

Observation of the Rotational Spectrum of KH Using a Tunable Far-Infrared Spectrometer

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Pure rotational transitions of KH were observed for the first time using a tunable far-infrared spectrometer. Transition frequencies of $R(J)$ with $J = 0$ to 12 were measured with an accuracy better than hundreds of kHz. These precise data have enabled us to determine improved rotational parameters of KH. © 1995 Academic Press, Inc.

1. INTRODUCTION

Metal hydride molecules have been the subject of extensive theoretical study, such as *ab initio* molecular theory, chemical bonding, and molecular structure. Accurate determination of the molecular constants requires precise measurement of their rotational transitions. These molecules are also important in astrophysics, because they are expected to exist in the interstellar medium (1–5). For their detection, precise measurements of rotational transitions are also necessary. Rotational spectra of these molecules fall mainly in the far-infrared (FIR) regions, where experimental difficulties have limited both the quantity and the quality of available data. The purpose of our work is to overcome these difficulties and to measure their rotational spectra precisely.

Alkali hydride is the simplest system of metal hydrides. Rotational transitions of LiH (6, 7) and NaH (8) have been measured precisely using tunable far-infrared radiation sources. As for KH, only an electronic spectrum and a rotational–vibrational spectrum have been observed in the visible and infrared (IR) regions, respectively. A number of studies on the $A^1\Sigma^+ - X^1\Sigma^+$ electronic spectrum have been made by using various techniques, such as arc discharge emission spectroscopy (9–11), laser-induced fluorescence spectroscopy (12–14), and time-resolved spectroscopy (15). The rotational–vibrational spectrum was first observed by Haese *et al.*, using a diode laser spectrometer (16). Fundamental bands and the first hot bands of the ^{39}KH and ^{41}KH isotopic molecules were measured to determine Dunham coefficients.

In the present paper, we report the first observation of pure rotational transitions of ^{39}KH (the most abundant species) in the far-infrared region. The accuracy of the observed frequencies is so high that the accuracy of the determined molecular parameters has been much improved in comparison with that attained in previous work (16).

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2. EXPERIMENTAL PROCEDURES AND RESULTS

Transition frequencies of $R(J)$ with $J = 1$ to 12 were measured using a tunable FIR spectrometer. Details of the spectrometer used in the present work have been already described (7). The tunable FIR radiation was generated by nonlinear mixing of two CO_2 lasers and microwave (MW) radiation on a metal-insulator-metal (MIM) diode (17). The generated tunable FIR radiation was introduced into a sample cell and detected by a liquid-helium-cooled silicon composite bolometer (Infrared Laboratories, Inc.). The FIR frequency and the absorption signal were modulated at 1 kHz due to the modulation used for frequency stabilization of the CO_2 lasers. The signal was demodulated by a lock-in amplifier operating in $1f$ mode. The absorption cell was a dc discharge cell made of a Pyrex glass tube with cylindrical stainless steel electrodes at both ends. Pieces of solid potassium placed in the central region were heated with external nichrome wires to about 520 K. The KH gas was produced in the dc discharge of the mixture of H_2 , He, and vaporized potassium. The partial pressure of H_2 was about 0.5–2 Torr and that of He was 0–1 Torr. When the color of the discharge in the central region was green, KH lines were observed with good signal-to-noise ratios. A typical tracing of the absorption line for the $R(9)$ transition at 2 003 548 MHz is shown in Fig. 1.

In addition to the submillimeter measurement for $R(1)$ – $R(12)$, the $R(0)$ transition in the millimeter-wave region was also observed using the sixth harmonic of a microwave synthesizer (HP83642A) as a wave source and a liquid-helium-cooled InSb hot electron bolometer (Infrared Laboratories, Inc.) as a detector. The millimeter wave was modulated at 50 kHz, and the absorption signal was demodulated by a lock-in amplifier operating in $2f$ mode. An observed signal of the $R(0)$ line at 202282 MHz is shown in Fig. 2. All the observed transitions are shown in Table I together with calculated values.

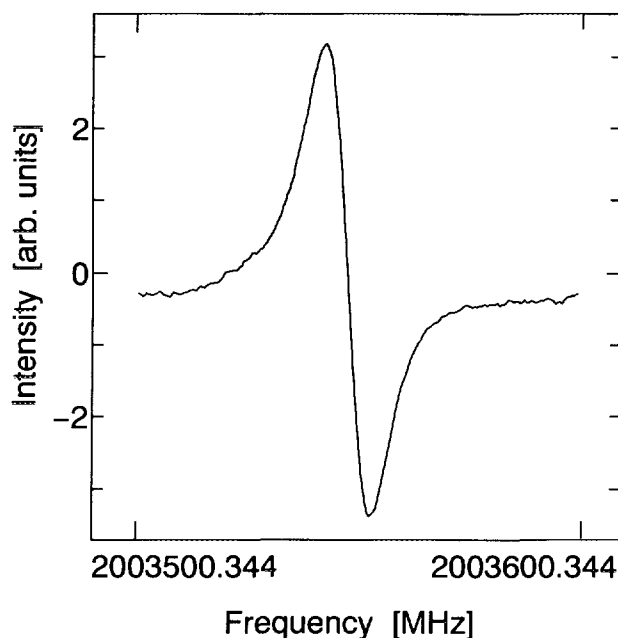
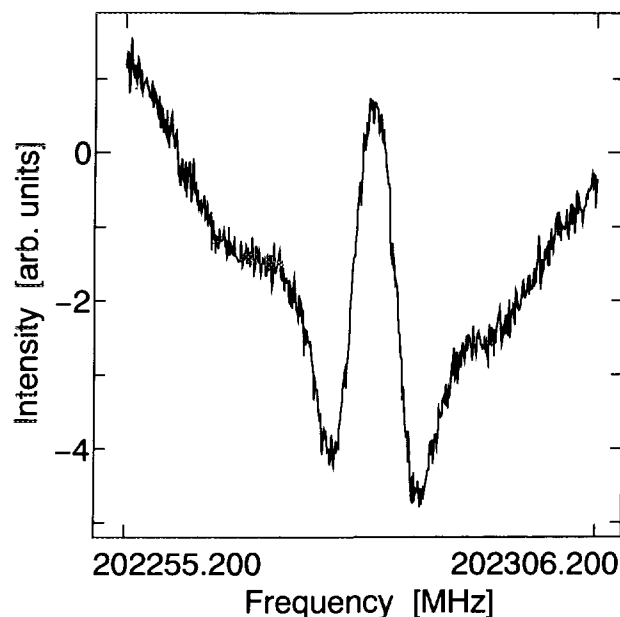


FIG. 1. Observed spectral line of the $R(9)$ transition.

FIG. 2. Observed spectral line of the $R(0)$ transition.

3. ANALYSIS AND DISCUSSION

The observed frequencies were fitted to the following effective Hamiltonian:

$$H_{\text{eff}} = BJ(J+1) - D[J(J+1)]^2 + H[J(J+1)]^3. \quad (1)$$

The determined rotational parameters B , D , and H are shown in Table II and are compared with those derived from the Dunham coefficients given by Haese *et al.* (16). The former parameters differ from the latter ones by a value slightly greater than three standard deviations. The transition frequencies calculated using the latter parameters systematically deviate from the observed values by tens of MHz, while the former parameters allow one to calculate the rotational transition frequencies up to $J = 12$ with much better accuracy.

The o-c values are a few hundreds of kHz, which are not decreased even if a higher-order term of $L[J(J+1)]^4$ is included in the effective Hamiltonian. This discrepancy in the fitting is due to the experimental uncertainties in observed frequencies, for which the following four origins are considered: wide linewidth, distortion of baseline, noise in a signal, and instability of the source frequency. (i) The observed linewidths are considerably wide. The half-width at half-maximum is 5 MHz for $R(0)$ and 10 MHz for $R(9)$, while the Doppler width at 520 K is as small as 0.3 MHz for $R(0)$ and 2.6 MHz for $R(9)$. The observed linewidths are explained by the pressure broadening caused by collisions of H_2 molecules with the KH molecule, whose pressure-broadening coefficient is 8 ± 3 MHz/Torr at 510 K (16). This wide linewidth gives rise to the experimental uncertainty of a few hundreds of kHz, provided that the line-center is determined with an accuracy of 1% of a spectral linewidth. The pressure of H_2 gas could not be reduced any more for a stable dc discharge. (ii) A distorted baseline due to the source modulation, as shown in Fig. 2, causes uncertainty in the observed frequency to a few hundreds of kHz. (iii) A low signal-to-noise ratio due to

TABLE I
Observed and Calculated Frequencies of Pure Rotational
Transitions of KH

R(<i>J</i>)	frequency (MHz)		
	obs.	calc. ^a	o-c
<i>J</i> =0	202282.255	202281.929	0.326
1	404446.389	404446.422	-0.033
2	606376.337	606376.177	0.160
3	807954.174	807954.158	0.016
4	1009063.695	1009063.730	-0.035
5	1209588.840	1209588.794	0.046
6	1409413.656	1409413.915	-0.259
7	1608424.265	1608424.463	-0.198
8	1806506.678	1806506.741	-0.063
9	2003548.060	2003548.121	-0.061
10	2199437.487	2199437.177	0.310
11	2394063.978	2394063.817	0.161
12	2587319.144	2587319.420	-0.276

^a Calculated frequencies were obtained using rotational parameters determined in this work, which are given in Table II.

random noise results in an uncertainty of typically several tens of kHz in the determination of the line-center. (iv) The fluctuations of the difference frequency of two CO₂ lasers are estimated to be less than a few tens of kHz by measuring the *R*(4) rotational transition of the CO molecule, which is determined accurately (18). This instability is negligibly small. Among these four origins of experimental uncertainties, origins (i) and (ii) are dominant.

TABLE II
Rotational Parameters of KH

	rotational parameters (MHz)	
	this work	Haese et al. ^a
<i>B</i>	101150.753(18) ^b	101146.33(77)
<i>D</i>	4.89465(20)	4.8858(28)
<i>H</i>	$1.8548(64) \times 10^{-4}$	$2.278(59) \times 10^{-4}$

^a Ref. (16).

^b The numbers in parentheses are the estimated 1 σ uncertainties in units of the last quoted digits.

Hyperfine structures due to the nuclear quadrupole moment of ^{39}K , the nuclear spin of which is $3/2$, were not resolved for any line. For the $R(0)$ transition, three hyperfine components of $F = \frac{5}{2} \leftarrow \frac{3}{2}$, $\frac{3}{2} \leftarrow \frac{3}{2}$, and $\frac{1}{2} \leftarrow \frac{3}{2}$ are expected, but they were not resolved within its observed linewidth of about 10 MHz. (See Fig. 2.)

ACKNOWLEDGMENT

This research was supported by the Grants-in-Aid for Scientific Research on Priority Areas (Interstellar Matter) of the Ministry of Education, Science, and Culture, Japan (Grants 03249209 and 04233212).

RECEIVED: December 6, 1994

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