Laser absorption spectroscopy using a molecular beam

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Infrared absorptions spectroscopy has been performed with the laser radiation propagating perpendicular to the molecular beam from a multiple-tube collimator source. A 1.3-MHz linewidth (HWHM) has been observed in NH_3 and $^{13}CH_3F$ absorption.

Although lasers give highly monochromatic radiation the resolution of laser spectroscopy is limited by Doppler broadening of absorption lines. The Lamb dip technique provides a powerful method to avoid this broadening. However, since the saturation of molecular transitions is required, the Lamb dip method cannot be applied when the laser radiation is weak or when the transition moment of the absorption is small. In this paper we report an alternative method to increase the resolution, that is, the use of a molecular beam. By using a molecular beam which is perpendicular to the direction of propagation of a laser beam we could reduce the Doppler width considerably. An experiment using a molecular beam technique has already been reported in the optical region by Youmans, Hackel, and Ezekiel[1] who detected fluorescence for an iodine beam.

In this work we employed a multiple-tube collimator[2-4] as the molecular beam source to achieve low divergence and high intensity. Since the number of molecules in the beam is high this technique enables us to observe absorption and should be widely applicable to many molecules.

A schematic diagram of the apparatus is shown in Fig. 1. The laser lines used are $P(13)$ of N_2O and $P(32)$ of CO_2 in the 9.4-μ region for the $aQ(8,7)$ transition of NH_3 and $R(4,3)$ of $^{13}CH_3F$, respectively. The laser frequency was swept by applying a linear ramp from the oscilloscope to the piezoelectric translator which supports the laser mirror. The laser cavity is 2 m long and the frequency could be swept for 75 MHz, covering one laser mode. The laser beam has a diameter of about 5 mm, and an output power of about 100 mW was used for spectroscopy. No attempt was made to stabilize the laser while sweeping.

The molecular beam apparatus is a high-vacuum chamber 25 cm in diameter and 120 cm long. It is pumped by a 3-in. diffusion pump and a liquid-nitrogen trap 8 cm above the gas collimators. The background pressure in the chamber during the observation is 2×10^{-6} Torr or less, depending on the flow rate of the gas. Multiple-tube gas beam collimators which consist of a bundle of tubes 0.18 cm long with 5 μ radii act as the molecular beam source. The source is 2 cm long and 0.5 cm wide. There are five such sources placed 15 cm apart along the path of the laser radiation, so that the total absorption length is 10 cm. The glass multiple-tube collimators (Bendix Corporation) have a transmission of 40%. The collimators are attached by epoxy to brass blocks which are connected with copper tubing to the gas handling system outside the vacuum chamber. The flow rate of the gas is controlled by a needle valve and the pressure behind the source is monitored by a Hasting thermocouple gauge.

The laser beam propagates 2 cm above the gas collimators and between two Stark plates which are separated by 0.85 cm. The Stark plates are used for Stark modulation to increase the sensitivity. Square-wave fields of 400 and 30 V/cm were provided for the NH_3 and $^{13}CH_3F$ experiments, respectively. The laser signal was detected by a Pb-Sn-Te detector and was synchronously processed by a phase-sensitive detector. A time constant of 300 msec was used in the detection. The observed absorption lines for NH_3 at different source pressures are shown in Fig. 2. The frequency widths of the absorption lines are estimated from the ratio of the line width to the width of the laser mode and are also calibrated by the Stark shift of the absorption line. The smallest width, 1.3 MHz (HWHM), is found in the case of the lowest source pressure, 10^{-2} Torr. This is a reduction of a factor of 35 from the room-temperature Doppler width which implies that the beam from the gas tube collimators must have a divergence, $\theta_{1/2}$, of about 2.5°. Assuming that the lead zirconate titanate (PZT) drive is linear with voltage, we find the NH_3 absorption line center to be +8 MHz from the center of the laser mode. This agrees with the result of +7.6 MHz from a two-photon Lamb dip measurement.[5] The $R(4,3)$ line of $^{13}CH_3F$ appeared about 25 MHz from the center of the laser mode of $P(32)$ CO_2 line. The width of the signal was 1.5 MHz.

The formation of molecular beams by multiple-tube collimators has been discussed extensively by Giordmaine and Wang.[3] For a source pressure for which the mean free path λ is not large compared to the length of

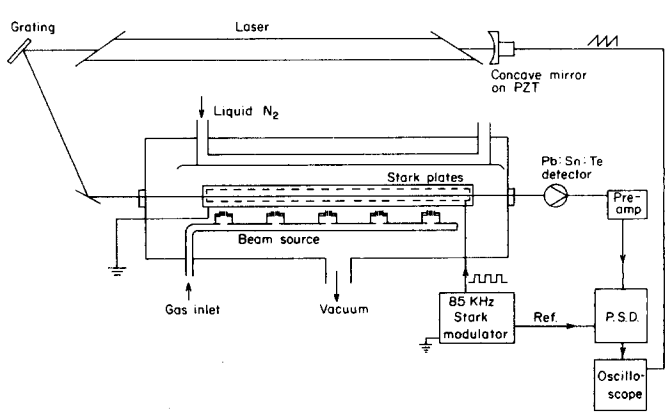

FIG. 1. Apparatus of the laser molecular beam experiment.

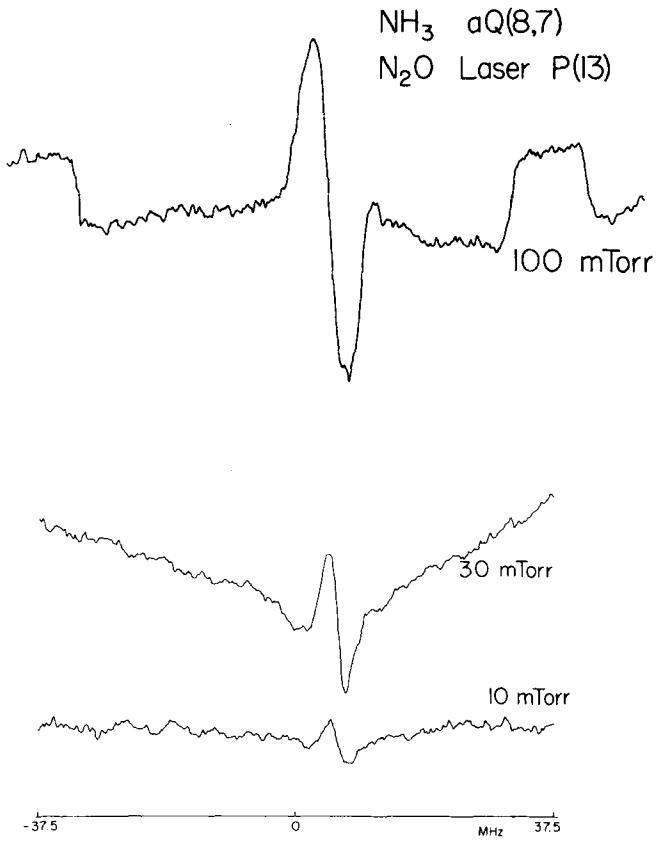

FIG. 2. Absorption lines of the $aQ(8,7)$ NH_3 transition (927.74 cm^{-1}) at various source pressures.

the tube l, but is much larger than the radius of the tube a ($l \gtrsim \lambda \gg a$), intermolecular collisions do not play a significant role. The divergence of the beam emerging from a single collimator tube can be derived from kinetic theory as

$$\theta_{1/2} = 3.78\delta(\pi n_0 a^2/2l)^{1/2}, \quad (1)$$

where δ is the collision diameter of the molecule and n_0 is the density of the gas at the high pressure end. Using $\delta = 4.4$ Å for NH_3,[6] we obtain a divergence of 2.6° and 0.8° for 100 and 10 mTorr, respectively. This is compared with the divergence of 5° and 2.5° estimated from experiment. Previous experiments with collimated beams[3,4] also show the observed divergence to be larger than calculated from Eq. (1). Other factors which might contribute to our linewidth are Stark field inhomogeneity and power broadening. However, the fact that the absorption linewidth increases with the driving pressure behind the source indicates that our line is still Doppler broadened. The width due to power broadening is calculated from $\mu E/h$ to be less than 1.2 MHz.

When the driving pressure behind the tube is 100 mTorr, the density of NH_3 molecules in the beam is calculated to be 1.3×10^{13} molecules cm^{-3}. Using the dimensions of the experimental setup given earlier and the percentage of the NH_3 molecules in the (8, 7) levels (0.3%) at room temperature, we find the number of molecules in the path of the laser beam to be 1.1×10^{10} molecules. The signal-to-noise ratio in Fig. 2 suggests that the number of molecules is several times smaller than this. This may be due to inefficiency of detection. Also, the pressure measurement was not done right behind the beam and the actual pressure may be somewhat lower.

We have demonstrated the possibility of high-resolution spectroscopy using a multiple-tube collimator. This method will be particularly useful for molecules when the Lamb dip technique is not applicable either because of low laser power or small absorption coefficients. The sensitivity of this method can be increased greatly by using a longer path length and a larger vacuum pump.

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[1]D.G. Youmans, L.A. Hackel, and S. Ezekiel, J. Appl. Phys. 44, 2319 (1973).
[2]J.G. King and J.R. Zacharias, Adv. Electron. Electron Phys. 6, 1 (1956).
[3]J.A. Giordmaine and T.C. Wang, J. Appl. Phys. 31, 463 (1960).
[4]G.R. Hanes, J. Appl. Phys. 31, 2171 (1960).
[5]S.M. Freund and T. Oka (private communication).
[6]C.H. Townes and A. Schawlow, *Microwave Spectroscropy* (McGraw-Hill, New York, 1956).