Abstract

Accurate absolute level energies of the $B^1\Sigma_u^+, v = 0 - 8, N$ and $EF^1\Sigma_g^+, v = 0 - 21, N$ rovibrational quantum states of molecular deuterium are derived by combining results from a Doppler-free two-photon laser excitation study on several lines in the $EF^1\Sigma_g^+ - X^1\Sigma_g^+ (0,0)$ band, with results from a Fourier-transform spectroscopic emission study on a low-pressure hydrogen discharge. Level energy uncertainties as low as 0.0005 cm$^{-1}$ are obtained for some low-lying $E^1\Sigma_g^+$ inner-well rovibrational levels, while uncertainties for higher-lying rovibrational levels and those of the $F^1\Sigma_g^+$ outer-well states are nominally 0.005 cm$^{-1}$. Level energies of $B^1\Sigma_u^+$ rovibrational levels, for $v \leq 8$ and $N \leq 10$ are determined at an accuracy of 0.001 cm$^{-1}$. Computed wavelengths of D$_2$ Lyman transitions in the $B^1\Sigma_u^+ - X^1\Sigma_g^+ (v,0)$ bands are also tabulated for future applications.

Keywords: molecular deuterium, Fourier-transform spectroscopy, accurate level energies

1. Introduction

Molecular hydrogen continues to be of relevance as it is the simplest neutral system yielding the most accurate results from molecular quantum theory. This benchmark molecule offers a natural setting for the confrontation of the most advanced first-principles theoretical calculations with accurate experimental investigations. Stable isotopologues of molecular hydrogen, H$_2$, HD, and D$_2$ are treated in analogous calculations, except for the additional
g/u symmetry breaking in HD [1]. For example, sustained efforts throughout the decades, in both the theoretical and experimental realm, have led to remarkable improvements in the determination of the dissociation energy $D_0$ of the molecular hydrogen isotopologues $\text{H}_2$ [2], HD [3], and $\text{D}_2$ [4]. At the present level of accuracy, subtle QED effects in molecular level energies need to be accounted for in calculations to obtain agreement with the measurements. Such calculations have now been performed by Pachucki and coworkers for the $X^1\Sigma^+_g$ electronic ground state of all three isotopomers yielding $10^{-3}$ cm$^{-1}$ uncertainties in the binding energies for bound rovibrational quantum states [5, 6]. However, for excited states as the $B^1\Sigma^+_u$ and the $EF^1\Sigma^+_g$ such accurate calculations have not been performed yet.

While $\text{H}_2$ and HD are of great interest in astronomical and cosmological investigations, see e.g. [7], $\text{D}_2$ has not been observed in space beyond the solar system. Since deuterium and tritium will be the main fuel for experimental fusion reactors, their spectra are important diagnostic tools to study the various molecular hydrogen isotopologues produced in the nuclear reactions. These $\text{D}_2$ and $\text{T}_2$ fuels will be heated to extremely high temperatures, so that it is important to characterize the plasma dynamics, for which the excitation cross-sections induced either by photons or electrons are of relevance [8].

The present work focuses on the determination of accurate level energies for the $B^1\Sigma^+_u$ and the $EF^1\Sigma^+_g$ states in the $\text{D}_2$ isotopologue. It builds on the long tradition of studies of the Lyman bands, associated with the $B^1\Sigma^+_u - X^1\Sigma^+_g$ system, that includes the strongest transitions in the molecule. Early, classical spectroscopic studies of the Lyman bands of $\text{D}_2$ were performed by Herzberg and coworkers [9, 10], later followed by XUV-laser spectroscopic studies at increasing resolution and precision [11, 12], albeit only for a relatively small subset of bands in the Lyman system. More comprehensive studies, delivering spectroscopic information on a large set of rovibrational levels, involved electron scattering induced emission studies [13] (with a full database provided [14]), laser probing of highly excited rovibrational levels in a plasma [15], and a VUV Fourier-transform absorption study [16].

The $EF^1\Sigma^+_g$ state, which is long-lived, since one-photon decay to the ground state is dipole forbidden, has been subject of many investigations over the years. Freund et al. [17] compiled a comprehensive data set of $\text{D}_2$ level energies from the studies performed by Dieke over many decades. Yu and Dressler have assembled the information, derived from classical spectroscopy, on the $\text{D}_2 EF^1\Sigma^+_g$ state in a comparison to an $ab initio$ model [18]. Two-photon laser excitation of the $EF^1\Sigma^+_g$ double-well state was vigorously
pursued leading to increased precision of level energies \[19, 20, 21\]. The most recent studies targeted excitation from the \(X^1\Sigma^+_g, v = 1\) level for a sensitive test of QED calculations in the \(D_2\) ground electronic state \[22, 23\]. The analogous 2+1 resonance-enhanced multi-photon ionization study by Heck \textit{et al.} was performed at much lower resolution and accuracy but provided information on a larger manifold of rovibrationally excited states \[24\].

In the present investigation, accurate level energies of the \(B^1\Sigma^+_u\) and \(EF^1\Sigma^+_g\) electronic states for \(D_2\) are derived from new high-resolution Fourier-transform (FT) spectroscopic data. These level energies are anchored with respect to the ground state \(X^1\Sigma^+_g\) using accurate \(EF - X\) transitions from previous UV spectroscopy investigations \[21, 22, 23\]. The FT spectroscopy setup has been discussed in detail in Ref. \[25\], while the anchoring method for the derivation of accurate level energies in the \(EF^1\Sigma^+_g\) and \(B^1\Sigma^+_u\) electronically excited states has been discussed in previous studies focusing on \(H_2\) \[26, 27\]. Here, the calibration procedures on the FT-spectra have been improved mainly by referencing against updated wavelength standards \[28, 29, 30\].

This work results in level energies for a large set of quantum levels for the \(B^1\Sigma^+_u, v = 0 - 8\) and \(EF^1\Sigma^+_g, v = 0 - 21\) vibrational states, being the most accurate to date. For future use, the transition wavelengths of the Lyman bands are calculated based on presently determined level energies and those of the \(X^1\Sigma^+_g\) ground electronic state \[5, 6\].

2. Method

The experimental determination of \(B^1\Sigma^+_u\) and \(EF^1\Sigma^+_g\) level energies is based on an approach that was previously employed for \(H_2\) \[26, 27\]. Accurate values are derived from two completely independent spectroscopic investigations. Relative level energies of a wide manifold of rovibrational quantum states in the \(B^1\Sigma^+_u\) and \(EF^1\Sigma^+_g\) states are determined via high resolution FT emission spectroscopy of transitions connecting \(B, EF, B'^1\Sigma^+_u,\) and \(GK^1\Sigma^+_g\) electronically excited states of \(D_2\). Levels from both the inner and outer wells of the \(EF^1\Sigma^+_g\) state are covered (see Fig. 1).

The relative energies are brought onto an absolute energy scale by anchoring them to the \(X^1\Sigma^+_g\) electronic ground state by results from two-photon UV laser spectroscopy on the \(EF^1\Sigma^+_g - X^1\Sigma^+_g\) system \[21\]. The general features of this measurement scheme include Doppler-free two-photon ionisation and use of a narrowband pulsed titanium-sapphire laser with pulse
frequency chirp measurement and correction [31], as well as absolute frequency calibration against a frequency comb laser. These two-photon UV laser experiments yield highly accurate level energies for two anchor levels used in the present D₂ study [21]: the \( \text{EF}^1\Sigma_g^+ - \text{X}^1\Sigma_g^+ \) Q(0) transition energy of 99 461.449 08 (1) cm\(^{-1}\) for ortho-D₂, and the \( \text{EF}^1\Sigma_g^+ - \text{X}^1\Sigma_g^+ \) Q(1) transition energy at 99 433.716 38 (10) cm\(^{-1}\) for para-D₂. The ortho-D₂ levels have total nuclear spin \( I_T = 0, 2 \), while para-D₂ have \( I_T = 1 \). For the \( \text{EF}^1\Sigma_g^+ \) electronic state symmetry, the even-\( N \) rotational levels belong to ortho-D₂ while the odd-\( N \) levels to para-D₂. For the latter para-state anchor transition, we have used in addition the D₂ \( \text{X}^1\Sigma_g^+ \), \( v = 0, N = 1 \) level energy of 59.780 615 (3) cm\(^{-1}\) from the accurate theoretical calculations of Komasa et al. [6]. The entire manifold of D₂ excited states becomes anchored to the \( \text{X}^1\Sigma_g^+ \), \( v = 0, N = 0 \) ground state with the use of the ortho and para anchor levels. The same two-photon UV experimental scheme has recently been employed for an accurate determination of the \( \text{EF}^1\Sigma_g^+ \) anchor against the \( v = 1 \) level in the \( \text{X}^1\Sigma_g^+ \) ground state [22, 23], thus verifying the values for the anchor levels.

In the FT emission investigation, an extremely broad wavelength range is covered, from 450 nm in the visible to 5 \( \mu \)m in the infrared. The entire
spectral data set includes a multitude of transitions belonging to mutually overlapping band systems. The experimental details have been described previously [25, 27] and only the general features are recalled here. A low-pressure microwave discharge \( f \sim 2450 \text{ MHz} \) was established in a quartz tube (diameter: 1 cm, length: 25 cm) where molecular deuterium flows through at moderate speed. The microwave power (about 70 W) and the gas pressure (about 5 mbar) were controlled in order to optimize the optical emission intensity of the molecular species (relative to the atomic emissions), as well as to maintain stability of the fluorescence. The discharge emission was focused onto the entrance iris of a Bruker IFS 120 FT spectrometer. The emission spectrum was recorded from 1 800 to 22 000 cm\(^{-1}\), with the data collection subdivided into smaller spectral range recordings using appropriate coloured or optical interference filters and detectors. Sample FT spectra are displayed in Fig. 2 showing the fluorescence transitions connecting some D\(_2\) \( EF^1\Sigma_g^+ \) and \( B^1\Sigma_u^+ \) levels. The spectral resolution is limited by Doppler widths, varying from about 0.02 cm\(^{-1}\) (infrared) to 0.2 cm\(^{-1}\) (violet).

Traces of CO or Ar were introduced with the deuterium flow for wavelength calibration purposes. The CO calibration transitions in the range between 1993 to 2254 cm\(^{-1}\) were referenced against the accurate microwave studies of Maki \textit{et al.} [32], which have uncertainties of \( 2 - 5 \times 10^{-5} \text{ cm}^{-1} \). The Ar lines were referenced against the more recent results of Whaling \textit{et al.} [28, 29] with estimated uncertainties of a few times \( 10^{-4} \text{ cm}^{-1} \). We note that the Whaling values [28] for Ar II show deviations with the older Norlen database [33] that can be as much as 0.01 cm\(^{-1}\), specifically in the range from 17 000 to 21 000 cm\(^{-1}\). For the Ar I calibrations using [29], the wavelengths must be corrected by a known factor as discussed by Sansonetti [34]. A recent compilation by Saloman [30] for (neutral and ionic) Ar includes the most recent determinations.

The line assignment and rotational analysis of the FT spectra was performed with the aid of Ref. [17] that was based on Dieke’s work. The analysis was verified through the combination differences of the transition energies from different vibrational bands for each level. For the \( EF^1\Sigma_g^+ \) level energies, transitions connecting \( EF \) to the \( B \) and \( B' \Sigma_u^+ \) electronic states were used, while for the \( B^1\Sigma_u^+ \) level energies, transitions from \( B \) to \( EF \) and \( G \Sigma_g^+ \) levels were used. The analysis then yielded a consistent set of \( EF \) and \( B \) level energies with respect to the \( EF^1\Sigma_g^+ \) \( v = 0, N = 0, 1 \) levels. Finally, the whole \( EF^1\Sigma_g^+ \) and \( B^1\Sigma_u^+ \) level manifold is anchored to the \( X^1\Sigma_g^+ \) \( (v = 0, N = 0) \) ground state using the accurate \( EF^1\Sigma_g^+ - X^1\Sigma_g^+ (0,0) \) band transition ener-
Figure 2: Fourier-transform spectra showing transitions connecting the D$_2$ $EF^1\Sigma^+_g$ and $B^1\Sigma^+_u$ electronic states. The two ranges represent small slices of the whole FT spectral range spanning from 1800 to 20000 cm$^{-1}$.

Energies from the VUV study of Hannemann et al. [21]. Since several transitions from different vibrational bands were used in the derivation of each level energy, the accuracy depends on the number of transitions, as well as the signal-to-noise ratio, connected to that particular level.

3. $EF^1\Sigma^+_g$ level energies

The level energies of the $EF^1\Sigma^+_g$ state of D$_2$ for vibrational levels $v = 0 – 21$ derived from FT spectroscopy are listed in Table I. The ortho-D$_2$ (even $N$ levels) were anchored to the $X^1\Sigma^+_g$ (0,0) level using the $EF^1\Sigma^+_g$ $v = 0, N = 0$ level energy of 99 461.44908 (10) cm$^{-1}$, while for para-D$_2$ (odd $N$ levels) the $EF^1\Sigma^+_g$ $v = 0, N = 1$ level energy of 99 493.49700 (10) cm$^{-1}$ is used. The $N = 0 – 2$ rotational levels of $EF, v = 0$ listed in Table I are derived from the results of Ref. [21] and ground state level energies of Komasa et al. [6], although the $EF, v = 0, N = 2$ value was not used as an anchor level energy. Note that the vibrational levels below the double-well barrier are labeled as belonging either to the inner $E$ or outer $F$ wells, in addition to the generalized $EF$ state vibrational quantum numbers. The energies for levels involved in transitions with good signal-to-noise ratio are most accurate, e.g. vibrational bands belonging to the inner well labeled
$E_0, E_1, E_2$ and $E_3$ with uncertainties as low as 0.0005 cm$^{-1}$ with the least accurate at 0.005 cm$^{-1}$. The transitions belonging to levels within the outer $F$-well and the higher-lying vibrational bands are in general weaker and have larger uncertainties, mostly in the 0.001 – 0.006 cm$^{-1}$ range.

Table 1: Level energies (term values) in the $EF^1\Sigma_g^+$ states of $D_2$ for vibrational levels $v = 0 - 21$. The vibrational assignment is given both in terms of a combined numbering in the $EF$ double-well potential (inside parentheses) and with alternative labels for vibrational bands bound within the separate $E$- and $F$-wells. The values are in cm$^{-1}$ with the 1σ-uncertainties in between parenthesis ( ) expressed in units of the last digit.

| N  | $(v = 0)$ $E0$      | $(v = 1)$ $F0$      | $(v = 2)$ $F1$      | $(v = 3)$ $E1$      |
|----|--------------------|--------------------|--------------------|--------------------|
| 0  | 99 461.4491 (1)†   | 99 829.136 (5)     | 100 686.239 (5)    | 101 149.6672 (5)   |
| 1  | 99 493.4970 (1)†   | 99 835.190 (5)     | 100 692.225 (5)    | 101 180.3488 (5)   |
| 2  | 99 557.4606 (1)†   | 99 847.581 (5)     | 100 704.409 (5)    | 101 241.5809 (5)   |
| 3  | 99 653.0778 (5)    | 99 865.990 (5)     | 100 722.567 (5)    | 101 333.1029 (5)   |
| 4  | 99 779.9595 (5)    | 99 890.577 (5)     | 100 746.741 (5)    | 101 454.5280 (5)   |
| 5  | 99 937.5933 (5)    | 99 921.241 (5)     | 100 776.969 (5)    | 101 605.1960 (5)   |
| 6  | 100 125.3510 (5)   | 100 814.897 (10)   | 101 784.9340 (5)   | 101 992.5515 (5)   |
| 7  | 100 342.4970 (5)   | 101 922.551 (5)    | 102 227.3623 (5)   | 102 488.4281 (5)   |
| 8  | 100 588.1951 (5)   | 102 227.3623 (5)   | 102 488.4281 (5)   | 102 488.4281 (5)   |
| 9  | 100 861.5180 (5)   | 102 488.4281 (5)   | 102 488.4281 (5)   | 102 488.4281 (5)   |
| 10 | 101 161.4531 (5)   | 102 488.4281 (5)   | 102 488.4281 (5)   | 102 488.4281 (5)   |
| 11 | 101 486.9391 (5)   | 102 488.4281 (5)   | 102 488.4281 (5)   | 102 488.4281 (5)   |

| N  | $(v = 4)$ $F2$      | $(v = 5)$ $F3$      | $(v = 6)$ $E2$      | $(v = 7)$ $F4$      |
|----|--------------------|--------------------|--------------------|--------------------|
| 0  | 101 516.074 (5)    | 102 318.268 (5)    | 102 741.6564 (5)   | 103 091.713 (2)    |
| 1  | 101 522.042 (5)    | 102 324.183 (5)    | 102 770.7862 (5)   | 103 097.588 (2)    |
| 2  | 101 533.990 (2)    | 102 336.000 (5)    | 102 828.9036 (5)   | 103 109.342 (2)    |
| 3  | 101 551.890 (2)    | 102 353.689 (5)    | 102 915.7214 (5)   | 103 126.972 (2)    |
| 4  | 101 575.746 (2)    | 102 377.272 (5)    | 103 030.7615 (5)   | 103 150.531 (2)    |
| 5  | 101 605.675 (2)    | 102 406.708 (5)    | 103 170.0036 (5)   | 103 183.462 (2)    |
| 6  | 103 344.3494 (5)   | 103 344.3494 (5)   | 103 344.3494 (5)   | 103 214.157 (5)    |
| 7  | 103 540.4663 (5)   | 103 540.4663 (5)   | 103 540.4663 (5)   | 103 214.157 (5)    |
| 8  | 103 761.8665 (20)  | 103 761.8665 (20)  | 103 761.8665 (20)  | 103 214.157 (5)    |
| 9  | 104 006.0941 (20)  | 104 006.0941 (20)  | 104 006.0941 (20)  | 103 214.157 (5)    |
| 10 | 104 273.0571 (50)  | 104 273.0571 (50)  | 104 273.0571 (50)  | 103 214.157 (5)    |

† Derived from Ref. [21] and Ref. [6]

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Table 1 – Continued from previous page

| N   | (v = 8) F5  | (v = 9) E3  | (v = 10)  | (v = 11)  |
|-----|-------------|-------------|-----------|-----------|
| 0   | 103 830.574 (5) | 104 196.634 3 (5) | 104 546.193 (5) | 105 158.038 (10) |
| 1   | 103 836.646 (5) | 104 222.511 2 (5) | 104 553.237 (5) | 105 167.538 (5) |
| 2   | 103 848.722 (5) | 104 273.802 1 (5) | 104 567.587 (5) | 105 186.262 (5) |
| 3   | 103 866.724 (5) | 104 349.206 9 (5) | 104 590.099 (5) | 105 213.063 (5) |
| 4   | 103 890.579 (5) | 104 445.043 9 (5) | 104 623.724 (5) | 105 247.353 (5) |
| 5   | 103 920.228 (5) | 104 548.420 1 (10) | 104 680.260 (5) | 105 288.197 (5) |
| 6   |              | 104 548.463 7 (10) | 104 787.933 (5) | 105 335.657 (5) |
| N   | (v = 12) | (v = 13) | (v = 14) | (v = 15) |
| 0   | 105 531.930 (1) | 105 977.638 (2) | 106 505.926 (2) | 106 985.727 (2) |
| 1   | 105 548.839 (1) | 105 988.775 (1) | 106 517.373 (2) | 106 998.539 (2) |
| 2   | 105 582.454 (1) | 106 011.360 (1) | 106 540.059 (2) | 107 024.061 (2) |
| 3   | 105 632.067 (1) | 106 046.122 (1) | 106 573.643 (2) | 107 062.045 (2) |
| 4   | 105 695.980 (1) | 106 094.346 (1) | 106 617.761 (2) | 107 112.023 (2) |
| 5   | 105 771.154 (1) | 106 158.770 (1) | 106 672.213 (2) |      |
| 6   | 105 853.413 (1) |              |      |      |
| 7   | 105 935.102 (10) |      |      |      |
| N   | (v = 16) | (v = 17) | (v = 18) | (v = 19) |
| 0   | 107 472.321 (2) | 107 980.549 (4) | 108 480.832 (4) | 108 972.673 (6) |
| 1   | 107 484.157 (2) | 107 991.879 (4) | 108 492.237 (4) | 108 984.013 (6) |
| 2   | 107 507.890 (2) | 108 014.491 (4) | 108 515.378 (4) | 109 006.729 (6) |
| 3   | 107 543.643 (2) | 108 048.307 (4) | 108 549.680 (4) | 109 040.717 (6) |
| 4   | 107 591.577 (2) | 108 093.270 (4) | 108 595.044 (4) | 109 085.952 (6) |
| 5   | 107 651.815 (2) | 108 149.381 (4) | 108 651.153 (4) | 109 142.203 (6) |
| N   | (v = 20) | (v = 21) |
| 0   | 109 466.309 (6) | 109 958.259 (6) |
| 1   | 109 477.214 (10) | 109 968.971 (6) |
| 2   | 109 498.981 (6) | 109 990.320 (6) |
| 3   | 109 531.610 (6) | 110 022.206 (6) |
| 4   | 109 575.054 (6) | 110 064.518 (6) |
| 5   | 109 629.317 (6) |      |      |      |

The FT-derived value for the D2 $EF^1\Sigma_g^+$ ($v = 0, N = 2$) level energy is compared to the accurate measurement results from Doppler-free two-photon $EF^1\Sigma_g^+ - X^1\Sigma_g^+$ spectroscopy by Hannemann et al. [21], Yiannopoulou et al. [20], and recently Niu et al. [23]. The comparison yields energy differ-
ences of $-0.0002 (2) \text{ cm}^{-1}$, $0.0000 (8) \text{ cm}^{-1}$, and $-0.00003 (2) \text{ cm}^{-1}$, respectively. For these comparisons, the ground state $X^1\Sigma_g^+, (v = 0, N = 2)$ and $(v = 1, N = 2)$ level energies used were taken from the theoretical values of Komasa et al. [6] in addition to the $EF^1\Sigma_g^+ - X^1\Sigma_g^+$ Q(2) transition energies determined from the respective investigations in Refs. [20, 21, 22]. Note that the $EF^1\Sigma_g^+ (v = 0, N = 0, 1)$ level energies are not included in the comparison as these are the anchor levels used as absolute references to the $X^1\Sigma_g^+$ ground state. These comparisons for $D_2$ confirm the agreement in the case of $H_2 EF^1\Sigma_g^+ (v = 0, N = 2 - 5)$ level energies as discussed in Refs. [26, 27] using identical methodologies described here. In addition, a comparison for $H_2 EF(v = 0, N = 6 - 12)$ FT results with that of $EF^1\Sigma_g^+ - X^1\Sigma_g^+$ UV spectroscopy in Ref. [35] shows very good agreement. Similarly, a comparison with the $H_2$ results of Dickenson et al. [36], detecting transitions up to the $EF(v = 10)$ level shows very good agreement that is limited by the experimental accuracy of the latter study. The favorable comparisons for the case of $H_2$ give confidence in the uncertainty estimated for the present $D_2$ case.

A comparison of the present level energies with the comprehensive data set from Yu and Dressler [18] was carried out for $EF, v > 0$, with a graphical representation of the differences shown in Fig. 3. For $D_2$, the compilation of Yu and Dressler [18] was based on the experimental results compiled by Freund et al. [17] and those of Senn et al. [37]. Yu and Dressler had already applied a correction of $-0.14 \text{ cm}^{-1}$ to the term values in consideration of their the $ab\ initio$ investigations. In Fig. 3, the present level energies $E_{FT}$ are systematically higher by $\sim 0.03 \text{ cm}^{-1}$ with respect to those of Ref. [18]. The standard deviation of $0.03 \text{ cm}^{-1}$ for the difference $\Delta E_{Yu}$ is consistent with the estimated statistical uncertainty of the experimental data used, i.e. $0.05 \text{ cm}^{-1}$ in Ref. [17] and $\sim 0.02 \text{ cm}^{-1}$ in Ref. [37].

Heck et al. [24] observed $D_2$ transitions between the $EF^1\Sigma_g^+ v' = 0, 1$ and $X^1\Sigma_g^+ v'' = 0$ states involving high rotational quantum numbers up to $N = 26$. The result of a comparison of the present results with that of Ref. [24] is plotted in Fig. 4. The upper panel (a) is a comparison with their experimental values, the lower panel (b) shows a comparison with their $ab\ initio$ calculations, for $EF, v = 0, 1$ (represented by circles and squares, respectively) for levels with rotational quantum numbers up to $N = 11$. The observed energy differences are within the estimated experimental uncertainty by Heck et al. of better than $2 \text{ cm}^{-1}$ [24]. The $ab\ initio$ calculations performed by Heck et al. in the same study [24] are the most accurate calculations for $D_2 EF^1\Sigma_g^+$ level energies. Although the accuracy was not
specified for the \textit{ab initio} values, the comparison in Fig. 3(b) suggests that the calculations are accurate within 1 cm\(^{-1}\) in the energy range accessed.

4. \(B^1\Sigma_u^+\) level energies

The \(\text{D}_2\) \(B^1\Sigma_u^+\) level energies derived from the present FT data set are listed in Table 2 covering vibrational quantum numbers \(v = 0 - 8\), with rotational states as high as \(N = 10\). The \(B\) levels are referenced to the \(EF\) anchor levels in the FT analysis, and are connected to \(X^1\Sigma_g^+\), \((v = 0, N = 0)\) ground state in a straightforward manner. Following the electronic symmetry of \(B^1\Sigma_u^+\), ortho-\(\text{D}_2\) levels have odd-\(N\) while para-\(\text{D}_2\) levels have even-\(N\) quantum numbers. Most level energies in Table 2 are accurate to 0.001 cm\(^{-1}\) while the least accurate have uncertainties better than 0.01 cm\(^{-1}\).

The recent work of de Lange et al. [16] presents an accurate and comprehensive data set for \(\text{D}_2\) \(B^1\Sigma_u^+\) level energies obtained from \(B^1\Sigma_u^+ - X^1\Sigma_g^+\) XUV FT spectroscopy using a synchrotron source. The database in Ref. [16] included all bound level energies in the \(B^1\Sigma_u^+\) potential well, covering vibrational quantum numbers \(v = 0 - 51\) with rotational quantum numbers \(N = 0 - 5\). An extensive comparison was carried out by de Lange et al. with the previous results by Hinnen et al. [11], which showed that the values of the
Figure 4: Difference $\Delta E_{\text{Heck}}^\text{exp,calc} = E_{\text{FT}} - E_{\text{Heck,calc}}$ (in cm$^{-1}$) between the level energies from the present dataset and those from Ref. [24] plotted against the rotational quantum number $N = 0 - 11$. Datapoints for $EF^1\Sigma^+_u$, $v = 0$ are denoted by circles, while those for $EF^1\Sigma^+_g$, $v = 3$ ($E1$) by squares. Comparison with experimental level energies $E_{\text{exp,Heck}}^\text{calc}$ are shown in (a), while a comparison with their ab initio calculations $E_{\text{Heck}}^\text{calc}$ is shown in (b).

Figure 5: Level energy differences $\Delta E_{\text{DeLange}} = E_{\text{FT}} - E_{\text{DeLange}}$ (in cm$^{-1}$) of $B^1\Sigma_u^+$ levels between the present dataset and those from Ref. [16]. The solid line indicates the average while the dashed lines indicate the $\pm 1\sigma$ standard deviations of $\Delta E_{\text{DeLange}}$. 
Table 2: Level energies (term values) in the $B^1\Sigma_u^+$ state of D$_2$ for vibrational levels $v = 0 - 8$. Values are in cm$^{-1}$ with estimated ($1\sigma$) uncertainties indicated in between parentheses.

| $N$ | $(v = 0)$          | $(v = 1)$          | $(v = 2)$          |
|-----|--------------------|--------------------|--------------------|
| 0   | 90 633.471 (1)     | 91 575.809 (1)     | 92 498.689 (1)     |
| 1   | 90 653.192 (1)     | 91 594.804 (1)     | 92 517.052 (1)     |
| 2   | 90 692.535 (1)     | 91 632.706 (1)     | 92 553.698 (1)     |
| 3   | 90 751.307 (1)     | 91 689.341 (1)     | 92 608.464 (1)     |
| 4   | 90 829.218 (1)     | 91 764.448 (1)     | 92 681.114 (1)     |
| 5   | 90 925.892 (1)     | 91 857.685 (1)     | 92 771.336 (1)     |
| 6   | 91 040.868 (1)     | 91 968.639 (1)     | 92 878.745 (1)     |
| 7   | 91 173.614 (1)     | 92 096.825 (1)     | 93 002.899 (1)     |
| 8   | 91 323.524 (1)     | 92 241.695 (1)     | 93 143.285 (1)     |
| 9   | 91 489.940 (1)     | 92 402.648 (1)     | 93 299.364 (1)     |
| 10  | 91 672.198 (10)    | 92 579.039 (5)     | 94 299.364 (1)     |

| $N$ | $(v = 3)$          | $(v = 4)$          | $(v = 5)$          |
|-----|--------------------|--------------------|--------------------|
| 0   | 93 403.321 (1)     | 94 290.405 (1)     | 95 160.388 (1)     |
| 1   | 93 421.117 (1)     | 94 307.683 (1)     | 95 177.183 (1)     |
| 2   | 93 456.633 (1)     | 94 342.167 (1)     | 95 210.710 (1)     |
| 3   | 93 509.723 (1)     | 94 393.720 (1)     | 95 260.832 (1)     |
| 4   | 93 580.164 (1)     | 94 462.133 (1)     | 95 327.358 (1)     |
| 5   | 93 667.664 (1)     | 94 547.135 (1)     | 95 410.033 (1)     |
| 6   | 93 771.870 (1)     | 94 648.390 (1)     | 95 508.539 (1)     |
| 7   | 93 892.368 (1)     | 94 765.515 (1)     | 95 622.505 (1)     |
| 8   | 94 028.682 (1)     | 94 898.060 (1)     | 95 751.516 (5)     |
| 9   | 94 180.302 (1)     | 95 045.539 (2)     | 95 895.107 (5)     |

| $N$ | $(v = 6)$          | $(v = 7)$          | $(v = 8)$          |
|-----|--------------------|--------------------|--------------------|
| 0   | 96 013.575 (1)     | 96 850.205 (1)     | 97 670.466 (1)     |
| 1   | 96 029.919 (1)     | 96 866.118 (1)     | 97 685.972 (1)     |
| 2   | 96 062.543 (1)     | 96 897.890 (1)     | 97 716.929 (1)     |
| 3   | 96 111.325 (1)     | 96 945.398 (1)     | 97 763.223 (1)     |
| 4   | 96 176.077 (1)     | 97 008.468 (1)     | 97 824.687 (1)     |
| 5   | 96 256.558 (1)     | 97 086.868 (1)     | 97 901.099 (1)     |
| 6   | 96 352.470 (1)     | 97 180.312 (1)     | 97 992.191 (1)     |
| 7   | 96 463.457 (2)     | 97 288.469 (2)     | 98 097.634 (2)     |
latter are systematically higher by 0.01 cm\(^{-1}\). De Lange et al. also made a comparison with the semi-empirical study of Abgrall et al. [13], based on the experimental results reported by Freund et al. [17]. The results of Abgrall et al. were shown to be shifted by 0.2 cm\(^{-1}\) higher with respect to the De Lange et al. values. This is not too surprising considering the estimated uncertainty of 0.5 cm\(^{-1}\) for the absolute calibration by Freund et al. [17]. A direct comparison of the present results with the Abgrall et al. values [13] show the same trend as the comparison presented by de Lange et al. for the \(B^1\Sigma_u^+\) levels as expected.

The comparison of the present data set and Ref. [16] reveals that the values of the latter are 0.02 cm\(^{-1}\) lower than the present data set (see Fig. 5). This offset is still within the estimated uncertainties of 0.03 cm\(^{-1}\) by de Lange et al. [16], nevertheless, the systematic trend is notable. We attribute this to systematic effects in the absolute energy calibration of the synchrotron XUV FT data which relies on laser data for correction. In the case of Ref. [16], the XUV laser results from Roudjane et al. [12] for the \(D^2B^1\Sigma_u^+, \nu = 9 - 11\) bands were utilized. In applying these corrections for the XUV FT, it is seen that systematic deviations increase the farther a certain transition is from the calibration line, and is probably limited by the FT relative energy calibration. In order to extract the most accurate results from the synchrotron XUV FT data, as is pursued for example in Ref. [38], a regular coverage of calibration lines throughout the full spectrum is then required.

5. Lyman band wavelengths

Derived \(D_2\) Lyman transition wavelengths connecting the \(B^1\Sigma_u^+ (\nu = 0 - 8, N = 0 - 5)\) levels to the \(X^1\Sigma_g^+ (\nu = 0, N)\) levels, for the R- and P-branches, are listed in Table 3 for \(\nu = 0 - 8, J = 0 - 5\) as a line list for future application. The transition wavelengths are derived using the present \(B^1\Sigma_u^+\) level energies and the ground state level energies from the calculations of Komasa et al. [6]. The wavelengths have relative accuracies of \(1 \times 10^{-8}\) or better, limited by the accuracy of the \(B^1\Sigma_u^+\) level energies. We note that although the Lyman values listed in Table 3 are only for the \(X^1\Sigma_g^+ (\nu = 0, N)\) levels, transition energies connecting vibrationally-excited ground state levels can equally well be derived, e.g. using the values of Komasa et al. [6].

Gabriel et al. [15] determined \(H_2\), HD and \(D_2\) Lyman transitions to high rovibrational levels in the \(B^1\Sigma_u^+\) state. A comparison show that the \(D_2\) values of Gabriel et al. [15] are systematically higher by 0.23 cm\(^{-1}\) with respect to
the present data set, with a scatter of 0.05 cm$^{-1}$. Note that this is at the accuracy limit estimated by Gabriel et al. [15] of 0.2 cm$^{-1}$.

6. Conclusions

Accurate level energies for the $D_2 B^1\Sigma_u^+, v = 0–8$ and $EF^1\Sigma_g^+ v = 0–21$ bands are presented. The present data set takes advantage of the extensive range covered by a highly-accurate FT spectroscopic investigation on $D_2$ excited state transitions, and the absolute accuracy $EF^1\Sigma_g^+ – X^1\Sigma_g^+$ UV spectroscopy to connect to the ground state. For $B^1\Sigma_u^+$ and $EF^1\Sigma_g^+$ levels connected with strong transitions, the accuracy is improved by more than order of magnitude with respect to previous studies. The energies the $B^1\Sigma_u^+$ levels obtained here will be useful calibration lines in XUV FT spectra, e.g. Ref. [16]. The accurate $EF^1\Sigma_g^+$ level energies will be important in future molecular tests of QED in $D_2$ vibrationally- and rotationally-excited quantum levels as in Ref. [35].

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Table 3: D$_2$ Lyman (B$^1\Sigma_u^+ - X^1\Sigma_g^+$) wavelengths. R- and P-branch transitions to the B$^1\Sigma_u^+$, ($v = 0 - 8, N$) rovibrational levels from the lowest X$^1\Sigma_g^+$, ($v = 0$) vibrational level. The wavelengths are given in nm with estimated uncertainties of 1 $\times$ 10$^{-6}$ nm. The X$^1\Sigma_g^+$, ($v = 0, N = 0 - 5$) level energies are taken from Ref. [6].

| $N$ | R($N$)  | P($N$)  | $N$ | R($N$)  | P($N$)  |
|-----|---------|---------|-----|---------|---------|
|     | $v = 0$ |         |     |         | $v = 1$ |
| 0   | 110.310511 | 0       | 109.176499 |
| 1   | 110.335386  | 1       | 109.202583  | 109.270476 |
| 2   | 110.409106  | 2       | 109.277348  | 109.390356 |
| 3   | 110.531553  | 3       | 109.400652  | 109.558555 |
| 4   | 110.702525  | 4       | 109.572267  | 109.774756 |
| 5   | 110.921739  | 5       | 109.791872  | 110.038561 |

|     | $v = 2$ |         |     |         | $v = 3$ |
| 0   | 108.088182 | 0       | 107.042180 |
| 1   | 108.115218  | 1       | 107.069990  | 107.131141 |
| 2   | 108.190687  | 2       | 107.145931  | 107.247750 |
| 3   | 108.314433  | 3       | 107.269839  | 107.412172 |
| 4   | 108.486203  | 4       | 107.441451  | 107.624082 |
| 5   | 108.705660  | 5       | 107.660409  | 107.883071 |

|     | $v = 4$ |         |     |         | $v = 5$ |
| 0   | 106.035899 | 0       | 105.067199 |
| 1   | 106.064350  | 1       | 105.096189  | 105.151800 |
| 2   | 106.140603  | 2       | 105.172638  | 105.265246 |
| 3   | 106.264484  | 3       | 105.296361  | 105.425852 |
| 4   | 106.435722  | 4       | 105.467079  | 105.633301 |
| 5   | 106.653953  | 5       | 105.684422  | 105.887175 |

|     | $v = 6$ |         |     |         | $v = 7$ |
| 0   | 104.134213 | 0       | 103.235272 |
| 1   | 104.163670  | 1       | 103.265131  | 103.316006 |
| 2   | 104.240224  | 2       | 103.341730  | 103.426466 |
| 3   | 104.363694  | 3       | 103.464880  | 103.583389 |
| 4   | 104.533796  | 4       | 103.634297  | 103.786460 |
| 5   | 104.750152  | 5       | 103.849604  | 104.035264 |

|     | $v = 8$ |         |
| 0   | 102.368844 |
| 1   | 102.399058  | 102.447800 |
| 2   | 102.475652  | 102.556840 |
| 3   | 102.598436  | 102.711993 |
| 4   | 102.767125  | 102.912943 |
| 5   | 102.981334  | 103.159282 |