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TITLE: COHERENT ANTI-STOKES RAMAN SCATTERING IN BENZENE AND NITROMETHANE SHOCK-COMPRESSED TO 10 GPa

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COHERENT ANTI-STOKES RAMAN SCATTERING IN BENZENE AND NITROMETHANE SHOCK-COMPRESSED TO 10 GPA*

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Abstract

The frequency shifts of the ring-stretching mode of shock-compressed liquid benzene and the CN stretching mode of nitromethane have been measured using coherent anti-Stokes Raman scattering. Shock pressures up to 11 GPa were achieved using a two-stage light gas gun. The frequency shifted Raman signal was generated using single pulse Nd YAG and broadband-type lasers.

PACS numbers 35.80.+s, 42.65.Cq, 78.35.+c

We have shown in previous work [1,2,3,4,5] that coherent optical scattering can be used to study the microscopic nature of shock-compressed molecular systems. In this paper, the results of using Reflected Broad Band Coherent Anti-Stokes Raman Spectroscopy (RBBCARS) to measure the vibrational frequencies of the ring stretching mode of benzene and the CN stretching mode of nitromethane at shock pressures up to 11 GPa are reported.

A schematic of the experimental apparatus is shown in Fig. 1. A two stage light gas gun was used to accelerate a polycarbonate projectile with 11-mm-thick AZ31B magnesium and 2024 aluminum impactors to a desired velocity. The projectile struck an approximately 2.4-mm-thick 304-stainless-steel target plate producing a shock wave which ran forward into a 2.7 to 3.3-mm-thick benzene (or nitromethane) sample. Lower pressures were achieved using previously described techniques. [2,4] Stainless steel was chosen as the target plate because of its ability to retain its reflectivity under shock compression. Reagent grade benzene (Mallinckrodt, Inc.) and commercial grade nitromethane were used. Standard data reduction techniques [6] using published shock-velocity, particle-velocity data [7] were used to determine the state of the shock-compressed samples.

Experiment design was greatly facilitated using the MACRAME one dimensional wave propagation computer code. [8]

The timing sequence for the experiment was determined by the incoming projectile. The interupted signals from 3 HeNe laser/photodiode detector assemblies located in the barrel approximately 2.8, 1.2, and 0.7 m from the target, in conjunction with appropriate time delays, triggered the laser flash lamps approximately 300 μs prior to projectile impact. A time-of-arrival pin activated just after the shock entered the liquid and another time delay served to Q-switch the laser approximately when the shock wave arrived at the quartz window.

Coherent anti-Stokes Raman Scattering [4,9,10] was used to measure the shift in vibrational frequency. Figure 2 shows the OMA recorded signals for the ring-stretching mode of benzene at pressures from ambient to 10.6 GPa. Up to pressures of approximately 10 GPa, the spectral data show no evidence for the presence behind the shock of decomposition product species [11] (at concentrations above the 10-20% level) having Raman active transitions within the vibrational frequency region spanned by the gain profile of the dye (i.e., between 800 and 1100 cm^{-1}.

The spectrum shown for 10.6 GPa is different than those obtained for lower pressures, in that preliminary results using a standard analyses for CARS data with a noresonant background contribution [9] suggest more than one spectral line will be required to fit the data. Previous work [12, 13] suggests chemical reaction occurs for benzene at pressures approaching 12 to 13 GPa. Results of analysis will be presented in a future publication.

The RBBCARS spectra for the CN stretching mode of nitromethane at pressures from ambient to 7.6 GPa are shown in Fig. 3. At 5 GPa the existence of the CN mode at microsecond times after shocking implies that decomposition of the nitromethane has not occurred as has been observed in static high temperature/high pressure studies. [14] Measurements are presently being extended to higher pressures where nitromethane is thought to be reactive after very short shock run distances. [12,15] Preliminary analysis indicate that the frequency shifts are comparable to those obtained using spontaneous Raman scattering for nitromethane shocked to pressures of 5 GPa. [15,16]

These experiments are part of an effort directed toward understanding the dynamic behavior and energy transfer mechanisms in shock-compressed molecular systems. With shock-wave techniques, materials can be rapidly pulsed in a well controlled laboratory environment to extreme pressures and temperatures. Under such conditions, intramolecular and intermolecular forces will have changed considerably and nonequilibrium conditions may be expected. Chemical behavior may be dramatically different from that expected on the basis of either extrapolations from ambient conditions or thermodynamic equiorium phenomena. In those experiments we have measured the change of the vibrational frequency of the ring stretch mode of benzene and the CN stretch mode of nitromethane for the shock-compressed liquids.

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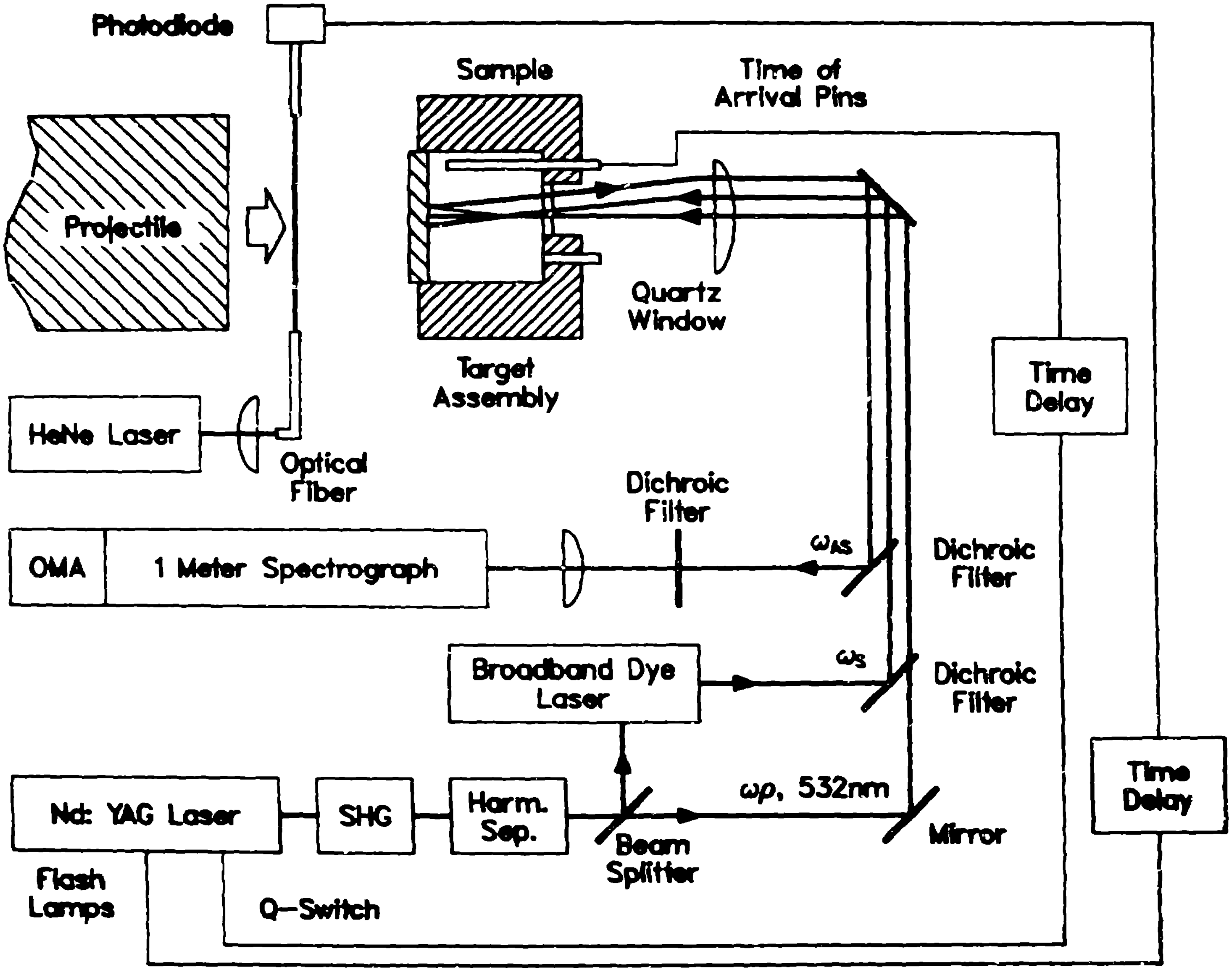
FIG. 1. Schematic representation of the reflected broadband coherent anti-Stokes Raman scattering experiment. SHG - second harmonic generator; Harm. Sep.-harmonic separator; OMA - optical multichannel analyzer; Sample - benzene and nitromethane.

FIG. 2. RBBCARS spectra of ambient and shock-compressed benzene. The ambient peak position of the benzene is 992 cm^{-1}. Shock pressure are indicated and the wavelength calibration is with respect to the 253.652 - nm Hg line in second order.

FIG. 3. RBBCARS spectra of ambient and shock-compressed nitromethane. The ambient peak position of the nitromethane is 921 cm^{-1}. Shock pressures are indicated and wavelength calibration is with respect to the 253.652 - nm Hg line in second order are indicated.


Photodiode
Sample
Time of Arrival Pins
Projectile
Quartz Window
Target Assembly
Time Delay
HeNe Laser
Optical Fiber
Dichroic Filter
OMA
1 Meter Spectrograph
ω_{AS}
Dichroic Filter
Broadband Dye Laser
ω_S
Dichroic Filter
Time Delay
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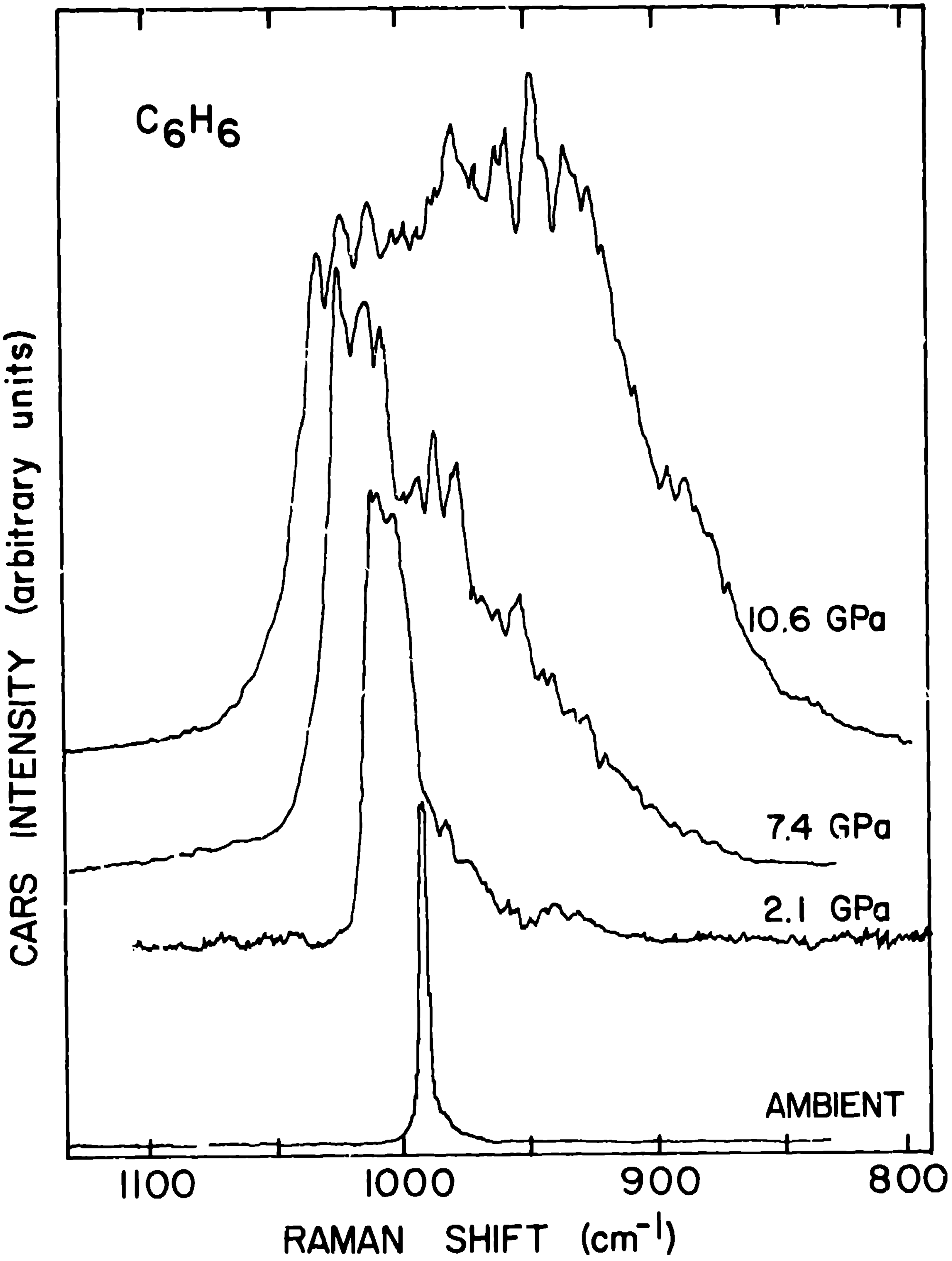
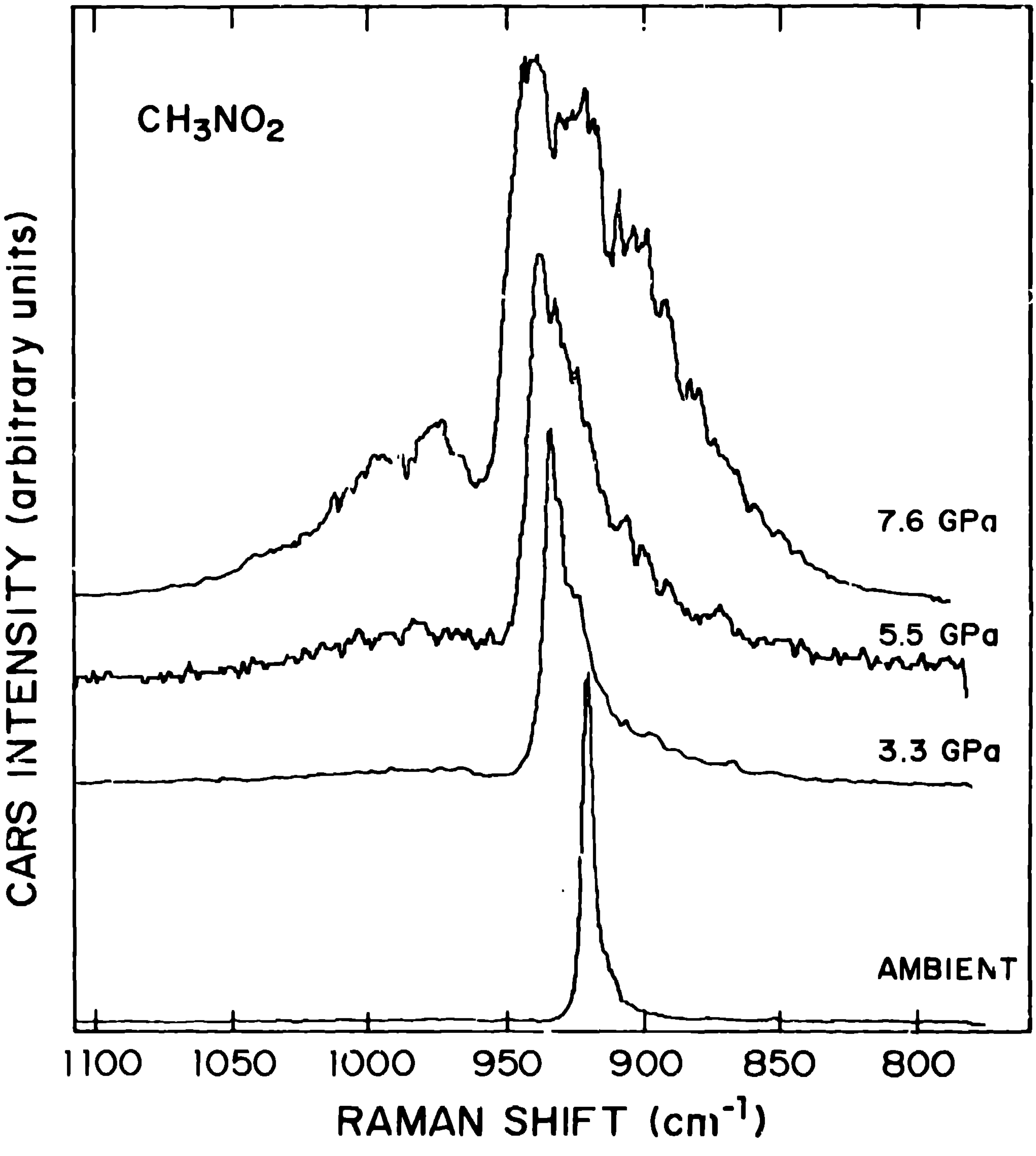
SHG
Harm. Sep.
ω_p, 532nm
Beam Splitter
Mirror
Flash Lamps
Q-Switch


C$_6$H$_6$
CARS INTENSITY (arbitrary units)
10.6 GPa
7.4 GPa
2.1 GPa
AMBIENT
1100
1000
900
800
RAMAN SHIFT (cm^{-1})

CHM-VG-8196



CH_3NO_2
CARS INTENSITY (arbitrary units)
7.6 GPa
5.5 GPa
3.3 GPa
AMBIENT
1100
1050
1000
950
900
850
800
RAMAN SHIFT (cm^{-1})

CHM-VG-8159