

ROTATIONAL FREQUENCIES OF TRANSITION METAL HYDRIDES FOR ASTROPHYSICAL SEARCHES IN THE FAR-INFRARED^{1,2}

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ABSTRACT

Accurate frequencies for the lowest rotational transitions of five transition metal hydrides (CrH, FeH, CoH, NiH, and CuH) in their ground electronic states are reported to help the identification of these species in astrophysical sources from their far-infrared spectra. Accurate frequencies are determined in two ways: for CuH, by calculation from rotational constants determined from higher J transitions with an accuracy of 190 kHz; for the other species, by extrapolation to zero magnetic field from laser magnetic resonance spectra with an accuracy of 0.7 MHz.

Subject headings: infrared: interstellar: lines — ISM: molecules — line: identification — molecular data

1. INTRODUCTION

The field of far-infrared astronomy is developing very rapidly. The first astronomical far-infrared spectroscopic observations were made with grating spectrometers (e.g., C⁺ by Russell et al. 1980) or Fabry-Perot spectrometers (e.g., OH by Storey, Watson, & Townes 1981) which had a fairly large, instrument-limited line width. Shortly afterward, heterodyne spectrometers capable of operating at much higher resolution were developed and are now sufficiently compact that they can be used for astronomical observations from an airborne platform (Röser 1991). Such instruments have recently been used to make the first heterodyne observations of atomic and molecular species in interstellar clouds. For example, fine-structure transitions have been detected in neutral C (Jaffe et al. 1985) and also in C⁺ (Boreiko, Betz, & Zmuidzinas 1988). Furthermore, Betz & Boreiko (1989) have detected the lowest rotational transition ($J = 5/2 \leftarrow 3/2$) of OH in its $^2\Pi_{3/2}$ ground state. To aid the search for such interstellar species, and to make a secure identification of an observed spectral line, the transition frequencies need to be known accurately. This depends on prior laboratory work on the species concerned.

We have recently made the first laboratory detection and measurement of the rotational spectra of several first-row transition metal hydrides in their electronic ground states (Beaton et al. 1988). Since the cosmic abundance of these elements is quite high (for example, Fe 0.003%, Ni 0.0002%), it is quite likely that these hydrides exist in significant amounts in astrophysical sources. Indeed, CrH and FeH have already been detected through their electronic spectra in the atmospheres of several cool M-type stars (Lindgren & Olofsson 1980; Carroll & McCormack 1972; Carroll, McCormack, & O'Connor 1976). We have therefore measured or determined the frequencies of the lowest rotational transitions of this series of compounds in order to aid their identification in remote astrophysical sources.

2. EXPERIMENTAL METHODS

We have used two methods to measure the rotational spectra of the transition metal hydrides. The first is tunable far-infrared spectroscopy, in which the far-infrared radiation is generated as the difference of two CO₂ frequencies by difference mixing in a metal-insulator-metal diode (Evenson et al. 1985). Details of the spectrometer are given in the paper by Evenson, Jennings, & Vanek (1988). The second method is far-infrared laser magnetic resonance (LMR) spectroscopy (Evenson 1981). A far-infrared laser is chosen close in frequency to that of the molecular transition under study. The small mismatch between these two frequencies is made up by applying a variable magnetic field to the paramagnetic sample, thereby allowing the transition to be detected by absorption of the laser radiation. Details of the spectrometer used to make the measurements described in this paper are given elsewhere (Sears et al. 1982). The tunable far-infrared experiment is based on a single-pass absorption cell and is therefore much less sensitive than the LMR experiment, which is performed within the laser cavity. However, it is the only method available for the study of the rotational spectra of light, closed-shell molecules (that is, those which are not magnetically tunable). The spectrum of CuH was recorded in this way. Those of all the other species were recorded using the LMR spectrometer.

All the hydrides are reactive species which were generated *in situ* by chemical reactions performed in the gas phase at a pressure of about 200 Pa (1.5 torr). The details of the reactions used to form each species are given in Table 1. Atomic hydrogen was generated in a flow system by a microwave discharge through a 5% mixture of molecular hydrogen in helium.

3. RESULTS

Rotational transitions between several levels of the five transition metal hydrides listed in Table 1 have been measured by tunable far-infrared spectroscopy for CuH and by LMR for the remaining four species. These measurements have been used to determine transition frequencies between the two lowest levels in the absence of a magnetic field. In the case of CuH five rotational transitions were recorded, the lowest being

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TABLE 1
METHODS USED FOR THE PRODUCTION OF TRANSITION METAL HYDRIDES

Molecule	Method	Reference
CrH	H atoms + Cr(CO) ₆	Corkery et al. 1991
FeH	H atoms + Fe(CO) ₅	Beaton et al. 1988
CoH	H atoms + Co ₂ (CO) ₈ or CoNO(CO) ₃	Beaton et al. 1988
NiH	H atoms + Ni(CO) ₄	Nelis et al. 1991
CuH	Cu (sputtered) + H ₂	Beaton & Evenson 1990

$J = 3 \leftarrow 2$, and their frequencies fitted to the standard formula for a molecule in a $^1\Sigma^+$ state (Beaton & Evenson 1990). The $J = 1 \leftarrow 0$ frequency was calculated from the constants and is given in Table 2. The uncertainty in this value is 190 kHz. No broadening from the electric quadrupole splitting for the ^{63}Cu nucleus ($I = 3/2$) was observed in the $J = 3 \leftarrow 2$ recording. The splitting is expected to be larger for the $J = 1 \leftarrow 0$ transition, and it may produce some broadening for this transition.

The other four molecules whose frequencies are presented in Table 2 all have open-shell ground states. The effective Hamiltonians for these molecules contain many more terms than that of a $^1\Sigma^+$ state, but, nevertheless, they are reasonably well defined. However, complications arise for these transition metal hydrides because there are several low-lying electronic states which originate from the redistribution of the valence electrons within the $3d$ shell. As a result, the ground electronic states of these molecules are all perturbed to a greater or lesser

extent, and their energy levels are hard to model with a single effective Hamiltonian. CrH is the best behaved; the others become progressively more perturbed through the series NiH, CoH, FeH. We have therefore recorded LMR spectra for the lowest rotational transition for each of these molecules on at least two laser lines. It is then possible to extrapolate to the zero field frequency by assuming a quadratic Zeeman effect. We estimate the uncertainty in this procedure to be 0.7 MHz. The results are given in Table 2 for the most abundant isotopomer. All the open-shell molecules show proton hyperfine structure on the order of 10 MHz which is resolved in the LMR spectra. This hyperfine structure is given in Table 2 for CrH and NiH. For CoH, the hyperfine splitting from the ^{59}Co nucleus ($I = 7/2$) is larger than the proton splittings, and is given instead in Table 2. Each of these CoH transitions also shows a small doubling from the proton hyperfine structure. In the case of FeH, we have been unable to fit the parameters of

TABLE 2
THE FREQUENCIES OF THE ROTATIONAL TRANSITIONS BETWEEN THE LOWEST LEVELS OF CrH, FeH, CoH, NiH, AND CuH

Molecule	State	Transition	Frequency (GHz)	Line Strength ^a	
^{52}CrH	$^6\Sigma^+$	$N = 1 \leftarrow 0$ $J = 7/2 \leftarrow 5/2$	$F = 4 \leftarrow 3$	362.6181	3.05
			$3 \leftarrow 2$	362.6277	2.26
		$5/2 \leftarrow 3/2$	$2 \leftarrow 2$	396.5409	1.47
			$3 \leftarrow 3$	396.5895	2.10
			$2 \leftarrow 3$	337.2601	1.63
			$1 \leftarrow 2$	337.2669	1.05
^{56}FeH	$^4\Delta_{7/2}$	$J = 9/2 \leftarrow 7/2$	$p = a \leftarrow a^b$	1411.0927	1.78 ^c
			$b \leftarrow b$	1411.3579	1.78
^{59}CoH	$^3\Phi_4$	$J = 5 \leftarrow 4$	$F = 17/2 \leftarrow 15/2^d$	2136.5269 ^e	2.95
			$15/2 \leftarrow 13/2$	2137.0755	2.38
			$13/2 \leftarrow 11/2$	2137.5296	1.88
			$11/2 \leftarrow 9/2$	2137.8863	1.46
			$9/2 \leftarrow 7/2$	2138.1431	1.10
			$7/2 \leftarrow 5/2$	2138.2981	0.81
			$5/2 \leftarrow 3/2$	2138.3497	0.58
$3/2 \leftarrow 1/2$	2138.2969	0.40			
^{58}NiH	$^2\Delta_{5/2}$	$J = 7/2 \leftarrow 5/2$	$F = 3^+ \leftarrow 3^-$	1613.666	0.07
			$3^+ \leftarrow 2^-$	1613.6998	1.43
			$4^+ \leftarrow 3^-$	1613.690	1.93
			$3^- \leftarrow 3^+$	1613.657	0.07
			$3^- \leftarrow 2^+$	1613.6904	1.43
			$4^- \leftarrow 3^+$	1613.6805	1.93
^{63}CuH	$^1\Sigma^+$	$J = 1 \leftarrow 0$	468.6522	1.00	

^a For definition see eq. (1). The values given do not take account of the mixing of nearby electronic states.

^b The absolute parity assignments have not yet been made for FeH. The labels a and b refer to the lower and upper lambda-doubling components, respectively.

^c Each rotational transition in FeH will be split into proton hyperfine component with a separation of about 10 MHz. The two dominant lines are $F = 5 \leftarrow 4$ and $F = 4 \leftarrow 3$, with estimated line strengths of 1.96 and 1.56, respectively.

^d Hyperfine structure arising from ^{59}Co nucleus. Each of these lines will be split by about 10 MHz by the proton hyperfine splitting.

^e There is a lambda-type doubling of about 2.5 MHz on each CoH transition.

an effective Hamiltonian to the experimental data and have not yet managed to model the hyperfine structure accurately. The transitions of FeH, CoH, and NiH show in addition a small lambda-type doubling which is given in each case in Table 2.

A splitting of 10 MHz corresponds to a velocity separation of 2.4 km s^{-1} at the FeH line frequency. This is slightly less than the line widths of many astrophysical sources which typically range from 4 to 10 km s^{-1} . The proton hyperfine splittings and the lambda doubling are therefore expected to show up only as a broadening of the line profile. Only in the case of FeH is the lambda doubling large enough to be resolvable for observations with typical astrophysical sources.

The line strength $S_{F'F''}$ can be used to assess the relative intensity of an individual transition. It is defined by

$$S_{F'F''} = |\langle \gamma' F' \| \mathcal{D}_q^1(\omega) * \| \gamma'' F'' \rangle|^2, \quad (1)$$

where the quantity on the right-hand side is the reduced element of the rotation matrix (Brink & Stachler 1968) and γ stands for the subsidiary quantum numbers. The intensity of a line in absorption can be obtained by multiplying the line strength by the square of the dipole momentum μ and by the

difference of the population factors for the two levels involved. The Einstein A coefficient for spontaneous emission from state i to state j can be calculated from the line strengths in Table 2 by the use of

$$A_{i \rightarrow j} = (16\pi^3 v_{ij}^3 / 3\epsilon_0 hc^3) (2F_i + 1)^{-1} S_{ij} \mu^2. \quad (2)$$

It is probable that these rotational transitions will be found in astrophysical sources. All five are thought to have large electric dipole moments (Chong et al. 1986); only that of NiH has been measured so far (2.4 debye; Gray, Rice, & Field 1985). The transition intensity is divided among the hyperfine and lambda-doubling components for the open-shell molecules. For the strongest transition in NiH ($J = 7/2 \leftarrow 5/2$, $F = 4^+ \leftarrow 3^-$ at 1613.690 GHz with a velocity spread of 4 km s^{-1}), a column density of $4.8 \times 10^{12} \text{ cm}^{-2}$ is required to produce an absorption of 20%. The hyperfine and lambda-doubling splittings produce uniquely characteristic patterns, and there should be no doubt about the identify of the carrier once the transitions are detected.

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