

Rovibronic energy levels for triplet electronic states of molecular deuterium

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An optimal set of 1046 rovibronic energy levels for 35 triplet electronic states of D_2 has been obtained by means of a statistical analysis of all available wavenumbers of triplet-triplet rovibronic transitions studied in emission, absorption, laser and anti-crossing spectroscopic experiments of various authors. We used a new method of the analysis (Lavrov, Ryazanov, JETP Letters, 2005), which does not need any *a priori* assumptions concerning the molecular structure being based on only two fundamental principles: maximum likelihood and Rydberg-Ritz. The method provides the opportunity to obtain the estimation of uncertainties of experimental wavenumbers independent from those presented in the original papers. 222 from 3842 published wavenumber values were found to be spurious, while the remaining set of the data may be divided into 15 subsets of uniformly precise data having close to normal distributions of random errors within the subsets. New experimental wavenumber values of 123 questionable lines were obtained in the present work. Optimal values of the rovibronic levels were obtained from the experimental data set consisting of 3743 wavenumber values (3620 old and 123 new). The unknown shift between levels of ortho- and para- deuterium was found by least squares analysis of the $a^3\Sigma_g^+$, $v = 0$, $N = 0 \div 18$ 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 $a^3\Sigma_g^+$ electronic state and presented in tabular form together with standard deviations (SD) of the semi-empirical determination. New energy level values differ sufficiently from those available in literature.

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Introduction

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 electronic-vibro-rotational (rovibronic) transitions, does not show a visible, easily recognizable band structure, but has the appearance of a multiline atomic spectra. 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 (H_2, D_2 and T_2) cause the known effect of the intensity alternation of neighbouring lines within the rotational structure of bands due 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 D_2). This effect also masks the visible structure of branches resulting in serious additional difficulties for 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 [1–4]. As an example, in the latest compilation of experimental data for molecular deuterium D_2 [4], the working list of 27488 measured 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 [1, 3], sometimes together with comparison of molecular constants obtained for different isotopic species [2]. Later the results of *ab initio* and semi-empirical calculations were taken into account [4].

Currently, available information concerning triplet rovibronic energy level values of D_2 molecule exists in the form of the list of molecular constants for Dunham expansions in the

NIST database [5], and tables of rovibronic levels obtained in Ref. [4].

In the case of the hydrogen molecule the Dunham coefficients are known to provide a very poor description of the rovibronic energy level values [6]. The data reported in Ref. [4], in general, give a rather good description of the D_2 spectrum (about 0.05 cm^{-1}), but they are also not free from criticism. The method of the analysis used in Ref. [4] is based on the common use of the combination differences, some selected wavenumbers for certain transitions and one by one multistage treating of separate branches, bands and band systems. The sequence of the steps chosen in Ref. [4] is not the only possible analytical arrangement. Therefore, the data thus obtained can not be considered as an optimal set of levels providing the best description of observed wavenumber values. It should also be mentioned that after publication of Ref. [4], new experimental data on the wavenumbers appeared [7, 8].

Recently, a new method of statistical analysis of the rovibronic transition wavenumbers has been proposed [9] and successfully applied for the derivation of rovibronic level values of the singlet states of the BH molecule [10]. The method is based on only two fundamental principles: Rydberg-Ritz and maximum likelihood. This approach differs from known techniques in several aspects: 1) does not need any assumptions concerning an internal structure of a molecule; 2) no intermediate parameters, such as molecular constants used in the traditional approach, are used; 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; 4) provides the opportunity of a rational selection of the experimental data in an interactive mode (thus allowing the user the option to eliminate obvious errors, to revise incorrect line identifications, and to compare various sets of experimental data for mutual consistency); 5) gives an opportunity of independent estimation of experimental errors by means of the analysis of the shape of error distributions; 6) provides an optimal set of rovibronic level values as well as the uncertainties of their determination (standard deviations SD) caused only by the quantity and quality of existing experimental data [11].

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

$s^3\Delta_g^+$, $s^3\Delta_g^-$, $u^3\Pi_u^+$, $u^3\Pi_u^-$, $(7p)^3\Pi_u^+$, $(7p)^3\Pi_u^-$, $(8p)^3\Pi_u^+$, $(8p)^3\Pi_u^-$, $(9p)^3\Pi_u^+$, $(9p)^3\Pi_u^-$, $(6d)^3\Sigma_g^+$, $(7d)^3\Sigma_g^+$, $(8d)^3\Sigma_g^+$ and $(9d)^3\Sigma_g^+$.

The method of analysis and determination of optimal set of rovibronic energy levels

The method of assessment is based on the minimization of the weighted mean-square deviation between observed $\nu_{n'v'N'}^{n''v''N''}$ and calculated (as differences of adjustable energy levels $E_{n''v''N''}$, $E_{n'v'N'}$) values of rovibronic line wavenumbers:

$$r^2 = \sum_{\nu_{n'v'N'}^{n''v''N''}} \left[\frac{(E_{n''v''N''} - E_{n'v'N'}) - \nu_{n'v'N'}^{n''v''N''}}{\sigma_{\nu_{n'v'N'}^{n''v''N''}}} \right]^2, \quad (1)$$

where n denotes the electronic state, v is the vibrational quantum number, and N is the rotational quantum number of total angular momentum of a molecule excluding spins of electrons and nuclei. Upper and lower rovibronic levels are marked by double and single primes, respectively. The values $\sigma_{\nu_{n'v'N'}^{n''v''N''}}$ are experimental root-mean-square (RMS) errors (one SD), and the summation is over all inputted experimental data. The $\nu_{n'v'N'}^{n''v''N''}$ and $\sigma_{\nu_{n'v'N'}^{n''v''N''}}$ values are the input data, while the optimal set of energy levels E_{nvN} and the calculated standard deviations of their determination $\sigma_{E_{nvN}}$ are output data from the computer code. Due to the linearity of the equations used, the optimization problem reduces to the solution of a system of linear algebraic equations [9].

It should be stressed, that for a realization of the method it is necessary to know the proper estimation of the SD for every experimental datum, or be able to divide the whole data set into a finite number of groups (subsets, samples) of data measured with the same precision. Then all data belonging to each subset may be characterized by a certain common value of SD. In the present study we assumed that systematic errors are eliminated (except occasional spurious data), and random errors should possess the normal (Gaussian) distribution function.

The method requires the known RMS errors of the wavenumbers in the process of determination the optimal level values for three purposes. Firstly, weighting of the input data depends on these values. Secondly, the rational selection of input data is based on a comparison of an experimental RMS uncertainty (common for a sample of data under the study) with differences between experimental wavenumbers of the lines (included into this

sample) and those calculated from the optimal values of the energy levels. Finally, estimates of uncertainties of the optimal level values, $\sigma_{E_{nvN}}$ are calculated by taking into account the input wavenumber RMS errors σ_ν .

Unfortunately only a few original works with experimental wavenumber data contain information on the accuracy of the listed values. And even in these cases the error estimations are of uncertain reliability. Therefore, it was necessary to obtain independent estimates of the wavenumber errors σ_ν . Our method provides the opportunity to obtain the estimates of uncertainties of experimental wavenumbers independent from those presented in the original papers.

Statistical analysis

The method of analysis consists of analyzing the distribution function $F(\xi)$ of the variable

$$\xi_{n''v''N''}^{n'v'N'} = \frac{\nu_{n''v''N''}^{n'v'N'} - (\tilde{E}_{n''v''N''} - \tilde{E}_{n'v'N'})}{\sigma_{\nu_{n''v''N''}^{n'v'N'}}}. \quad (2)$$

Energy level values $\tilde{E}_{n''v''N''}$ and $\tilde{E}_{n'v'N'}$ are obtained by the minimization of Eq.(1) without using the $\nu_{n''v''N''}^{n'v'N'}$ wavenumber value. In favorable cases this distribution should be close to the normal distribution with an average value equal to zero and variance equal to unity, namely

$$F_0(\xi) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\xi} e^{-\frac{x^2}{2}} dx. \quad (3)$$

The analysis of the shape of the distribution function $F(\xi)$ for various groups (samples) of experimental data provides an opportunity to estimate the RMS errors of experimental data reported in various works by the rational selection of experimental data and determination of proper values of experimental errors $\sigma_{\nu_{n''v''N''}^{n'v'N'}}$. Experimental data which have shown unreasonably large deviations (ξ larger then 3) were excluded as spurious results. Then the value of an experimental RMS uncertainty (unique for all lines belonging to the same sample) was adjusted in such a way that the distribution function $F(\xi)$ of a certain sample becomes close to the normal distribution function represented by Eq.(3).

All available values of rovibronic transition wavenumbers studied in emission, absorption, laser and anticrossing spectroscopic experiments of various authors were analyzed [4, 7, 8, 12–

16] . Fine and hyperfine structures of rotational levels were ignored. In the case of resolved and partly resolved fine structure, the wavenumber of the strongest component was used.

The statistical analysis of the 3842 published wavenumber values has shown that 222 experimental data (for 218 spectral lines) should be excluded from further consideration as being spurious. The remaining set of 3620 wavenumber values could be divided into 15 subsets (samples) of uniformly precise data having close to the normal distribution functions for random experimental errors. All the wavenumber data within each sample may be characterized by the same value of standard deviation (SD).

Experimental determination of wavenumbers for questionable lines

138 of the 218 questionable lines are located within the wavelength range available for us (430-730 nm). Therefore we decided to provide an independent experimental determination of their wavenumbers. For that purpose we used the emission spectra of D_2 obtained during our previous studies of translational and rotational temperatures in hydrogen and deuterium containing plasmas [17]. A detailed description of the experimental setup has been reported elsewhere [18]. Capillary arc discharge lamps DDS-30 described in Ref. [19] have been used as light sources. They were filled with about 6 Torr of spectroscopically pure $D_2 + H_2$ (9:1) mixture. The range of the discharge current was from 50 to 300 mA (current densities $j = 1.6 \div 10 \text{ A/cm}^2$). Light from the axis of the plasma inside the capillary was directly focused by an achromatic lens on the entrance slit of the 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 the Optical Multichannel Analyser (Princeton Appl. Res., OMA-Vision-CCD System).

Assignments and wavelength values from Ref. [4] were used for identification of D_2 spectral lines in the spectrum. These values show a certain spread around monotonic dependence of the wavenumber from the distance along the direction of dispersion in the focal plane of the spectrograph. For the majority of strong, unblended lines, this scatter was within the error bars of 0.05 cm^{-1} reported in Ref. [4].

Assuming the dispersion of the spectrograph to be a monotonic function of the coordinate in the focal plane of the spectrograph, new wavenumber values for 123 of the questionable spectral lines were obtained by polynomial approximation of the dispersion curve. The

intensities of the remaining 15 questionable lines were too weak to be detectable in the experimental conditions.

Statistical analysis of the deviations given by Eq.(2) have shown that the 123 new wavenumber values represent the sample of the experimental data with the distribution function $F(\xi)$ close to normal distribution, corresponding to the value of standard deviation $\sigma_\nu = 0.06 \text{ cm}^{-1}$ common for all 123 lines. Such a relatively high value of the experimental uncertainty arises because most of questionable lines are quite weak and are partly blended with stronger lines. Nevertheless, our new data are in better agreement with the optimal set of energy levels, obtained by the minimization of Eq.(1) with the input data set in which wavenumbers of questionable lines were omitted. Thus, new experimental data obtained in the present work are in good agreement with the wavenumbers of all other lines referencing the initial and final rovibronic levels of those questionable lines.

Results

Optimal values of 1046 triplet rovibronic energy levels of D_2 have been obtained by the minimization of Eq.(1) with the input experimental data set consisting of 3743 wavenumber values (3620 old and 123 new). The unknown shift between levels of ortho- and para-deuterium was obtained by least squares analysis of the $a^3\Sigma_g^+$, $v = 0$, $N = 0 - 18$ levels with odd and even values of the rotational quantum number N . All the energy levels were obtained relative to the lowest vibro-rotational level ($v = 0$, $N = 0$) of the $a^3\Sigma_g^+$ state and presented in tabular form together with the SD of the semi-empirical determination. Absolute values of the triplet rovibronic levels relative to the $X^1\Sigma_g^+$, $v = 0$, $N = 0$ ground rovibronic state of D_2 may be obtained by adding the difference $(E_{a00} - E_{X00}) = 95348, 22 \text{ cm}^{-1}$ from Ref. [4] to our level values.

Energy level values obtained in the present work are now incorporated into the database of the Atomic and Molecular (A+M) Data Unit of the IAEA, and are also available through the link located on the previous page. Moreover, further improvements in our knowledge of rovibronic energy levels of D_2 molecule will appear on that link when completed.

Conclusion

A detailed comparison of the optimal set of rovibronic levels with the data reported in Ref. [4, 5] will be presented in a separate paper. Most of the differences between our data and those from Ref. [4] are less than 0.05 cm^{-1} , the values reported in Ref.[4] as an estimation of the one standard deviation uncertainty of the energy levels. On the other hand, most of those differences are sufficiently larger than the SD of our data, which normally are within the range of $0.004 \div 0.03 \text{ cm}^{-1}$ and depend on the value of the rotational and vibrational quantum numbers. Therefore, the deviations of the data obtained in Ref.[4] from our optimal level values are significant.

Thus, the optimizational approach to the problem allows us to obtain significantly higher precision in derivation of the energy level values from measured wavenumbers of rovibronic spectral lines of D_2 molecule.

Acknowledgments

The authors are indebted to Prof. S. Ross for providing the electronic version of the wavelength tables for lines of the D_2 emission spectrum measured and assigned by G.H. Dieke and co-workers (Appendix C. from Ref.[4]), and to Mr. M.S. Ryazanov for development of the computer code and helpful discussions. We also acknowledge financial support from the Russian Foundation for Basic Research (the Grant #06-03-32663a). BPL is thankful to Dr. R.E.H. Clark, Dr. A. Nichols and Mr. D. Humbert for useful discussions, and to the A+M Data Unit of IAEA for financial support of his visits and hospitality.

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