

Doppler-free spectroscopy of the ν_2 band in $^{14}\text{NH}_3$: Application to 16- μm generation^{a)}

J. Bokor,^{b),c)} W.K. Bischel, and C.K. Rhodes^{c)}

Molecular Physics Laboratory, SRI International, Menlo Park, California 94025

(Received 22 May 1978; accepted for publication 5 December 1978)

Several two-photon transitions leading to various (J,K) rotational sublevels of the $\nu_2 = 2^-$ state in $^{14}\text{NH}_3$ have been observed using the high-resolution technique of Doppler-free two-photon spectroscopy. It is shown that these transitions can be both tuned into resonance with the optical Stark effect and saturated with intensities of order $1\text{--}10\text{ MW/cm}^2$, so that laser action on many wavelengths in the vicinity of $16\ \mu\text{m}$ is obtainable. This method of excitation is generally applicable for the excitation of molecular systems in frequency-conversion processes.

PACS numbers: 33.80.Kn, 42.55.Hq, 42.55.Hq, 33.55.+c, 33.20.Ea

Two-photon optical pumping of molecular vibrational states has many attractive properties for down conversion in the infrared. CO_2 or N_2O lasers at either 9 or $10\ \mu\text{m}$ are well suited as the primary sources of radiation from which the down conversion can be generated. Recently, laser action at 15.88 and $15.95\ \mu\text{m}$ has been demonstrated^{1,2} in ammonia ($^{14}\text{NH}_3$) following such excitation.

The two-photon pumping process utilizing $\sim 10\text{-}\mu\text{m}$ radiation offers significant advantages over the single-photon analogue in the generation of $16\ \mu\text{m}$. Specifically, they are (1) that the excitation requirements for reaching threshold are substantially reduced without gas cooling because the thermal population of the lower laser level is ~ 150 times smaller, (2) the lower laser level can relax by fast $V\text{-}V$ processes which could allow these systems to be operated in the cw mode, and (3) the available combinations of two CO_2 or N_2O laser wavelengths constitute a nearly continuously tunable pump source in the $1800\text{--}2100\text{-cm}^{-1}$ region, thereby allowing considerable flexibility in the excitation of the available vibrational-rotational states.

The two-photon method of excitation, however, requires accurate spectroscopic knowledge of the vibrational/rotational excited-state manifold. In this investigation we report new high-resolution spectroscopic data on the $\nu_2 = 2^-$ excited state in $^{14}\text{NH}_3$, obtained using Doppler-free two-photon spectroscopy in combination with molecular Stark tuning. These data conclusively demonstrate that many rotational sublevels of the $\nu_2 = 2^-$ state can be efficiently populated, leading to several new laser transitions in the $16\text{-}\mu\text{m}$ band ($2^- \rightarrow 1^-$). Furthermore, it is clear that this method can be utilized generally in other molecular systems in frequency-conversion processes for both up and down conversion.

The experimental conditions were equivalent to that reported by Bischel *et al.*³ in earlier studies. Two stable cw CO_2

or N_2O lasers operating on different rotational transitions were frequency stabilized^{3,4} above and below their respective line centers, so that the two-photon transitions were observed at a frequency which precisely coincided with the sum of the line-center laser frequencies.^{5,6} The tuning of the molecular resonance required to achieve this condition was provided by an external static Stark field, applied in a specially constructed cell capable of generating fields up to $80\ 000\ \text{V/cm}$, with a homogeneity of approximately one part in 10^4 . Both laser intensities were monitored using lock-in detection techniques referenced to a modulation voltage on the Stark cell. For Q -branch two-photon transitions, both lasers were linearly polarized parallel to the static field. For R -branch transitions, one laser is polarized parallel and the other perpendicular to the static applied field. These configurations correspond to the conditions of maximum signal strength.³

Under typical operating conditions at pressures of $10\ \text{mTorr}$, electric fields on the order of $60\ 000\ \text{V/cm}$ were obtained before gas breakdown occurred. Using the previously determined³ field of $5253.4\ \text{V/cm}$ required to shift the $0^2\text{-}Q(5,4,5)$ transition into resonance with the $^{12}\text{C}^{16}\text{O}_2P(18)$ and $^{12}\text{C}^{16}\text{O}_2P(34)$ sum sum frequency, we determined the Stark cell plate spacing to be $0.150975 \pm 0.00015\ \text{cm}$.

Using this apparatus, we observed and identified four additional two-photon resonances leading to states in the $\nu_2 = 2^-$ manifold. The data obtained are shown in Table I along with previously obtained data for comparison. These transitions were identified by examining the M_J substate patterns and by comparison with existing Stark spectroscopy,^{7,8} diode spectroscopy,⁹ and hot-band spectra.¹⁰ For each of the four transitions reported, at least one additional M_J state was observed beyond that shown in Table I. Note that for the $0^2\text{-}Q(7,5,6)$ transition, the $M_J = J$ transition was observed but not included in the data analysis due to interference from the $0^1\text{-}Q(7,5,6)$ single-photon transition.

The $0^2\text{-}Q(3,3,3)$, $0^2\text{-}Q(4,2,4)$, and $0^2\text{-}R(5,3,5)$ are reported with somewhat larger uncertainties compared to the others. For the $0^2\text{-}R(5,3,5)$,¹¹ the uncertainty is due to the fact that one of the lasers was free running when the measurement was made. The open loop frequency stability of the laser is conservatively estimated at $\pm 10\ \text{MHz}$. For the oth-

^{a)}Work supported by the U.S. Department of Energy under Contract No. AT(04-71-115), (99).

^{b)}Department of Electrical Engineering, Stanford University, Stanford, Calif. 94305. Support by the Fanny and John K. Hertz Foundation is gratefully acknowledged.

^{c)}Present address: Department of Physics, University of Illinois at Chicago Circle, Box 4348, Chicago, Ill. 60680.

TABLE I. Parameters for two-photon resonance in $^{14}\text{NH}_3$.

Two-photon resonance ($\Delta M = 0$) ^b	ω_1	ω_2	Stark field (V/cm)	Total Stark ^a shift δ (GHz)	Intermediate detuning at resonance Δ (GHz)	Zero field two-photon frequency (cm^{-1})
0-2 Q (2,2,2) ^c	10.4- μm CO ₂ P(34)	10.4- μm CO ₂ P(14)	24420 \pm 10	5.032 \pm 0.005	4.91	1880.6486 \pm 0.0002
0-2 Q (3,3,3) ^d	10.4- μm N ₂ O P(10)	10.4- μm CO ₂ P(14)	29011 \pm 60	8.1000 \pm 0.03	3.90	1880.106 \pm 0.001
0-2 Q (4,2,4) ^d	10.4- μm CO ₂ P(32)	10.4- μm CO ₂ P(20)	30005 \pm 60	3.170 \pm 0.015	0.29	1877.2601 \pm 0.0005
0-2 Q (4,4,4) ^c	10.4- μm CO ₂ P(34)	10.4- μm CO ₂ P(14)	24670 \pm 10	- 6.887 \pm 0.005	- 2.22	1880.2510 \pm 0.0002
0-2 R (5,3,5) ^d	9.4- μm CO ₂ P(12)	10.4- μm CO ₂ P(26)	16917 \pm 1	- 1.716 \pm 0.010	- 0.777	1992.5545 \pm 0.0003
0-2 Q (5,4,5) ^c	10.4- μm CO ₂ P(34)	10.4- μm CO ₂ P(18)	5253.4 \pm 1	0.29285 ^e \pm 0.0001	4.95	1876.991441 ^f \pm 8 \times 10 ⁻⁶
0-2 Q (7,5,6) ^d	10.4- μm CO ₂ P(32)	10.4- μm CO ₂ P(24)	43978 \pm 1	- 9.956 \pm 0.001	2.31	1873.17641 \pm 3 \times 10 ⁻⁵

^aCalculated from Eq. (6) of Ref. 3.

^bIn our notation for labeling these two-photon transitions, the first two symbols denote the quantum number and parity of the lower and upper vibrational states, respectively, the third symbol denotes the overall ΔJ in the transition (using standard convention), and the quantum numbers of the lower state follow: (J, K, M) .

^cTaken from the results of Bischel *et al.*¹

^dThis work.

er two transitions, the uncertainty is due to severe line-shape distortions, the precise nature of which will require further analysis. These distortions, which are presumed to arise from a complicated interplay of the quadrupole hyperfine effect,¹² the dc Stark effect,¹³ and the ac Stark effect,^{14,15} apparently do not follow lowest-order theory. In order to more accurately locate these levels, careful measurements of the dependence of the line shape on the various experimental

^eThe value of the total Stark Shift is slightly different from that given in Ref. 3 due to the fact that the Stark-effect constant given in Eq. (3) of Ref. 3 is in error. The correct value is $\mu E = 0.5034021$ MHz/D V/cm.

^fThe value in cm^{-1} of this measurement is limited by the value of the speed of light taken to be $c = 299\,792\,456.2$ (1.1) m/sec from K.M. Evenson, J.S. Wells, F.R. Peterson, B.L. Danielson, G.W. Day, R.L. Barges, and J.L. Hall, Phys. Rev. Lett. **29**, 1346 (1972).

parameters will be required, as well as the use of more sophisticated theory.

With these seven levels now located with a resolution of better than 30 MHz (the Doppler width for these transitions is ~ 170 MHz), we can identify efficient optical pumping channels which will lead to 16- μm oscillation in the Q branch of the $\nu_2 = 2^+ \rightarrow \nu_2 = 1^-$ band. Pumping transitions other than those used for spectroscopy need to be identified

TABLE II. Important parameters for pumping selected rotational sublevels of the $\nu_2 = 2$ state in $^{14}\text{NH}_3$, including expected 16- μm laser transition frequencies.

Pump transition	Δ (MHz)	δ (MHz)	I_1 (MW/cm ²) Laser line	I_2 (MW/cm ²) Laser line	Σ	λ 16 μm (cm^{-1})
0-2 Q (2,2)	3352	- 1559	5.1 10- μm P 9 N ₂ O	0.5 10- μm P 14 CO ₂	307	629.16 Q (2,2) 630.90 Q (3,2)
0-2 Q (3,3)	12 000	8100	0.5 10- μm P 10 N ₂ O	16.3 10- μm P 14 CO ₂	123	628.38 Q (3,3) 630.63 Q (4,3)
0-2 Q (4,2)	3457	3170	0.5 10- μm P 32 CO ₂	1.7 10- μm P 20 CO ₂	12	633.31 Q (4,2) 630.90 Q (3,2) 636.44 Q (5,2)
0-2 Q (4,4)	- 2851	1823	0.1 10- μm R 22 CO ₂ ^d	3.3 10- μm R 12 N ₂ O	114	627.17 Q (4,4) 629.83 Q (5,4)
0-2 R (5,3)	953	- 1943	10.9 10- μm P 32 CO ₂	0.5 9- μm P 6 CO ₂	1780	637.27 Q (6,3) 633.56 Q (5,3) 641.87 Q (7,3)
0-2 Q (5,4)	5250	293	0.5 10- μm P 34 CO ₂	1.3 10- μm P 18 CO ₂	31	629.83 Q (5,4) 627.17 Q (4,4) 633.20 Q (6,4)
0-2 R (6,5)	3846	1538	0.5 9- μm R 8 CO ₂	2.3 10- μm P 24 CO ₂	24	632.16 Q (7,5) 628.47 Q (6,5) 636.73 Q (8,5)

^dIsotopic form $^{13}\text{C}^{18}\text{O}_2$.

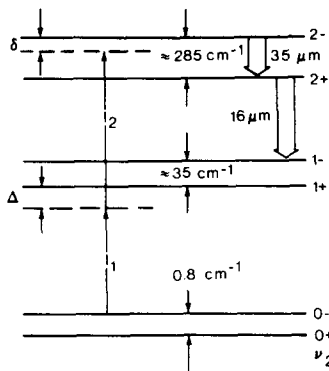


FIG. 1. Schematic of levels involved in two-photon pumped 16- μm laser.

for the three $+ \rightarrow -$ transitions observed. In the spectroscopic work, violation of the parity rule for two-photon transition is induced by the static Stark field. The use of a static field in optical pumping experiments at higher pressures (~ 3 Torr for the laser in Ref. 2) is not practical due to the occurrence of electrical breakdown of the gas. However, using this measurement of the two-photon frequency and the spectroscopic constants of Schnabel¹⁶ and Ueda⁸ for the ground and first excited state, respectively, we can confidently predict the transition frequencies for all allowed two-photon transitions leading to the same upper state. We then search to find a suitable combination of two CO_2 or N_2O laser frequencies using the CO_2 laser frequencies determined by Freed *et al.*⁵ and the N_2O laser frequencies determined by Whitford *et al.*⁶

In Table II we display the pump transitions which have been identified in this way. Figure 1 shows a schematic of the levels involved. The molecular tuning achieved with the use of the static Stark field in the spectroscopic observations in obtained in the optical pumping process through the control of the ac (optical) Stark effect induced by the high-intensity pump radiation. This shift is given in lowest-order perturbation theory^{14,15} as

$$S = 4.773 \times 10^7 \left[\left(\frac{\mu_{12}^2}{\Delta} \right) I_1 - \left(\frac{\mu_{23}^2}{\Delta - \delta} \right) I_2 \right], \quad (1)$$

where S is the Stark shift in MHz, μ_{12} and μ_{23} are the dipole matrix elements in Debye of the $0 \rightarrow 1$ and $1 \rightarrow 2$ transition, respectively, Δ and δ are the detunings in MHz as defined in Fig. 1, and I_1 and I_2 are the intensities of the two light fields in MW/cm^2 . We emphasize that this control of the ac Stark shift allows line-center pumping conditions to be achieved without the introduction of an additional static Stark field. It is further noted, however, that the magnitude of the shift does depend upon the angular momentum projection quantum number M_j .

Under such conditions, the two-photon transition is strongly saturated with intensities readily achievable for CO_2 and N_2O TEA lasers. To describe this aspect we define the saturation parameter

$$\Sigma = 2W_{fg}\tau, \quad (2)$$

in which W_{fg} is the two-photon transition rate and τ is the upper-state lifetime. The pressure-broadened lifetime is given

by $\tau = (\pi\Delta\nu_p)^{-1}$, where $\Delta\nu_p$ is the pressure-broadened linewidth ($\Delta\nu_p = 30 \text{ MHz/Torr}$).³ Using perturbation theory we obtain

$$\Sigma = 2.69 \times 10^{16} (\mu_{12}\mu_{23}/\Delta)^2 (I_1 I_2 / \Delta\nu\Delta\nu_p), \quad (3)$$

where $\Delta\nu$ is the two-photon transition linewidth in MHz, and $\Delta\nu_p$ is also in MHz. Since, in this experiment, the beams are copropagated through the cell,² the two-photon transition is Doppler broadened in the low-pressure regime ($P \lesssim 5$ Torr). Typical Doppler widths for the transitions studied here are ~ 168 MHz. For higher pressures, of course, the pressure-broadened width must be used for $\Delta\nu$ in Eq. (3).

In Table II we show typical intensities required to achieve $S = -\delta$ (line-center pumping) and a value for Σ using these intensities at a pressure of ~ 3 Torr. We also show expected 16- μm laser frequencies¹⁷ calculated using spectroscopic constants obtained by Ueda⁸ and Taylor.¹⁸ These frequencies are accurate to 0.01–0.1 cm^{-1} . The results shown in Table II do not constitute an exhaustive list of the available two-photon transitions. In fact, a computer analysis of low-resolution hot-band spectroscopy^{9,18} indicates that a great many more transitions can be observed under high resolution and can also be efficiently pumped.

In summary, we have identified several new two-photon pumping channels to obtain 16- μm laser action in $^{14}\text{NH}_3$. Our results show that these transitions can be easily saturated with intensities readily available from CO_2 or N_2O TEA lasers, resulting in an efficient line-tunable optically pumped 16- μm laser system.

The authors wish to thank W. Birkeley for his expert technical contributions.

¹R.R. Jacobs, D. Prosnitz, W.K. Bischel, and C.K. Rhodes, *Appl. Phys. Lett.* **29**, 710 (1976).

²H. Pummer, W.K. Bischel, and C.K. Rhodes, *J. Appl. Phys.* **49**, 976 (1978).

³W.K. Bischel, P.J. Kelley, and C.K. Rhodes, *Phys. Rev. A* **13**, 1829 (1976); W.K. Bischel, R.R. Jacobs, and C.K. Rhodes, *Phys. Rev. A* **14**, 1294 (1976).

⁴C. Freed and A. Javan, *Appl. Phys. Lett.* **17**, 33 (1970).

⁵C. Freed, A.H.M. Ross, and R.G. Donnell, *J. Mol. Spectrosc.* **49**, 438 (1974).

⁶B.G. Whitford, K.J. Siemson, H.D. Riccius, and G.R. Hanes, *Opt. Commun.* **14**, 70 (1975).

⁷F.J. Shimizu, *J. Chem. Phys.* **51**, 2754 (1969); *ibid.* **52**, 3572 (1970).

⁸Y. Ueda and K. Shimoda, in *Laser Spectroscopy* (Springer, Berlin, 1975).

⁹Norris Nereson, *J. Mol. Spectrosc.* **69**, 489 (1978); J.P. Sattler and K.J. Ritter, *J. Mol. Spectrosc.* **69**, 486 (1978)F

¹⁰J.S. Garing, H.H. Nielson, and K.N. Rao, *J. Mol. Spectrosc.* **3**, 496 (1959).

¹¹An accurate value for the $0^2R(5,3,5)$ two-photon transition frequency can be obtained by summing the two single-photon transitions: $0^1R(5,3)$ at $1053.8403 \text{ cm}^{-1}$ from Ref. 7 and the $1^2Q(6,3)$ at 938.7285 cm^{-1} obtained from J.J. Hillman, Theodor Kostuik, David Buhl, J.L. Faris, J.C. Navaco, and M.J. Mumma, *Opt. Lett.* **1**, 81 (1977). This sum is 1992.5688 ± 0.0005 , a value which disagrees with the present result in Table I by 0.0143 cm^{-1} . The source of this discrepancy is yet to be determined.

¹²S.G. Kukolich and S.C. Wofsky, *J. Chem. Phys.* **52**, 5477 (1970); P. Grigolini and R. Moccia, *J. Chem. Phys.* **57**, 1369 (1972); M. Ouyahan and C.J. Borde, *Mol. Phys.* **33**, 597 (1977).

¹⁴J.M. Jauch, Phys. Rev. **72**, 715 (1947).

¹⁵J.S. Bakos, Phys. Reports **31**, 209 (1977).

¹⁶P.F. Liao and J.E. Bjorkholm, Opt. Commun. **16**, 392 (1976); C.K. Rhodes and C.D. Cantrell, in *The Significance of Nonlinearity in the Natural Sciences*, edited by Behram Kursunoglu, Arnold Perlmutter, and Linda F. Scott (Plenum, New York, 1977), p. 293.

¹⁶E. Schnabel, T. Topping, and N. Wilke, Z. Phys. **188**, 167 (1965).

¹⁷We have very recently observed 16- μ m laser emission subsequent to excitation on the 0-2 R (6,5) pump transition shown in Table II. This work will be described in a future publication.

¹⁸F.W. Taylor, J. Quant. Spectrosc. Radiat. Transfer. **13**, 1181 (1973).