Generation of 16-μm radiation in $^{14}NH_3$ by two-quantum excitation of the $2\nu_2^-(7,5)$ state

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Stimulated emission at 15.82 and 15.91 μm has been obtained in $^{14}NH_3$ following two-photon excitation of the $2\nu_2^-(7,5)$ state. Total output energies on the order of 3 mJ have been observed in a simple experimental arrangement. A discussion of the experimental findings concerning the laser output spectrum, the pressure dependence, the utilization of the optical Stark effect, and the influence of the spectral width and spatial profiles of the CO_2 radiation providing the nonlinear excitation is given.

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Previous work[1-3] has described the production of stimulated emission in the 16-μm region following two-photon excitation of the $2\nu_2^-$ (5,4) state of $^{14}NH_3$ with 9–10-μm radiation. A recent study[4] utilizing two-photon spectroscopic techniques has accurately determined the location of six additional states in the $2\nu_2^-$ manifold of $^{14}NH_3$. The date provided by these measurements[4] establish the conditions required for selective two-quantum excitation of these specific $2\nu_2^-$ levels, thereby providing pathways for conversion of CO_2 radiation to the 16-μm range.[1-3] In the discussion below we describe experimental findings concerning the excitation of the $2\nu_2^-$ (7,5) state, including the down-converted spectrum, the pressure dependence, the utilization of the optical Stark effect, and the influence of the spectral width of the CO_2 radiation providing the nonlinear excitation.

Efficient energy conversion by the two-quantum processes considered in this work requires that three conditions must be satisfied: (1) the saturation of the transition used for excitation, (2) the establishment of the necessary resonance condition, and (3) a constraint on medium density arising from collisional redistribution of the absorbed energy.

In both the current and previous experiments,[1,2] the optical Stark effect has been used to establish the appropriate resonance condition. Since this aspect is a central consideration in these experiments, we briefly review below the main characteristics of the optical Stark effect.

In the simplest first-order perturbative analysis, the frequency shift S of a two-photon transition can be written[4-6] as

$$S \cong 4.8\times 10^7\left[\left(\frac{\mu_{12}^2}{\Delta}\right)I_1 - \left(\frac{\mu_{23}^2}{\Delta-\delta}\right)I_2\right], \tag{1}$$

in which μ_{12} and μ_{23} denote electric dipole matrix elements in Debye units, I_1 and I_2 represent optical intensities in MW/cm^2, and S, Δ, and δ are frequencies expressed in MHz (see Fig. 1). The result stated in expression (1) is valid in the regime for which the shifts of the participating levels are all significantly smaller than the detuning parameters Δ or $\Delta - \delta$. As we observe from Fig. 1, however, the specific case under consideration may involve an appreciable correction as the parameters δ and $\Delta - \delta$ are comparable. We note that this situation is in contrast to that applicable to the $2\nu_2^-$ (5,4) level previously investigated.[1,2] Therefore, in the following we use the more accurate expression[5]

$$S = \frac{44.8\times 10^7\mu_{12}^2 I_1}{2} - \frac{\Delta-\delta}{2} \times\left[\left(1+\frac{1.9\times 10^8}{(\Delta-\delta)^2}\sum_m \mu_{23}^2 I_2\right)^{1/2} - 1\right], \tag{2}$$

which is now applicable in the region explored by our experiments. If we evaluate this expression with the relevant matrix elements[7,8] and frequency factors for the intensity range of our studies[4] ($\leqslant 10$ MW/cm^2), we find that the second term in expression (2) dominates the shift, so that in this case we may write

$$S \cong -\frac{(\Delta-\delta)}{2}\left[\left(1+\frac{1.9\times 10^8}{(\Delta-\delta)^2}\sum_m \mu_{23}^2 I_2\right)^{1/2} - 1\right]. \tag{3}$$

Within the framework of this approximation, we see that the optical Stark shift S is governed entirely by the intensity I_2.

At this point we may make an estimate of the optical intensities required to achieve the resonance condition. We note, however, that the strong applied field splits the spatial degeneracy of the molecular states and causes the optical Stark shift to be magnetic sublevel (M) dependent. This effect originates from the M dependence[7] of the matrix elements involved in Eq. (2). Table I illustrates the intensity I_2 required to achieve resonance for the magnetic sublevels of the $2\nu_2^-$ (7,5) state. It is evident that for intensities $\leqslant 10$ MW/cm^2 that only the states $|M| = 7$, 6, and 5 are of practical concern.

The experimental apparatus shown in Fig. 2 is configured differently from that used previously.[1,2] The two Lumonics 103 TEA lasers equipped with intracavity gain cells were operated on the P(24) 10.6-μm (I_2) and R (8) 9.6-μm (I_1) transitions and produced 5.5 MW/cm^2 (1 J) and 1.5 MW/cm^2 (0.5 J), respectively. These output beams were combined on a ZnSe window, as shown in Fig. 2. Since the first transi-

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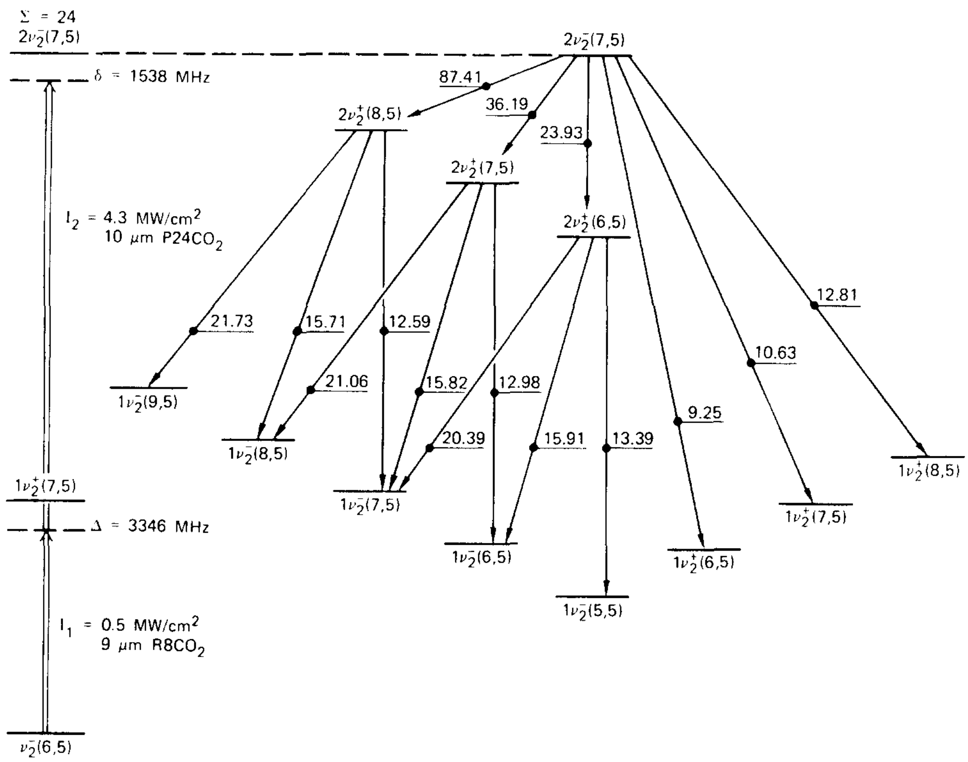

FIG. 1. Pump scheme and cascading transitions in $^{14}NH_3$.

tion optically tuned into resonance involves the states $0\nu_2^-$ (6,5,6)→$1\nu_2^+$ (7,5,7)→$2\nu_2^-$ (7,5,7), the largest matrix elements occur for the situation of orthogonal polarization vectors for the two CO_2 frequencies. To accomplish this, we set the ZnSe window at Brewster's angle for the polarized P(24) radiation while simultaneously achieving a reflectivity of greater than 50% for the orthogonally polarized R (8) radiation. The combined beams traversed a 3-m cell equipped with either KCl or antireflection-coated ZnSe windows. The beams are then incident on a LiF flat with an angle of incidence of ~10°. The refelcted 9.6- or 10.6-μm light (0.5%) is then completely blocked by 16-μm bandpass filters.

The NH_3 laser excited in this fashion by the CO_2 lasers is expected to exhibit optical gain on cascading transitions, as shown in Fig. 1. The laser emission is also incident on the LiF flat, which is highly reflective at wavelengths of interest[9] (72 ± 5% from 16 to 22 μm). The reflected signal then passes through the ir filters and is measured with a Laser Precision μJ meter or throught a Spex $\frac{3}{4}$-m spectrometer using a Cu-Ge detector having high sensitivity from2 to 22 μm. In the latter case, the signal was recorded using a transient digital converter connected to a PDP-11/34 computer.

In order to examine the influence of the spectral width of the CO_2-laser radiation on NH_3-laser performance, the output energy as a function of NH_3 pressure, both with and without CO_2-laser-pulse smoothing, has been studied. A plot of these data is shown in Fig. 3, where each point is an averge of at least 20 shots. The CO_2 lasers had significant timing uncertainty, which we believe caused most of the variation in the output energy. We note that without the pulse smoothing, the peak is at ~3.5 Torr, and is very similar to the pressure dependence measured in previous NH_3 two-photon work.[1] With pulse smoothing, the peak was at ~5 Torr, with almost twice the output energy. One possible explanation for this is that *linear* absorption present on the 9-μm R (8) line may be significantly reduced with the use of pulse smoothing due to the accompanying spectral narrowing, thereby allowing the system to run at higher pressures.

The output spectrum of the NH_3 laser was also experimentally determined. This was done by replacing the LiF reflector with an NaCl reflector whose index of refraction is known to vary smmothly from 10 to 25 μm.[10] The output was directed through the spectrometer and measured by integrating the output from the Cu : Ge dectector. The energy spectrum, when corrected for the reflectivity of NaCl and the filter transmission, is the following: 15.82 μm—55%, 12.98 μm—38%, 15.91 μm—2.7%, 21.06 μm—2.4%, 20.39 μm—2.0%, 12.81 μm—0.7%, and 12.98 μm—0.7% (± 20% of the stated percentage). No signal was observed at 13.39 μm, nor from any transition emanating from the $2\nu_2^+$ (8,5) state, and no attempt was made to measure the 10.63- or 9.25-μm transitions due to their close proximity to the CO_2 pump transitions. The maximum total output from this laser was greater than 3.8 mJ. Average total outputs were obtained in excess of 2.5 mJ. Using absorbing gases to

TABLE I. Intensities required to achieve resonance.

M level	∓7	∓6	∓5	∓4	∓3	∓2	∓1	0
Intensity I_2 (MW/cm²)	4.3	5.9	8.4	13.2	23	52	212	Unshifted

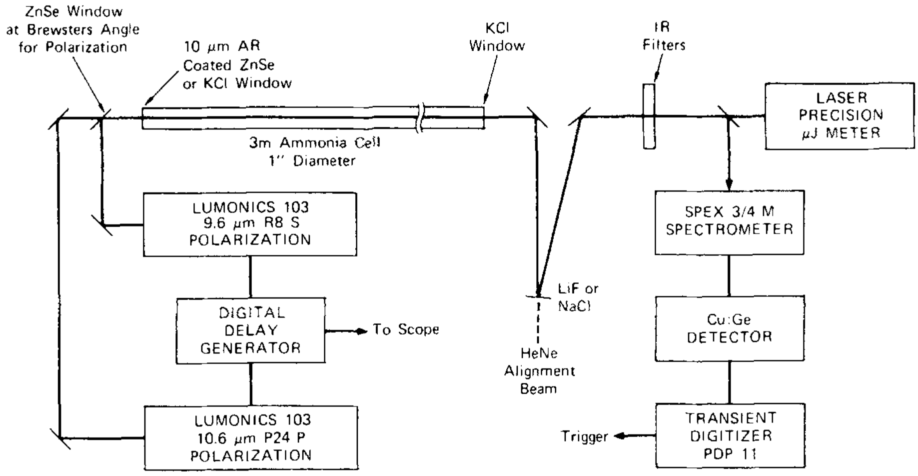

FIG. 2. Experimental setup.

control the radiative cascade dynamics as described previously,[1] almost all of this energy could be diverted to either 15.82 or 15.91 μm.

In order to determine the efficiency of this system, several additional measurements were made. Linear absorption at the previously stated intensities was measured on both the 9-μm R (8) and 10-μm P (24) CO_2 lines. The absorption of the P (24) line was small and below our detection limit ($< 2\%$) at an NH_3 pressure of 3 Torr. The absorption on R (8) was significant (12% at 3 Torr in a 3-m cell) and was measured versus NH_3 pressure from 0.75 to 15 Torr. These data indicate that the R (8) pump pulse saturates the NH_3 linear absorption. Also measured was the energy absorbed by the medium through the two-photon channel. This was done by removing the ir filters and allowing the reflected 9-μm R (8) signal from the LiF window to enter the spectrometer. In this way, the R (8) transmission could be monitored independent of the presence of the P (24) pulse. With 3.12 Torr NH_3 in the cell, we measured an abosrption of $\sim 10\%$, attributable to a two-photon process. The R (8) energy was measured at 350 mJ per pulse, and (therefore) assuming one P (24) photon absorbed for each R (8) photon absorbed, we find the deposited energy to be 60 ± 15 mJ. Since the quantum efficiency of the system for 16-μm generation is $\sim 30\%$, then in the absence of losses the 16-μm output would be 18 ± 5 mJ. However, we observed about 3 mJ, or 15% of the deposited energy. Possible loss mechanisms to account for this include collisional redistribution of the energy and unobserved oscillation at 10.63 and 9.25 μm.

Data were also taken to illustrate the validity of our assumptions in estimating the ac Stark effect [Eq. (3)]. If the P (24) laser controls the optical Stark shift instead of the R (8) laser, then the NH_3-laser output energy should show a much stronger dependence on the P (24) pump intensity than on the R (8) intensity. Data were taken by measuring the NH_3-laser output while varying the attenuation of one of the pump beams with salt windows or CaF_2 attenuators while

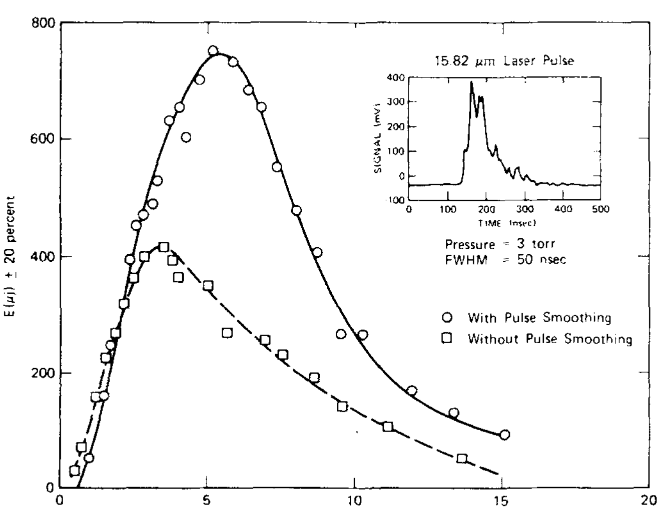

FIG. 3. Pressure dependence of laser output, uncorrected ro LiF reflectivity or filter transmission. For this data, 85% of the output energy is at 15.82 μm. Inset is a typical pulse shape of the 15.82-μm signal.

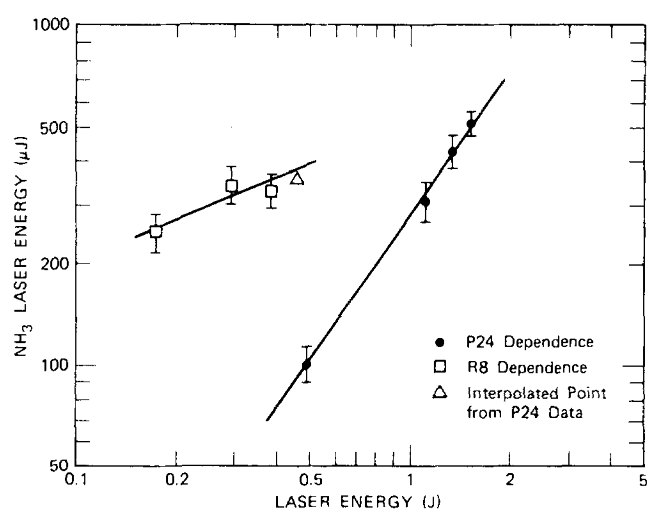

FIG. 4. Laser output versus pump energy. For P (24) dependence, the R (8) energy was 450 mJ. For R (8) dependence, the P (24) energy was 1.21 J. The Δ data point is interpolated from the P (24) dependence with R (8) and P (24) energies of 450 mJ and 1.21 J, respectively.

maintaining the other pump beam at constant intensity. The beams were then switched and the process repeated. The results are displayed in Fig. 4. It is clearly evident that the output is much more susceptible to variations in the $P(24)$ (I_2) intensity, as expected.

In conclusion,we have examined additional two-photon excitation channels in $^{14}NH_3$ as in illustration of the generality of this method for down conversion in the infrared. In addition, the influence of the optical Stark effect has been examined and is found to be crucial to the operation of this system with fixed-frequency CO_2 lasers. The use of the continuously tunable high-pressure CO_2-laser technology should enable the creation of a fully line-tunable source in the 16-μm region.

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