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Infrared-Microwave Double Resonance of NH_3 Using an N_2O Laser

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The infrared vibration-rotation transitions ν_2 [6Q_2 (8, 7)] of $^{14}\text{NH}_3$ and ν_2 [6Q_2 (4, 4)] of $^{15}\text{NH}_3$ have been pumped by the $P(13)$ and $P(15)$ lines, respectively, of an N_2O laser, and the resulting changes in the molecular populations of the rotational levels have been monitored by observing the microwave inversion lines. Large variations of the intensities of the monitored lines have been observed. In addition, small variations of neighboring inversion lines due to collision-induced transitions have also been found. The dependence of the efficiency of pumping on the frequency difference between the laser line and the NH_3 absorption line (which was varied by using a Stark field) and on the pressure of the sample was studied. The results can be explained by using Karplus and Schwinger's theory of saturation and by taking into account a "hole burning" on the Doppler profile of the absorption line.

INTRODUCTION

Since the advent of infrared lasers, infrared-microwave double-resonance experiments have been attempted by several workers; an infrared-laser line pumps molecules in certain rotational levels of the ground vibrational state into an excited vibrational state and the resulting non-Boltzmann rotational distribution is monitored by microwave absorption lines. Although small variations of the intensities of microwave absorption lines have been reported for CH_3Br ^{1,2} and NH_3 ,³ obtained with powerful but not exactly resonant laser radiations, there has been no observation of a clear-cut effect of the resonant laser pumping on a microwave absorption line. In this paper, we report the observation of such double-resonance effects in some three-level systems of $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$. The most important information needed for the experiment is the degree of coincidence of the laser frequencies with those of molecular absorption. Although conventional infrared absorption spectra of $^{14}\text{NH}_3$ ⁴ and $^{15}\text{NH}_3$ ⁵ provide approximate information on the degree of coincidence, more exact information has had to await the development

of laser Stark spectroscopy.⁶ Recently, Shimizu has made extensive studies of laser Stark spectroscopy of $^{14}\text{NH}_3$ ⁷ and $^{15}\text{NH}_3$,⁸ using 10- μm CO_2 and N_2O lasers, and discovered one almost exact coincidence and several near coincidences; these coincidences are used in the present work.

EXPERIMENTAL

The experimental arrangement is shown in Fig. 1. The laser consists of a water-cooled 1.8-m discharge tube sealed with a concave mirror (radius 5 m) and with a NaCl Brewster window, and a plane grating blazed at 10 μm . A mixture of 5% N_2O , 15% N_2 , and 80% He is passed through the discharge tube at a pressure of 13 Torr. The laser power was coupled out from the zeroth-order reflection of the grating and sent into the double-resonance cell; the typical output power was 80 mW. The double-resonance cell is made of a 30-cm K -band waveguide in which an electrode for Stark modulation is supported by Teflon strips. The normal method of 125-kHz Stark modulation and phase detection was used to monitor the microwave absorption lines. The cell is sealed by two NaCl windows having a thickness of 1 mm.

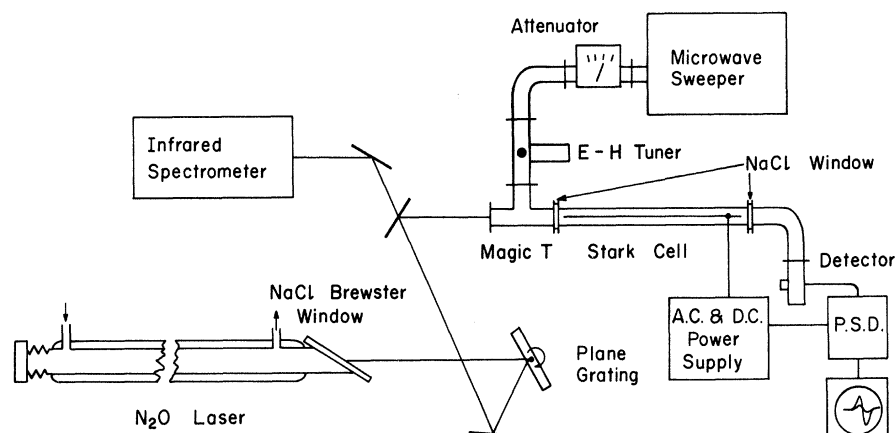


FIG. 1. Schematic diagram of the infrared-microwave double-resonance experiment.

RESULTS

The three-level systems and the observed effects of laser pumping on microwave absorption lines are shown in Fig. 2. In the three-level system shown in Fig. 2(a), the infrared transition $\nu_2[{}^aQ_-(8,7)]$ of ${}^{14}\text{NH}_3$ coincides almost exactly with the N_2O -laser $P(13)$ line at 927.739 cm^{-1} .⁷ When the

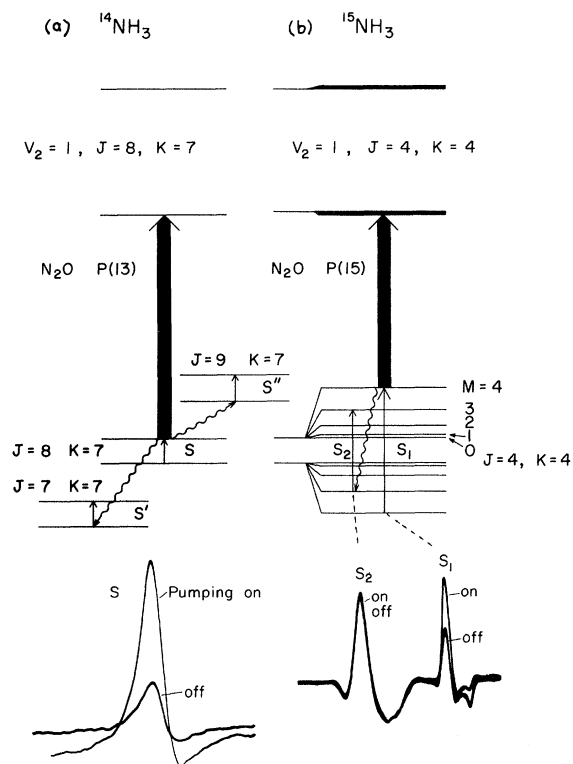


FIG. 2. Schematic energy levels and observed effect of laser pumping on microwave-absorption lines. For the sake of clarity, the separation of inversion doublet levels and Stark shift of lines are magnified.

pumping power was turned on, the intensity of the (8,7) inversion line at 23 232.20 MHz increased by a factor of 2–8, depending on the pressure of NH_3 . A broadening of the microwave absorption line due to the laser pumping was noticed at low pressure, but the splitting due to the modulation effect⁹ was not resolved. By applying a dc electric field, it was possible to monitor the effect of the laser pumping on the individual M components of the microwave line. When the electric field of the laser radiation was parallel to that of the microwave radiation (and thus, to the dc electric field), the component with the largest M values was pumped most efficiently; whereas, if they were perpendicular to each other, the components with lower M values were pumped more efficiently as expected from the relevant matrix elements of the direction cosine.

In addition to the large effect of the laser pumping on the (8,7) inversion line, a small effect was also observed in the neighboring (9,7) and (7,7) lines which are connected to the pumped level via collision-induced transitions [wavy arrows in Fig. 2(a)]. Because of the parity selection rules governing the transitions induced by $\text{NH}_3\text{-NH}_3$ collisions,¹⁰ the decrease of molecular population in the upper component of the (8,7) levels is transferred more readily to the lower component of the (9,7) and the (7,7) levels; therefore, unlike the (8,7) line, the intensities of the (9,7) and the (7,7) lines are *decreased* by the pumping. A decrease up to 3% was observed which is about 10 times larger than the values obtained by the microwave double-resonance method.¹⁰ Since the deviation from a Boltzmann distribution produced by laser pumping is much larger than that produced by microwave pumping, the laser-pumping method should be a powerful tool for detailed studies of rotational relaxation.

In the three-level system shown in Fig. 2(b), the frequency of the $P(15)$ line of the N_2O -laser at

925.979 cm^{-1} is 332 MHz lower than the infrared transition $\nu_2[{}^aQ_-(4,4)]$ of ${}^{15}\text{NH}_3$,⁸ and therefore, it is necessary to apply an electric field on ${}^{15}\text{NH}_3$ to "pull" the absorption line to the laser line. Under an electric field of 4.565 kV/cm, the laser pumping increased the intensity of the $M=4$ component [S_1 in Fig. 2(b)] by a factor of 2, while the $M=3$ component [S_2 in Fig. 2(b)] was only slightly affected by the collisional transfer (wavy arrow) of the molecular population.

The relative variation of the signal $\Delta I/I$ due to the laser pumping depends on the frequency difference between the laser line and the absorption line (which can be varied by applying an electric field) and on the pressure of NH_3 . The dependences observed for the (8,7) line are shown in Fig. 3. The dependence of $\Delta I/I$ on the square of the electric field (and thus, on the frequency difference between the laser line and the absorption line) shown in Fig. 3(a) gives the Doppler profile of the infrared spectral line of NH_3 . We see that the laser frequency is only about 10 MHz lower than the frequency of the NH_3 transition at zero electric field, and that the Doppler width is about 40 MHz, which agrees with the calculated value of 41.7 MHz. The deviation from the calculated Gaussian curve in the low-field region [dashed curve in Fig. 3(a)] is due to the fact that in this region we are monitoring all the unresolved M components; whereas, in the higher-field region where the M components are split, we are monitoring only the $M=8$ component which is pumped more efficiently than the others. Figure 3(b) indicates that the values of $\Delta I/I$, and therefore the efficiency of pumping, is a monotonically decreasing function of the pressure; this dependence is different from that reported for CH_3Br .^{1,2} On the other hand, when He

gas at a pressure of about 100 mTorr was mixed with NH_3 at 10 mTorr, an increase of $\Delta I/I$ by about 50% was observed.

DISCUSSIONS

Although the observed relative variation of the signal $\Delta I/I$ is several orders of magnitude larger than the thermal effect previously observed,³ it is still much smaller than $\frac{1}{2}(kT/h\nu_m)$ (ν_m is the frequency of the microwave transition) which is expected if the laser pumping completely saturates the infrared transition and half of the molecules in the upper level of the microwave transition are depleted. This fact together with the observed Gaussian profile [Fig. 3(a)] having the expected Doppler width suggests that a "hole burning" on the Doppler profile of the infrared line is occurring; only 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 of the infrared absorption and ν_L is the frequency of the laser line. We shall calculate the value of $\Delta I/I$ on the basis of the following simplifying assumptions: (i) A molecule does not change its velocity during the time between inelastic collisions; and (ii) the population changes occur only in the pumped levels. In order to estimate the efficiency of pumping $\Phi(v)$ for molecules with velocity component v , we use Karplus and Schwinger's formula¹¹

$$\Phi(v) = - \frac{[\delta n_{p1}(v) - \delta n_{pu}(v)]}{[n_{p1}^0(v) - n_{pu}^0(v)]} = \frac{\gamma^2}{[\nu_0(1+v/c) - \nu_L]^2 + (1/2\pi\tau)^2 + \gamma^2}, \quad (1)$$

where $\gamma = |\mu E|_p/h$ ($\gamma \sim 290\text{ kHz}$), τ is the relaxation

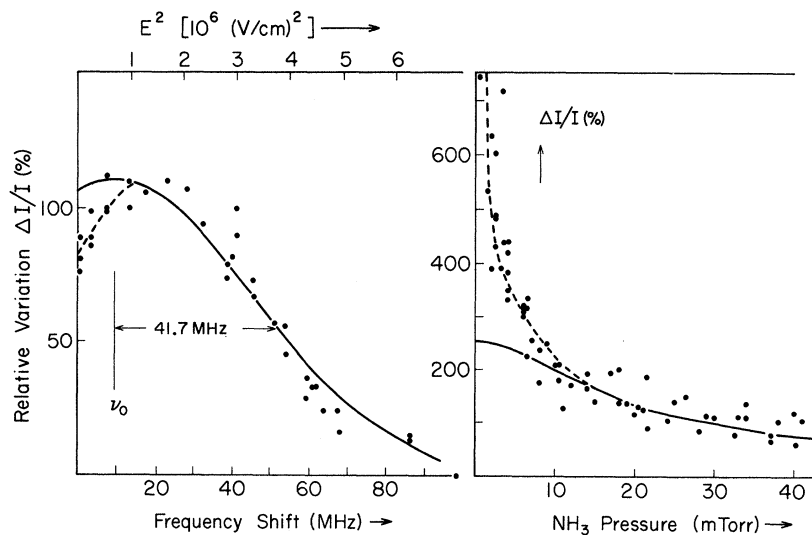


FIG. 3. Observed dependence of $\Delta I/I$ (a) on the center frequency of absorption ν_0 which is varied by Stark field, and (b) on the pressure of sample. The solid curves are theoretical curves based on Eq. (4). The deviations (dashed lines) from the theoretical curve are discussed in the text.

time of the saturation ($1/2\pi\tau \sim 26 \text{ MHz Torr}^{-1}$),¹² $n_{p_l}(v)$ and $n_{p_u}(v)$ are the molecular populations in the lower and upper levels of the pumping transition, the superscript 0 denotes the populations in the equilibrium state, and δn denotes the deviation from the Boltzmann population, i. e., $\delta n_{p_l} = n_{p_l} - n_{p_l}^0$, etc. Approximating $n_{p_u}^0 \approx 0$ and using the assumption (ii), i. e., $\delta n_{p_l}(v) + \delta n_{p_u}(v) = 0$, we have

$$\delta n_{p_l} = \frac{-n_{p_l}^0 \gamma^2}{2\{[\nu_0(1+v/c) - \nu_L]^2 + (1/2\pi\tau)^2 + \gamma^2\}}. \quad (2)$$

For a microwave absorption line in which the pressure broadening is much larger than the Doppler broadening, the intensity is merely a function of total number of molecules. Averaging Eq. (2) over the Maxwellian distribution of molecular velocities and using the fact that the magnitude of $1/2\pi\tau$ and γ are much smaller than the Doppler width, we obtain the population change in the lower level of the pumping transition, and thus the upper level of the signal transition, to be

$$\delta N_{p_l} = \delta N_{s_u} = -N_{p_l}^0 \sqrt{\pi} \gamma^2 (2\delta\nu)^{-1} [(1/2\pi\tau)^2 + \gamma^2]^{-1/2} \times \exp[-(\nu_L - \nu_0)^2 / (\delta\nu)^2], \quad (3)$$

where $\delta\nu = (2kT/mc^2)^{1/2} \nu_0$. The value of $\Delta I/I = (\delta N_{s_l} - \delta N_{s_u}) / (N_{s_l}^0 - N_{s_u}^0)$ is calculated by using the assumption (ii) (i. e., $\delta N_{s_l} = 0$) as follows:

$$\Delta I/I = \frac{1}{2} (kT/h\nu_m) \sqrt{\pi} \gamma^2 (\delta\nu)^{-1} [(1/2\pi\tau)^2 + \gamma^2]^{-1/2} \times \exp[-(\nu_L - \nu_0)^2 / (\delta\nu)^2]. \quad (4)$$

The physical implication of this formula is obvious. The value of $\Delta I/I$ is smaller than the ideal value $\frac{1}{2}(kT/h\nu_m)$ by a factor of the efficiency of saturation $\gamma^2[(1/2\pi\tau)^2 + \gamma^2]^{-1}$, a factor of the width of pumping $\sqrt{\pi}[(1/2\pi\tau)^2 + \gamma^2]^{1/2}/\delta\nu$, and a factor of frequency mismatch $\exp[-(\nu_L - \nu_0)^2 / (\delta\nu)^2]$. The pressure dependence of $\Delta I/I$ is introduced through $1/2\pi$, which is equal to $\Delta\nu p$, where p is the pressure and $\Delta\nu$ is the relaxation parameter. The best fits of the formula to the observed values are shown in Fig. 3 by the solid lines. These fits give the value of $\Delta\nu/\gamma$ to be 77 Torr^{-1} and $\frac{1}{2}(kT/h\nu_m)\sqrt{\pi}\gamma(\delta\nu)^{-1}$ to be 2.5. The calculated values for these quantities by using $\Delta\nu = 26 \text{ MHz Torr}^{-1}$,¹² the infrared-transition dipole moment

$$\langle \mu \rangle = KM[J(J+1)]^{-1} \frac{\partial \mu}{\partial Q} Q = 0.208 \text{ D} \left(\frac{\partial \mu}{\partial Q} Q = 0.238 \text{ D} \right)$$

(where the value 0.238 D is from Ref. 13), and estimated power density in the waveguide of 20 mW/cm^2 , are 89 and 1.3 Torr^{-1} , respectively.

In view of the rather crude approximations used in deriving Eq. (4) and the uncertainty of the estimated laser field in the double-resonance cell, the agreement is satisfactory.

It is likely that the condition for "hole burning" is not strictly met in the actual system due to the velocity changes of the pumped molecules [breakdown of the assumption (i)] and the instability of the laser frequency; in this respect, Eq. (4) underestimates the value of $\Delta I/I$. It is also possible that the molecular population in the lower level of the signal transition N_{s_l} is also decreased because of collision-induced transitions between the inversion levels [breakdown of the assumption (ii)]; in this respect, Eq. (4) overestimates the value of $\Delta I/I$. It is known¹⁴ that in $\text{NH}_3\text{-NH}_3$ collisions, the transition β between the inversion doublet levels has a much larger probability than other transitions α , γ , and ξ , with $\Delta J \neq 0$ or $\Delta K \neq 0$; whereas, in wall collisions these "selection rules" do not exist.¹⁴ The sharp increase of the observed values of $\Delta I/I$ in the low-pressure region [dashed line in Fig. 3(b)], where the wall collisions (about $1.2 \times 10^5 \text{ sec}^{-1}$) become dominant, is probably due to variation of the ratio of the probability of the transition β , which depletes the population N_{s_l} , to that of other $\Delta J \neq 0$ transitions which supply the population. Collisions without selection rules, such as wall collisions, or with less rigorous selection rules, such as $\text{NH}_3\text{-He}$ collision¹⁵ tend to increase $\Delta I/I$ by maintaining molecular populations, other than that directly pumped, closer to Boltzmann distribution.

In view of its capability of producing a large non-Boltzmann distribution in a single rotational level of the ground state and easiness of separating the laser radiation from the microwave radiation, the laser-pumping method developed in this paper will be a powerful tool for the studies of rotational energy transfer.^{10,14,15}

Note added in proof: (i) After this paper was submitted we learned of two other observations of the infrared-microwave double resonance. A clear signal has been detected in CH_3Cl by Frenkel, Marantz, and Sullivan.¹⁶ They have also seen small signals in CH_3Br . Lemaire *et al.* reported their observation for CH_3Br and N_2O .¹⁷ They interpret the signals as due to thermal effect. (ii) Recently Shimizu has reported the absorption coefficient of the $\nu_2^{[a]Q_-(8,7)}$ transition to be $0.7 \text{ cm}^{-1} \text{ Torr}^{-1}$.¹⁸ The net infrared absorption in the double resonance cell used in the present experiment is of the order of 80% at 10 mTorr. The sharp increase of $\Delta I/I$ at the low-pressure region shown in Fig. 3 may be partly due to the decrease of the absorption in the region and thus to the increase of the laser power at the exit end of the cell.

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Excitation Transfer and Decay in Molecular Dimers Optically Excited

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The transfer of excitation in a dimer is treated as a resonance, using Feshbach's nuclear reaction formalism. The radiation field-matter interaction is treated simultaneously with the intermonomeric potential. This gives a unified point of view and allows one to see what the interference effects are. The Förster vibrational-relaxation mechanism and the Frenkel exciton are studied for the dimers, and explicit expressions for the decay probability are obtained.

I. INTRODUCTION

Excitation transfer in dimers can be understood as a nonradiative transition process. As such, it is extremely difficult to detect directly in an experiment. What is observed instead is the molecular luminescence. Thus, a thorough study of the radiative processes in dimers should show the features of excitation transfer. From a theoretical point of view, both potentials which cause radiative decay and excitation transfer should be treated on an equal basis. Essentially, it is the intermolecular interaction in the dimer which produces the excitation transfer, and the radiation field-matter interaction which causes the

fluorescence decay. Up to now, the two mechanisms have always been separated, and the excitation transfer has been studied considering only the intermolecular interaction.

The excitation transfer in molecular dimers has been studied, introducing simplifying assumptions¹⁻³. Each of the interacting molecules is a system of two levels; one is the ground state and the other is the considered excited state. Furthermore, when each of the monomers is individually electronically excited, there is only one vibrational mode Q of the molecule which is perturbed by the electronic excitation.

Depending on the importance of the interaction between the two molecules composing a dimer,