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TITLE COHERENT ANTI-STOKES RAMAN SCATTERING (CARS) DETECTION OR HOT ATOM REACTION PRODUCT INTERNAL ENERGY DISTRIBUTIONS

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COHERENT ANTI-STOKES RAMAN SCATTERING (CARS) DETECTION OF HOT ATOM REACTION PRODUCT INTERNAL ENERGY DISTRIBUTIONS*

by

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ABSTRACT

Coherent anti-Stokes Raman spectroscopy (CARS) is being utilized to investigate the rovibrational energy distributions produced by reactive and nonreactive collisions of translationally hot atoms with simple molecules. Translationally hot H atoms are produced by ArF laser photolysis of HBr. Using CARS we have monitored, in a state-specific and time-resolved manner, rotational excitation of HBr (v=0), vibrational excitation of HBr and H_2, rovibrational excitation of H_2 produced by the reaction H + HBr → H_2 + Br, and Br atom production by photolysis of HBr.

*Work performed under the auspices of the US DOE.

INTRODUCTION

Recently, a new experimental technique has been developed for the investigation of the collision dynamics associated with translationally "hot" atoms and radicals.[1-5] The technique makes use of a short-pulse ($\lesssim$20 ns) uv excimer laser to photolyze simple molecules. As molecular bonds break, the fragments-to-be repel each other and acquire large amounts of translational energy (up to a few eV), if excitation of the internal degrees of freedom of the fragments is negligible. The availability of these high-energy excimer lasers makes it possible to generate large quantities of hot atoms and radicals. When a translationally hot atom (or radical) collides with a molecule, a number of interesting kinetic events can take place, including rovibrational excitation of the "target" molecule and chemical reactions that do not occur appreciably under room temperature thermal equilibrium conditions. Infrared fluorescence detection techniques have been applied to investigate the translation-to-vibration (T-V) energy transfer process between hot H atoms and simple di- and triatomic molecules (e.g. HCl, HBr, CO, CO_2, N_2O).[1-5] Since this detection technique relies on vibrational spontaneous emission, it cannot provide information concerning rotational excitation of the ground vibrational state and, in addition, is limited in its applicability to the study of molecules with infrared active vibrational modes (which excludes all homonuclear diatomics). One experimental technique that overcomes some of the shortcomings of infrared detection is coherent anti-Stokes Raman spectroscopy (CARS). CARS is a sensitive, highly state-specific and non-intrusive probe of the internal energy states of a molecule, with outstanding time-resolution capability. It is especially useful for examining kinetic processes involving homonuclear diatomics. A description of the theory and applications (through 1977) of CARS can be found in the review article by Tolles et al.[5] Examples of more recent applications of CARS include temperature and species concentration measurements in combustion gases,[7] measurements of H_2 rovibrational state distributions in a low pressure plasma,[8] C_2 fragment detection in the uv multiphoton dissociation of benzene,[9] nascent O_2 internal energy distributions from O_3 uv photolysis,[10] and Cl atom detection in a microwave discharge.[11]

The main purpose of this first report is to demonstrate the applicability of CARS to the investigation of the chemical kinetics associated with hot atoms or radicals. The emphasis here is on the rovibrational energy distributions produced by reactive and non-reactive collisions of hot H atoms with simple molecules. We will illustrate, with several examples pertaining to the ArF laser photolysis of HBr, the wealth of time-resolved state-specific information that CARS is capable of providing. Detailed analysis of the kinetic processes occurring in simple uv photolysis systems will be the subject of future reports.

PRELIMINARY CONSIDERATIONS

Absorption of ArF laser light by HBr produces translationally hot H atoms with a quantum yield of unity in the following manner:

$$\begin{aligned} HBr \xrightarrow[0.85]{193\ nm} \; & H + Br\ (^2P_{3/2}) + \Delta E = 2.63\ eV \\ \xrightarrow[0.15]{} \; & H + Br\ (^2P_{1/2}) + \Delta E = 2.17\ eV \end{aligned}$$

Conservation of linear momentum dictates that the H atom receives ~99% of the available excess energy. Recent experiments[2] indicate that ~15% of the Br atoms are produced in the lowest excited state ($^2P_{1/2}$, hereafter referred to as Br^*). Since the available energy is much larger than the average room temperature translational and rovibrational energies (~0.04 eV each) of the absorbing HBr molecules, the initial velocity of the H atoms is a very narrow distribution centered at ~2.2×10^6 cm/sec (or ~2.0×10^6 cm/sec for the Br^* channel), which is approximately 9 times faster than the average H atom velocity at room temperature and is equivalent to a translational temperature of ~20,000 K. For the first collision that each H atom participates in, the collision velocity is well known. However, the H atom velocity distribution will broaden and shift to lower values as translation-to-translation (T-T'), translation-to-rotation (T-R), and translation-to-vibration (T-V) energy transfer collisions take place.[12] In addition, chemical and exchange reactions which proceed at a rate that depends on the relative collision velocity will also affect the velocity distribution of the H atoms. In the case of uv photolysis of HBr, the H atoms produced will react readily with undissociated HBr:

$$\begin{aligned} H + HBr &\xrightarrow{k} H_2 + Br \qquad \Delta H = -16.7\ \text{kcal/mole} \\ &\xrightarrow{k^*} H_2 + Br^* \qquad \Delta H = -6.2\ \text{kcal/mole.} \end{aligned}$$

The reaction exothermicities[13] shown above apply to H atoms at 300 K. Infrared chemiluminescence experiments by Bly et al.[14] have determined the branching ratio k^*/k to be $\lesssim 0.013$ at 300 K. The reaction rate constant k at 300 K[15] is 1-2 × 10^5 $torr^{-1}$ sec^{-1}. The rovibrational energy distribution in the H_2 reaction product has not, to our knowledge, been reported in the literature. The reaction rate for hot H atoms with HBr will depend on how the reaction cross section varies with relative collision velocity. Potential energy surface trajectory calculations by White et al.[16] suggest a significant increase in the reaction cross section for the hot H atoms considered here. It is conceivable that the large excess translational energy of H atoms produced by uv photolysis will influence both the Br^*/Br branching ratio and the H_2 rovibration energy distribution of the H + HBr chemical reaction.

EXPERIMENTAL

In a CARS experiment signals are produced at an anti-Stokes frequency (ω_{as}) by four-wave mixing[6] induced by the presence of frequencies ω_p and ω_s, the pump and Stokes frequencies, respectively, where $\omega_{as} = 2\omega_p - \omega_s$. The signals are greatly enhanced when the difference between the pump and Stokes frequencies corresponds to a molecular or atomic resonance, and are proportional to the square of the population difference between the two levels involved in each transition.

The experimental apparatus used here is similar to one used previously[10] and is shown schematically in Fig. 1. The pump frequency (~20 mJ, ~1 cm^{-1} line width) is provided by splitting off 30% of the output beam of a frequency-doubled commercial Nd:YAG laser (Quanta-Ray DCR-2A). The remaining 70% excites a commercial dye laser (Quanta-Ray PDL-1) whose output (~1 to 2 mJ, ~0.5 cm^{-1} line width) is used as the tunable Stokes frequency. The two beams are expanded in Galilean telescopes and combined collinearly on a dichroic filter after the pump laser is spatially delayed to maximize their temporal overlap. The combined beams are focused to a common point in the sample cell using a 600-mm focal length achromatic lens. After exiting the sample cell, the majority of the pump and Stokes beams' energy is separated from the anti-Stokes beam by a dichroic filter and dumped into a power meter. The anti-Stokes beam is then passed through another dichroic filter, focused into a double 0.1 m monochromator (Instruments, SA DH-10) and detected by a RCA 1P28 photomultiplier tube whose dynode chain was wired for fast response. The signal was processed by a boxcar and ratioed to the energy in the Stokes beam.

CARS spectra are obtained by scanning the frequency difference $\omega_p - \omega_s$ while monitoring the intensity at ω_{as}. The dye laser (Stokes frequency) and monochromator (anti-Stokes frequency) are scanned with synchronously driven stepper motors.

The photodissociation wavelength is provided by a rare-gas-halide excimer laser (Lumonics 861-T) through which the laser gas mix is flowed to provide approximately constant power output. The beam is focused with a Galilean telescope and combined collinearly with the CARS laser beams at a dichroic mirror. In order to prevent photodissociation and subsequent depletion of the excimer laser energy except near the focus of the CARS laser beams where the majority of the CARS signal is produced,[17] the sample cell was constructed in three sections separated by 2-mm apertures. The sections near the Brewster's angle windows are swept clear of reactant gas by a flowing stream of Ar. The center section contains a flow of reactant gas plus the flow of Ar which passes through the apertures. A large overpressure of Ar is dropped across a small needle valve to prevent changes in Ar flow rate with reactant gas pressure in the center section. The total pressure in the center section is measured with a Baratron gauge. Delay times between the excimer laser pulse and the Nd:YAG laser pulse are set by two channels of a digital delay generator (Nanofast 568-702). Jitter between the photolysis pulse ($\lesssim$10 ns) and the CARS probe pulses (4~5 ns) was measured to be less than 10 ns. Thus, this CARS arrangement allows one to examine kinetic processes occurring on a 10-ns time scale.

The reactant gas in these experiments was HBr which was freeze-pumped twice at 77 K to remove residual H_2 and stored in blackened 5-ℓ glass bulbs. The photodissociation wavelength of 193 nm was provided by the ArF excimer. Very slight focusing of the excimer beam was used to obtain a constant ca. 20% dissociation[18] of the HBr per shot. The total flow rate was ca. 0.15 torr-l/s and was found adequate to replace the dissociated or reacted HBr in the photolysis zone between the 10-Hz laser pulses.

RESULTS AND DISCUSSION

We have examined the rotational excitation of HBr(v=0) produced by collisions with translationally hot H atoms produced by ArF excimer laser photodissociation of HBr. Figure 2 shows the CARS spectrum of the v=0 to v=1 Q-branch transitions of HBr before the excimer laser is fired (room temperature rotational distribution) (a), and 0.8 μs after the laser pulse (b). The relative amplitude of (b) has been adjusted so that the height of the largest peak is roughly the same as in (a). The rotational excitation caused by the hot H atoms is clear. By varying the delay time between the CARS probe pulse and the photodissociation pulse one could examine the behavior of each individual rotational state as a function of time.

CARS can also be used to examine vibrational excitation processes initiated by collisions with hot atoms. Figure 3 shows the vibrational excitation of HBr observed 1 μs after ArF photolysis of 2 torr HBr with 0.5 torr Ar. Transitions pertaining to HBr(v=0,1,2) are clearly visible. Higher vibrational levels have not been investigated yet. The data in Fig. 3 suggests vibrational level populations monotonically decreasing with increasing v quantum number. A more detailed analysis of vibrational level populations as a function of time will be the subject of subsequent reports.

As mentioned in the introduction, CARS can be used to investigate rovibrational populations in homonuclear diatomics. Some preliminary results involving the H_2 molecule are described below. We have detected prompt formation of rovibrationally excited H_2 produced by the H + HBr reaction following ArF laser photolysis of HBr. Figure 4 shows a CARS spectrum with peaks belonging to high J states of $H_2(v=0)$ and a sequence of peaks belonging to $H_2(v=1)$ observed 0.5 μs after photolysis of a mixture of 2 torr HBr and 0.5 torr Ar. Note the intensity alternation between odd and even J lines, as expected for ortho- and para-H_2. A Boltzmann analysis of the $H_2(v=1)$ rotational distribution suggests rotational temperatures on the order of 3000 K. The strong feature near 3700 cm^{-1} is due to Br atoms $(^2P_{3/2} \rightarrow {}^2P_{1/2})$. Higher vibrational levels of H_2 have not been investigated yet. Figure 5 shows a CARS spectrum of H_2 observed 2 μs after ArF laser photolysis of a mixture of 0.67 torr H_2, 0.33 torr HBr, and 0.5 torr Ar. The strong feature on the right is the aforementioned Br atom transition. Rovibrational excitation of H_2 under these conditions is most likely due to a direct T-V or exchange process between hot H atoms and H_2 molecules.

As illustrated in Figs. 4 and 5, we have also monitored the production of Br atoms in the ArF laser photolysis of HBr. By fixing the dye laser frequency on the Br atom CARS transition and scanning the delay time we can examine the production and depletion of Br atoms.

SUMMARY

Coherent anti-Stokes spectroscopy was applied to the state-specific and time-resolved investigation of reactive and non-reactive collisional processes involving translationally hot H atoms produced by ArF laser photolysis of HBr. We have demonstrated the capability to examine in great detail the rotational and vibrational state distributions produced by inelastic or reactive collisions between hot H atoms and simple diatomic molecules such as HBr and H_2. We have also demonstrated CARS detection of Br atoms and of rovibrationally excited H_2 produced by the H + HBr reaction for the first time.

In future experiments, rovibrational state distributions produced directly by T-V, T-R, and H-atom exchange and reaction collisions will be carefully examined. Of special interest will be systems involving the H_2 molecule and its isotopic variants.

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17. Given the laser beam parameters in our system, we estimate (as shown in Ref. 5) that >70% of the CARS signal is generated within ~1 cm of the laser focal point

18. A quick estimate of the percent dissociation is obtained by examining the decrease in the HBr non-resonant CARS signal immediately after the photolysis pulse.

FIGURE CAPTIONS

Fig. 1. Schematic of the CARS experimental arrangement.

Fig. 2. CARS spectrum of 0.5 torr HBr plus 0.5 torr Ar before the excimer laser pulse (a), and 0.8 μs after the laser pulse (b). The amplitude of (b) has been adjusted so that the maximum peak height is roughly the same as in (a).

Fig. 3. CARS spectrum obtained 1 μs after ArF photolysis of 1 torr HBr with 0.5 torr Ar showing vibrational excitation of HBr. Transitions corresponding to HBr (v=0,1,2) are indicated.

Fig. 4. CARS spectrum observed 0.5 μs after photolysis of 2.0 torr HBr and 0.5 torr Ar. Transitions corresponding to H_2 (v=0,1) are indicated. The dip and strong feature near 3700 cm^{-1} are due to a Br atom transition.

Fig. 5. CARS spectrum observed 2 μs after the photolysis pulse, with ~70% HBr dissociation. Transitions due to H_2(v=0,1) are indicated. The strong feature on the right is due to a Br atom transition. This spectrum is uncorrected for dye laser pulse energy variation with wavelength.

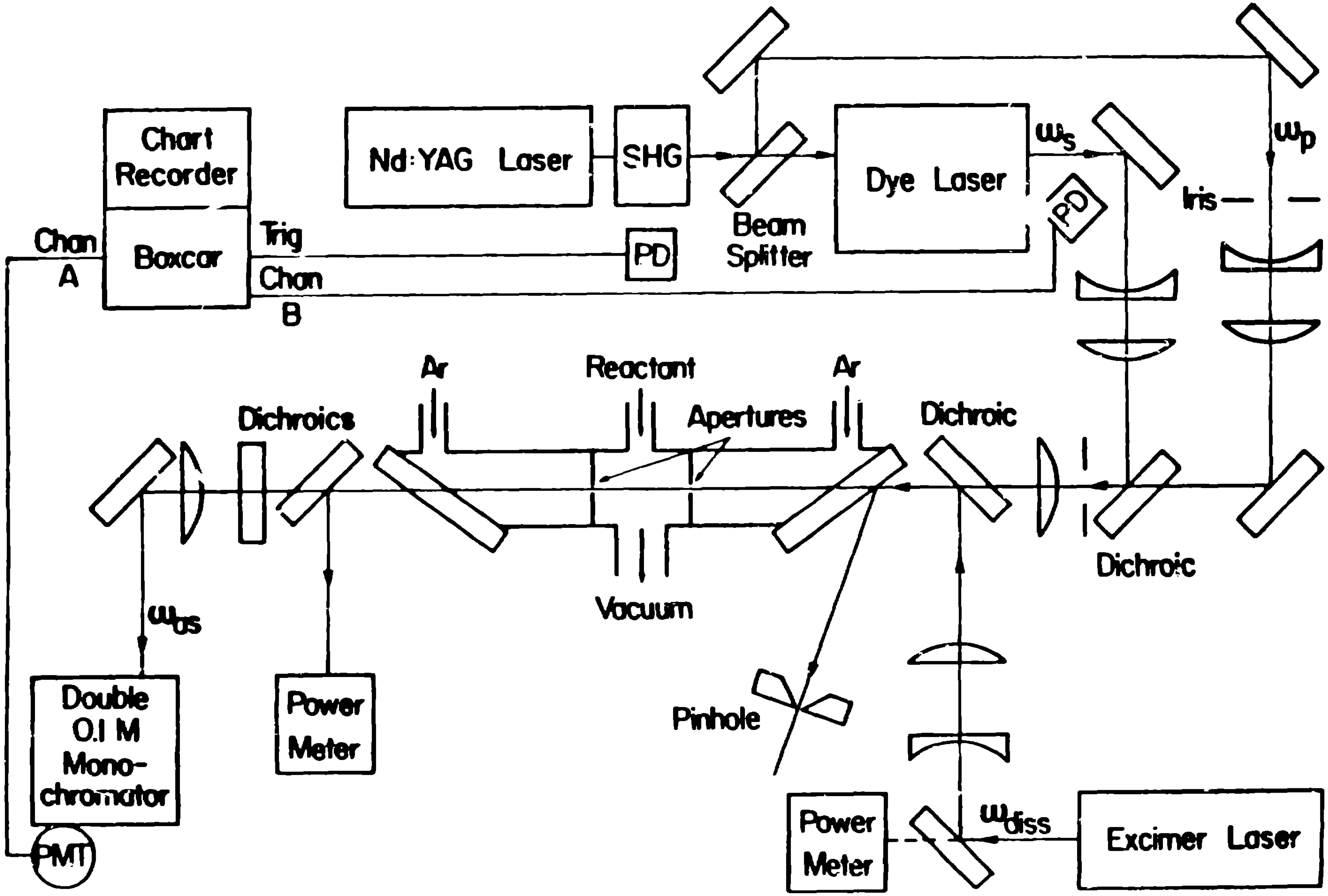


Figure 1

CHM-VG-1568

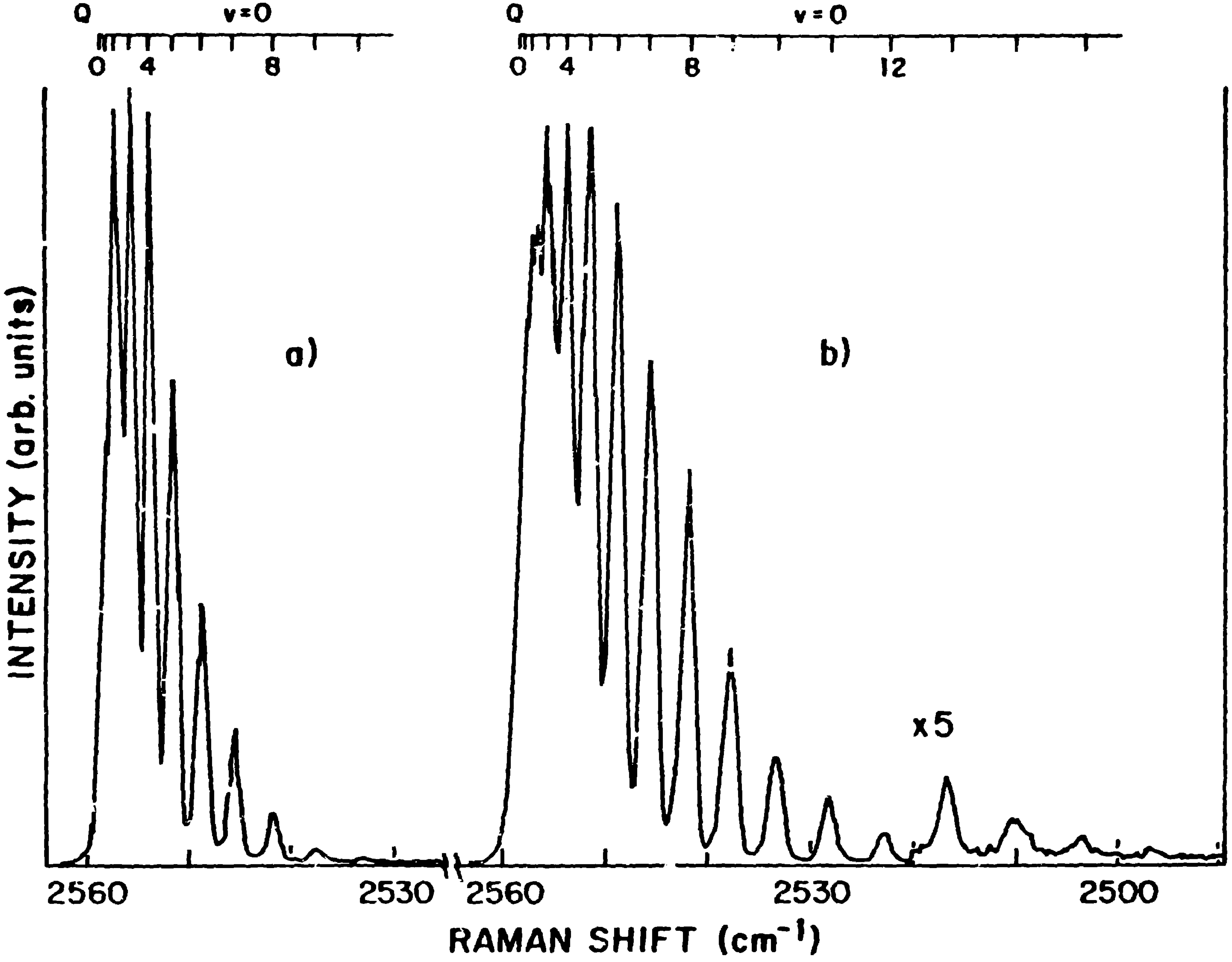


Figure 2

CHM-VG-1565

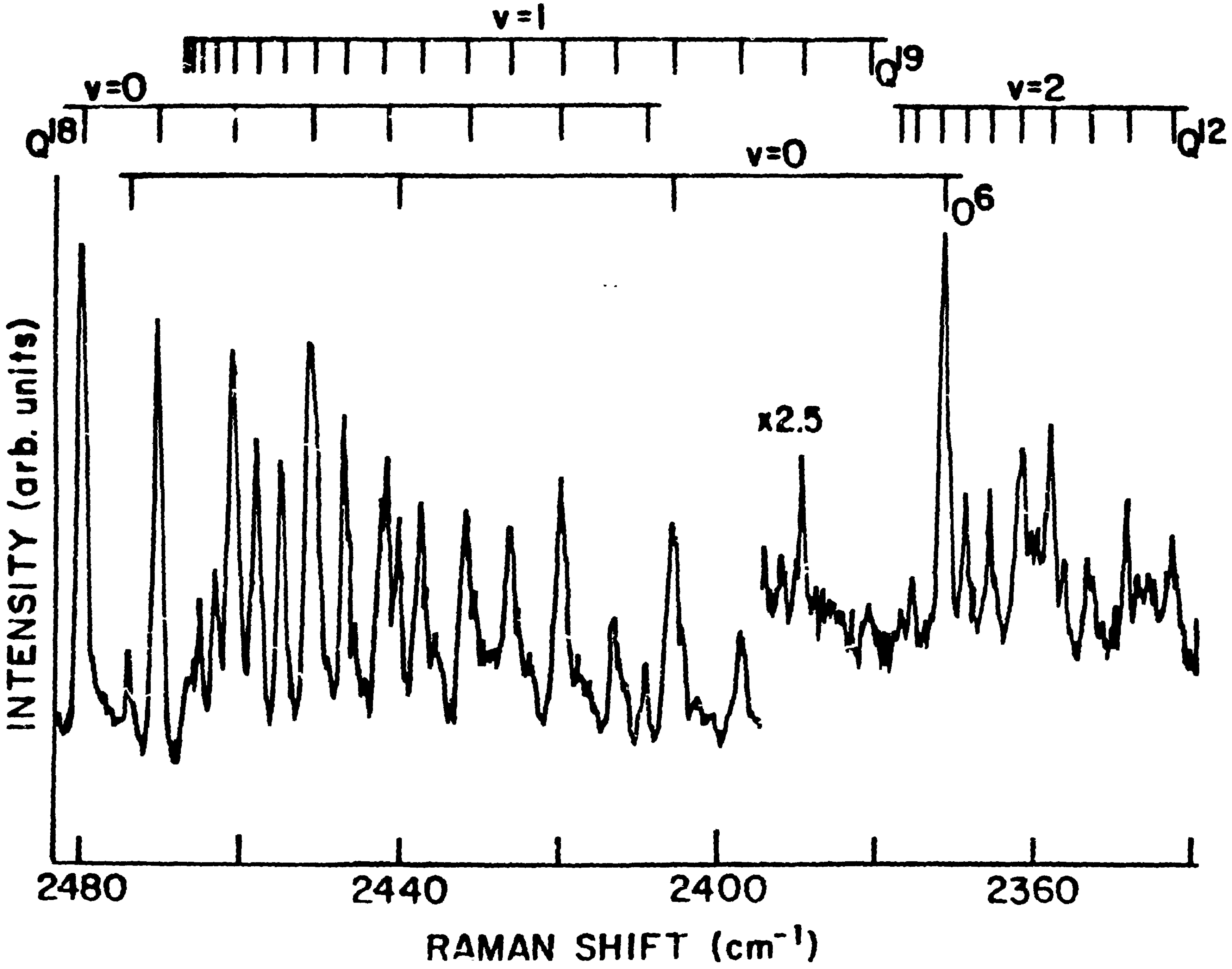
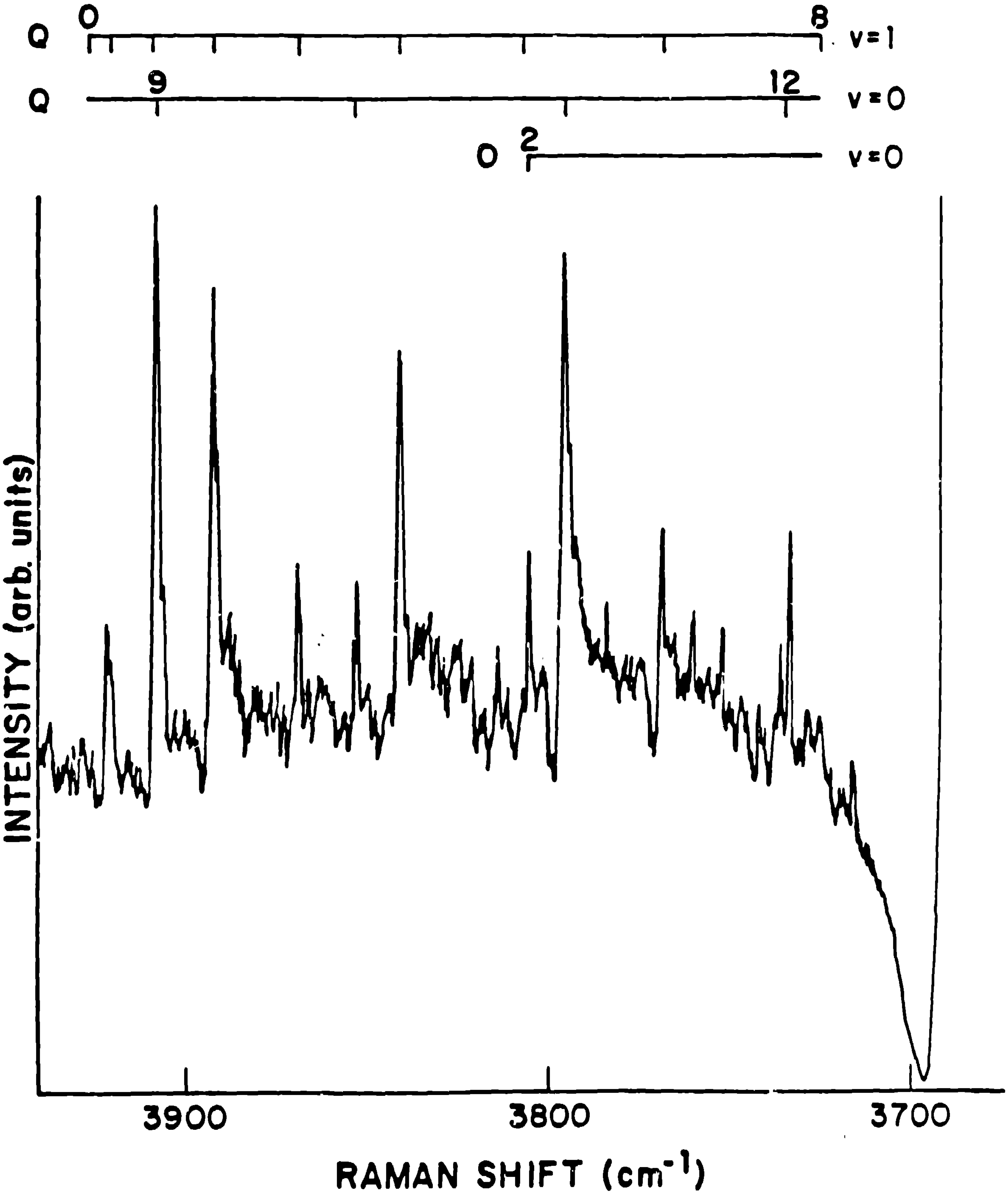


Figure 3

CHM-VG-1569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0
8
v=1
Q
9
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v=0
O
2
v=0
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3900
3800
3700
RAMAN SHIFT (cm^{-1})

Figure 4

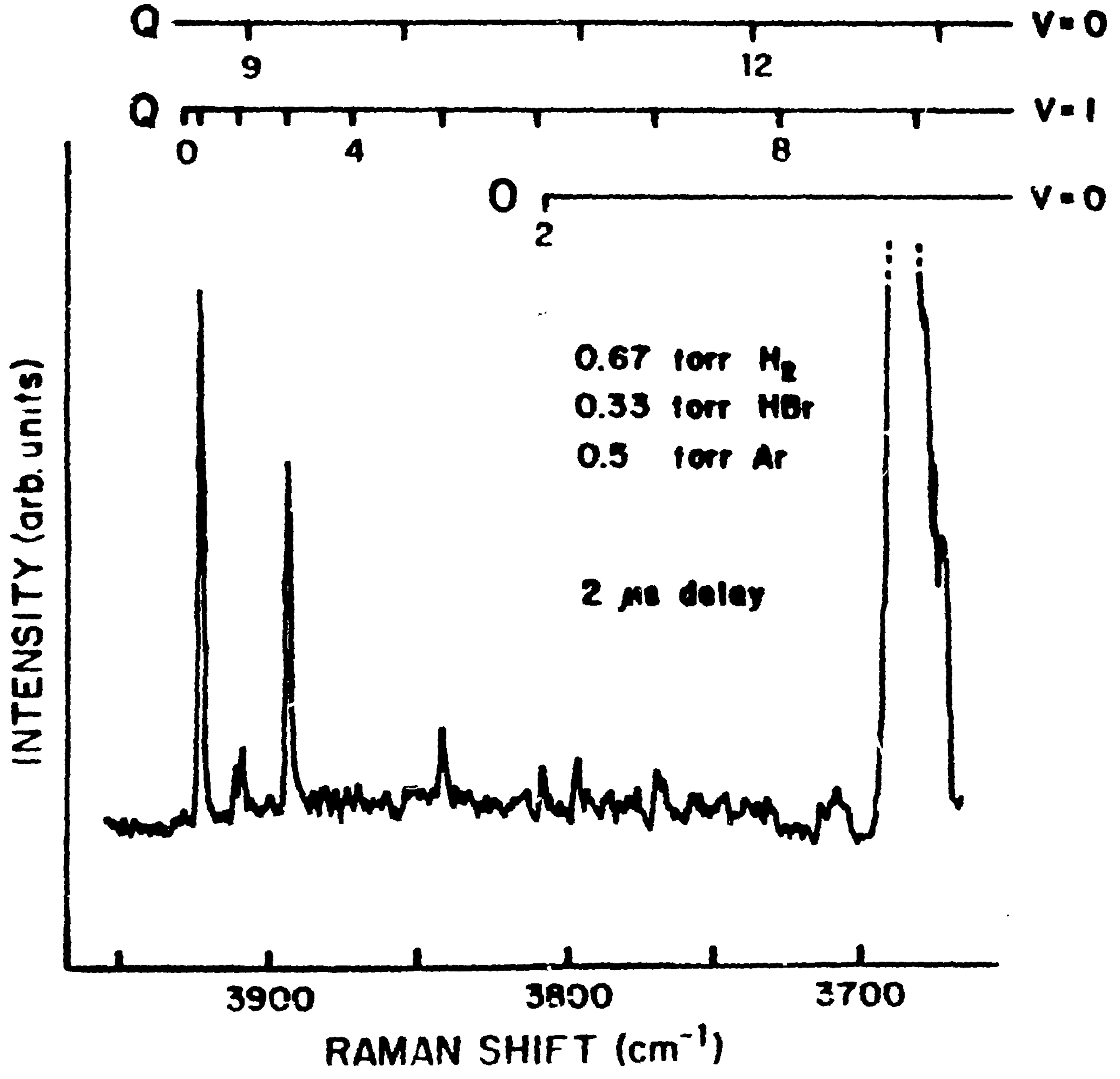

Figure 5

CHM-VG-1579