Effect of Laser Irradiation on Infrared Spectrum of Ammonia

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Although a few observations have been reported on the laser-induced fluorescence of vibration-rotation transitions,[1-3] they have been limited to the region where laser frequencies locate, and hardly have they been extended to the region of pure rotational transitions. In this communication, we report on the observation of emission spectrum of ammonia as well as the change in the absorption spectrum in the far-infrared by irradiation of a CO_2 laser. Similar measurements have also been made for the ν_2 band in the 10 μ region, with which the laser frequencies coincide.

The CO_2 laser used consists of a 1.5 m discharge tube with two internal mirrors; one is a concave mirror of radius 3.5 m and the other is a flat germanium plate from which the laser beam is taken out. A leakage transformer (15 kV) was used for ac-excitation. The laser output is distributed among a few vibration-rotation transitions of the 10.6 μ band, of which the P(20) line at 944.25 cm^{-1} is the strongest.

For spectroscopic measurements a cross-cell similar to that described by Ronn[1] was used. The emission perpendicular to the incident laser beam was observed. With this cell we also made absorption measurements with or without laser irradiation. In Fig. 1, we show the emission spectrum of NH_3 (150 mmHg) obtained in the 340—200 cm^{-1} region with a Hitachi EPI-L spectrophotometer, along with the absorption spectra of NH_3 at the same pressure with and without the laser irradiation. The emission is strongest at about 275 cm^{-1} ($J=13\rightarrow14$), where the difference between the normal and irradiated absorption spectra is largest.

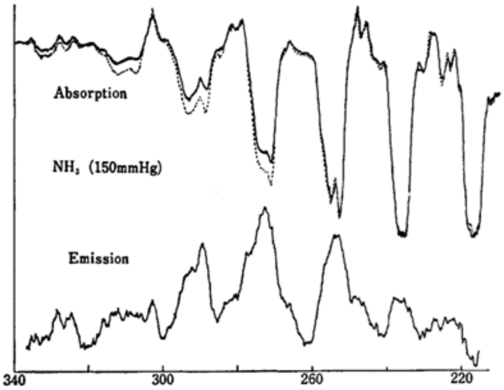

Fig. 1. Infrared spectra of ammonia (150 mmHg) in the 340—200 cm^{-1} region: laser-induced emission (below), and absorption spectra (above). Dotted line indicates the irradiated spectrum.

In the 10 μ region we have also observed rather strong emission. As reported by Ronn,[1] the spectrum is quite complex, probably due to the coincidence of the laser lines with "hot transition" $\nu_2{}^s\rightarrow2\nu_2{}^a$ of NH_3. The change in the absorption spectrum is also complex; however, a few remarks can be made: (1) Remarkable change in intensity was observed for the R(12)-R(16) lines of $0^s\rightarrow1^a$ band, and their intensities increased up to twice. (2) The Q-lines with $J=\sim10$ at about 950 cm^{-1} also exhibited intensity increase under the same conditions, whereas the changes were not appreciable for the corresponding P-lines. (3) Every absorption band associated with $1^s\rightarrow2^a$ transitions increases its intensity when irradiated. (4) Some fundamental lines with low J showed intensity decrease.

The above results may be interpreted as follows: since the CO_2 laser serves as a pumping source, the molecules absorb the light of characteristic frequencies and are exicted to the corresponding vibration-rotation levels. The collison relaxation time, however, is sufficiently short to allow the redistributions of the molecules among all the vibration-rotation levels. We may say that a dynamical equilibrium is established, in which the populations of the upper vibrational levels as well as the rotational temperature of each vibration level are higher than those in the thermal equilibrium. Thus, the CO_2 laser irradiation affects not only the vibration rotation transitions around the laser frequencies but also the other vibration-rotation transitions. The observed pure rotational emission and the intensity change in the absorption spectrum can also be explained on the same basis.

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