

## Laser Magnetic Resonance Spectroscopy

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**Abstract** The technique of laser resonance magnetic resonance allows one to study the high-resolution spectroscopy of transient paramagnetic species, viz, atoms, radicals, and molecular ions. This article is a brief exposition of the method, describing the principles, instrumentation and applicability of the IR and FIR - LMR and shows results for  $\text{HF}^+$ .

Laser Magnetic Resonance (LMR) spectroscopy is a new technique developed during the last decade for high-resolution studies of transient paramagnetic species, viz. atoms, radicals, and molecular ions. LMR is closely related to the technique of gas-phase electron paramagnetic resonance (EPR). In both experiments the paramagnetic energy levels of atoms or molecules contained in a resonant cavity are tuned by a DC magnetic field until their energy difference matches that of a fixed frequency source. The final product of the spectrometer is then an absorption spectrum of the species as a function of magnetic flux density. The principal distinction between the LMR and EPR experiments is that EPR transitions occur between different magnetic sublevels ( $M_J$ ) of a single angular momentum state ( $J$ ), whereas LMR transitions occur between different rotational (molecules) or fine-structure (atoms) angular momentum states.

The concept of far-infrared laser magnetic resonance (FIR-LMR) originated when Professor M. Mizushima first pointed out the near coincidence of the  $N = 5, J = 5, M = -4$   $N = 3, J = 4, M = -4$  magnetic dipole transition of  $\text{O}_2$  with the frequency of the  $339 \mu\text{m}$   $\text{HCN}^-$  laser line, and the possibility of Zeeman tuning these levels into coincidence

with the laser<sup>1</sup>. In 1968, Evenson and co-workers<sup>2</sup>, actually demonstrated this effect using a fixed-frequency far-infrared laser, instead of the microwave source normally employed in EPR.

Several kinds of information can be extracted from an LMR-spectrum. Important molecular information, such as rotational constants, fine-structure interactions, hyperfine parameters, spin densities, field gradients and molecular g-factors can be obtained with a high degree of accuracy from the measured line positions; kinetic and dynamic data are extracted from intensities and linewidths. This technique not only effects a precise determination of these molecular constants, but also makes it possible to detect weak free-radical spectra in the presence of many strong neutral absorbers; this selectivity makes LMR an important tool for use in reaction kinetics studies, in reactive intermediate are monitored.

LMR is one of the most sensitive spectroscopic methods in existence, relative to other competing techniques, such as conventional optical and microwave spectroscopy and gas-phase EPR. Its sensitivity is similar to that of laser-induced fluorescence. The resolution attainable with LMR, however, is comparable with that of microwaves spectroscopy and gas-phase EPR. Hence its sensitivity - resolution product is far greater than for any other direct spectroscopy method. Furthermore, the only rigorous constraint on the applicability of the method is that the species of interest must be paramagnetic.

In his Spiers Lecture to the Faraday Society, Evenson<sup>3</sup> presents a list of atoms, molecules, free radicals, ions studied by the LMR technique, including: atoms: O, C; ground state radicals: O<sub>2</sub>, NO, CH, PH, NH, CRO, CF, CH, OD, SeH, SeD, SH, NQ, HQ, HCO, PH, NH, CH, COH, CH<sub>3</sub>O, CH<sub>2</sub>F, CH<sub>2</sub>OH; metastable states of: O<sub>2</sub>, PH, H<sub>2</sub>O<sub>2</sub>, CO, NF; molecular ions: HBr<sup>+</sup> and DBr<sup>+</sup>. Species studied since this review include: He<sup>4+</sup>, SeO<sup>5</sup>, CH<sup>6</sup>, OH<sup>7</sup>, FSO<sup>8</sup>, ClSO<sup>8</sup>, SHF<sup>9</sup>, CH<sub>2</sub><sup>10</sup>, NHD<sup>11</sup>, O<sub>2</sub><sup>12</sup>, PO<sub>2</sub><sup>13</sup>, PD<sup>13</sup>, PO<sup>13,14</sup>, AsH<sup>13</sup>, and the molecular ions HCl<sup>+</sup><sup>15</sup>, and HF<sup>+</sup><sup>16</sup>.

A LMR-spectrum is assigned and analyzed with the use of a non-linear least squares routine incorporating an accurate molecular Hamiltonian. The standard procedure for theoretical work in this field is to consider the Zeeman and hyperfine Hamiltonian as perturbations to the rotational-fine structure<sup>17</sup>. The Zeeman effect, in the first-order,

takes the form

$$H_z = U_0 B (g_J^+ M_J + g_I M_I)$$

where  $g_J^+$  is a complex functions of molecular g-factors, the rotational quantum number, and fine-structure parameters. The  $g_J$  factors are determined for each rotational level J. This first-order correction is clearly not sufficient accurate, and several complicated higher-order corrections are required. Most of the theory required to analyze LMR-spectra was worked out earlier by Carrington and co-workers and is contained in the review by Carrington, Levy and Miller<sup>18</sup>. J. M. Brown<sup>19</sup> and L. Veseth<sup>20,21</sup> have since developed more precise formalisms. The high precision of the experimental data requires a very detailed theoretical description of Zeeman effect in a molecular state which is subject to both a complex fine and a hyperfine structure, particularly when a strong magnetic field is applied.

The LMR-spectrometer consists essentially of a FIR-laser pumped by a CO<sub>2</sub>-laser, an electromagnet, and associated electronics and vacuum equipment (Fig.1). The FIR-laser is a symmetric near-confocal Fabry-Perot resonator, designed to contain the absorption cell. The absorption cell is separated from the gain cell by a 12.5μm polypropylene beamsplitter, set at the Brewster angle; the beamsplitter can be rotated about the laser axis, to provide parallel (v) and perpendicular (a) polarization of the FIR-laser electrical field relative to the transverse DC magnetic field; hence, electric dipole transitions with either  $\Delta M = 0$  (v) or  $\pm 1$  (a) can be selected<sup>22</sup>. The gain cell of the FIR-laser is pumped by a line-tunable CO<sub>2</sub>-laser. A micrometer-driven mirror is translated to select a single longitudinal mode of the desired laser line. An intracavity iris diaphragm eliminates higher order transverse modes. The detection volume is a small region (~ 2 cm<sup>3</sup>) defined by the intersection of the mutually perpendicular FIR-laser beam, homogeneous magnetic field, and the sample flow tube. Transient species are produced in the detection volume by flames or DC discharges suitable installed into the intracavity absorption cell.

The first derivative of the laser absorption is observed because an A.C. magnetic field is superimposed on the DC field of the electromagnet, and phase sensitive (PSD) detection is employed. The

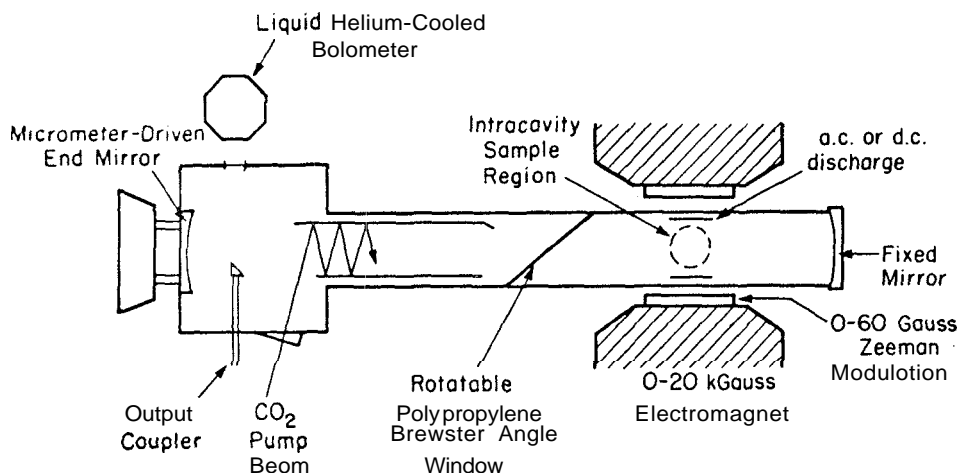


Fig.1 - Far-infrared laser magnetic resonance spectrometer

large sensitivity enhancement obtained with AC magnetic field modulation is necessary for this experimental because the attenuation of the FIR-laser radiation by absorption of the sample is generally only a small fraction of the output power. A NMR-gaussmeter is used to make magnet-flux density measurements.

The extremely high sensitivity of the FIR-LMR technique results from two principal factors: 1) Absorption strengths for pure rotational transitions generally vary as  $\nu^n$  with  $n = 1-3$ , depending on the molecule linewidth, and temperature. 2) Intracavity detection provides a nonlinear enhancement of 1-50 over that determined from the passive Q of the cavity.

An obvious extension of FIR-LMR is infrared LMR (IR-LMR) which uses CO ( $\lambda = 5-7 \mu\text{m}$ ) and CO<sub>2</sub> ( $\lambda = 9-11 \mu\text{m}$ ) lasers as source. This extension makes possible the study of vibration-rotation and electronic spectra of atoms and molecules. The general arrangements of the IR-LMR

spectrometer are the same as those of a FIR-LMR spectrometer except for some finer details. For example, the detector must be appropriate for wavelength regions  $\lambda = 5-7 \mu\text{m}$  and/or  $\lambda = 9-11 \mu\text{m}$ . Reference 23 presents a design for this type of spectrometer.

The sensitivity of the FIR-LMR spectrometer ( $\sim 2 \times 10^5$  molecules/cm<sup>3</sup>) Ref. 1 is about 1-2 orders of magnitude higher than that of IR-LMR spectrometer, but these estimates are dependent on the particular molecule and on the sophistication of the apparatus. The resolution of the IR-LMR spectrometer is determined by the dominant source of line broadening; typical Doppler widths and pressure broadening linewidths are 40-150 MHz, and 2-20 MHz, respectively<sup>24</sup>, whereas the FIR-LMR spectrometer exhibits 0.5-5 MHz and 1-20 MHz for these parameters.

The analysis of the spectra from IR-LMR is similar to that for FIR-LMR, but is greatly simplified, since hyperfine structure is not usually observed and the level of precision is much less demanding.

From reference 24, the atoms and molecules studied up to 1980 by the IR-LMR technique are: CR, Hg\*, He\*, NO, NO<sub>2</sub>, NF<sub>2</sub>, HCO, DCO, NH<sub>2</sub>, ND<sub>2</sub>, PH<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, DO<sub>2</sub>, SeH, SeD, FO, CRO, BrO, SD, CRQ, SeO, NSe, SO, SO\*, CH<sub>4</sub>, CH<sub>3</sub>O(?), FCO(?), NCO. And now, must be included: Kr<sup>25</sup>, Xe<sup>25</sup>, FO<sup>26</sup>, CF<sup>27</sup>, HSO<sup>28</sup>, FO<sub>2</sub><sup>29</sup>, CH<sub>2</sub><sup>30</sup>, SiH<sub>3</sub><sup>31</sup>, NCO<sup>32</sup>, SeD<sup>33</sup>, DO<sub>2</sub><sup>34</sup>, BrO<sup>35</sup>, NF<sub>2</sub><sup>36</sup>, FD<sup>37</sup>, and NH<sub>2</sub><sup>38</sup>.

The high sensitivity of LMR-spectroscopy make it a powerful technique for detecting molecular ions, transient atoms, and free radical. Their short life-times and small densities observed in the laboratory were previously formidable obstacles to their discussion. The experiment of Saykally and Evenson<sup>39</sup> demonstrated a suitable way to obtain molecular ions *in situ* with a DC glow discharge maintained inside the laser cavity, using a cooled solenoid magnet to provide the magnetic field. They were able to produce and detect far-infrared LMR-spectra of HBr<sup>+</sup> and DBr<sup>+</sup> ions. Later, other ions, HCl<sup>+</sup><sup>15</sup> and HF<sup>+</sup><sup>16</sup> were produced and detected by the Saykally group at Berkeley using a new design for the FIR-LMR-spectrometer, with an electromagnet instead of a solenoid, providing the advantage of large range of magnetic field ( $\sim 2 \text{ T}$ ) and with the possibility of using both polarizations of the laser radiation. In the case of the molecular ion HF<sup>+</sup>, the FIR-LMR-technique was able to provide a spectrum with both the F-hyperfine and H-hyperfine structure resolved.

Figure 2 shows the FIR-LMR spectrum of the rotational transition  $J = 3/2 \rightarrow 5/2$ ,  $M_J = -3/2 \rightarrow -1/2$ , of the state  $X^2\Pi_{3/2}$  of the molecular ion  $\text{HF}^+$ , tuned into resonance with the  $122.4 \mu\text{m}$  ( $\text{CH}_2\text{F}_2$ ) line of the FIR-laser by the magnetic field. The splitting due to lambda-doubling of the electronic state and the large F-hyperfine intersections are indicated. The smaller four doublets splitting are due to the hyperfine interactions of the H-nucleus.

From measurements of the magnetic field and the laser frequency it is possible to determine the value of the molecular constants through a non-linear least squares analysis. The uncertainties result from a laser frequency uncertainty of  $\pm 0.5 \text{ MHz}$  and an uncertainty in the magnetic flux density measurements of about  $0.5 \text{ G}$  at values less than  $10 \text{ KG}$  and about  $2 \text{ G}$  at values above  $10 \text{ KG}$ .

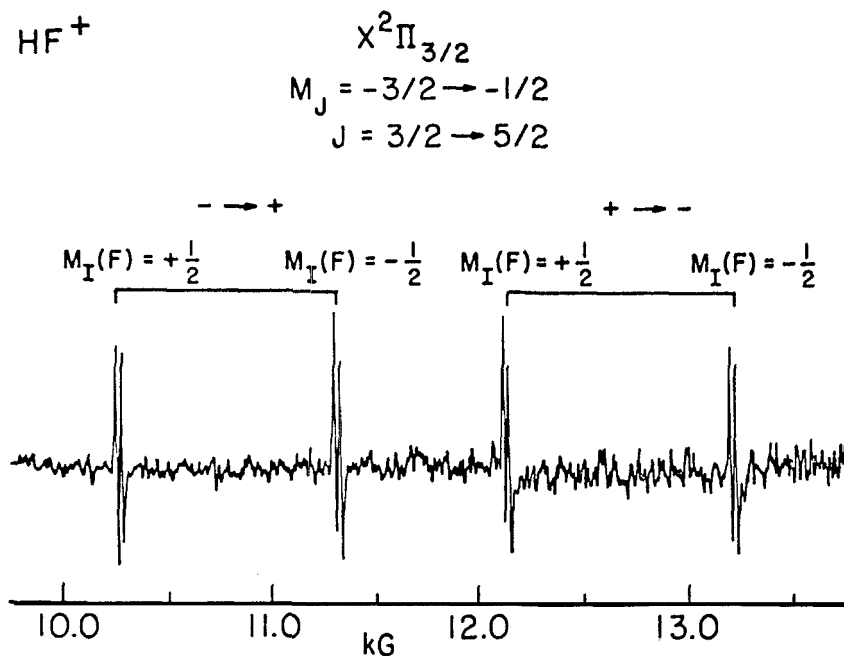


Fig.2 - The  $\text{HF}^+$  spectrum recorded with the  $122.5 \mu\text{m}$   $\text{CH}_2\text{F}_2$  laser.  $\text{HF}^+$  was generated in a  $60 \text{ Hz}$  discharge operating with  $500 \text{ V}$  and  $9 \text{ mA}$  (r.m.s. values) in  $94 \text{ Pa}$  of helium containing a trace of  $\text{HF}$ .

Given the recent success with the molecular ions  $\text{HBr}^+$ ,  $\text{HC}^+$ ,  $\text{HF}^+$  and other isotopes of the Group VII of the Table of the Elements, the ions  $\text{HI}^+$  is a natural candidate for a LMR search. This search, unsuccessful until now, is certainly due to the lack of good optical data for the molecular constants necessary to predict the coincidences between transitions and the far-infrared lasers.

Radio-astronomical observations, have been extended into the far-infrared region<sup>40, 41</sup>. Such investigations require an accurate knowledge of the frequencies of transitions of the excited states of atoms and molecules. This accuracy can be obtained from LMR measurements. The discovery of atomic carbon<sup>40</sup> in Orion was made possible from LMR measurements of C which yielded a precise value of the fine-structure separation<sup>42</sup>. As the nuclear spin of the  $^{12}\text{C}$  isotope is zero, the ground electronic state has no hyperfine spectra that can be detected by radioastronomy.

Chemical processes taking place in the earth's atmosphere are of importance in many ways, involving air pollution, communications and meteorology. The identification of some chemical species present in the earth's atmosphere and the measurements of their abundance as function of time is important in the study of these problems. It is apparent from recent research that ions have important roles in the nucleation process that lead to soot formation<sup>43</sup>; hence a cognizance of ionic properties and reactions will be useful in the design of energy-efficient and pollution-free combustion systems.

## SUMMARY

From a LMR-spectrum we can directly obtain accurate values for the rotational constants, centrifugal distortions, hyperfine constants, lambda-doubling constants, electron spin-rotation constants, quadrupole coupling parameters, and molecular g-factors. In addition, measurements of cross-spin transitions ( $\Delta\Omega \neq 0$ ) directly determine the spin-orbit parameter and the spin-spin parameter for state with  $s \geq 1$ <sup>44</sup>. Once these parameters are determined, intimate details of the geometrical and electronic structures of the molecules are revealed.

The high sensitivity and resolution attainable by the LMR technique make it applicable to the study of very reactive species; how-

ever, there are limitations: a) transitions to be studied must have Zeeman effects large enough to bring them into resonance with laser lines; b) for Hund's case (a) diatomic and linear polyatomic molecules, the Zeeman effect rapidly decreases with the increase of rotational quantum number. When the electron spin is decoupled by large Zeeman fields from the molecular framework, as in case (b) molecules, electric dipole transitions to be observed<sup>4,5</sup>.

Another limitation is the number of far-infrared laser lines available, which limits the possibilities of coincidence with relevant molecular transitions; it must be noted that the FIR laser technology is in a stage of strong development, and much effort is being expended in the development of tunable FIR laser sources. Hence LMR should become an even more powerful tool for investigating transient species in the future.

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#### Resumo

A técnica de ressonância magnética com laser (LMR) permite-nos estudar espectroscopia de alta-resolução de espécies paramagnéticas de transição, a saber, átomos, radicais e íons moleculares. Este artigo é uma breve exposição do método, descrevendo os princípios, instrumentação e aplicação do LMR na região do infravermelho e infravermelho longo, apresentando resultados para o íon molecular  $\text{HF}^+$ .