "Cavity-Ringdown Laser Spectroscopy: History, Development, and Applications," *1997 ACS Symposium Series 720 on Cavity-ringdown spectroscopy: an ultratrace-absorption measurement technique*, Kenneth W. and Marianna A. Busch, editor, pp. 71-92 (**1999**).

222. D. Kraus, R.J. Saykally, and V.E. Bondybey, "Cavity ringdown spectroscopy search for transition metal dimers," *Chemical Physics* 247, 431-434 (**1999**).

225. R.A. Provencal, K. Roth, J.B. Paul, C.N. Chapo, R.N. Casaes, R.J. Saykally, G.S. Tschumper, and H.F. Schaefer, III, "Hydrogen Bonding in Alcohol Clusters: A Comparative Study by Infrared Cavity Ringdown Laser Absorption Spectroscopy," *J. Phys. Chem. A* 104, 1423 (**2000**).

229. D.R. Wagner, and R.J. Saykally, "Ringing the changes," *Chemistry in Britain* 36, 47-49 (July **2000**).

Submitted/In Press Papers

M00.4 E. Michael, C.J. Keoshian, D.R. Wagner, S.K. Anderson, A.J. Huneycutt, and R.J. Saykally, "Infrared Water Lasers," *Nature* (submitted **2000**).

Figure Captions

Figure 1. **Design of Medium Resolution IR Cavity Ringdown Spectrometer**
Tunable infrared radiation is generated by Raman shifting an ND:YAG pumped dye laser. The tunable infrared light is injected into the ringdown optical cavity where the beam intersects a supersonic expansion in which the transient molecules are formed. Light exiting the cavity is monitored using a detector (InSb or HgCdTe). The signal is amplified, digitized, and sent to a PC computer for determination of cavity losses.

Figure 2. **CRLAS Spectra of Methanol Clusters in the O-H Stretching Region**
Spectrum obtained using the medium resolution Cavity Ringdown spectrometer. Features from the dimer to tetramer were assigned along with a broad band from the pentamer and larger clusters.

Figure 3. **The ν_3 Band of C_5**
The R(12) to R(26) transitions of the ν_3 band. The sensitivity of the medium resolution CRLAS spectrometer is as good as the previous diode laser experiment. The high resolution CRLAS spectrometer should be 10 times more sensitive.

Figure 4. **IR Spectrum of Al NH Molecule**
Spectra assigned to Al NH on the basis of IR matrix data. This HEDM molecule was generated by laser vaporization of Al into a mixture of He and NH_3.

Figure 5. **The High Resolution IR Cavity Ringdown Spectrometer**
500 micro joules of infrared radiation (20700 cm^{-1} to 1900 cm^{-1}) are generated by stimulated Raman shifting of the Alexandrite laser (100 mJ/40 MHz) in deuterium and hydrogen.

Figure 6. **Spectrum of OCS Confirming Instrument Linewidth <250 MHz**
Linewidth vary from 350 MHz to 150 MHz. This is probably due to variations in the Alexandrite linewidth during the scan. This problem will be fixed once we install a new OEM.

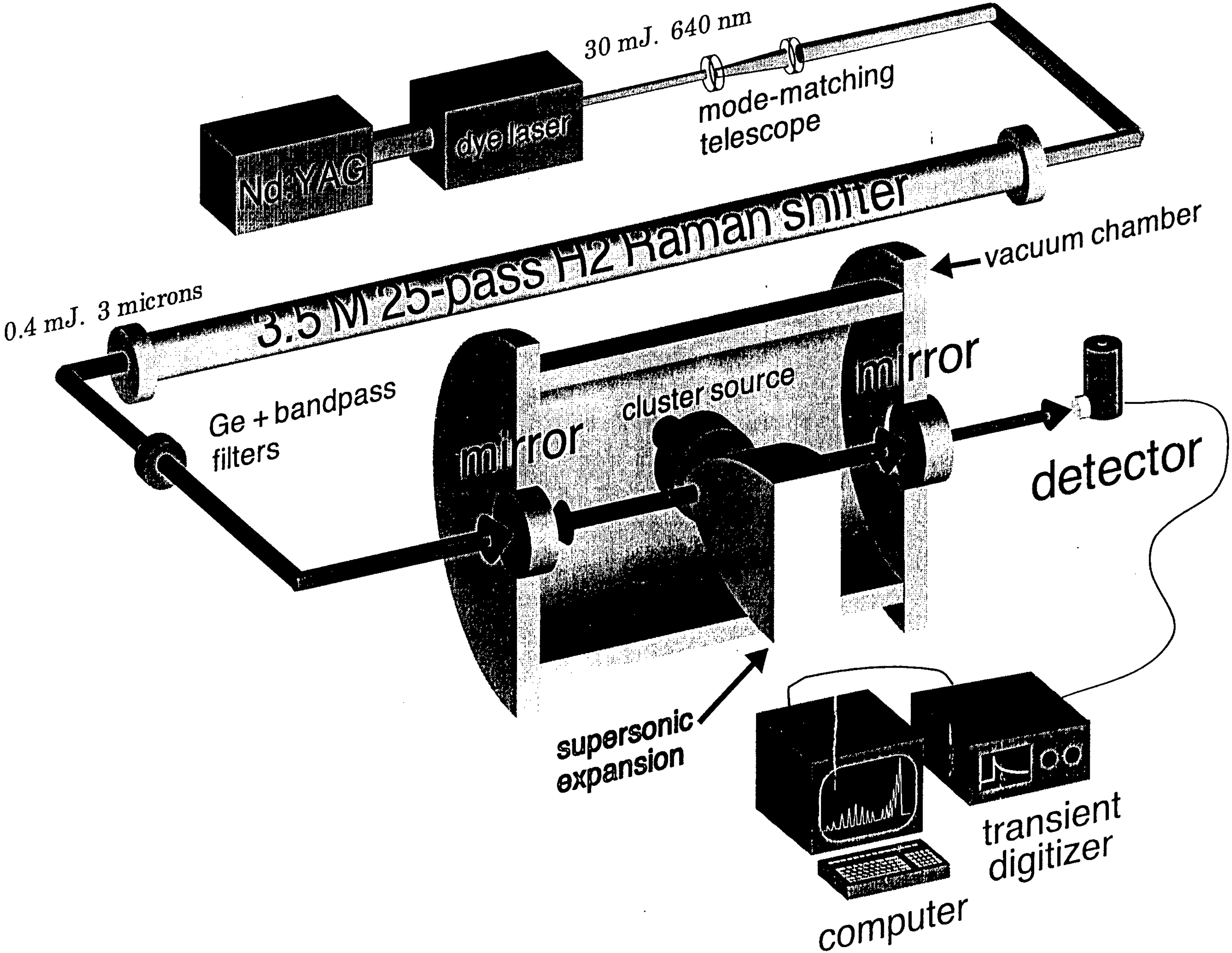
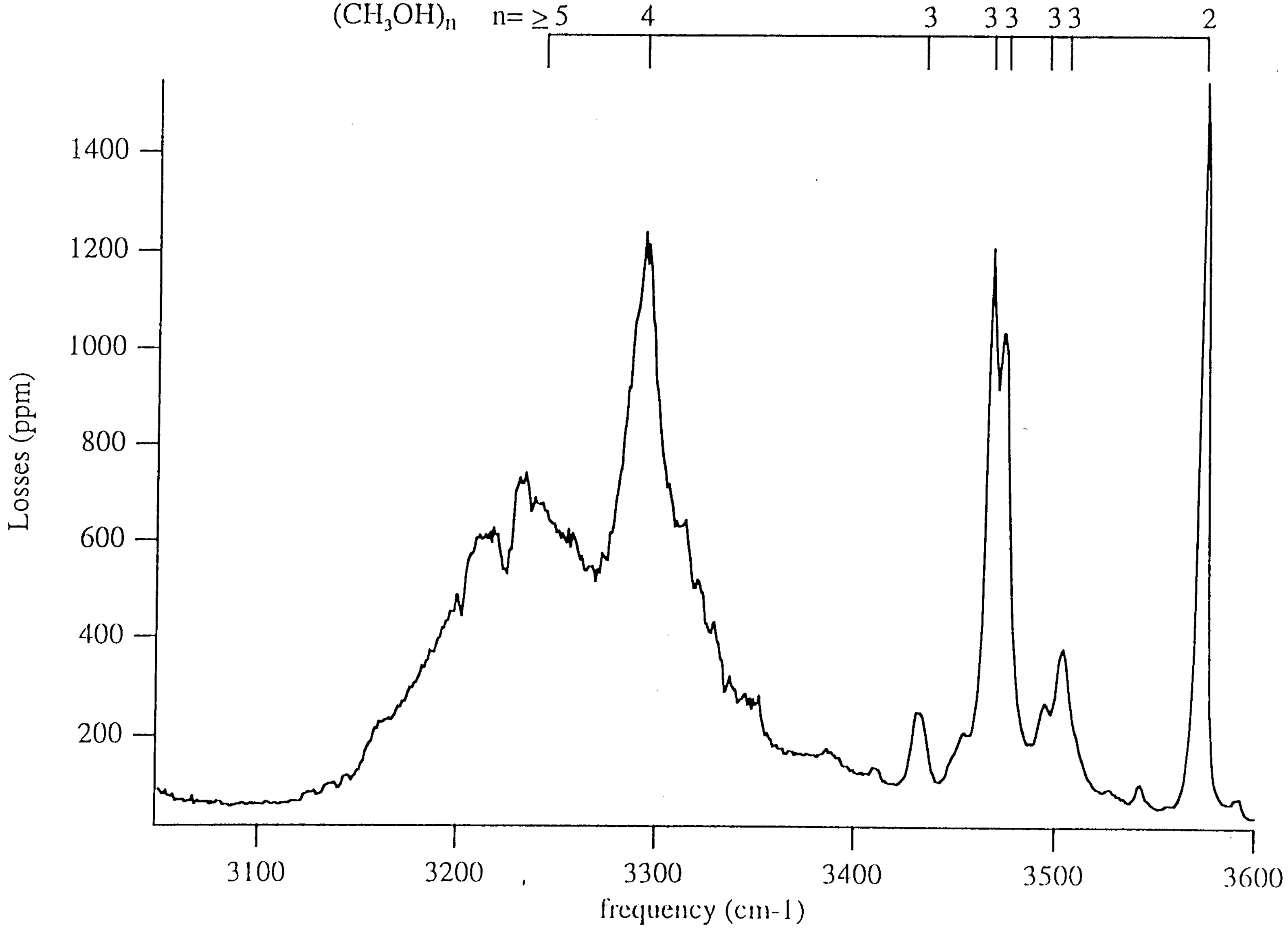
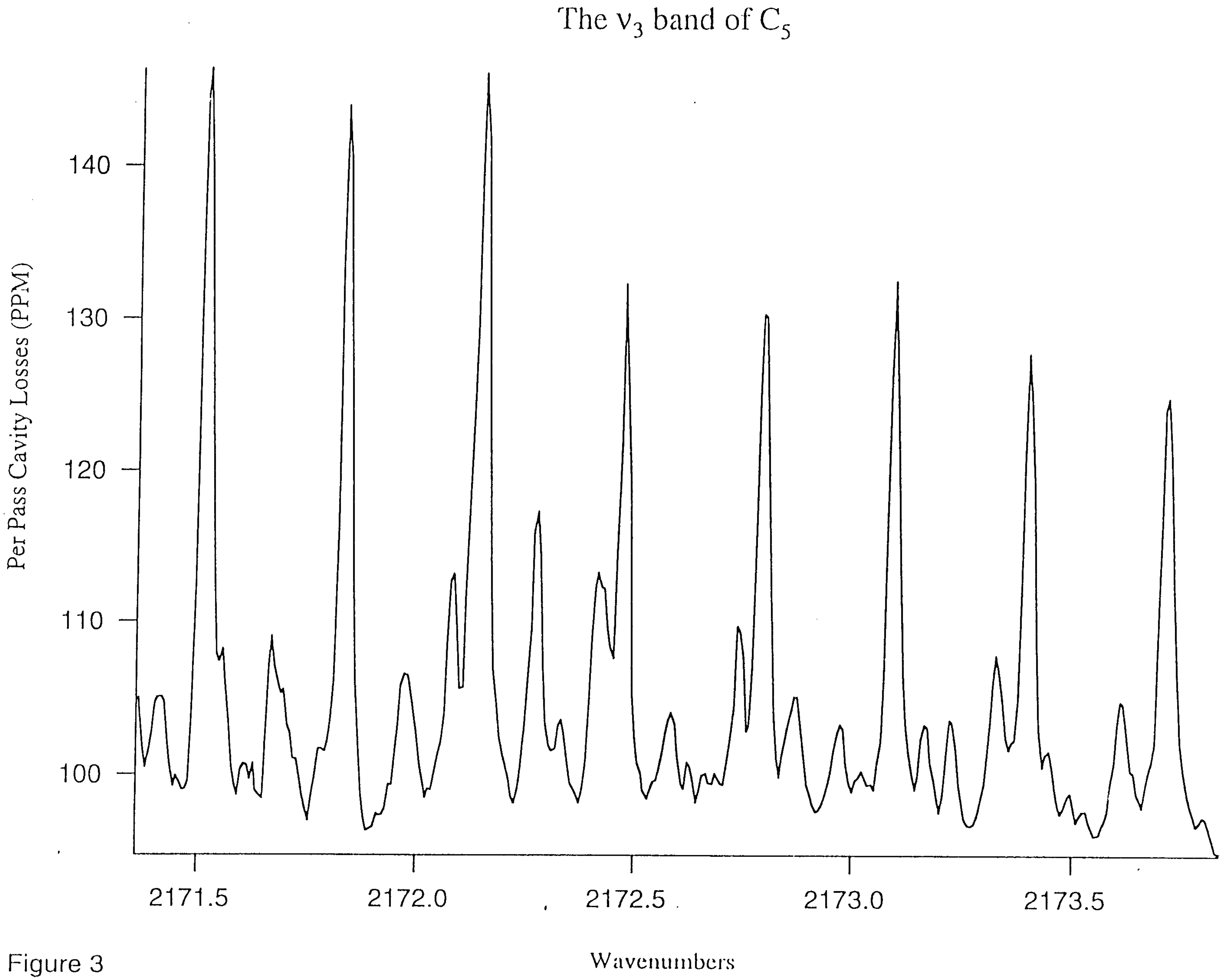

30 mJ. 640 nm
Nd:YAG
dye laser
mode-matching
telescope
3.5 M 25-pass H2 Raman shifter
0.4 mJ. 3 microns
vacuum chamber
Ge + bandpass
filters
mirror
cluster source
mirror
detector
supersonic
expansion
transient
digitizer
computer

Figure 1



$(CH_3OH)_n$ n= ≥ 5
4
3
3 3
3 3
2
1400
1200
1000
800
600
400
200
Losses (ppm)
3100
3200
3300
3400
3500
3600
frequency (cm-1)

Figure 2


The ν_3 band of C_5
Per Pass Cavity Losses (PPM)
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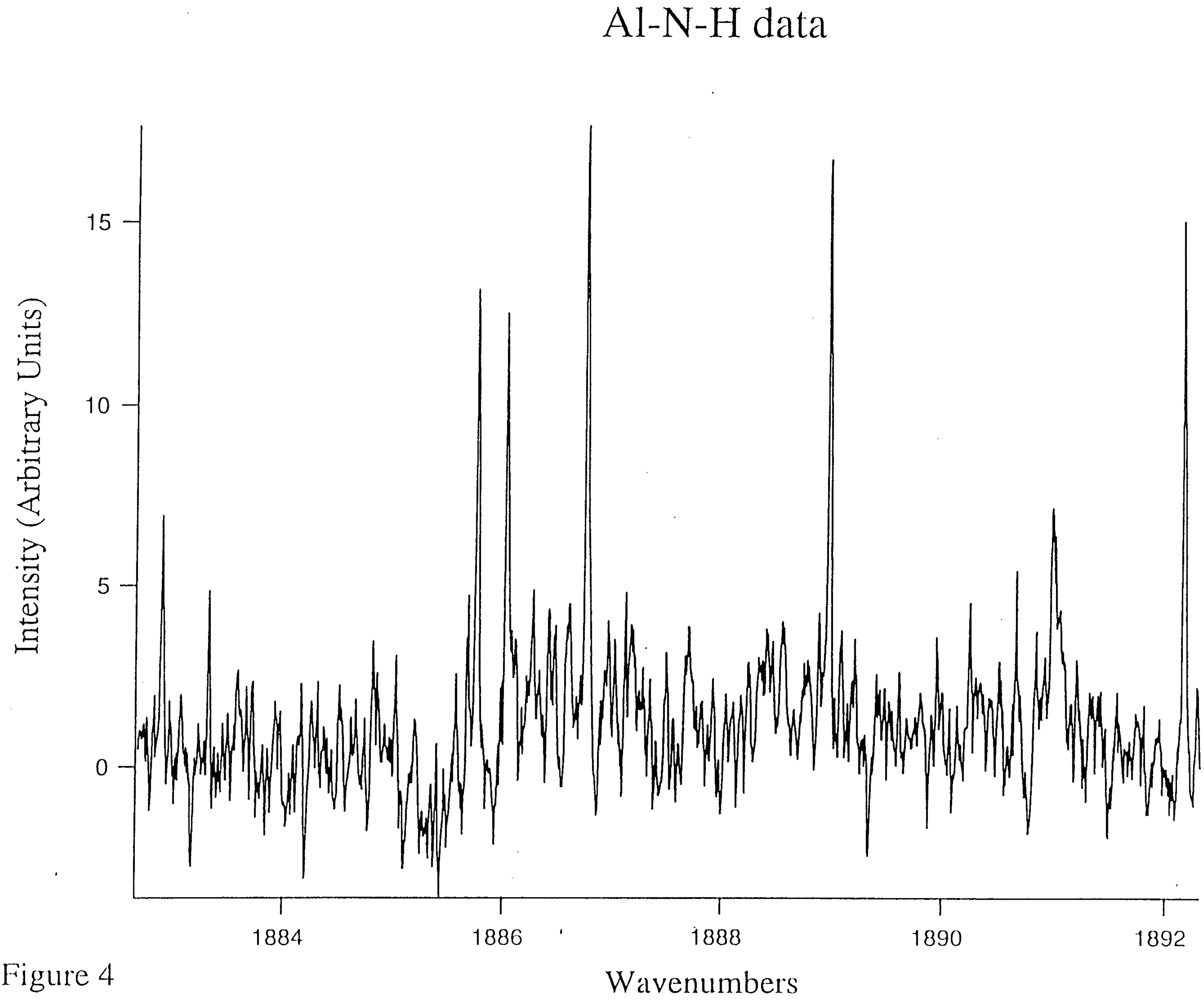
130
120
110
100
2171.5
2172.0
2172.5
2173.0
2173.5
Wavenumbers

Figure 3


Al-N-H data
Intensity (Arbitrary Units)
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5
0
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1886
1888
1890
1892
Wavenumbers

Figure 4

High Resolution Cavity Ringdown Spectrometer

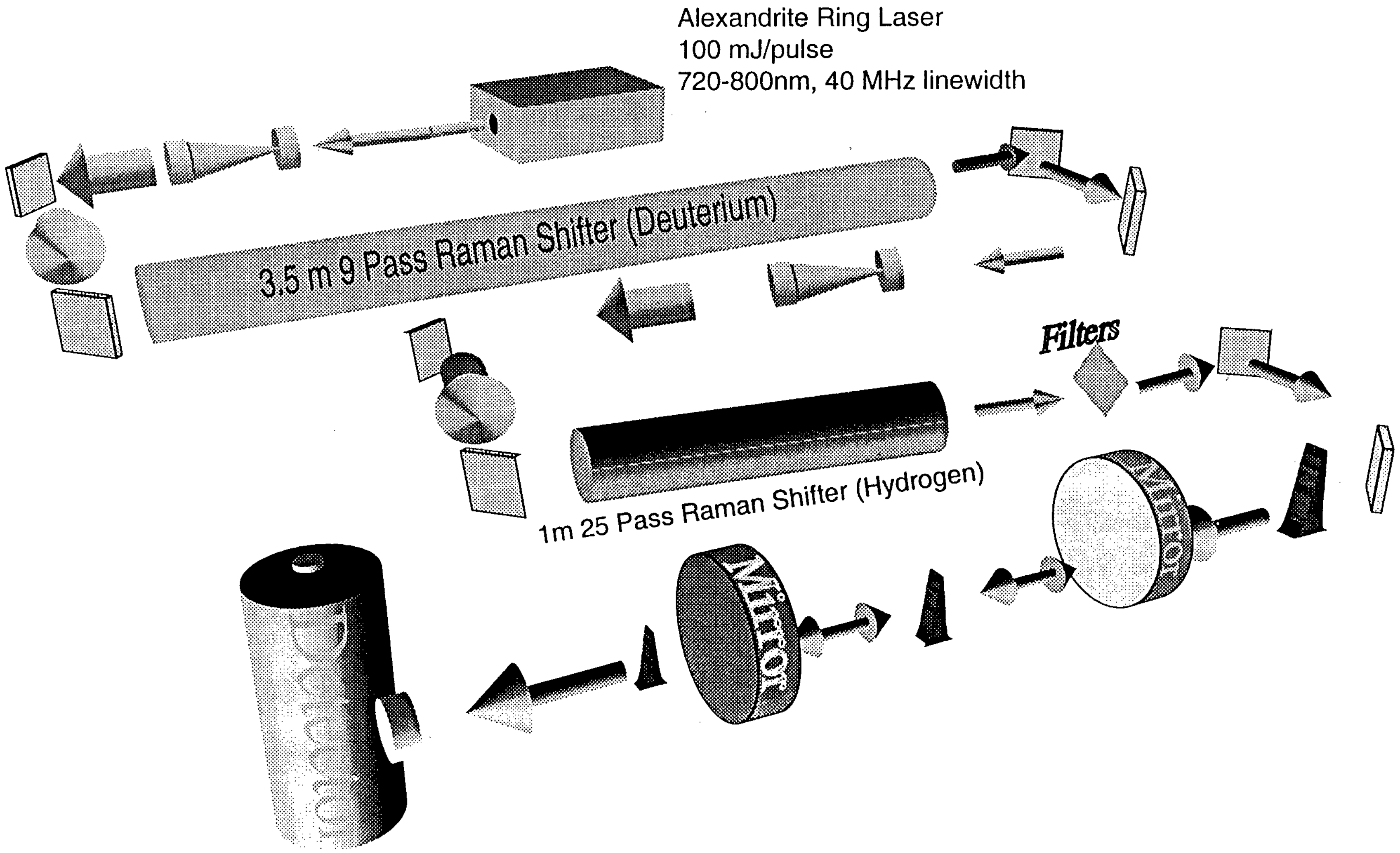

Figure 5

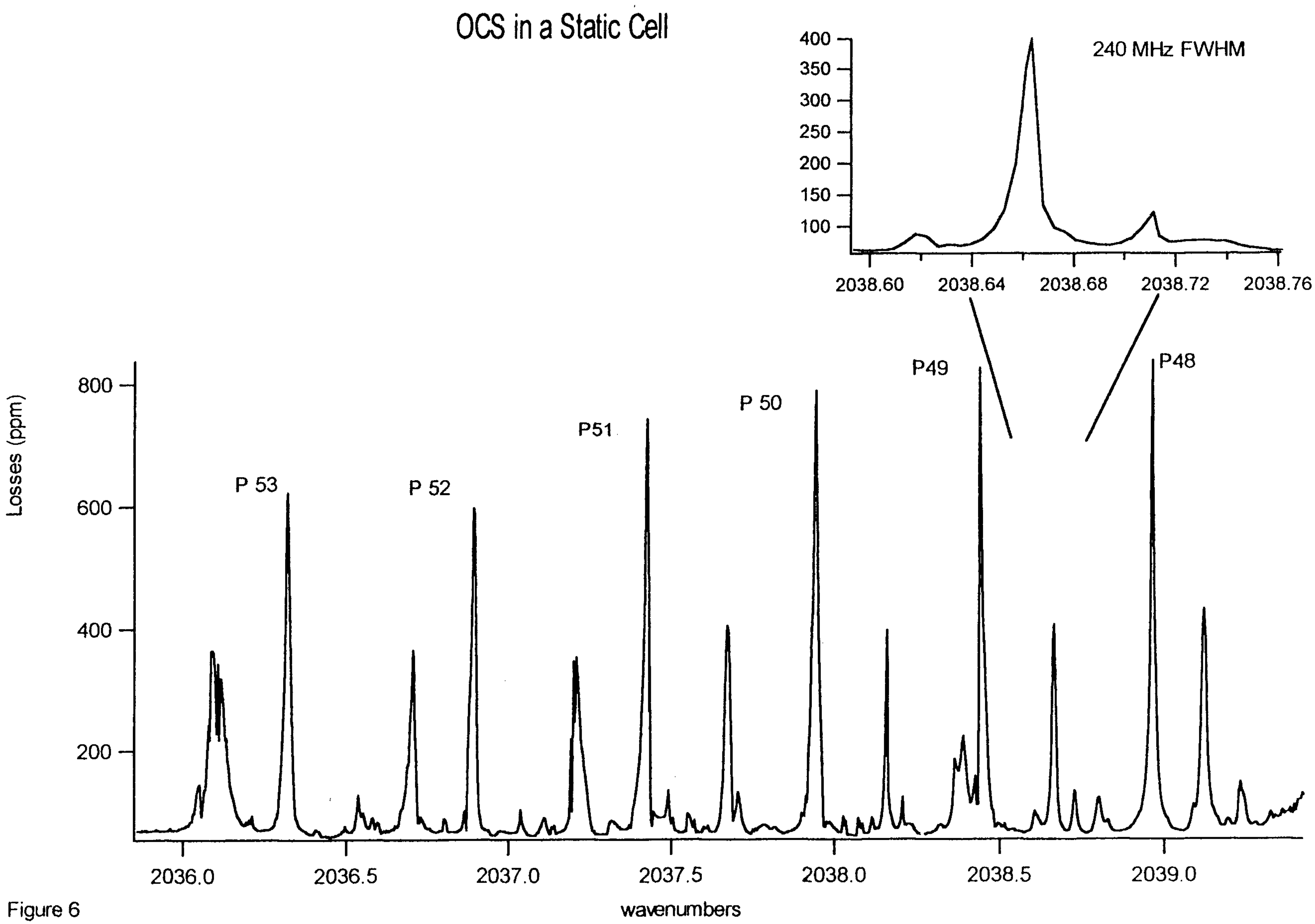
OCS in a Static Cell
240 MHz FWHM
400
350
300
250
200
150
100
2038.60
2038.64
2038.68
2038.72
2038.76
Losses (ppm)
800
600
400
200
P 53
P 52
P51
P 50
P49
P48
2036.0
2036.5
2037.0
2037.5
2038.0
2038.5
2039.0
wavenumbers

Figure 6