MEASUREMENT OF THE LOWEST MILLIMETER-WAVE TRANSITION FREQUENCY OF THE CH RADICAL

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ABSTRACT

The CH radical offers a sensitive way to test the hypothesis that fundamental constants measured on earth may differ from those observed in other parts of the universe. The starting point for such a comparison is to have accurate laboratory frequencies. Here, we measure the frequency of the lowest millimeter-wave transition of CH, near 535 GHz, with an accuracy of 0.6 kHz. This improves the uncertainty by roughly two orders of magnitude over previous determinations and opens the way for sensitive new tests of varying constants.

Key words: methods: laboratory: atomic – molecular data – submillimeter: general

Online-only material: color figures

1. INTRODUCTION

The CH radical is an important constituent of stellar atmospheres and interstellar gas clouds and plays an essential role in most combustion processes. It is a well-established tracer for molecular hydrogen and a basic constituent of interstellar chemistry, being one of the building blocks for more complex species. Recently, the lowest-lying Λ-doublet transitions of CH, and the lowest rotational transition, have been identified as highly sensitive to a possible variation of the fine-structure constant, α, or of the electron-to-proton mass ratio, μ (Kozlov 2009; de Nijs et al. 2012). Such variations—in time, in space, or with local matter density—are expected in some higher-dimensional theories that aim to unify gravity with the other forces, and in some theories of density—are expected in some higher-dimensional theories that aim to unify gravity with the other forces, and in some theories of density—are expected in some higher-dimensional theories that aim to unify gravity with the other forces, and in some theories of density—are expected in some higher-dimensional theories that aim to unify gravity with the other forces, and in some theories of density—are expected in some higher-dimensional theories that aim to unify gravity with the other forces, and in some theories of density—are expected in some higher-dimensional theories that aim to unify gravity with the other forces, and in some theories of density—are expected in some higher-dimensional theories that aim to unify gravity with the other forces, and in some theories of density—are expected in some higher-dimensional theories that aim to unify gravity with the other forces, and in some theories of

Figure 1 shows the relevant energy levels in the ground state of CH. The two lowest levels, having angular momenta J = 1/2 and J = 3/2, are separated by a combination of rotational and spin–orbit energy. Each of these is split into a Λ-doublet, consisting of two levels of opposite parity, p. The magnetic moment of the hydrogen nucleus causes a further splitting into hyperfine components labelled by F, the total angular momentum quantum number. We use the notation (Jp, F) to label these levels. Precise measurements of the Λ-doubling frequencies are given in Truppe et al. (2013). The previous most precise measurements of the J = 3/2–1/2 transitions are given by Amano (2000), with uncertainties between 30 and 100 kHz. Rotational and spin–orbit transitions between higher-lying rotational levels were measured with similar precision by Davidson et al. (2001), who then used all the available data on the v = 0 level of the X2Π state to determine a precise set of molecular parameters. Here, we measure the J = 3/2–1/2 frequencies with a precision of 0.6 kHz.

2. EXPERIMENT

Figure 2 shows the experimental setup. We produce a supersonic beam of CH by photodissociating bromoform. At 4 bar pressure, a carrier gas of He, Ne, Ar, or Kr is bubbled through liquid bromoform (CHBr3, 96% purity stabilized in ethanol) and then expands through the 1 mm-diameter nozzle of a pulsed solenoid valve into a vacuum chamber (Lindner et al. 1998; Romanzin et al. 2006). Light from an excimer laser (wavelength of 248 nm, duration 20 ns, and energy up to 220 mJ) is focused in front of the nozzle to a spot 1 mm high (along y) and 4 mm wide (along z), where it dissociates the bromoform to produce the CH. This source is pulsed with a repetition rate of 10 Hz. At z = 86 mm, the molecules pass through a 2 mm-diameter skimmer into a second vacuum chamber where the pressure is below 10−7 mbar. Here, they enter a magnetically shielded region, and then, at z = 241 mm, they pass through a beam of millimeter-wave radiation that drives a selected hyperfine component of the 3/2+–1/2− transition. The radiation propagates along x and is linearly polarized along y. After leaving the magnetic shield, the molecules are detected at z = 780 mm by driving the ΛΔv(= 0) − X2Π(v = 0) transition with a cw laser beam (from a frequency-doubled titanium-sapphire laser) and imaging the resulting fluorescence onto a photomultiplier tube. This probe light propagates along x, is linearly polarized
along \( z \), has a wavelength near 430.15 nm, and has a power of about 5 mW in a rectangular cross section 4 mm high and 1.4 mm wide. The pulse of fluorescence is recorded with a temporal resolution of about 5 \( \mu \)s. To measure the depletion of the \( J = 1/2 \) population, or the increase in the \( J = 3/2 \) population, the laser drives the transitions to the \( J = 3/2 \) or \( J = 5/2 \) levels of the \( A^2 \Delta(v = 0, N = 2) \) state, respectively. The frequencies of these transitions are given by Zachwieja (1995), where they are designated as \( R_{22\text{ff}}(1/2) \) and \( R_{11\text{ff}}(3/2) \).

The millimeter-wave radiation comes from an amplifier-multiplier chain (Virginia Diodes, AMC) that generates the 54th harmonic of a frequency synthesizer, phase-locked to a 10 MHz GPS reference. A WR1.5 diagonal horn antenna delivers about 7 \( \mu \)W in a rectangular cross section 4 mm high and 1.4 mm wide. The electric field at the output is approximately Gaussian with a waist of 1 mm. This beam is collimated by a plano-convex teflon lens of 30 mm focal length and then passes into the vacuum chamber through a quartz window. At the position of the molecular beam, the electric field profile of the millimeter-wave beam is approximately 

\[
e^{-\left(\frac{y^2+z^2}{w^2}\right)/2},
\]

where \( w \approx 5 \) mm. After accounting for reflection and absorption losses in the lens and window, the power delivered to the molecules is about 7 \( \mu \)W. For the transition between \( (3/2^+, 2, M = 1) \) and \( (1/2^-, 1, M = 1) \), we estimate a Rabi frequency of \( 2\pi \times 23 \text{ kHz} \).

3. RESULTS AND DISCUSSION

With Ar as the carrier gas, Figure 3 shows the time-of-flight profile for molecules in the \( J = 3/2 \) state, both with and without the millimeter-wave radiation applied. From the peak and width of these profiles, we deduce that the molecules have a mean speed of 567 m s\(^{-1}\) and a translational temperature of 0.4 K. When Kr is the carrier gas, the speed is 412 m s\(^{-1}\), and for Ne it is 791 m s\(^{-1}\). When the millimeter-wave radiation is on, the \( J = 3/2 \) fluorescence signal is about 5% of the \( J = 1/2 \) signal. When the millimeter-wave radiation is off, the \( J = 3/2 \) signal increases by a factor of 8.

Figure 4 shows how the laser-induced fluorescence signal from the \( (3/2^+ \) state depends on the millimeter-wave frequency, which is tuned near the \( (3/2^+, 2)-(1/2^-, 1) \) transition and stepped between shots of the experiment in a random order. Each point in the spectrum is the integral of the time-of-flight profile between the limits indicated by the dashed lines in Figure 3. To understand the line shape, we have modeled the experiment taking into account the Gaussian intensity distribution and wavefront curvature of the millimeter-wave beam and the Doppler broadening due to the range of transverse velocities that are detected. Broadening due to the Zeeman effect (see below) is negligible. This model predicts a Gaussian line shape with an FWHM of 44 kHz for a speed of 412 m s\(^{-1}\), 58 kHz for 567 m s\(^{-1}\), and 79 kHz for 791 m s\(^{-1}\). Gaussian fits to our data

![Figure 1. Relevant energy levels in the \( X^2\Pi(v = 0, N = 1) \) ground state of CH, using Hund’s case (b) notation. Transition frequencies are in kHz and are given by the present measurement in combination with the \( \Lambda \)-doublet transitions given in Truppe et al. (2013).](image1)

![Figure 2. Schematic of the experiment.](image2)

![Figure 3. Time-of-flight profiles for molecules having \( J = 3/2 \) before (red points) and after (blue points) driving the \( (3/2^+, 2)-(1/2^-, 1) \) transition. The solid lines are Gaussian fits to the data. The molecules used in the analysis are those that arrive between the dashed lines.](image3)

![Figure 4. \( J = 3/2 \) signal vs. millimeter-wave frequency, showing the \( (3/2^+, 2)-(1/2^-, 1) \) transition. The line is a Gaussian fit to the data.](image4)
give reasonably good agreement with these predictions: we find FWHMs of $51 \pm 4$ kHz, $62 \pm 2$ kHz, and $79 \pm 4$ kHz for these three speeds, where the uncertainties are the standard deviations of several measurements. The fit indicated by the solid line in Figure 4 determines the line center with a precision of $0.3$ kHz.

Inevitably, there is a Doppler shift because the millimeter-wave beam is not exactly perpendicular to the molecular beam. We correct for this by measuring at all three beam velocities and extrapolating the line center to zero velocity, as plotted in Figure 5. For each velocity, we repeat the measurement a number of times and take the weighted mean of the line centers. As expected, we observe a linear shift of the frequency with velocity due to the Doppler shift. To check the reliability of this method, we change the propagation direction of the millimeter-wave beam and repeat the measurements, as also plotted in Figure 5. The two sets of data have different slopes due to the magnetic field, and the excitation zones.

Next, we consider systematic shifts due to the Zeeman effect. The $g$-factor is close to zero when $J = 1/2$, whereas for $J = 3/2$ it is 1.081 when $F = 1$ and 0.648 when $F = 2$. The $(3/2^+, 2)$→$(1/2^−, 1)$ transition is therefore split by a small magnetic field into five equally spaced components separated by 9.07 Hz/nT. In the shielded region where the molecules interact with the millimeter-wave beam, we measure a magnetic field component along $z$ of 13 nT, with the components along $x$ and $y$ being at least 10 times smaller. The linear Zeeman splitting in this field is only $120$ Hz. Furthermore, this linear splitting should not shift the line center because, for a linearly polarized millimeter-wave beam, the shifted components are symmetric about the line center. We have verified this by applying a field large enough to resolve the Zeeman splitting. We have also measured the effect of the quadratic Zeeman shift due to magnetic dipole matrix elements off diagonal in $F$. We apply magnetic fields along $z$ that are large enough to observe a shift of the line center. As expected, this shift is quadratic and has a curvature of $-20$ Hz/nT$^2$. We conclude that in our residual setup, the quadratic Zeeman shifts are negligible at the current level of precision.

The dc Stark shift due to stray static electric fields, the motional Stark shift due to the motion of the molecules through the magnetic field, and the ac Stark shift due to frequency sidebands are all negligible in the experiment. Also negligible are frequency shifts due to collisions, blackbody radiation, and the second-order Doppler shift.

Our measured frequencies for the $(3/2^+, 2)$→$(1/2^−, 1)$ and $(3/2^+, 1)$→$(1/2^−, 1)$ transitions are $532,723,889.3 \pm 0.7$ kHz and $532,721,588.6 \pm 1.4$ kHz, respectively. When taken together with the measured $J = 1/2$ and $J = 3/2$ doublet transition frequencies (Truppe et al. 2013), these results determine the frequency for all components of the $(N = 1, J = 3/2)$→$(N = 1, J = 1/2)$ transition in $^{13}$CH. These are given in Table 1. The uncertainties in the table are slightly smaller than those of the individual measurements quoted above because there are more measurements than independent frequencies. Our results are between 50 and 150 times more precise than the previous best measurements (Amano 2000) and differ from those by up to 3.6 standard deviations. Subtracting our results from those of Amano (2000) and taking the weighted mean, we find a difference of $79 \pm 15$ kHz, indicating an uncontrolled systematic error in those previous measurements.

The absolute accuracy of these new laboratory frequencies is improved to almost one part per billion, at which level the uncertainty no longer hinders the search for varying fundamental constants. This improvement will also allow more accurate velocity determinations to be made in astrophysical measurements. If some need were to emerge for measuring the laboratory frequency even more accurately, then this could be readily achieved using Ramsey’s method (Ramsey 1950) of two excitation zones. In the present apparatus, this would increase the frequency resolution by a factor of 100 without any loss of molecular flux. The use of resonant cavities around the two excitation zones would eliminate the residual Doppler shift and increase the amount of available power for driving the transition. With careful shielding to reduce systematic shifts due to magnetic fields (Truppe et al. 2013), a measurement of this THz frequency interval with an accuracy of 1 Hz is feasible. Precise measurements of submillimeter-wave transition frequencies in other molecules could also be made using this method.

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Table 1

| Transition  | Frequency (kHz) |
|-------------|-----------------|
| $(3/2^+, 1)$→$(1/2^+, 0)$ | 536,795,569.5 ± 0.6 |
| $(3/2^+, 1)$→$(1/2^+, 1)$ | 536,781,856.3 ± 0.6 |
| $(3/2^+, 2)$→$(1/2^+, 1)$ | 536,761,046.3 ± 0.6 |
| $(3/2^+, 1)$→$(1/2^−, 0)$ | 532,793,274.6 ± 0.6 |
| $(3/2^+, 2)$→$(1/2^−, 1)$ | 532,723,889.3 ± 0.6 |
| $(3/2^+, 1)$→$(1/2^−, 1)$ | 532,721,588.6 ± 0.6 |

Figure 5. Doppler shift of the $(3/2^+, 2)$→$(1/2^−, 1)$ transition frequency as a function of velocity, for two different angles of the millimeter-wave beam. (A color version of this figure is available in the online journal.)
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