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Detection of the free radicals FeH, CoH, and NiH by far infrared laser magnetic resonance^{a)}

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We report the detection of rotational transitions of the free radicals FeH, CoH, and NiH. The measurements were made in the far infrared (FIR) between 50–90 cm^{-1} using laser magnetic resonance. Signal-to-noise ratios of over 1000 with a 1 s time constant were obtained on the strongest lines of all three species. These metal hydrides are expected to be abundant in the interstellar medium and optical emission spectra of FeH have been detected in many stellar spectra.^{1,2} Precise ground state rotational transition frequencies are needed for radio and FIR astronomical searches and will be provided from an analysis of our spectra.

The radicals were formed from the reaction of hydrogen atoms with the three metal carbonyl compounds, $\text{Fe}(\text{CO})_5$, $\text{Co}_2(\text{CO})_8$, and $\text{Ni}(\text{CO})_4$, in a low pressure atomic flame. The atoms were produced in a 50 W microwave discharged mixture of 270 Pa of helium and 10–20 Pa of hydrogen; 0.3 Pa of the metal carbonyl was added downstream producing the hydrides. The pressures were not critical; however, excess carbonyl destroyed the signal. The iron carbonyl produced a green–yellow flame; the nickel, a dull red flame; but the cobalt, no noticeable flame.

FeH has a $^4\Delta$ electronic ground state,³ with $^4\Delta_{7/2}$ the

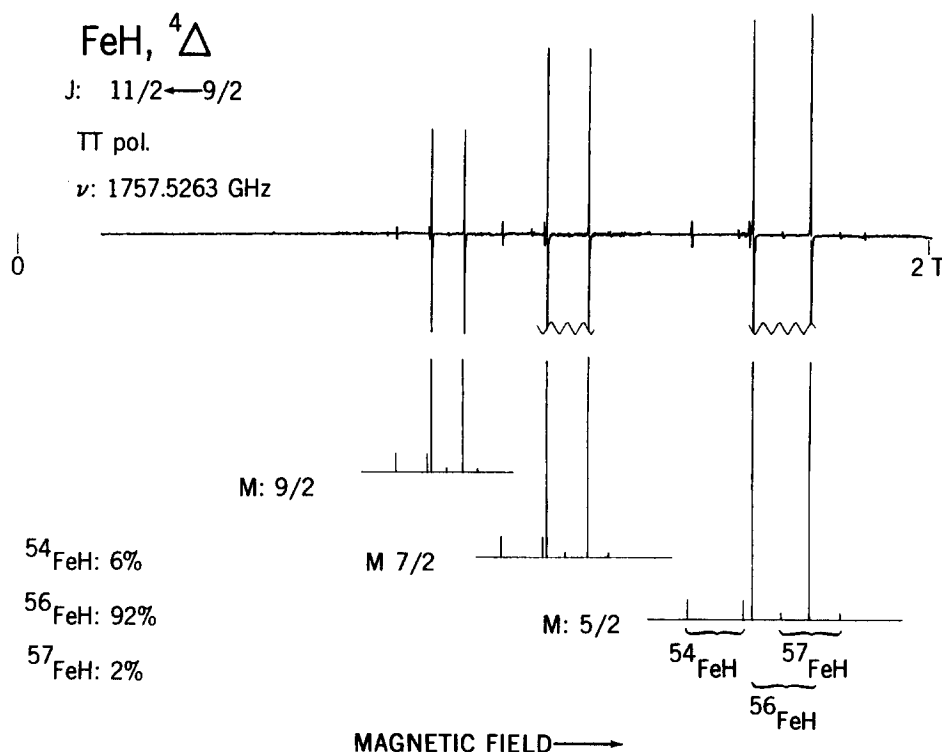


FIG. 1. LMR spectrum of iron hydride, $\Omega = 7/2:0-2 \text{ T}$, 0.1 s time constant, 170.6 μm in π polarization.

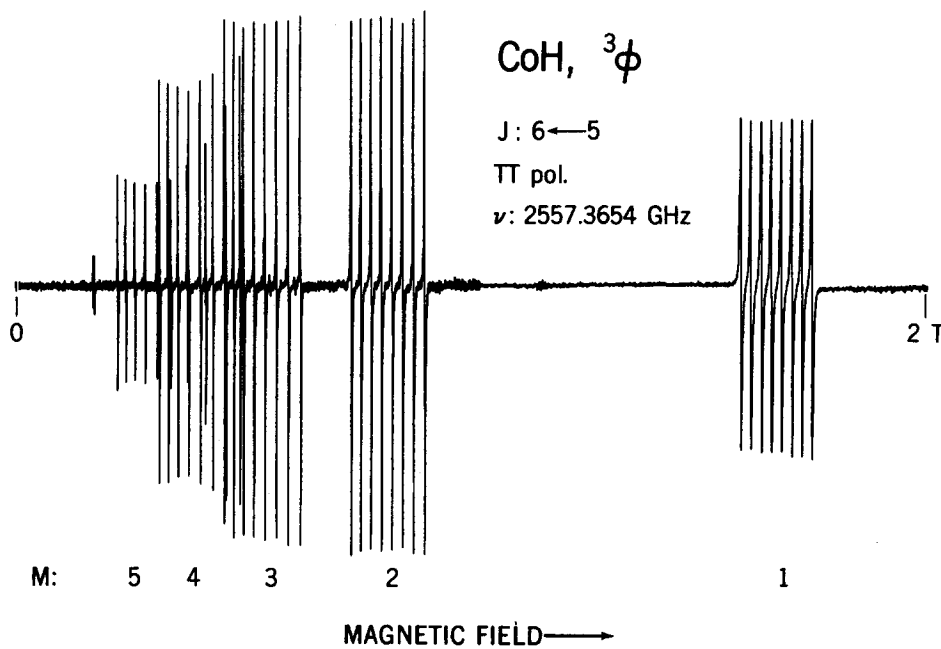


FIG. 2. LMR spectrum of cobalt hydride, $\Omega = 4:0-2$ T, 0.1 s time constant, 117.2 μm in π polarization.

lowest spin component. Its rotational spectrum has been predicted by Phillips and Davis.⁴ The spectrum in Fig. 1 is from the $J = 11/2 \leftarrow 9/2$ transition, in the $\Omega = 7/2$ level, in π polarization, taken with the 1757.5263 GHz (170.6 μm) laser line. This line is from methanol pumped by the 9P(36) line of the CO_2 laser. Lines from three of the naturally occurring iron isotopes are visible in the figure; ^{54}FeH (5.82%), ^{56}FeH (91.66%), and ^{57}FeH (2.19%). The signal from ^{58}FeH (0.33%) is just at the noise level in this survey scan. The very large Λ doubling is probably due to mixing with

other low-lying electronic levels. The transition frequency for each isotope is less than the laser frequency. This same rotational transition was also observed with the 1745.4395 GHz laser line [171.8 μm ; this line is from $^{13}\text{CH}_3\text{OH}$ pumped by the 10R(18) line of the CO_2 laser]. In this case the transition frequency was greater than the laser frequency. The observation of the same transition with the two laser lines allows us to calculate the zero-field frequencies and g factors with great precision. A preliminary calculation yielded 1745.80 and 1746.65 GHz as the zero-field frequencies for

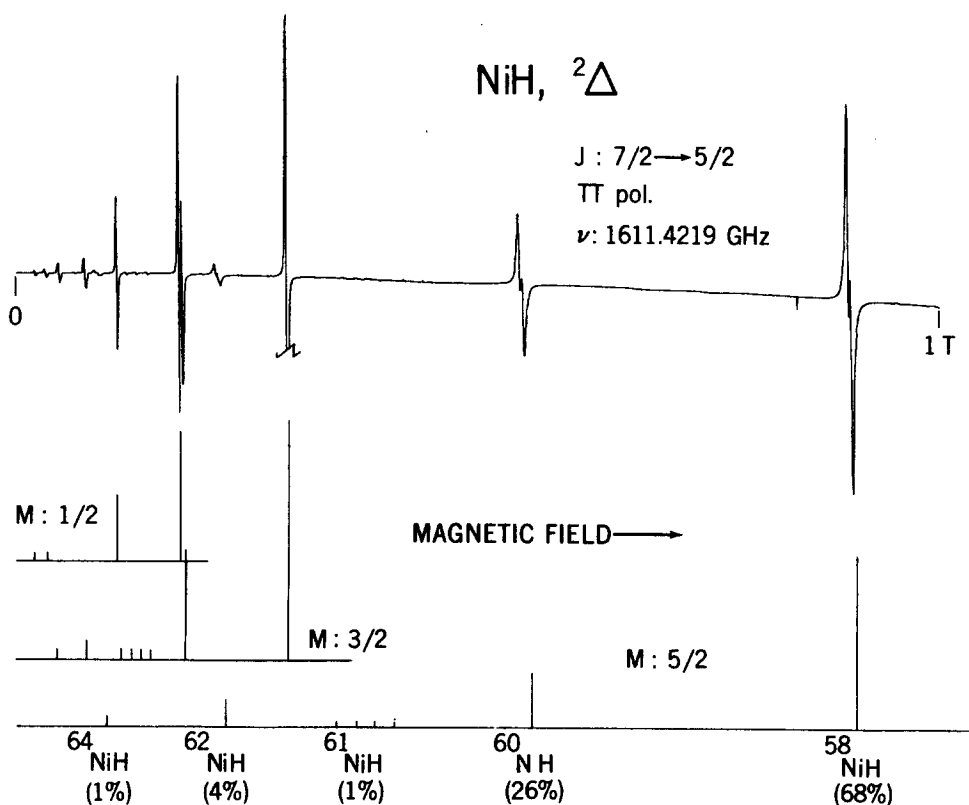


FIG. 3. LMR spectrum of nickel hydride, $\Omega = 5/2:0-1$ T, 0.1 s time constant, 186.0 μm in π polarization.

this Λ -doublet pair.

CoH has a $^3\Phi$ electronic ground state,⁵ with $^3\Phi_4$ the lowest component. In Fig. 2, LMR spectra from the $J = 6 \leftarrow 5$ transition in the $\Omega = 4$ level are recorded. There is only one naturally occurring isotope of cobalt, ^{59}Co . The large eightfold hyperfine splitting caused by the cobalt nuclear spin of $7/2$ is very evident. The spectrum shown was taken at 2557.3654 GHz ($117.2 \mu\text{m}$). This frequency is from the CH_3OD laser, pumped by the $9P(26)$ line of CO_2 . The Paschen-Back effect is evident here; the nuclear spin remains partially coupled to the molecule for transitions below 1 T; but, at higher flux densities, the hyperfine splitting becomes constant. The first line (actually a triplet) at 0.17 T in Fig. 2 is an impurity, possibly NH or CN. The nitrogen is present either as a contaminant in the gases used or is introduced through small leaks in the vacuum plumbing.

NiH has a $^2\Delta$ electronic ground state, with $^2\Delta_{5/2}$ as the lower component. Scullman *et al.*⁶ have analyzed the electronic spectra of NiH, and, recently Nelis *et al.*⁷ detected NiH using infrared laser magnetic resonance. The analysis by Nelis *et al.* yielded very accurate rotational predictions and provided the impetus for the work now being reported. Figure 3 shows three M components of the $J = 7/2 \leftarrow 5/2$ transition in the $\Omega = 5/2$ level, in π polarization with lines of all five naturally occurring nickel isotopes recorded (^{58}Ni :68.0%, ^{60}Ni :26.2%, ^{61}Ni :1.1%, ^{62}Ni :3.7%, ^{64}Ni :1.0%). Under high resolution, each line is seen to be split into doublets of doublets due to Λ -type doubling and

the hydrogen hyperfine splitting. Each ^{61}NiH line is seen to split into four additional hyperfine components due to its nuclear spin of $3/2$. All transitions, except the ^{64}NiH isotope, have a zero-field frequency greater than the laser frequency of 1611.4219 GHz. The $186.0 \mu\text{m}$ line of methanol pumped by the CO_2 $9R(18)$ line was used to record this spectrum.

We are analyzing these and other spectra to obtain information on the nature of the low lying electronic states of these important interstellar molecules. Furthermore, we will calculate the zero-field frequencies of the ground state rotational transitions with sufficient precision to allow astronomical heterodyne measurements for the possible detection of these hydrides in the interstellar medium. The hydrides of other metals such as chromium and manganese may also be observable using these same methods.

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A new technique for state-to-state studies of unimolecular reactions

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Critical tests of both statistical theories and dynamical calculations of unimolecular reactions require experiments that prepare reactant molecules in specific states above their dissociation threshold and determine the reaction rate into individual states of the products.¹² Many current techniques have been limited in their state specificity by the distribution of energy in the reactant molecules,³⁻¹² either from the initial thermal distribution^{3,4,7-12} or from the excitation method itself.⁵⁻⁸ This distribution of reactant energies may obscure dynamical effects related to subtle features of the potential energy surface and limit the degree to which the observed dynamics can test calculated results. We have recently developed a double-resonance technique to selectively excite reactant molecules in particular states from a room temperature gas sample. Combining this selective excitation with laser induced fluorescence product detection permits state-to-

state studies of unimolecular dissociation dynamics. This communication describes our initial results in applying this approach to the unimolecular dissociation of hydrogen peroxide (HOOH).

The experimental scheme is as follows. An optical parametric oscillator (OPO) excites the fundamental of a normal mode involving light atom stretching motion, in this case asymmetric OH stretch of hydrogen peroxide. After a delay of 10 ns, a visible dye laser excites the $6 \leftarrow 1$ vibrational overtone transition of the same light atom oscillator and puts the reactant molecules above the threshold for dissociation at the O-O bond. A second dye laser, further delayed by 7 ns, probes the nascent OH reaction products via laser induced fluorescence.

Shown in Fig. 1(a) is the vibrational overtone excitation spectrum of hydrogen peroxide obtained by directly deposit-