Millimeter-wave spectroscopy of titanium dioxide, TiO$_2$

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ABSTRACT

The millimeter-wave rotational spectrum of TiO$_2$ in its ground vibrational state has been recorded in the frequency range from 248 to 345 GHz using the Cologne Supersonic Jet Spectrometer for Terahertz Applications (SuJeSTA). Forty-two b-type rotational transitions of the main isotopologue ^{48}TiO$_2$ and five transitions of ^{46}TiO$_2$ in natural abundance have been measured up to J = 22 and K_a = 8 which corresponds to excitation temperatures of 170 K. TiO$_2$ was formed by laser ablation and adiabatically cooled in a supersonic jet of helium to rotational temperatures of 20 K. The new transitions have been analyzed together with previously reported data obtained from Fourier-transform microwave spectroscopy in the frequency range from 7 to 42 GHz. The improved and extended set of spectroscopic parameters provides accurate transition frequencies for future astronomical searches in the millimeter-wave region.

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1. Introduction

The cosmic abundance of titanium is relatively high ([Ti]/[H] $\approx 9 \times 10^{-8}$) [1] compared to other transition metals, so that Ti-containing molecules should have column densities sufficient for detection. Surprisingly, to date only two species, TiO [2] and TiH [3], were detected in atmospheres of cool M-type stars. Some of the abundant TiO might be converted to other stable gas-phase molecules such as TiO$_2$, which is the subject of the present manuscript. The tentative detection of TiO$_2$ in the oxygen-rich circumstellar shell around the late type star VY CMa via rotational transitions at 218.1 GHz and 255.9 GHz [4] prompted us to extend the laboratory measurements of the rotational spectrum of TiO$_2$ into the submm-wavelength region to provide accurate rest frequencies for further astronomical searches. At the low rotational temperature ($\sim$20 K) prevalent in our experiment, the strongest rotational lines of TiO$_2$ are located in the mm- and submm-wavelength region (see Fig. 1), where experimental data are in high demand.

Beside astronomical reasons there is a more general interest in the chemical and physical properties of small transition metal oxides and dioxides because of their importance in catalytic and biological processes (see Gong and Zhou [5] for a recent review on spectroscopic and theoretical studies of transition metal oxygen compounds). Titanium dioxide, TiO$_2$, was the first triatomic transition metal dioxide investigated spectroscopically in the gas phase by both optical emission and infrared absorption spectra [6,7]. The low resolution of these studies prevented the determination of structural data beyond the conclusion that TiO$_2$ must be nonlinear. Its infrared and visible spectra were also studied in rare gas matrices [8–10].

The first gas phase high resolution spectroscopic study on TiO$_2$ was reported by Brünken et al. [4]. The rotational spectrum of titanium dioxide was detected by laser-ablation molecular beam Fourier-transform microwave spectroscopy. Rotational transitions in the X^{1}A$_1$ electronic ground state of the ^{48}TiO$_2$ most abundant isotopic species and also of the ^{46}TiO$_2$ and ^{50}TiO$_2$ rare isotopic species were reported in the frequency range from 7 to 42 GHz. Rotational and centrifugal distortion parameters were obtained together with the first accurate experimental determination of its molecular structure. More recently, Wang et al. [11] and Zhuang et al. [12] recorded high resolution visible spectra and determined the electric dipole moments in the X^{1}A$_1$ and A^{1}B$_2$ electronic states to be substantial, i.e. 6.33(7) D and 2.55(8) D, respectively.
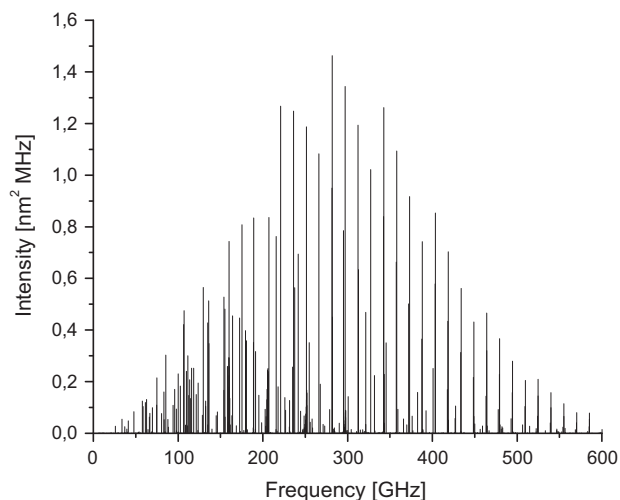
2. Experimental details

Pure rotational transitions of TiO$_2$ were measured in the frequency region from 248 GHz to 346 GHz using the Cologne Supersonic Jet Spectrometer for Terahertz Applications (SuJeSTA). The general experimental setup has been described in detail previously [13]. For the measurements presented here we implemented a
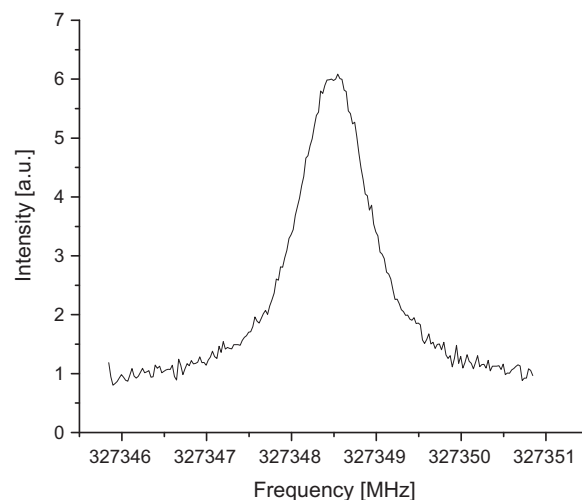
Fig. 1. Calculated overview spectrum for the main isotopologue $^{48}TiO_2$ at 20 K rotational temperature.

Fig. 2. Rotational transition $8_{5,3} \leftarrow 7_{4,4}$ of TiO_2 recorded with SuJeSTA. The line profile is given by a Voigt profile.

laser ablation source into the system, which allows for the gas-phase characterization of non-volatile samples. Titanium dioxide was produced by laser ablation of TiO_2 powder (99.9%, Sigma Aldrich) mixed with low concentrations of methyl cellulose (mass mixing ratio 20:1) to form a solid rod. Alternatively, a pure titanium rod (99.7%, Sigma Aldrich) was used as ablation target and a few percent of molecular oxygen was added to the helium buffer gas to form TiO_2 molecules. This latter production method of TiO_2 turned out to be more stable and was applied in all measurements presented here. The strongest lines of TiO_2 were observed at a concentration of 2–3% O_2 in helium.

Light of the fundamental mode of a Q-switched Nd:YAG laser (Inlite III-30, Continuum) was focused by a 30-cm focal length CaF_2 lens onto the surface of the probe. Highest yields and stable conditions were achieved at Nd:YAG laser power of 35–40 mJ per pulse (~10 ns pulse duration). To allow for homogenous ablation the rod was constantly rotated and translated. The vaporized products – formed in the high pressure regime of a 6 mm-long reaction channel – were diluted in a 500 µs long pulse of helium and collisionally and adiabatically cooled to a rotational temperature of ~20 K in a supersonic expansion into the vacuum chamber. Best results were obtained for helium backing pressures of 2 bars at a background pressure of 50 µbar in the vacuum chamber. Operation of the pulsed valve, ablation laser, and signal recording was controlled and synchronized by a TTL timer unit at 30 Hz repetition rate.

The millimeter-wave beam probed the molecular jet approximately 3 cm downstream and almost perpendicular to the direction of jet propagation to reduce Doppler broadening of recorded lines. The sensitivity of the spectrometer was enhanced by multipass optics using a Herriott-type cell [14] with 10 passes through the jet, and an absorption path length of roughly 100–200 mm. The output signal from a liquid He cooled InSb detector was amplified and the short pulses of signal were recorded by a pair of gated boxcar integrators. The strongest lines were observed with a signal-to-noise ratio of about 25 after 30 min of integration (see Fig. 2).

3. Results and data analysis

Titanium dioxide is an asymmetric prolate top with C_{2v} symmetry and Ray's asymmetry parameter of $\kappa = -0.8445$. A large permanent electric dipole moment of 6.33(7) D is pointing
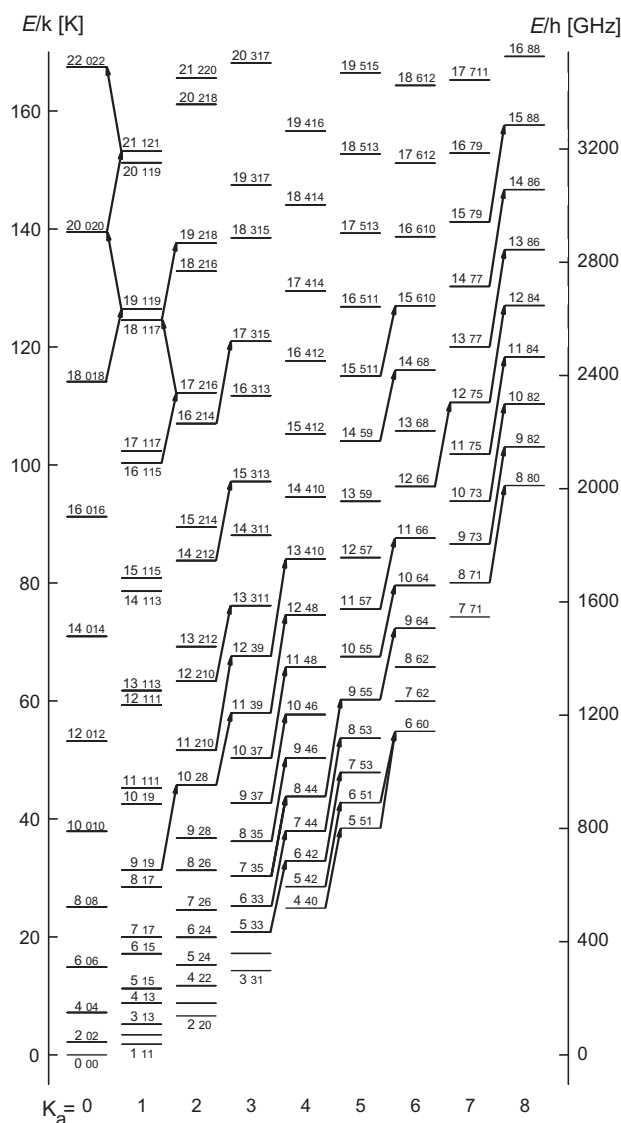
Fig. 3. Energy level diagram and measured transitions of $^{48}TiO_2$.

along the molecular b-axis [4,11]. Only rotational levels with $K_a + K_c$ even exist for isotopologues containing two ^{16}O atoms because of spin-statistics and the zero nuclear spin of ^{16}O. A sample in natural isotopic abundance (73.72% ^{48}Ti, 8.25% ^{46}Ti, 7.44% ^{47}Ti, 5.41% ^{49}Ti and 5.18% ^{50}Ti) was used for the present measurements. In total, 42 new transitions with quantum numbers J from 4 up to 22 and K_a up to 8 were measured for the main isotopologue $^{48}TiO_2$ (see Fig. 3), and five transitions were recorded for the second most abundant isotopic species $^{46}TiO_2$ to confirm the adequacy of the constraints employed for the centrifugal distortion parameters, see below. The previous predictions turned out to be very good. The newly measured lines had initial uncertainties of up to 1 MHz. In particular for transitions with high J, the lines were usually observed within the predicted uncertainties. For transitions with high K_a and $J \approx K_a$, the deviations were slightly larger, around twice the predicted uncertainties. Voigt line profiles were numerically fit to the data to obtain precise line center frequencies. All results and experimental uncertainties are given in Tables 1 and 2, and an exemplary spectrum is shown in Fig. 2. The new data were analyzed together with previously reported microwave data [4] using an A-reduced Watson type Hamiltonian model which contains the molecular rotation of a rigid rotor and the associated centrifugal correction terms. Pickett's programs [15] SPFIT and SPCAT were used to derive rotational and leading centrifugal distortion constants. The ratios of quartic distortion constants for all

three isotopologues have been obtained by empirical force field calculations using the NCA program routine by Christen [16] and were fixed in the SPFIT routine. Details of the force field calculation will be presented in a subsequent publication. Sextic centrifugal distortion parameters were evaluated from B3LYP calculations with Gaussian03 [17] employing Bauschlicher's cc-pVTZ basis set [18]. Isotopic ratios of these parameters were also kept fixed in the combined fit of three isotopic species.

All quartic and three sextic distortion parameters were varied in the fit, albeit with the isotopic ratios constrained; only the rotational constants were varied without constraints. As it was possible to reproduce the experimental lines on average within the uncertainties, there was no need to release any of the isotopic constraints. Strictly speaking, these ratios hold only in the hypothetical equilibrium state, but any deviations in the ground vibrational state were apparently not significant in the present data set. Improved spectroscopic parameters were thus obtained for $^{48}TiO_2$, $^{46}TiO_2$, and $^{50}TiO_2$. The uncertainties of the centrifugal distortion parameters among the isotopic species reflect their constraint in the combined fit. Moreover, the uncertainties of the rotational constants of $^{46}TiO_2$ and $^{50}TiO_2$ are only slightly larger than those of $^{48}TiO_2$ because these have been determined already by the previous FTMW data [4].

The new spectroscopic parameters are given in Table 3, they are consistent within error bars with parameters obtained from

Table 1
Observed transition frequencies of $^{48}TiO_2$. Uncertainties are estimated from signal-to-noise ratios of measured lines.

J'	K_a'	K_c'		J''	K_a''	K_c''	Frequency (MHz)	Uncertainty (MHz)	Obs.–calc. (MHz)
17	2	16	←	16	1	15	248664.553	0.050	−0.042
15	6	10	←	15	5	11	249028.641	0.100	0.159
14	6	8	←	14	5	9	249402.792	0.100	0.121
11	6	6	←	11	5	7	251185.390	0.060	−0.042
6	4	2	←	5	3	3	251359.335	0.060	−0.091
10	6	4	←	10	5	5	251473.636	0.030	−0.023
9	6	4	←	9	5	5	251708.056	0.050	0.023
6	6	0	←	6	5	1	252046.992	0.050	0.039
11	3	9	←	10	2	8	254646.740	0.040	0.058
18	1	17	←	17	2	16	255866.063	0.080	0.181
19	1	19	←	18	0	18	257976.544	0.100	0.111
7	4	4	←	6	3	3	266139.682	0.040	0.039
13	3	11	←	12	2	10	267832.201	0.080	0.010
20	0	20	←	19	1	19	271110.740	0.100	0.064
19	2	18	←	18	1	17	273064.125	0.080	0.044
15	3	13	←	14	2	12	278954.166	0.060	0.067
8	4	4	←	7	3	5	281736.326	0.050	−0.019
5	5	1	←	4	4	0	282012.150	0.040	−0.056
21	1	21	←	20	0	20	284371.901	0.050	−0.063
17	3	15	←	16	2	14	290299.493	0.030	−0.020
9	4	6	←	8	3	5	295043.012	0.020	0.013
12	7	5	←	12	6	6	297027.465	0.080	−0.023
6	5	1	←	5	4	2	297139.588	0.030	−0.025
22	0	22	←	21	1	21	297553.951	0.050	0.025
10	2	8	←	9	1	9	300625.113	0.030	−0.000
7	5	3	←	6	4	2	312248.341	0.020	0.013
10	4	6	←	9	3	7	312732.066	0.060	−0.020
11	4	8	←	10	3	7	321401.936	0.050	0.089
8	5	3	←	7	4	4	327348.499	0.010	−0.009
12	3	9	←	11	2	10	331599.580	0.040	0.026
15	8	8	←	15	7	9	342217.332	0.060	0.017
9	5	5	←	8	4	4	342344.863	0.010	0.008
14	8	6	←	14	7	7	342490.878	0.060	−0.036
13	8	6	←	13	7	7	342708.238	0.060	−0.052
6	6	0	←	5	5	1	342861.788	0.030	−0.004
12	8	4	←	12	7	5	342876.765	0.050	0.060
11	8	4	←	11	7	5	343004.056	0.050	0.022
10	8	2	←	10	7	3	343097.014	0.030	−0.026
9	8	2	←	9	7	3	343162.011	0.080	0.018
8	8	0	←	8	7	1	343204.527	0.030	0.015
13	4	10	←	12	3	9	343243.361	0.020	−0.005
12	4	8	←	11	3	9	345580.864	0.010	−0.008

Table 2
Observed transition frequencies of $^{46}TiO_2$. Uncertainties are estimated from signal-to-noise ratios of measured lines.

J'	K'_a	K'_c		J''	K''_a	K''_c	Frequency (MHz)	Uncertainty (MHz)	Obs.–calc. (MHz)
6	4	2	←	5	3	3	255126.577	0.080	−0.068
7	4	4	←	6	3	3	269955.281	0.050	0.015
8	4	4	←	7	3	5	285530.191	0.080	−0.016
5	5	1	←	4	4	0	286793.797	0.080	−0.005
7	5	3	←	6	4	2	317077.439	0.100	0.012

Table 3
Ground state molecular parameters[a] (MHz) of $^{48}TiO_2$, $^{46}TiO_2$, and $^{50}TiO_2$.

Parameter	$^{48}TiO_2$	$^{46}TiO_2$	$^{50}TiO_2$
A	30520.54096 (132)	31051.47943 (168)	30031.66458 (164)
B	8471.758010 (305)	8471.56434 (36)	8471.93513 (41)
C	6613.58728 (41)	6638.20087 (48)	6590.31930 (48)
$\Delta_J \times 10^3$	8.34807 (129)	8.37951 (129)	8.31921 (128)
$\Delta_{JK} \times 10^3$	−94.6176 (261)	−96.7359 (267)	−92.6802 (255)
$\Delta_K \times 10^3$	732.662 (61)	757.404 (63)	710.238 (59)
$\delta_J \times 10^3$	2.97997 (66)	2.96422 (66)	2.99444 (66)
$\delta_K \times 10^3$	16.798 (48)	17.283 (49)	16.345 (47)
$\Phi_K \times 10^6$	60.89 (76)	64.04 (80)	58.02 (73)
$\Phi_{KJ} \times 10^6$	−7.49 (35)	−7.81 (37)	−7.20 (34)
$\phi_K \times 10^6$	5.64 (200)	5.89 (209)	5.42 (192)

^{a} Isotopic ratios of the centrifugal distortion parameters were kept fixed in the fit, see text. Numbers in parentheses are one standard deviation in units of the least significant figures.

Fourier-transform microwave data alone, except for the sextic parameter Φ_K whose value changed more because of the inclusion of the additional parameters Φ_{KJ} and ϕ_K. The experimental values of 61 kHz, −7.5 kHz and ∼5.6 kHz for Φ_K, Φ_{KJ}, and ϕ_K, respectively, for $^{48}TiO_2$ compare very favorably with calculated values of 59.9 kHz, −7.75 kHz, and 5.6 kHz. All other sextic distortion parameters were calculated to be much smaller in magnitude, were not determinable from the experimental data, and their inclusion as fixed parameters does not affect the values of the remaining parameters significantly. They have thus not been included in the final fit.

4. Conclusion

The present millimeter-wave measurements add 47 new entries to the list of known rotational transitions of TiO_2 (see Tables 1 and 2). These data were combined with microwave data from earlier measurements [4] and analyzed together. The new data lead to an improved and extended set of spectroscopic parameters for TiO_2. Most significantly, the centrifugal distortion parameters have been improved by up to one order of magnitude. The rotational spectrum of TiO_2 can now be calculated accurately through large portions of the millimeter- and submillimeter-wave region for astronomical searches for TiO_2 in, e.g., O-rich circumstellar shells. For 20 K, the strongest lines occur in a wide range around 300 GHz with R-branch transitions having in particular $J \approx K_a$, with K_a = 3, 4, 5. At higher temperatures, $J \approx K_a$ transitions also dominate the spectrum, albeit at higher frequencies and higher K_a values.

SuJeSTA proves to be a sensitive instrument for high resolution spectroscopic measurements of transient species formed in a supersonically cooled molecular beam. Rotationally resolved spectra of molecular ions, radicals, and transition metal compounds at rotational temperatures as low as 20 K can be studied in the mm- and submm-wavelength region. SuJeSTA will be used to investigate short-lived molecules relevant to astrophysical observations, such as unsaturated hydrocarbons, low bending modes of pure carbon chains, carbon–silicon and transition metal compounds, and weakly bound van-der-Waals complexes, as well. Experimental data and line predictions will be made available through the catalog section of the Cologne Database for Molecular Spectroscopy, CDMS, [19,20] to foster future detection of molecules in space.

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