Letters to the Editor

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Communications

Infrared-Microwave Double Resonance of NH_3 Using an N_2O Laser

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In 1967 Ronn and Lide[1] reported the first observation of infrared-microwave double resonance in CH_3Br by using a CO_2 laser. This experiment has since been checked by several workers. Although Lemaire *et al.*[2] reported positive results, the experiments conducted by Winnewisser *et al.*[3] and by Flygare and his co-workers[4] gave negative result. More recently Fourier *et al.*[5] reported infrared-microwave double resonance in NH_3 by using a CO_2 laser. They have observed small nonresonant changes of microwave signals (of the order of 0.5%) due to thermal effect of the infrared pumping. In the present paper we report on what we believe to be the first clear-cut observation of infrared-microwave double resonance signal in some three level systems of $^{14}NH_3$ and $^{15}NH_3$.

Recently detailed studies of laser Stark spectroscopy of $^{14}NH_3$ [6] and $^{15}NH_3$ [7] have been made by Shimizu. He discovered near coincidences between the $P(13)$ and the $P(15)$ lines of N_2O laser with the $\nu_2[^qQ_-(8,7)]$ transition of $^{14}NH_3$ and the $\nu_2[^qQ_-(4,4)]$ transition of $^{15}NH_3$, respectively. These coincidences are used in the present work. An N_2O laser which consists of a plane grating and a water cooled 1.8-m discharge tube sealed with a concave mirror and a NaCl window provided the pumping power of about 80 mW. The double resonance cell is made of a 30-cm K-band Stark cell sealed by two NaCl windows.

The energy levels and the observed effect of the laser pumping on microwave absorption lines are shown in Fig. 1. In the system shown in Fig. 1(a), the infrared transition $\nu_2[^qQ_-(8,7)]$ of $^{14}NH_3$ coincides almost exactly with the N_2O-laser $P(13)$ line at 927.739 cm^{-1}. The infrared pumping *increased* the intensity of the (8, 7) inversion line by a factor from 2 to 8 depending on the pressure of NH_3. A small effect of the laser pumping was also observed in the neighboring (9, 7) and (7, 7) lines due to the collision-induced transitions shown by wavy arrows in Fig. 1(a). Because of the "selection rules" governing the transitions induced by NH_3–NH_3 collisions,[8] the decrease of the molecular population in the pumped level is transferred more readily to the lower components of the (9, 7) and the (7, 7) levels, and therefore these lines *decreased* in intensity.

In the system shown in Fig. 1(b), the infrared transition $\nu_2[^qQ_-(4,4)]$ of $^{15}NH_3$ is about 332 MHz higher than the N_2O-laser $P(15)$ line,[7] and therefore it is necessary to apply an electric field of 4.565 kV/cm[7] on $^{15}NH_3$ to "pull" the absorption line to the laser frequency. Under the electric field the laser pumping *increased* the intensity of the $M=4$ component [S_1 in Fig. 1(b)] by a factor of 2. A small effect of the pumping due to collision-induced transitions was also observed for the $M=3$ component [S_2 in Fig. 1(b)]. Because of the "selection-rules" governing collision-

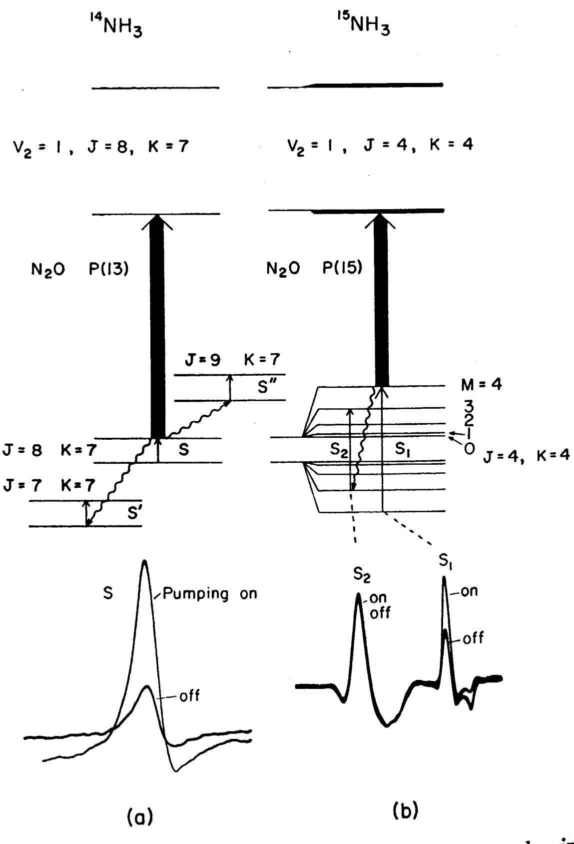

Fig. 1. Schematic energy levels and oscilloscope traces showing the observed effect of laser pumping on microwave absorption lines. For the sake of clarity the separation of inversion doublet levels and Stark shift of the levels are magnified.

induced transitions between various M levels,[9] the latter *decreased* the intensity.

The observed relative variation of the signal $\Delta I/I(=2\sim8)$ is several orders of magnitude larger than the thermal effect observed by Fourier *et al.*,[5] in spite of the fact that we are using much smaller laser power. However, the observed value of $\Delta I/I$ is still much smaller than $\frac{1}{2}(kT/h\nu)(=\sim130)$ which is expected if the laser pumping completely saturates the infrared transition. This fact together with other observed characteristics suggests that a "hole burning" on the Doppler profile of the infrared transition is occurring; only those molecules with velocity component v in the direction of the propagation of the laser light such that $\nu_0(1+v/c)\simeq\nu_L$ are pumped efficiently, where ν_0 is the center frequency and ν_L is the laser frequency. More detailed discussions of the observed characteristics and analysis will be published elsewhere.[10]

As already pointed out by Ronn and Lide,[1] the infrared-microwave double resonance provides a powerful means for the studies of rotational energy transfer. An obvious advantage of using laser pumping is that we can create by this method a much larger deviation from a Boltzmann distribution than by microwave pumping. Indeed in the present work, we could observe collision-induced signals in the (9, 7) and (7, 7) lines which are about 10 times larger than those observed by microwave double resonance.[8] However, in order to take full advantage of the merit of laser pumping, some method has to be devised to avoid the "hole burning."

We wish to thank F. Shimizu for informing us of the result of his laser spectroscopic studies of $^{14}NH_3$ and $^{15}NH_3$ prior to publication.

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