

The Submillimeter-wave Rotational Spectra of Interstellar Molecules

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Abstract

We discuss past and recent progress in our long-term laboratory program concerning the submillimeter-wave rotational spectroscopy of known and likely interstellar molecules, especially those associated with regions of high-mass star formation. Our program on the use of spectroscopy to study rotationally inelastic collisions of interstellar interest is also briefly mentioned.

1. Introduction

More than 120 molecules have been discovered in interstellar and circumstellar clouds by the methods of high resolution spectroscopy. Although most of these molecules are unsaturated (hydrogen-poor), saturated and near-saturated molecules can be found in regions of star formation, especially those associated with high-mass stars. These hydrogen-rich molecules are especially prominent in so-called hot cores, which are quiescent regions at densities ($\approx 10^6$ cm⁻³) and temperatures (100-300 K) higher than standard values in dense interstellar clouds. Some well-studied hot cores are the Hot Core and Compact Ridge in Orion, and the molecular Heimat source Sgr B2(N-LMH) in Sagittarius B2. It is generally thought that the saturated molecules are formed via a two-stage process in which the first stage occurs at low temperatures before the onset of star formation. In this stage, the molecule CO is hydrogenated on grain surfaces to form formaldehyde (H₂CO) and methanol (CH₃OH), which develop large abundances in grain mantles. As temperatures begin to rise during star formation, the grain mantles evaporate and the particularly high abundance of methanol makes it an important precursor of still larger saturated organic molecules that form from it via gas-phase chemical processes (Millar & Hatchell 1998).

Many if not most of the saturated organic molecules in hot cores have complex rotational spectra due to a large-amplitude motion known sometimes as torsion and sometimes as internal rotation. This motion is most prominent in methyl (-CH₃) groups; the hydrogens of a methyl group rotate around the bond connecting the carbon to another heavy atom. The rotation

is not free, but is constrained by a potential of three-fold symmetry. If one considers torsion as a one-dimensional motion, one can easily determine the energy levels and eigenstates of the system. The torsional levels are typically separated by ≈ 100 K, and each level is split into two sublevels, characterized by the letters A and E. Molecules with two rotating methyl groups have torsional sublevels characterized by two letters, e.g. AA, AE, etc. In any case, rotational transitions occur within each torsional sublevel. Since the rotational constants are not the same for different torsional levels, there are more rotational spectral lines than in rigid molecules of the same size. Moreover, torsional and rigid (end-over-end) rotational motions interact with one another, making the quantum mechanics of the overall system rather complex, especially for molecules such as methanol with rather small barriers against torsional motion. The result is that the laboratory analysis of common internal rotors such as methanol and methyl formate has taken long periods of time to be even partially understood. Nevertheless, we have managed to study and analyze the spectra of a long list of internal rotors up to frequencies of 500 GHz - 1 THz. The molecules include: methanol (CH_3OH) and several of its isotopomers ($^{13}\text{CH}_3\text{OH}$, CH_3OD , CH_2DOH , and CHD_2OH), methyl mercaptan (CH_3SH), acetaldehyde (CH_3CHO), methyl formate (HCOOCH_3) and one of its isotopomers (DCOOCH_3), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), dimethyl ether (CH_3OCH_3), and acetone (CH_3COCH_3). In addition to these internal rotors, we have studied a number of more rigid species detected in hot cores, including ethyl cyanide ($\text{C}_2\text{H}_5\text{CN}$), ethylene oxide ($\text{C}_2\text{H}_4\text{O}$), and glycolaldehyde (CH_2OHCHO).

2. Laboratory Program

The microwave laboratory at the Ohio State University, which moved from Duke University more than a decade ago, has long been involved with the extension of rotational spectroscopy of gas-phase species into the millimeter-wave and submillimeter-wave regions of the electromagnetic spectrum. We currently have a variety of spectrometers that operate at frequencies through 1 THz. In addition, a close collaboration with the spectroscopy group in Cologne, Germany, allows us to utilize their spectrometers at frequencies to 2 THz. One of the more exciting recent developments in our laboratory at Ohio State has been a fast-scan spectrometer with the acronym of FASSST (Fast Scan Submillimeter-wave Spectroscopic Technique) (Petkic *et al.*, 1997). With this technique, a frequency range of 100 GHz can be swept in a matter of seconds, and a large number of spectral lines recorded. The rate-limiting step in the analysis of the spectrum then becomes the determination of the quantum numbers for each transition and the fitting of the frequencies of the assigned spectral transitions to calculated values obtained with an effective Hamiltonian. Such a Hamiltonian normally contains a number of adjustable parameters, known as rotational and distortion constants, which multiply assorted kinetic and potential operators. For molecules that undergo internal rotation, these sets of constants are joined by constants relating to the torsional motion and its interaction with the end-over-end rigid-body rotation (De Lucia *et al.*, 1989). Once a large number of spectral lines are fit to an effective Hamiltonian, one can obtain their intensities, normally in the form of transition strengths, and one can predict frequencies for many lines not measured or assigned in the laboratory (Groner *et al.*, 1998).

At the current time, we are studying rotational-torsional spectra of the molecules *trans*-ethyl methyl ether ($\text{CH}_3\text{OC}_2\text{H}_5$) and methyl carbamate ($\text{H}_2\text{NCOOCH}_3$). Neither of these species has been detected in hot cores, possibly because their millimeter-wave spectra have not yet been measured. Since dimethyl ether has a high abundance in hot cores, it is likely that methyl ethyl ether, the next member of the ether series, is also detectable. Methyl ethyl ether possesses two rotating methyl groups and these groups are not in similar environments. Such a situation is rather complex spectroscopically, and the analysis of the spectrum is taking some time to complete. Methyl carbamate is being studied because it is an isomer of glycine, the simplest amino acid. Although glycine has not been detected in space, methyl carbamate may be much more abundant since it is a simple derivative of the abundant methyl formate.

3. Inelastic Collisions

We also use submillimeter-wave spectroscopy to monitor rotationally inelastic collisions by pressure-broadening experiments and by pump-probe double-resonance studies. Astronomers need cross sections for inelastic collisions to analyze spectral lines excited collisionally under non-LTE conditions. Since our laboratory studies cannot be undertaken under all conditions relevant to astronomy, they are also used to constrain intermolecular potentials so that detailed quantum mechanical calculations can be undertaken for the conditions not studied in the laboratory. Examples of collisional systems studied under this program are $\text{CO} + \text{H}_2$, $\text{H}_2\text{CO} + \text{H}_2$, and $\text{HDO} + \text{H}_2$, as well as the ion-molecule system $\text{HCO}^+ + \text{H}_2$ (Oesterling *et al.*, 2001).

4. Some Future Spectroscopic Plans

Our future spectroscopic plans include the study of newly detected interstellar molecules such as ethylene glycol and vinyl alcohol, both of which were identified on the basis of lines not measured in the laboratory, as well as the study of common internal rotors in excited torsional states, since these states are at energies relevant to warm star-formation regions. Finally, we plan to push our spectral studies to higher frequencies so that the future analysis of Herschel data will be feasible.

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