MOLECULAR ROTATION IN THE PRESENCE OF INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION: TECHNIQUES AND EXPERIMENTAL DESIGN

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As an ongoing effort to develop high sensitivity techniques for dynamic rotational spectroscopy based on Fourier transform microwave (FTMW) spectroscopy we will describe the general methods and experimental setup used to record rotational spectra in vibrationally excited molecules. These techniques are used to measure the rotational spectrum of a single eigenstate where the lineshape analysis yields information on the intramolecular dynamics. The rotational spectra are recorded after infrared excitation of the acetylenic C-H fundamental. The methods presented are similar to those developed by Endo for electronic transitions.[a] The mechanisms involved depend on the timing of the MW pulse relative to the FTMW polarizing pulse. As a means to minimize interference problems, detection of the molecular emission takes place when there are no light sources being coupled into the cavity. A comparison of the techniques will be discussed in light of recent results for phenylacetylene.

[a] M. Nakajima, Y. Sumiyoshi, Y. Endo, Rev. Sci. Instrum. 73, 165 (2002).