Observation of the Rotational Spectra of ^{4}HeH$^+$, ^{4}HeD$^+$, ^{3}HeH$^+$, and ^{3}HeD$^+$

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Low J rotational transitions of ^{4}HeH$^+$, ^{4}HeD$^+$, ^{3}HeH$^+$, and ^{3}HeD$^+$ were observed in the 2–5 THz region with a high-precision far-infrared spectrometer. Dunham coefficients Y_{kl} and isotopically independent parameters U_{kl}, Δ_{kl}^{He}, and Δ_{kl}^{H} were determined. In particular, Δ parameters with $k = 0$ and $l = 1, 2$ were determined with unprecedented accuracy, and provide important information for breakdown of the Born-Oppenheimer approximation. The lowest $J = 1 \leftarrow 0$ transition of ^{4}HeH$^+$ observed at 2010.1839(2) GHz will be an important future probe for detecting this species in space. [S0031-9007(97)02533-7]

The protonated helium molecular ion HeH$^+$ is the simplest polar molecule. Together with H$_2$ and H$_3^+$, which also have two electrons, it is one of the most fundamental species in molecular quantum mechanics. Since it is the only well bound system of the two elements that are most abundant in the Universe, its presence in astronomical objects such as planetary nebulae [1–4], super novae [5], white dwarfs [6], and QSO (quasistellar object) envelopes [7] has been suggested. HeH$^+$ is expected to play an important role in primordial star formation [8] because of its capability for efficient spontaneous emission of low energy photons. For these reasons HeH$^+$ has been studied by many researchers both experimentally and theoretically.

Spectroscopy of HeH$^+$ was first reported by Tolliver, Kyrala, and Wing [9] who applied the technique of Doppler-tuned ion-beam laser spectroscopy to observe its vibration rotation spectrum; five P branch lines in the fundamental band and hot bands were observed in 5.3–5.7 μm region. A similar technique with a different detection method has been used to observe vibration-rotation lines of HeH$^+$ and its isotopic species near the dissociation limits by Carrington *et al.* [10,11]. Bernath and Amano [12] used a tunable infrared difference-frequency laser source to observe vibration-rotation transitions in the fundamental band and determined molecular constants for the $v = 0$ and $v = 1$ vibrational states of HeH$^+$. By using a similar technique Crofton *et al.* [13] observed vibration-rotation transitions of HeH$^+$ in the fundamental and hot bands and those of its isotopic species HeD$^+$, ^{3}HeH$^+$, and ^{3}HeD$^+$ in their fundamental bands. They determined Dunham coefficients Y_{kl} and isotopically independent parameters U_{kl}, Δ_{kl}^{He}, and Δ_{kl}^{H}, which demonstrate the breakdown of the Born-Oppenheimer approximation. Liu, Ho, and Oka [14] observed a high-J-rotational line of HeH$^+$ in the ground vibrational state with a tunable diode laser spectrometer.

In the present paper we report the first observation of low J rotational transitions of the HeH$^+$ molecule and its isotopic species HeD$^+$, ^{3}HeH$^+$, and ^{3}HeD$^+$ with an accuracy of about 0.3 MHz (1×10^{-5}cm^{-1}) by using a

far-infrared spectrometer with a tunable radiation source. The observed transitions have been analyzed together with infrared transitions [12,13] to determine Dunham coefficients Y_{kl} for HeH$^+$ and its isotopic species. The large fractional changes in isotopic masses between H and D and between ^{4}He and ^{3}He have allowed us to determine the isotopically invariant parameters U_{kl}, Δ_{kl}^{He}, and Δ_{kl}^{H} for $k = 0$ and $l = 1, 2$ with unprecedented accuracy. These values will provide most accurate experimental information for the theoretical studies of this most fundamental species [15] and of the breakdown of the Born-Oppenheimer approximation [16,17].

The far-infrared spectrometer used in this work is based on a tunable far-infrared (referred to as TuFIR) technique developed by Evenson *et al.* [18]. Since it has been described in a previous work [19], a brief description is given here. Far-infrared radiation of high spectral purity is generated as a difference of two CO$_2$ laser radiations ν_{I} and ν_{II} which are mixed in a metal-insulator-metal (MIM) diode. A microwave radiation from a synthesizer with a frequency of ν_{MW} which is tunable up to 18 GHz is added to generate tunable sidebands at the frequencies of

$$\nu_{\text{FIR}} = |\nu_{\text{I}} - \nu_{\text{II}}| \pm \nu_{\text{MW}}, \qquad (1)$$

where ν_{FIR} is the generated FIR frequency. With an appropriate choice of the pair of CO$_2$ laser lines, tunable FIR radiation up to 5.7 THz can be generated.

The sample cell is an ac discharge tube made of Pyrex glass with a length of 140 cm and inner diameter of 1.6 cm and is cooled with liquid nitrogen. A signal generator followed by an audio power amplifier and a step-up transformer was used as the power supply for discharges. The sinusoidal ac discharge had a frequency of 1.2 kHz, the peak to peak voltage of ~5 kV, and the current density of ~180 mA/cm^2. A gas mixture of He:H with the typical mixing ratio of 100:1 and the total pressure of ~200 Pa was used. A mechanical booster pump was used to exhaust the sample gas. We found that the ion velocity modulation technique developed by Gudeman

et al. [20] is effective to observe light ions such as HeH$^+$ with large Doppler widths.

Figure 1 shows an observed line for the $J = 1 \leftarrow 0$ transition in the ground vibrational state of ^{4}HeH$^+$. We observed nine rotational lines in total for all the four isotopic molecules; $J = 1 \leftarrow 0, 2 \leftarrow 1$ of ^{4}HeH$^+$, $J = 2 \leftarrow 1, 3 \leftarrow 2, 4 \leftarrow 3$ of ^{4}HeD$^+$, $J = 1 \leftarrow 0, 2 \leftarrow 1$ of ^{3}HeH$^+$, and $J = 2 \leftarrow 1, 3 \leftarrow 2$ of ^{3}HeD$^+$. Observed spectral line shapes were fitted to Voigt line profiles using a computer program to determine their center frequencies. Measured frequencies are listed in Table I.

The uncertainty of measured frequencies, estimated to be about 0.3 MHz, results mainly from the large Doppler width and small S/N ratio of a spectral line. The synthesized FIR frequency has an accuracy of about 10 kHz [21], and its contribution to the uncertainty is negligible.

In order to obtain molecular parameters of the HeH$^+$ isotopic species, observed frequencies in Table I were analyzed together with vibration-rotation transition frequencies listed in Table I of Crofton *et al.* [13] where measurements by other authors, Bernath and Amano [12], and Tolliver, Kyrala, and Wing [9], have been also included. Observed frequencies for each isotopic species were fitted separately by a least squares analysis using the vibration-rotation term values of a $^1\Sigma$ state given by

$$E_V(J) = T_V + B_V J(J + 1) - D_V[J(J + 1)]^2$$
$$+ H_V[J(J + 1)]^3 + L_V[J(J + 1)]^4. \quad (2)$$

Obtained molecular parameters are listed in Table II. All the L_V and some H_V values were fixed to those used by Crofton *et al.* [13], which were obtained from the *ab initio* term values [11,15]. The uncertainties of the infrared measurements were all assumed to be 150 MHz in the best fit analysis. Those of the TuFIR measurements were set to the uncertainties in Table I. It is noted that the accuracy of the rotational parameters, especially that of B_0 in the ground state, has been improved by more than 1 order of magnitude from those obtained previously [13].

A simultaneous fit of all the isotopic data gives us information relating to a validity of the Born-Oppenheimer approximation. The vibration-rotation term values are
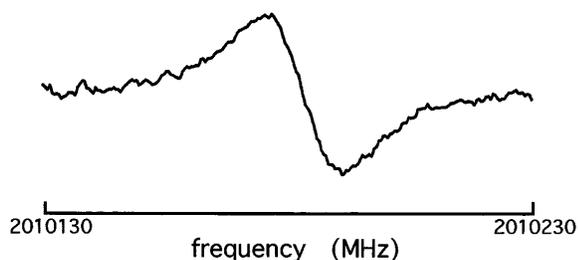

FIG. 1. Observed $J = 1 \leftarrow 0$ rotational transition of ^{4}HeH$^+$. One min scan with a PSD time constant of 0.3 sec was accumulated 6 times.

TABLE I. Observed frequencies of rotational transitions of HeH$^+$ isotopic species in the vibrationally ground state. [a]

	Transition	Frequency (MHz)	Obs-calc [b]
^{4}HeH$^+$	$J = 1 \leftarrow 0$	2 010 183.873 (202)	0.108
	$J = 2 \leftarrow 1$	4 008 733.084 (194)	−0.148
^{4}HeD$^+$	$J = 2 \leftarrow 1$	2 434 626.571 (143)	0.077
	$J = 3 \leftarrow 2$	3 641 427.274 (384)	−0.210
	$J = 4 \leftarrow 3$	4 835 691.417 (166)	0.039
^{3}HeH$^+$	$J = 1 \leftarrow 0$	2 139 522.472 (300)	−0.213
	$J = 2 \leftarrow 1$	4 265 839.060 (300)	0.330
^{3}HeD$^+$	$J = 2 \leftarrow 1$	2 696 099.975 (255)	−0.021
	$J = 3 \leftarrow 2$	4 031 223.001 (511)	−0.650

[a] The numbers in parentheses are the estimated 1σ uncertainties in units of the last quoted digits.
[b] Calculated values result from the simultaneous fitting of all isotope frequencies.

expressed in power series using Dunham parameters Y_{kl} as

$$E_{kl} = \sum_{kl} Y_{kl}(v + 1/2)^k[J(J + 1)]^l. \quad (3)$$

According to Watson's expression, isotopically variant parameters Y_{kl} are written in terms of isotopically invariant parameters as

$$Y_{kl} = \mu_c^{-(k/2+l)} U_{kl}\left[1 + \frac{m_e \Delta_{kl}^A}{M_A} + \frac{m_e \Delta_{kl}^B}{M_B}\right], \quad (4)$$

where U_{kl}, Δ_{kl}^A, and Δ_{kl}^B are the invariant parameters and μ_c is given by

$$\mu_c = \frac{M_A M_B}{(M_A + M_B - Cm_e)}, \quad (5)$$

where M_A and M_B are atomic masses of atoms A and B, respectively, m_e is the electron mass, and C is the charge number of the ion, which is 1 for HeH$^+$. The terms including Δ parameters in Eq. (4) are very small compared to 1 but they demonstrate breakdown of the Born-Oppenheimer approximation. The rotational transition frequencies in the present work were combined with the vibration-rotation transition frequencies in Table I of Crofton *et al.* [13] to determine values of the isotope invariant parameters by the least squares method. The results are listed in Table III.

In the first stage of the least squares analysis to test our computer program, we fit the IR transition frequencies in Table I of Ref. [13] using the same eighteen parameters and obtained a consistent result. We then included our FIR data in the calculation and noted that this produced larger and systematic discrepancies between the observed and calculated values for IR data. The large discrepancies were not reduced when one or two more higher order parameters, such as U_{41}, U_{32}, and U_{14}, were included in the calculation. However, an inclusion of Δ_{02}^H greatly reduced the discrepancies. So, we obtained the values of

TABLE II.   Molecular parameters (in cm^{-1}) of HeH$^+$ isotopic species. [a]

	^{4}HeH$^+$	^{4}HeD$^+$	^{3}HeH$^+$	^{3}HeD$^+$
B_1	30.839 982 (47)	19.083 895 (84)	32.728 20 (12)	21.061 35 (57)
$D_1 \times 10^2$	1.586 062 (88)	0.575 680 (67)	1.798 33 (43)	0.7069 (18)
$H_1 \times 10^6$	5.5289 (68)	1.187[c]	6.538 (44)	1.677[c]
$L_1 \times 10^9$	-3.206[b]	-0.355[c]	-4.17[c]	
B_0	33.558 670 00 (98)	20.349 486 2 (11)	35.720 188 3 (16)	22.540 741 8 (34)
$D_0 \times 10^2$	1.621 774 (14)	0.586 906 4 (41)	1.841 163 (31)	0.722 276 (27)
$H_0 \times 10^6$	5.9311 (33)	1.266[c]	7.202 (24)	1.807[c]
$L_0 \times 10^9$	-2.832[b]	-0.345[c]	-3.67[c]	
$T_1 - T_0$	2910.957 42 (55)	2310.4858 (18)	2995.048 49 (70)	2423.4244 (33)

[a]The numbers in parentheses are the estimated 1σ uncertainties in units of the last quoted digits.
[b]The values fixed to those given by Crofton *et al.* [13] as obtained from the *ab initio* term values of Bishop and Cheung [15].
[c]The values fixed to those given by Crofton *et al.* [13] as obtained from the *ab initio* term values of Fournier and Richard [11].

nineteen parameters in the least squares analysis. The value of Δ_{02}^{He} was much less than Δ_{02}^{H} and was not determinable; it was fixed to 0 in the analysis. As for other Δ parameters, inclusion of Δ_{11}^{H} or Δ_{11}^{He} did not improve the fit significantly.

Finally, we point out that the lowest $R(0)$ rotational transition of HeH$^+$ observed in this paper at 2010.1839 GHz (67.05252 cm^{-1}) will be a powerful probe to detect HeH$^+$ in astronomical objects from airborne or satellite observatories. Because of the large permanent dipole moment of 1.78 debye [22], the transition will be strong both in absorption and emission. So far the negative results by Moorhead *et al.* [23] who searched for the infrared vibration-rotation $R(0)$ transition in the planetary nebula NGC7027 seems to be the only reported attempt to detect this important ion.

TABLE III.   Isotopically invariant parameters of HeH$^+$. [a]

U_{10}	2888.95 (14)	U_{03}	3.2070 (91) $\times 10^{-6}$
U_{20}	-124.233 (93)	U_{13}	-1.70 (12) $\times 10^{-7}$
U_{30}	0.142 (19)	U_{23}	-3.52 (59) $\times 10^{-8}$
U_{01}	28.115 425 (95)	U_{04}	-1.237 (39) $\times 10^{-9}$
U_{11}	$-1.967 71$ (23)	Δ_{10}^{He}	1.048 (18)
U_{21}	6.26 (16) $\times 10^{-3}$	Δ_{10}^{H}	-0.613 (20)
U_{31}	-2.658 (32) $\times 10^{-3}$	Δ_{01}^{He}	0.7736 (18)
U_{02}	$-1.065 58$ (13) $\times 10^{-2}$	Δ_{01}^{H}	-0.1459 (19)
U_{12}	2.999 (26) $\times 10^{-4}$	Δ_{02}^{H}	2.346 (91)
U_{22}	-3.84 (11) $\times 10^{-5}$	Δ_{02}^{He}	0.0 (fixed)

[a]The unit of U_{kl} is cm^{-1}(amu)$^{(k/2+l)}$. Parameters Δ_{kl} are nondimensional. The numbers in parentheses are the estimated 1σ uncertainties in units of the last quoted digits.

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