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CARS spectroscopy of the ($\nu = 0 \rightarrow 1$) band in T_2

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Abstract

Molecular hydrogen is a benchmark system for bound state quantum calculation and tests of quantum electrodynamical effects. While spectroscopic measurements on the stable species have progressively improved over the years, high-resolution studies on the radioactive isotopologues T_2 , HT and DT have been limited. Here we present an accurate determination of T_2 $Q(J = 0-5)$ transition energies in the fundamental vibrational band of the ground electronic state, by means of high-resolution coherent anti-Stokes Raman spectroscopy. With the present experimental uncertainty of 0.02 cm^{-1} , which is a fivefold improvement over previous measurements, agreement with the latest theoretical calculations is demonstrated.

Keywords: coherent anti-Stokes Raman spectroscopy, tritium, hydrogen molecule, high resolution

(Some figures may appear in colour only in the online journal)

1. Introduction

Molecular hydrogen and its isotopologues are benchmark systems where the most refined quantum chemical theories can be applied. Its energy level structure can be calculated to the highest accuracy of any neutral molecule, which include the Born–Oppenheimer (BO) contribution, nonrelativistic BO corrections as well as relativistic and radiative (quantum electrodynamical (QED)) contributions [1, 2]. Adiabatic and nonadiabatic effects are prominent in molecular hydrogen due to the lightness of the nuclei, and thus analogous studies on the different isotopologues provide a handle for a better understanding of these contributions to the level energies.

The ground state level energies and transitions in H_2 , HD and D_2 have been determined at ever increasing accuracies, with the recent accurate studies employing cavity-enhanced techniques (e.g. [3–7]) or pulsed molecular beam spectroscopies [8, 9]. The dissociation energy D_0 , a benchmark quantity in quantum molecular calculations, have also been determined to a

high accuracy [10–12] by combining the results of several precision spectroscopies. The comparison of the results from measurements and calculations enable precision tests of QED, and even test of new physics beyond the standard model [13].

While numerous precision spectroscopic studies on the stable molecular hydrogen isotopologues have been performed, the tritium-bearing species HT, DT and T_2 are not as well studied because of the limited access to radioactive tritium. The comprehensive classical spectroscopy of Dieke [14] on all isotopologues of molecular hydrogen included tritium-containing species. Laser Raman spectroscopic studies were carried out on the pure rotational (0-0) and fundamental vibrational (1-0) bands by Edwards *et al* [15] for T_2 and later for HT and DT [16]. Veirs and Rosenblatt [17] also performed Raman spectroscopy on all molecular hydrogen species, however, they reported discrepancies with [15, 16] that exceeded the claimed uncertainties of those previous determinations. Chuang and Zare [18] performed high-resolution measurements on the (1-0), (4-0) and (5-0) bands of HT using photoacoustic techniques. They pointed out discrepancies when comparing to the *ab initio* calculations by Schwartz and

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LeRoy [19] that may stem from the treatment of nonadiabatic corrections.

The molecular structure of the tritiated hydrogen isotopologues in the electronic ground state is also relevant in experiments which aim at the determination of the mass of the neutrino, like the Karlsruhe tritium neutrino experiment [20]. The mass is deduced from high-resolution electron spectroscopy of the decay electrons from the molecular beta-decay of tritium, $T_2 \rightarrow {}^3\text{HeT}^+ + e^- + \bar{\nu}_e$. After the decay, the helium–tritium ion remains in an excited electronic, vibrational and/or rotational state [21]. This internal excitation energy reduces the kinetic energy carried away by the electron, which acts as the central kinematic observable in the neutrino mass measurements. The probability of excitation of these states is currently only accessible via theory [22, 23]. These calculations crucially depend on the energy levels of the initial states of T_2 and final states of ${}^3\text{HeT}^+$.

In this contribution, we present our determination of the Q -branch transitions of the T_2 fundamental band ($v = 0 \rightarrow 1$) in the ground electronic state. We employed coherent anti-Stokes Raman spectroscopy (CARS) [24] using narrowband pulsed lasers on a low-pressure gas cell containing tritium. Comparison with previous experimental determinations demonstrate agreement with [17], while comparison with calculations in [25] indicate that relativistic and QED contributions are smaller than the present measurement accuracy.

2. Experiment

For the high resolution CARS measurements a new tritium compatible cell was developed based on the concept of the standard Raman cells at the Tritium Laboratory Karlsruhe (TLK) [26, 27]. Tritium-compatibility is guaranteed by employing well-proven materials only, such as stainless steel or certain fused silica windows with metal-to-window sealings. It should be noted that rubber- or plastic-based materials cannot be used due to deterioration by radiochemical reactions induced by the beta-emitter. The inner volume of the cell should be as small as possible to reduce the activity of the tritium gas sample at a certain pressure. On the other hand the length of the cell needs to be long enough, so that the energy density of the laser pulses at the window surface does not exceed the damage threshold. In our design a good compromise was found at a length of 80 mm, which resulted in a total inner cell volume of 4 cm³. Tritium gas was prepared at high purity by performing displacement gas chromatography and getting on uranium beds at the TLK [28] and filled into the cell at about 2.5 mbar. This corresponds to an activity of less than 1 GBq which is the legal limit for handling tritium outside of a licensed lab. The composition of the sample was measured by Raman spectroscopy [29]: T_2 : 93.4%, DT: 4.9%, HT: 1.4%, H_2 : 0.2% and D_2 : 0.1%. Subsequently, the cell was decontaminated to allow transporting to the CARS setup at LaserLab Amsterdam.

A schematic diagram of the setup is shown in figure 1. The frequency-doubled output, at 532 nm, of an injection-

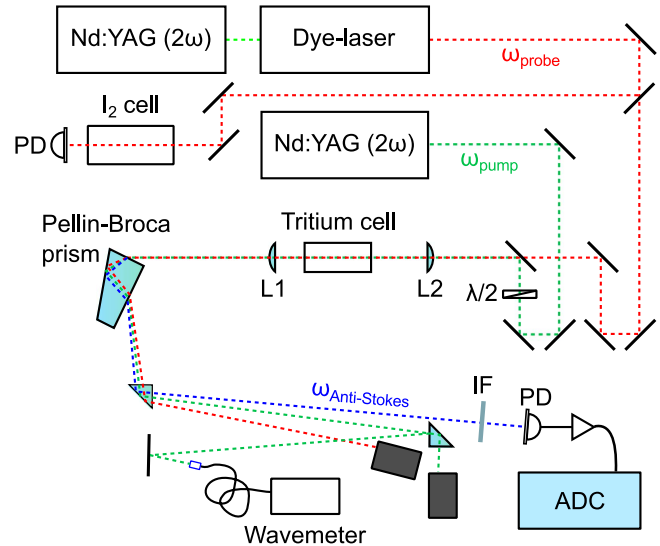


Figure 1. Schematic diagram of CARS setup. $\lambda/2$: half-wave plate; L1, L2: lenses; IF: interference filter; PD: photodiode.

seeded Nd:YAG pulsed laser (Spectra Physics 250-10 PRO, 10 Hz repetition rate) was used as the pump radiation ω_{pump} . The tunable probe beam ω_{probe} , at ~ 612 nm, is the output of a pulsed dye laser (Lioptec LiopStar) running on a mixture of Rhodamine B and Rhodamine 640 that is pumped by another Nd:YAG pulsed laser. The pump and probe beams are spatially combined and subsequently focused by a lens L2, focal length $f = 30$ cm, into the tritium cell and collimated by another lens L1, focal length $f = 10$ cm, after the cell. The probe, pump and anti-Stokes signal $\omega_{\text{anti-Stokes}} = 2\omega_{\text{pump}} - \omega_{\text{probe}}$ beams are then dispersed by a Pellin–Broca prism, where the signal beam (~ 470 nm) passes through an optical interference filter (bandwidth 10 nm) before collection onto a photodetector. The temporal overlap of the pump and probe pulses is optimized by changing the trigger timings of the Nd:YAG lasers.

During the measurement, the wavelength of ω_{pump} is measured continuously (around $18\,789.0302(10)\text{ cm}^{-1}$) using a wavemeter (High Finesse Angstrom WSU-30). The probe radiation ω_{probe} wavenumber is scanned, while simultaneously a portion of ω_{probe} is diverted into an I_2 absorption cell, where the Doppler-broadened absorption lines of the latter are used as calibration [30]. The iodine calibration lines are shown together with a selected Raman line in figure 3. The wavenumber calibration of ω_{pump} is estimated to be better than 0.002 cm^{-1} , while the calibration accuracy of ω_{probe} is estimated at 0.01 cm^{-1} .

3. Results and discussion

The observed $Q(0) - Q(5)$ transitions ($v = 0 \rightarrow 1$, $\Delta J = 0$), plotted against the Raman shift ($\omega_{\text{anti-Stokes}}$), are shown in figure 2. Good signal-to-noise ratio is obtained even for the weakest lines for 7.5 mJ pulse energy for both the pump and probe beams, where the linewidths are observed to be $\sim 0.15\text{ cm}^{-1}$. The relative intensities of the CARS signal follow the expected behavior of $I_{\text{CARS}} \propto N^2$ with N being the number

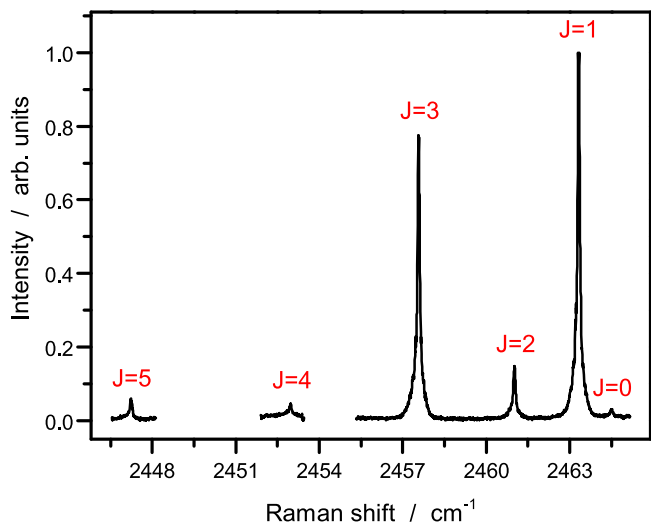


Figure 2. High-resolution spectrum of Q -branch in the fundamental band of T_2 . The lines shown were recorded at pump/probe pulse energies of 5 mJ, except for $J = 4$ which was recorded at 7.5 mJ.

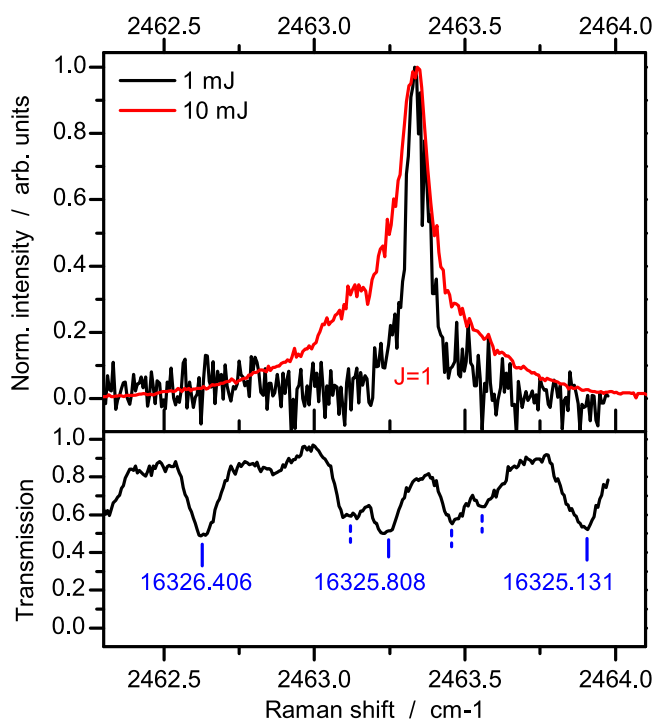


Figure 3. Top: $Q(1)$ transition recorded at 1 and 10 mJ for the pump and probe beams. Bottom: transmission through I_2 calibration cell. Blue lines indicate I_2 absorption lines which have been included in the calibration of the tuneable probe laser (in cm^{-1}). Note, that the wavenumber axis of the iodine spectrum is given by the wavenumber of the pump ($18789.0302(10) \text{ cm}^{-1}$)—Raman shift.

density by considering Placzek–Teller Raman line strength coefficients and a room temperature partition function [31].

The Doppler width of the T_2 Q transitions at room temperature is 0.014 cm^{-1} . In order to estimate the effect of ac-Stark broadening, the $Q(1)$ transition was recorded at lower pulse energies of 1 mJ for both pump and probe beams, see figure 3. Even at these reduced pulse energies, the line-width is observed to be $\sim 0.1 \text{ cm}^{-1}$, which we attribute to be

mainly limited by the probe laser (ω_{probe}) instrument bandwidth. This is confirmed by the fitted linewidths of the I_2 calibration resonances of $\sim 0.08 \text{ cm}^{-1}$, used for calibrating ω_{probe} , while the expected I_2 Doppler width is $\sim 0.03 \text{ cm}^{-1}$. The instrument linewidth of the pump laser ω_{pump} is estimated to be $\sim 0.005 \text{ cm}^{-1}$, and thus has a minor contribution to the T_2 linewidths.

The ac-Stark effect shifts the $v = 0$ and $v = 1$ energy levels due to effects of the polarizability derivative and by a smaller contribution of the polarizability anisotropy [32, 33]. Both these properties are different in ground and excited states and the resulting ac-Stark coefficient for H_2 are found: $\Delta\alpha = 20 \text{ MHz GHz}^{-1} \text{ cm}^{-2}$ for the polarizability derivative and $\Delta\gamma = 9 \text{ MHz GHz}^{-1} \text{ cm}^{-2}$ for the polarizability anisotropy. Since this property is different in the ground- and excited state, a shift of the resulting Raman lines appears. Dyer and Bischel [34] showed that the experimentally determined ac-Stark shifts are in perfect agreement with *ab initio* calculated polarizabilities and that the ac-Stark effect for hydrogen always leads to a red-shift of the Raman line. Using the formulas of Dyer and Bischel with polarizability values for T_2 by Schwartz and Le Roy [19], one obtains a shift which is 40% smaller than that of H_2 . When calculating the expected shift for a CARS signal with typical pulses (pump/probe pulse energy $E = 10 \text{ mJ}$, pulse duration $\tau = 8 \text{ ns}$, beam diameter in focus $d_{\text{focus}} = 35 \mu\text{m}$) we should expect a shift of about 0.1 cm^{-1} . A shift like this should have been visible in figure 3. The effect on our spectrum is less a shift, but more a broadening towards the red (lower wavenumber) side of the CARS resonance. This observation may be ascribed to a difference in our CARS experiment as compared to the dedicated setup by Dyer and Bischel with a well-controlled auxiliary laser for quantifying the ac-Stark effect. In our approach temporal and spatial integration over the power densities has to be considered for the quantitative assessment of the ac-Stark phenomenon, leading to the observed red-side broadening as demonstrated by Li *et al* [35]. As we measured the line profiles for energies for 1–10 mJ while accounting for the asymmetric broadening, we did not observe a shift above the uncertainty of the probe laser calibration of 0.01 cm^{-1} .

May *et al* [36] developed a model for the collisional shift in H_2 as a function of pressure. They measured the linear shift coefficient of the Q -branch to be about $\sim 0.003 \text{ cm}^{-1}/\text{atm}$ at room temperature (see also Rahn *et al* [37]). They predicted that the shift is proportional to the fundamental vibrational transition ω_e and thus to the inverse square root of the reduced mass ($\propto \mu^{-1/2}$)—a behavior which has been verified by Looi *et al* [38] when comparing shifts in D_2 and H_2 . Therefore, the linear shift coefficient in T_2 is expected to be about 1.7 smaller as compared to that of H_2 . At a pressure of 2.5 mbar, we estimate the collision shift to be negligible ($< 1 \times 10^{-5} \text{ cm}^{-1}$).

The accuracy of the present line position determination is then limited by the line fitting uncertainty and by the Doppler-broadened I_2 calibration reference. We provide a conservative estimate of 0.02 cm^{-1} for the transitions measured. Multiple measurements of the $Q(1)$ transition demonstrate reproducibility of the line positions to within 0.01 cm^{-1} at the highest

Table 1. Transition energies of the Q -branch in the fundamental band ($\nu = 0 \rightarrow 1$) of T_2 extracted from measurement with lowest possible pump/probe pulse energies at sufficient high signal-to-noise ratio ($J = 0, 1, 2, 3, 5$: 5 mJ; $J = 4$: 7.5 mJ). The present results are compared to the previous experimental determination in [17] as well as calculations in [19, 25]. See text for the discussion of uncertainties in the *ab initio* calculations. The energies are given in cm^{-1} .

J	This work	[17]	[19]	[25]
0	2464.50 (2)		2464.498 (10)	2464.502
1	2463.33 (2)		2463.343 (10)	2463.346
2	2461.01 (2)	2461.0 (1)	2461.034 (10)	2461.037
3	2457.57 (2)	2457.5 (1)	2457.575 (10)	2457.579
4	2452.97 (2)	2452.0 (1)	2452.976 (10)	2452.980
5	2447.23 (2)	2447.3 (1)	2447.245 (10)	2447.249

pulse energy of 10 mJ, at lower pulse energies the reproducibility increases.

The fitted line positions of the Q transitions are listed in table 1. The transition values from the previous determination of Veirs and Rosenblatt [17], as well as the calculations of Schwartz and LeRoy [19] and by Pachucki and Komasa [25] are also included in the table. There is good agreement with the previous experimental values of [17], with the present results representing a fivefold improvement. The calculation of Schwartz and LeRoy [19] include early estimates of the relativistic and radiative corrections to the potentials, where they estimate a 0.01 cm^{-1} contribution to the level energies. They also evaluate the nonadiabatic corrections by an isotopic scaling procedure and estimate a total uncertainty of 0.015 cm^{-1} for the level energies of low rotational J states. The calculations of Pachucki and Komasa [25] only dealt with nonrelativistic contributions including nonadiabatic corrections for which they assign an uncertainty of 10^{-7} cm^{-1} , which is effectively exact for our purpose. Although [25] does not include relativistic and radiative (QED) contributions, good agreement is found with the present results. This suggests that relativistic and QED corrections are below the present experimental uncertainty of 0.02 cm^{-1} . Since the corresponding relativistic and QED corrections for Q transitions is $\sim 0.002 \text{ cm}^{-1}$ in D_2 [2], the present agreement with [25] is reasonable as it is expected that the analogous corrections are less for T_2 . It is worth noting that the calculation by Schwartz and Le Roy [19] agrees to within 0.004 cm^{-1} when compared to [25].

The previous measurements of Edwards *et al* [15] deviate by -0.2 cm^{-1} in comparison to the present results on average, despite their claimed accuracy of 0.005 cm^{-1} . As the same disagreement persists when comparing [15] with the experimental results of Veirs and Rosenblatt [17], we believe that determinations of Edwards *et al* [15] may have unrecognized systematic errors.

4. Conclusions

We have determined the transition energies of the $Q(0) - Q(5)$ lines in the fundamental band ($\nu = 0 \rightarrow 1$) of the ground

electronic state of molecular tritium by employing CARS spectroscopy. The present results are in good agreement with Veirs and Rosenblatt [17] and represent a five-fold improvement over their previous experimental determination. Agreement with the most accurate nonrelativistic calculation [25] implies that relativistic and radiative effects for these transitions are below the present accuracy of 0.02 cm^{-1} , but may manifest in planned measurements using a narrowband probe laser source. Our present results on T_2 , with the addition of spectroscopies on tritiated species HT and DT, expand our ongoing program on testing the most accurate quantum chemical theory.

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