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RESEARCH ARTICLE

Extreme ultraviolet laser calibration of D₂ Lyman and Werner transitions

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Some 39 lines in the $B^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+(v', 0)$ Lyman bands for $v' = 9\text{--}11$, and in the $C^1\Pi_u \leftarrow X^1\Sigma_g^+(0, 0)$ Werner band of the D₂ molecule were measured using a narrowband tunable extreme-ultraviolet laser source, at an unprecedented accuracy of $\Delta\lambda/\lambda = 6 \times 10^{-8}$. The results bear relevance for future use in the calibration of dense classical spectra obtained for the HD and D₂ hydrogen isotopologues.

Keywords: vacuum UV; molecular spectroscopy; hydrogen isotopologues; precision metrology

1. Introduction

The hydrogen molecule is a benchmark system for the investigation of molecular structure. Notwithstanding the fact that it is the smallest neutral molecule, its spectrum is complex: H₂ and its natural isotopologues HD and D₂ do not exhibit band structures normally associated with molecules in the gas phase, but rather atomic-like spectra without obvious regularities. Moreover, due to the low nuclear masses application of the Born–Oppenheimer approximation becomes somewhat questionable. Hence, adiabatic and non-adiabatic effects on the level structure are most pronounced in hydrogen, thus making the hydrogen molecule an ideal testing ground for assessing mass-dependent effects in spectra of diatomic molecules. Finally, due to the large energetic separation between $1s$ and $2p$ levels in the H-atom, and the large binding energy of the singly-bonded ground state of the hydrogen molecule, the electronic absorption and emission spectra of H₂ and its isotopologues are in the vacuum ultraviolet (VUV) domain, which for many years has been difficult to access with high-resolution methods. A detailed understanding of the hydrogen VUV-spectra is important in astrophysics due to the large abundance of hydrogen, with the strongest absorption features formed by the Lyman and Werner band systems of H₂ and HD. D₂ is of relevance for plasma science, most notably in Tokamak environments aiming at deuterium nuclear fusion.

Over the years the VUV spectrum of D₂ has been investigated by a number of spectroscopists, namely, Bredohl and Herzberg [1], Dabrowski and Herzberg [2], Takezawa and Tanaka [3], and Larzilliere *et al.* [4], all in connecting wavelength regions. Hinnen *et al.* [5] thereupon performed a study of a limited part of the D₂ spectrum using a tunable laser source in the vacuum ultraviolet at a somewhat better resolution than in the classical spectroscopic studies.

At the Meudon Observatoire in the last decade techniques of high-resolution grating spectroscopy have been applied to produce a comprehensive database on the VUV emission spectrum of hydrogen, culminating in an atlas for H₂ [6]. Work is in progress to extend these studies to HD and D₂. Before the HD lines can be assigned, the D₂ spectrum has to be investigated, because an HD emission discharge spectrum will always be contaminated by H₂ and D₂ transitions. Recently investigations on the $D^1\Pi_u \rightarrow X^1\Sigma_g^+$ and $D^1\Pi_u \rightarrow X^1\Sigma_g^+$ [7] and the $B^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ systems [8] have been published. In such studies several thousand spectral lines are recorded. An internal calibration standard for such comprehensive spectra may be provided by accurately calibrated wavelength positions for a limited subset. This is precisely the purpose of the present laser-based investigation of D₂; some 39 D₂ lines in the wavelength range 99.98–102.07 nm have been calibrated with an accuracy of $\Delta\lambda/\lambda = 6 \times 10^{-8}$. These transitions may

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serve as a calibration standard in the ongoing emission studies on the $B^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ Lyman and $C^1\Pi_u \rightarrow X^1\Sigma_g^+$ Werner band systems in D_2 .

2. Experiments

The methods of performing high-resolution spectroscopy with a narrowband tunable extreme-ultraviolet (XUV) laser source on diatomic molecules in a pulsed and skimmed molecular beam have been developed at the Laser Center (Vrije Universiteit, Amsterdam) and described previously [9]. Coherent XUV-radiation is produced by harmonic upconversion of the output of a pulsed dye amplifier, which is injection seeded by a stabilized ring-dye laser. The visible output in pulses of 5 ns duration is frequency-doubled in a KD*P-crystal and thereupon tripled in a xenon gas jet. The pulsed XUV-radiation of nearly Fourier-transform limited bandwidth ($\Delta\nu \sim 250$ MHz) then perpendicularly intersects a molecular beam of D_2 . It should be noted that the XUV-radiation produced with the present laser system possesses a resolution and accuracy more than an order of magnitude better than with the system used in [5]. Possible Doppler shifts on the central resonance wavelengths are carefully addressed through probing of different velocity clusters in the beam by delaying the laser pulses with respect to the molecular beam pulses. The absolute frequency calibration is derived from a reference standard in the visible range, based on saturation spectroscopy of molecular iodine [10]; interpolation is performed with the use of a stabilized étalon and the calibration in the XUV-domain is then derived from multiplication by the harmonic order. The full analysis of the uncertainty budget of the XUV-spectroscopic measurements has been discussed in recent studies performed by the group of the Laser Center, for limited sets of rotational lines of Lyman and Werner bands in H_2 and HD [11–13] and for the recently published work on frequency calibration of Lyman transitions in H_2 [14]. In Figure 1 a typical recording of a D_2 spectral line is displayed, with the I_2 and étalon traces used for the calibration.

3. Results and discussion

The wavelengths of the 39 accurately determined rotational lines and the corresponding frequencies in wavenumber units are listed in Table 1. From the error budget, the uncertainty in the line positions is estimated to be $\pm 0.000\,006$ nm or ± 0.006 cm^{-1} in wavenumbers. Note that all wavelength values pertain to vacuum. Combination differences Δ_{20} between

$P(J'' + 2)$ and $R(J'')$ lines can further be verified with ground-state rotational splittings from far-infrared FTS-Raman spectroscopy [15] to test the accuracy and the internal consistency of our results. The present set of Lyman and Werner band transitions contains measurements of four pairs of $R(0)$ and $P(2)$ lines whose combination differences are plotted in Figure 2. This shows the consistency of the set of results involving these eight spectral lines. The deviation of the combination differences from their average value is 0.002 cm^{-1} . This suggests that the determination of transition frequencies is more accurate than would follow from our estimated error budget for these pairs of transitions. A statistical analysis yields a value for the combination difference of 179.066 (1) cm^{-1} , in agreement with the IR data [15] given by 179.068 (2) cm^{-1} for the Δ_{20} energy splitting. A similar procedure can be performed for the $R(1)$ – $P(3)$ combination differences, where an average value of 297.533 (2) cm^{-1} is derived from a set of four pairs of transitions, in agreement with 297.533 (3) cm^{-1} given for the Δ_{31} energy splitting [15]. This result provides an independent validation of the calibration procedures followed in the present study. Note also that the present XUV results yield improved values for the ground-state combination differences.

In the spectral range 99.98–102.07 nm the most accurate VUV wavelength measurements of D_2 were performed by Dabrowski and Herzberg [2], using a spectrograph with concave grating. They claimed

Figure 1. Recording of the $R(3)$ line in the $B \leftarrow X$ (10,0) Lyman band in D_2 via 1 XUV + 1' UV ionization spectroscopy, using a narrowband laser system tunable in the XUV domain. The absolute calibration of this line is performed by comparing the visible laser radiation before harmonic conversion to the i -hyperfine component in the I_2 $B \leftarrow X$ (11,2) $R(85)$ line, marked with (*) and corresponding to $16,508.79510$ cm^{-1} .

Table 1. Measured wavelengths and the corresponding frequencies of rotational lines belonging to the $B^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ Lyman bands (Lv for B-X($v'-0$)) and $C^1\Pi_u \leftarrow X^1\Sigma_g^+$ Werner bands (Wv for C-X($v'-0$)) for D_2 . The figures in parentheses represent the uncertainties in the last digit. Δ_{o-h} refers to the difference between the present laser-based results and the previously obtained classical values for the transition frequencies [2]. Δ_{o-c} lists the difference between the observed and calculated frequencies obtained in the present work.

Transition	λ (nm)	ν (cm^{-1})	Δ_{o-h} (cm^{-1})	Δ_{o-c} (cm^{-1})
L11R0	99.950 845 (6)	100049.179 (6)	0.389 ^a	-1.091
L11R1	99.981 898 (6)	100018.106 (6)	0.076	-1.094
L11P1	100.024 982 (7)	99975.024 (7)	0.044	-1.086
L11R2	100.058 279 (6)	99941.755 (6)	0.035	-1.095
L11P2	100.130 055 (6)	99870.114 (6)	0.004	-1.086
L11R3	100.179 786 (6)	99820.536 (6)	0.056	-1.094
L11P3	100.280 205 (6)	99720.578 (6)	0.098	-1.092
L11R4	100.346 139 (6)	99655.055 (6)	0.145	-1.105
L11P4	100.475 135 (6)	99527.112 (6)	0.002	-1.088
W0R1	100.576 139 (6)	99427.161 (6)	-0.119	-0.209
W0R0	100.578 369 (6)	99424.957 (6)	-0.023	-0.203
W0R2	100.603 099 (6)	99400.517 (6)	0.017	-0.213
W0Q1	100.639 168 (6)	99364.891 (6)	0.111	-0.199
W0R3	100.659 135 (6)	99345.181 (6)	0.101	-0.219
W0Q2	100.697 795 (7)	99307.041 (7)	-0.069	-0.199
L10R0	100.727 943 (6)	99277.318 (6)	0.248	-1.040
W0R4	100.744 037 (7)	99261.458 (7)	0.118	-0.232
L10R1	100.758 767 (7)	99246.947 (7)	0.207	-1.043
W0P2	100.759 840 (6)	99245.890 (6)	-0.190 ^a	-0.200
W0Q3	100.785 478 (6)	99220.644 (6)	0.184	-0.206
L10P1	100.803 590 (6)	99202.816 (6)	0.116	-1.044
L10R2	100.835 261 (7)	99171.658 (7)	0.108	-1.042
W0P3	100.878 014 (6)	99129.628 (6)	0.108	-0.202
W0Q4	100.901 911 (6)	99106.151 (6)	0.161	-0.209
L10P2	100.909 950 (6)	99098.255 (6)	0.055	-1.045
L10R3	100.957 239 (6)	99051.837 (6)	0.057	-1.053
W0P4	101.024 522 (6)	98985.868 (6)	0.118	-0.212
L10P3	101.061 745 (7)	98949.409 (7)	0.189	-1.051
L10R4	101.124 405 (7)	98888.097 (7)	0.077	-1.063
L10P4	101.258 641 (6)	98757.004 (6)	0.324	-1.056
L9R0	101.533 513 (6)	98489.648 (6)	0.188	-0.992
L9R1	101.564 042 (6)	98460.044 (6)	0.124	-0.996
L9P1	101.610 783 (7)	98414.752 (7)	0.122	-0.998
L9R2	101.640 597 (6)	98385.884 (6)	0.034	-1.006
L9P2	101.718 451 (6)	98310.581 (6)	0.231	-0.999
L9R3	101.762 986 (7)	98267.557 (7)	0.157	-1.013
L9P3	101.871 885 (6)	98162.511 (6)	0.171	-0.999
L9R4	101.930 917 (6)	98105.661 (6)	0.191	-1.009
L9P4	102.070 772 (6)	97971.239 (6)	0.229	-1.001

^aBlended line in [2].

an uncertainty of 0.15cm^{-1} on transition energies of unblended lines. The differences between the presently observed transitions with these previously reported data, Δ_{o-h} , are listed in Table 1 and are plotted in Figure 3. From this comparison, we find that the transition energies of the $B(v'=9-11) \leftarrow X(0)$ Lyman bands from [2] are on average lower by 0.14cm^{-1} compared to the present laser-based results, with a

standard deviation of $\sigma = 0.10\text{cm}^{-1}$. The transition energies of $C(0) \leftarrow X(0)$ Werner band lines from [2] are on average smaller by 0.04cm^{-1} than the laser-based results, with a standard deviation of $\sigma = 0.12\text{cm}^{-1}$. In the work on the H_2 molecule by Philip *et al.* [12], the authors pointed out a systematic shift of $+0.06\text{cm}^{-1}$ with respect to previous data from the Meudon Observatory group [6], also using a concave

Figure 2. Energy splitting Δ_{20} between the $J'' = 2$ and $J'' = 0$ ground-state levels derived from combination differences between four pairs of R(0) and P(2) transitions measured in the Lyman and Werner bands. Indicated are the (weighted) average value of Δ_{20} from the four pairs and the resulting uncertainty: $179.066 (1) \text{ cm}^{-1}$.

Figure 3. Comparison between transition frequencies obtained in the present laser-based study and those obtained from the classical work of [2].

grating spectrograph. This shift was attributed to the calibration procedure where reference lines emitted by an auxiliary discharge, probably with a different illumination of the grating, were superimposed on the experimental spectrum. Since a similar procedure was also used by Dabrowski and Herzberg [2] for calibration of their D_2 spectrum, a systematic shift of their data with respect to the present laser-based results may have the same origin.

A second comparison is made between the observed transition frequencies and calculations based on the theoretical framework as presented in [7,8]. The upper-level energies belonging to the excited states $\text{B}^1\Sigma_u^+$ and $\text{C}^1\Pi_u$ were calculated [7] by solving a set of coupled

equations using the newest *ab initio* potentials by Wolniewicz and co-workers [17], taking into account the nonadiabatic coupling terms between $\text{B}^1\Sigma_u^+$, $\text{C}^1\Pi_u$, $\text{B}^1\Sigma_u^+$ and $\text{D}^1\Pi_u$ states [18]. The differences between the observed and calculated transition energies, $\Delta_{\text{o-c}}$, for the investigated lines belonging to the Lyman and Werner bands, are given in Table 1. For most of the transitions satisfactory agreement was obtained. The remaining discrepancies, are probably due to nonadiabatic couplings with higher electronic states, that were neglected in the calculations.

4. Conclusion

We present highly accurate transition wavelengths ($\Delta\lambda/\lambda = 6 \times 10^{-8}$) and frequencies of some 39 rotational lines of D_2 in the $\text{B}^1\Sigma_u^+ \leftarrow \text{X}^1\Sigma_g^+, (v', 0)$ Lyman bands, for $v' = 9-11$, and in the $\text{C}^1\Pi_u \leftarrow \text{X}^1\Sigma_g^+(0, 0)$ Werner band. The present values of the transition wavelengths are substantially more accurate than the previously published data of Dabrowski and Herzberg [2], and will be used, together with the highly accurate XUV measurements on H_2 [19], as calibration lines for VUV emission studies, in particular for the D_2 and HD molecules.

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