

FAR INFRARED LASER MAGNETIC RESONANCE SPECTROSCOPY*

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I. INTRODUCTION

Within the last few years, laser magnetic resonance (LMR) has emerged as a powerful technique for the study of pure rotational spectra of transient species in the gas phase. The sensitivity of this method is considerably higher than that of competing techniques, such as conventional optical and microwave spectroscopy and gas-phase EPR, while the resolution attainable is comparable with that of the latter two methods. Its domain of applicability presently includes atoms, ground states of molecules with up to 5 atoms, and most recently, metastable molecular electronic states in the millisecond lifetime range, and molecular ions. The only rigorous constraint on this applicability is that the species of interest must be paramagnetic.

While LMR had its inception and early development in the far-infrared (FIR) region of the spectrum (50-1000 μm), it has recently been extended to include vibrational transitions in the mid-IR (9-10 μm), where it similarly has exhibited substantial capabilities. Furthermore, the laser Stark analogue of this experiment has been developed quite effectively in the mid- and near- IR regions, although not yet in the far-infrared. In this paper, we focus on the magnetic resonance experiment in the far-IR.

II. DESCRIPTION OF THE METHOD

The LMR experiment itself is intimately related to the technique of gas-phase electron paramagnetic resonance, (EPR)¹, so successfully exploited by Radford and by Carrington and his collaborators a decade ago. In EPR, appropriate paramagnetic energy levels of an absorbing sample are tuned by a DC magnetic field until their difference frequency equals that of a fixed-frequency source in the microwave region. The principal difference between these two experiments is that in EPR the relevant transitions are between different magnetic sublevels (M_J) of the same angular momentum state (J), typically occurring in the microwave region for normally accessible laboratory magnetic fields

(2 tesla), while the transitions in LMR are between rotational states (in molecules) or fine-structure levels (in atoms), and occur in the far-infrared. In EPR, the transition can in principle be tuned to coincidence with any frequency lower than its maximum tunability (10 GHz, on the average), but in LMR one must rely on a coincidence between the laser frequency and the transition frequency to within about 1%, given the same tunability. In both EPR and LMR the sample is contained inside a resonant cavity. The increased sensitivity of LMR is mainly derived from operating at frequencies roughly 100 times higher than those of the microwaves normally used in EPR, since absorption coefficients normally depend on either the square or the cube of frequency for $h\nu \ll kT$. Also, by placing the absorbing sample inside the laser cavity, additional sensitivity (up to 3 orders-of-magnitude) can result from its interaction with the gain medium of the laser. With a one second time constant, the detection limit for OH radicals by LMR is presently about $1 \times 10^6 \text{ cm}^{-3}$, whereas for EPR it is about $2 \times 10^{12} \text{ cm}^{-3}$, for optical absorption it is about 10^{11} cm^{-3} , and for uv resonance fluorescence with a water vapor discharge source it is $3 \times 10^9 \text{ cm}^{-3}$. High sensitivity for spectroscopic detection of OH radicals is obtained by laser induced fluorescence, $3 \times 10^6 \text{ cm}^{-3}$ in ambient air, but probably less than 10^6 cm^{-3} with optimum conditions.

III. FREE RADICALS

Twenty-five free radicals have been detected with LMR techniques in the three laboratories using FIR LMR Spectrometers: atoms: $\text{O}(^3\text{P})^{2,3}$, $\text{C}(^3\text{P})^4$; diatomics: $\text{O}_2(^3\Sigma^-)^{5,6,7}$, $\text{OH}(^2\Pi)^8$, $\text{NO}(^2\Pi)^9$, $\text{CH}(^2\Pi, v=0, 1, \dots)^{10,11}$, $\text{PH}(^3\Sigma^-)^{12}$, $\text{NH}(^3\Sigma^-)^{13,14}$, $\text{ClO}(^2\Pi)^{15}$, $\text{CF}(^2\Pi)^{16}$; triatomics: $\text{NO}_2(^2\text{A}_1)^{17}$, $\text{HO}_2(^2\text{A}'')^{18,19,20}$, $\text{HCO}(^2\text{A}')^{21}$, $\text{PH}_2(^2\text{B}_1)^{22}$, $\text{NH}_2(^2\text{B}_1)^{23,24}$, $\text{CH}_2(^3\text{B}_1)^{25}$, $\text{CCH}(^2\Sigma^+)^{26}$; polyatomics CH_3O^{27} , CH_2F^{28} ; metastables: $\text{O}_2(^1\Delta_u)^{29}$, $\text{PH}(^1\Delta)^{12}$, $\text{HO}_2(^2\text{A}_1)^{18}$, $\text{CO}(^3\Pi)^{30}$, and ions: $\text{HBr}^+(^2\Pi)^{31}$, and $\text{DBr}^+(^2\Pi)^{31}$.

We will discuss four of these: two have been discovered in the interstellar medium (CH and CCH); and two more (C and CH_2) will probably be discovered via the frequencies provided by LMR.

Perhaps the single most important development of the LMR method occurred in 1971 with the detection of the $J = 5/2 \rightarrow 7/2$, $N = 2 \rightarrow 3$, pure rotational transition of the extremely elusive CH radical in a low-pressure oxyacetylene flame using the $118.6 \mu\text{m}$ H_2 laser. Although EPR had yielded spectra of many similar transient radicals with $^2\Pi$ ground states, all attempts to observe such spectra from CH had failed. Similarly, astronomical searches for the 10 cm lambda-doubling transition had resulted only in frustration. The successful detection of CH clearly demonstrated the high sensitivity of the LMR technique;

CH in the ground vibrational and rotational state yielded signals 260 times noise for an absorption path of 5 cm - roughly 30 times the S/N reported for an optical absorption experiment! This experiment used the water vapor laser powered by an electrical discharge. The course of LMR was dramatically altered by the invention³² of the optically-pumped far-infrared laser by Chang and Bridges in 1970. The sensitivity of LMR was quite evident from the experiments performed with the dozen or so H₂O and HCN laser lines, but because the method relies on a close coincidence between a cw laser line and a relevant molecular transition, the general application of LMR as a spectroscopic technique seemed quite limited. Furthermore, these lines were all shorter than 337 μm (891 GHz), ostensibly limiting applications mainly to paramagnetic hydrides. With the advent and rapid development of CO₂-pumped FIR lasers, the number of useful cw laser lines has grown rapidly to the present total of nearly 1000 - many of these in the wavelength region from 500 to 1000 μm .

In 1977 an optically-pumped LMR spectrometer was constructed using a transversely-pumped gain cell.³³ This system has the advantage of accommodating high CO₂ laser powers, and consequently operates on a large number of FIR lines. With this new system CH spectra were observed¹¹ with 8 optically-pumped laser lines with an improved signal-to-noise ratio, resulting from a more intense source of CH from a F atom/CH₄ flame. A rather complete analysis of all nine LMR spectra in this work was obtained deducing values for the 4 hyperfine constants a, b, c, and d, as well as improved values for lambda doubling intervals in J = 3/2, 5/2, and 7/2 states. A fit of all the data now available should provide a complete set of improved molecular constants of this important species in the near future.

The important methylene radical (CH₂) was first observed in the LMR system by Mucha et al.,²⁵ who reported the detection of several hyperfine triplets. The identity of the carrier of these triplets was established as the ³B₁ ground state of CH₂ from a series of isotopic substitution experiments. Several other sets of triplets, have subsequently been found which have been shown to be from ¹³CH₂.³⁴ A tentative assignment of the spectrum observed at 85.3 μm (¹³CH₂OH) has yielded a structure for the radical, which, however, must be viewed as extremely tentative because of the obvious perils of using only one observed transition as the basis for such a determination. Another interesting result obtained in this study was the observation of a series of triplets at 171.8 μm (¹³CH₃OH) occurring in stimulated emission.

The detection of the ethynyl radical (CCH) by LMR was reported in 1978.²⁶ The N = 6 \rightarrow 7 pure rotational transition in the X² Σ^+ ground state was found using the 490 μm laser line of CD₃I. The identity of the carrier was again established through isotopic substitution experiments. This work constitutes the first spectroscopic detection of

gaseous CCH in the laboratory, although the observation of its microwave emission spectrum by radio astronomy has established it as a ubiquitous constituent of interstellar clouds.³⁵

The $2^3P_0 - 2^3P_1$ and $2^3P_1 - 2^3P_2$ fine-structure transitions within the carbon atom ground state were detected in the same F atom/CH₄ flame that produced CCH, CH₂, CH, CH₂F and CF spectra. The $J=0 \rightarrow 1$ transition was measured with six different laser lines near 610 μm , while the $J=1 \rightarrow 2$ was measured with 4 lines near 370 μm . Mass shifts and hyperfine splittings were observed for the ¹³C isotope. Analysis of these measurements has yielded precise frequencies for the zero-field fine-structure transitions in both isotopic forms.

In 1978 a new technique for studying transient species in a laser magnetic resonance system was developed.³ The positive column of a DC glow discharge was sustained in the sample region of the laser cavity, and the transverse magnetic field used in the previously described LMR experiments was replaced by a longitudinal field, provided by a 7.6 cm diameter and 33 cm long liquid nitrogen cooled solenoid magnet. This magnet was capable of producing a 5 kG field with a 0.1% homogeneity over a 15 cm length. The optically-pumped gain cell was essentially the same. The longitudinal magnetic field configuration readily accommodates the live intracavity discharge, although producing some visible plasma constriction, and also provides an increased detection length (~ 15 cm instead of 1.5 cm). This apparatus permitted the observation of the first laser magnetic resonance spectra of a molecular ion.³¹ Four isotopic forms of HBr⁺ (H^1Br^+ , D^2Br^+ , H^{81}Br^+ , D^{81}Br^+) in its $2\Pi_{3/2}$ ground state were detected in glow discharges through a dilute (1%) mixture of HBr (DBr) in helium. For the hydrogen isotopes, the $J=3/2 \rightarrow 5/2$ transition was observed with laser lines at 251.1 μm (CH_3OH) and 253.7 μm (CD_3OH), and the $J=5/2 \rightarrow 7/2$ transition in $v=1$ was found with the 186.2 μm line of CH_3OH . The $J=3/2 \rightarrow 5/2$ transition of DBr^+ was detected with the 496.1 μm line of CH_3F . All of the spectra showed hyperfine lines from both bromine isotopes and exhibited small lambda doublings. The proton hyperfine structure was not resolved. On a single Zeeman component of this transition, a signal-to-noise ratio of ~ 100 was achieved with a 1 sec time constant on a single scan. While this was quite a difficult experiment, because of the extremely specific condition required to produce the spectra, with a potential signal of this magnitude, other molecular ions should be detectable by the same method.

Since laser magnetic resonance spectroscopy exhibits a very high sensitivity with nearly microwave resolution, it has produced detailed spectroscopic information on a number of interesting transient species which have eluded detection by other high resolution techniques. In the future, these same qualities of LMR augmented by the fact that it is much easier to search for unknown spectra using swept-field rather than swept-frequency techniques, should make it possible to detect certain astrophysically important radicals for which only theoretical (ab initio)

estimates of parameters are available. Analysis of these spectra will produce precise rest frequencies which can then serve as a basis for astronomical searches for these species in the interstellar medium.

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DISCUSSION FOLLOWING EVENSON

Kuiper: In June 1979 de Graauw and Lidholm (ESTEC), van Vliet, Nieuwenhuizen, and van der Stadt (U. of Utrecht), and myself attempted to detect the 492 GHz CI line with an InSb hot electron bolometer on the Kuiper Airborne Observatory. Instrumental difficulties precluded obtaining any useful data.

Hollenbach: Can you measure the wavelength of the C⁺ fine structure line at ~156μ?

Evenson: We are very anxious to try C⁺, and we will soon.

Phillips: Would it be easier to examine CHD, which has both a and b transitions, to help in the understanding of the CH₂ experiment?

Also, can you look for HCl^+ as well as HBr^+ ?

Evenson: That is a very good suggestion. We must eventually look for CHD and CD_2 to arrive at the structure of the molecule. HCl^+ is the next ion on our list of molecular ions to investigate.

Huntress: Were any of the searches for interstellar HO_2 or CH_3O successful?

Evenson: No. However I believe that searches are continuing.

Wootten: Have you been able to measure a frequency for CCD ?

Evenson: We have not yet looked at CCD .

Wootten: Can you measure the frequency of the $^3\text{D}_{5/2} - ^3\text{D}_{3/2}$ transition of NI at ~ 250 GHz?

Evenson: No. The lowest frequency our laser will operate at is 340 GHz.

Shivanandan: Has the C^+ line been accurately identified in the laboratory?

Evenson: No, but we shall make a search for it. It will not be easy since we will be looking for magnetic dipole transition of an ion, and obtaining a sufficient number density will be difficult.