LABORATORY MEASUREMENT OF THE $J = 1$–0 TRANSITIONS OF SODIUM HYDRIDE AND POTASSIUM HYDRIDE

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ABSTRACT

The $J = 1$–0 transitions of ^{23}NaH and ^{39}KH were measured in the millimeter-wave region with a source modulation millimeter-wave spectrometer. The NaH and KH molecules were generated from sodium grains and a potassium ingot, respectively, in a DC glow discharge through hydrogen gas. The line splittings caused by the hyperfine structure due to the ^{23}Na and ^{39}K nuclei ($I = 3/2$) were observed in the rotational transitions for the first time. The central transition frequency, the nuclear electric quadrupole coupling constant, and the nuclear magnetic spin-rotation coupling constant were determined for each species by line-shape simulation.

Subject headings: ISM: molecules — molecular data

1. INTRODUCTION

About 120 molecular species have been identified through radio astronomy in interstellar molecular clouds and in circumstellar envelopes. Species containing metallic elements were detected in the envelope of the red giant star IRC +10216: a fluoride (AlF), chlorides (NaCl, AlCl, KCl), and cyanides (NaCN, MgCN, MgNC) (Cernicharo & Guélin 1987; Kawaguchi et al. 1993; Turner, Steimle, & Meerts 1994; Ziurys et al. 1995). However, no metal hydrides have been observed in interstellar space. Since hydrogen is the most abundant element in space, it is likely that metal hydrides exist in significant amounts in astrophysical sources (Tsuji 1973). Indeed, chromium hydride (CrH) and iron hydride (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). Since the 1980s, laboratory rotational spectra have been reported for the alkali-metal hydrides. Millimeter-wave (Sastry, Herbst, & De Lucia 1981a, 1981b) and tunable far-infrared (TuFIR) spectra (Leopold et. al. 1987) were reported for the NaH molecule. The $J = 1$–0 transition frequencies reported by Sastry et al. had systematic deviations against the TuFIR results. Leopold et al. suggested that this discrepancy was probably caused by a nuclear hyperfine effect of the sodium nucleus. Microwave and TuFIR spectra of KH were also observed (Odashima et al. 1995). Although they gave no comment, the $J = 1$–0 transition frequency of KH observed showed large residual with respect to the calculated frequency from the molecular constants determined by a least-squares method.

Based on the laboratory measurements, astrophysical searches for NaH have been carried out since the early 1980s (Plambeck & Erickson 1982; Turner 1991), but without success. However, recent development of millimeter-wave radio telescopes may enable the astronomical detection of NaH and KH. The rest frequencies of the $J = 1$–0 transition of both species (Sastry et al. 1981a; Odashima et al. 1995) were not very accurate, because their analysis ignored the line-broadening effect of the hyperfine structure due to the ^{23}Na or ^{39}K nucleus ($I = 3/2$). Observation of the hyperfine-split line will be of importance in the astronomical study of these molecules.

In this study we measured the precise $J = 1$–0 rest transition frequencies of NaH and KH with millimeter-wave spectroscopy for astronomical use. The precise transition frequencies as well as the nuclear electric quadrupole and nuclear magnetic spin-rotation coupling constants were determined from the analysis of the line shapes.

2. LABORATORY EXPERIMENT

The rotational transitions of NaH and KH were observed using a 100 kHz source modulation millimeter-wave spectrometer at Shizuoka University (Okabayashi & Tanimoto 1993). The second and third harmonics of the 100V10A klystron output generated by a multiplier were used as the millimeter-wave source near 202 and 290 GHz, respectively. The radiation transmitted through a free space cell was detected by an InSb detector cooled to 4.2 K by liquid helium. A phase-sensitive detector (PSD) demodulated the microwave signal in the 2-f mode, and the PSD output was accumulated in a desktop microcomputer.

The NaH molecule was generated from sodium grains (about 20 g) in the free space cell in a DC glow discharge through hydrogen gas. For the KH production, a potassium ingot (5 g) was used instead of sodium grains. Sodium or potassium placed on the cathode was vaporized by the heat of an electric discharge. Rotational transitions of the two species were easily observed at room temperature. The intensity of the lines of NaH and KH grew while the discharge was operating. This was explained by the increase in metal vaporization in the cell heated by the discharge, because sodium and potassium have low melting points (98°C for Na and 64°C for K). The discharge current was adjusted to about 400 mA. Optimum pressure of the hydrogen gas was about 30 mtorr.

3. OBSERVED SPECTRA AND ANALYSIS

A least-squares analysis for each species was carried out for the observed line shape. Since both the Na and K nuclei have nonzero nuclear spin $I = 3/2$, the $J = 1$–0 rotational transitions of NaH and KH split into three hyperfine components, $F = 5/2$–$3/2$, $F = 3/2$–$3/2$, and $F = 1/2$–$3/2$. According to the monograph of Gordy & Cook (1984), the transition frequencies of the three hyperfine components are

represented as follows,

$$v(F = 5/2\text{--}3/2) = v_0 - 0.05eQq + 1.5C_I, \quad (1)$$

$$v(F = 3/2\text{--}3/2) = v_0 + 0.20eQq - C_I, \quad (2)$$

and

$$v(F = 1/2\text{--}3/2) = v_0 - 0.25eQq - 2.5C_I, \quad (3)$$

where v_0 is the central transition frequency, eQq the nuclear electric quadrupole coupling constant, and C_I the nuclear magnetic spin-rotation coupling constant. Although the hydrogen atom also possesses nonvanishing nuclear spin $I = 1/2$, the hyperfine effect due to hydrogen was omitted because of its small contribution. The intensity ratio of the $F = 5/2\text{--}3/2$, $F = 3/2\text{--}3/2$, and $F = 1/2\text{--}3/2$ hyperfine components was assumed to be 3:2:1 (Townes & Schawlow 1955) in the analysis.

Each hyperfine component was assumed to have the Lorentzian shape function (Gordy & Cook 1984)

$$\alpha_v = \alpha_0 \left[\frac{\Delta v}{(v_0 - v)^2 + (\Delta v)^2} \right], \quad (4)$$

where α_v is the absorption coefficient, α_0 concerns the line strength, and Δv is a Lorentzian width. Although the α_0 term depends on the microwave frequency v, it is quite reasonable to regard α_0 as a constant in the narrow frequency region.

The experimental spectral line shape observed in the present measurement is shown in Figure 1. The line shape observed for the KH or NaH molecule was composed of 256 data points. A least-squares analysis was carried out so as to reproduce these 256 observed data using the equations noted above. The small contribution of the baseline undulation was simultaneously removed using a polynomial equation in the least-squares fit. Since the PSD was operated in the 2-f mode, the recorded signal had a line shape like a second derivative. Therefore, the deformation caused by the modulation/demodulation process had to be considered in the analysis. The time-constant effect due to the electronic circuit of the spectrometer was also taken into account, employing an empirical instrumental function. Figure 1 displays the simulated spectra and residual of the analysis together with the observed spectra.

4. RESULTS AND DISCUSSION

Table 1 summarizes the molecular constants of ^{23}NaH and ^{39}KH determined by the least-squares analysis: the central transition frequency v_0, the nuclear electric quadrupole coupling constant eQq, and the nuclear magnetic spin-rotation coupling constant C_I. The uncertainties in the three constants mainly originate from the disturbed line shape. These constants yield the transition frequencies of the hyperfine components through equations (1), (2), and (3). The obtained frequencies are also listed in Table 1 with their uncertainties calculated from those of the molecular constants.

The central transition frequencies v_0 of ^{23}NaH and ^{39}KH are determined to be 289,863.949(4) and 202,281.977(4) MHz, respectively. They are in poor agreement with the previous millimeter-wave frequencies (Sastry et al. 1981a; Odashima et al. 1995), 289,864.34 and 202,282.255 MHz, respectively. The frequencies reported previously are in good agreement with the $F = 5/2\text{--}3/2$ component frequencies, 289,864.264(5) and 202,282.248(7), whose intensity is strongest among the three hyperfine components. This is

TABLE 1

MOLECULAR CONSTANTS OF NaH AND KH IN MHz

Constant	^{23}NaH	^{39}KH
v_0	289,863.949(4)	202,281.977(4)
eQq	$-5.571(30)$	$-5.296(32)$
C_I	0.0243(19)	0.0041(32)
Derived Transition Frequencies		
$F = 5/2\text{--}3/2$	289,864.264(5)	202,282.248(7)
$F = 3/2\text{--}3/2$	289,862.798(8)	202,280.914(8)
$F = 1/2\text{--}3/2$	289,865.281(10)	202,283.291(12)

NOTE.—Values in parentheses represent 3 standard deviations in units of the last digit.

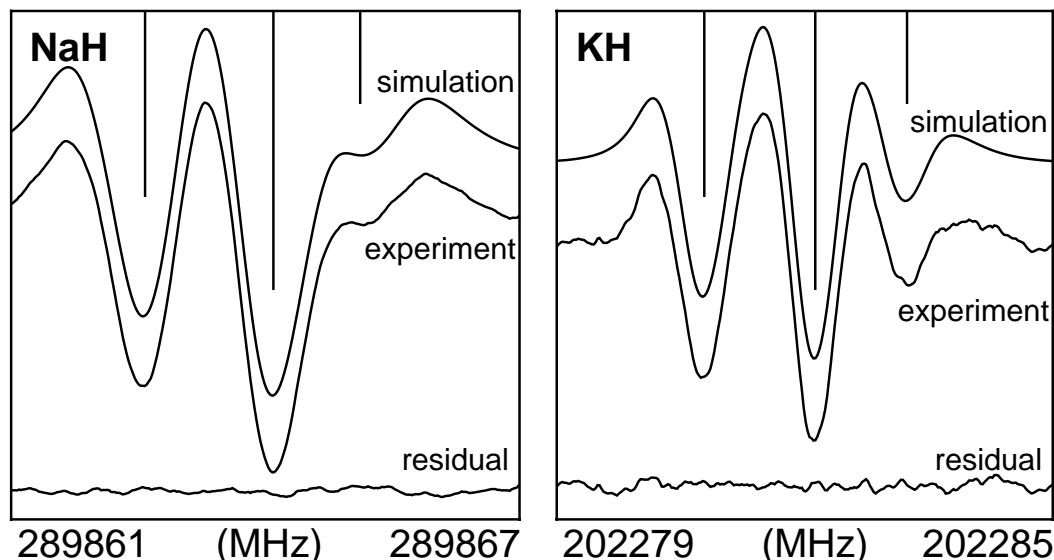

FIG. 1.—Observed and simulated spectra of the $J = 1\text{--}0$ transitions of ^{23}NaH and ^{39}KH. Positions and relative intensities of the hyperfine structure lines are indicated by the vertical bars.

explained by the low resolution in the previous experiments, in which hyperfine splittings were not observed.

The nuclear electric quadrupole coupling constant eQq of NaH, $-5.571(30)$ MHz, is similar to those of sodium halides NaX (X = F, Cl, Br, I), which range from -8.4 to -4.1 MHz (Gräff & Werth 1965; Cederberg & Miller 1969; Cederberg et al. 1987; Miller & Zorn 1969). The eQq value of NaH has been predicted to be -4.1 MHz by an ab initio study (Sundholm, Pyykkö, & Laaksonen 1985). The predicted value is a little smaller in the absolute value than the present experimental value. The eQq value of KH, $-5.296(32)$ MHz, is also similar to those of potassium halides KX (X = F, Cl, Br, I), which range from -8.0 to -4.1 MHz (Paquette et al. 1988; Nitz et al. 1984; de Leeuw, van Wachem, & Dymanus 1969; Tiemann et al. 1973). The value of eQq reflects the gradient of the electric field at the nucleus. The present results indicate that electric charge distribution in an alkali-metal hydride is close to that in an alkali-metal halide.

The nuclear magnetic spin-rotation coupling constant C_I of NaH, $0.0243(19)$ MHz, is much greater than those of NaX (X = F, Cl, Br, I), which range from 0.002 to 0.0007 MHz (Gräff & Werth 1965; Cederberg & Miller 1969; Cederberg et al. 1987; Miller & Zorn 1969). The C_I value of KH, $0.0041(32)$ MHz, is also much greater than those of KX (X = F, Cl, Br), about 0.0002 MHz (Paquette et al. 1988; Nitz et al. 1984; de Leeuw et al. 1969). The value of C_I is proportional to both the rotational constant and the nuclear magnetic g-factor. Since the rotational constants of NaH (145 GHz) and KH (101 GHz) are 10 times as large as those of NaX and KX (X = F, Cl, Br, I), which range from 13 to 2 GHz (Honig et al. 1954; Veazey & Gordy 1965), it is reasonable that the C_I values of NaH and KH are much larger than those of halides.

In conclusion, the $J = 1-0$ transitions of NaH and KH were precisely measured in the 290 and 202 GHz regions, respectively. The frequencies of the hyperfine components have been derived for the first time. The combination of a recent millimeter-wave telescope with high sensitivity and the precise rest frequencies obtained in the present millimeter-wave study will help in the astrophysical identification of NaH and KH molecules in the interstellar and circumstellar regions.

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