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► **To cite this version:**

Raul Z. Martinez, Dionisio Bermejo, Piotr Wcislo, Franck Thibault. Accurate wavenumber measurements for the S-0(0), S-0(1), and S-0(2) pure rotational Raman lines of D-2. *Journal of Raman Spectroscopy*, 2019, 50 (1), pp.127-129. <10.1002/jrs.5499>. <hal-02049443>

HAL Id: hal-02049443

<https://univ-rennes.hal.science/hal-02049443v1>

Submitted on 1 Sep 2020

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**Accurate wavenumber measurements for the $S_0(0)$, $S_0(1)$ and $S_0(2)$
pure rotational Raman lines of D_2**

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(Dated: September 10, 2018)

Abstract

We present accurate measurements for the wavenumbers of the $S_0(0)$, $S_0(1)$ and $S_0(2)$ pure rotational Raman lines in D_2 . Our measurements improve the accuracy of the previously available experimental data by an order of magnitude. They also show complete agreement with the state-of-the-art *ab initio* calculations of the D_2 rotational splitting, which include both relativistic and QED corrections.

Keywords: D_2 , Rotational Raman Spectrum, Stimulated Raman Spectroscopy.

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I. INTRODUCTION

Molecular hydrogen, H_2 , is the simplest stable molecule known. Due to this reason, this species and its isotopologues constitute excellent benchmark systems for the testing and development of computational methods and approaches. As a result, a large body of data resulting from calculations, normally in the form of energy levels, has been amassed for these molecules¹⁻⁶. Some of these data boast enormous accuracy⁶, and their availability highlights the need for equally accurate experimental data, in the form of spectroscopic parameters and energy levels, that can be used for comparison and validation of the calculations.

The main obstacle to obtain accurate experimental data on the H_2 isotopologues is the absence (or in the case of HD, the small magnitude) of a dipole moment, which limits the techniques that can be used to either Raman spectroscopy or ultra-sensitive absorption techniques that allow the observation of the extremely weak quadrupole or collision-induced transitions (weak dipole transitions for HD). The availability of such techniques has prompted, in recent years, the completion of a number of studies on these molecules⁷⁻¹⁷. Specifically, most of them have used cavity ring-down spectroscopy or cavity-enhanced saturated absorption to measure quadrupole and collisionally-induced rovibrational transitions in the first and second overtones of H_2 , HD and D_2 . There is, however, a conspicuous absence of purely rotational data, with the most accurate measurements of the rotational Raman spectrum of these molecules dating back over 30 years. This inspired the measurements presented in this article, which were conducted in the course of a larger experimental work whose aim was the determination of broadening and shift coefficients in D_2 , and that is already in the process of being published¹⁸.

II. EXPERIMENTAL

The measurements were carried out using the technique of stimulated Raman spectroscopy (SRS). The experimental apparatus is a *quasi*-continuous (cw) SRS setup, whose basic configuration has already been described in detail in a number of prior articles^{19,20}. The configuration was modified for these experiments so that the pump and probe beams could operate at frequencies close to each other and also with polarizations perpendicular to each other. This is critical to reach the relatively low frequencies of the rotational lines to

be studied. A detailed description of the modified setup can be found in the parent article mentioned in the introduction¹⁸.

The accuracy of a wavenumber measurement in this type of experiment can be affected by a number of sources of error, of which the main ones are collisional shift of the spectral lines, alternating current (AC) Stark shift/broadening of the lines, uncertainty in the determination of the maximum of the peak when a given function is fitted to the experimental line profile and finally the accuracy of the devices (in our case, Fizeau wavemeters) used to perform the wavenumber measurement of the laser sources. In the following paragraphs we describe the conditions under which the measurements were performed and briefly analyze the possible impact of each one these sources of error.

The measurements were conducted at room temperature and a D₂ pressure of 5 mbar, low enough to prevent any detectable shift of the line positions due to molecular collisions. Extrapolations of the self-shift coefficients measured by Van den Hout²¹ for H₂ and D₂ at different temperatures allowed us to roughly estimate a ceiling of ~ 15 MHz/atm for the self-shifting of D₂ at room temperature. Even if these shift coefficients were an order of magnitude larger, we would still be hard-pressed to detect their effect at a sample pressure of 5 mbar.

AC Stark shift and broadening/splitting of hydrogen lines has been observed in coherent Raman experiments when high intensities are used in the laser sources^{22,23}. In order to prevent this, we worked with intensities of the focused pump beam around 1 GW/cm², or approximately 1 mJ/pulse of energy, which is over 2 orders of magnitude lower than the intensities used in the two cited studies. We also performed several trial scans with slightly higher fluences without observing any apparent shift, broadening or asymmetry (a telltale of Stark effect due to the different splitting of the M_J states for each J value) of the spectral lines in this range.

Two high-accuracy wavemeters were used to determine the wavenumbers of the pump and probe lasers, and thus the Raman wavenumber, at every point of the scans. The absolute accuracy of a properly calibrated wavemeter is quoted as 10 MHz (3σ), which translates into an accuracy of 14 MHz (3σ) for the joint two-wavemeter Raman measurement. This is the single largest contributing factor to the uncertainty of the wavenumber measurement in our experiment. A single-mode Ar⁺ ion laser frequency-locked to a known hyperfine transition of ¹²⁷I₂, the a₃ component of the P(13), 43-0 transition at 19429.79512 cm⁻¹, was used for

wavemeter calibration²⁰. For each Raman line, several scans were performed on different days to ensure that the wavenumber values obtained were reproducible within the claimed uncertainty interval. A scan speed of 5 MHz/s and a sampling rate of 10 Hz provided over 120 points per full width at half maximum for the narrowest $S_0(0)$ line, and over 180 for the widest $S_0(2)$.

The experimental line profiles were fitted with gaussian functions to obtain the maxima of the peaks. The gaussian profile accounts very satisfactorily for the convolution of the Doppler broadening and the nearly-gaussian apparatus function of the SRS spectrometer, with typical uncertainties in the peak determination of $\pm 3 \times 10^{-5} \text{ cm}^{-1}$ or $\pm 0.9 \text{ MHz}$ (3σ).

The overall uncertainty of our measurements is thus dominated by the $\pm 14 \text{ MHz}$ of the wavemeters, with all the other potential contributions being negligible compared to it. We have rounded up this uncertainty interval to 0.0002 cm^{-1} (1σ) in table I.

III. RESULTS AND DISCUSSION

Table I presents the wavenumbers obtained for the $S_0(0)$, $S_0(1)$ and $S_0(2)$ Raman lines of D_2 together with the most accurate experimental values available²⁴ prior to this work and also the results of the most advanced calculation performed in this system⁶ up to this day.

A comparison of the two sets of experimental values clearly shows that our results and those of Jennings are in complete agreement within the quoted experimental uncertainties. However, our measurements provide an improvement of an order of magnitude in accuracy.

An even more interesting comparison is the one between our values and those calculated by Komasa *et al.*⁶: the level of detail of the calculation is such that allows the authors to claim accuracies that exceed ours by an order of magnitude. Our measurements agree perfectly, within our uncertainty intervals, with these theoretical results. In fact, the magnitudes of the relativistic and QED corrections included in the calculation, also shown in table I, make it clear that such an agreement would not be possible if these effects had not been taken into consideration. Thus, our experimental results are also a validation of these corrections.

To summarize, in this work we provide the most accurate experimental values for the wavenumbers of the $S_0(0)$, $S_0(1)$ and $S_0(2)$ Raman lines of D_2 measured up to today. Our figures are consistent not only with the results of prior measurements, but also validate, to the limit of our experimental accuracy, those provided by the best calculation available.

ACKNOWLEDGMENTS

RZM and DBP acknowledge the funding received from Vicepresidencia de Investigación Científica y Técnica of Consejo Superior de Investigaciones Científicas through the Fondo de Apoyo Extraordinario and from Project FIS2017-84391-C2-1-P of Ministerio de Economía y Competitividad. PW contribution is supported by the National Science Centre, Poland, Project no. 2015/19/D/ST2/02195.

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	Jennings <i>et al.</i> ²⁴	This work	Komasa <i>et al.</i> ⁶	Magnitude of corrections ⁶	
	(FT-Raman)	(SRS)	(calculated)	α^2 (relativistic)	α^3 (QED)
$S_0(0)$	179.068(2)	179.0669(2)	179.06710(1)	0.0039	-0.0015
$S_0(1)$	297.533(3)	297.5336(2)	297.53374(1)	0.0065	-0.0026
$S_0(2)$	414.648(2)	414.6484(2)	414.64845(2)	0.0090	-0.0036

Table I. Comparison of the absolute wavenumbers measured in this work for the $S_0(0)$, $S_0(1)$ and $S_0(2)$ pure rotational transitions of D_2 to those reported in the bibliography. The two rightmost columns show the magnitude of the relativistic and QED corrections included in the calculations of Komasa⁶, taken from the supplementary material of their article. Units are cm^{-1} . Errors in parentheses are given in units of the last significant digit and correspond to one standard deviation.