Doppler-free two-photon resonances in the ν_2 bands of $^{14}NH_3$ at high Stark fields*

William K. Bischel
Molecular Physics Center, Stanford Research Institute, Menlo Park, California 94025

Ralph R. Jacobs
Lawrence Livermore Laboratory, University of California, Livermore, California 94550

Charles K. Rhodes
Molecular Physics Center, Stanford Research Institute, Menlo Park, California 94025

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Additional two-photon resonances have been observed and identified in the ν_2 bands of $^{14}NH_3$ at high Stark fields with the Doppler-free technique. With an excitation energy of 1880.481 cm^{-1} provided by two CO_2 10.4-μm laser quanta [$P(14)$ and $P(34)$] the observed $(\nu_2, J, K) \rightarrow (\nu_2', J', K')$ resonances are identified as $(0^+,4,4) \rightarrow (2^-,4,4)$ and $(0^-,2,2) \rightarrow (2^-,2,2)$. Violation of the parity rule in the former case is induced by the static Stark field.

In a previous work,[1,2] a technique for applying Doppler-free two-photon absorption to the study of molecular spectroscopy and collisional phenomena was reported. This technique involves combining the tunability provided by the static Stark effect with fixed-frequency CO_2 lasers. It was noted that excited states containing more than one quanta above the ground state could be effectively studied, allowing for the determination of spectroscopic constants and collisional data in a manner similar to the single-photon infrared Stark spectroscopy that has been performed[3-5] on CH_3F, NH_3, and NH_2D.

In this Addendum we report additional Doppler-free two-photon resonances in the ν_2 bands of NH_3 that supplement those of the earlier study.[2] These data illustrate that this method can easily provide rotational constants for the $\nu_2 = 2^-$ excited state of NH_3 which are as accurately known as those of the $\nu_2 = 1$ vibrational state.[6]

The experimental arrangement is the same as that illustrated in Fig. 3 of Ref. 1 and described in Sec. II D of Ref. 2. In this configuration, the two lasers were operated on the $P(34)$ 10.6-μm (probe) and $P(14)$ 10.6-μm (pump) transitions of $^{12}C\,^{16}O_2$. These lasers were actively stabilized and locked 500 kHz below and above 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 CO_2 frequencies. The tuning of the molecular resonance required to achieve this condition was provided by an external static Stark field. For the purpose of eliminating interference from single-photon Doppler-broadened resonances, both the $P(34)$ and $P(14)$ laser intensities were monitored using lock-in detection techniques referenced to the modulation voltage on the Stark cell. Hence any genuine two-photon transition simultaneously manifests narrow resonances on both recording systems, thereby simplifying the identification of any signal observed.

Typical operating pressures in the Stark cell were 10 mTorr. The plate spacing in the Stark cell was calibrated from our previous work[2] to be 0.9983 mm. With this spacing and the above operating pressures, electric fields on the order of 40 kV/cm were obtained before breakdown occurred. The experimental procedure entailed sweeping the Stark field in units of 300 V over the entire 4 kV range and observing resonances on a strip-chart recorder. Voltage sweep rates are

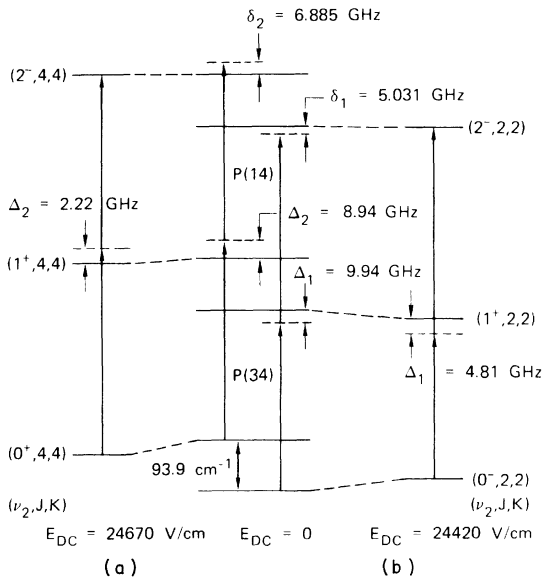

FIG. 1. Schematic diagram of the two-photon resonances $(\nu_2, J, K) \rightarrow (\nu_2', J', K')$ in the $NH_3 Q$ branch for (a) the $(0^+, 4, 4) \rightarrow (2^-, 4, 4)$ transition and (b) the $(0^-, 2, 2) \rightarrow (2^-, 2, 2)$ transition.

TABLE I. Parameters for two-photon resonance.

Two-photon resonance ($\Delta M=0$) $0 \rightarrow 2\nu_2 Q(J,K,M)$	Stark field[a] (V/cm)	Stark shifts[b] (GHz) $\Delta W_g^{(1)}$	$\Delta W_g^{(2)} - \Delta W_f^{(2)}$	Total	Predicted[c] off resonance (GHz) $\nu_{NH_3} - (\nu_1 + \nu_2)_{laser}$	Intermediate-state detuning (GHz) $E_{dc}=0$	$E_{dc} \neq 0$ (resonance)
$aaQ(2,2,2)$	24 420 ± 10	5.052	−0.021	5.031 ± 0.005	5.7	9.94	4.81
$saQ(4,4,4)$	24 670 ± 10	−6.873	−0.012	−6.885 ± 0.005	−7.1	−8.94	−2.22
$saQ(4,4,3)$	32 870 ± 10	−6.865	−0.021	−6.886 ± 0.005	−7.1	−8.94	−2.21

[a] Plate spacing was 0.099 83 cm.
[b] Calculated from Eq. (6) of Ref. 2; all $\Delta W = W - W_0$, where W_0 is the energy of the unshifted level.
[c] Predicted from Refs. 4, 6, and 7.

determined from the lock-in time constant and the width of the resonances being observed. For a time constant of 400 msec and an estimated resonance width of 3 MHz, it was estimated and confirmed that a sweep rate of 0.3 V/sec would be sufficient to observe these resonances.

Using this experimental apparatus, we observed and identified two separate two-photon resonances from the Q branch of the ν_2 vibrational-rotational manifold. These two resonances are illustrated in Fig. 1 and are the $(\nu_2, J, K) \rightarrow (\nu_2', J', K') = (0^-,2,2) \rightarrow (2^-,2,2)$ and $(0^+,4,4) \rightarrow (2^-,4,4)$ transitions. The large Stark field required to shift these transitions into resonance breaks the parity selection rule in the ground state, allowing the $saQ(4,4)$ two-photon transition to occur with appreciable strength. It is noteworthy that these two resonances occur within 250 V/cm of each other. As indicated in Table I, the $M_J = 3$ component of the $saQ(4,4)$ two-photon transition was observed, but not the $M_J = 1$ component of the $aaQ(2,2)$ two-photon transition, because of electrical breakdown problems arising from the Stark field. These transitions were identified from the existing Stark spectroscopy of NH_3,[4,6] and from the hot-band spectra given in Ref. 7. The $saQ(4,4)$ two-photon transition was assigned to the 24 670-V/cm signal, since the $M_J = 3$ component occurred at $\frac{4}{3}$ times this voltage (see Table I). The $aaQ(2,2)$ two-photon transition was assigned to the 24 420-V/cm signal, since this resonance occurred close to the value predicted from Refs. 4 and 7. Even though we were not able to observe the $M_J = 1$ component of this transition, we are confident of the assignment, since the only other two-photon transition $aaQ(1,1)$, which would give a similar M_J pattern, is expected to occur at much higher voltages.

The Stark shifts for these transitions are given in Table I and are calculated from Eq. (7) of Ref. 2. For those fields, second-order corrections can contribute significantly (~10 linewidths) to the tuning. It is satisfying to note that the 2^- excited-state dipole moment measured in Ref. 2 correctly predicts the second-order ($\Delta W_f^{(2)}$) correction to the tuning rate (see Table I). It would be possible to improve the value of this dipole moment by an order of magnitude if computer fitting techniques such as those outlined in Ref. 2 were used to reduce these data.

In conclusion, we have observed and identified two new two-photon resonances in the ν_2 bands of NH_3. These results extend the findings of our previous study[2] and indicate that the two-photon spectroscopy of vibrational levels not accessible from the ground state by linear techniques can provide a precise and generally useful method for studying these excited levels. Finally, we note that the use of near-resonant transitions of this nature may be utilized for optical up-conversion to the 5-μm region by either optical pumping or parametric processes.

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