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Critical evaluation of measured line positions of $^{14}N^{16}O$ in $X^2\Pi$ state

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ABSTRACT

All available line positions for unresolved and resolved Λ-doublets of the $^{14}N^{16}O$ molecule in the $X^2 \Pi$ state were collected from the literature and tested using the RITZ computer code. These data have been critically analysed and used to obtain the most complete set of 1789 experimental energy levels of unresolved Λ-doublets covering the 0–35,866 cm^{-1} interval. A set of 425 experimental energy levels of resolved Λ-doublets covering the 0–5957 cm^{-1} interval for two states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ also have been obtained. These levels together with calculated correlation matrix can be used to generate the precise list of transitions with confidence intervals. Comparisons with the HITRAN as well as with Amiot calculations are discussed. The systematic shift between experimental energy levels of unresolved Λ-doublets and those calculated by Amiot for $^2\Pi_{3/2}$ state was found. The same systematic shift for transitions frequencies of unresolved Λ-doublets in forbidden subbands $^2\Pi_{1/2}\leftrightarrow{}^2\Pi_{3/2}$ is also established in the HITRAN database. Comparison of the RITZ energy levels with calculated energy levels by Wong at al. was also done. It was found, that experimental RITZ energy levels for resolved Λ-doublets of $^{14}N^{16}O$ coincide with those calculated by Wong at al. within experimental uncertainties.

1. Introduction

The goal of the present work is to improve the knowledge of nitric oxide experimental energy levels in view to atmospheric applications. Nitric oxide molecule plays a significant role in photophysical, chemical and biochemical processes therefore its spectrum is the subject of a number of numerous investigations by different spectroscopic techniques. NO is an especially interesting molecule due to the unpaired electron in the ground electronic state $^2\Pi$ state is split by a spin-orbit interaction into $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states separated by about 123 cm^{-1}. In addition, the interaction with other electronic states leads to a Λ-doubling which splits each level into a doublet of components whose separation can reach a few 10^{-2} cm^{-1}. Up to now there is no representative set of experimental energy levels of this molecule including Λ-doubling.

The basic goal of this work is a via critical evaluation of published experimental line positions to obtain accurate set of experimental energy levels. According to the resolution of the experimental line positions the appropriate set of energy levels including Λ-doubling and hyperfine splitting or without it could be obtain. As a rule some data from the publications can contain errors caused by improper calibration, identification, pressure shifts, misprints etc. They are not always agreed with each other within experimental accuracies. For the critical evaluation of the measured line positions of $^{14}N^{16}O$ in $X^2\Pi$ state we followed the papers [1,2] and have used the fundamental Rydberg–Ritz combination principle in order to have accurate set of experimental energy levels for further improving molecular constants. First we have made a critical analysis of the measured line positions representing unresolved Λ-doublets for rotation-vibration, pure rotation and magnetic dipole transitions because the majority of the experimental positions are Λ- unresolved data. After that we have gathered and analysed the data with Λ-doubling. Thus two sets of experimental energy levels with and without Λ splitting have been obtained. The data of the hyperfine Λ-doubling transitions were ignored in the analysis, as they are insufficient to use the RITZ combination principle.

2. Dataset of measured line position

All measured line positions in the $X^2\Pi$ state available in the literature are collected from the papers [3–34]. The data used in the analysis were separated into two sets of line positions with the Λ-doublets unresolved and Λ-doublets resolved. The measured line positions of the unresolved Λ-doublets collected from the papers [3–20] were presented in the first set. The wavenumbers of forbidden subbands $^2\Pi_{1/2} - {}^2\Pi_{3/2}$, $^2\Pi_{3/2} - {}^2\Pi_{1/2}$ [3,4,10] and magnetic dipole transitions [11] were also included in this set. The most data

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for unresolved doublets came from three papers [17–19]. In total a set of 5310 transitions covering 18–208 $cm^{-1,}$ 1554–7372 cm^{-1} and 12,472–12,566 cm^{-1} spectral ranges was constructed. Accuracy of the data ranged from 0.13×10^{-3} cm^{-1} [20] to 50×10^{-3} cm^{-1} [8]. The most excited vibrational band is for $v = 19 \rightarrow v^{'} = 22$ and the maximum value of the rotational quantum number J is equal to 76.5 for the 2–0 vibrational band in the $^2\Pi_{3/2}$ state. The summary of collected data for the isolated unresolved Λ-doublets is given in Table 1.

The second set of the measured line positions represents the available data on the rotation-vibration and pure rotational lines with the Λ-doubling resolved. The frequencies of the magnetic dipole transitions observed in the far infrared region in the subband $^2\Pi_{3/2} - ^2\Pi_{1/2}$ were also added to the second set. A complete set of 1341 Λ- doublets covers the two spectral ranges 11–198 cm^{-1} and 1704–5544 cm^{-1}. The highest rotational quantum number J is 41 for the vibrational band 1–0. The data experimental uncertainty of the second set varies from 0.67×10^{-6} cm^{-1} [29,31] to 5×10^{-3} cm^{-1} [14]. A summary of the Λ- doublets transitions collected from $v = 0$ up to $v = 2$ and a few transitions from the bands 3–0, 3–1, as well as of the pure rotational transitions and magnetic dipole transitions are given in Table 2 [14–16,20–33]. The sources of the data are listed in the first column of Tables 1 and 2. Experimental techniques used to measure the line positions are presented in column 2. Uncertainties of the measurements and numbers of lines are listed in columns 3 and 4. The extent of measurements for each source is given in columns 6 and 7.

3. Method for extracting experimental energy levels

Transition frequencies are directly observable quantities and contain the information about energy levels of the molecule which are unobservable in the experiment. Therefore obtaining the energy levels from observed transition frequencies is very important in molecular spectroscopy. The method of the extracting information on the energy levels is known in spectroscopy as a fundamental Rydberg-Ritz combinational principle:

$$\nu_{i \to j} = E_i - E_j, \qquad (1)$$

where $\nu_{i \to j}$ is the observed transition frequency, E_i and E_j are the upper and lower energy levels respectively. The composite quantum number indexes *i* and *j* define the spectroscopic assignment of the observed transition frequency. In the case of the NO molecule, if we neglect the hyperfine structure, these indexes represent the quantum numbers v, Ω, J as well as-the parity (e or f) of the rotational levels. Since the number of transitions N usually is greater than the number of energy levels, it is possible to consider a set of Eq. (1) written for each measured transition as an overdetermined system of linear equations with unknown energy levels E_i. This approach arises from the work [35] and was applied to CO_2, H_2O and CO molecules [1,2,36,37]. We followed these works and have used the RITZ computer code created by S. Tashkun [1,2,36]. When collecting a complete set of observed transitions we have to take into account that each source has its own set of observed transitions recorded under definite conditions. So, for the real spectra taking into account the correction factors the Rydberg-Ritz combinational principle (1) can be presented as [2]:

$$c^s \nu^s_{i \to j} = (E_i - E_j) + \varepsilon^s_{i \to j} \qquad (2)$$

where s is the source index, because the data come from various sources; $c^s \approx 1$ is a correction factor of the source corresponding to the index s; $\varepsilon^s_{i \to j}$ is the error of the measurement from the source with the index s; indexes i and j enumerate the energy levels from 1 up to n, $i \to j$ count the number of the transitions N, which is greater than the number n of energy levels. The inclusion

Table 1
Experimental line positions data for the $X^2\Pi$ state of $^{14}N^{16}O$ molecule (unresolved Λ-doublets).

Reference 1	Type of measurements 2	Uncertainty 10^{-3} cm^{-1} 3	N- number of lines 4	N- del 5	ν_{min} cm^{-1} 6	ν_{max} cm^{-1} 7	RMS1 dimensionless 8	RMS2 (10^{-3} cm^{-1}) 9
James 1964 [3]	IR absorption	10	20	1	1972.0	2030.3	0.55	5.5
James et al., 1964 [4]	IR absorption	10	139	1	1794.4	2075.7	0.7	7.0
Olman et al., 1964 [5]	IR absorption	10–15	149	18	3632.3	5589.8	1.25	12. 5
Meyer et al., 1964 [6]	IR absorption	30	66	33	5438.2	5593.6	0.47	14.2
Meyer et al., 1965 [7]	IR absorption	1–17	95	3	3651.1	7371.8	0.83	6.8
Deutsch 1966 [8]	IR, NO laser	50	60	2	1554.7	1710.5	0.79	39.7
Hall et al., 1966 [9]	MW, absorption	3	45	1	18.4	93.9	0.98	2.95
Keck 1967, 1968 [10]	IR absorption	4	14	0	1713.9	2075.7	0.78	3.1
Brown et.al., 1972[11]	MW, FIR absorption	30	64	10	80.3	207.7	1.11	33.3
Patel et al., 1977 [12]	Opto-acoustic absorption	20	13	0	1877.7	1894.9	1.2	24
Guerra et al., 1977 [13]	CO laser absorption	5	4	0	1880.7	1892.1	1.15	5.7
Dale et al., 1977 [14]	IR-RF DR	0.6–5	4	0	1863.7	1884.3	0.11	0.48
Valentin et al., 1978 [15]	IR absorption	5	133	0	1741.2	1979.9	0.2	0.99
Henry et al., 1978 [16]	IR absorption	5	198	0	3612.3	5595.6	0.19	0.94
Hallin et al., 1979 [17]	FT emission	7	609	183	3199.5	3801.3	1.25	8.7
Amiot et al., 1980 [18]	FT emission	2	1844	0	1741.2	5594.6	0.41	0.82
Amiot 1982 [19]	FT emission	5	1580	0	3814.2	5000.5	0.33	1.65
Hinz et al., 1986 [20]	CO laser heterodyne	0.13–0.3	6	0	1750.1	1927.3	0.11	0.034
Bood et al., 2006 [34]	NICE-OHMS	2.5	14	1	12,472.2	12,565.8	1.16	2.9