# THE PURE ROTATIONAL SPECTRUM OF KH ($X^1\Sigma^+$): QUADRUPOLE COUPLING IN ALKALI HYDRIDES

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## ABSTRACT

The pure rotational spectrum of KH ($X^1\Sigma^+$) has been recorded using millimeter/submillimeter direct absorption techniques. The species was created by the reaction of potassium vapor and $H_2$ in a d.c. discharge. The $J = 0 \rightarrow 1$ and $1 \rightarrow 2$ transitions were measured near 202 and 404 GHz, and electric quadrupole splittings were resolved in the $J = 0 \rightarrow 1$ line and partly resolved in the other transition. For comparison, the quadrupole structure in the $J = 0 \rightarrow 1$ transition of NaH ($X^1\Sigma^+$) was also recorded. Very accurate rotational and quadrupole hyperfine constants were determined for KH, and $eqQ$ was established for NaH as well. Diatomic hydride species are the building blocks for interstellar chemistry in both dense and diffuse gas. Knowledge of the rest frequencies of KH will enable its detection in such objects.

*Subject headings:* ISM: molecules — line: identification — methods: laboratory — molecular data

## 1. INTRODUCTION

Because hydrogen is so much more abundant than any of the other elements, diatomic hydride molecules of the general form MH are usually the first species to be synthesized in interstellar chemical networks (e.g., van Dishoeck 1995). Such hydrides, in fact, are not only readily created by ion-molecule reactions through the intermediate $H_3^+$ (e.g., Dalgarno & Black 1976), but also are formed from $H_2$ via "shock" chemistry, and perhaps from H atoms on dust grain surfaces. Hence, they exist in many interstellar environments and must be the precursors for more complicated molecules.

Although several diatomic hydrides have been identified via their electronic transitions at optical wavelengths (e.g., NH; Meyer & Roth 1991), many have escaped observation because as light molecules, their rotational transitions lie in the submillimeter and infrared regions. At such wavelengths, atmospheric transmission is poor if not nonexistent, making ground-based measurements difficult. However, new developments in receiver technology at submillimeter/THz frequencies, along with improved facilities such as the space-borne platforms SWAS and SOFIA (e.g., Melnick et al. 2000), are making observations in this part of the electromagnetic spectrum more feasible. Therefore, studies of interstellar hydrides have significantly increased. For example, HCl has recently been observed via its $J = 1 \rightarrow 0$ transition at 625 GHz towards various molecular clouds using ground-based telescopes (e.g., Zmuidzinas et al. 1995; Schilke, Phillips, & Wang 1995). In one instance, the sensitivity was sufficient to measure both chlorine isotopomers $H^{35}Cl$ and $H^{37}Cl$, and to determine the respective Cl isotope ratio (Salez, Frerking, & Langer 1996). In contrast, the initial detection of HCl in Orion in 1985 required difficult airborne observations with the KAO (Blake, Keene, & Phillips 1985).

Because of their fundamental role in interstellar chemistry, many diatomic hydrides have been extensively studied in the laboratory at high spectral resolution, including such species as SiH (Brown, Curl, & Evenson 1985), LiH (Plummer, Herbst, & DeLucia 1984), NaH (Sastry, Herbst, & DeLucia 1981), and, more recently, MgH (Ziurys, Barclay, & Anderson 1993) and CaH (Barclay, Anderson, &

Ziurys 1993). One diatomic hydride, however, that never has been investigated by pure rotational spectroscopy is KH, although various infrared studies of its rovibrational transitions have been carried out (Haese, Liu, & Altman 1984; Essig et al. 1993; Uehara, Horiai, & Konno 1997). Given the detection of KCl in circumstellar gas at millimeter wavelengths (Cernicharo & Guélin 1987), KH would seem an obvious candidate for an astronomical search. Tsuji (1973), in fact, predicts KH to be the most abundant potassium-containing species at $T = 2000$ K. Moreover, the abundance of potassium relative to hydrogen is non-negligible with K/H $\sim 1.9 \times 10^{-7}$ (Anders & Grevesse 1989). In addition, CrH and FeH have been observed via their electronic spectra in atmospheres of several M-type stars (e.g., Lindgren & Olofsson 1980). Other metal hydrides therefore may be present.

Here we present measurements of the pure rotational spectrum of the KH molecule. The $J = 0 \rightarrow 1$ and $J = 1 \rightarrow 2$ transitions of potassium hydride in its $X^1\Sigma^+$ ground electronic state for the $v = 0$ level were recorded, as well as the $J = 1 \rightarrow 2$ line in the $v = 1$ vibrational state. The quadrupole hyperfine (hf) structure was completely resolved in the $J = 0 \rightarrow 1$ transition of KH ($v = 0$), enabling an accurate determination of $eqQ$ for the $^{39}K$ nucleus. Quadrupole hyperfine splitting in the $J = 0 \rightarrow 1$ transition of NaH near 298 GHz was also measured, resulting in a determination of $eqQ$ for this molecule as well. In this paper we discuss our results.

## 2. EXPERIMENTAL

The measurements of the alkali hydrides were conducted using one of the millimeter/submillimeter direct absorption spectrometers of the Ziurys group (e.g., Ziurys et al. 1994). The instrument used consists of a phase-locked Gunn oscillator/Schottky diode multiplier as the source of radiation, an evacuated reaction chamber that incorporates a Broida-type oven for metal vapor production, and a liquid helium-cooled InSb bolometer as the detector. The radiation is modulated at 25 kHz to achieve phase-sensitive detection and is propagated quasi-optically through the cell using a scalar feedhorn, a polarizing grid, and a series of Teflon lenses. After transmission through this double-pass

system, the resultant radiation is recorded at $2f$, thus obtaining second derivative spectra.

The KH and NaH were both produced by reaction of the appropriate metal vapor with a mixture of $H_2$ and argon in a gas glow discharge. $H_2$ was introduced through an inlet tube directed above the Broida oven actively producing metal vapor, while argon was fed in from beneath the oven in such a manner as to achieve a partial pressure of 8–10 mTorr of $H_2$ and 25–30 mTorr argon. The d.c. discharge was then applied from a cathode placed above the electrically grounded oven. A voltage range of 20–50 V was found to achieve optimum discharge conditions at a corresponding current of approximately 400 mA, depending on the type of electrode used and the physical condition of the tungsten filament and crucible of the oven. Extensive experimentation was typically necessary to produce KH, while NaH was much less sensitive to reaction conditions and was readily synthesized. The manner in which the potassium metal was prepared before introduction to the cell, the geometry of how the $H_2$ was introduced in relationship to the molten metal, and the flow rate of $H_2$ were the most important factors to the production of KH.

All measurements were made from an average of an even number of 5 MHz scans, half of which were taken in increasing frequency and the other half in decreasing frequency, in alternation. Typically four such scans were averaged, but in the case of the $J = 0 \rightarrow 1$ line of KH, 32 scans were necessary to achieve sufficient sensitivity for the quadrupole coupling measurement. Line widths ranged from 500 to 1,000 kHz.

## 3. RESULTS AND ANALYSIS

The transition frequencies measured for KH and NaH are listed in Table 1. Here $J$ is the rotational quantum number and $F$ indicates the hyperfine structure, which for both molecules arises from the electric quadrupole moment of alkali metal nuclei ($^{39}K : I = 3/2$; $^{23}Na : I = 3/2$). As can be seen in the table, the $J = 0 \rightarrow 1$ transitions of KH and

NaH ($v = 0$) have been resolved into three hyperfine components ($F'' \rightarrow F'$): $3/2 \rightarrow 5/2$, $3/2 \rightarrow 1/2$, and $3/2 \rightarrow 3/2$. Observation of such hf splitting enables the determination of the electric quadrupole coupling constant, $eqQ$. (Although the $J = 1 \rightarrow 0$ transition of NaH had been previously observed in the laboratory by Sastry et al. (1981), these authors were not able to resolve the quadrupole structure). The quadrupole splitting in the $J = 1 \rightarrow 2$ transition of KH ($v = 0$) on the other hand, has only been partially resolved, in part because the interaction gets smaller at higher $J$. In this case two spectral features were recorded, each consisting of a blend of hf components ($1/2 \rightarrow 3/2$ and $5/2 \rightarrow 5/2$; $3/2 \rightarrow 5/2$, $5/2 \rightarrow 7/2$, and $1/2 \rightarrow 1/2$). The $v = 1$ line was somewhat weaker in intensity; thus, only one spectral line was observed, that of the strongest hf blend.

The quadrupole splitting for KH and NaH is illustrated in Figure 1. Here representative spectra of the $J = 0 \rightarrow 1$ transitions of KH and NaH are shown on the same frequency scale. The three hf components and their 3:5:1 intensity ratio, indicated underneath the spectra, are easily identified in the KH spectrum (*lower panel*). For NaH (*upper panel*), the splitting is comparable but the $F = 3/2 \rightarrow 1/2$ component does not appear as prominent.

In Figure 2 the $J = 1 \rightarrow 2$ transitions of KH in its $v = 0$ and $v = 1$ vibrational states are presented. The $v = 0$ spectrum (*upper panel*) consists of a strong feature and, to its left, a weaker line. As indicated underneath the two features, the weaker signal consists of two blended hf components which comprise 17.3% of the total intensity of the transition. The stronger feature is comprised of three hf lines (70% of the transition intensity). The remaining intensity results from one hf component ($F = 3/2 \rightarrow 3/2$), which lies in the wing of the strong line at higher frequency but was too weak to detect. The position of this component is shown on the spectrum. For the $v = 1$, $J = 1 \rightarrow 2$ transition of KH (*lower panel*), only the stronger feature, comprised of the three hf lines, has been clearly detected. (Any hf component with an intensity of $\leq 2\%$ was not considered).

## TABLE 1
### TRANSITION FREQUENCIES FOR KH AND NaH ($X^1\Sigma^+$)[a]

| Molecule | $J''$ | $F'' \rightarrow$ | $J'$ | $F'$ | $v$ | $v_{obs}-v_{calc}$ |
|---|---|---|---|---|---|---|
| KH ($v = 0$) ....... | 0 | 3/2 | 1 | 3/2 | 202,280.922 | 0.029 |
| | | 3/2 | | 5/2 | 202,282.237 | −0.013 |
| | | 3/2 | | 1/2 | 202,283.318 | −0.017 |
| | 1 | 1/2 | 2 | 3/2 | 404,445.049[b] | 0.017 |
| | | 5/2 | | 5/2 | | −0.099 |
| | | 5/2 | | 7/2 | 404,446.546[c] | 0.041 |
| | | 3/2 | | 5/2 | | 0.041 |
| | | 1/2 | | 1/2 | | ...[d] |
| KH ($v = 1$) ....... | 1 | 5/2 | 2 | 7/2 | 394,344.601[c] | ...[d] |
| | | 3/2 | | 5/2 | | |
| | | 1/2 | | 1/2 | | |
| NaH ($v = 0$) ...... | 0 | 3/2 | 1 | 3/2 | 289,862.675 | −0.062 |
| | | 3/2 | | 5/2 | 289,864.264 | 0.139 |
| | | 3/2 | | 1/2 | 289,865.157 | −0.077 |

[a] In MHz.
[b] Blended lines.
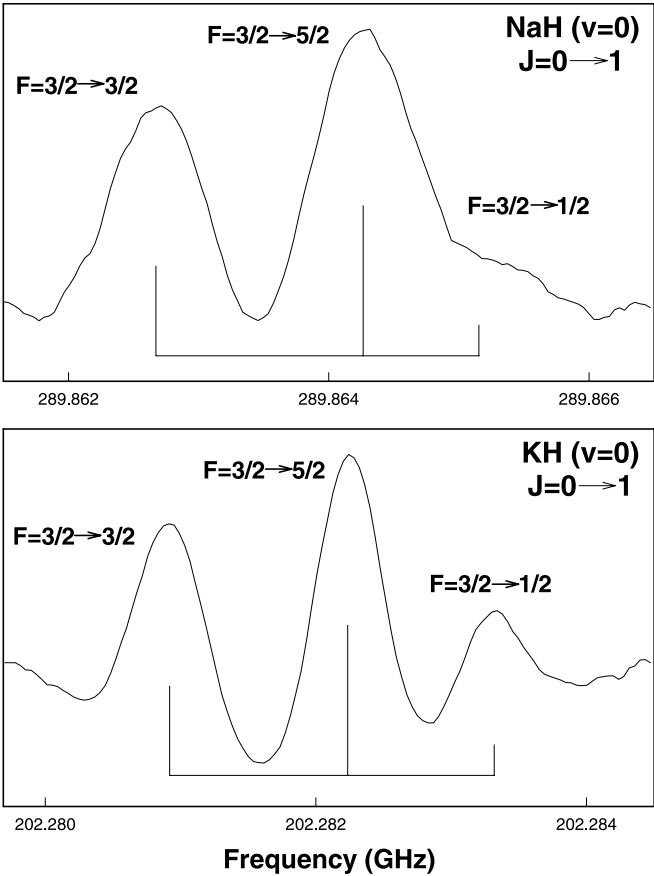[c] Blend of three hyperfine components.
[d] Not fit (see text).

Fig. 1.—Spectra of the $J = 0 \to 1$ rotational transition of KH and NaH ($X^1\Sigma^+$: $v = 0$) observed in the laboratory in this work. Each transition is split into three hyperfine components, labeled by quantum number $F$, because of electric quadrupole interactions of the metal nuclei. The quadrupole pattern is indicated under each spectrum. The KH spectrum is an average of 32 30 s scans, 5 MHz in frequency coverage; the NaH data is an average of four such scans.
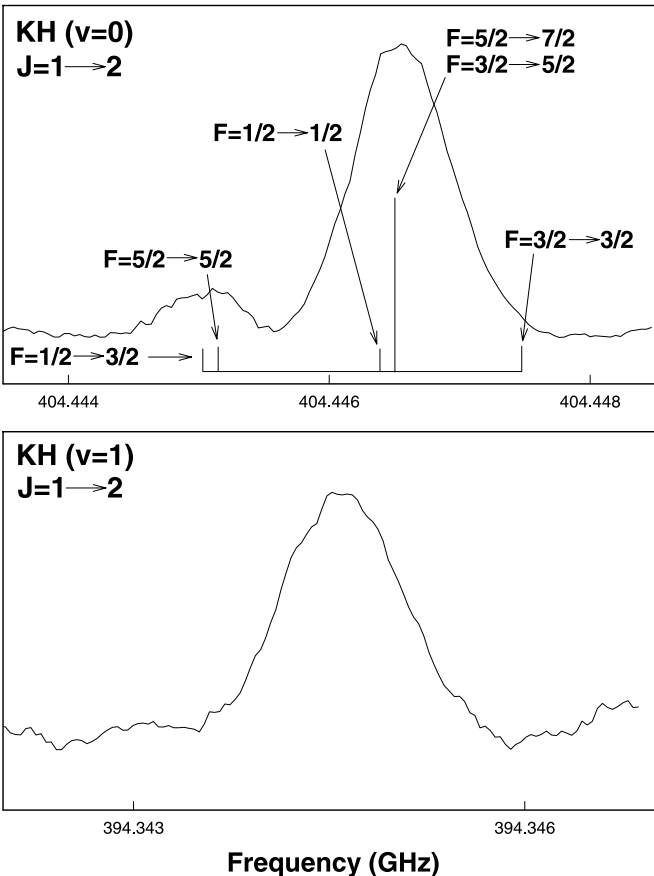


Fig. 2.—Spectra of the $J = 1 \to 2$ transition of KH ($X^1\Sigma^+$) in its $v = 0$ and $v = 1$ vibrational states. In the $v = 0$ data, the quadrupole hyperfine structure is only partly resolved. Therefore only two features appear in the spectrum, both which are comprised of several hf components, as indicated under the spectrum. The $v = 1$ line is weaker in intensity, and hence only the stronger feature is observed. These data comprise four ($v = 0$) and eight ($v = 1$) scan averages, respectively, each 5 MHz in frequency coverage and lasting 30 s.

The data were fitted with a simple linear Hamiltonian that included an electric quadrupole term. For KH ($v = 0$), all $J = 0 \to 1$ hf components of the transition were incorporated into the fit, but only four out of the eight total hf lines of the $J = 1 \to 2$ transition were used. These four transitions were the $F = 1/2 \to 3/2$ and $5/2 \to 5/2$ lines that compose the weaker feature in Figure 2, and the $F = 3/2 \to 5/2$ and $5/2 \to 7/2$ components that comprise the stronger line (see Fig. 2). The stronger feature, as mentioned, consists of an additional hf component, but this line is much weaker than the other two components (9% vs. 61% of total intensity), and was not included in the data fit.

The spectroscopic constants derived from the analysis are presented in Table 2. For KH ($v = 0$), $B_0$, $D_0$, and $eqQ$ were determined. In the case of NaH, only $B_0$ and $eqQ$ could

be established, since a single rotational transition was recorded. (This was also the case in the Sastry et al. 1981 study). A $B_0$ constant has additionally been determined for KH in its $v = 1$ state, fixing $D_0$ to be that of the $v = 0$ state. The rotational constants obtained for KH are consistent with previous values obtained from infrared rovibrational spectra, within their quoted errors of $\pm 5$ MHz (Haese et al. 1984; Essig et al. 1993). The $B_0$ parameter found for NaH is also in agreement with that of Sastry et al. (1981).

## 4. DISCUSSION

This study has resulted in the measurement of the $J = 0 \to 1$ and $2 \to 1$ transitions of KH. Highly accurate spectroscopic constants have also been determined for this hydride species such that other transitions can be predicted with very high precision ($< 500$ kHz), in particular those in the submillimeter region. Furthermore, the quadrupole hf splittings have been measured in the $J = 0 \to 1$ transition of both KH and NaH. This hf structure may be helpful to the identification of these molecules in the ISM.

Measurement of the quadrupole structure for NaH and KH can yield some insight into the type of bonding present in metal hydride molecules. The quadrupole constant is a measure of the electric field gradient across the nucleus with

TABLE 2

Spectroscopic Constants for KH and NaH ($X^1\Sigma^+$)[a]

| Molecule | $B_0$ | $D_0$ | $eqQ$ |
|---|---|---|---|
| KH ($v = 0$) ....... | 101,150.786 (60) | 4.8987 (90) | $-5.43$ (41) |
| KH ($v = 1$) ....... | 98,625.342 (60) | 4.899[b] | ... |
| NaH ($v = 0$)...... | 144952.484 (44) | 10.28[b] | $-5.55$ (47) |

[a] In MHz.
[b] Held fixed in data fit.

the quadrupole moment. Because the major contributor to the gradient are electrons in $p$ orbitals, large $eqQ$ values usually indicate more covalent character to a bond. On the other hand, as discussed by Gordy & Cook (1984), there are many subtleties in evaluating the percent ionic (or covalent) character from quadrupole constants, including shielding factors, orbital overlap, etc. However, when the quadrupole moment is on the positive pole of a diatomic molecule, $eqQ$ becomes more positive with increasing covalent character. Therefore, relative comparisons can be reliably made.

Quadrupole coupling constants have been obtained for the potassium and sodium nuclei for the highly ionic species KF and NaF. For KF, $eqQ = -7.932$ (9) MHz and for NaF, $eqQ = -8.435$ (9) MHz (Bauer & Lew 1963). In comparison, those of KH and NaH are $eqQ = -5.43$ (41) MHz and $-5.55$ (47) MHz, respectively. Hence, the alkali hydrides are less ionic than the halides by at least 30%. Electronegativity differences between hydrogen and fluorine are consistent with this change in bonding character.

The quadrupole constants of the alkali hydrides themselves can also be compared to ascertain changes in bonding. Differences in $Q$, the quadrupole moment of the nuclei, however, must be considered. The quadrupole moment of the $^{23}$Na nucleus is somewhat larger than that of

$^{39}$K ($0.11 \times 10^{-24}$ cm$^2$ vs. $0.09 \times 10^{-24}$ cm$^2$; Gordy & Cook 1984). The $eqQ$ parameter of KH is consequently slightly more negative than that of NaH, after normalizing by the difference in quadrupole moments. Therefore, potassium hydride is the more ionic species, but only marginally so. In comparison, the quadrupole constant of LiH is $eqQ = 0.346$ (1) MHz (Wharton, Gold, & Klemperer 1962). The change in sign occurs because $Q$ for $^7$Li is $-0.04 \times 10^{-24}$ cm$^2$. Normalizing by the sign and magnitude of the quadrupole moment of lithium yields $eqQ \sim -1$ MHz. Hence, LiH is clearly far more covalently bonded than the other alkali hydrides. This trend only qualitatively mimics that of the metal electronegativities (Li: 0.98; Na: 0.93; K: 0.82 [Gordy & Cook 1984]).

*Note added in manuscript.*—At the time of our measurements and data analysis, the $J = 1 \rightarrow 0$ transition of KH was also being recorded by Okabayashi & Tanimoto (2000). Our results are in excellent agreement with their measurements.

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