Observation of the inverse Lamb dip for infrared-microwave two-photon transitions

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(Received 14 April 1972)

An inverse Lamb dip has been observed for infrared-microwave two-photon transitions in $^{14}NH_3$ and $^{15}NH_3$. The signal was sufficiently strong to be observed on an oscilloscope with a detector time constant of 3 msec. The observations establish a method of measuring differences between laser frequencies and molecular absorption frequencies with high accuracy even if this absorption is outside of the tuning range of the laser lines. A double resonance experiment involving the two-photon inverse Lamb dip has also been conducted.

Most of the observations of an inverse Lamb dip in the infrared and optical regions of spectra have been limited to absorption lines which lie within the tuning range of a laser line.[1] When the absorption line is outside of this range, an electric[2] or magnetic[3] field has been used to tune the spectral lines into resonance. More recently, the inverse Lamb dip has been observed by using pulsed tunable lasers.[4,5] In this letter we report the observation of the inverse Lamb dip for infrared-microwave two-photon transitions. The advantage of this method is that we can measure the frequency of a Lamb dip outside the tuning range of the laser directly and accurately by measuring the microwave frequency.

Since the initial observation of infrared-microwave two-photon transitions,[6] the technique has been used to obtain high-resolution infrared spectra of $^{14}NH_3$ and $^{15}NH_3$.[7] In the experiment, microwave radiation having a tunable frequency is "added" to infrared laser radiation of fixed frequency by using the nonlinearity of a molecular transition process; in effect, we render the laser tunable about the original laser frequency.

An inverse Lamb dip in the absorption is observed when the transition moment of the two-photon transition,

$$(\mu E)_{if} = \langle i|\mu_p\cdot \mathbf{E}_m|m\rangle\langle m|\mu_v\cdot \mathbf{E}_l|f\rangle/2h\Delta\nu, \qquad (1)$$

is on the order of, or greater than, the pressure-broadening $\Delta\nu_P P$. In Eq. (1) $\mathbf{E}_m$ and $\mathbf{E}_l$ represent the electric field of the microwave and the laser radiation, respectively, which are parallel in this experiment, and μ_p and μ_v are the permanent dipole moment (1.467D)[8] and the vibrational transition dipole moment (0.24D),[9] respectively. The letters i, m, and f represent the initial, intermediate, and final molecular states involved in the two-photon transitions, and $\Delta\nu$ is the difference between the frequency of the laser and that of molecular transition (see Fig. 2). With $E_m \simeq 30$ V/cm and $E_l \simeq 100$ V/cm, $(\mu E)_{if}/h$ is on the order of $100/\Delta\nu$ MHz for transitions with high M value (M is the quantum number for the projection of the total angular momentum along the field). Since the pressure-broadening parameter $\Delta\nu_P$ is on the order of 30 MHz/Torr,[8] these electric fields can saturate two-photon transitions with $\Delta\nu \simeq 500$ MHz in ammonia at a pressure, P, of 10 mTorr or lower. The observable $\Delta\nu$ can be increased by simul-

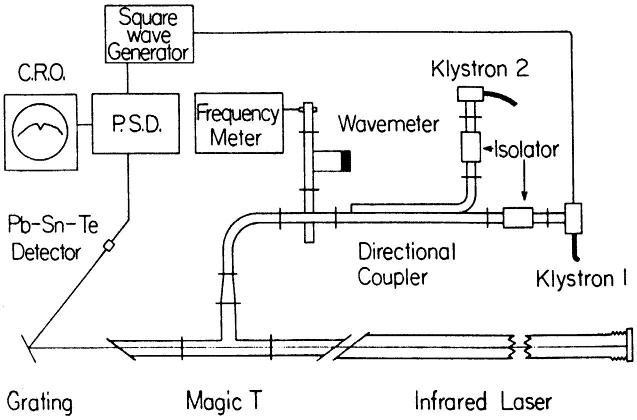

FIG. 1. Block diagram of the apparatus.

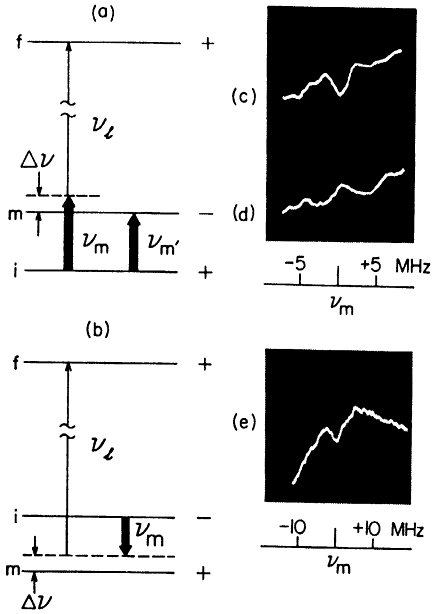

FIG. 2. Energy level diagrams for two-photon transitions, (a) and (b), and the corresponding observed two-photon inverse Lamb dips, (c) and (e). (a) shows the two-photon transition involving the vibrational transition $\nu_2[{}^qQ_-(4,4)]$ in $^{15}NH_3$; the Lamb dip for this transition is shown in (c). When the second microwave radiation ν_m' is applied, the dip splits into a doublet as shown in (d). (b) shows the two-photon transition involving the vibrational transition $\nu_2[{}^qQ_+(5,4)]$ in $^{14}NH_3$; the Lamb dip for this transition is shown in (e).

taneously reducing the gas pressure and increasing the sensitivity of the apparatus.

A block diagram of the apparatus is shown in Fig. 1. The CO_2 or N_2O gas laser consists of a water-cooled 1.8-m gain cell with a concave mirror of 5-m radius at one end, and a plane grating blazed at 10 μm at the other. The absorption cell, which is 30 cm long, is constructed using a commercial magic T and two waveguide extensions (RG-91U) sealed with NaCl windows at the Brewster angle. The use of the oversized waveguide was necessitated by the size of the laser beam. The cell was placed in the laser cavity so that molecules experience infrared radiation travelling in two directions. Since the Doppler broadening is very small for microwave, no care was taken to make the microwave field travel both directions in all parts of the cell. Microwave power of about 1 W, generated by an OKI 24-V11 klystron (klystron 1 in Fig. 1) was introduced into the cell through the E-arm of the magic T. The frequency of the microwave was modulated and swept by applying a 20-kHz square-wave voltage and a low-frequency sawtooth voltage to the reflector of the klystron. Klystron 2 in Fig. 1 is another OKI 24-V11 klystron which was used for a double resonance experiment to be described later. The two-photon inverse Lamb dip was detected by monitoring the output power of the laser using a Pb-Sn-Te detector. The modulated signal was processed by a phase-sensitive detector and displayed on an oscilloscope.

The near coincidence between the $P(15)$ line of the N_2O laser at 925.9824 cm^{-1} and the $\nu_2[{}^qQ_-(4,4)]$ transition of $^{15}NH_3$ ($\Delta\nu \simeq 300$ MHz), and that between the $R(6)$ line of the CO_2 laser at 966.2511 and the $\nu_2[{}^qQ_+(5,4)]$ transition of $^{14}NH_3$ ($\Delta\nu \simeq 500$ MHz) was used in this experiment. The energy level diagrams for these two-photon transitions are shown in Figs. 2(a) and 2(b), respectively, and the observed inverse Lamb dips are shown in Figs. 2(c) and 2(e), respectively. The pressure of the sample was typically 5–20 mTorr, and the time constant of the detection was 3–10 msec. It was not possible to use much longer time constants because of the frequency instability of the laser. This limited the observable value of $\Delta\nu$ to about 500 MHz; however, by using a stabilized laser,[10] longer time constant, and reduced sample pressure, it should be possible to measure transitions with considerably larger $\Delta\nu$ values.

Since the sum of the laser frequency and the microwave frequency $\nu_l + \nu_m$ is defined, tuning the laser frequency appears as a shift of the microwave frequency for the dip. It was possible to alter the microwave frequency over a range of 20 MHz by this tuning. The microwave frequency ν_m for the dip was measured either at the center of this frequency range or at the point of maximum output power of the laser (emission line center); the two measurements agreed well. The value of ν_m, $\Delta\nu$, and the frequency of the infrared transition $\nu = \nu_l + \Delta\nu$ are listed in Table I. $\Delta\nu$ is determined by subtracting the known inversion frequency of NH_3 from ν_m. Although the microwave frequency of the dip ν_m, and thus $\Delta\nu$, can be measured to within 0.1 MHz, the values listed in Table I have uncertainty on the order of 5 MHz because of the uncertainty of ν_l. This uncertainty will be greatly reduced if we stabilize the laser at the Lamb dip using the technique developed by Freed and Javan.[10] The value of $\nu = \nu_l + \Delta\nu$ is calculated using the reported value of the CO_2 laser frequencies.[11] The uncertainty of the listed values of ν are on the order of 25 MHz, which results from the uncertainty in the absolute value of ν_l.[11] The frequency of the N_2O laser was calculated from our results of two-photon spectroscopy[7] and Chang's CO_2 laser frequencies.[11]

The observed half-width at half-maximum of the Lamb dip is approximately 0.8 MHz, which is considerably larger than the broadening expected from collisions or transit time; this is presumably due to frequency instability and inhomogeneity of the laser field.

By applying a second microwave radiation generated by klystron 2 in Fig. 1 at the inversion frequency ν_m' [see Fig. 2(a)], a coherency splitting[12] of the two-photon inverse Lamb dip has been observed as shown in Fig. 2(d). The characteristics of such a splitting are well known for normal microwave double resonance; the

TABLE I. Observed two-photon inverse Lamb dips.

Infrared transition	Laser line	ν_m (MHz)	$\Delta\nu$ (MHz)	ν (MHz)
$^{15}NH_3$; $\nu_2[{}^qQ_-(4,4)]$	N_2O $P(15)$	23 360	+314	27 760 572
$^{14}NH_3$; $\nu_2[{}^qQ_+(5,4)]$	CO_2 $R(6)$	22 095	+558	28 968 039

splitting is equal to the matrix element of $\mu E/h$, i.e., $KM\mu_p E_{m'}/J(J+1)$. Recently such a splitting has been observed for a normal inverse Lamb dip by Takami and Shimoda.[13] An interesting feature of this splitting for a two-photon transition is that the relative intensities of the M components of the split line have a higher power dependence on M than that for a single-photon transition. For a single-photon transition of the Q-branch type, the relative intensity of the M components is proportional to M^2, whereas for a two-photon transition, which involves two Q-branch transitions like those discussed in this letter, it is proportional to M^4. Although the individual M components are not resolved in this experiment because of the inhomogeneity of the microwave field in the cell,[14] the signal shown in Fig. 2(d) is primarily due to the strongest component (i.e., $M=4$).

The two-photon Lamb dip reported in this letter will be a powerful technique for the accurate measurement of the infrared spectra of simple molecules with respect to precisely measured laser frequencies. Using this method and stabilizing the laser at the emission Lamb dip,[10] it will be possible to measure the frequency difference between laser lines and the molecular absorption line to within 0.1 MHz. When the frequencies of the laser lines at the emission Lamb dip are measured accurately by using frequency beating methods,[15] it will be possible to determine the absolute frequency of the infrared transitions with high accuracy.

Compared with other methods of high-resolution laser spectroscopy, this method has an advantage in that we can measure frequency differences easily and accurately by measuring the frequency of added microwave radiation. Furthermore, there is no broadening of the inverse Lamb dip due to dc field inhomogeneity as in the case of Stark or Zeeman tuning, because here we simply "add" frequency rather than shift it by means of a field. Use of rf instead of microwave radiation for molecules with degenerate rotational levels is an obvious extension of this method and is being carried out in our laboratory.

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