Observation of the fine structure for rovibronic spectral lines in visible part of emission spectra of \( D_2 \)

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For the first time in visible part of the \( D_2 \) emission spectrum the pseudo doublets representing partly resolved fine structure of rovibronic lines have been observed. They are characterized by splitting values about 0.2 cm\(^{-1}\) and relative intensity of the doublet components close to 2.0. It is shown that they are determined by triplet splitting in lower rovibronic levels of various \( ^3\Pi_u \rightarrow ^3\Pi_u \) electronic transitions. It is proposed to use an existence of such partly resolved fine structure patterns for identification of numerous unassigned spectral lines of the \( D_2 \) molecule coming from great variety of triplet "gerade" electronic states to vibro-rotational levels of the \( c^3\Pi_u \) state.

The present paper reports new observations concerning triplet-triplet electronic-vibro-rotational (rovibronic) spectral lines in visible part of the emission spectrum of the \( D_2 \) molecule. There are several peculiarities of current knowledge of triplet rovibronic states and radiative transitions between them which make it possible to consider this knowledge as insufficient and which motivated our experimental studies.

Most of spectral lines in visible and near infrared parts of the emission spectrum of molecular deuterium are not classified so far. Thus, for example in the latest compilation of experimental data \( ^1 \) the working list of 27488 recorded lines (within the wavelength ranges \( \approx 309-1192 \) and 1647 – 2780 nm) contains only 8243 assignments. In our opinion it is difficult to consider such situation as normal for an isotopomer of simplest neutral molecule (four-particle quantum system).

Almost all experimental data on wavenumbers for triplet rovibronic transitions of \( D_2 \) (3117 lines in \( ^1 \)) were obtained by means of traditional technique – photographing an image located in a focal plane of long-focus spectrographs \( ^2 \). The only exceptions are wavenumbers of the 81 rovibronic lines in \( ^3 \) and 3 lines in \( ^4 \) obtained in middle IR (about 4.5 \( \mu m \)) by FTIR (Fourier transform infrared) and laser spectroscopy.

In contrast to the \( H_2 \) spectrum where both fine (FS) and hyperfine (HFS) structures of triplet lines and levels were studied for many electronic states and by various methods (see e.g. bibl. in \( ^3 \)), for the \( D_2 \) molecule only fragmentary data concerning only FS were obtained, namely: fine structure splitting values for 11 rovibronic levels of the \( d^3\Pi_u \) state measured by MOMRIE (microwave optical magnetic resonance induced by electrons) method \( ^6 \); pseudo doublets of partly resolved triplet structure for 18 from 81 recorded triplet lines in \( ^3 \), and completely resolved FS for 3 rovibronic lines in \( ^4 \). Most complete sets of data concerning wavenumber values in visible and near IR together with empirical values of rovibronic energy levels were reported in \( ^1 \) for the \( H_2 \) and in \( ^1 \) for the \( D_2 \) molecules. They are based on experimental results of G.H. Dieke and co-workers first reported in \( ^8 \). Describing his experimental setup in \( ^8 \) G.H. Dieke mentioned that ”In the low pressure, low temperature discharge the lines are considerably sharper and for instance the pseudo doublet structure of the \( 2p^3\Pi \) state which is about 0.2 cm\(^{-1}\) is well resolved under these conditions. This requires a resolving power of 100000 in the visible.” But in later compilations of the data for both \( H_2 \) \( ^1 \) and \( D_2 \) \( ^4 \) isotopomers the fine structure of lines and empirical rovibronic energy levels was not mentioned at all. Moreover, in both cases the reported values of experimental errors (“few hundredth cm\(^{-1}\) for \( H_2 \) \( ^1 \) and 0.05 cm\(^{-1}\) for \( D_2 \) \( ^4 \)) are about one order of magnitude smaller than splitting in partly resolved fine structure earlier reported in \( ^8 \) and mentioned in \( ^9 \). It is unclear how empirical rovibronic energy values were obtained with such precision when more pronounced effect of the FS splitting was not taken into account.

There is noticeable asymmetry in studies of visible and near IR spectra of light (\( H_2 \)) and heavy (\( D_2 \)) isotopomers of hydrogen molecule. The FS of the \( H_2 \) spectral lines was discovered by O.W. Richardson and W.E. Williams as early as in 1931 \( ^10 \) exactly in visible part of the spectrum (see also \( ^9 \)). Although both isotopomers should have similar values of the FS splitting it’s observation in visible spectrum of the \( D_2 \) molecule was not reported in the literature known to authors.

The goal of present work was to study an opportunity of resolving the fine structure in visible spectrum of the \( D_2 \) molecule by means of spectroscopic technique developed in \( ^11 \). It is based on achieving certain level of “optical resolution” of a spectrograph, recording spectral intensity distributions by matrix photoelectric detector, and by numerical deconvolution (inverse to the convolution operation) of recorded spectra. In dense multiline rovibronic spectra of \( H_2 \) and \( D_2 \) molecules actual ”digital resolution” achievable by our technique could be much higher than ”optical resolution” of spectrometer which is limited not by its resolving power but by large Doppler broadening of spectral lines (see below). Thus it is possible to speak about some kind of sub-Doppler high res-
olution spectroscopy.

The spectroscopic part of our experimental setup was described in [13]. The 2.65 m Ebert–type spectrograph with 1800 line/mm diffraction grating 100 mm wide was equipped with additional camera lens and computer-controlled CMOS matrix detector (22.2 × 14.8 mm², 1728 × 1152 triples of the Red, Green and Blue (RGB) photo detectors) [14]. The calibrated spectrometer makes it possible in the fully automatic regime to record sets of individual windows (sections of a spectrum about 1.6 nm wide) at the experimentalist’s choice, or survey spectra by measuring sequences of successive windows with a specified overlap. Thus we obtained digital automatic spectrometer with following characteristics: effective focal length about 7 meters, linear dispersion 0.077 ± 0.065 nm/mm (for the wavelength region 400 ± 700 nm). Maximal optical resolving power (up to 180000) was achieved in resolving HFS components of Hg lines 546.1 and 404.6 nm, FWHM of the instrumental profile for those wavelengths being 0.021 cm⁻¹ and 0.028 cm⁻¹ respectively.

When the entrance slit is uniformly illuminated, signals of one type photo detectors (B, G, or R), located in the same vertical column, carry information concerning the brightness of the radiation at the same wavelength. Averaging makes it possible to increase the sensitivity of the spectrometer and the signal-to-noise ratio (SNR) for data obtained by single exposure. To reach required value of SNR we made many records (up to 150 shots for the same wavelength fragment and the same discharge conditions). Averaging of those results made it possible to reach SNR value up to 10⁴ (see [13]).

For recording the D₂ spectra with low resolution, high sensitivity and large population of high rotational levels we used hot-cathode capillary-arc discharge lamp LD-2D described in [15] (pure D₂ under pressure ≈ 6 Torr, capillary inner diameter Ø2 mm, current density ≈ 10 A/cm²). Gas temperature T = 1890 ± 170 K was obtained from the intensity distribution in the rotational structure of the (2 – 2) Q-branch of Fulcher-α band system (see e.g. [16, 17]). It corresponds to Doppler linewidths (FWHM) ΔνD = 0.22 ± 0.37 cm⁻¹ for 1/ν = 420 ± 700 nm. Therefore we were able to open the entrance slit of the spectrometer up to 60 µm for gaining more signal (and corresponding decrease in data accumulation time) without significant loss in resolution.

To achieve best possible optical resolution we have to decrease Doppler broadening by diminution of the gas temperature in plasma. It is obviously favorable for increasing spectral resolution, but lowering the temperature automatically leads to lower population densities of high rotational levels in ground and exited electronic states and to much smaller intensities of corresponding spectral lines. Therefore we had to use some compromise plasma conditions. Thus in high resolution experiments we used glow discharge with cold cathode and water cooled walls. Additional third electrode with the axial cylindrical hole Ø4 mm was located on discharge axes between cathode and anode. Through a hole in an anode the flux of radiation emitted by plasma inside additional electrode was focused on the entrance slit of the spectrometer. With this geometry we got current density as low as 0.4 A/cm² and T = 610 ± 20 K.

It should be emphasized once more that the overwhelming majority of data on the wavenumbers for rovibrionic transitions of the D₂ molecule is obtained by photographic recording of spectra up to now (see e.g. [18, 19]). Our way of determining wavenumber values is based on linear response of CMOS matrix photo detector on the spectral irradiance and digital intensity recording. Both things provide an extremely important advantage of our technique over traditional photographic recording with microphotometric or visual comparator reading. It not only makes it easier to measure the relative spectral line intensities but also makes it possible to investigate the shape of the individual line profiles and, in the case of overlap of the contours of adjacent lines (so-called blending), to carry out numerically the deconvolution operation and thus to measure the intensity and wavelength of blended lines. As is well known, it is this blending that makes it very hard to analyze dense multiline spectra of the D₂ molecule [1].

We are treating the problem of wavenumber determination as that of conditional optimization: parameterization of a model for an intensity distribution and determination of optimal set of parameters by searching a global minimum of an objective function under specified conditions. Thus for small regions of the spectrum (≈ 0.5 nm wide, about one-third of a window, containing 500 ± 600 vertical columns of photodetectors, see Fig. II) the observed spectral intensity distribution (dependence of the photoelectric signal of k-th photodetector I_k^{exp} on the detector position x_k) was approximated by a superposition of a finite number M of line profiles f_i(x) with a width Δx common for all lines within an analyzed region:

\[ I_{\text{calc}}(x) = I_{bg} + \sum_{i=1}^{M} A_i f_i(x, x_i^0, \Delta x), \]

where \( I_{bg} \) is a constant background intensity, \( A_i \) – amplitude of i-th profile (intensity in the line center \( x_i^0 \))

We used an objective function in the form of a sum of squares of deviations between experimental and "synthesized" intensity distributions

\[ \Phi\{\{A_i, x_i^0\}_{i=1}^{K}, \Delta x, I_{bg}\} = \sum_{k=1}^{K} (I_k^{exp} - I_{\text{calc}}(x_k))^2, \]

where \( K \) indicates a number of experimental intensity values \( I_k^{exp} \) in the spectral region under the study.

If the experimental errors of the \( I_k^{exp} \) values are random and distributed according to a normal (Gaussian) law, the solution obtained by the least-squares criterion for \( \Phi \) corresponds to the maximum likelihood principle. For determining a global minimum of the objective function \( \Phi \) in multidimensional parameter space
FIG. 1. Part of the $D_2$ spectrum containing first 10 lines of the R-branch for $(1-1)$ band of the $i^3\Pi_u \rightarrow c^3\Pi_u$ electronic transition obtained in high (a, b, c) and low (d) resolution experiments. Experimental data $I_{\text{expt}}^k$ in relative units are shown by circles. Solid line represents the intensity distribution calculated as a sum of optimal Voigt profiles. Wavenumber values reported in [1] are marked by short vertical line segments above $I_{\text{expt}}^k$, those of them shown in bold were used for calibration of our spectrometer. Spectral lines obtained by the deconvolution are presented as "stick diagrams" indicating their wavenumber positions $\nu^0$ and amplitudes $A_i$. Pairs of sticks painted in bold represent the pseudo doublets having specific characteristics (see text).
TABLE I. Wavenumber values (in cm\(^{-1}\)) and relative intensities \(I_S/I_W\) for strong and weak components for pseudo doublets of the R-branch lines for the (1−1) band of the \(^3\Pi_g \rightarrow e^3\Pi_u\) electronic transition (the T-3e-2c (1-1) RN' rovibronic transitions in G.H.Dieke notation \([1]\)). The \(\nu_S\) and \(\nu_W\) are wavenumbers of strong and weak components; \(\Delta\nu_{SW} = \nu_S - \nu_W\); \(\Delta\nu_{LR}\) – the wavenumbers obtained in low resolution experiments. Experimental errors (one SD) are shown in brackets in unites of last significant digit.

| Assignment    | \(\nu\)   | \(\nu_{LR}\) | \(\nu_S, \nu_W\) | \(\Delta\nu_{SW}\) | \(I_S/I_W\) |
|---------------|-----------|--------------|-------------------|-------------------|-------------|
| T- 3e-2c (1-1) R1 | 16996.58 | 16996.57(2) | 16996.58(3)s | 0.22(5) | 1.93(5) |
| T- 3e-2c (1-1) R2 | 16996.38 | 16996.31(2) | 16996.36(4)w | 0.18(4) | 1.88(2) |
| T- 3e-2c (1-1) R3 | 17010.36 | 17010.37(2) | 17010.39(3)s | 0.17(5) | 1.99(4) |
| T- 3e-2c (1-1) R4 | 17019.71 | 17019.73(2) | 17019.74(3)s | 0.17(4) | 1.94(3) |
| T- 3e-2c (1-1) R5 | 17025.11 | 17025.12(2) | 17025.13(3)s | 0.17(5) | 2.05(7) |
| T- 3e-2c (1-1) R6 | 17026.97 | 17026.98(2) | 17026.99(3)s | 0.17(5) | 1.84(4) |
| T- 3e-2c (1-1) R7 | 17027.51 | 17027.60(2) | 17027.70(3)s | 0.18(6) | 1.82(11) |
| T- 3e-2c (1-1) R8 | 17021.56 | 17021.56(2) | 17021.57(4)s | 0.21(6) | 1.90(60) |
| T- 3e-2c (1-1) R9 | 17014.87 | 17014.88(2) | 17014.91(4)s | 0.17(5) | 1.84(4) |
| T- 3e-2c (1-1) R10 | 16994.53 | 16994.54(2) | 16994.57(4)s | 0.16(6) | 1.89(14) |

The analysis of line profiles obtained in high resolution experiments showed that Gaussian function is insufficient and we had to use more flexible Voigt profiles:

\[
f_x(x) = \frac{1}{\sqrt{2\pi} \Delta x_L} \int_{-\infty}^{+\infty} \frac{\exp(-t^2)}{\left(\frac{\Delta x_G}{\sqrt{2\Delta x_G}} + \frac{x-x^0}{\sqrt{2\Delta x_G}} - t\right)^2} \, dt,
\]

where \(\Delta x_L\) — Lorentzian linewidth.

The values for all the \(2M + 3\) parameters \((\{A_i, x_i^0\}_{i=1,M}, \Delta x_G, \Delta x_L, \text{ and } I_{bg}\) obtained by minimizing \([2]\) are optimal for the observed intensity distribution under the condition of identical \(\Delta x_G\) and \(\Delta x_L\) values for all the lines. Thus it is possible to obtain optimal values of the amplitude and a line center for each spectral line as well as common value of total “observed” line width \(\Delta x\) calculated from optimal values of \(\Delta x_G\) and \(\Delta x_L\). In the case of long-focus spectrometers the dependence of the wavelength on the coordinate along direction of dispersion is close to linear in the vicinity of the center of the focal plane. It can be represented as a power series expansion over of the small parameter \(x/F\) (The \(x\)-coordinate represents small displacement from the center of the matrix detector, \(F\) is the focal length of the spectrometer), which in our case does not exceed \(2 \times 10^{-3}\) nm. On the other hand, the wavelength dependence of the refractive index of air \(n(\lambda)\) is also close to linear inside a small enough part of the spectrum. Thus, when recording narrow spectral intervals, the product \(\lambda \cdot \nu_{vac} = \lambda(\nu)\) has the form of a power series of low degree. This circumstance makes it possible to calibrate the spectrometer directly in vacuum wavelengths \(\nu_{vac} = 1/\nu\), thereby avoiding the technically troublesome problem of accurate measuring the refractive index of air for various experimental conditions. For spectrometer calibration the experimental vacuum wavelength values \((1/\nu)\) of bright, non-blended \(D_2\) lines from \([1]\) were used as the standard reference data \([22]\). They show small random spread around smooth curve representing dependence of the wavelengths on positions of corresponding lines in the focal plane of the spectrometer. Moreover these random deviations are in good accordance with normal distribution. Thus it is possible to obtain precision for new wavenumber values better than that of the reference data due to smoothing. The calibration curve of the spectrometer was obtained by polynomial least-squares fitting the data with accuracy better than \(2 \times 10^{-3}\) nm.
Following the way described above we measured the $D_2$ spectra in low and high resolution experiments for wavenumber regions $14378.80 \div 23894.65$ cm$^{-1}$ $(695 \div 418$ nm) and $15948.82 \div 18331.28$ cm$^{-1}$ $(627 \div 545$ nm) respectively. Within these intervals 11986 and 3518 spectral lines were distinguished after the deconvolution. Detailed analysis of the data will be reported in subsequent papers. In the present short communication we shall restrict ourselves to consideration of one particular, but rather typical case which allow to illustrate some general features of our first observations.

As an example four fragments of the $D_2$ spectrum containing first 10 lines of the $R$-branch for $(1-1)$ band of the $i^3\Pi^g_{→} c^3\Pi^c$ electronic transition are shown in Fig. 1. First fragments $(a,b,c)$ are three parts of the same window recorded in the high resolution experiment (discharge current $I = 30$ mA, entrance slit $\Delta S = 15 \mu$m, observed FWHM $\Delta \nu = 0.18$ cm$^{-1}$). They were used separately in the deconvolution procedure described above. Fourth fragment $(d)$ is identical to the third one $(c)$, but it was obtained in low resolution experiment $I = 300$ mA, $\Delta S = 60 \mu$m, $\Delta \nu = 0.39$ cm$^{-1}$). One may see that two identical fragments measured with different spectral resolution are qualitatively different. In the low resolution case all lines look like singles having symmetrical profiles. In high resolution experiments the partly resolved fine structure of some lines becomes apparent as asymmetry of their profiles, although some other lines remain single with symmetric profiles (see Fig. 1(a, b)). This is a result of so-called "optical resolution" only. The deconvolution of measured intensity distributions based on numerical optimization technique described above provides an opportunity to recognize narrow substructures within observed asymmetric profiles. The results of such "digital resolution" are shown in Fig. 1 as "stick diagrams" of the individual components indicating their wavenumber positions $\nu^0$ and amplitudes $A_i$. Numerical data concerning the $(1-1)$ $R$-branch lines under the study are presented also in Tab. 1. One may see from the table that in our conditions this technique is able to provide high enough precision in wavenumbers and relative intensities of latent spectral lines. Moreover, additional resolving power obtained by the deconvolution is sufficiently higher than that corresponding to Rayleigh criterion.

Among many lines shown in Fig. 1(a, b, c) the 22 pairs of recognized lines (sticks) catch one’s eye, because they have distinguishing features: the splitting value is about 0.2 cm$^{-1}$, and intensity ratios of the violet (strong) and red (weak) components are close to 2:1. The sticks representing such pseudo doublets are shown in bold. 10 of them (painted as black dash sticks) were previously classified as single vibronic lines belonging to the $(1-1)$ $R$-branch of the $i^3\Pi^g_{→} c^3\Pi^c$ electronic transition [1]. 4 other cases (painted black) were also classified as triplet lines coming to vibro-rotational levels of the $c^3\Pi^c$ state [1]. Recently these assignments were confirmed by statistical analysis of the experimental wavenumbers in the framework of Rydberg-Ritz combination principle [11]. 8 other pairs (painted in red) are not assigned so far.

The splitting values obtained in present work for the $(1-1)$ $R$-branch lines are shown in Fig. 2 together with analogous data obtained in middle IR for the $a^3\Sigma^\pm \rightarrow c^3\Pi^c$ transitions of $D_2$ (points 1) and those for the $a^3\Sigma^+_{→}, \nu'' = 2, N'' \rightarrow c^3\Pi^c_{→}, \nu'' = 1$ transitions of $D_2$ obtained by FTIR spectroscopy in [3] (points 2). 3 – the splitting values in pseudo doublets of the $c^3\Pi^c_{→}, v = 1, N = 2, 4$ vibronic levels of the $H_2$ molecule, calculated from the data reported in [2].

FIG. 2. Values of the splitting in pseudo doublets observed in the present work for the $i^3\Pi^g_{→}, \nu'' = 1, N'' + 1 \rightarrow c^3\Pi^c_{→}, \nu'' = 1, N''$ vibronic transitions of $D_2$ (points 1) and those for the $a^3\Sigma^+_{→}, \nu'' = 2, N'' \rightarrow c^3\Pi^c_{→}, \nu'' = 1$ transitions of $D_2$ obtained by FTIR spectroscopy in [3] (points 2). 3 – the splitting values in pseudo doublets of the $c^3\Pi^c_{→}, v = 1, N = 2, 4$ vibronic levels of the $H_2$ molecule.
rule for intensities within narrow multiplets when one assumes that the triplet splitting in upper rovibronic states may be neglected while in the lower rovibronic states \( \tilde{c}^3\Pi_u, v = 1, N' \) two fine structure sublevels \( J'' = N'' - 1 \) and \( J'' = N'' + 1 \) are close to each other and located noticeably lower than that with \( J'' = N'' \). These assumptions are in agreement with IR tunable laser observations \( (E_{J''=2} \approx E_{J''=0} < E_{J''=1}) \) for the fine structure of the \( \tilde{e}^3\Sigma^+_g, v' = 4, N' = 3 \rightarrow \tilde{c}^3\Pi_u, v'' = 3, N'' = 1 \) rovibronic transition reported in [3]. Thus our ability to measure both the intensities and splitting values gives an opportunity to get information about an order and separation of the fine structure sublevels.

Finally, two main results of our observations may be formulated as follows. The deconvolution of intensity distributions recorded by a matrix photoelectric detector by means of numerical optimization procedure is a powerful tool for determining wavenumbers and intensities of substructures within apparent line profiles masked by overlapping of adjacent lines (blending) and line broadening in traditional photographic recording of spectra. In contrast to fragmentary results of tunable laser techniques, such Doppler-free classic spectroscopy is able to provide huge volumes of data for broad regions of molecular spectra. It should be stressed that we are working in visible part of the spectrum, most suitable for various applications. Even partly resolved fine structure of spectral lines provides an opportunity to expand the existing identification of triplet rovibronic lines by detecting those doublets in experimental spectra. The doublets analyzed above are especially promising because they are easily recognizable in the spectrum due to their distinguishing features. Within the spectral region under the study \( (545 \div 627 \text{ nm}) \) we already found more than 200 pairs of unassigned lines which may represent pseudo doublets of partly resolved FS of rovibronic transitions between \( ^3\Lambda_{g}^\pm \) and \( \tilde{c}^3\Pi_u \) electronic states of the \( D_2 \) molecule [23].

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