Untangling the overtone spectra using the two-temperature technique in supersonic jets: methane and ammonia

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Near-infrared spectroscopy in supersonic jets is established as a powerful tool to untangle the complicated ro-vibrational structure of the overtone molecular absorption bands. Low temperatures in the supersonic expansions lead to reduction of higher rotational states populations and the measured spectra thus contain only spectral lines that originate from the lowest rotational states. In addition spectral line Doppler broadening is reduced at low temperatures. Consequently the spectra are in general less congested and easier to assign.

In this contribution we demonstrate the application of two-temperature technique using slit jet molecular beams: The spectra are measured at two different temperatures and the changes in line intensities are used to determine empirical values of lower state energies which further aides the spectral assignments. Supersonic jet experiments are perfectly suited to apply this approach to species with high boiling points, which have very low vapor pressures at reduced temperatures and therefore weak absorptions in the cold cell experiments. High level of supersaturation can be achieved in the jet expansion before condensation (clustering) onset, and even condensable species such as H_2O, NH_3 or halo-methane molecules can be cooled to temperatures close to the absolute zero. We demonstrate the technique for spectra of $^{12}CH_4$ and 13CH4 species in the lower icosad region (7050 – 7350 cm^{-1}) and for NH_3 in $^2n_3$ spectral region (6600-6900cm^{-1}). The measurements were carried out by cw-diode laser spectrometer in combination with slit jet supersonic expansion. We demonstrate that by controlling the expansion conditions the temperature can be varied over a wide range - between 20K and 140K - and we show how the temperature dependence of the line intensities is used to determine the lower state rotational energies and to estimate the lower state rotational quantum numbers.

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