Doppler-free two-photon absorption of NH_3 using a CO_2 and diode laser

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A successful two-photon spectroscopy experiment using combined CO_2 and diode lasers operating in the 10-μm region is reported. Beams from the two lasers were passed in nearly opposite directions through a sample cell while the intensity of the transmitted diode laser beam was monitored as a function of its frequency. Doppler-free two-photon absorption signals were observed for the rovibrational transitions of NH_3, $T(v_2,J,K) = (2^-,7,7) \leftarrow (0^-,7,7,)$ and $(2^-,1,1) \leftarrow (0^-,1,1)$.

In the past decade it has become possible to exploit multiphoton-absorption techniques for gas-phase atomic and molecular spectroscopy. The features of high sensitivity and/or high spectral resolution has permitted the investigation of a wide variety of problems such as the spectroscopy of electronically excited states, the study of state-to-state relaxation processes, and the observation of forbidden transitions. The initial microwave-microwave double-resonance experiments of Oka,[1] have been extended to infrared-microwave,[2–4] and visible-visible[5] double-resonance experiments. Related phenomena, first shown in the visible region using fixed frequency and tunable dye lasers, involve two-photon absorption events where the intermediate state is not in resonance; when the light beams propagate in opposite directions through the sample the Doppler effect is eliminated and very high resolution (sub-Doppler) spectra are obtained.[6–8] Recently, this technique has been extended to the infrared region by Bischel *et al.*[9,10] By combining two fixed-frequency CO_2 lasers (wavelength near 10 μm) with molecular Stark tuning, they observed Doppler-free rovibrational transitions in NH_3 and CH_3F. In the present paper we report the first detection of Doppler-free two-photon absorption signals in the v_2 band of NH_3 by using a fixed-frequency CO_2 laser and a diode laser. Because of the tunability of the diode this technique promises to have a wide field of application. In particular, two-photon spectra, obeying different selection rules than ordinary spectra, are of great help in making unequivocal level assignments in complex molecules.

A block diagram of the experiment is shown in Fig. 1. A CO_2 pump beam and a diode laser probe beam propagate in nearly opposite directions through the sample cell. The angle between the beams (178°) was chosen to maximize the volume in which they overlap, while permitting them to be separated far from the cell. The length of interaction achieved was about 5 cm. The CO_2 laser was tuned to the appropriate CO_2 pump line by means of a grating and was frequency modulated at 1.6 kHz by means of a piezoelectric transducer on the cavity output mirror; the peak-to-peak modulation was about 7.5 MHz. The diode laser frequency was, on the other hand, swept through the resonance region by applying a ramp current to the diode, while the transmitted intensity was measured by synchronous detection of the signal from a cooled Hg-Cd-Te ir detector. A critical element in the adjustment of the CO_2 laser beam was to ensure that a minimum of scattered CO_2 laser radiation fell on the laser diode, whose frequency of oscillation was affected by it, probably through a minute heating effect. Most of the residual CO_2 ra-

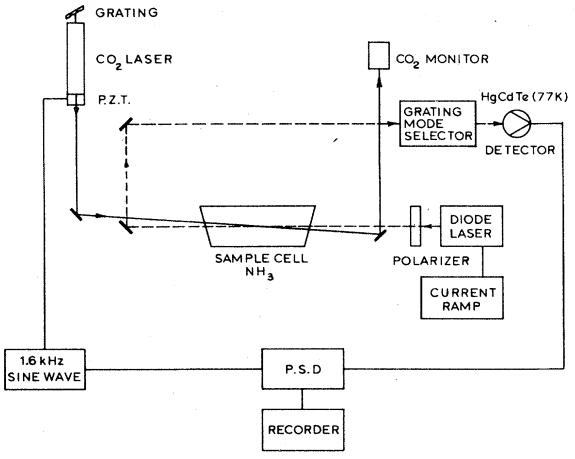

FIG. 1. Schematic of experimental apparatus. CO_2 laser (ca. 15-W power) and diode laser (ca. 1 mW) beams propagating in nearly opposite directions are focused in a 10-cm-long cell containing NH_3 gas. The transmitted intensity of the diode laser beam is measured with a cooled detector and a phase-sensitive detector. The CO_2 laser is frequency modulated. The polarizer reduces CO_2 power leakage into the diode laser system.

diation was suppressed by orienting the polarizations of the two laser beams at right angles and placing a polarizer in front of the diode. The diode frequency, nevertheless, remained slightly dependent on the CO_2 laser power.

Ammonia gas was chosen as the sample because of its large electric dipole moment, and because some transitions in the ν_2 band are known to lie near CO_2 laser frequencies. Furthermore, since the molecule is of considerable astrophysical significance, it is important to have as precise information as possible on its energy-level structure. The relevant energy levels and the transitions involved in this experiment are shown in Figs. 2 and 3. The frequency shift of the intermediate levels from the CO_2 lines has been measured using heterodyne spectroscopy by Hillman *et al.*[11] The pertinent data are summarized in Table I.

The recorded absorption signals are shown in Figs. 4 and 5. The most prominent feature lies at the already known one-photon absorption frequency, the two-photon absorption being the weaker, much narrower feature. The absorption at the single-photon frequency does not arise directly from two-photon processes; nevertheless it could be expected in this experiment from either an ac Stark shift of the NH_3 levels by the intense CO_2 laser field, or by a modulation of the population of the intermediate level. The observed peak is believed to be, however, largely due to another mechanism—a very weak modulation of the diode laser frequency due to scattered CO_2 radiation, sufficient to give a signal when scanning through the frequency region of the very strong one-

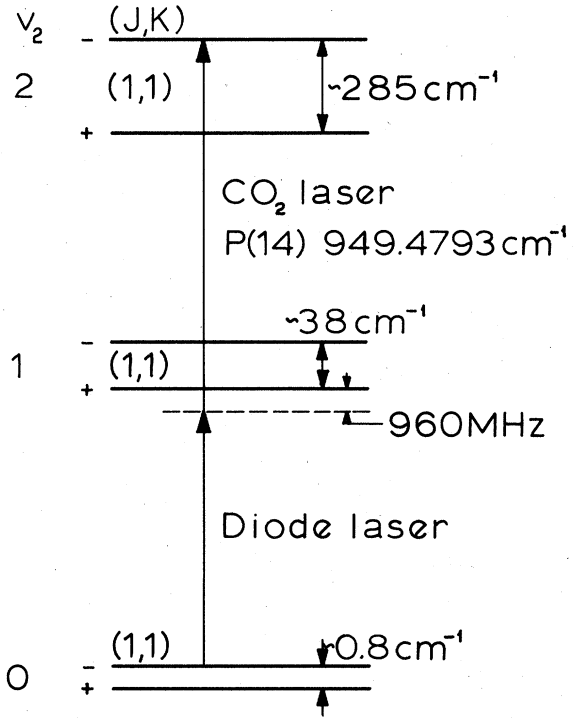

FIG. 2. Energy-level diagram (not to scale) showing the two-photon transition in the ν_2 band of NH_3 for the $J,K=1,1$ manifold. The intermediate level lies below the $v_2=1$ inversion doublet.

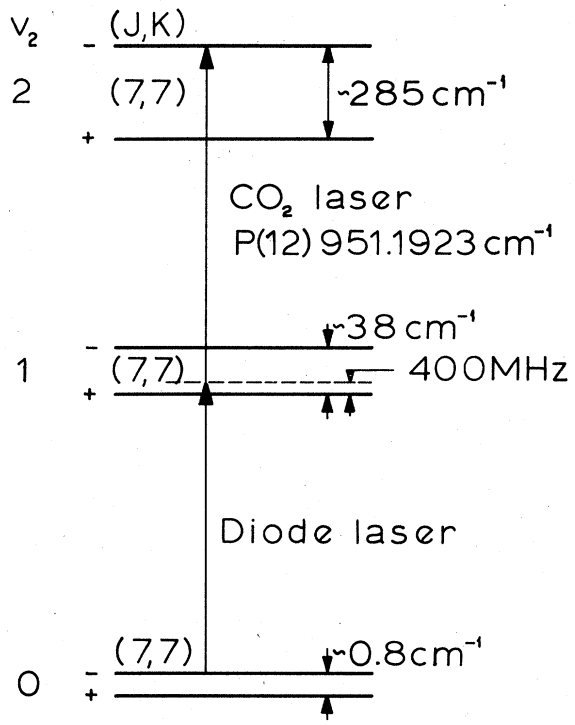

FIG. 3. Energy levels for the $J,K=7,7$ manifold, and observed two-photon transition.

TABLE I. NH_3 transitions and CO_2 pump lines, cm^{-1}.

Transition $(v_2'',J'',K'')-(v_2',J',K')$			Observed wave number
$aQ(1,1)$	$1^+,1,1$	$0^-,1,1$	931.627 78[a]
$2sQ(1,1)$	$2^-,1,1$	$1^+,1,1$	949.477 32[b]
$aQ(7,7)$	$1^+,7,7$	$0^-,7,7$	925.599 61[a]
$2sQ(7,7)$	$1^+,7,7$	$1^+,7,7$	951.204 2[b]
CO_2 pump lines			
$P(14)$		949.479 313[c]	
$P(12)$		951.192 264	

[a] S. Urban, V. Spirko, and D. Papousek (private communication).
[b] Reference 11.
[c] F. R. Peterson, D. G. McDonald, J. D. Cupp, and B. L. Danielson, in *Laser Spectroscopy*, edited by R. G. Brewer and R. Mooradian (Plenum, New York, 1974).

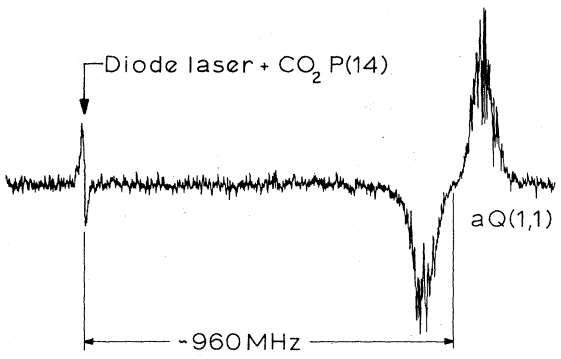

FIG. 4. Recorder tracing of observed NH_3 spectra near 11-μm wavelength. Two-ir-photon absorption $(v_2,J,K) = (2^-,1,1) \leftarrow (0^-,1,1)$, and a single-photon transition, $(v_2,J,K) = (1^+,1,1) \leftarrow (0^-,1,1)$ referred to in the literature as $aQ(1,1)$ (Ref. 12) are observed simultaneously. The phase of the two-photon transition is inverted with respect to the single-photon transition.

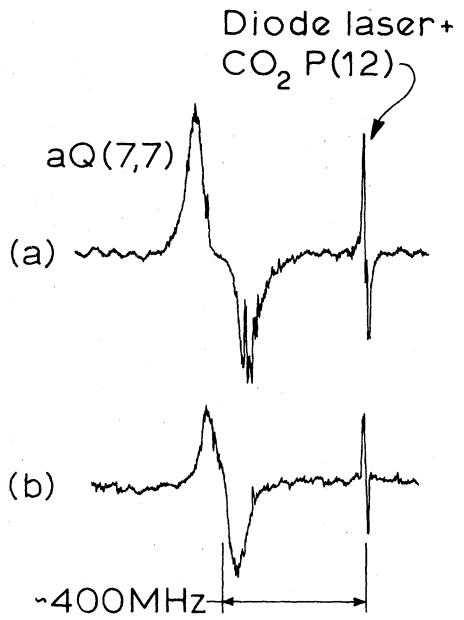

FIG. 5. Recorder tracings of the two-photon transition $(v_2,J,K) = (2^-,7,7) \leftarrow (0^-,7,7)$ and the single-photon transition $aQ(7,7)$ or $(v_2,J,K) = (1^+,7,7) \leftarrow (0^-,7,7)$. The single-photon and the two-photon transition have the same phase. Traces (a) and (b) are for NH_3 pressures of about 0.1 and 0.4 torr, respectively.

photon absorption line. Although of little intrinsic interest here, its center provides a frequency marker, and its width is a measure of normal line broadening. It will be noticed that the relative phase of the single- and two-photon transitions is different in Figs. 4 and 5; the reason for this will be discussed in a later publication.

Because of partial cancellation of the Doppler effect the width of the observed two-photon line arises mainly from pressure broadening and instrumental effects. The precision of our measurements is not yet adequate to obtain reliable pressure-broadening data; nevertheless the measured linewidths are consistent with the following considerations. The residual Doppler width may be shown to equal

$$\Delta\nu = 2(\nu_1^2 + \nu_2^2 + 2\nu_1\nu_2\cos\theta)^{1/2}[(2\ln 2)kT/mc^2]^{1/2} ,$$

where ν_1 and ν_2 are the CO_2 and diode laser frequencies, respectively, and θ is the angle between the beams. Here, $\Delta\nu$ equals 3.7 MHz, whereas the Doppler width of the single-photon transition equals 82.5 MHz (the observed feature is much wider due to saturation). At the pressure at which spectra were taken, ~0.2 torr, the linewidth due to pressure broadening is expected to be ~6 MHz.[10] Further, a small amount of transit-time broadening, of the order of 1 MHz, can be expected since the CO_2 laser beam was focused in the cell. These three effects together can be expected to give a linewidth of 7 MHz, the line itself being approximately Lorentzian in shape. Since the FM deviation of the CO_2 laser equaled 7.5 MHz the expected separation between the positive and negative peaks of the observed two-photon feature equaled 7 MHz; the measured separation is instead 8.5 MHz. The excess width is believed to arise from frequency jitter of the diode laser. Such jitter is also believed responsible for the strong noise spikes on the peaks of the one-photon feature. It is clear that to obtain precise line profile measurements the diode must be stabilized.

The frequency separation between the one- and two-photon features could in principle be measured quite accurately from our records; unfortunately we did not possess an infrared wavemeter of sufficient precision to enable us to improve the values which can be calculated from known frequencies of one-photon transitions. Nevertheless, it is clear that the potential for making this type of measurement has been demonstrated.

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