

Optically Pumped Far-Infrared Lasers Through High Resolution Molecular Spectroscopy of Methanol

Indra Mukhopadhyay
Department of Physics and Engineering
Albany State University (West Campus)
Albany, GA 31707, USA

Abstract: *In this paper, we have reviewed the details of experimental and theoretical aspects of the high resolution molecular spectroscopy of methanol isotopic species. The methods of spectroscopic assignments and analysis have been discussed. The applications of the spectroscopic techniques, particularly of Fourier transform spectroscopy in the field of optically pumped methanol far infrared lasers have been discussed. New assignments have been deduced for TEA-CO₂ laser pumped methanol and CW CO₂ pumped ¹³CD₃OD. Stark effect analyses and the determination of accurate dipole moment values have been discussed for CH₃OH, ¹³CH₃OH and CH₃¹⁸OH. The importance of high resolution spectroscopy is also discussed in terms of astrophysical detection [1-54].*

Keywords: Astrophysics, Synchrotron Radiation, Spectroscopy, Interstellar Space, Methanol.

I. INTRODUCTION

Although Methyl Alcohol is one of the simplest asymmetric molecules capable of hindered internal rotation, its energy level structure is extremely complicated and leads to strong interest to the study of FIR and IR spectra. It has been the subject of great spectroscopic interest in the microwave (MW) to infrared (IR) region of the electromagnetic spectrum. A significant discovery, which brought a strong practical aspect to the study of the spectrum of methanol, was made by Chang et al.[1] when they obtained intense FIR laser radiation from methanol optically pumped by a CO₂ laser. This led to study of the molecule in two new directions: (a) high resolution spectroscopy in the FIR and IR regions, and (b) experiments exploring the range of possibilities of optically pumped methanol FIR laser transitions. In fact methanol and its isotopic derivatives are the richest source of optically pumped FIR lasers, accordingly one third of the total number of FIR laser lines known [2]. There are two main reasons for this high performance: (i) methanol has a strong IR band corresponding to the C-O stretch which overlaps extremely well with the CO₂ laser lines operating in the 10 μm region, and (ii) the internal rotation and the small asymmetry in the molecule offer strong and dense FIR spectrum in a wide frequency range. High resolution spectroscopy provides detailed knowledge of the energy level pattern and help in identifying and predicting FIR laser lines.

In the present work the application of high resolution IR and FIR spectroscopy of methanol to optically pumped far infrared lasers has been reviewed. In unraveling the complexity of energy level structure of methanol and its isotopic species various spectroscopic methods were applied: (i) high resolution Fourier transform spectroscopy of the vibrational IR bands and the torsional-rotational FIR band, (ii) the frequencies, relative intensities of the emission FIR lines along with the pump laser frequencies, (iii) Stark effect measurements of the emission as well as absorption lines, and (iv) microwave and MMW spectra on the pure rotational transitions. The analysis of the above complementary types of data is beginning to provide significant understanding of the detailed picture of the energy level structure of methanol and its isotopic species and in turn providing valuable information for the identification and prediction of optically pumped FIR emission lines. The identification of quantum states is of importance to experimental laser scientists for optimization of laser efficiency through informed control of operating conditions, while the predictions make future discovery of new emission lines unambiguous. Our study of the FIR absorption spectrum (20-350 cm⁻¹) resulted in an atlas [2] of about 20,000 precise line positions with an accuracy of about ±6 MHz. This atlas is identified by the International Union of Pure and Applied Chemistry (IUPAC) as a secondary wavenumber standard in the FIR region [3].

In this paper, an overview is presented on the torsion-rotation-distortion Hamiltonian model for slightly asymmetric molecules capable of hindered internal rotation in three-fold potential barrier. The detailed discussion on the Hamiltonian for symmetric and slightly asymmetric molecules undergoing three fold internal rotation will be the subject of another paper. The application of the model in the case of methyl alcohol and its isotopic species resulted in the analysis and interpretation of torsion-rotation and vibration-torsion-rotation high resolution Fourier transform spectra. Accurate molecular parameters were

thereby obtained for these species. The IR analysis provided the assignments and predictions of many optically pumped FIR laser lines. Using accurate combination loops of measured transitions the frequency of the FIR emission lines are improved by at least an order of magnitude better than can be obtained from direct wavelength measurements. The typical accuracy of our calculated FIR laser frequencies is in of the order of ± 6 MHz. Many of the predicted FIR laser lines have been subsequently realized by others, some of these examples will be discussed.

Out of the isotopic derivatives, the asymmetrically substituted species e.g., CH_2DOH and CHD_2OH , the problem becomes even more complicated. This is due to the fact that torsional potential is not three fold more and this results in a large relaxation of the selection rules. These molecular species offer even better choice for FIR emission media due to more possibility of coincidence with CO_2 laser and dense FIR spectrum. A brief outline of the spectroscopic problems will be presented for these asymmetric species. The results will be valuable for exploring new emission lines in the FIR region.

Synchrotron Radiation (SR) sources are now available in handful of facilities around the world. These provide intense and highly collimated source in the far infrared (FIR) and infrared (IR) region of the electromagnetic spectrum. These makes the SR sources very attractive for Fourier transform (FT) spectroscopy. The conventional FT spectrometers use thermal sources e.g. Globar and Hg discharge source operating at high pressure, which are rather weak in brightness and divergent. Most facilities use the commercial FT spectrometer or home built spectrometer coupled with FIR beamline in an electron storage ring or even linear accelerations using deflectors or wigglers. These offer very high resolution and excellent signal/noise (S/N) ratio. Thus the uses of SR source based FT spectrometers are suitable for spectroscopy of highly crowded region of a spectrum and for very weak lines.

In the FIR region very high resolution spectroscopy is possible using the SR sources where spectroscopy with conventional sources with rather low brightness is particularly difficult. Spectrometers used at IR beamlines are virtually always Fourier transform instruments, for conventional high spectral resolution facilities. For the gaseous sample the sharp spectral lines impose coherence on the IR continuum radiation from the synchrotron. The optimum resolution obtained in the transformed spectra is limited the approximate instrumental line shape achieved by an apodization function applied in the time domain. In the FIR region the low line width (Doppler) provides its own apodization and hence sub Doppler spectra can be achieved.

In the field of astrophysics a large variety of molecules have been discovered in cold interstellar clouds especially near the star forming regions, out of these molecules methanol and its isotopic derivatives are present almost everywhere. Hence, methanol has become known as an interstellar “weed” in the radio astrophysical landscape. Recent advancements in a number of facilities, e.g., the Heterodyne Instrument for the Far-Infrared (HIFI) with extended spectral coverage, extreme sensitivity and resolution in the FIR region on board the Herschel Space Observatory, the ALMA (Atacama Large Millimeter Array) and the SOFIA (Stratospheric Observatory for Infrared Astronomy) have created substantial demand for accurate laboratory databases for the methanol and its isotopic derivatives. The present paper provides a catalog of the most accurate wavenumbers for the asymmetrically deuterated species known so far using the synchrotron based FT spectrometer at the Canadian Light Source. This will make it well suited for development of extensive FIR and IR spectral atlases for astrophysical discovery.

The deuterated methanol species have been observed in most interstellar sources where the parent species (CH_3OH) has been detected. These observations are a powerful diagnostic of evolution of chemistry in those clouds using the ratio of D/H abundances. The deuterated species have lower zero-point vibrational energy compared to the parent species makes the D/H ratio quite higher than the average cosmic value. It is noteworthy that the deuterated species are present in cometary tails and star forming regions.

In fundamental spectroscopy the symmetrically deuterated methanol species poses a challenge to theoretical scientists because of the complex asymmetry interactions with various degrees of freedom. These complexities have been outlined in our previous papers. Nevertheless, a complete mapping of the ground vibrational state (in the three lowest torsional sub-states) allowed us to have a global analysis of the energy levels. The complete atlas is for about 4279 assigned transition with an accuracy reaching microwave accuracies has been prepared. This atlas can be had from the author vis e-mail. The readers are referred to the bibliography presented for further information [4-54].

II. THEORETICAL ASPECTS

The two main criteria for a molecule to be an efficient source of optically pumped FIR laser lines are: (i) the molecule should have a strong absorption band in the region of operation of a strong pump laser (almost invariably a CO_2 laser) and (ii) the molecule should have a permanent dipole moment. These conditions are very well suited in Methanol and its isotopic derivatives making these molecular species the best known source of FIR laser emission lines. In fact methanol and its isotopic species account for more than one third of the 4500 CW optically pumped FIR laser emission. In addition, there remains a large number of lines obtained from methanol using TEA CO_2 laser. Furthermore, the large angle internal rotation in the molecule provides the possibility of torsional transitions in addition to the pure rotational transitions. These make it possible to

obtain FIR transitions in a much wider frequency range compared to any other media. In methanol species the strong band corresponding to the C-O stretch vibration overlaps very well with the CO₂ laser lines operation in the 9.6 and 10.6 μm bands. There remains a definite but random probability of coincidence between the discrete CO₂ laser lines and the absorption lines in the C-O stretch band. As an example we present in Table 1, the location of the band head of the C-O stretch band for some of the isotopic species of methanol. It can be noticed that useful tuning of the absorption bands can be achieved by isotopic substitution in the absorbing media. This tuning can also be achieved by using isotopic CO₂ lasers but experimentally it is difficult. We present in Table 2, a list of strong optically pumped FIR laser lines in methanol and its isotopic derivatives arranged in terms of increasing wavelength.

When CO₂ laser is efficiently absorbed in methanol vapor media the molecules are excited to the first excited C-O stretch state and subsequent radiative transition produces FIR laser radiation in a cavity. High resolution Fourier transform spectroscopy has proven to be a very powerful tool for the identification, prediction and frequency refinement of optically pumped FIR laser lines.

The internal rotational motion of the OH group with respect to the CH₃ top makes the energy level structure of methanol very complicated. This torsional motion is opposed by a potential barrier with a period of 2/3γ, because of the three equivalent positions of the OH group with respect to the methyl top. This kind of potential as shown in Fig. 1, can be represented in terms of the internal rotational angle γ by a Fourier series expansion :

$$V(\gamma) = \sum_{\ell=0}^{\infty} (V_3/2) (1 - \cos 3\ell\gamma) \dots\dots (1)$$

The dominant contribution is due to the first term V₃, called the barrier height, while the V₆ term gives the departure of the potential curve from being a sinusoid and is usually very small. In the infinite barrier limit, the stationary states would be the torsional levels like the vibrational levels of a harmonic oscillator, labeled n = 0, 1, 2,, where n is the torsional vibrational quantum number. Each n state would be threefold degenerate, because of the threefold symmetry of the potential function. The finite height of the barrier potential introduces probability of tunneling between the three wells of the potential and thereby splits each n state into three states labeled A, E₁ And E₂ .

The internal rotation can interact with the remaining vibrational degrees of freedom, and these in turn can interact with the overall rotation of the molecule. Thus a coupling between internal and overall rotation exists in an indirect way through the non-rigid nature of the molecule. The coupling between torsion and overall rotation can be removed to zeroth order by using an internal axis method (IAM) in which the methyl top and the OH framework have equal and opposite torsional angular momentum. Higher order interaction terms are then included as first order perturbations to the zeroth order Hamiltonian H⁰. This zeroth order Hamiltonian within a given vibrational state can be written as a sum of three terms representing a symmetric rotor H⁰_{Rsym}, the torsion H⁰_T, and the molecular asymmetry H⁰_{Rasym} :

$$H^0 = H^0_{Rsym} + H^0_T + H^0_{Rasym} \dots\dots\dots (2)$$

Where,

$$H^0_T = Fp^2 + (V_3/2)(1 - \cos 3\gamma) \dots\dots\dots (3)$$

and the other terms can be represented in terms of various moment of inertia elements of the molecule. The axis system is chosen in such a manner that it has its origin at the center of mass of the molecule, the a axis along the CH₃ top axis, the c axis perpendicular to the COH plane, and the b axis mutually perpendicular to a and c axes. Pγ is the torsional angular momentum, K is used to denote the projection of overall angular momentum J along the CH₃ top axis, and F is a reduced rotational constant.

Methanol has permanent dipole moment components both along the near symmetry a-axis (μ_a) and along the b-axis (μ_b). This gives rise to two kinds of transitions, viz. the parallel a-type and the perpendicular b-type. In the a-type transition, the a-component of the dipole moment is responsible, hence no torque can be produced along the symmetry axis, consequently, K cannot change. In the b-type transitions the responsible dipole moment is μ_b and K can however change by ±1. In any transition, the torsional symmetry species must be conserved, so that we have the additional selection rule E₁ ↔ E₁, E₂ ↔ E₂ and A ↔ A. It should be noted that for K=0, E₁ and E₂ species are essentially identical. Precise dipole moments were determined for the methanol species using the MW and FIR laser Stark spectroscopic measurements. These dipole moment values are useful for the calculation of line strengths of astrophysically significant lines and potential optically pumped FIR emissions.

For the levels belonging to the A - symmetry species the +K and -K degeneracy is broken by the ΔK=±2 matrix element due the asymmetry of the molecule and the levels become split. This splitting is generally termed as the asymmetry splitting and is most pronounced for K=1 and for the excited torsional states its value decreases.

When deuterium is substituted for one of the hydrogen atoms in the methyl top, the 3-fold symmetry of the molecule is broken. The torsional potential barrier of the molecule must then be extended to include the terms $\frac{1}{2}V_1(1-\cos\gamma)$ and $\frac{1}{2}V_2(1-\cos2\gamma)$ in addition to the 3-fold term $\frac{1}{2}V_3(1-\cos3\gamma)$, where γ is the torsional angle. The effect of the V_1 and V_2 term is to lift the degeneracy of the $\sigma=-1$ and $+1$ levels and strongly mix the $\sigma=0$ and ± 1 levels. The molecules are localized in the symmetric 'trans' and asymmetric 'gauche' configuration for the relative orientation of the -OH and the CH₂D- groups. Hence the first three torsional vibrational states in increasing order in energy are then given by the symmetry species (σ) e_0 , e_1 and o_1 . These correspond to the ground torsional state for the parent methanol species CH₃OH. $1/\lambda = \nu/c$ (in cm⁻¹) the wavenumber of transitions. J is the overall rotational angular momentum quantum numbers, K is the components of J along the quasi-symmetric axis. The asymmetry mixing of the states due to $\Delta K=\pm 2$ and ± 1 matrix elements causes the levels to split into the "+" and "-" components.

III. SELECTION RULES

Fourier transform spectrometer: The Fourier transform spectrometers used were the BOMEM DA.004 model at the Herzberg Institute of Astrophysics and the University of British Columbia in Canada and the Brüker IFS 120 HR model at the Justus Liebig Universität. The IFS 120 HR was developed and built by the Brüker Analytische company in Germany. The IFS 120 instrument is a Michelson-type interferometer. The source in the FIR region is a high pressure mercury lamp whose radiation is imaged onto the plane of the aperture and then collimated. The FIR beam-splitters are mylar films. After traversing the interferometer the radiation passes through the absorption cell and is focused onto a liquid helium cooled silicon bolometer. The mirror movement and the sampling of the data points of the interferogram are controlled using the interferogram of a single frequency He-Ne laser. The He-Ne laser radiation passes through the same interferometer as the FIR radiation. In the detection and amplification systems of the interferometer, the AC component of the detector signal passes through an electronic bandpass filter after amplification and is digitized in a 16-bit analog to digital converter. For the IR region the Globar source together with a Ge-Cu detector and a KBr/Ge beam-splitters was used. Path lengths used varied from 20 cm to about 16 m in a multipass cell. The sample pressure was typically 1 torr or less. The interferograms obtained were coadded and transformed to give a resolution of 0.0017 cm⁻¹. The absorption frequencies were calibrated using measured CO lines and naturally occurring water vapour lines. The calibration factor was typically of the order of 1.000002. The accuracy of the line positions varies between 0.0001 and 0.0003 cm⁻¹. The spectra recorded with the BOMEM spectrometer were at a resolution of 0.004 cm⁻¹ and the accuracy of unblended lines was of the order of 0.0005 cm⁻¹.

Microwave, millimeterwave and sub-millimeterwave spectrometers: High resolution millimetre (MM) and submillimetre (SUBMM) spectroscopy has had a major impact on many important fields of science and technology. Because the strength of the interaction between electromagnetic radiation and molecular rotation peaks sharply in the MM/SUBMM region, a variety of spectroscopically based remote sensing applications have grown out of this more basic work. The least remote of these have involved laboratory studies of molecular lasers and the collision induced rotational and vibration processes which are central to their operation. This spectral region has also played an important role in the study of the chemical processes in the upper atmosphere which are important in ozone formation and destruction. Lastly, the vast majority of the over one hundred molecular species which have been identified and studied in the interstellar medium have been observed by means of MM/SUBMM "radio" astronomy. In spite of these and other applications, the MM/SUBMM spectral region is by far the least explored region. This is because of the difficulty of generating and detecting radiation at these frequencies. However, over the years, a number of approaches have been developed. High resolution spectroscopy was first extended into the SUBMM region by means of nonlinear harmonic generation. In the present work millimeterwave (MMW) measurements have been carried by the MMW spectrometer at the Justus Liebig Universität, Giessen, Germany, was used. It covers the range 90-500 GHz and uses Klystrons and Gordy-type frequency multiplier.

A new high resolution spectroscopic system for the MM/SUBMM region has been developed recently by the group of F.C. De Lucia [18] at the Ohio State University, in the USA. This system is a fast, broadband, sensitive, and simple. It is based on the broadband, voltage tunable backward wave oscillators (BWO) produced by the ISTOK research and Development Company of Fryazino, Moscow region, Russia and uses very fast sweep ($\approx 10^5$ Doppler limited spectral resolution elements per second) and optical calibration methods to replace the phase and frequency lock techniques more commonly used. This technique is called fast scan submillimetre spectroscopic technique (FASSST). Because the fast scan effectively freezes frequency instability on the time scale of the optical calibration period, resolution, and frequency measurements accuracy are comparable to that of the much slower and more complex phase/ frequency locked systems. The FASSST approach makes it possible to fully utilize the inherent instantaneous bandwidth of the BWOs and to achieve a spectroscopic system of unprecedented capabilities. Furthermore, the resultant system is much simpler and has the potential for wide application.

The lower frequency MW rotational measurements were done using the Stark modulated spectrometer at New Brunswick in Canada. For the dipole moment studies careful measurements were made using the same MW Spectrometer. The MW Stark cell was made of two flat, 10 cm wide stainless steel plates of 60 cm length, and separated by quartz spacers placed at the edges. The plate spacing was 5.180(1) mm as was determined from the thickness of the quartz spacers and by test measurements on OCS lines. A dc potential ranging from 50 to 200 V was applied to the Stark plates and a 5 kHz square wave with a maximum peak to peak of 20 V was used as modulation. The Stark plates were placed in a 25 cm cylindrical glass cell that was evacuated to better than 0.1 mtorr. For a set of measurements, the cell was isolated from the pump with a valve and the sample was admitted to the cell until a pressure of 5-15 mtorr was attained.

FIR Stark spectrometer: The laser Stark spectroscopy was carried out with the electrically discharge pumped HCN laser at the University of Wisconsin. A direct discharge molecular gas laser in the FIR region has been developed to perform high resolution molecular spectroscopy. The laser cavity consists of a 10 cm diameter, 4 m long Pyrex glass tube. Several CW laser oscillations have been observed using HCN (337 and 311 μm), DCN (195, 195' μm 190 and 190' μm), H₂O (118.6 μm), and D₂O (107 μm) as lasing media. The Stark cell is a stainless-steel cylinder with 0.1 mm Mylar windows. The Stark plates are made of silvered glass, 60 cm long, 7.5 cm wide, and spaced at 0.051508 cm. Stark fields up to 60,000 V/cm are used. The molecular absorption is modulated by a 20 Hz square wave generator. The detector is a Golay cell with a quartz window and polyethylene lens optics. This highly sensitive Stark system can detect molecular resonances which have very small transition moments and not visible in normal absorption spectra.

IV. STRUCTURE OF THE SPECTRA

***a*-type spectra :** Since the effective B-values change little within a given vibrational state the frequency of the *a*-type transitions is a relatively weak function of ($n\tau K$) states and hence depends primarily on J. Thus in the spectrum, they occur in a fairly narrow range for a given J. For low J the frequency of *a*-type transitions will be in the MW and MMW regions but for higher J these fall in the FIR region. The assignments of these FIR transitions become easier once the low-J *a*-type and strong *b*-type transitions are assigned.

***b*-type Spectra :** For the *b*-type spectrum it can be shown that for stronger transitions, K and J have to change in the same direction. In a given torsional state, a K+1 state usually has higher energy than a K state, so the ^rR-branch transitions would be stronger than the ^rP-branch transitions. For a torsional band where n changes by unity, however, in addition to the case of stronger ^rR-branches for K+1 \leftarrow K transitions, one expects to find the ^rP-branches for K-1 \leftarrow K transitions. Consecutive lines in an R-branch or P-branch series are separated by approximately (B+C), where B and C are the rotational constants. This helps a great deal in the analysis of the spectrum. The separation between a Q(J+1) line and the corresponding R(J) line is approximately (B+C)(J+1). For transitions within a given torsional state, the Q-branch lines are usually grouped in a very small frequency region, whereas for a torsional band, the Q-branch lines are well resolved because of a significant difference between the effective rotational constants in the upper and lower states involved.

Infrared Spectra: Because the C-O stretch vibration is being executed parallel to the near symmetry axis, the selection rules followed by this band are of the parallel *a*-type. In the spectrum strong ^rP, ^rQ and ^rR branches are observed. The overall structure has the typical appearance of a parallel band of a near symmetric top molecule. In the spectrum each J-multiplet is resolved into a very complicated substructure and this is because of the strong torsion-vibration-rotation interaction in the molecule.

The study of overtone bands allowed by the anharmonicity of the vibrational potential are indicated. The high resolution spectroscopy of overtones of polyatomic molecules is one of today's fields of research interest. The main reason behind this interest is to be able to investigate molecular dynamics such as intramolecular vibrational energy redistribution (IVR). The understanding of the IVR dynamics is particularly interesting at chemically significant energies, accessing regions of the potential energy surface where large amplitude, anharmonic coupling effects are very efficient and may encounter high barrier chemical transformations. Spectroscopic access to high energy states of the stretching vibration through overtone bands allows the investigation of the energy flow from these anharmonic modes to other vibrational modes of the molecule.

A pulse TEA-CO₂ laser was used to selectively dissociate methanol molecules that have been first excited to a high vibrational overtone level without dissociating the large excess of ground-state molecules. The overtone transition is then monitored by detecting the dissociation fragments as an usual implementations of photofragment spectroscopy. This method is called the IR-laser assisted photofragment spectroscopy (IRLAPS).

The O-H overtone frequencies up to $\nu^{\text{OH}} = 5 \leftarrow 0$. It was discovered that there was a strong "Fermi" interaction between $\nu^{\text{OH}} = 5$ and the combination state $4 \nu^{\text{OH}} + 1 \nu^{\text{CH}}$ both for the stretch state. The interaction

causes the 5 ν^{OH} state to shift in the lower wavenumber side by about 30 cm^{-1} . The following band positions fundamental and overtone band are obtained : $\nu^{\text{OH}} = 1 \leftarrow 0, 2 \leftarrow 0, 3 \leftarrow 0, 4 \leftarrow 0$ and $5 \leftarrow 0$, respectively, at 3681.5, 7200, 10540, 13707 and 16703 cm^{-1} . These band origins have been fitted with the following vibrational energy (in cm^{-1}):

$$E(v) = w_e (v+1/2) - \omega_e x_e (v+1/2)^2 - \omega_e y_e (v+1/2)^3 \dots \dots \dots (11)$$

and we obtained the three vibrational parameters as $\omega_e = 3884.84 \pm 3.76$, $\omega_e x_e = 93.56 \pm 1.16$ and $\omega_e y_e = 0.63 \pm 0.11 \text{ cm}^{-1}$. Thus the first order anharmonicity parameter is $\omega_e x_e = 93.56 \text{ cm}^{-1}$. This can be compared with the value obtained for the C-O stretch state as $\omega_e x_e = 3.97 \text{ cm}^{-1}$. This proves that the O-H stretch is much more anharmonic than the C-O stretch.

V. APPLICATION TO FIR LASERS

From the peak positions in the IR band one can get the absorption lines in close coincidence with the emission lines of the CO_2 laser. These coincidences offer the possibility of the molecule to be optically pumped to emit FIR laser lines. The absorption intensity gives an idea of the pumping efficiency. The analyses of the IR bands provide us with the quantum numbers associated with the pump transition, which in turn yields the assignments of observed FIR laser lines. It is also possible to find the frequencies of yet unobserved FIR laser transitions. The FIR absorption assignments of the torsion-rotation bands provide the precise locations of the ground state energy levels. Having the assignments of the IR absorption lines one can form close combination loops of accurately measured transitions to calculate the FIR laser frequencies with much better precision than can be obtained by direct wavelength measurement. Typically the accuracy of the wavelength measurement with an Febyr-Perot (FP) interferometer in the FIR region is of the order of $\pm 1 \mu\text{m}$. At a wavelength of 100 μm this represents an accuracy of $\pm 30 \text{ GHz}$. The precision of the FTIR peaks is of the order of 0.0002 cm^{-1} , yielding an accuracy of the loop calculated FIR laser line frequencies of the order of $\pm 15 \text{ MHz}$, representing an improvement by a factor of about 2000. The frequencies of the predicted FIR laser transitions are also calculated with the combination loop with similar precision. The usefulness of the spectral assignments of FIR laser lines can be demonstrated with the 127 μm FIR laser lines in $^{13}\text{CD}_3\text{OH}$. In an open structure resonator this line shows efficiency comparable to the well-known 119 μm line in CH_3OH , and is the second most strongest FIR laser line. Some years ago an assignment was put forward for this line. Two accompanied FIR laser lines were predicted for the 10P(8) CO_2 pump line in $^{13}\text{CD}_3\text{OH}$ at 21.6318 and 57.1087 cm^{-1} , later these lines were observed at 21.61 and 57.06 cm^{-1} , respectively. The predicted line positions gave the experimenter an idea of the precise location to search for the emission lines. In the following we present some such applications in CH_3OH , $^{13}\text{CH}_3\text{OH}$, CD_3OH and $^{13}\text{CH}_3\text{OH}$.

Refilling FIR laser transitions in CH_3OH : When high power TEA CO_2 lasers are used to pump CH_3OH , numerous high frequency FIR laser lines around 200 cm^{-1} are produced. This emission is puzzling because such frequencies would be expected for torsional transitions, yet the observed pump frequencies do not correspond to observed excited torsional lines in the IR band, and indeed seem more often to match better with known torsional ground state absorptions. An explanation put forward [43], which is somewhat a novel one, is that the FIR laser emission occurs by a refilling process into the lower pumped level whose populations are strongly depleted by the strong TEA pumping. A simple steady state equilibrium argument would indicate that only those levels lying less than 140 cm^{-1} above the lower pumped level would have enough population at room temperature to yield a population inversion. However, it seems not unlikely that short, powerful TEA pulses could produce sufficient nonlinear and transient effects to allow lasing on the higher frequency torsional transitions.

Table 1

Location of the C-O Stretch Q-branch in Methanol Species	
Species	Q-branch Head (cm^{-1})
CH ₃ OH	1033
¹³ CH ₃ OH	1018
CH ₃ ¹⁸ O	1008
CD ₃ OH	985
¹³ CD ₃ OH	980

Table 2
Strong Optically Pumped CW FIR Laser Lines in Methanol Isotopic Species

Pump	Molecule	λ (μm)	ν (GHz)	FIR Power (mw)	Pump Power (w)
9P(32)	CH ₃ OH	37.85	7919.6602	10	
10R(18)	CD ₃ OD	41.36	7249.2660	60	33
9P(32)	CH ₃ OH	42.16	7110.9814	10	
9R(8)	CH ₃ OD	46.7		10	
9R(8)	CH ₃ OD	57.0		10	
9R(18)	CH ₃ OH	64.0		>20	
9P(34)	CH ₃ OH	65.6		10	
9P(34)	CH ₃ OH	70.51	4251.6740	100	30
9R(8)	CH ₃ OH	96.52	3105.9368	300	
9P(30)	CH ₃ OD	103.13	2907.0889	10	
9P(36)	CH ₃ OH	118.83 [#]	2522.7816	1250	125
10P(8)	¹³ CD ₃ OH	127.02 [%]	2360.1748	8	33
10R(38)	CH ₃ OH	163.03	1838.8393	18	31
9P(36)	CH ₃ OH	170.58	1757.5263	10	
9R(18)	CH ₃ OH	186.04	1611.4219	10	
9P(38)	CH ₃ OH	198.66	1509.0402	10	
9P(34)	CH ₃ OH	237.60		10	
9P(12)	¹³ CH ₃ OH	238.52	1256.8720	10	
10R(36)	CD ₃ OD	255.0		19	25
9R(18)	CD ₃ OH	297.0		10	
9P(36)	CH ₃ OH	392.07	764.6426	10	
10R(36)	CD ₃ OH	418.71	715.9876	10	
9P(12)	¹³ CH ₃ OH	461.38	649.7667	10	
10R(38)	CH ₃ OH	469.02	639.1846	10	
10R(8)	CD ₃ OH	553.0		10	
10P(46)	CH ₂ DOH	509.37	588.5534	10	
9P(16)	CH ₃ OH	570.57	525.42790	40	
9P(16)	CH ₃ OH	627.46	477.79088	10	
9P(34)	CH ₃ OH	669.42		10	
9R(14)	CD ₃ OH	871.59	343.9624	10	
9P(16)	CH ₃ OH	1223.66	244.9966	10	

Frequency is given if it is measured accurately.

The pump power is provided if available.

[#] Highest efficiency line reported to date.

[%] This is the second highest efficient line.

VI. APPLICATION TO ASTROPHYSICS

The high resolution spectroscopy of methanol became of interest to astrophysicists, when methanol was discovered in interstellar space. More than 200 interstellar lines of methanol have been observed, and nowadays methanol is regarded as an astronomical “weed”. Thus the high resolution spectroscopic map of methanol is desirable to allow astronomers to identify them and allow such important measurement as D/H ratio in interstellar clouds. The discoveries of interstellar methanol and optically pumped FIR methanol FIR lasers has been capped by the discovery of interstellar methanol laser emission, recognized in 1975, but actually observed even earlier in 1971. The interpretation and evaluation of these interstellar emissions require detailed knowledge of the energy levels and transition probabilities of methanol over wide range of spectrum.

VII. SUMMARY

To sum up, continued interest in optically pumped FIR laser and measurement of methanol spectra in interstellar space will keep motivating further studies on high resolution spectroscopy of methanol and its isotopic species which will further the knowledge of fundamental understanding of torsion-rotation-vibration interactions in slightly asymmetric molecules.

REFERENCES

1. N.G. Douglas, Springer Series in Optical Sciences, 61 (Springer, Berlin, 1989)
2. G. Moruzzi, B.P. Winnewisser, M. Winnewisser, I. Mukhopadhyay and F. Strumia, "Microwave, Infrared, and Laser Transitions of Methanol : Atlas of Assigned Lines from 0 to 1258 cm⁻¹," CRC Press, Florida, (Aug 1995) ISBN. 0-8493-2478-5 and the references therein
3. G. Guelachvili, et al., " High Resolution Wavenumber Standards for the Infrared (Technical Report)," Pure and Appl. Chem. 68 (1996) 193-208.
4. I. Mukhopadhyay, P.K. Gupta and R.M. Lees, J. Mol. Spectrosc. 157, (1993) 290-300
5. I. Mukhopadhyay and R.M. Lees, Opt. Commun. 97, (1994) 194-198.
6. I. Mukhopadhyay, J. Mol. Spectrosc. 166, (1994) 107-119.
7. I. Mukhopadhyay, Opt. Commun. 110, (1994) 303-308.
8. M. Inguscio, et al., Int. J. IR. MM. Waves, 5, (1984) 1289-1296.
9. N. Ioli, A. Moretti and F. Strumia, Appl. Phys. B48, (1989) 305-309.
10. J.C.S. Moraes. et al., Appl.Phys. B54, (1992) 24-28.
11. G.W. Chantry, "Long Wave Optics- The Science and Technology of Infrared and Near-millimeter Wanes", Vol. 2, Academic Press (1984).
12. R.M Lees and J.G. Baker, J. Chem. Phys. 48, (1968) 5299-5318.
13. L.H. Johnston, R.P. Srivastava and R.M. Lees, J. Mol. Spectrosc. 84 (1980) 1-40.
14. D.T. Petke, et al., Rev. Sci. Instrum. 68 (1997) 1675-1683.
15. I. Mukhopadhyay, R.M. Lees and W. Lewis-Bevan, Int. J. IR. MM. Waves, 9, (1988) 545-553.
16. J.O. Henningsen and J.C. Petersen, Infrared Physics, 18, (1978) 475.
17. J.O. Henningsen, J.C. Petersen, F.R. Petersen, D.A. Jennings and K.M. Evenson, J. Mol. Spectrosc., 77, (1979) 298-307.
18. I. Mukhopadhyay and R.M. Lees, Opt. Commun. 97, (1993) 194.
19. A. Predoi, R.M. Lees and L.H. Xu, Infrared Phys. & Tech. 37 (1996) 351-366.
20. J.C. Petersen, J. Opt. Soc. Am. B, 6, (1989) 350-354.
21. I. Mukhopadhyay, R.M. Lees, W. Lewis-Bevan and J.W.C. Johns, J. Chem. Phys. 102, (1995) 6444-6455.
22. I. Mukhopadhyay, R.M. Lees and J.W.C. Johns, Int. J. Infrared Millimeter waves, 9, (1988) 1119.
23. I. Mukhopadhyay, R.M. Lees, W. Lewis-Bevan, J.W.C. Johns and G.Moruzzi, Int. J. Infrared Millimeter Waves, 8, (1987) 1483-1502.
24. J.C.S. Moraes, et al., J. Mol. Spectrosc. 177 (1996) 302-306.
25. N. Ioli, A. Moretti, F. Strumia and F.D. Amato, Int. J. Infrared Millimeter Waves, 7, (1986) 459-466.
26. D. Pereira and A. Scalabrin, Appl. Phys. B, 44, (1987) 67-75.
27. R.M. Lees, I. Mukhopadhyay, J. Chem. Phys. 102, (1996) 6444-3418.
28. I. Mukhopadhyay and R.M. Lees, Int. J. Infrared Millimeter Waves, 16, (1995) 99-115.
29. R.M. Lees, Private Communication.
30. I. Mukhopadhyay, et al., IR. Phys. & Tech. 38 (1997) 107-111.
31. I. Mukhopadhyay, Spectrochimica Acta A, 53 (1997) 2467-2469.
32. P. Bernard and J.R. Izatt, Int. J. Infrared and MM. Waves, 4 (1983) 21-36.
33. I. Mukhopadhyay, M. Mollabashi, R.M. Lees, and J.W.C. Johns, J. Mol. Spectrosc. 138, 521-540 (1989).
34. I. Mukhopadhyay, M. Mollabashi and R.M. Lees, J. Opt. Soc. Am. B 14 (1997) 2227-2237.
35. D. Pereira, et al., Int. J. Infrared Millimeter Waves 15, 1-44 (1994).
36. S.C. Zerbetto and E.C.C. Vasconcellos, Int. J. Infrared Millimeter Waves 15, 889-933 (1994).
37. D. Pereira, et al., Int. J. Infrared Millimeter Waves 13, 497-506 (1992).
38. W.H. Weber and P.D. Maker, J. Mol. Spectrosc. 93, 131-153 (1982).
39. T. Kachi and S. Kon, Int. J. Infrared Millimeter Waves 4, 767-777 (1983).
40. Indra Mukhopadhyay, Infrared Physics & Technology, 75 (2016) 139-144., Infrared Physics & Technology, 75 (2016) 193-201., Infrared Physics & Technology, 75 (2016) 145-149., Infrared Physics & Technology, 76 (2016) 82-90., Infrared Physics & Technology, 76 (2016) 116-121., Infrared Physics & Technology, 77 (2016) 283-295., Infrared Physics & Technology 77 (2016) 03-218, Infrared Physics & Technology 79 (2016) 216-241., Infrared Physics & Technology, 85, (2017), 184-210.
41. P. R. Roelfsema, et al., Astronomy and Astrophysics 537, (2012) A17
42. New Herschel Maps and Catalogues Reveal Stellar Nurseries Across the Galactic Plane, ESA report, 22 April 2016
43. First Detection of Methyl Alcohol in a Planet-forming Disc, eso1619 — Science Release, 15 June 2016

44. The Jet With a 17-Ton Telescope That NASA Uses as a Flying Observatory, SOFIA, www.sofia.usra.edu, and Astrochemistry, W. T. Reach, Newsletter June 2016 • Volume 1, No. 1
45. T.E. May, "Infrared facility at the Canadian light source," *Infrared Phys. Technol.* 45 (2004) 383–387.
46. B. Parise et al., 16293–2422, *Astronomy & Astrophysics*, 393 (2002) L49–L53,
47. C.R. Quade, M. Liu, Indra Mukhopadhyay, and N. Suenram, *J. Mol. Spectrosc.* 192 (1998) 378-385
48. C.R. Quade, private communication.
49. Indra Mukhopadhyay, *Optics Communications*, 110, (1994) 303-308
50. C. Uranga,, C. Connell,, G.M. Borstad, L.R. Zink,, M. Jackson,, *Appl. Phys. B* 88, (2007) 503–505
51. L. Bizzocchi P. Caselli, S. Spezzano and E. Leonardo, *Astronomy & Astrophysics*, A27 (2014) 569
52. M. McKnight, et al., *IEEE J. Quantum Electron.* 50 (2014) 42-46.
53. M. Liu and C.R. Quade, *J. Mol. Spectrosc.* 146 (1991) 238-251
54. M. Liu and C.R. Quade, *J. Mol. Spectrosc.* 146 (1991) 252-263

Personal Profile of Dr. Indra Mukhopadhyay



Dr. Indra Mukhopadhyay received the B.S. and M.S. degrees in Physics and Radio Physics and Electronics from Burdwan University. He completed M.Tech.(Engng.) degree in Electronics and Electrical Communication Engineering from the IIT, Kharagpur and received his Ph.D. degree in Physics (Laser Physics and Spectroscopy) from the University of New Brunswick. In 1990, he joined as a Senior Scientist at the Atomic Energy Department. He was involved in various projects including optically pumped molecular lasers, atomic and molecular physics and solid state electronics. In recent years his research interests included Stark Effect, high resolution MMW, FIR and IR Spectroscopy and Radio Astronomy.

Dr. Mukhopadhyay was involved with the detection of methanol in a distant Star forming region and the calculation of D/H ratio which has important significance to the "Big Bang" theory. He spent time in various laboratories in USA, Germany, and Canada and is a member of the Canadian Association of Physicists, Indian Laser Association and Laser and Spectroscopy Society of India. He is a member Physics and Astronomy Advisory Committee of the University System of Georgia.

Presently he is the Professor of Engineering and Physics at Albany State University, University System of Georgia, USA. He has been nominated for the "US professor of the year" and for the "Excellence in Teaching" award by the Georgia Board of Regents. Dr. Mukhopadhyay has published more than 150 papers in referred journals.