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A new analysis of the ν_2 fundamental band of H_2O^{+*}

Zheng Rui(郑 锐), Li Song(李 松), Hou Shun-Yong(侯顺永),
Huang Guang-Ming(黄光明), and Duan Chuan-Xi (段传喜)[†]

College of Physical Science and Technology, HuaZhong Normal University, Wuhan 430079, China

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This paper reports that the absorption spectra of H_2O^+ have been measured by tunable mid-infrared diode laser spectroscopy in the spectral range of 1100–1380 cm^{-1} . The H_2O^+ ions are generated in an AC glow discharge of the gaseous mixtures of $\text{H}_2\text{O}/\text{He}$ and detected with the velocity modulation technique. Forty new lines are assigned to the ν_2 fundamental band of H_2O^+ (\tilde{X}^2B_1). The observed lines together with other data published previously are fitted to the standard effective Hamiltonian of an asymmetric top, yielding a set of improved rotational constants, spin-rotation constants and their quartic and sextic centrifugal distortion constants for the $\nu_2=1$ vibrational state of H_2O^+ .

Keywords: infrared spectra, water cations, rotational analysis

PACC: 3320E, 3520P, 3310E

1. Introduction

The water cation (H_2O^+) has been extensively studied for many decades since it was postulated to be present in comet tails by Whipple in 1950.^[1] The first high resolution electronic emission spectrum of the $\tilde{A}^2A_1 - \tilde{X}^2B_1$ band system of H_2O^+ was reported by Lew and Heiber in 1973.^[2] Later, Lew performed a detailed analysis of the emission spectrum in 1976.^[3] The high resolution absorption spectrum of H_2O^+ has been reported in visible,^[4,5] near-infrared,^[6,7] mid-infrared,^[8–10] and far-infrared region.^[11,12] Das and Farley^[4] and Wu *et al*^[5] measured the $\tilde{A}^2A_1 - \tilde{X}^2B_1$ transition in the visible range with a dye laser. Huet *et al*^[6] and Gan *et al*^[7] measured the $\tilde{A}^2A_1 - \tilde{X}^2B_1$ transition in the near-infrared range with a Ti:Sapphire laser. Dinelli *et al* observed the ν_3 band in the region 3100–3400 cm^{-1} with a tunable difference frequency spectrometer.^[8] Brown *et al* recorded the ν_2 and $2\nu_2 - \nu_2$ bands in the region 1270–1750 cm^{-1} with a diode laser spectrometer.^[9] Huet *et al* measured the ν_1 and $\nu_2 + \nu_3 - \nu_2$ bands in the region 3180–3390 cm^{-1} with a colour centre laser spectrometer.^[10] The far-infrared laser magnetic resonance spectroscopy has also been used to measure the pure rotational transitions of H_2O^+ in the ground state.^[11,12]

From a theoretic point of view, H_2O^+ is also a prototype for studying the Renner–Teller effect. The

ground and the first excited electronic states of H_2O^+ are degenerated into a $^2\Pi_u$ state in the linear configuration. Several *ab initio* calculations have been carried out on this system.^[13–17] Among them, the calculations by Weiss *et al*^[16] and Brommer *et al*^[17] were widely used to guide and compare with the experimental measurement. Recently, Wu *et al* performed an *ab initio* calculations of the electronic dipole moment components for the \tilde{A}^2A_1 and \tilde{X}^2B_1 electronic states and the electronic transition moment for the $\tilde{A}^2A_1 - \tilde{X}^2B_1$ transition of H_2O^+ .^[18]

During our previous work on H_3O^+ , we observed some lines of molecular ions which could not be assigned to the $\nu_2(1^- \leftarrow 0^+)$ band of H_3O^+ .^[19] They were most probably from the ν_2 fundamental or hot bands of H_2O^+ in a glow discharge of the mixtures of $\text{H}_2\text{O}/\text{He}$. Though Brown *et al* have derived a set of molecular constants for the $\nu_2 = 0, 1$ and 2 vibrational states by recording 85 lines of the ν_2 fundamental band and 20 lines of the $2\nu_2 - \nu_2$ hot-band of H_2O^+ in the region 1270–1750 cm^{-1} ,^[9] the discrepancies between our observed line positions and the predicted frequencies based on their molecular parameters were quite large. Therefore we performed a spectral scan from 1100 to 1380 cm^{-1} with our available laser diodes in order to make an extension to their measurement and refine the molecular parameters.

In this paper, we present a new measurement and

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[†]Corresponding author. E-mail: cxduan@phy.ccnu.edu.cn

analysis of the ν_2 fundamental band of H_2O^+ . Our observed lines together with those reported in Ref.[9] are fitted to the standard effective Hamiltonian of an asymmetric top. It derives a set of improved rotational constants, spin-rotation constants and their quartic and sextic centrifugal distortion constants for the $\nu_2 = 1$ vibrational state of H_2O^+ .

2. Experiment

The tunable mid-infrared diode laser spectrometer used to investigate the absorption spectra of H_2O^+ is identical to that used in our previous work on H_3O^+ [19] and D_2O^+ [20]. The velocity modulation technique is used to eliminate signals from neutral species.[21] Briefly, the mid-infrared radiations are emitted from a tunable lead-salt diode laser which is mounted in a liquid-nitrogen cooled Dewar (Model L5736, Laser Components). After a single pass through a 10 mm bore, 1 m long water-cooled discharge cell, the main part of the laser beam is detected by a liquid-nitrogen cooled HgCdTe detector. A small portion of laser beam is reflected by the front CaF_2 window of the discharge cell. Then it is modulated by a mechanical chopper at a frequency of about 600 Hz. This chopped beam is split into two parts further before they transmit through a referential gas cell and a Ge etalon separately. The absorption of the reference gas and the interference fringes are also detected by two liquid-nitrogen cooled HgCdTe detectors. Three lock-in amplifiers are used to demodulate signals from three HgCdTe detectors separately. The scan of the current of the diode laser and the data acquisition from three lock-in amplifiers are controlled by a home-developed LabView program simultaneously.

In this paper, the H_2O^+ ions were generated by an AC glow discharge with a flowing gas mixture of distilled water vapour and high-purity helium (> 99.999%). The typical discharge frequency and peak-to-peak current were 42 kHz and 300 mA respectively. The optimal gas mixture was at a total pressure of ~ 1.5 Torr (1 Torr = 133 Pa), which was measured

by a Pirani vacuum gauge at the downstream of the discharge cell. The H_2O^+ ions have been also observed in a $\text{He}/\text{H}_2/\text{O}_2$ discharge.[8–10] The main differences of the plasma chemistry between these two discharge systems have been qualitatively illustrated by Huet *et al.*[10] Four laser diodes were used to cover about 20% of the 1100–1380 cm^{-1} region. The absorption spectra of H_2O^+ were calibrated by using the accurate line positions of N_2O and SO_2 from the HITRAN database[22] and the Ge etalon fringes (FSR $\sim 0.049 \text{ cm}^{-1}$). The absolute accuracy of the calibration was estimated to be better than 0.005 cm^{-1} .

3. Results and analysis

Under the experimental conditions described above, more than one hundred lines of molecular ions were recorded in the range 1100–1380 cm^{-1} , in which 40 new lines were assigned to the ν_2 fundamental band of H_2O^+ with the aid of molecular parameters reported in Ref.[9]. Fourteen lines were re-measured at better accuracy. The measured frequencies and their assignment are listed in Table 1. Due to our improved signal-to-noise ratio, some blended lines reported in Ref.[9] were well resolved in this work, as shown in Fig.1.

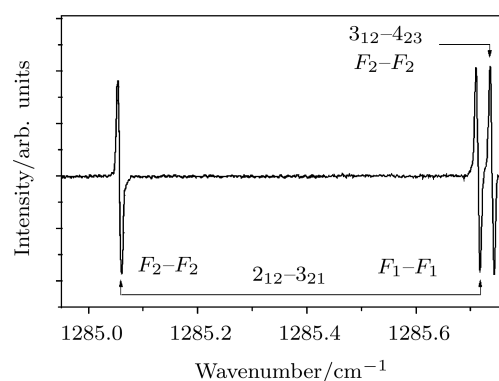


Fig.1. A typical spectrum of the ν_2 fundamental band of H_2O^+ . The assigned transitions are $2_{12}\text{F}_2 \leftarrow 3_{21}\text{F}_2$ (1285.059 cm^{-1}), $2_{12}\text{F}_1 \leftarrow 3_{21}\text{F}_1$ (1285.713 cm^{-1}) and $3_{12}\text{F}_2 \leftarrow 4_{23}\text{F}_2$ (1285.739 cm^{-1}). The latter two transitions are well resolved in this work, but were blended with each other in Ref.[9] and observed at 1285.713 cm^{-1} .

Table 1. Transitions of the ν_2 fundamental band of H_2O^+ .

N'	K'_a	K'_c	J'	N''	K''_a	K''_c	J''	Obs./ cm^{-1}	Obs. - Calc./ 10^{-3}cm^{-1}
5	3	3	5.5	6	4	2	6.5	1193.067 ^a	-10
5	3	3	4.5	6	4	2	5.5	1193.081 ^a	6
6	2	4	5.5	7	3	5	6.5	1205.111 ^a	6
6	2	4	6.5	7	3	5	7.5	1205.395 ^a	11

Table 1 *Continued*

N'	K'_a	K'_c	J'	N''	K''_a	K''_c	J''	Obs./ cm^{-1}	Obs. - Calc./ 10^{-3}cm^{-1}
4	2	3	4.5	5	3	2	5.5	1224.693 ^a	16
8	1	7	8.5	9	2	8	9.5	1231.022 ^a	0
8	1	7	7.5	9	2	8	8.5	1231.081 ^a	3
3	3	1	3.5	4	4	0	4.5	1236.775 ^a	-1
3	3	0	3.5	4	4	1	4.5	1236.830 ^a	0
3	3	1	2.5	4	4	0	3.5	1237.088 ^a	0
3	3	0	2.5	4	4	1	3.5	1237.141 ^a	0
8	0	8	8.5	9	1	9	9.5	1245.328 ^a	-1
8	0	8	7.5	9	1	9	8.5	1245.432 ^a	3
3	2	2	2.5	4	3	1	3.5	1248.748 ^a	-3
3	2	2	3.5	4	3	1	4.5	1249.019 ^a	0
3	2	1	3.5	4	3	2	4.5	1252.144 ^a	-1
3	1	3	2.5	4	2	2	3.5	1252.541 ^a	0
3	1	3	3.5	4	2	2	4.5	1253.167 ^a	0
8	2	7	7.5	9	1	8	8.5	1253.243 ^a	-5
2	2	1	1.5	3	3	0	2.5	1271.516 ^a	0
2	2	1	2.5	3	3	0	3.5	1271.618 ^a	-3
2	2	0	1.5	3	3	1	2.5	1272.136 ^a	1
2	2	0	2.5	3	3	1	3.5	1272.237 ^a	-3
4	1	3	3.5	5	2	4	4.5	1272.901 ^a	-1
8	1	8	8.5	8	2	7	8.5	1279.167 ^a	-11
6	0	6	6.5	7	1	7	7.5	1279.188 ^{a,c}	-11
6	0	6	5.5	7	1	7	6.5	1279.277 ^{a,c}	2
2	1	2	1.5	3	2	1	2.5	1285.059 ^a	-2
2	1	2	2.5	3	2	1	3.5	1285.713 ^{a,c}	-4
3	1	2	2.5	4	2	3	3.5	1285.739 ^{a,c}	0
3	1	2	3.5	4	2	3	4.5	1286.142 ^b	2
8	0	8	7.5	8	1	7	7.5	1287.300 ^{b,d}	-49
8	0	8	8.5	8	1	7	8.5	1287.768 ^a	6
5	0	5	4.5	6	1	6	5.5	1294.918 ^b	-10
5	0	5	5.5	6	1	6	6.5	1294.999 ^b	-7
7	1	7	6.5	7	2	6	6.5	1295.035 ^b	-2
7	1	7	7.5	7	2	6	7.5	1295.583 ^b	-1
2	1	1	1.5	3	2	2	2.5	1300.551 ^b	-1
2	1	1	2.5	3	2	2	3.5	1301.071 ^b	-3
5	1	5	5.5	6	0	6	6.5	1302.414 ^{a,c}	-4
5	1	5	4.5	6	0	6	5.5	1302.571 ^{a,c}	-2
7	0	7	7.5	7	1	6	7.5	1308.744 ^a	14
4	0	4	3.5	5	1	5	4.5	1309.859 ^{a,c}	5
4	0	4	4.5	5	1	5	5.5	1309.937 ^{a,c}	6
6	1	6	5.5	6	2	5	5.5	1310.064 ^a	-3
6	1	6	6.5	6	2	5	6.5	1310.642 ^b	3
1	1	1	0.5	2	2	0	1.5	1312.728 ^b	1
1	1	1	1.5	2	2	0	2.5	1313.334 ^b	-3
6	4	2	5.5	6	5	1	5.5	1315.175 ^a	-1
6	4	2	6.5	6	5	1	6.5	1315.301 ^a	1
7	2	6	7.5	7	3	5	7.5	1316.877 ^b	-5
1	1	0	0.5	2	2	1	1.5	1317.563 ^b	10

Table 1 *Continued*

N'	K'_a	K'_c	J'	N''	K''_a	K''_c	J''	Obs./cm ⁻¹	Obs. - Calc./10 ⁻³ cm ⁻¹
1	1	0	1.5	2	2	1	2.5	1318.064 ^b	1
5	3	3	5.5	5	4	2	5.5	1320.807 ^b	0
4	3	1	3.5	4	4	0	3.5	1321.642 ^{b,d}	323
4	3	1	4.5	4	4	0	4.5	1321.759 ^b	0
5	3	2	5.5	5	4	1	5.5	1322.029 ^b	4
4	1	4	4.5	5	0	5	5.5	1322.175 ^b	0
4	1	4	3.5	5	0	5	4.5	1322.391 ^b	2
6	3	3	6.5	6	4	2	6.5	1323.162 ^a	-3
5	1	5	4.5	5	2	4	4.5	1323.388 ^b	3
5	2	4	5.5	6	1	5	6.5	1323.808 ^a	9
5	1	5	5.5	5	2	4	5.5	1324.001 ^{a,c}	0
3	0	3	2.5	4	1	4	3.5	1324.097 ^b	5
3	0	3	3.5	4	1	4	4.5	1324.248 ^b	7
7	3	4	6.5	7	4	3	6.5	1325.266 ^{b,d}	81
5	2	4	4.5	5	3	3	4.5	1328.375 ^b	1
5	2	4	5.5	5	3	3	5.5	1328.830 ^b	1
6	0	6	5.5	6	1	5	5.5	1328.872 ^b	2
6	0	6	6.5	6	1	5	6.5	1329.211 ^b	9
3	2	2	3.5	3	3	1	3.5	1334.356 ^{a,c}	2
4	1	4	3.5	4	2	3	3.5	1334.688 ^{a,c}	-4
4	1	4	4.5	4	2	3	4.5	1335.372 ^{a,c}	-9
2	0	2	1.5	3	1	3	2.5	1338.392 ^b	-2
4	2	2	4.5	4	3	1	4.5	1339.503 ^b	2
8	1	7	8.5	8	2	6	8.5	1340.772 ^a	-11
5	2	3	4.5	5	3	2	4.5	1343.064 ^a	-10
3	1	3	2.5	4	0	4	3.5	1343.355 ^a	-14
3	1	3	3.5	3	2	2	3.5	1344.606 ^b	1
2	1	2	2.5	2	2	1	2.5	1351.526 ^b	-1
7	2	5	6.5	7	3	4	6.5	1351.984 ^b	-5
7	2	5	7.5	7	3	4	7.5	1352.281 ^b	-6
1	0	1	1.5	2	1	2	2.5	1354.064 ^{a,c}	4
8	2	6	8.5	8	3	5	8.5	1354.077 ^a	8
6	1	5	5.5	6	2	4	5.5	1361.607 ^b	8
6	1	5	6.5	6	2	4	6.5	1361.833 ^b	-3
2	1	1	1.5	2	2	0	1.5	1362.314 ^b	1
4	0	4	4.5	4	1	3	4.5	1363.567 ^b	4
5	1	4	4.5	5	2	3	4.5	1366.171 ^a	1
3	1	2	3.5	3	2	1	3.5	1366.192 ^a	0
5	1	4	5.5	5	2	3	5.5	1366.474 ^a	-8
4	1	3	3.5	4	2	2	3.5	1367.248 ^b	-1
4	1	3	4.5	4	2	2	4.5	1367.673 ^b	-5
0	0	0	0.5	1	1	1	1.5	1371.206 ^{a,c}	1
3	0	3	2.5	3	1	2	2.5	1374.935 ^b	4
2	0	2	1.5	2	1	1	1.5	1382.782 ^b	2
2	0	2	2.5	2	1	1	2.5	1383.286 ^b	4
5	2	4	5.5	4	3	1	4.5	1434.414 ^b	7
1	1	1	0.5	0	0	0	0.5	1450.851 ^b	2

Table 1 *Continued*

N'	K'_a	K'_c	J'	N''	K''_a	K''_c	J''	Obs./ cm^{-1}	Obs. - Calc./ 10^{-3}cm^{-1}
3	0	3	2.5	2	1	2	1.5	1454.826 ^b	-1
3	0	3	3.5	2	1	2	2.5	1455.126 ^b	4
2	1	2	2.5	1	0	1	1.5	1466.346 ^b	-13
4	2	2	4.5	4	1	3	4.5	1468.959 ^b	-4
5	2	3	5.5	5	1	4	5.5	1469.888 ^b	-10
4	2	2	3.5	4	1	3	3.5	1469.992 ^b	4
2	2	0	2.5	2	1	1	2.5	1474.109 ^b	-2
6	2	4	6.5	6	1	5	6.5	1474.844 ^b	2
4	0	4	4.5	3	1	3	3.5	1476.678 ^b	9
2	2	0	1.5	2	1	1	1.5	1476.823 ^{b,d}	60
3	1	3	2.5	2	0	2	1.5	1481.556 ^b	-4
3	1	3	2.5	2	0	2	2.5	1481.733 ^{b,d}	37
7	2	5	6.5	7	1	6	6.5	1485.070 ^b	-4
2	2	1	2.5	2	1	2	2.5	1485.302 ^b	1
3	2	2	3.5	3	1	3	3.5	1491.607 ^b	19
3	2	2	2.5	3	1	3	2.5	1493.171 ^b	-3
4	2	3	3.5	3	1	2	2.5	1552.053 ^b	-0
3	2	1	2.5	2	1	2	1.5	1552.154 ^b	2
8	2	7	7.5	8	1	8	7.5	1552.365 ^b	10
5	2	4	5.5	4	1	3	4.5	1563.864 ^b	-5
4	2	2	3.5	3	1	3	2.5	1583.320 ^b	1
3	3	1	3.5	2	2	0	2.5	1596.114 ^b	-6
3	3	0	3.5	2	2	1	2.5	1596.795 ^b	6
4	3	1	3.5	3	2	2	2.5	1620.706 ^b	-5
4	4	0	3.5	3	3	1	2.5	1677.566 ^b	1

^a: From this work.^b: From Ref.[9].^c: Lines are also reported in Ref.[9] but our measured frequencies are adopted in the final fit.^d: Lines are not in accord with the others and omitted in the final fit.

H_2O^+ has three vibrational modes in the \tilde{X}^2B_1 state: **symmetric stretching (ν_1)**, **bending (ν_2)** and **asymmetric stretching (ν_3)**. The ν_2 fundamental mode obeys the b -type selection rules for an asymmetric top: $\Delta N = 0, \pm 1$; $\Delta K_a = \pm 1(\pm 3, \pm 5, \dots)$; $\Delta K_c = \pm 1(\pm 3, \pm 5, \dots)$. The interaction of the single unpaired electron and the rotation motion splits each rotational level into two spin components (F_1 : $J = N + 1/2$; F_2 : $J = N - 1/2$). The $\Delta J = \Delta N$ doublets have the dominant intensity while the $\Delta J \neq \Delta N$ doublets only have reasonable intensity at low N . The nuclear spin of the hydrogen atom ($I = 1/2$) gives a nuclear spin statistical weight of 3 for rotational levels with $(K_a, K_c) = (e, e), (o, o)$, and 1 for levels with $(K_a, K_c) = (e, o), (o, e)$, when the vibrational eigenfunction of the lower level is totally symmetric.

The rotational structure of the ground and $\nu_2 = 1$ vibrational states of H_2O^+ (\tilde{X}^2B_1) can be described by the A -reduced asymmetric top Hamiltonian H_R

of Watson^[23] with additional A -reduced spin-rotation Hamiltonian H_{SR} of Brown and Sears:^[24]

$$\begin{aligned}
H_R = & AN_a^2 + BN_b^2 + CN_c^2 - \Delta_N N^4 \\
& - \Delta_{NK} N^2 N_a^2 - \Delta_K N_a^4 \\
& - \frac{1}{2} [\delta_N N^2 + \delta_K N_a^2, (N_+^2 + N_-^2)]_+ \\
& + H_N N^6 + H_{NK} N^4 N_a^2 \\
& + H_{KN} N^2 N_a^4 + H_K N_a^6 + \dots, \quad (1)
\end{aligned}$$

$$\begin{aligned}
H_{SR} = & \varepsilon_{aa} N_a S_a + \varepsilon_{bb} N_b S_b + \varepsilon_{cc} N_c S_c \\
& + \Delta_N^S N^2 (N \cdot S) + \frac{1}{2} \Delta_{NK}^S [N^2, N_a S_a]_+ \\
& + \Delta_{KN}^S N_a^2 (N \cdot S) + \Delta_K^S N_a^3 S_a + \dots, \quad (2)
\end{aligned}$$

where A, B, C are rotational constants, $\Delta_N, \Delta_{NK}, \Delta_K, \delta_N, \delta_K$ are quartic rotational centrifugal distortion constants, and H_N, H_{NK}, H_{KN}, H_K are sextic rotational centrifugal distortion constants; $\varepsilon_{aa}, \varepsilon_{bb}, \varepsilon_{cc}$ are spin-rotation interaction constants, and $\Delta_N^S,$

Δ_{NK}^S , Δ_{KN}^S , Δ_K^S are quartic spin-rotational centrifugal distortion constants.

Our measured lines together with those reported in Ref.[9] were used to determine molecular parameters for the ground and $\nu_2 = 1$ vibrational states of H_2O^+ simultaneously by using Pickett's program SPFIT.[25] In the final fit, 120 lines were fitted to 35 parameters. Five lines measured by Brown *et al*

were excluded from the fit since they were not in accord with the others.[9] Our measured frequencies were adopted for those re-measured 14 lines. The standard deviation of the fit was 0.0057 cm^{-1} , close to the accuracy of measurement. The resulting parameters are listed in Tables 2 and 3. The differences between all the observed line positions and their calculated values are listed in Table 1.

Table 2. The molecular constants (in cm^{-1}) for the ground vibrational state of H_2O^+ . (Figures in parentheses represent one standard deviation in units of the last digit.)

Parameter	This work	Ref.[9]	Ref.[10]	Ref.[3]	Ref.[12]
A	29.03970(57)	29.0366(37)	29.0359(21)	29.0256(9)	29.039508(19)
B	12.41917(22)	12.4170(15)	12.42298(58)	12.4224(5)	12.420949(14)
C	8.46877(24)	8.4684(13)	8.46921(58)	8.4693(5)	8.468088(14)
$10^3\Delta_N$	0.9515(58)	0.937(50)	1.015(13)	1.000(7)	0.97396(30)
$10^3\Delta_{NK}$	-5.037(33)	-5.63(19)	-5.007(71)	-4.73(3)	-5.0788(32)
$10^3\Delta_K$	45.466(80)	45.72(73)	44.20(63)	41.87(6)	45.7162(81)
$10^3\delta_N$	0.34916(89)	0.312(10)	0.3817(24)	0.3700(3)	0.37477(28)
$10^3\delta_K$	1.689(13)	1.60(12)	1.795(50)	1.97(6)	1.9308(52)
10^6H_N	0.334(42)	1.89(60)	0.33(14)	—	—
10^6H_{NK}	-7.15(44)	-9.7(29)	-5.1(11)	—	—
10^6H_{KN}	-4.03(90)	52(21)	—	—	-24.21(26)
10^5H_K	20.52(30)	20.3(27)	15.1(44)	—	25.935(95)
ε_{aa}	-1.0763 (19)	-1.1049(72)	-1.0882(43)	-1.092(6)	-1.088215(63)
ε_{bb}	-0.1153(11)	-0.1237(37)	-0.1130(19)	-0.120(3)	-0.114439(41)
$10^3\varepsilon_{cc}$	3.06(81)	-6.1(25)	3.2(19)	4(3)	1.294(41)
$10^3\Delta_{KN}^s$	-0.307(36)	-0.98(4)	-0.72(23)	—	-0.543(12)
$10^3\Delta_K^S$	5.83(14)	12.6(8)	6.32(71)	5.0(3)	7.456(28)

Table 3. The molecular constants (in cm^{-1}) for the $\nu_2 = 1$ vibrational state of H_2O^+ . (Figures in parentheses represent one standard deviation in units of the last digit.)

Parameter	This work	Ref.[9]	Ref.[3]
A	33.40521(73)	33.3930(42)	33.3601(20)
B	12.47766(24)	12.4765(12)	12.4765(12)
C	8.31554(24)	8.3138(11)	8.3188(20)
$10^3\Delta_N$	1.0247(68)	0.944(44)	1.22(10)
$10^3\Delta_{NK}$	-7.850(41)	-8.13(29)	-7.35(31)
$10^3\Delta_K$	97.37(12)	92.6(10)	82.13(32)
$10^3\delta_N$	0.39854(97)	0.372(8)	0.26(7)
$10^3\delta_K$	4.579(18)	5.00(18)	4.96(43)
10^6H_N	0.479(62)	1.34(57)	—
10^6H_{NK}	-32.27(48)	-3.7(7)	—
10^6H_{KN}	14.3(32)	-13.5(59)	—
10^5H_K	106.26(68)	94.1(36)	—
ε_{aa}	-1.6158(24)	-1.621(10)	-1.645(10)
ε_{bb}	-0.1171(11)	-0.1349(39)	-0.125(4)
$10^3\varepsilon_{cc}$	3.55(93)	-9.4(28)	13(5)
$10^3\Delta_{KN}^s$	-1.04(11)	2.92(72)	—
$10^3\Delta_K^S$	17.33(33)	7.05(205)	18(13)
ν_0	1408.4074(14)	1408.4153(65)	1408.404(10)

4. Discussion and conclusions

Molecular constants for the ground state of H_2O^+ are compared with previous studies in Table 2. Our results are more precise than those of Brown *et al.*^[9] from the analysis of the ν_2 fundamental band, and those of Huet *et al.*^[10] from the analysis of the combination differences from the ν_1 and ν_3 fundamental bands and the electronic emission spectrum. The rotational constants and quartic centrifugal distortion rotational constants from our fit are very close to those of Mürtz *et al.* from a weighted nonlinear, least-squares analysis with the LMR data and the combination differences from the ν_3 band and the electronic emission spectrum.^[12] We didn't fix the molecular parameters for the ground vibrational state at the values reported in Ref.[12] in our fitting, because transitions with $N = 9$ and $K_a = 5$ have been measured in this work, but their term values cannot be extrapolated

accurately with the molecular parameters reported in Ref.[12]. All the sextic rotational centrifugal distortion constants have been determined significantly in this work.

Molecular constants for the $\nu_2 = 1$ vibrational state are compared with those of Brown *et al.*^[9] and of Lew^[3] in Table 3. Our results show better precision than others. The band centre of the ν_2 fundamental band was determined to be $1408.4074(14)\text{ cm}^{-1}$, which agrees well with the value $1408.4153(65)\text{ cm}^{-1}$ determined by Brown *et al.*^[9]

In summary, we have reported an extension of the previous measurement of the ν_2 fundamental band of H_2O^+ . Forty new lines have been assigned and analysed together with the data published previously. Molecular constants for the $\nu_2 = 1$ vibrational state have been better determined, which can be used to characterize the rotational levels up to $N = 9$ and $K_a = 5$ precisely.

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