Observation of Infrared-Microwave Two-Photon Transitions in NH_3

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An infrared-microwave two-photon absorption is observed in $^{15}NH_3$. A tunable frequency of microwave radiation is "added" to a fixed frequency of laser radiation utilizing the nonlinearity of the molecular absorption. This method will be useful for high-resolution infrared spectroscopy and for experiments which use laser radiation for pumping molecular energy levels.

Recently, several experiments have been reported in which molecules are pumped with infrared radiation from a CO_2 or N_2O laser.[1-5] The limiting feature of such experiments is that it is necessary to rely on coincidences between the laser frequency and the frequency of the molecular absorption to at least within the Doppler half-width, which is of the order of 40 MHz. The Stark effect has been used[1] to tune the molecular absorption line to the laser line, but this method has the drawback that the absorption line splits into M components under the applied high electric field. In this paper, we report the observation of infrared-microwave two-photon absorption in which a tunable frequency of microwave radiation is "added" to a fixed frequency of laser radiation utilizing the nonlinearity of the molecular absorption; we therefore make the laser, in effect, tunable about the original laser frequency.

The energy diagram for the two-photon absorption is given in Fig. 1. The transition moment for the process is[6,7]

$$(\mu E)_{1\text{-}3} = \langle 1|\mu_p E_m|2\rangle\langle 2|\mu_v E_l|3\rangle/2h\Delta\nu, \qquad (1)$$

where μ_p and μ_v are the permanent dipole moment and the vibrational transition moment of the molecule, E_m and E_l are the electric field of the microwave and the laser radiation, respectively, and $\Delta\nu$ is the difference between the laser frequency and the frequency of the molecular transition (see Fig. 1). It is assumed in deriving Eq. (1) that the two radiations are both linearly polarized in the same direction. It is seen from Eq. (1) that a two-photon transition is weaker than a normal vibrational transition by a factor of $|\langle 1|\mu_p E_m|2\rangle/2h\Delta\nu|^2$. If microwave radiation of sufficiently high-power density (large E_m) is used, this factor is not very small,

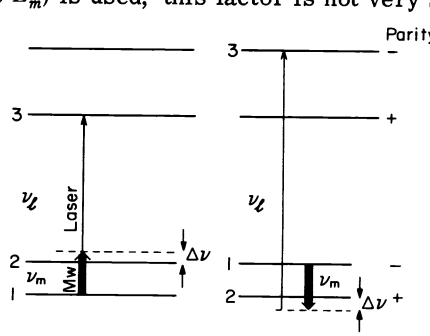

FIG. 1. Energy-level schemes for infrared-microwave two-photon transitions.

even for relatively large $\Delta\nu$. Such two-photon absorption processes have already been observed by using two microwave frequencies with the molecule $(CH_2)_2O$, in which $\Delta\nu \sim 100$ MHz,[8] and with CD_3CN and PF_3, in which $\Delta\nu \sim 8000$ MHz.[7]

The apparatus used in the present experiment is shown in Fig. 2. The laser consisted of a water-cooled 1.8-m gain cell with a concave mirror of radius 5 m at one end and a plane grating blazed at 10 μm at the other end. The laser was tuned to individual vibration-rotation lines of N_2O or CO_2 by adjusting the angle of the grating. The laser light was passed through a 1-m absorption cell, containing $^{15}NH_3$ at a pressure of between 10 mTorr and 1 Torr, and was detected by a Ge:Au detector. The absorption cell was sealed by two 1-mm-thick NaCl windows. The high-power microwave radiation (20 W at 23 GHz) was generated by a floating drift tube klystron (Elliott 12 TFK2) and coupled into the absorption cell by a 3-dB directional coupler. The matching of the microwave circuit was done by an E-H tuner at the end of the cell. It was found that the Ge:Au infrared detector was also sensitive to the microwave power reflected from the absorption cell; therefore a cutoff filter was placed in front of the detector. For the purpose of lock-in detection the microwave power was modulated by a 30-Hz chopper; this also made the video detection much easier.

The observed absorption of the $P(15)$ line of the N_2O laser due to the two-photon process in $^{15}NH_3$ is shown in Fig. 3. The frequency of the infrared transition $\nu_2[{}^qQ_-(4,4)]$ is about 300 MHz higher than the frequency of the laser line.[9] This difference requires that the microwave frequency for the two-photon transition be about 300 MHz higher than the frequency of the (4, 4) inversion transition, which is 23 046.10 MHz.[10] The value of $\langle 1|\mu_p E_m|2\rangle/h$ is of the order of 60 MHz for the microwave power used in the experiment; therefore, a strong absorption was observed.

Figure 3(a) shows an oscilloscope trace of the signal obtained by video detection. The higher-frequency square wave of the Fig. 3(a) corresponds to the 120-Hz chopping of the laser light which was done for the purpose of oscilloscope display (the chopper for this is not shown in Fig. 2). The lower-frequency square wave corresponds to the 30-Hz on-off

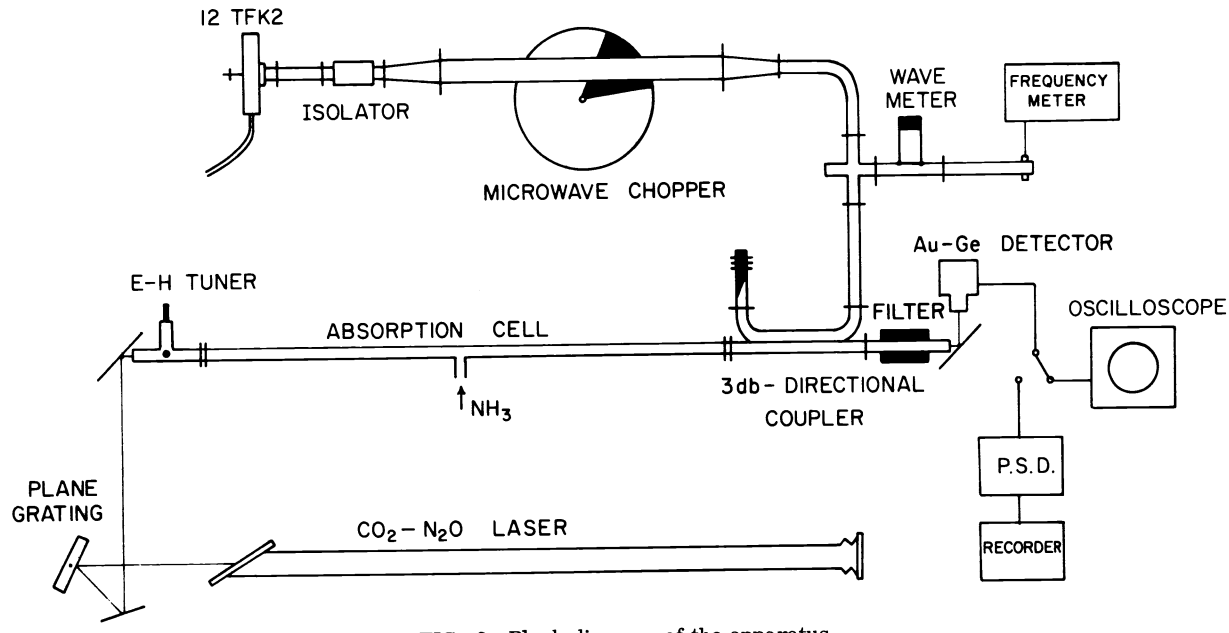

FIG. 2. Block diagram of the apparatus.

switching of the microwave power. It is seen that about 60% of the laser power was absorbed by the two-photon transition in $^{15}NH_3$ gas when the pressure was 150 mTorr. The signal increased with ammonia pressure in the low-pressure region, reached a maximum, and then decreased with further pressure increase. The decrease in the high-pressure region is due to the fact that major portion of the laser light was absorbed by the tail of pressure-broadened single-photon transition. The magnitude of the absorption, and the pressure dependence of the signal, agreed with that expected from a Lorentzian lineshape, if the transition moment of Eq. (1) and an appropriate pressure-broadening parameter are used (see Refs. 7 and 8).

Figure 3(b) shows a typical signal from a phase-sensitive detector. The microwave frequency at the maximum of the two-photon absorption given in the Fig. 3(b) is 23 305 MHz which means $\Delta\nu = 259$ MHz; this value changes considerably depending on the adjustment of the laser. Also by using a different mode of the laser a two-photon absorption was observed for which the microwave frequency was about 80 MHz higher than the one shown in Fig. 3(b) which means $\Delta\nu = 340$ MHz. This latter value agrees better with the value of $\Delta\nu$ determined by Stark laser spectroscopy.[9] It should be possible to remove the uncertainty of the laser frequency by using the inverse-Lamb dip technique[11] and thereby to measure $\Delta\nu$ with a precision of the order of 1 MHz. The ob-

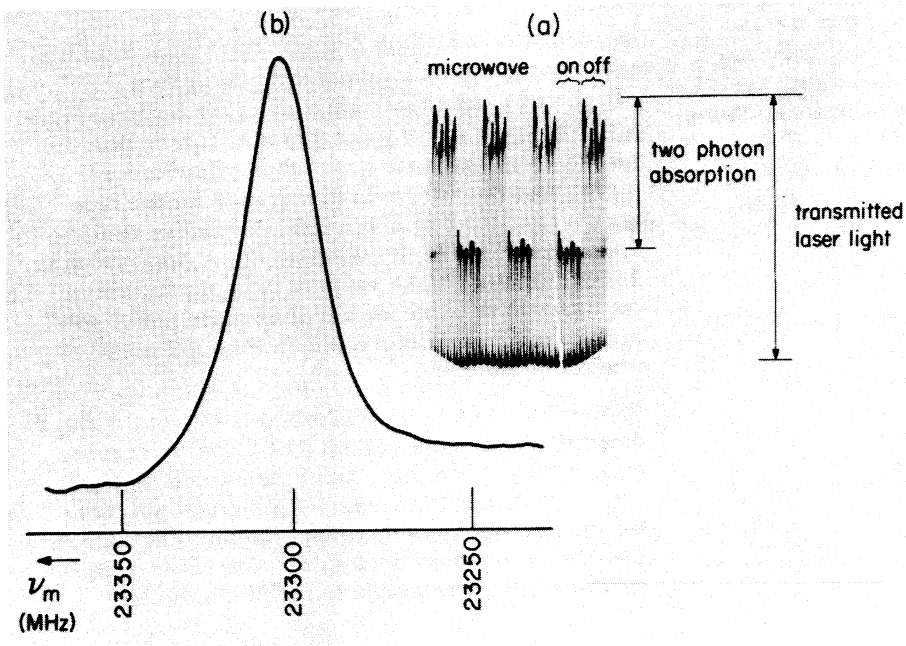

FIG. 3. Observed signals of the infrared-microwave two-photon transitions. (a) Oscilloscope trace showing the two-photon transition obtained by video detection with the following experimental conditions: The laser line was the $P(15)$ line of N_2O laser. The microwave frequency was 23305 MHz, and the pressure of the $^{15}NH_3$ gas was 150 mTorr. When the microwave power was on, about 60% of the laser light was absorbed. (b) Recorder trace showing the two-photon transition obtained by the phase sensitive detection. The pressure of the $^{15}NH_3$ gas was 150 mTorr. The time constant of the detection was 0.1 sec and the sweep speed was about 3 MHz/sec.

served half-width of the two-photon absorption was appreciably smaller than the Doppler width of 40 MHz.[1] This "narrowing" was probably due to the relatively narrow-banded microwave circuit.

Infrared-microwave two-photon transitions such as that observed in the present paper ought to be useful for high-resolution infrared spectroscopy. By using a more sensitive method of detection and by extending this technique to other lines of the CO_2 and N_2O laser, it ought to be possible to observe all of the infrared transitions of ammonia appearing in the 9—11-μm region. This method has the advantages over Stark laser spectroscopy[9] that the frequencies are measured directly and both sides of an absorption can be covered. This technique could also be useful for an experiment in which a laser is used for pumping.[1-5]

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