

the pore diameter, and β is a constant. Values of the parameters D_p and β for some acid media and temperatures are known.⁸ In most cases pore densities fall in the range 10^{10} – 10^{11} pores/cm². This technique allows one to make a well-defined surface. These surfaces of well-defined particle dimensions can then be used to study the SERS enhancement effect as functions of the particle size and the distance between particles.

In conclusion, we have demonstrated that highly-enhanced Raman spectra can be observed from the surfaces of silver deposited in anodic aluminum oxide pores whose oxide layers were partly removed after the deposition of silver. This preparatory method for new SERS-active surfaces may have advantages in that the size of and the distance between Ag particles can be controlled.

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CARS Spectra of HCl, N₂, and C₂H₂ in the Gas Phase

Sun Jong Baek, Joong Hee Kim, Ju Yeon Park, Sungyul Lee[†], and Hong Lae Kim

Department of Chemistry, Kangwon National University, Chuncheon 200-701, Korea

[†]*Department of Chemistry, Kyunghee University, Kyungki-Do 449-701, Korea*

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Coherent anti-Stokes Raman scattering (CARS) spectra of HCl, N₂, and the ν_1 fundamental of C₂H₂ have been measured in the gas phase. The measured spectra show rotational structures which originate from the Q-branch transitions. The spectra have successfully been simulated with proper selection rules, line positions, and relative intensities from room temperature Boltzmann population distributions. The vibration-rotation interaction constant α of HCl in the ground electronic state has been measured from the rotationally resolved CARS spectra which is $\alpha=0.3076$ cm⁻¹. Possibilities of optical pumping and of measuring state specific energy distributions of molecules are discussed.

Introduction

Rovibrational spectra of molecules in the gas phase provide rich information about molecular structures and the dynamics when the spectra can particularly be observed in a chemically changing system. Absorption or Emission of light due to spectroscopic transitions between the rovibrational states in the ground electronic state of the molecules would produce such spectra in the infrared.¹ However, it is not easy to obtain the IR absorption spectra of the molecules in the gas phase because of intrinsically low absorption coefficients of the molecules in this spectral region. Since the

radiative lifetime in the excited rovibrational states are in general long (longer than 1 ms in many cases), it is even more difficult to measure the emission spectra of the molecules in IR.² Moreover, the fact that the blackbody radiation at ambient temperatures peaks in near IR decreases the signal-to-noise in the IR emission spectra. Vibrational Raman spectra may be alternatives to study the molecular structures but the Raman scattering signals from the molecules in the gas phase are too small to be measured in the rotationally resolved spectra. However, with a recent advent of coherent high power lasers, a stimulated Raman scattering technique greatly enhances the signal. Various laser Raman spectro-

scopic techniques have been thus far developed to obtain the rovibrational spectra under high resolution.^{3,4}

Coherent anti-Stokes Raman Scattering (CARS) spectroscopy utilizes a nonlinear property of a medium with an aid of the intense laser light at a frequency of the ordinary Raman Stokes scattering frequency.^{5,6} With the two laser frequencies tuned to the pump (ω_1) and the Stokes frequency (ω_2), the strong CARS signal at $2\omega_1 - \omega_2$ can be generated when the three wavevectors are phase-matched. Since dispersion of these three waves are not large in the gaseous medium, the phase matching condition can be relatively easily fulfilled compared to the one in the condensed media. The CARS spectra of some hydrocarbons and oxygen containing molecules in the flame have been measured, from which combustion processes have directly been studied.^{7,8} Recently, the rotationally resolved CARS spectra of O_2 have been measured from photodissociation of ozone in the gas phase and the dynamics of the photodissociation has been studied in detail.⁹

In this report, the rotationally resolved CARS spectra of homonuclear, heteronuclear diatomics, N_2 and HCl , and a linear polyatomic molecule, C_2H_2 in the gas phase are presented. The rotational population distributions are identified by using proper selection rules and room temperature Boltzmann distributions. Measured spectroscopic constants are found to be in good agreement with the ones previously measured in IR and Microwave.

Experiment

CARS spectra have been measured in a static cell which is a cube made of stainless steel with two windows on each side. The cell has been evacuated with a mechanical pump whose pressure is about 10^{-3} Torr and then a few Torr of the gaseous sample has been filled at ambient temperatures.

The pump laser, ω_1 is the second harmonic of an Nd : YAG laser (532 nm, green) from Lumonics (YM-800) of which about 10% of the beam is splitted from a quartz plate and directly introduced into the sample cell. The light at the Stokes frequency is an output of a dye laser (Lumonics HD-500) pumped by the rest of the green, which is tuned to the molecular rovibrational transition frequencies ($\omega_1 - \omega_2$). Pulse energies of the pump and the dye laser output are typically about 20 mJ/pulse and 8 mJ/pulse, respectively. Since the dye laser output is delayed about 6 ns from the green, the green light is optically delayed to obtain correct temporal overlap and to obtain the maximum CARS signal. The two laser beams are colinearly propagated and focused with a lens ($f=200$ mm) at the center of the cell. Since the CARS signal strength depends on the sample length, various lenses of different focal lengths have been employed. Another lens on the opposite side of the cell collimates the green, the dye laser output, and the CARS signal. The three beams are separated through a prism and the CARS signal is detected with a photodiode through a proper filter. A schematic diagram of the experimental apparatus is in Figure 1. As expected, the CARS signal strength depends on the square of the pump laser power and linearly on the laser power of the Stokes frequency.

HCl is purchased from Aldrich, N_2 and C_2H_2 are from

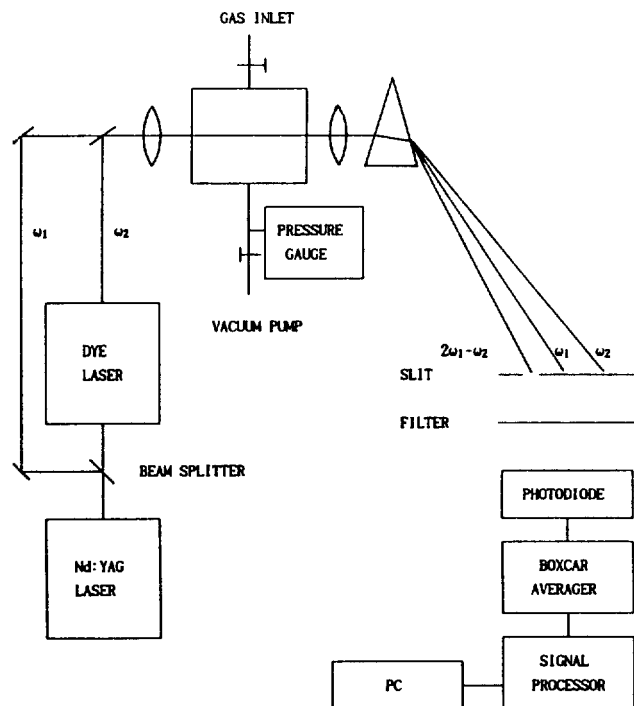


Figure 1. A schematic diagram of the experimental apparatus.

Kwaksan Sanso Co. in Korea and used without further purification.

Results and Discussion

CARS spectra of HCl , N_2 , and the ν_1 fundamental of C_2H_2 are presented in Figure 2 and Figure 3. As seen in the figures, the spectra reveal rotational structures which originate from the Q-branch transitions of different J values. The ordinary Raman selection rules for linear molecules are $\Delta J=0$ (Q-branch), ± 2 (O,S-branch) but the O- and S-branch transitions are not observed in the spectra.¹⁰ In Figure 2, simulated spectra of N_2 are shown under the measured spectra with sticks and with convolution of the Gaussian laser lineshape of about 0.6 cm^{-1} linewidth. As shown in the figures, the measured spectra of N_2 , HCl , and C_2H_2 can be well reproduced by the simulation.

The CARS signal strength for a low density gaseous sample is given by

$$P_{CARS}(\omega) = (8\pi^2 c^2 \omega_{CARS}^3 / 15 \omega_1 \omega_2^3) (\Delta N)^2 (d\sigma/d\Omega)^2 I_1^2 I_2^2 [1/(2\omega^2 + \Gamma^2)]$$

where ΔN is the population difference between ground and excited molecular states and $d\sigma/d\Omega$ is the ordinary differential Raman scattering cross sections.¹¹ Thus the relative intensities of the rotational transitions are proportional to the square of ΔN and $d\sigma/d\Omega$, which are given by

$$I(J) \propto (\Delta N)^2 (d\sigma/d\Omega)^2 \propto [S_J \exp(-B_0 J(J+1)/kT)]^2$$

where

$$S_J = (2J+1) + \frac{J(J+1)(2J+1)}{(2J-1)(2J+3)}$$

for the Q-branch Raman transitions.¹² The spectral line posi-

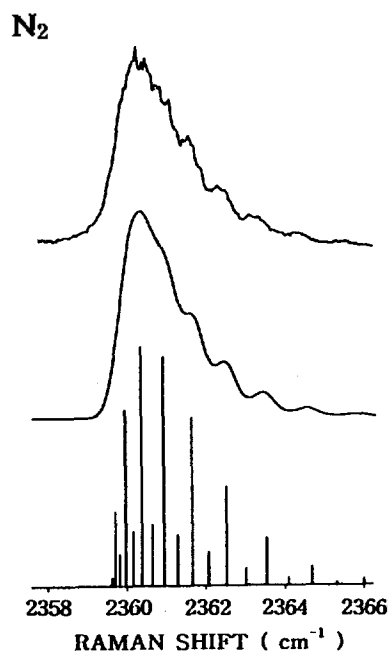


Figure 2. Experimental and simulated CARS spectra of N_2 at room temperature. Partially resolved Q-branch rotational transitions are shown.

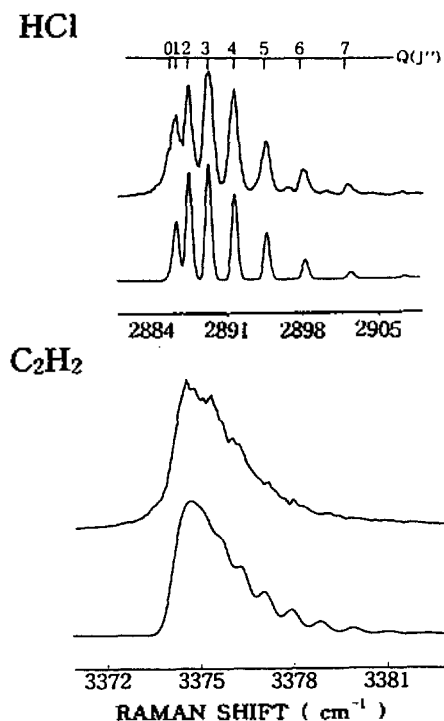


Figure 3. Experimental and simulated CARS spectra of HCl and the ν_1 fundamental of C_2H_2 at room temperature (see text). Q-branch rotational transitions are assigned on top of the HCL spectra.

tions are calculated by term values of the rotational energy levels in the upper and lower vibrational states, which are given by

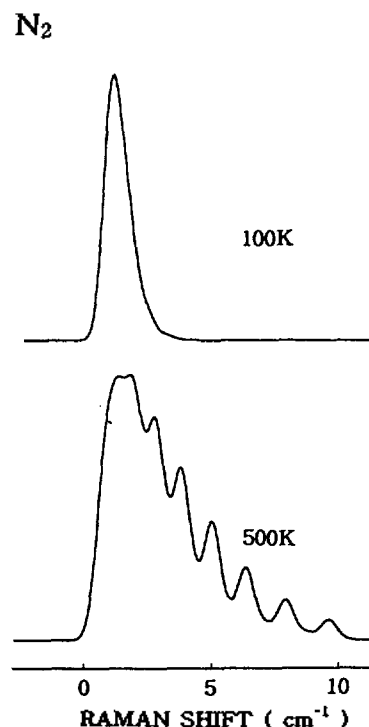


Figure 4. Simulated spectra of N_2 at 100 K and 500 K. The band origin is at 0 cm^{-1} .

$$\Delta\omega = \omega_1 - \omega_2 = (B_1 - B_0)J(J+1) - (D_1 - D_0)J^2(J+1)^2$$

where B and D are the rotational and centrifugal distortion constants, respectively.

The CARS spectra of N_2 is well reproduced by the simulation with the convolution of the Gaussian laser linewidth of 0.55 cm^{-1} at 300 K as represented in Figure 2. The rotational constants are adapted from the literature.¹³ In the simulated spectra, the intensity variation of 1:4 is clearly shown for the odd: even J values according to the nuclear spin statistical weights for homonuclear diatomics of the nuclear spin of $I=1$. This intensity variation is also shown in the spectra of C_2H_2 as 1:9 for the even: odd J values since C_2H_2 has an inversion center with two nuclei of $I=1/2$ (Figure 3). The alternating intensity variation in the even and odd J 's helps resolving the rotational transitions under our spectral resolution of 0.6 cm^{-1} . In the case of HCl, the rotational transitions are completely resolved as shown in the figure. The assignments of each rotational transition are on top of the spectra. From the line positions, the vibration-rotation interaction constant has been measured from the plot $\Delta\omega$ vs $J(J+1)$ as $\alpha = 0.3076\text{ cm}^{-1}$ since $B_1 - B_0 = -\alpha$ neglecting the centrifugal distortion. The measured α is in good agreement with the value measured from the high resolution IR spectra.¹⁴

Studies of chemical reaction dynamics require measuring the rovibrational distribution of the reaction products among quantum states.¹⁵ Various high resolution spectroscopic techniques have been employed such as laser induced fluorescence, resonance enhanced multiphoton ionization, and so forth to measure the distribution. However, it is not easy to measure such a distribution of the products if the products

are specially homonuclear diatomic molecules whose absorption frequencies do not lie in the easily accessible spectral region. In Figure 4, the simulated CARS spectra of N₂ at two different rotational temperatures are presented. The spectra show distinct shapes for different rotational temperatures from which the rotational population distributions can be deduced. As shown in the figure, the CARS technique can serve as a sensitive measure of the rovibrational distribution of the molecules of interest in the ground electronic states. In addition to the precise energy distribution of the products, the initial states of the reactants should be specified to study chemical dynamics in detail. The stimulated Raman scattering can pump the molecules in the desired rovibrational states by tuning the Stokes frequency. Thus the initial states of the reactants can be prepared as well as identified in this process. In our laboratory, various chemical and photochemical reaction dynamics have been studied by this technique.

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Synthesis of Diamond-Like Carbon Films on a TiO₂ Substrate by DC-Discharge Plasma Enhanced Chemical Vapor Deposition

Su-Jin Ku, Changmin Kim, and Jong-Gi Jee*

Department of Chemistry, College of Natural Sciences, Kyungpook National University, Taegu 702-701, Korea

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A diamond-like carbon (DLC) film was produced on a TiO₂ substrate using a plasma enhance chemical vapor deposition (PECVD) method. The CH₄-H₂ plasma was produced by applying 400 V DC. The DLC film with the best crystalline structure was obtained when the concentration of CH₄ in H₂ was 0.75 percent by volume and total pressure was 40 torr. The presence of the diamond structure was confirmed by Raman spectroscopy, X-ray diffraction, and scanning electron microscopy methods. It was found that the diluting gas H₂ played an important role in producing a DLC film using a PECVD method.

Introduction

The hard or diamond-like carbon films have attracted a rapidly growing interest in the past few years because of their unique properties. Their characteristic properties are¹⁻³ high electrical resistivity of the order of 10³-10¹² Ωcm, extreme hardness, high optical transparency over a wide spectral range, especially in IR region, chemical inertness to both acids and alkalis, and a high refractive index.

Diamond-like carbon (DLC) films are metastable amor-

phous materials. They can be synthesised by various methods such as ion beam deposition (IBD),⁴ sputtering,⁵ chemical vapor deposition (CVD),⁶ and *rf*- or *dc*-plasma CVD methods.⁷ These methods employ a variety of carbon bearing solid or gaseous source materials.⁸ The gas-phase synthesis of diamond has clear advantages over the high-pressure and high-temperature method. It is possible to grow the film on large area substrates and highly pure diamond-like carbon can be obtained. DLC films contain *sp*³-, *sp*²- and even *sp*¹ coordinated carbon atoms and sometimes have medium range order. Depending on the precursor materials, many of these films contain a significant amount of hydrogen from

*To whom correspondences should be addressed