Optimal values of rovibronic energy levels for triplet electronic states of molecular deuterium

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Abstract
An optimal set of 1050 rovibronic energy levels for 35 triplet electronic states of D₂ has been obtained by means of a statistical analysis of all available wavenumbers of triplet–triplet rovibronic transitions studied in emission, absorption, laser and anticrossing spectroscopic experiments of various authors. We used a new method of analysis (Lavrov and Ryazanov 2005 JETP Lett. 81 371–4), which does not need any a priori assumptions concerning the molecular structure, being based on only two fundamental principles: Rydberg–Ritz and maximum likelihood. The method provides the opportunity to obtain the root-mean-square estimates for uncertainties of the experimental wavenumbers independent from those presented in the original papers. A total of 234 from 3822 published wavenumber values were found to be spurious, while the remaining set of the data may be divided into 20 subsets (samples) of uniformly precise data having close to normal distributions of random errors within the samples. New experimental wavenumber values of 125 questionable lines were obtained in the present work. Optimal values of the rovibronic levels were obtained from the experimental data set consisting of 3713 wavenumber values (3588 old and 125 new). The unknown shift between levels of ortho- and para-deuterium was found by least-squares analysis of the \( a^3 \Sigma^+_1, v = 0, N = 0 \div 18 \) rovibronic levels with odd and even values of \( N \). All the energy levels were obtained relative to the lowest vibro-rotational level \( (v = 0, N = 0) \) of the \( a^3 \Sigma^+_1 \) electronic state, and presented in tabular form together with the standard deviations of the empirical determination. New energy-level values differ significantly from those available in the literature.

1. Introduction

The present work is devoted to studies of the wavenumbers of the triplet–triplet radiative electronic-vibro-rotational (rovibronic) transitions and empirical determination of the optimal set of the triplet rovibronic energy levels of the D₂ molecule.

Studies of the spectra and structure of molecular deuterium represent not only understandable general interest (an isotopomer of the simplest neutral diatomic molecule), but have also direct practical value in connection with wide use of D₂ in physical experiments and in various technical applications: from gas-discharge sources of ultraviolet radiation [1] up to tokamak reactors [2].

The spectrum of the D₂ molecule is caused by both singlet–singlet and triplet–triplet rovibronic transitions. The intercombination lines have not yet been observed. The most interesting resonance singlet band systems are located in the vacuum ultraviolet (VUV), while the triplet transitions are responsible for the major part of light emission of ionized gases and plasma in the near infrared, visible and near ultraviolet. They are often used for spectroscopic diagnostics of nonequilibrium plasmas [1–6]. Therefore, the triplet rovibronic levels and optical transitions between them were chosen as the object of the present research.

The energy-level values evaluated from experimental wavenumbers are often called observed energy levels irrespective of the method used for data processing. Such rather disputable terminology implicitly assumes that all spurious experimental results and systematic errors are absent, and random errors are negligibly small. (Otherwise, several different sets of the observed energy-level values may be
obtained from the same set of experimental wavenumbers by applying different methods of data processing.) Therefore, we prefer to use the term empirical level values (for any values obtained from experimental data) and optimal level values (for the values obtained by a purely statistical approach [8, 9]), leaving the word ‘observed’ for experimental values of the wavenumbers which are unambiguously linked with the wavelengths—real observables in spectroscopy. (It should also be mentioned that in molecular spectroscopy energy levels in cm⁻¹ are often called molecular terms (see, e.g. [10]).) Absolute values of both levels and terms are always positive and calculated relative to the lowest vibro-rotational level of the ground-electronic state considered as a zero level. That is in contrast to original meanings of terms and energies adopted in atomic spectroscopy.

Generally speaking, the best set of empirical values of energy may be named a set of optimum values (optimal for available experimental data) only if these values do not depend on the procedure whereby they are obtained, and are defined only by the amount and quality of available experimental data. In such a favourable case the energy-level values may be considered as secondary experimental data.

It is well known that diatomic hydrogen, being the simplest neutral molecule, has a most sophisticated emission spectrum. The hydrogen band spectrum, caused by spontaneous emission due to rovibronic transitions, does not show a visible, easily recognizable band structure, but has the appearance of a multilane atomic spectrum. The peculiarity of molecular hydrogen and its isotopic species—abnormally small nuclear masses—leads to high values of vibrational and rotational constants and large separation between vibrational and rotational levels of various excited electronic states. As a result, various rovibronic spectral lines belonging to different branches, bands and band systems are located in the same spectral regions, leading to the overlap of various band systems, bands and branches, as well as the mixing of rovibronic spectral lines having different origins. The small nuclear masses stimulate a breakdown of the Born–Oppenheimer approximation due to electronic–vibrational and electronic–rotational perturbations having both regular and irregular character; this combination seriously complicates the interpretation of the spectra of hydrogen isotopomers and the unambiguous identification of rovibronic spectral lines. Symmetry rules for permutation of identical nuclei in homonuclear isotopomers (H₂, D₂ and T₂) cause the known effect of the intensity alternation of neighbouring lines within the rotational structure of bands to the alternation in degeneracy of successive rotational levels with odd and even values of rotational quantum number (e.g. 1:2 in the case of D₂). This effect also masks the visible structure of branches resulting in serious additional difficulties for the identification of rovibronic spectral lines.

Thus, most of the lines in the optical spectra of hydrogen isotopomers have not yet been assigned in spite of tremendous efforts by spectroscopists over the previous century [11–17]. As an example, in the latest compilation of experimental data for molecular deuterium D₂ [16], the working list of 27,488 recorded lines contains only 8243 assignments. These assignments were obtained by traditional methods of analysis using wavenumber combination differences (method of common differences) and Dunham series expansions [11, 13], sometimes together with the comparison of molecular constants obtained for different isotopic species [12]. Later on, the traditional methods were supplemented by taking into account the line intensities [18] and the results of ab initio and semi-empirical calculations [16, 17].

Recently in [19, 20], the identification of rovibronic lines of three singlet VUV band systems of D₂ has been obtained by the common use of non-adiabatic calculations (of the levels and the transition probabilities) together with the program IDEN [21, 22] developed for the visual identification of complex atomic spectra. Although the approach seems to be a rather powerful and prospective tool for finding new assignments in the spectra of hydrogen isotopomers, the final results of [19, 20] cannot be considered as optimal values of the rovibronic energy levels for the D² Π₁, D² Π₂, and B² Σ₁ electronic states studied in [19, 20]. They were simply calculated as the average of values derived from different observed line wavenumbers added to the corresponding lower vibro-rotational levels of the Χ₁ Σ₁ ground-electronic state from [14], assumed to be known with negligible uncertainty. Actually, those lower levels were obtained from wavelengths of two other VUV band systems (B¹ Σ⁺ₓ – Χ¹ Σ⁺ₓ, C¹ Π⁻ₓ – Χ¹ Σ⁺ₓ) by two independent methods of the analysis which gave noticeably different results (compare columns two and four of table 4 from [14]). It is evident that the common use of experimental data for the five singlet band systems mentioned above may give another set of rovibronic levels for the Χ¹ Σ⁺ₓ ground-electronic state. Then the level values for the excited states will be changed somehow. In our opinion, the assignments found in [19, 20] also should be confirmed by the appropriate statistical analysis of all experimental data available in the literature on the wavenumbers for all other singlet band systems of D₂. For this purpose it is possible to use the approach proposed and realized in our papers [8, 9, 23, 24].

Currently, the available information concerning triplet rovibronic energy-level values of D₂ molecule exists in the form of a list of molecular constants for Dunham series expansions in [15, 25], and tables of rovibronic levels obtained in [16].

In the case of the hydrogen molecule the Dunham coefficients are known to provide a very poor description of the rovibronic energy-level values [26]. Moreover any set of molecular constants depends not only on molecular properties but also on the theoretical model used in the analysis of the spectrum (the type and length of the series expansion, form of a model Hamiltonian, etc), as well as on the number of measured wavenumbers and even on the distribution of the spectral lines over the vibrational and rotational levels (see, e.g. [8, 9, 26, 27]). Therefore, the molecular constants are rather conditional and the procedures used for their determination are subjective in character. In practical use of reference data on molecular constants, the question arises as to how many rovibronic levels of a particular type can be described by a given set of constants with the required accuracy. In the best

1 Compare with the term experimental level values in [7].
case, this question can be answered only by the researcher who obtained the given set of molecular constants. However, series expansions and molecular constants may be useful both in the process of classifying rovibronic lines in unknown spectra and in calculations which do not claim a high accuracy.

The data reported in [16], in general, give a rather good description of the D₂ spectrum, but they are also not free from criticism. The method of the analysis used in [16] is based on the common use of the combination differences, some selected wavenumbers for certain transitions and one by one multistage treatment of separate branches, bands and band systems. The sequence of the steps chosen in [16] is not the only possible analytical arrangement. Therefore, the data thus obtained cannot be considered as an optimal set of levels providing the best description of all observed wavenumber values. In our opinion the uncertainty σ = 0.05 cm⁻¹ reported in [16] for all levels and all wavenumbers of lines is the overestimation caused by the randomization of various deviations when working with many thousands of levels and lines. It should also be mentioned that after publication of [16], new experimental data on the wavenumbers appeared [28, 29].

Recently, a new method of a pure statistical analysis of experimental data on the rovibronic transition wavenumbers for the empirical determination of the optimal energy-level values has been proposed [8] and successfully applied for the derivation of rovibronic level values of the singlet states of the BH [23] and the triplet states of the H₂ [24] molecules. The method is based on only two fundamental principles: Rydberg–Ritz and maximum likelihood. This approach differs from known techniques in several aspects: (1) it does not need any assumptions concerning the internal structure of a molecule; (2) it does not employ intermediate parameters, such as molecular constants in the traditional methods; (3) a one-stage optimization procedure can be used for all available experimental data obtained for various band systems, by various methods and authors, and in various works (simultaneous adjustment of all levels eliminates the possibility of accumulative errors in traditional methods, caused by multi-step treating of various bands one by one, as well as by transfer of any occasional error for one level, appeared on one step, for all higher levels obtained during further steps); (4) it provides the opportunity for a rational censoring of the experimental data in an interactive mode (thus allowing the user the option to eliminate obvious errors (outliers) and misprints, to revise incorrect line assignments, and to compare various sets of experimental data for mutual consistency); (5) it gives an opportunity for independent estimation of experimental uncertainties by analysing the shapes of error distributions within various samples of the experimental data (this means that our statistical estimates of the root-mean-square (RMS) experimental errors are totally independent from the estimates reported in original experimental papers); (6) provides an optimal set of rovibronic level values as well as the uncertainties of their determination (standard deviations SD and the covariance matrix) caused only by the amount and quality of existing experimental data [9].

A necessary precondition for an application of the method [8] is the existence of more or less dependable assignments for majority of the rovibronic spectral lines under study. Therefore, the new method should be considered as complementary to the traditional and new methods of identifying unknown spectra. However, since the new, pure statistical method is objective, it is better to consider any identification of a rovibronic spectrum as preliminary until it is not corroborated by the fact that the use of certain assignments in the framework of this method does not lead to contradictions with the Rydberg–Ritz principle or with normal distribution of random experimental errors.

The goal of the present paper is to report the results of applying the new method [8] for statistical analysis of the rovibronic spectral line wavenumbers of triplet band systems and determining the optimal set of rovibronic energy levels for all known 35 triplet electronic states of molecular deuterium: $a^3\Sigma_g^+, c^3\Pi_u^+, d^3\Pi_u^+, d^3\Pi_u^-, d^3\Sigma_g^+, f^3\Sigma_u^+, g^3\Sigma_g^+, h^3\Sigma_u^+, i^3\Pi_u^+, j^3\Delta_g^+, j^3\Delta_u^+, k^3\Pi_u^-, k^3\Pi_u^+, n^3\Pi_u^+, n^3\Pi_u^-, p^3\Sigma_u^+, q^3\Sigma_g^+, r^3\Pi_u^+, r^3\Pi_u^-, s^3\Delta_g^+, s^3\Delta_u^+, u^3\Pi_u^-, u^3\Pi_u^+, (7p)^3\Pi_u^+, (7p)^3\Pi_u^-, (8p)^3\Pi_u^+, (8p)^3\Pi_u^-, (9p)^3\Pi_u^+, (9p)^3\Pi_u^-, (6d)^3\Sigma_g^+, (7d)^3\Sigma_g^+, (8d)^3\Sigma_g^+$ and $(9d)^3\Sigma_g^+$.

2. Statistical approach to empirical determination of optimal values of the rovibronic energy levels

In principle the analysis of experimental data on wavenumbers of spectral lines may be considered as consisting of two separate parts: (1) an identification (classification, assignment) of spectral lines (an establishment of a correspondence between observed spectral lines and pairs of the initial and final levels responsible for the occurrence of these lines in a spectrum) and (2) the determination of energy-level values from measured wavenumbers (or some other magnitudes related to the levels, like molecular constants [26], or potential curves [30]). The aim of the first stage of the analysis is to find the most likely identification and to prove the correctness of the assignments. The goal of the second is to obtain the best possible values of the energy levels as well as the uncertainties of their empirical determination. In spite of the difference in objectives these two parts of the analysis are closely connected because the quality of final results in both cases is determined by their ability to reproduce observed spectra. Therefore, quite often the parts are not distinguished in the original papers.

The main part of the present work represents the second stage of the analysis of the triplet–triplet spectrum of D₂ molecule, based on the results of the first stage reported in [16, 28, 29, 31–35]². Therefore in further considerations it is supposed that more or less reliable identification is already established for the majority of lines. Then only a few cases of wrong assignments may be revealed as outliers and corrected during the statistical analysis (see below).

All spectroscopic methods of empirical determination of energy levels of atoms and molecules are based on the Rydberg–Ritz combination principle corresponding to the

² In some cases discussed below, we have had to do the job of the first stage when it was necessary to change earlier assignments and to obtain new experimental values of the wavenumbers of some questionable lines.
Bohr frequency rule in quantum mechanics. For rovibronic transitions of diatomic molecules between electronic states corresponding to Hund’s case ‘b’ for angular momenta coupling (negligible multiplet splitting) it may be written as

\[ v^{\nu',N'}_{n',\nu'} = E_{n',\nu'} - E_{n',\nu'}^{N}. \]

where \( n \) indicates an electronic state, and \( \nu \) is the vibrational quantum number. In the case of diatomic hydrogen isotopomers the multiplet splitting and hyperfine structure of levels and lines are negligibly small and usually unresolved in experiments, therefore in the present work rotational levels are characterized by the quantum number \( N \) of the total angular momentum of a molecule excluding spins of electrons and nuclei. Upper and lower rovibronic levels are marked by single and double primes, respectively. The \( v^{\nu',N'}_{n',\nu'} \) is the wavenumber (recalculated for vacuum conditions) of the \( n', \nu', N'-n', \nu', N' \) rovibronic transition, and \( E_{n',\nu'} \) are corresponding energy-level values.

One may see that the experimentally measured wavenumbers of the spectral lines are related only to the differences between pairs of rovibronic energy levels. So the values of the levels cannot be directly obtained by means of the Rydberg–Ritz principle only. Therefore, traditional methods of empirical determining the rovibronic energy levels require the introduction of some additional (with respect to the Rydberg–Ritz combination principle) assumptions regarding properties of molecules and, hence, are semiempirical and allow some subjectivity of the researcher (see details in [9]).

The classification of the levels and lines by certain sets of quantum numbers \((n, \nu, N)\) is important for the assignment of the wavenumbers to the rovibronic levels between which the transitions occur and, in particular, for the application of the selection rules. When this assignment is carried out, the specific designations of the levels and lines are no longer important. The rovibronic levels may be denoted by single numbers in an arbitrary order. The notation \( E_{n',\nu'} \) may be changed to a more compact notation \( E_{n\nu N} \), and the wavenumbers are designated by pairs of indices corresponding to the initial and final levels. Then the expression (1) becomes

\[ v_{ij} = E_i - E_j. \]

Suppose that the set of available experimental data consists of \( n_e \) wavenumber values obtained for \( n_T \) transitions caused by the combinations of \( n_E \) energy levels. \( n_e > n_T > n_E \) because the number of transitions allowed by selection rules usually considerably exceeds the number of combining levels. Furthermore, experimental data for the same transitions may be obtained and reported in various publications. One may insert all experimental wavenumbers into the left-hand side of (1) one by one, and consider the energy levels as adjustable parameters to be obtained from the experimental data. Then (1) turns into a system of \( n_e \) equations with \( n_E \) unknown quantities \( E_i \). This system of equations is overdetermined and, hence, is inconsistent because the experimental data always involve measurement errors.

The straightforward general solution for solving such problems is well known in mathematical statistics. That is the least-squares method based on the assumption of finite second moment of the distribution function for random errors [36]. In our case, it consists of the minimization of the weighted mean-square deviation between the observed \( v_{ij}^{\text{exp}} \) and calculated (as differences of adjustable energy levels \( E_i, E_j \)) values of rovibronic line wavenumbers, or the sum

\[ r^2 = \sum_{ij} \left[ (E_i - E_j) - v_{ij}^{\text{exp}} \right]^2 / \sigma_{ij}^{\text{exp}}. \]

The values \( \sigma_{ij}^{\text{exp}} \) are the RMS estimates of experimental errors (one standard deviation—SD) for each experimental datum, and the summation is performed over all available experimental data. Due to the linearity of equations (2), the optimization problem amounts to solving a system of linear algebraic equations. The complete solution involves the inversion of the \( n_E \times n_E \) sparse matrices. When the number of desired levels \( n_E \) is of the order of a thousand, as is usually the case, this problem can be solved even using modern personal computers (see [9] for details)). If the experimental errors are random and distributed according to a normal (Gaussian) law, the obtained solution corresponds to the maximum likelihood principle [36].

The attempts to apply such a statistical approach for the determination of the energy-level values appeared almost simultaneously in atomic (e.g. the spectra of the Er I, Er II [37], Cl II [38] by the inversion method, and the spectra of the Si I [39], Cl I [40] by the iterative method) and in molecular [14, 41] spectroscopy when the first digital computers became available. It is interesting to note that in spite of obvious disadvantages of the iterative method (the problems of convergence and lack of the covariance matrix (see p 6 in [42])), its usage can be found in current publications (see, e.g. [43]).

In several studies reviewed by Åslund in [41], it was proposed to determine the rovibronic levels of molecules on the basis of the combination principle by solving the overdetermined system of equations with the use of a computer. Owing to the limited capabilities of the computers of the day, the optimization procedure was realized for processing the wavenumbers for separate bands only. As a result, those authors overlooked the opportunity to overcome the problem of the limitations for the method of common differences caused by Laporte’s selection rule allowing rovibronic transitions only between levels with different + and − parities [8]. (Only recently, it was shown that, if it is possible to use experimental data on rovibronic lines that pairwise couple three or more different electronic-vibrational states, then the system of equations (1) contains the link between the line wavenumbers and the values of all rovibronic levels involved [8]. Thus, in the case of heteronuclear molecules the above problem of the existence of uncoupled sets of the levels with even and odd rotational quantum numbers disappears.) Consequently, the relative positions of unrelated odd and even rotational levels, as in traditional approaches, were obtained using the Dunham approximation and molecular constants. It should be noted that the attempts to directly empirically determine the rovibronic levels in [41] were inconsistent from the very outset. The level values were considered as some intermediate parameters of a molecule, and the procedure of
The empirical determination of the energy-level values by means of the least-squares method looks natural and simple, but its correct realization in practice encounters serious difficulties. The problem is that the result of the minimization of (3) (i.e. the optimal set of the level values and the matrix of co-variances) depends not only on the values of experimental data, but also on weighting of various data (i.e. from what co-variances) depends not only on the values of experimental data set). Therefore, for the correct optimization of the adjusted parameters (required level values) it is necessary to know a dependable RMS error estimate for each experimental wavenumber value, or to have the set of the wavenumbers consisting of several subsets (statistical samples) of uniformly precise data with known RMS error estimates for each sample.

Unfortunately, authors of experimental works usually limit themselves to some remarks of general character (concerning resolving power of a spectograph, linear dispersion, typical line widths, etc) and, at best, to some rough estimates of an order of magnitude or the upper limit of possible experimental uncertainty. Most often the real accuracy of the reported data is uncertain. The situation in the literature containing experimental data analysed in the present work will be illustrated below, but it should be mentioned that the same uncertainty may be met even in current publications. (To substantiate, a very recent paper [43] may be used as a typical example. In the part describing the experimental setup one may read: ‘the estimated error is ±0.005 Å for single lines, but many lines are blended in complex emission peaks’; while in the part describing data processing one may find: ‘as input to the code, 1314 classified lines were used with uncertainties in their wave numbers smoothly decreasing from 0.33 to 0.10 cm$^{-1}$ between 1150 and 2800 Å’. The attentive reader can easily recognize that the wavenumber uncertainties correspond to wavelength uncertainties 0.0044 and 0.0078 Å not equal to those for single lines. But a lot of questions remain. What about blended lines? Why does the weighting of various data depend only on wavenumber values? What kind of smooth decrease was chosen and why? We hope that the authors have some answers and did their best to get the best possible level values they are interested in. But what can an independent researcher do with those wavenumbers after several decades?)

The problem of weighting various experimental data according to their accuracy in the framework of the least-squares fitting has been mentioned from the very beginning [37]. But in practical applications it was always considered as an issue of secondary importance, leaving a lot of room for the author’s subjectivity. Maybe it is because researchers process their own experimental data and have certain opinions concerning their accuracy. Then, irrespective of the method of data processing, the empirical level values are considered as optimal when they are able to reproduce experimental wavenumbers with an accuracy corresponding to the author’s estimates for the experimental errors (‘chosen tolerance’). That is certainly reasonable, but only if the author’s expectations coincide with real experimental uncertainty caused by all possible sources of errors. Thus, in spite of the principal objectivity of the least-squares method the results of its application have subjective character reflecting the author’s individuality. The Achilles’ heel of all papers (known to the authors of the present work) devoted to the determination of the level values by means of the least squares adjustment is ignoring or subjectively estimating the experimental errors.

The development of a purely statistical approach to the problem of empirical determination of energy-level values [8] was motivated by the author’s desire to overcome the subjectivity discussed above. The main ideas of the approach may be formulated in the following way. Since optimal values of rovibronic levels are to be entirely defined only by the amount and quality of available experimental data, the procedure to obtain them should be based only on the fundamental principles. The Rydberg–Ritz combination principle provides the link between experimental wavenumbers of rovibronic transitions and desired energy levels. The maximum likelihood principle gives the optimization criterion in the form (3) for the normal distribution function of random errors. The set of input data for minimizing (3) should be prepared by means of statistical analysis: (1) the data having systematic errors and spurious results (outliers) should be uncovered and eliminated; (2) the whole set of available experimental data should be divided into a finite number of subsets (samples) of uniformly precise data with normal error distributions; (3) the values of the experimental RMS uncertainty for the samples (unique for all data belonging to the same sample) are obtained, being independent from those named in the original papers. An optimal set of rovibronic level values is obtained from the prepared input data set in the one-stage optimization procedure. The accuracy of the empirical determination of the optimal level values is characterized by the covariance matrix $D(E)$; the square roots of its diagonal elements are used as the uncertainties (one SD) of the level values ($\sigma_{E_i} = \sqrt{D_{ii}(E)}$). (The method may be easily generalized for other types of the distribution function of random errors.)

The computer code developed for the practical realization of the method is based on the minimization of the weighted mean-square deviation (3) by the inversion of the $n_E \times n_E$ sparse matrices [8, 9]. The $v_{ij}^{\text{exp}}$ and $\sigma_{ij}^{\text{exp}}$ values are the input data, while the optimal set of the energy levels $E_i$ and their covariance matrix $D(E)$ are the output data of the minimization. The latter is used for calculating and visualization of various quantities suitable for interactive statistical analysis of the experimental data including rational censoring of various groups (samples) of the data and the derivation of the RMS uncertainties of experimental data independent from those reported in the original papers.
The interactive analysis consists of the studies of the shape of the distribution functions of the weighted unbiased deviations

\[ \xi_{ij}^{\text{exp}} = \frac{u_{ij}^{\text{exp}} - (E_i - E_j)}{\sigma_{ij}}, \]  

for various sets (statistical samples) of the experimental wavenumbers, \( k \) being the number of the sample. Here \( u_{ij}^{\text{exp}} \) is a certain experimental datum for the wavenumber of the \( i - j \) transition, while the level values \( E_i \) and \( E_j \) are obtained by the minimization of (3) without using the particular datum under consideration. \( \sigma_{ij} \) is an adjustable value of the estimate for experimental uncertainty (RMS error estimate) common for all the data included in the sample. The dimensionless deviation \( \xi_{ij}^{\text{exp}} \) characterizes the degree of co-ordination of the particular experimental datum \( u_{ij}^{\text{exp}} \) with all other experimental data in the framework of the Rydberg–Ritz principle. Among all, the most important are certainly the data obtained for the same rovibronic transition in various works, and the wavenumbers of other lines directly connected with the upper \( n', v' \), \( N' \) or the lower \( n'', v'', N'' \) rovibronic levels.

The values \( E_i \) and \( E_j \) may be expressed through the corresponding level values and the covariance matrix \( D(E) \) obtained with the use of all experimental data:

\[ \xi_{ij}^{\text{exp}} = \frac{u_{ij}^{\text{exp}} - (E_i - E_j)}{\sqrt{\sigma_{ij}^2 - (D_{ii}(E) + D_{jj}(E) - 2D_{ij}(E))}}, \]

where \( D_{ij}(E) \) are elements of the covariance matrix. This makes it possible to obviate the need for repeated minimizing (3).

The empirical accumulative distribution function for each data sample is defined by

\[ F(\xi) = \frac{1}{n_v} \sum_{\xi_{ij}^{\text{exp}}} I(\xi_{ij}^{\text{exp}} \leq \xi), \]

where \( n_v \) is the number of elements in the sample, \( I(A) \) is the indicator of event \( A \). Here the sum is over all data included in the sample. After each minimization of (3) it is possible to calculate and to see \( F(\xi) \) for any sample of the \( \xi_{ij}^{\text{exp}} \) values chosen by the user of the computer code. That gives an opportunity to study various data samples selected from the complete set of all experimental data by some physical considerations: the data reported in the particular paper, wavenumbers of lines from the particular interval of wavelengths, or belonging to the particular band, or to the particular band system.

It is evident that if all the data \( u_{ij}^{\text{exp}} \) included in some sample are free from systematic errors and have normal distribution of random errors with RMS estimate equal to \( \sigma_{ij} \); then the empirical distribution \( F(\xi) \) should be close to the normal cumulative distribution function with the zero mean and variance equal to unity, namely

\[ F_0(\xi) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\xi} \exp \left(-\frac{x^2}{2}\right) \, dx, \]

\( I(\xi_{ij}^{\text{exp}} \leq \xi) = 1 \) for \( \xi_{ij}^{\text{exp}} \leq \xi \) and \( I(\xi_{ij}^{\text{exp}} \leq \xi) = 0 \) for \( \xi_{ij}^{\text{exp}} > \xi. \)

Therefore, it is useful and convenient to provide the interactive analysis of experimental wavenumber values by studies of the shape of the empirical functions

\[ \Phi(\xi) = F_0^{-1}(F(\xi)), \]

calculated for various groups (samples) of available data. Here \( F_0^{-1} \) is the reverse function to \( F_0(\xi) \), i.e. \( F_0^{-1}(F_0(\xi)) = \xi \).

If the empirical distribution function \( F(\xi) \) is close to the normal distribution, the empirical function (8) is close to the linear function

\[ \Phi(\xi) = \xi. \]

The method of dividing (sampling) the whole set of experimental data into the subsets is not determined, leaving some subjectivity for a researcher. But the shape of the function \( \Phi(\xi) \) is an objective characteristic of the sample, being determined by the experimental values of the wavenumbers, the Rydberg–Ritz principle and only one arbitrary parameter \( \sigma_{ij} \). If for a certain data sample adjusting the value of \( \sigma_{ij} \) leads to the shape of \( \Phi(\xi) \) fulfilling the criterion (9), the data included in the sample are to be considered as measured with uniform precision and characterized by the normal distribution of random experimental errors. The obtained value \( \sigma_{ij} \) is their experimental uncertainty (RMS error estimate). Thus, the method of \( a \ posteriori \) statistical analysis proposed in [8, 9] gives the objective mean to get proper results by the studies of the \( \Phi(\xi) \) functions, trying various kinds of sampling and adopting or rejecting various guesses. First applications of the approach in our recent studies of rovibronic spectra of BH and \( \text{H}_2 \) molecules [8, 9, 23, 24] showed that the method allows revealing and rejecting both single outliers (caused by wrong assignments, blending, spurious readings and misprints) and large data sets, including data of some experiments (probably caused by systematic error of the wavelength calibration [9]).

3. Statistical analysis of published wavenumbers of triplet rovibronic transitions

All available values of rovibronic transition wavenumbers studied in emission, absorption, laser and anticrossing spectroscopic experiments of various authors [16, 28, 29, 31–35] were analysed in the present work. In the overwhelming majority of the works the fine and hyperfine structures of lines have not been resolved, and the reported experimental wavenumbers correspond to intensity maxima of the observable line profiles. In cases of partly resolved structure of lines [28, 29] we used wavenumbers of the brightest components.

All the identified triplet electronic transitions are naturally divided into three groups of band systems. These are: (i) the 9 band systems having one common low electronic state \( n^3 \Lambda_u - a^3 \Sigma_a^+ \), with \( \Lambda = 0, 1 \) and \( n = 3 - 9 \); (ii) the 12 band systems having another common low state \( n^3 \Lambda_g - c^3 \Pi_u \), with
$\Lambda = 0 - 2$ and $n = 3 - 9$); and (iii) the 7 band systems connecting various $n^3\Lambda_u$ and $n^3\Lambda_g$ electronic states (with $\Lambda = 0 - 2$ and $n = 2 - 4$) including the $a^3\Sigma_g^+ - c^3\Pi_u$ transitions. Therefore, the whole set of available experimental data possesses different informational content about rovibronic levels of different electronic states. Thus, the information on rovibronic levels of the $c^3\Pi_u$ electronic state is contained in the wavenumber values of the 13 band systems, on the $a^3\Sigma_g^+$ state—10 band systems, and on for example the $e^3\Sigma_u^+$ state—6 band systems. For some electronic states as a source of the information on rovibronic levels we can use wavenumbers of lines from very few or even only one band system. In such cases the obtained values of the rovibronic levels are essentially less reliable.

Most of the data used in our statistical analysis are those collected from earlier works (partly unpublished) and reported in [16]. This compilation contains wavenumbers of 3117 rovibronic spectral lines assigned as triplet-to-triplet transitions. Thirty-one of them have upper electronic and vibrational states. They were not used in the analysis, so only 3086 experimental data were taken from [16]. The 83 wavenumber values obtained in [33] coincide with those reported in [16] (although 12 of them appeared in appendix C of [16] as unassigned). To prevent duplication of the same experimental results we excluded 71 wavenumbers from the data sets of [33]. The data reported in [31, 32] and [16] are obtained for the lines of the same band systems, but wavenumber values are different. Taking into account the random character of the differences we decided to consider the data of those papers as the results of independent experiments. Thus, the initial data set used for the start of the statistical analysis contains: 350 wavenumbers from paper [32], 285 from [31], all 37 data from [34], 12 from [33], 1 from [35], 3086 from [16], 81 from [28] and 3 from [29]. It should be stressed that the wavenumbers of spectral lines used in the present work are spread over the very wide range 0.896—28 166.84 cm$^{-1}$ from radio frequencies up to the ultraviolet.

On the first iteration of our statistical analysis we assumed that all sets of experimental data presented in various papers represent the samples of uniformly precise data with RMS error uncertainty equal to the estimates presented in the original experimental works. In the review [16] there are two remarks concerning accuracy of the wavenumbers. In the experimental part it is written: ‘...the widths of the lines themselves limited the attainable accuracy, which was a few hundreds of a cm$^{-1}$’. At the end of the analysis the authors of [16] wrote: ‘the mean (O–C) value for all triplets is $-0.001 \pm 0.051$ cm$^{-1}$, and came to the conclusion that ‘the precision of the measurements appear to be roughly uniform from the infrared to the ultraviolet’. In spite of the doubtfulness of such estimations we have accepted the value $\sigma_\nu = 0.05$ cm$^{-1}$ in the first iteration of our analysis for all wavenumbers taken from [16]. In papers [31, 32, 34] experimental errors are not mentioned at all. Therefore, we used the same value 0.05 cm$^{-1}$ taking into account the estimates made by the same scientific group. In [33] it is written: ‘...the errors in the wave number of good lines should not exceed a few times 0.01 cm$^{-1}$’. We certainly do not know which lines are good or bad, therefore in this case we again took $\sigma_\nu = 0.05$ cm$^{-1}$. For the data taken from [28, 29, 35] we used author’s estimates $\sigma_\nu = 0.01, 0.003, 0.0003$ cm$^{-1}$, respectively. Under these assumptions we obtained a set of energy levels by minimization of (3) and the empirical function $F(\xi)$ shown in figure 1.

One may see that the distribution function $F(\xi)$ is far from the normal distribution $F_0(\xi)$ ($F(\xi)$ is too far from the dotted straight line representing the case of normal distribution). Too many experimental wavenumber values significantly exceed those calculated as differences of corresponding energy-level values. The distribution is not close to normal even in the area of small deviations ($\xi < 3$). We suppose that this disagreement is caused by the deviations of real experimental wavenumber errors from their estimates, reported in the original works. (At this stage of our analysis it was observed that 33 lines with wavenumbers measured in [16] are the combinations of 55 rovibronic levels representing the blocks of levels totally disconnected with all other triplet rovibronic levels of $D_2$. Therefore these wavenumbers were excluded from further consideration as useless. So only 3053 from the data reported in [16] are useful for further analysis.)

Thus there is the necessity of independent estimation of experimental uncertainties of the measured wavenumbers. To carry out this estimation we need to divide the data set used in the first iteration into some groups (subsets, samples) so that all experimental data inside one subset can be considered as uniformly precise. We tried to sort the experimental data into subsets taking into account various criteria, selecting the data obtained in various papers, in various wavelength regions and in various band systems. But acceptable results for error estimates were obtained only when we considered each band as a group of uniformly precise data. Maybe that method of sampling is fruitful because the lines of each band are located in narrow parts of the spectrum, and different bands are usually measured and treated by different people even within the same
scientific group. It should be also mentioned that such an approach gave reasonable results in a similar analysis of BH [23] and Hg [24] spectra.

Each \( m \)th iteration consists of: (1) the minimization of (3) with a certain \( m \)th set of the input data prepared at the last stage of the previous \((m-1)\)th iteration. It includes certain amount of experimental wavenumbers divided into finite number of samples characterized by certain RMS estimates for experimental errors in each \( k \)th sample \( \sigma_{ik}^{(m-1)} \); (2) the output data (optimal energy levels \( E_{expt}^{(m)} \) and the covariance matrix \( D_{ij}^{(m)} \)) are used for calculating the \( \Phi^{(m)}(\xi) \) functions for each sample. That gives us an opportunity to analyze the shapes of the \( F^{(m)}(\xi) \) distribution function for all the samples and to find outliers. The data with \( \xi_{ij}^{(m)} \) larger than 3 were qualified as outliers. In all cases this criterion of censoring was less strong than the commonly adopted Chauvenet’s and Peirce’s criterions [45]; (3) the new set of input data for the next \((m+1)\)th iteration is prepared by excluding the outliers from the current \( m \)th data set, and by obtaining for each sample new values of RMS estimates for experimental errors \( \sigma_{ik}^{(m)} \) by multiplying \( \sigma_{ik}^{(m-1)} \) by the factor which should move \( \sigma_{ik} \) closer to unity in the next iteration. Usually we used the expression 

\[
\sigma_{ik}^{(m)} = \sigma_{ik}^{(m-1)} \rho_{ik},
\]

where \( \rho_{ik} \) is closer than 3 were excluded. Then the value (4) for these lines is equal to zero. We do not take into account such lines when calculating empirical distribution functions \( \Phi^{(m)}(\xi) \).

The square of the second moments \( \sigma_{ik}^{(m)} \) for empirical distribution functions \( F^{(m)}(\xi) \) (for each sample in each iteration) are calculated as 

\[
\sigma_{ik}^{(m)} = \sum_{\xi_{ij}^{(m)}} \left( \xi_{ij}^{(m)} - \mu_{ij}^{(m)} \right)^2 F^{(m)}(\xi_{ij}^{(m)}),
\]

where \( \mu_{ij}^{(m)} = \sum_{\xi_{ij}^{(m)}} \xi_{ij}^{(m)} F^{(m)}(\xi_{ij}^{(m)}) \), and the summing is performed over all the data included in the \( k \)th sample.

The method of independent error estimation of wavenumbers belonging to the same \( k \)th sample may be illustrated by considering one typical example—an analysis of the \((0 - 1)\) band of the \( e^3 \Sigma_u^+ - a^3 \Sigma_g^+ \) electronic transition. Thirty spectral line wavenumber values for \( R- \) and \( P- \) branch lines from this band are reported in [16]. The lines R18 and R19 are caused by the transitions between \((E_e,0,19)\) and \((E_e,0,20, E_a,1,19)\) pairs of rovibronic levels, respectively. Mutual positions of these levels can be derived using wavenumber values of these lines only, because there are no other lines which provide information about these levels. Then the value (4) for these lines is equal to zero. We may try to shift \( \sigma_{ik}^{(2)} \) to unity by changing the error estimation in the following way: 

\[
\sigma_{ik}^{(1)} = \sigma_{ik}^{(2)}, \quad \sigma_{ik}^{(1)} = 0.028(8) \text{ cm}^{-1}.
\]

In the second iteration for the band under consideration we used the same set of experimental data but a new value of \( \sigma_{ik}^{(1)} \) instead of \( \sigma_{ik}^{(2)} \). The empirical function \( \Phi_{ik}^{(1)}(\xi) \) is shown in figure 2(b). One may see that now the majority of lines show the deviations sufficiently closer to the normal distribution, and the square root of the second moment \( \sigma_{ik}^{(2)} = 0.9(3) \) is closer to unity. But one point located in the bottom left corner of the figure is in contradiction with the rest of the distribution. This point represents the \( \xi \) value for the line \( P \)10. The measured
wavenumber value of this line \( v_{a,10}^{0.9} = 9292.16 \text{ cm}^{-1} \) deviates from the difference of corresponding energy-level values derived in this iteration \( v_{a,10}^{0.9} - (E_{S+0.9}^{(2)} - E_{S+1.10}^{(2)}) = -0.0950 \text{ cm}^{-1} \). The deviation exceeds our estimate for RMS error \( \sigma_{\nu}^{(1)} = 0.028(8) \text{ cm}^{-1} \) by more than three times. Thus the experimental wavenumber for the \( P \) 10 line should be excluded from the input data set as an outlier.

In the third iteration we used 27 wavenumber values and common uncertainty \( \sigma_{\nu k}^{(2)} = \sigma_{\nu k}^{(1)} = 0.028(8) \text{ cm}^{-1} \). The function \( \Phi_3(\xi) \) thus obtained is shown in figure 2(c). One may see that this distribution function is not close to the normal distribution function mainly because \( \sigma_{\nu k}^{(3)} = 0.60(8) \) is too far from unity. Therefore we have to correct the experimental uncertainty as \( \sigma_{\nu k}^{(3)} = \sigma_{\nu k}^{(2)} \sigma_{\nu k}^{(3)} \). After a certain number of iterations we are coming to \( \sigma_{\nu k} = 0.012(1) \text{ cm}^{-1} \). Then in the next iteration we have empirical \( \Phi_k(\xi) \) function shown in figure 2(d) and the square root of the second moment \( \sigma_{\nu k} = 1.0(1) \). One may see that now the experimental distribution function \( F_2(\xi) \) is close to the normal distribution function with zero mean and the variance equal to unity.

Thus, the sample of the 27 wavenumbers under the study may be considered as a group of uniformly precise experimental data with RMS estimate for random errors \( \sigma_{\nu k} = 0.012(1) \text{ cm}^{-1} \). It should be underlined that our estimate is less than a quarter of the value 0.05 cm\(^{-1}\) declared in [16].

In this way we estimated RMS uncertainties of experimental data by the rational censoring of experimental data and the determination of proper values of \( \sigma_{\nu k} \).

After several dozens of iterations described above we came to the conclusion that 234 experimental data representing 228 spectral lines have to be excluded as outliers. Remaining 3588 wavenumbers were organized as 317 samples of uniformly precise data with RMS uncertainties obtained by the statistical analysis. RMS errors for many bands are so close that it seems reasonable to provide the enlargement of the samples by merging studied samples having close values of RMS error. This also helps to improve the statistics because some bands have small amounts of data. It is reasonable to combine into the same sample wavenumbers of various bands with RMS errors approaching the particular wavenumber interval. The amount and widths of such intervals are uncertain. The choice of these parameters may lead to some subjectivity. On one hand, the widths of intervals should be large enough for the amount of data included in each interval to be sufficient for the statistics. But on the other hand, it should be as small as possible, so as not to disturb the close-to-normal error distributions obtained for separate bands. Our computational experiments show that the intervals \( (0.00 \div 0.01) \text{ cm}^{-1}, (0.01 \div 0.02) \text{ cm}^{-1}, (0.02 \div 0.03) \text{ cm}^{-1} \), etc fulfil the requirements mentioned above. It is important that all energy-level values, obtained by the minimization of (3) with experimental data divided into the such enlarged samples of this size, have been changed significantly less then one SD of their determination with the original 317 samples.

After that, the whole set of the 3588 experimental data was reorganized into the 17 enlarged samples of uniformly precise data from [16, 28, 31–34]. The RMS error estimates for each of these 17 subsets were derived by a method similar to that described above. The results of the distribution of the data among the 17 samples together with the list of RMS error estimates for the wavenumbers of lines belonging to various vibronic bands are presented in table 1 of [46]. Also 1 wavenumber from [35] and 3 wavenumbers from [29] were used in further analysis as two separate samples (18th and 19th) with RMS errors reported in the original papers, because the errors were unchanged during the analysis.

The amount of experimental data \( n_i \) in each of the new samples is presented in figure 3. It is seen that the amount of data in most samples obtained by the enlargement is sufficient for carrying out the statistical analysis. Moreover, the distribution of data over the error steps looks quite plausible: the number of too precise data \( \sigma_{\nu k} = (0.00 \div 0.01) \text{ cm}^{-1} \) is small (\( \approx 9\% \)), most of the data (\( \approx 85\% \)) are measured with realistic accuracy \( (0.01 \div 0.06) \text{ cm}^{-1} \), and the quantity of data falls down almost monotonously with further increase in the error estimate \( \sigma_{\nu k} \).

Empirical functions \( \Phi(\xi) \) for the first six combined samples representing vast majority of usable experimental data are shown in figure 4. The corresponding values of RMS error estimates for each sample are shown in the figure. One may see that the error distribution functions are in much better accordance with the normal distribution function than those obtained for the data samples representing separate bands (see figure 2).

Thus, splitting of experimental data into the samples and the subsequent enlargement of the samples as a whole were justified. Taking into account high enough statistics of the samples we are coming to the conclusion that the obtained error estimates with a high probability are close to the values of the real experimental uncertainty.

4. Experimental determination of wavenumbers for questionable lines

The statistical analysis of the 3822 published wavenumber values known to the authors has shown that 3588 of them are usable for empirical determination of the level values, while the 234 experimental data (concerning 228 spectral lines) have to be excluded as outliers. 161 of those questionable lines are located within the wavelength range 4300 \( \div \) 7300 Å available to us. 26 of them are the data
Figure 4. Empirical functions $\Phi(\xi)$ representing the error distributions within the first six enlarged samples corresponding to the intervals $(0 \div 0.01)$, $(0.01 \div 0.02)$, $(0.02 \div 0.03)$, $(0.03 \div 0.04)$, $(0.04 \div 0.05)$, $(0.05 \div 0.06)$ (from left to right, and top to bottom). The values of the experimental uncertainty obtained in the present work for every sample are shown near the appropriate graphs together with SDs of their statistical determination (in brackets).

Figure 5. Fragments of the D$_2$ spectrum in the neighbourhood of the questionable lines. Experimental intensity $J$ in relative units is shown by open circles ($\circ$). Dotted lines represent Gaussian profiles for separate lines obtained by deconvolution, while the solid line corresponds to the total intensity obtained by summing over the components. The wavenumber values from the appendix C of [16] are shown and marked by dash-dot vertical lines. Sections of bold vertical lines denote maxima of the separate line profiles. Bold underlined wavenumbers represent the new wavenumber values for the questionable lines obtained in the present work.

For the identification of the D$_2$ spectral lines in our spectrum we used the assignments and wavelength values from [16]. Those values show a certain spread around the monotonic dependence of the wavenumber from the distance along the direction of dispersion in the focal plane of the spectrograph. The dispersion function of the spectrograph was obtained by a polynomial least-squares fitting of wavelength versus distance for strong unblended lines. Such a wavelength calibration allows us to get new experimental values for the wavenumbers of 125 questionable spectral lines. The new values differ from those reported in [16] not only because of the smoothing procedure. In contrast to previous works we used a digital intensity registration providing a linear response of the CCD detector. This gave us the opportunity of digital deconvolution of the recorded spectra to resolve most of the blended lines. The observed line profiles were determined mainly by Doppler and instrumental broadening. For strong unblended lines they were close to the Gaussian shape except for insignificant far wings (see, e.g., the bottom graph in figure 5). Therefore, the parts of spectra in the neighbourhood of the blended questionable lines under study were reported in old papers [31, 32] and the wavenumber values for these lines were measured once more and corrected in the compilation [16]. For the remaining 135 lines we decided to provide independent experimental determination of their wavenumbers. For this purpose we used the emission spectra of D$_2$ obtained during our studies of translational and rotational temperatures in hydrogen and deuterium containing plasmas [3]. A detailed description of the experimental setup has been reported elsewhere [47]. Capillary arc discharge lamps DDS-30 described in [48] were used as a light source. They were filled with about 6 Torr of a spectroscopically pure D$_2$ + H$_2$ (9:1) mixture. The range of the discharge current was from 50 to 300 mA (current densities $j = 1.6 \div 10$ A cm$^{-2}$). The light from the plasma axis inside the capillary was directly focused by an achromatic lens on an entrance slit of a Czerny–Turner type 1 m double monochromator (Jobin Yvon, U1000). The intensity distribution in the focal plane of the spectrometer was recorded by a cooled CCD matrix detector of an Optical Multichannel Analyser (Princeton Appl. Res., OMA-Vision-CCD System).
Figure 6. Empirical function $\Phi(\xi)$ for the sample containing new wavenumber values for questionable lines. The frequency diagram $N$ versus $\xi$ is constructed with uniform width intervals equal to 0.4. $N$ represents the number of deviations $\xi_{i,\text{exp}}$ within each interval. The columns show experimental results while the solid line with circles corresponds to the normal distribution with zero mean and variance equal to unity.

approximated by superpositions of a certain number of lines having Gaussian profiles with fixed half-width and adjustable intensity and wavelength values. Then we obtained new values for the maximum intensities of $D_2$ lines. A typical example is shown in figure 5. One may see that the new values of the rovibronic transition wavenumbers are a little different from those reported in [16]. In our experimental conditions the intensities of 10 questionable lines were too weak to detect, as well as to obtain an unambiguous separation of the lines by the deconvolution.

The uncertainty of our experimental data is mainly determined by errors of the deconvolution process. It should be underlined that most of the questionable lines are blended lines of relatively low intensity. In this case it is not easy to obtain reliable RMS estimates for experimental errors. Therefore we used the statistical method for the derivation of experimental uncertainty described above. The new wavenumber values were included in the input data set obtained in the last part of the previous section as a separate (20th) sample of uniformly precise experimental data. After several iterations the RMS estimate of experimental uncertainty 0.06 cm$^{-1}$ was obtained without any evidence for the existence of outliers. The experimental $\Phi(\xi)$ function for the sample of new wavenumbers for questionable lines is shown in figure 6 together with the corresponding frequency diagram. One can see that the distribution function of random errors is close to the normal distribution. Moreover new wavenumber values do not contradict the rest of the data set and may be used for the determination of optimal values of rovibronic levels.

The new wavenumber values of questionable lines obtained in the present work are listed in table 1 together with those from [16]. One may see that in most cases the differences between the new and old data are significant. Most often small differences (<0.05 cm$^{-1}$) are probably caused by errors of reading from photographic plates and/or by round-up errors, when the vacuum wavenumbers were calculated from the wavelengths measured in air. In our case, they were eliminated by a digital reading of the intensity profiles and smoothing procedure of the determination of the dispersion curve. Differences higher than 0.05 cm$^{-1}$ are caused by blending (by shifts of the intensity maxima or by disappearance of a weak line within the profile of the strong one, see, e.g. figure 5), misprints and wrong assignments. The differences (O–C) between observed wavenumber values and those calculated as differences of corresponding optimal energy-level values obtained in the present work are also shown in table 1. One may see that in the framework of the Rydberg–Ritz principle the new experimental data for 125 questionable lines are in much better co-ordination with the 3588 wavenumbers of other lines than those reported in [16].

5. Results and discussion

Information on the amount of experimental data reported in the original papers and the amount of outliers revealed by statistical analysis is presented in table 2.

Overall, the input data set consists of 3713 wavenumber values (3588 old and 125 new) divided into 20 subsets of uniformly precise data with known RMS estimates of experimental uncertainties obtained in the present work by pure statistical analysis, i.e. independent from the estimates reported in the original papers. This data set was used for the determination of optimal values of all experimentally studied triplet rovibronic levels by minimizing (3). The empirical function $\Phi(\xi)$ thus obtained is presented in figure 7. One can see that the final distribution function $F(\xi)$ is close to the normal distribution $F_0(\xi)$. Small deviations from the linear plot are caused by insufficient statistics for the data showing too high values of the weighted deviations $|\xi_{i,\text{exp}}|$ without any contradiction with Chauvenet’s criterion. Thus, optimal values of the 1050 rovibronic energy levels have been obtained from the 3713 values of the experimental wavenumbers. All the energy levels were obtained relative to the lowest vibro-rotational level ($v = 0, N = 0$) of the $a^3\Sigma^+_g$ electronic state.

The shift (33.631 ± 0.004) cm$^{-1}$ between uncoupled levels of ortho- and para-deuterium was obtained by the least-squares analysis of the $a^3\Sigma^+_g$, $v = 0, N = 0 \div 18$ levels with odd and even values of the rotational quantum number $N$. According to [16] the difference $E_{000} - E_{000} = (33.62 ± 0.10)$ cm$^{-1}$. Both values coincide within error bars, but our
Table 1. Experimental values of the wavenumbers (in cm\(^{-1}\)) of some spectral lines of \(\text{D}_2\) obtained in the present work (P.W.) and those reported in [16]. O–C denotes the differences between observed wavenumber values and those calculated as differences of corresponding optimal energy-level values obtained in the present work.

| Electronic transition | Band Line | [16] | O–C | P.W. | O–C |
|-----------------------|-----------|------|-----|------|-----|
| \(e^1 \Sigma_u^+ - a^1 \Sigma_g^+\) | 2–0 | P11 | 13 751.08 | -0.14 | 13 751.29 | 0.07 |
| | 3–0 | R6 | 15 868.98 | -0.05 | 15 869.01 | -0.02 |
| | | R9 | 15 705.21 | 0.23 | 15 704.98 | 0.00 |
| | 4–1 | P8 | 14 862.89 | -0.08 | 14 862.95 | -0.02 |
| | 5–2 | P6 | 14 524.31 | 0.07 | 14 524.26 | 0.02 |
| | 6–2 | R4 | 15 977.48 | -0.06 | 15 977.56 | 0.02 |
| | 6–3 | P9 | 13 703.95 | 0.09 | 13 703.87 | 0.01 |
| | 7–3 | P5 | 15 107.67 | -0.04 | 15 107.71 | 0.00 |
| | 8–3 | R0 | 16 354.21 | 0.05 | 16 354.19 | 0.03 |
| | 8–4 | P5 | 14 468.77 | -0.10 | 14 468.86 | -0.01 |
| | 9–5 | P4 | 13 861.27 | -0.19 | 13 861.45 | -0.01 |
| | R4 | 14 002.82 | -0.11 | 14 002.91 | -0.02 |
| | 10–4 | P4 | 16 124.14 | 0.25 | 16 123.94 | 0.05 |
| | 1–1 | R2 | 20 346.49 | 0.07 | 20 346.42 | 0.00 |
| | 1–2 | R0 | 18 564.54 | 0.21 | 18 564.19 | -0.14 |
| | 2–1 | P3 | 21 653.13 | 0.20 | 21 653.04 | 0.11 |
| | 2–3 | P3 | 18 242.42 | 0.09 | 18 242.40 | 0.07 |
| \(f^3 \Sigma_u^+ - a^3 \Sigma_g^+\) | 0–1 | R9 | 15 019.54 | 0.10 | 15 019.44 | 0.00 |
| | 1–0 | P2 | 18 207.70 | 0.10 | 18 207.60 | 0.00 |
| | 1–5 | P5 | 18 065.38 | 0.06 | 18 065.36 | 0.04 |
| | 1–1 | Q1 | 16 460.87 | -0.07 | 16 460.93 | -0.01 |
| | 1–2 | Q10 | 14 582.86 | 0.03 | 14 582.84 | 0.01 |
| | 2–0 | Q1 | 19 823.53 | 0.09 | 19 823.45 | 0.01 |
| | 2–1 | R1 | 18 065.70 | 0.07 | 18 065.68 | 0.05 |
| | 3–0 | R5 | 18 109.66 | 0.04 | 18 109.64 | 0.02 |
| | 3–1 | R6 | 18 107.89 | -0.04 | 18 107.97 | 0.04 |
| | 3–2 | R8 | 18 089.06 | -0.05 | 18 089.10 | -0.01 |
| | 2–2 | R7 | 16 386.78 | 0.05 | 16 386.78 | 0.05 |
| | 2–3 | Q6 | 16 383.63 | 0.05 | 16 383.58 | 0.00 |
| | 3–0 | Q9 | 14 538.55 | 0.05 | 14 538.51 | 0.01 |
| | 3–1 | Q9 | 14 481.26 | 0.09 | 14 481.19 | 0.02 |
| | 3–2 | R4 | 19 576.76 | 0.17 | 19 576.61 | 0.02 |
| | 4–0 | Q7 | 17 842.03 | -0.08 | 17 842.10 | -0.01 |
| | 3–3 | R5 | 16 180.93 | -0.10 | 16 181.08 | 0.05 |
| | 3–4 | Q6 | 14 415.64 | 0.15 | 14 415.48 | -0.01 |
| | 4–3 | P8 | 18 788.84 | -0.05 | 18 788.84 | -0.05 |
| | 4–3 | P3 | 17 401.87 | 0.11 | 17 401.74 | -0.02 |
| | 5–3 | R6 | 17 586.74 | 0.07 | 17 586.69 | 0.02 |
| | 5–4 | Q7 | 14 280.99 | 0.06 | 14 280.94 | 0.01 |
| | 5–2 | Q3 | 20 510.44 | -0.14 | 20 510.57 | -0.01 |
| | 5–3 | Q6 | 18 757.31 | -0.17 | 18 757.49 | 0.01 |
| | 6–4 | Q8 | 18 677.56 | 0.08 | 18 677.49 | 0.01 |
| | 6–6 | Q7 | 18 420.01 | -0.11 | 18 420.10 | -0.02 |
| | 7–6 | Q5 | 16 727.50 | 0.18 | 16 727.38 | 0.06 |
| \(k^3 \Pi_u - a^3 \Sigma_g^+\) | 0–0 | P8 | 21 966.23 | -0.01 | 21 966.21 | -0.03 |
| | 0–1 | Q8 | 22 180.52 | 0.16 | 22 180.39 | 0.03 |
| | 0–2 | R6 | 22 452.89 | 0.17 | 22 452.75 | 0.03 |
| | 0–1 | Q8 | 20 406.67 | -0.04 | 20 406.68 | -0.03 |
| | 3–0 | R3 | 19 613.91 | 0.19 | 19 613.78 | 0.06 |
| | 1–2 | P4 | 20 217.44 | 0.11 | 20 217.32 | -0.01 |
| | 2–3 | R2 | 20 822.53 | 0.21 | 20 822.45 | 0.13 |
| | 1–2 | P4 | 20 320.54 | 0.09 | 20 320.48 | 0.03 |
| | 3–3 | Q6 | 21 592.35 | 0.22 | 21 592.19 | -0.02 |
| | 3–3 | Q4 | 22 761.98 | 0.13 | 22 762.13 | 0.02 |
| \(n^3 \Pi_u - a^3 \Sigma_g^+\) | 1–2 | Q5 | 22 881.68 | -0.05 | 22 881.71 | -0.02 |
| | 2–3 | P3 | 22 670.82 | -0.12 | 22 670.88 | -0.06 |
| \(h^3 \Sigma_u^+ - c^3 \Pi_u\) | 3–3 | P4 | 16 779.23 | -0.09 | 16 779.32 | 0.00 |
| Electronic transition | Band | Line [16] | O-C | This work | O-C |
|-----------------------|------|-----------|-----|-----------|-----|
| $g^{3} \Sigma_g^+ - c^{3} \Pi_u$ | 0–0 | P5 | 16 588.93 | 0.13 | 16 588.87 | 0.07 |
| | 0–1 | P3 | 15 064.96 | –0.18 | 15 065.27 | 0.13 |
| | 1–1 | P4 | 16 502.17 | 0.13 | 16 502.08 | 0.04 |
| | 2–1 | P5 | 17 846.80 | –0.27 | 17 847.07 | 0.00 |
| | 2–2 | P6 | 16 164.95 | 0.22 | 16 164.69 | –0.04 |
| | 3–2 | P4 | 17 652.53 | 0.09 | 17 652.43 | –0.01 |
| | 3–3 | P3 | 17 765.57 | –0.05 | 17 765.67 | 0.05 |
| | 3–3 | P8 | 16 450.63 | 0.09 | 16 450.62 | –0.09 |
| | 3–4 | Q2 | 17 107.09 | –0.07 | 17 107.06 | 0.05 |
| | 2–2 | P3 | 17 200.68 | –0.27 | 17 200.97 | 0.00 |
| | 3–2 | P9 | 16 045.63 | –0.03 | 16 045.64 | –0.02 |
| $i^{3} \Pi_g^+ - c^{3} P_u$ | 0–0 | P11 | 16 902.38 | –0.03 | 16 902.34 | –0.07 |
| | 1–0 | P7 | 18 524.43 | 0.16 | 18 524.27 | 0.00 |
| | 1–1 | Q10 | 17 214.20 | 0.13 | 17 214.14 | 0.07 |
| | 2–1 | Q2 | 18 425.10 | –0.17 | 18 425.19 | –0.08 |
| | 3–3 | P6 | 16 450.63 | 0.08 | 16 450.62 | –0.09 |
| | 2–2 | P10 | 17 431.73 | 0.10 | 17 431.72 | 0.09 |
| | 3–2 | P4 | 18 750.25 | –0.20 | 18 750.51 | 0.06 |
| | 3–3 | P3 | 18 598.78 | 0.13 | 18 598.69 | 0.04 |
| | 3–3 | Q12 | 17 667.66 | 0.00 | 17 667.68 | 0.02 |
| | 2–2 | P14 | 16 369.80 | –0.08 | 16 369.84 | –0.04 |
| | 2–1 | Q3 | 17 071.29 | –0.09 | 17 071.28 | –0.10 |
| | 2–2 | Q9 | 16 988.78 | 0.13 | 16 989.69 | 0.04 |
| | 3–3 | R9 | 17 150.62 | 0.17 | 17 150.53 | 0.08 |
| | 1–0 | P3 | 18 525.88 | 0.22 | 18 525.72 | 0.06 |
| | 2–1 | R1 | 18 451.87 | 0.23 | 18 451.60 | 0.00 |
| | 2–2 | R2 | 18 464.46 | 0.13 | 18 464.34 | 0.01 |
| | 2–2 | P10 | 16 345.66 | –0.04 | 16 345.72 | 0.02 |
| | 2–1 | R4 | 16 864.08 | 0.21 | 16 863.92 | 0.05 |
| | 2–2 | R8 | 16 857.89 | –0.59 | 16 858.46 | –0.02 |
| | 3–2 | R3 | 15 207.72 | 0.05 | 15 207.75 | 0.08 |
| | 3–3 | P3 | 16 517.58 | 0.06 | 16 517.57 | 0.05 |
| | 3–3 | R5 | 16 693.01 | –0.16 | 16 693.13 | –0.04 |
| | 3–3 | Q2 | 16 599.70 | 0.05 | 16 599.70 | 0.05 |
| | 3–3 | Q14 | 16 369.80 | 0.02 | 16 369.84 | –0.02 |
| $j^{3} \Delta_g^+ - c^{3} \Pi_u$ | 0–0 | P13 | 17 309.93 | –0.02 | 17 309.93 | –0.02 |
| | 1–0 | Q12 | 17 667.66 | 0.00 | 17 667.68 | 0.02 |
| | 1–1 | Q2 | 19 060.17 | 0.14 | 19 060.15 | 0.12 |
| | 2–1 | P10 | 17 192.24 | 0.09 | 17 192.26 | 0.04 |
| | 2–2 | Q7 | 17 439.67 | 0.11 | 17 439.65 | 0.09 |
| | 2–2 | R8 | 17 722.82 | –0.04 | 17 722.82 | –0.04 |
| | 2–1 | Q5 | 18 907.85 | –0.11 | 18 907.90 | –0.06 |
| | 2–2 | P9 | 17 081.06 | –0.10 | 17 081.14 | –0.02 |
| $j^{3} \Delta_g^- - c^{3} \Pi_u$ | 0–0 | P14 | 17 182.21 | –0.01 | 17 182.26 | 0.04 |
| | 1–0 | Q13 | 17 564.20 | –0.02 | 17 564.24 | 0.02 |
| | 1–1 | Q4 | 17 654.95 | –0.13 | 17 655.06 | –0.02 |
| | 2–1 | R12 | 17 922.15 | 0.22 | 17 921.87 | –0.06 |
| | 2–2 | P7 | 18 863.60 | 0.26 | 18 863.37 | 0.03 |
| | 3–4 | Q4 | 19 066.14 | –0.18 | 19 066.26 | –0.06 |
| | 1–1 | Q8 | 17 423.59 | 0.10 | 17 423.54 | 0.05 |
| | 2–2 | Q10 | 17 431.73 | –0.09 | 17 431.78 | –0.04 |
| | 3–3 | P4 | 18 786.75 | –0.14 | 18 786.94 | 0.05 |
| | 3–4 | Q4 | 18 903.82 | –0.28 | 18 904.14 | 0.04 |
| | 2–2 | P5 | 17 200.68 | –0.10 | 17 200.72 | –0.06 |
| | 3–3 | P1 | 15 783.87 | –0.25 | 15 784.09 | –0.03 |
| | 3–4 | P4 | 17 107.09 | –0.04 | 17 107.11 | –0.02 |
| | 3–4 | Q2 | 15 692.04 | 0.16 | 15 691.96 | 0.08 |
values (see table 3), this increase of precision in obtaining the account the values of the SD uncertainties of our optimal level value is obtained with much higher precision. Taking into

Figure 7. Empirical function $\Phi(\xi)$ obtained for the final set of all available experimental data (see the text) with RMS errors estimates obtained in the present work by the statistical analysis.

value is obtained with much higher precision. Taking into account the values of the SD uncertainties of our optimal level values (see table 3), this increase of precision in obtaining the shift value is significant.

Optimal values of the rovibronic levels for the triplet electronic states corresponding to principal quantum numbers $n = 2, 3$ of the united atom are listed in table 3. Radiative transitions between those levels are located in the visible part of the spectra, which is most convenient for spectroscopic studies of non-equilibrium gases and plasmas [4, 5]. The expanded version of table 3 including all 1050 optimal level values is presented in [46]. For each rovibronic level we introduced into table 3 the standard deviation of the empirical determination (in brackets), the number of spectral lines $n_v$ which originate or terminate on that level, and the difference $\Delta E$ between energy-level values reported in [16] and those obtained in the present work.

Several interesting things can be seen from table 3.

(1) In many cases the number of the lines, directly connected with a certain level, is high enough for the statistics. In some cases there are very few lines. In these cases the levels are obtained with less accuracy. It is important to stress that the SD uncertainties of empirical determination of optimal level values partly reflect the influence of $n_v$ on the SD values. This is the trend (not straightforward dependence) because there are more factors of influence. The levels with $n_v < 4$ should be considered as unreliable. The SDs of such levels are mainly determined by experimental uncertainties of a few lines directly connected with those levels. Additional experimental studies are needed to obtain more reliable results.

(2) The differences $\Delta E$ are generally less than the value $0.05 \text{ cm}^{-1}$, reported in [16] as the SD uncertainty of the energy levels. This confirms our assumption that the unique SD uncertainty for all the levels declared in [16] is only an upper-limit estimate of the real uncertainties of various levels.

(3) The vast majority of the $\Delta E$ are much higher than SD error bars of our optimal values, which normally are within the range of $0.004 \div 0.03 \text{ cm}^{-1}$ depending on the value of the rotational and vibrational quantum numbers. Thus, the deviations of the data reported in [16] from the optimal level values obtained in the present work are significant.

Currently it is not possible to find and list reasons for those deviations for each and every level, because [16] does not contain information on the details of calculating the common differences in various bands. We may presume that they appeared for the following reasons: errors of reading from photo plates, round-up errors in calculating the wavenumbers from measured wavelengths, lack of deconvolution of blended lines, subjective preferences in eliminating some of the controversial experimental data, some additional assumptions (like neglecting $\Lambda$-doubling for some states), transfer and accumulation of experimental errors in the method of common differences adopted in [16] for wavenumber analysis of separate bands, quite subjective multi-step procedure of the analysis of the band systems. It is clear that for various rovibronic states all these factors may multiply or compensate each other.

Sometimes the nature of the differences $\Delta E$ may be easily recognized. One typical example is illustrated in figure 8, in which the differences $\Delta E$ are shown for rotational levels in the ground vibrational states ($v = 0$) of the $a^3\Sigma_u^+ (d), c^3\Pi_u^-$ (c) and $j^3\Delta_u^-$ (b) electronic states. The error bars represent our estimates (one SD) of the empirical determination of the optimal energy-level values obtained by the pure statistical approach in the present work. One may see that, as already mentioned, quite often the deviations $\Delta E$ are less than $0.05 \text{ cm}^{-1}$, but significantly higher than SD uncertainties of optimal level values (figure 8(d)). In figure 8(b) and (c) one can see interesting behaviour of the deviation $\Delta E$—periodical changes for rotational levels with odd and even values of $N$ (for uncoupled levels of ortho- and para-molecules). A similar

| Reference  | [16] | [32] | [31] | [28] | [34] | [33] | [29] | [35] | P.W. Total |
|------------|------|------|------|------|------|------|------|------|-----------|
| Reported   | 3117 | 350  | 285  | 81   | 37   | 83   | 3    | 1    | 125       | 4082      |
| Usable     | 3053 | 350  | 285  | 81   | 37   | 12   | 3    | 1    | 125       | 3947      |
| Excluded   | 179  | 18   | 18   | 5    | 4    | 10   | 0    | 0    | 0         | 234       |
| Used       | 2874 | 332  | 267  | 76   | 33   | 2    | 3    | 1    | 125       | 3713      |
| %          | 94.1 | 94.9 | 93.7 | 93.8 | 89.2 | 16.7 | 100  | 100  | 100       | 94.1      |
Table 3. Optimal values $E_{mN}$ of rovibronic energy levels (in cm$^{-1}$) for various triplet electronic states of the D$_2$ molecule obtained in the present work. The uncertainties of the $E_{mN}$ value determination (one SD) are shown in brackets in units of least significant digit. $n_v$—the number of various spectral lines directly connected with a particular level. $\Delta E$ is the difference between energy-level values obtained in the present work and those reported in [16].

| $N$ | $E_{mN}$ | $n_v$ | $\Delta E$ | $E_{mN}$ | $n_v$ | $\Delta E$ | $E_{mN}$ | $n_v$ | $\Delta E$ |
|-----|----------|-------|-----------|----------|-------|-----------|----------|-------|-----------|
| 0   | 1814.908(5) | 21  | 0 | 5601.726(6) | 26  | −0.016  |
| 1   | 1847.36(4)  | 55   | −0.014 | 3592.036(8) | 56   | −0.016  |
| 2   | 1912.172(5) | 66   | −0.012 | 3654.573(5) | 70   | −0.003  |
| 3   | 2009.042(8) | 63   | −0.002 | 3748.034(8) | 64   | −0.004  |
| 4   | 2137.628(6) | 57   | −0.008 | 3872.103(6) | 64   | −0.003  |
| 5   | 2297.385(9) | 46   | −0.005 | 4026.245(9) | 49   | −0.005  |
| 6   | 2487.748(6) | 42   | 0.002 | 4209.894(7) | 44   | 0.006   |
| 7   | 2707.967(10) | 27   | −0.007 | 4422.319(10) | 25   | 0.001   |
| 8   | 2957.220(7) | 27   | 0.020 | 4662.756(7) | 22   | 0.014   |
| 9   | 3234.634(11) | 21   | −0.004 | 4930.308(11) | 14   | −0.008  |
| 10  | 3539.206(8) | 15   | 0.024 | 5224.035(9) | 10   | 0.015   |
| 11  | 3869.902(14) | 6   | 0.008 | 5542.94(2) | 4   | −0.010  |
| 12  | 4225.651(16) | 3   | 0.069 | 5885.903(3) | 3   | 0.010   |
| 13  | 4605.20(2)  | 3   | −0.010 | 6251.85(3) | 2   | 0.040   |
| 14  | 5007.43(3)   | 3   | −0.050 | 6639.59(3) | 2   | 0.020   |
| 15  | 5431.37(3)  | 3   | 0.010 | 7048.04(3) | 2   | 0.030   |
| 16  | 5875.164(6) | 2   | 0.050 | 7475.59(17) | 2   | 0.050   |
| 17  | 6338.324(2) | 2   | 0.040 |                     |      |         |
| 18  | 6818.594(9) | 2   | 0.080 |                     |      |         |

| $N$ | $E_{mN}$ | $n_v$ | $\Delta E$ | $E_{mN}$ | $n_v$ | $\Delta E$ | $E_{mN}$ | $n_v$ | $\Delta E$ |
|-----|----------|-------|-----------|----------|-------|-----------|----------|-------|-----------|
| 0   | 6851.077(6) | 21   | −0.007 | 8398.070(7) | 14   | −0.000  |
| 1   | 6880.190(9) | 48   | 0.000 | 8426.100(9) | 37   | 0.000   |
| 2   | 6938.313(6) | 57   | −0.013 | 8482.065(6) | 37   | 0.015   |
| 3   | 7025.178(9) | 49   | 0.002 | 8565.721(9) | 35   | −0.011  |
| 4   | 7140.470(6) | 54   | −0.020 | 8676.731(6) | 40   | 0.019   |
| 5   | 7283.696(9) | 36   | 0.004 | 8814.632(9) | 31   | −0.012  |
| 6   | 7454.309(6) | 32   | −0.009 | 8978.894(7) | 27   | 0.016   |
| 7   | 7651.638(10) | 17   | 0.012 | 9168.832(11) | 13   | −0.012  |
| 8   | 7874.926(8) | 10   | −0.016 | 9383.741(8) | 11   | 0.029   |
| 9   | 8122.780(18) | 5   | 0.010 | 9622.02(3) | 1   | 0.030   |
| 10  | 8395.992(2) | 5   | 0.040 | 9884.34(4) | 1   | 0.040   |
| 11  | 8691.85(6)  | 2   | −0.030 |                     |      |         |
| 12  | 9006.99(7)  | 2   | −0.010 |                     |      |         |
| 13  | 9189.89(6)  | 2   |         |                     |      |         |

| $N$ | $E_{mN}$ | $n_v$ | $\Delta E$ | $E_{mN}$ | $n_v$ | $\Delta E$ | $E_{mN}$ | $n_v$ | $\Delta E$ |
|-----|----------|-------|-----------|----------|-------|-----------|----------|-------|-----------|
| 0   | 11299.845(16) | 6   | −0.045 | 12655.467(18) | 5   | −0.007  |
| 1   | 11325.784(11) | 18   | −0.004 | 12680.356(12) | 12   | −0.036  |
| 2   | 11377.500(8) | 18   | 0.000 | 12729.972(9) | 13   | −0.052  |
| 3   | 11454.821(12) | 14   | −0.010 | 12804.129(13) | 14   | −0.059  |
| 4   | 11557.399(9) | 14   | −0.009 | 12902.503(9) | 13   | −0.143  |
| 5   | 11684.766(13) | 8   | −0.036 | 13024.059(14) | 4   | −0.049  |
| 6   | 11836.493(10) | 7   | −0.033 | 13170.42(5) | 2   | −0.000  |
| 7   | 12011.941(19) | 3   | −0.051 |                     |      |         |
| 8   | 12210.76(3)  | 2   | −0.060 |                     |      |         |
| 9   | 1257.802(2)  | 2   | 0.010 |                     |      |         |
| 10  |                     |      |         |                     |      |         |
| 11  | 11594.7(3)  | 2   |         |                     |      |         |
| 12  | 11894.2(3)  | 2   |         |                     |      |         |
Table 3. (Continued).

\[
\begin{array}{cccccc}
\hline
v = 9 & & & & & v = 10 \\
N & E_{\nu N} & n_v & \Delta E & E_{\nu N} & n_v & \Delta E \\
0 & 13947.39(4) & 1 & 0.000 & & & \\
1 & 13971.35(15) & 4 & -0.035 & & & \\
2 & 14018.88(12) & 4 & -0.013 & & & \\
3 & 14089.86(15) & 3 & 0.024 & & & \\
4 & 14184.03(13) & 4 & -0.088 & & & \\
5 & 14300.93(17) & 3 & 0.017 & & & \\
6 & 14440.11(13) & 1 & 0.028 & & & \\
\hline
\end{array}
\]

\[
\begin{array}{cccccc}
\hline
v = 1 & & & & & v = 2 \\
N & E_{\nu N} & n_v & \Delta E & E_{\nu N} & n_v & \Delta E \\
0 & & & & & & \\
1 & -132.611(18) & 12 & 0.021 & & & \\
2 & -71.553(12) & 17 & -0.007 & & & \\
3 & 19.675(15) & 20 & -0.015 & & & \\
4 & 140.787(11) & 19 & -0.027 & & & \\
5 & 291.332(16) & 17 & -0.002 & & & \\
6 & 470.743(13) & 16 & -0.083 & & & \\
7 & 678.29(2) & 11 & 0.000 & & & \\
8 & 913.480(17) & 8 & -0.090 & & & \\
9 & 1175.21(2) & 7 & 0.010 & & & \\
10 & 1462.81(2) & 7 & -0.130 & & & \\
11 & 1775.19(3) & 6 & 0.040 & & & \\
12 & 2111.33(4) & 4 & -0.120 & & & \\
13 & 2470.34(5) & 3 & 0.080 & & & \\
14 & 2851.05(7) & 5 & 0.100 & & & \\
15 & 3252.43(6) & 1 & 0.080 & & & \\
\hline
v = 3 & & & & & v = 4 \\
N & E_{\nu N} & n_v & \Delta E & E_{\nu N} & n_v & \Delta E \\
1 & 4727.022(9) & 7 & 0.108 & & & \\
2 & 4782.112(9) & 10 & 0.038 & & & \\
3 & 4864.307(13) & 11 & 0.073 & & & \\
4 & 4973.456(10) & 12 & 0.054 & & & \\
5 & 5109.097(16) & 9 & 0.093 & & & \\
6 & 5270.732(15) & 5 & 0.028 & & & \\
7 & 5457.24(2) & 5 & -0.032 & & & \\
8 & 5669.46(2) & 4 & 0.030 & & & \\
9 & 5905.35(5) & 1 & -0.020 & & & \\
10 & 6164.52(3) & 1 & 0.080 & & & \\
\hline
v = 5 & & & & & v = 6 \\
N & E_{\nu N} & n_v & \Delta E & E_{\nu N} & n_v & \Delta E \\
1 & 9090.44(2) & 1 & - & & & \\
2 & 9099.75(17) & 1 & - & & & \\
3 & 9173.43(2) & 1 & - & & & \\
4 & 9271.249(18) & 1 & - & & & \\
\hline
v = 1 & & & & & v = 2 \\
N & E_{\nu N} & n_v & \Delta E & E_{\nu N} & n_v & \Delta E \\
1 & -132.586(12) & 22 & -0.004 & & & \\
2 & -71.584(14) & 26 & 0.014 & & & \\
3 & 19.662(11) & 28 & -0.032 & & & \\
4 & 140.727(15) & 27 & -0.026 & & & \\
5 & 291.217(12) & 24 & -0.087 & & & \\
6 & 470.542(16) & 19 & -0.022 & & & \\
7 & 678.114(15) & 15 & -0.094 & & & \\
8 & 913.12(2) & 10 & 0.022 & & & \\
\hline
\end{array}
\]
Table 3. (Continued).

| \(N\) | \(E_{n\nu}\) | \(n\nu\) | \(\Delta E\) | \(E_{n\nu}\) | \(n\nu\) | \(\Delta E\) | \(E_{n\nu}\) | \(n\nu\) | \(\Delta E\) |
|-------|-------------|----------|------------|-------------|----------|------------|-------------|----------|------------|
| \(v = 0\) | \(v = 1\) | \(v = 2\) | \(v = 3\) | \(v = 4\) | \(v = 5\) |
| 9 | 1174.80(2) | 8 | 0.120 | 2812.35(2) | 5 | 0.030 | 4388.78(6) | 3 | 0.200 |
| 10 | 1462.24(2) | 5 | 0.010 | 3090.18(6) | 2 | 0.330 | 4657.07(4) | 5 | 0.080 |
| 11 | 1774.48(3) | 6 | 0.170 | 3345.84(6) | 2 | 0.110 |          |            |            |
| 12 | 2110.45(4) | 4 | 0.010 |          |            |            |          |            |            |
| 13 | 2469.04(7) | 3 | 0.120 |          |            |            |          |            |            |
| 14 | 2849.68(6) | 2 | 0.080 |          |            |            |          |            |            |
| 15 | 3250.67(8) | 2 | 0.100 |          |            |            |          |            |            |
| \(v = 3\) | \(v = 4\) | \(v = 5\) | \(v = 6\) | \(v = 7\) |
| 1 | 4727.07(7) | 14 | 0.052 | 6226.42(10) | 7 | 0.081 | 7667.29(13) | 2 | 0.053 |
| 2 | 4782.08(12) | 16 | 0.109 | 6279.55(10) | 9 | 0.007 | 7718.54(13) | 2 | 0.016 |
| 3 | 4864.44(8) | 15 | 0.104 | 6359.07(11) | 7 | 0.133 | 7795.17(10) | 1 | 0.008 |
| 4 | 4973.60(14) | 9 | 0.084 | 6464.40(14) | 8 | 0.079 | 8023.16(16) | 1 | 0.000 |
| 5 | 5109.36(18) | 10 | 0.092 | 6595.37(13) | 6 | 0.009 |          |            |            |
| 6 | 5271.03(2) | 5 | 0.110 | 6751.56(18) | 4 | 0.059 |          |            |            |
| 7 | 5458.14(18) | 7 | 0.035 |          |            |            |          |            |            |
| 8 | 5670.02(3) | 5 | 0.030 |          |            |            |          |            |            |
| 9 | 5905.61(2) | 3 | 0.070 |          |            |            |          |            |            |
| \(v = 6\) | \(v = 7\) |
| 0 | 2071.83(17) | 1 | 0.037 | 10376.62(2) | 1 | 0.083 |          |            |            |
| 1 | 2010.32(16) | 2 | 0.100 | 2061.75(12) | 2 | 0.099 | 2036.48(2) | 2 | 0.143 |
| 2 | 2010.10(17) | 2 | 0.053 | 2070.79(8) | 3 | 0.032 | 2012.98(10) | 4 | 0.088 |
| 3 | 2024.87(15) | 3 | 0.113 | 2152.92(9) | 13 | 0.061 | 2109.37(13) | 4 | 0.083 |
| 4 | 2036.07(13) | 2 | 0.063 | 2181.83(9) | 3 | 0.051 | 2303.28(13) | 3 | 0.009 |
| 5 |            |    |        | 2342.23(16) | 2 | 0.059 |          |            |            |

(1s2p\(\sigma\)
\(2\Sigma\)_0^+ \(1s2p\(\sigma\)
\(2\Pi\)_0^+ \(1s2p\(\sigma\)
\(2\Pi\)_2^+ \(1s2p\(\sigma\)
\(3\Sigma\)_2^+ \(1s3p\(\sigma\)
\(3\Sigma\)_0^+ \(1s3p\(\sigma\)
\(3\Sigma\)_2^+ \(1s3p\(\sigma\)
\(3\Sigma\)_2^+ \(1s3p\(\sigma\)

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Table 3. (Continued).

\[(1\sigma 3\rho \tau)d^3\Sigma_u^+\]

| \(N\) | \(E_{\text{mol}}\) | \(n\) | \(\nu\) | \(\Delta E\) | \(E_{\text{mol}}\) | \(n\) | \(\nu\) | \(\Delta E\) | \(E_{\text{mol}}\) | \(n\) | \(\nu\) | \(\Delta E\) |
|------|-----------------|------|-------|--------|-----------------|------|-------|--------|-----------------|------|-------|--------|
| 17   | 15 428.58(4)    | 2    | 0.050 |        | 16 763.73(4)   | 4    | 0.060 |        | 18 408.097(10)| 10   | -0.002|        |
| 18   | 15 832.13(3)    | 2    | 0.020 |        | 17 150.23(4)   | 2    | 0.040 |        |                  |      |        |        |
| 19   | 16 249.09(4)    | 2    | 0.060 |        | 17 549.32(5)   | 1    | 0.080 |        |                  |      |        |        |
| 20   | 16 624.556(14)  | 4    | 0.006 |        | 17 666.052(10)| 15   | -0.002|        |                  |      |        |        |
| 21   | 17 566.118(4)   | 7    | 0.018 |        | 17 820.186(7)  | 13   | 0.004 |        |                  |      |        |        |
| 22   | 17 748.977(11)  | 10   | 0.007 |        | 17 994.639(11)| 12   | -0.008|        |                  |      |        |        |
| 23   | 17 952.546(8)   | 9    | 0.014 |        | 18 188.800(8)  | 12   | 0.000 |        |                  |      |        |        |
| 24   | 18 176.041(12)  | 3    | -0.011|        | 18 402.006(14)| 5    | -0.036|        |                  |      |        |        |
| 25   | 17 418.674(9)   | 4    | 0.016 |        | 18 633.901(11)| 3    | -0.001|        |                  |      |        |        |
| 26   | 17 679.65(2)    | 1    | 0.010 |        |                  |      |        |        |                  |      |        |        |
| 27   | 17 958.06(3)    | 1    | 0.030 |        |                  |      |        |        |                  |      |        |        |
| 28   | 19 546.641(11)  | 7    | -0.001|        | 20 605.338(10)| 8    | -0.008|        | 21 575.310(13)| 9    | -0.030|        |
| 29   | 19 567.047(7)   | 16   | -0.007|        | 20 624.515(6)  | 15   | -0.015|        | 21 593.153(7)  | 19   | -0.013|        |
| 30   | 19 607.728(10)  | 16   | -0.008|        | 20 662.787(9)  | 16   | -0.017|        | 21 628.745(10)| 19   | -0.005|        |
| 31   | 19 668.569(7)   | 16   | 0.001 |        | 20 720.289(6)  | 14   | -0.009|        | 21 681.957(7)| 20   | -0.007|        |
| 32   | 19 749.319(10)  | 16   | -0.019|        | 20 795.613(9)  | 12   | -0.023|        | 21 752.568(11)| 18   | -0.038|        |
| 33   | 19 849.642(8)   | 15   | -0.012|        | 20 889.773(6)  | 14   | -0.003|        | 21 840.510(8)  | 16   | -0.010|        |
| 34   | 19 969.098(11)  | 14   | -0.028|        | 21 001.748(10)| 9    | -0.008|        | 21 946.349(12)| 7    | -0.029|        |
| 35   | 20 107.185(7)   | 12   | 0.005 |        | 21 131.071(7)  | 9    | -0.001|        | 22 074.088(14)| 2    | 0.002 |        |
| 36   | 20 263.354(13)  | 8    | 0.006 |        |                  |      |        |        |                  |      |        |        |
| 37   | 21 440.901(17)  | 1    | 0.029 |        |                  |      |        |        |                  |      |        |        |
| 38   | 22 442.451(11)  | 8    | -0.011|        | 23 181.37(2)    | 4    | 0.004 |        |                  |      |        |        |
| 39   | 22 458.482(7)   | 17   | -0.002|        | 23 195.302(13)| 11   | -0.022|        |                  |      |        |        |
| 40   | 22 490.446(10)  | 16   | -0.006|        | 23 223.064(16)| 10   | -0.024|        |                  |      |        |        |
| 41   | 22 538.192(7)   | 18   | -0.002|        | 23 264.357(13)| 11   | -0.017|        |                  |      |        |        |
| 42   | 22 601.388(10)  | 18   | -0.038|        | 23 318.792(19)| 6    | -0.042|        |                  |      |        |        |
| 43   | 22 679.660(7)   | 14   | -0.040|        | 23 385.89(2)   | 3    | -0.030|        |                  |      |        |        |
| 44   | 22 772.422(11)  | 10   | -0.022|        |                  |      |        |        |                  |      |        |        |
| 45   | 22 879.153(11)  | 3    | 0.037 |        |                  |      |        |        |                  |      |        |        |

\[(1\sigma 3\rho \tau)\]
Table 3. (Continued).

(1s\,3\,p\,\pi)d3\,\Pi_u^-

\begin{tabular}{cccccc}
\hline
\hline

| $v=0$ | $E_{\nu N}$ & $E_{\nu}$ & $\Delta E$ & $n_\nu$ & $\Delta$ & $E_{\nu N}$ & $E_{\nu}$ & $\Delta E$ & $n_\nu$ & $\Delta$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 10 | 18 250.742(14) & 2 & 0.008 & & & & & & & |
| 11 | & & & & & & & & & |
| 12 | 18 881.99(2) & 1 & −0.040 & & & & & & & |
| 13 | 19 231.13(2) & 1 & −0.020 & & & & & & & |
| 14 | 19 601.19(2) & 1 & −0.050 & & & & & & & |
| 15 | 19 991.19(3) & 1 & 0.010 & & & & & & & |
| 16 | 20 399.80(4) & 1 & 0.070 & & & & & & & |
| 17 | 20 825.83(4) & 1 & 0.010 & & & & & & & |
| 18 | 21 267.81(4) & 1 & 0.080 & & & & & & & |
| $v=3$ | $E_{\nu N}$ & $n_\nu$ & $\Delta E$ & $E_{\nu N}$ & $E_{\nu}$ & $\Delta E$ & $n_\nu$ & $\Delta$ & $E_{\nu N}$ & $E_{\nu}$ & $\Delta E$ & $n_\nu$ & $\Delta$ |
| 7 | 21 533.645(12) & 9 & 0.005 & & & & & & & |
| 8 | 21 396.902(9) & 8 & −0.002 & & & & & & & |
| 9 | 21 476.477(12) & 8 & −0.007 & & & & & & & |
| 10 | 21 582.13(13) & 8 & −0.008 & & & & & & & |
| 11 | 24 713.423(13) & 7 & −0.013 & & & & & & & |
| 12 | 21 869.803(9) & 8 & 0.057 & & & & & & & |
| 13 | 22 050.667(15) & 4 & −0.007 & & & & & & & |
| 14 | 22 255.379(12) & 4 & 0.011 & & & & & & & |
| 15 | 22 483.185(19) & 2 & −0.035 & & & & & & & |
| 16 | 22 733.258(15) & 3 & 0.002 & & & & & & & |
| 17 | 23 004.67(5) & 2 & −0.050 & & & & & & & |
| 18 | 23 403.97(6) & 2 & 0.010 & & & & & & & |
| 19 | 23 603.42(6) & 1 & 0.030 & & & & & & & |
| 20 | 23 930.61(6) & 1 & 0.090 & & & & & & & |
| $v=6$ | $E_{\nu N}$ & $n_\nu$ & $\Delta E$ & $E_{\nu N}$ & $E_{\nu}$ & $\Delta E$ & $n_\nu$ & $\Delta$ & $E_{\nu N}$ & $E_{\nu}$ & $\Delta E$ & $n_\nu$ & $\Delta$ |
| 11 | 25 443.364(10) & 9 & −0.004 & & & & & & & |
| 12 | 25 490.706(7) & 9 & −0.006 & & & & & & & |
| 13 | 25 561.485(11) & 8 & −0.005 & & & & & & & |
| 14 | 25 655.396(7) & 8 & −0.006 & & & & & & & |
| 15 | 25 772.049(11) & 9 & −0.019 & & & & & & & |
| 16 | 25 910.990(8) & 7 & −0.020 & & & & & & & |
| 17 | 26 071.762(19) & 3 & −0.082 & & & & & & & |
| 18 | 26 253.93(3) & 2 & −0.080 & & & & & & & |
| $v=9$ | $E_{\nu N}$ & $n_\nu$ & $\Delta E$ & $E_{\nu N}$ & $E_{\nu}$ & $\Delta E$ & $n_\nu$ & $\Delta$ & $E_{\nu N}$ & $E_{\nu}$ & $\Delta E$ & $n_\nu$ & $\Delta$ |
| 19 | 29 023.33(5) & 4 & −0.040 & & & & & & & |
| 20 | 29 064.97(4) & 4 & 0.010 & & & & & & & |
| 21 | 29 127.43(6) & 2 & −0.170 & & & & & & & |
| 22 | 29 209.88(5) & 2 & −0.170 & & & & & & & |
| 23 | 29 313.31(7) & 1 & −0.050 & & & & & & & |
| $v=0$ | $E_{\nu N}$ & $n_\nu$ & $\Delta E$ & $E_{\nu N}$ & $E_{\nu}$ & $\Delta E$ & $n_\nu$ & $\Delta$ & $E_{\nu N}$ & $E_{\nu}$ & $\Delta E$ & $n_\nu$ & $\Delta$ |
| 1 | 16 695.884(8) & 8 & −0.014 & & & & & & & |
| 2 | 16 755.61(11) & 8 & −0.011 & & & & & & & |
| 3 | 16 844.912(9) & 8 & −0.002 & & & & & & & |
| 4 | 16 963.424(13) & 5 & −0.004 & & & & & & & |
| 5 | 17 110.685(9) & 4 & 0.005 & & & & & & & |
| 6 | 17 286.063(13) & 4 & −0.013 & & & & & & & |
| 7 | 17 488.918(10) & 4 & 0.002 & & & & & & & |
| 8 | 17 718.45(9) & 4 & 0.023 & & & & & & & |
| 9 | 19 973.80(12) & 3 & 0.030 & & & & & & & |

\end{tabular}
Table 3. (Continued).

\( (1s\sigma^3p\pi)d^3\Pi_u^+ \)

| \( v = 0 \) | \( v = 1 \) | \( v = 2 \) |
|----------|----------|----------|
| \( N \) | \( E_{eN} \) | \( n_\nu \) | \( \Delta E \) | \( E_{eN} \) | \( n_\nu \) | \( \Delta E \) | \( E_{eN} \) | \( n_\nu \) | \( \Delta E \) |
| 10 | 18 254.078(18) | 3 | -0.048 | 21 306.503(13) | 3 | -0.023 |
| 11 | 18 557.648(15) | 2 | -0.078 | 21 588.485(18) | 1 | 0.015 |
| 12 | 18 885.46(2) | 1 | -0.050 | 21 891.41(3) | 1 | -0.010 |
| \( v = 3 \) | \( v = 4 \) |
| \( N \) | \( E_{eN} \) | \( n_\nu \) | \( \Delta E \) | \( E_{eN} \) | \( n_\nu \) | \( \Delta E \) | \( E_{eN} \) | \( n_\nu \) | \( \Delta E \) |
| 1 | 21 343.795(7) | 15 | -0.005 | 22 769.695(7) | 14 | -0.015 |
| 2 | 21 397.294(11) | 14 | 0.006 | 22 821.398(10) | 15 | 0.002 |
| 3 | 21 477.206(7) | 16 | 0.004 | 22 898.632(7) | 15 | -0.012 |
| 4 | 21 583.081(11) | 14 | -0.001 | 23 000.957(10) | 16 | -0.007 |
| 5 | 21 714.214(8) | 14 | 0.006 | 23 127.895(7) | 15 | -0.005 |
| 6 | 21 868.935(14) | 5 | -0.025 | 23 278.629(11) | 14 | 0.001 |

\( (1s\sigma^3d\pi)g^3\Sigma_g^+ \)

| \( v = 0 \) | \( v = 1 \) | \( v = 2 \) |
|----------|----------|----------|
| \( N \) | \( E_{eN} \) | \( n_\nu \) | \( \Delta E \) | \( E_{eN} \) | \( n_\nu \) | \( \Delta E \) | \( E_{eN} \) | \( n_\nu \) | \( \Delta E \) |
| 1 | 16 716.76(3) | 2 | 0.040 | 18 225.643(18) | 1 | 0.017 | 19 649.58(3) | 2 | 0.030 |
| 2 | 16 731.26(2) | 5 | 0.009 | 18 242.564(13) | 6 | 0.046 | 19 662.30(2) | 4 | 0.070 |
| 3 | 16 761.132(14) | 9 | -0.022 | 18 269.116(9) | 9 | 0.034 | 19 690.552(19) | 6 | 0.045 |
| 4 | 16 809.506(19) | 7 | -0.006 | 18 315.063(14) | 8 | 0.041 | 19 805.556(18) | 6 | 0.054 |
| 5 | 16 974.92(2) | 4 | -0.030 | 18 475.553(13) | 8 | 0.027 | 19 896.30(2) | 6 | 0.053 |
| 6 | 17 095.52(2) | 4 | -0.060 | 18 592.497(12) | 7 | -0.007 | 20 010.457(10) | 6 | 0.083 |
| 7 | 17 242.11(2) | 4 | -0.001 | 18 734.375(16) | 4 | 0.025 | 20 148.302(14) | 5 | 0.048 |
| 8 | 17 414.75(2) | 3 | -0.100 | 18 901.123(3) | 3 | -0.003 | 20 309.845(11) | 3 | -0.015 |
| 9 | 17 612.97(3) | 2 | 0.020 | 19 093.108(17) | 1 | 0.094 | 20 494.868(17) | 3 | 0.092 |
| 10 | 17 836.31(2) | 3 | -0.130 | 19 309.527(17) | 1 | 0.025 | 20 702.83(7) | 2 | – |
| 11 | 18 084.04(3) | 2 | 0.010 | 19 333.73(6) | 1 | – |
| 12 | 18 355.33(3) | 2 | -0.180 | 19 333.73(6) | 1 | – |
| 13 | 18 649.99(9) | 2 | 0.010 | 19 333.73(6) | 1 | – |
| 14 | 18 964.55(7) | 1 | – | 19 333.73(6) | 1 | – |
| 15 | 19 300.83(6) | 1 | – | 19 333.73(6) | 1 | – |
| 16 | 19 656.91(8) | 1 | – | 19 333.73(6) | 1 | – |

\( (1s\sigma^3d\pi)i^3\Pi_g^- \)

| \( v = 0 \) | \( v = 1 \) | \( v = 2 \) |
|----------|----------|----------|
| \( N \) | \( E_{eN} \) | \( n_\nu \) | \( \Delta E \) | \( E_{eN} \) | \( n_\nu \) | \( \Delta E \) | \( E_{eN} \) | \( n_\nu \) | \( \Delta E \) |
| 0 | 1 16 968.914(17) | 4 | -0.004 | 18 497.025(19) | 5 | 0.025 | 19 952.756(14) | 6 | 0.034 |
| 1 | 17 017.47(2) | 5 | -0.032 | 18 545.33(2) | 9 | 0.076 | 20 000.436(15) | 9 | 0.124 |
| 2 | 17 091.044(17) | 5 | -0.014 | 18 618.163(16) | 8 | 0.017 | 20 072.116(12) | 8 | 0.054 |
| 3 | 17 190.22(2) | 5 | 0.007 | 18 715.69(2) | 7 | 0.074 | 20 167.775(15) | 7 | 0.055 |

20
Table 3. (Continued).

\[(1s\sigma 3d\pi)^3\Pi_g^−\]

\[\begin{array}{cccccc}
\hline
v &=& 0 & v &=& 1 & v &=& 2 \\
\hline
N & E_{\nu N} & n\nu & \Delta E & E_{\nu N} & n\nu & \Delta E & E_{\nu N} & n\nu & \Delta E \\
\hline
\hline
5 & 17 315.208(16) & 4 & −0.068 & 18 838.130(16) & 7 & 0.020 & 20 287.31(2) & 4 & 0.190 \\
6 & 17 466.29(2) & 5 & −0.034 & 18 985.45(2) & 5 & 0.024 & 20 430.99(3) & 2 & 0.110 \\
7 & 17 643.211(17) & 4 & −0.091 & 19 157.50(2) & 4 & 0.010 & 20 598.47(4) & 2 & 0.010 \\
8 & 17 845.71(2) & 4 & −0.000 & 19 355.99(2) & 4 & 0.030 & 20 789.05(7) & 1 & 0.060 \\
9 & 18 073.46(2) & 4 & −0.120 & 19 574.38(2) & 3 & 0.010 & 21 002.86(6) & 2 & −0.500 \\
10 & 18 325.64(3) & 3 & 0.010 & 19 818.25(5) & 1 & 0.040 & & & \\
11 & 18 601.48(3) & 3 & −0.140 & 20 084.73(5) & 2 & 0.110 & & & \\
12 & 18 900.26(4) & 3 & 0.060 & & & & & & \\
13 & 19 220.93(6) & 2 & −0.210 & & & & & & \\
14 & 19 562.52(5) & 1 & 0.080 & & & & & & \\
15 & 19 923.94(7) & 1 & − & & & & & & \\
\hline
\end{array}\]

\[(1s\sigma 3d\pi)^3\Pi_g^+\]

\[\begin{array}{cccccc}
\hline
v &=& 3 & v &=& 4 \\
\hline
N & E_{\nu N} & n\nu & \Delta E & E_{\nu N} & n\nu & \Delta E \\
\hline
\hline
1 & 21 335.02(2) & 2 & 0.050 & 22 626.81(3) & 2 & 0.140 \\
2 & 21 381.83(4) & 2 & 0.130 & 22 689.88(4) & 1 & 0.100 \\
3 & 21 452.060(17) & 3 & 0.030 & 22 755.33(4) & 1 & 0.120 \\
4 & 21 545.60(2) & 2 & 0.078 & 22 846.55(4) & 1 & 0.070 \\
5 & 21 662.35(2) & 2 & 0.070 & & & & & \\
6 & 21 802.26(3) & 3 & −0.060 & & & & & \\
7 & 21 964.76(2) & 3 & 0.030 & & & & & \\
8 & 22 148.61(4) & 1 & −0.030 & & & & & \\
9 & 22 351.80(3) & 1 & 0.020 & & & & & \\
\hline
\end{array}\]

\[(1s\sigma 3d\delta)^3\Delta_g^-\]

\[\begin{array}{cccccc}
\hline
v &=& 0 & v &=& 1 & v &=& 2 \\
\hline
N & E_{\nu N} & n\nu & \Delta E & E_{\nu N} & n\nu & \Delta E & E_{\nu N} & n\nu & \Delta E \\
\hline
\hline
1 & 16 998.00(2) & 4 & 0.024 & 18 539.50(2) & 5 & 0.040 & 20 033.06(2) & 5 & 0.070 \\
2 & 17 086.474(17) & 5 & −0.014 & 18 617.862(19) & 6 & 0.008 & 20 130.70(3) & 3 & 0.080 \\
3 & 17 202.627(19) & 5 & −0.007 & 18 725.790(19) & 7 & 0.010 & 20 254.70(3) & 5 & 0.040 \\
4 & 17 343.627(15) & 6 & −0.047 & 18 860.377(15) & 7 & 0.033 & 20 403.22(4) & 3 & −0.030 \\
5 & 17 508.18(2) & 4 & −0.026 & 19 019.62(2) & 7 & 0.048 & 20 597.14(5) & 1 & 0.050 \\
6 & 17 695.856(15) & 5 & −0.086 & 19 202.388(17) & 7 & −0.018 & 20 795.15(5) & 1 & 0.140 \\
7 & 17 906.63(2) & 4 & −0.011 & 19 407.97(2) & 6 & −0.044 & 21 037.01(4) & 1 & 0.080 \\
8 & 18 140.58(2) & 3 & −0.110 & 19 635.73(2) & 5 & 0.030 & 21 258.76(6) & 1 & − \\
9 & 18 397.46(2) & 3 & 0.010 & & & & & & \\
10 & 18 676.88(5) & 2 & 0.000 & & & & & & \\
11 & 18 978.67(4) & 1 & 0.040 & & & & & & \\
\hline
\end{array}\]
Table 3. (Continued).

\[
\begin{array}{cccccc}
\text{\textit{(1s\sigma 3d\delta)j}} & \Delta E & \text{\textit{v = 0}} & \Delta E & \text{\textit{v = 1}} & \Delta E & \text{\textit{v = 2}} \\
N & E_{\text{envN}} & n_\nu & \Delta E & E_{\text{envN}} & n_\nu & \Delta E & E_{\text{envN}} & n_\nu & \Delta E \\
8 & 18.450.74(2) & 3 & 0.000 & 19.983.01(3) & 2 & -0.010 & 21.452.03(2) & 3 & 0.130 \\
9 & 18.721.33(2) & 3 & -0.110 & 20.240.85(2) & 3 & 0.010 & 21.691.00(8) & 1 & -0.450 \\
10 & 19.016.08(3) & 3 & 0.020 & 20.522.00(6) & 3 & -0.420 & 21.963.82(5) & 1 & 0.080 \\
11 & 19.333.82(3) & 2 & -0.150 & 20.779.34(6) & 1 & 0.110 & & & \\
12 & 19.673.28(4) & 2 & 0.050 & & & & & & \\
13 & 20.033.26(6) & 3 & 0.100 & & & & & & \\
14 & 20.413.33(5) & 3 & 0.080 & & & & & & \\
15 & 20.810.64(7) & 2 & 0.100 & & & & & & \\
\end{array}
\]

\[
\begin{array}{cccccc}
\text{\textit{(1s\sigma 3d\delta)j}} & \Delta E & \text{\textit{v = 3}} & \Delta E & \text{\textit{v = 4}} & \Delta E & \text{\textit{v = 5}} \\
N & E_{\text{envN}} & n_\nu & \Delta E & E_{\text{envN}} & n_\nu & \Delta E & E_{\text{envN}} & n_\nu & \Delta E \\
2 & 21.971.43(3) & 4 & 0.087 & 23.370.57(3) & 3 & 0.070 & 24.709.17(5) & 2 & 0.070 \\
3 & 22.054.90(3) & 4 & 0.087 & 23.448.57(3) & 3 & 0.090 & & & \\
4 & 22.165.21(16) & 4 & 0.080 & 23.551.78(4) & 2 & 0.060 & & & \\
5 & 22.301.69(15) & 2 & 0.041 & 23.679.34(4) & 2 & 0.030 & & & \\
6 & 22.463.39(2) & 2 & 0.040 & 23.830.38(4) & 2 & 0.060 & & & \\
7 & 22.649.12(18) & 3 & 0.032 & & & & & & \\
8 & 22.858.24(3) & 3 & -0.020 & & & & & & \\
9 & 23.089.12(2) & 3 & 0.060 & & & & & & \\
\end{array}
\]

Small alternations of the deviations $\Delta E$ (less than 0.1 cm$^{-1}$) are connected with the difference in the values of the shift between levels of ortho- and para-molecules obtained in the present work and in [16]. More pronounced cases of the alternations appear as a result of experimental errors due to the non-optimal method of energy-level derivation used in [16]—the sequential, multi-step procedure based on calculating common differences. The error appearing in one common difference due to one spurious experimental wavenumber value is transferred from the previous energy-level value to the next one. The mechanism is valid also for small random errors with various final results, because subsequent pairs of lines within a band may have experimental errors of various values and signs. Sometimes random errors may partially compensate each other, but in principle this method has the possibility of an accumulation of experimental wavenumber errors and transferring them into the errors of the empirical values of rovibronic energy levels.

A typical example of the alternating appearance caused by spurious experimental wavenumber values is illustrated...
The excellent agreement between the observed and calculated wavenumbers reported in [16] seen in figure 8(a) is evidence that the wavenumbers of the R4 and R12 spectral lines were used in the determination of the level values. Experimental wavenumbers reported in [16] for both lines were classified as outliers by our statistical analysis. Results of our independent experiments confirmed that this is caused by occasional errors in [16]. The wavenumber values from [16] for the lines R4 and R12 are underestimated and overestimated, respectively (see figure 8(a) and table 1). From figures 8(b) and (c) one can see how those experimental errors are transferred into the wrong values of the empirical energy levels via sequential adding of the common differences $\Delta E$ between optimal values of the energy levels obtained in the present work and those calculated with molecular constants from [25] for various rotational and vibrational levels of the $a'$ $\Sigma^+$ electronic state of the D$_2$ molecule.

In figures 8(a)–(c). They demonstrate the influence of two significant errors in wavenumbers of the R-branch lines of the (0–0) band of the $j^3 \Delta_g - c^3 \Pi_u$ electronic transition on the empirical values of the rotational levels obtained in [16] for the upper $j^3 \Delta_g$, $v = 0$ and lower $c^3 \Pi_u$, $v = 0$ electronic–vibrational states of the band.

The excellent agreement between the observed and calculated wavenumbers reported in [16] seen in figure 8(a) is evidence that the wavenumbers of the R4 and R12 spectral lines were used in the determination of the level values. Experimental wavenumbers reported in [16] for both lines were classified as outliers by our statistical analysis. Results of our independent experiments confirmed that this is caused by occasional errors in [16]. The wavenumber values from [16] for the lines R4 and R12 are underestimated and overestimated, respectively (see figure 8(a) and table 1). From figures 8(b) and (c) one can see how those experimental errors are transferred into the wrong values of the empirical energy levels via sequential adding of the common differences $\Delta E(N)$ and $\Delta E(N)$ calculated for upper and lower rovibrionic levels. The cases of appearance, accumulation and partial compensation of experimental errors may be found in figures 8(b) and (c).

Taking into account the results of our previous studies of some triplet states of the H$_2$ molecule [26] it is easy to expect that the Dunham series expansions with empirical molecular constants from [15, 25] have rather limited ability to describe rovibrionic levels of the D$_2$ isotopomer. These expectations were confirmed by the results of the present work. A typical example of the contradictions is illustrated in
figure 9 representing the differences $\Delta E$ between optimal values of the energy levels obtained in the present work and those calculated with molecular constants from [15, 25] for various rotational and vibrational levels of the $a^3 \Sigma_g^+$ electronic state of the $D_2$ molecule. One can see that the deviations show strong dependences on vibrational and rotational quantum numbers, achieving values of about 100 cm$^{-1}$. It should be stressed that according to our previous studies of the potential curves [30] the $a^3 \Sigma_g^+$ electronic state is almost free from the non-adiabatic effect of perturbations. Higher electronic states are mainly perturbed due to the electronic–rotational and electronic–vibrational interactions, and simple Dunham expansions are non-applicable.

For the determination of precise absolute values of the triplet rovibronic levels of $D_2$, it is desirable to make a purely statistical analysis of all currently available experimental data on the wavenumbers of singlet rovibronic transitions and to use the data of anticrossing spectroscopy [49–51] for establishing the link between the singlet and triplet states. The approach used in the present work is most appropriate for solving this problem in the future. Nowadays the absolute values of the triplet rovibronic levels (relative to the $X^1 \Sigma_g^+$, $v = 0$, $N = 0$ ground rovibronic state) may be obtained only by adding an absolute value $E_{\text{rot}}$ of energy of the $a^3 \Sigma_g^+$, $v = 0$, $N = 0$ rovibronic level to the relative energy-level values obtained in the present work. According to [16] $E_{\text{rot}} = 95348.2(4)$ cm$^{-1}$, while in [52] $E_{\text{rot}} = 95348.3(1)$ cm$^{-1}$. These values coincide within the uncertainties reported in the original papers and can be used. The precision of such absolute calibration should be better than 1 cm$^{-1}$.

Our relative values of triplet rovibronic levels of the $D_2$ molecule can be used not only in comparisons with results of non-empirical calculations. They are recommended for calculating accurately the wavenumbers of triplet–triplet optical transitions for computer simulations of emission and absorption spectra in applied spectroscopy of non-equilibrium gases and plasmas. Moreover, the high precision of optimal level values achieved in the present work provides the opportunity to expand the existing identification of triplet rovibronic lines by calculating accurately wavenumbers of all currently unassigned rovibronic transitions allowed by the selection rules for electric dipole transitions and detecting corresponding lines in experimental spectra. From the Grotrian diagram of the $D_2$ molecule it may be seen that several new band systems may be discovered and investigated.

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