

Line parameters of 15N216O from Fourier transform measurements in the 5800 - 7600 cm-1 region and global fitting of line positions from 1000 to 7600 cm-1

Oleg M. Lyulin, David Jacquemart, Nelly Lacome, Sergei A. Tashkun, Valerii I. Perevalov

▶ **To cite this version:**

Oleg M. Lyulin, David Jacquemart, Nelly Lacome, Sergei A. Tashkun, Valerii I. Perevalov. Line parameters of 15N216O from Fourier transform measurements in the 5800 - 7600 cm-1 region and global fitting of line positions from 1000 to 7600 cm-1. Journal of Quantitative Spectroscopy and Radiative Transfer, 2010, 111 (3), pp.345-356. 10.1016/j.jqsrt.2009.10.010 . hal-00746036

HAL Id: hal-00746036

https://hal.sorbonne-universite.fr/hal-00746036

Submitted on 29 Oct 2012

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Line parameters of $^{15}N_2{}^{16}O$ from Fourier transform measurements in the 5800 - 7600 cm^{-1} region and global fitting of line positions from 1000 to 7600 cm^{-1}

O.M. Lyulin[1], D. Jacquemart[2,3,*], N. Lacome[2,3], S.A. Tashkun[1], V.I. Perevalov[1]

[1] *Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, 1, Akademicheskii av., 634055 Tomsk, Russia*

[2] UPMC Univ Paris 06, UMR 7075, Laboratoire de Dynamique, Interactions et Réactivité, Case Courrier 49, 4 Place Jussieu, 75252 Paris Cedex 05, France

[3] CNRS, UMR 7075, Laboratoire de Dynamique, Interactions et Réactivité, Case Courrier 49, 4 Place Jussieu, 75252 Paris Cedex 05, France

Revised 2009

[*] Corresponding author. Tel.: + 33-1-44-27-36-82; fax: + 33-1-44-27-30-21.
E-mail address: david.jacquemart@upmc.fr

Abstract

Using FT spectra (unapodized resolution ~ 0.0056 cm^{-1}) of nitrous oxide isotopologue $^{15}N_2{}^{16}O$, the line positions and intensities have been measured for 511 lines of 8 cold and one hot bands lying between 5800 and 7600 cm^{-1}. A multispectrum fitting procedure has been used to retrieve line parameters from 5 experimental spectra recorded at different pressures. An absolute wavenumber calibration has been performed using acetylene line positions around 6500 cm^{-1} and water line positions in the 7100-7300 cm^{-1} region. The average absolute accuracy of the line parameters obtained in this work has been estimated to be ± 0.0005 cm^{-1} for the line positions, 2-5% for the line intensities depending on the transitions. For each studied band, the vibrational transition dipole moment squared value and the empirical Herman-Wallis coefficients have been adjusted. Moreover the line positions measured in this work and those collected from the literature allowed the global fitting of the effective Hamiltonian parameters for this isotopologue.

Key words: Nitrous oxide, $^{15}N_2{}^{16}O$; Infrared; Fourier transform spectroscopy; Line positions, Line intensities; Global modeling

1. Introduction

The nitrous oxide is a minor constituent of the earth atmosphere but it plays an essential role in the physical and chemical processes. The isotopologue $^{15}N_2{}^{16}O$ of nitrous oxide has a very small natural abundance (0.0013%), but the line parameters of this isotopologue can be useful for having a better accuracy of the atmospheric spectra simulation and also for developing theoretical models describing the influence of the isotopic substitution on the spectral line parameters.

To our knowledge only two works [1,2] are available in the literature for the line positions measurements of this isotopic species. No works have been found in the literature concerning the line intensity measurements. This explains why spectroscopic databases as HITRAN [3] or GEISA [4] do not contain any line parameters of $^{15}N_2{}^{16}O$.

In the present work, 511 lines of 9 bands, namely the $3\nu_3$, $\nu_2+3\nu_3-\nu_2$, $\nu_1+3\nu_3$, $2\nu_1+2\nu_3$, $3\nu_1+\nu_3$, $4\nu_1+\nu_3$I, $4\nu_1+\nu_3$II, $5\nu_1$I and $5\nu_1$III bands, have been studied between 5800 and 7600 cm^{-1} for the $^{15}N^{15}N^{16}O$ isotopologue. The line positions, intensities, self-broadening and self-shifting coefficients have been measured using a multispectrum fitting procedure [5] applied to five experimental spectra recorded at different pressures of $^{15}N_2{}^{16}O$. In this paper we publish only the line positions and line intensities. For each studied band, the vibrational transition dipole moment squared and empirical Herman-Wallis coefficients have been obtained. Using the measured line positions of this work and those from the literature, the global fitting of the effective Hamiltonian parameters has been performed.

The experimental procedure and the methodology of the analysis are presented in Sections 2 and 3 respectively. The Section 4 is devoted to the analysis and the modelling of the spectral line parameters. In Section 5 the results of the global fitting of the effective Hamiltonian parameters are presented.

2. Experimental procedure

To record the spectra, the rapid scan Bruker IFS 120 HR interferometer of the LADIR (Paris) has been used. The unapodized spectral resolution used for each spectrum was equal to $5.6\ 10^{-3}$ cm^{-1} ($1/2\Delta_{max}$) that corresponds to a maximal optical path difference Δ_{max} of 90 cm. The interferometer was equipped with a CaF_2 beam splitter, an InGaAs detector, a Tungsten source, and no optical filter in order to cover the whole 5500 - 9000 cm^{-1} spectral region. Five spectra have been recorded at room temperature with various gas pressures; experimental

conditions are summarized in Table 1. The whole optical path was under vacuum and a multipass cell of one meter base length was used for a total absorption path of 2015 ± 1 cm. The cell was equipped with KCl windows. The commercial gas sample has been furnished by Campro Scientific Gmbh, the given isotopic assay is: 99.9% of ^{15}N, 0.1% of ^{14}N and 98.3% of ^{16}O, 0.1% of ^{17}O and 1.6% of ^{18}O. The stated purity of the sample of N_2O is 99.1%. Using these specifications, the partial pressure of the various isotopologues can be calculated for each spectrum (the partial pressures of the more abundant isotopologues are given as percentage of the total pressure in Table 1). The temperature of the gas in the cell was monitored with the help of four platinum probes at different places in the cell. The accuracy of the averaged temperature is estimated to be ± 1 K (this accuracy takes into account small temperature gradients inside the cell). The pressure of the gas was measured with a capacitive MKS Baratron manometer with an accuracy equal to ± 1%. For each spectrum, a total of 300 scans have been recorded and individually transformed using the Fourier transform procedure included in the Bruker software OPUS package [6], selecting a Mertz phase error correction [7,8]. The final spectrum is then the result of the co-addition of the 300 spectra.

3. Line parameter measurements

In this study, the line assignment has been performed on the basis of the predictions performed using global effective Hamiltonian for $^{15}N_2{}^{16}O$ isotopologue obtained in Ref. [9].

The wavenumber calibration has been performed using $^{12}C_2H_2$ transitions around 6500 cm^{-1} and $H_2{}^{16}O$ transitions between 7100-7350 cm^{-1} (these two gases are present in the sample as impurities). The reference values of the line positions have been taken from the HITRAN 2004 database [3]. Using the values of the line intensities of Ref. [3], the partial pressures of $^{12}C_2H_2$ and $H_2{}^{16}O$ have been determined in each spectrum (see Table 1). For the wavenumber calibration, the quantity $\varepsilon = (\nu_{\text{HITRAN}} - \nu_{\text{this work}})/\nu_{\text{HITRAN}}$ has been calculated individually in each spectrum for 35 isolated lines of H_2O and 10 isolated lines of $^{12}C_2H_2$. The uncertainties of these reference lines vary from 0.0001 cm^{-1} to 0.001 cm^{-1}. The plot of ε for each line versus pressure demonstrates its linear dependence on pressure (see Fig.1). Taking into account that the same experimental set up was used to record all spectra this calibration factor ε has to be the same (ε_0) for all lines at zero pressure. Averaging ε_0 over all 45 transitions it has been found $\langle \varepsilon_0 \rangle = 1.15\times10^{-6}$ with 1 SD = 2×10^{-8} (see Fig.1). This value was used for the calibration of all spectra. Considering the dispersion of the calibration factor

and the uncertainties of the reference lines the accuracy of the wavenumber calibration was estimated to be about 5×10^{-4} cm^{-1}.

Concerning the apparatus function, its calculation [10] has been performed numerically by the Fourier transform of the optical weighting function of the interferogram, due to the throughput, truncated at the maximum optical path difference. The treatment of the apparatus function is the same as what has been done in Refs. [10-12]. An effective radius of the aperture has been obtained from the fit of 36 isolated lines. The fitted values vary from spectra to spectra between 0.59 and 0.72 mm. These values of the effective radius of the aperture with nominal value of the focal length (418 mm) have been used for the calculation of the apparatus function in each spectrum.

Line parameters have been retrieved using a multispectrum procedure [5] that adjusts a calculated spectrum simultaneously to each laboratory spectrum. In this way, line positions, line intensities, self- broadening and -shifting coefficients have been directly retrieved from the simultaneous fit of the five experimental spectra.

At 296 K in the spectral domain 5800-7600 cm^{-1} the Doppler half-width at half-maximum (HWHM) is between 0.005 and 0.007 cm^{-1} for $^{15}N_2{}^{16}O$. The half-width at half-maximum of the apparatus function is mainly due to the limitation of the optical path difference and is equal to 0.003 cm^{-1}. Since the values of the self-broadening coefficients of the principal isotope are about 0.1 $cm^{-1}atm^{-1}$, the collisional half-width at half-maximum (equal to the product: self-broadening coefficient × partial pressure of $^{15}N_2{}^{16}O$) was supposed to be between 0.0008 and 0.004 cm^{-1} depending on the experimental conditions (see Table 1). Therefore, in the case of the highest experimental pressures, the collisional width leads to non negligible contribution in the line profile and can be measured for the strongest lines. The background was modeled by the second order polynomial that has been fitted for each line and each spectrum. A Voigt profile has been used in all fits. Since the spectra are recorded at temperatures slightly different from 296 K, a temperature conversion of the line intensities has been done neglecting the temperature dependence of the total partition function. The weak temperature effect on the broadening and shifting coefficients has been neglected because the temperatures were very close to 296 K. Note that the broadening contribution of the other isotopologues of N_2O and impurities was taken into account by assuming that their broadening coefficients were the same as the $^{15}N^{15}N^{16}O$ self-broadening coefficients.

4. Results

The parameters of 511 lines belonging to 8 cold bands and one hot band lying between 5800 and 7600 cm^{-1} have been found using a multispectrum fitting procedure [5]. The position, intensity, half-width and self-shift coefficients of each line have been adjusted simultaneously in the five spectra. In the case of the strongest $3\nu_3$ band, the line parameters have been obtained with small statistic uncertainty and small residuals between simulated and observed spectra. Slightly worse results have been obtained for $3\nu_1+\nu_3$, $3\nu_1+\nu_3$, $5\nu_1$I and $5\nu_1$III bands. The uncertainty of the measured line parameters have been estimated to be about 5×10^{-4} cm^{-1} for the line positions, 2-5% for the line intensities depending on the intensity value. The complete set of the line parameters measured in this work is available as Supplementary Materials. In Tables 2-4 we present line positions and line intensities for three strongest bands $3\nu_3$, $3\nu_1+\nu_3$, and $5\nu_1$I. The line intensities are given for 296 K and for pure $^{15}N_2{}^{16}O$ isotopologue.

4.1. Spectroscopic constants

In addition to the global modeling of the line positions which is presented in Section 5 the spectroscopic constants G_v, B_v, D_v and H_v appearing in the equation

$$E_v(J) = G_v + B_v J(J+1) - D_v\left[J(J+1)\right]^2 + H_v\left[J(J+1)\right]^3 \quad (1)$$

for the rotational energy levels of a given vibrational state have been obtained in this paper for all observed bands. They are given in Table 5. The spectroscopic constants of the ground state have been fitted simultaneously with the spectroscopic constants of the upper state to the line positions of the $3\nu_3$ band.

4.2. Vibrational transition dipole moment squared, and Herman-Wallis factor

In this section, the empirical treatment of the measured line intensities is presented. From each line intensity $S(T_0)$, obtained from the multispectrum fitting procedure, in cm·molecule^{-1} at the standard temperature T_0 = 296 K, the transition dipole moment squared $|R|^2$, in D^2 (1 debye = 3.33546×10^{-30} C·m) has been deduced using the following equation:

$$S(T_0) = (1/4\pi\varepsilon_0)\,(8\pi^3/3hc)\,[\nu_0/Q(T_0)]\,|R|^2\,L(J,\ell)\,\exp(-hcE''/kT_0)\,[1-\exp(-hc\,\nu_0/kT_0)], \quad (2)$$

where $1/4\pi\varepsilon_0 = 10^{-36}$ erg·cm^3·D^{-2}; h is Planck's constant equal to $6.6260755 \times 10^{-27}$ erg·s (1 erg = 10^{-7} J); c is vacuum speed of light equal to $2.99792458 \times 10^{10}$ cm·s^{-1}; ν_0 is the transition wavenumber in cm^{-1}; $Q(T_0)$ is the total partition function at temperature T_0; $L(J,\ell)$ is the Hönl-London factor, J being the rotational quantum number of the lower state of the transition and λ is the quantum number of its projection on the molecular axis; E'' , in cm^{-1}, is the energy of the lower level; k is Boltzmann's constant equal to 1.380658×10^{-16} erg·K^{-1}.

For the parallel bands ($\Delta\lambda = 0$), which are studied in this paper, the Hönl-London factors are given by:

$$L(J,\lambda) = (J+1+\lambda)(J+1-\lambda)/(J+1) \quad (R\text{-branch}), \tag{3}$$

$$L(J,\lambda) = (J+\lambda)(J-\lambda)/J \quad (P\text{-branch}). \tag{4}$$

For linear molecule the rotational dependence of the transition dipole moment squared can be expressed by the well known expansion:

$$\left|R\right|^2 = \left|R_0\right|^2 F(m), \tag{5}$$

where $|R_0|^2$ is the vibrational transition dipole moment squared. $F(m)$ is the empirical Herman-Wallis factor which can be expressed for P and R branches as following:

$$F^{RP}(m) = (1 + A_1^{RP} m + A_2^{RP} m^2)^2, \tag{6}$$

where A_1^{RP} and A_2^{RP} are the Herman-Wallis coefficients.

For each band, the vibrational transition dipole moment squared and the Herman-Wallis coefficients have been fitted to the observed line intensities. These parameters are given in Table 5 for the 9 bands studied in this work. For the $3\nu_3$, $3\nu_1 + \nu_3$, and $5\nu_1$I bands, the line intensities measurements together with the calculated intensities using parameters of Table 5 and Eqs. [2-6] are given respectively in Tables 2-4. In Figs.2-3, the plot of the transition dipole moment squared versus rotational quantum number m is given respectively for the two bands $5\nu_1$I and $5\nu_1$III.

5. Global fitting of $^{15}N_2{}^{16}O$ line positions

The measured line positions obtained in this work have been used to improve the parameters of the polyad model of effective Hamiltonian obtained recently in Ref. [9] for

the $^{15}N_2{}^{16}O$ isotopologue. The clustering in the case of nitrous oxide molecule arises due to the following approximate relations among the harmonic frequencies [14]

$$\omega_3 \approx 2\omega_1 \approx 4\omega_2. \tag{7}$$

As a result, the vibrational states are grouped into vibrational polyads with the pseudo quantum number *P*:

$$P = 2V_1 + V_2 + 4V_3 . \tag{8}$$

The effective Hamiltonian within the framework of the polyad model takes into account two types of accidental resonance interactions: anharmonic resonance interactions and anharmonic $+\ell$-type resonance interactions [15,16]. The matrix elements of this effective Hamiltonian in the basis of the eigenfunctions of harmonic oscillators and rigid rotor operators are given in Ref. [17].

The effective Hamiltonian parameters have been determined by a least-squares fitting program [18] using the measured line positions of this work as well as other line positions collected from Refs. [1,2]. The initial values of the effective Hamiltonian parameters were taken from Ref. [9]. The aim of the fitting procedure was to minimize the weighted standard deviation defined according to the usual formula

$$\chi = \sqrt{\frac{\sum_{i=1}^{N}\left[\left(\nu_i^{obs} - \nu_i^{calc}\right)/\varepsilon_i\right]^2}{N-n}} , \tag{9}$$

where ν_i^{obs} and ν_i^{calc} are the observed and calculated line positions, ε_i is the experimental uncertainty of the ν_i^{obs}, *N* is the number of the fitted line positions, and *n* is the number of the adjusted parameters. To describe the quality of a fit, two additional statistics characteristics have been used: the root mean squares of the residuals of the fit (*RMS*) and the root mean squares of residuals for a given experimental source. The *RMS* is defined according to the usual equation

$$RMS = \sqrt{\frac{\sum_{i=1}^{N}\left(\nu_i^{obs} - \nu_i^{calc}\right)^2}{N}} , \tag{10}$$

where *N* is the number of the fitted line positions in the first case and the number of the line positions of a given source in the second case.

In Table 6 we present the characteristics of the input data. Note that used in the fit the line list of Ref. [2] contains the calculated line positions. Those calculations were performed using the spectroscopic parameters G_v, B_v, D_v and H_v obtained in the result of the fittings of the observed line positions. This is the reason why for the weighting we have taken the value equal to 0.0001 cm^{-1} as uncertainty of the discussing data though the author has declared slightly low uncertainty of his data. Using 61 adjustable parameters we have managed to reproduce 2162 line positions with global *RMS* = 0.0012 cm^{-1} and a weighted standard deviation $\chi = 0.83$. This statistics shows that the observed line positions are reproduced within their experimental uncertainties. The residuals of the global fit are presented in Fig. 6. The fitted set of effective Hamiltonian parameters is given in Table 7. No evidence of any interpolyad resonance interaction has been observed for the treated $^{15}N_2{}^{16}O$ line positions.

6. Conclusion

In this work, the line positions and absolute line intensities of 511 lines belonging to 8 cold bands and one hot band of rare isotopic species $^{15}N_2{}^{16}O$ of nitrous oxide molecule have been measured. These bands are belonging to the 5800-7600 cm^{-1} spectral region. The measured line positions of this work together with those collected from the literature have been used to improve the set of the effective Hamiltonian parameters of $^{15}N^{15}N^{16}O$ isotopologue recently published in Ref. [9]. The measured line intensities have been modeled for each band using a semi-empirical approach involving vibrational transition dipole moment squared and Herman-Wallis coefficients. The full set of measured line parameters is available as Supplementary Materials.

Acknowledgments

This study has been performed in the framework of a financial support given by the City of Paris, France (2006-2007).

References

[1] Amiot C. Vibration-rotation bands of $^{15}N_2{}^{16}O$ - $^{14}N_2{}^{18}O$. J Mol Spectrosc 1976;59:380-95.

[2] Toth RA. http://mark4sun.jpl.nasa.gov

[3] Rothman LS, Jacquemart D, Barbe A, Benner DC, Birk M, Brown LR, Carleer MR, Chakerian C Jr, Chance KV, Dana V, Devi VM, Flaud JM, Gamache RR, Goldman AA, Hartmann JM, Jucks KW, Maki A, Mandin JY, Massie ST, Orphal J, Perrin A, Rinsland CP, Smith MAH, Tennysson J, Tolchenov RN, Toth RA, Vander Auwera J, Varanasi P, Wagner G. The HITRAN 2004 molecular spectroscopic database. JQSRT 2005;96:139-204.

[4] Jacquinet-Husson N, Scott NA, Chédin A, Crépeau L, Armante R, Capelle V, Orphal J, Coustenis A, Boonne C, Poulet-Crovisier N, Barbe A, Birk M, Brown LR, Camy-Peyret C, Claveau C, Chance K, Christidis N, Clerbaux C, Coheur PF, Dana V, Daumont L, De Backer-Barilly MR, Di Lonardo G, Flaud JM, Goldman A, Hamdouni A, Hess M, Hurley MD, Jacquemart D, Kleiner I, Köpke P, Mandin JY, Massie S, Mikhailenko S, Nemtchinov V, Nikitin A, Newnham D, Perrin A, Perevalov VI, Pinnock S, Régalia-Jarlot L, Rinsland CP, Rublev A, Schreier F, Schult L, Smith KM, Tashkun SA, Teffo JL, Toth RA, Tyuterev VlG, Vander Auwera J, Varanasi P, Wagner G The GEISA spectroscopic database: Current and future archive for Earth and planetary atmosphere studies. JQSRT 2008;109:1043-59.

[5] Jacquemart D, Mandin JY, Dana V, Picqué N, Guelachvili G. A multispectrum fitting procedure to deduce molecular line parameters. Application to the 3-0 band of $^{12}C^{16}O$. Eur Phys J D 2001;14:55-69.

[6] Wartewig S. IR and Raman Spectroscopy: Fundamental Processing. Wiley-VCH, Weinheim, 2003.

[7] Mertz L. Transformations in Optics. Wiley, New York, 1965.

[8] Griffiths PR, De Haseth JA. Fourier Transform Infrared Spectrometry. Wiley, New York, 1986.

[9] Vlasova AV, Perevalov BV, Tashkun SA, Perevalov VI. Global fittings of the line positions of the rare isotopic species of the nitrous oxide molecule. In: Proceedings of the XVth Symposium on High-Resolution Molecular Spectroscopy, Nizhny Novgorod, Russia. SPIE 2006;6580:658007.

[10] Mandin JY, Dana V, Claveau C. Line intensities in the ν_5 band of acetylene $^{12}C_2H_2$. JQSRT 2000;67:429-46.

[11] Jacquemart D, Mandin JY, Dana V, Régalia-Jarlot L, Thomas X, Von Der Heyden. Multispectrum fitting measurements of line parameters for 5-μm cold bands of acetylene. JQSRT 2002;75:397-422.

[12] Jacquemart D, Kwabia Tchana F, Lacome N, Kleiner I. A complete set of line parameters for CH_3Br in the 10-μm spectral region. JQSRT 2007;105:264-302.

[14] Pliva J. Molecular constants of nitrous oxide, $^{14}N_2{}^{16}O$. J Mol Spectrosc 1968;27:461-88.

[15] Teffo JL, Chedin A. Internuclear potential and equilibrium structure of the nitrous oxide molecule from rovibrational data. J Mol Spectrosc 1989;135:389-409.

[16] Perevalov VI, Tashkun SA, Teffo JL. Global fittings of rovibrational line positions of nitrous oxide. In: Program and Abstracts of Sixteenth Colloquium on High Resolution Molecular Spectroscopy, Dijon, France. 1999:103.

[17] Ni HY, Song KF, Perevalov VI, Tashkun SA, Liu AW, Wang L., Hu SM. Fourier-transform spectroscopy of $^{14}N^{15}N^{16}O$ in the 3800 – 9000 cm^{-1} region and global modeling of its absorption spectrum. J Mol Spectrosc 2008;248:41-60.

[18] Tashkun SA, Tyuterev VG. GIP a program for experimental data reduction in molecular spectroscopy. In: Proceedings of Eleventh Symposium and School on High-Resolution Molecular Spectroscopy, Moscow, Russia. SPIE 1994 ;2205:188-191.

Captions of tables

Table 1. Experimental conditions and characteristics of the recorded spectra.

Table 2. Line parameters obtained for the $3\nu_3$ band of $^{15}N_2{}^{16}O$[a].

Table 3. Line parameters obtained for the $3\nu_1 + \nu_3$ band of $^{15}N_2{}^{16}O$[a].

Table 4. Line parameters obtained for the $5\nu_1$I band of $^{15}N_2{}^{16}O$[a].

Table 5. Summary of vibrational transition dipole moments squared and Herman-Wallis coefficients obtained for the 9 bands of $^{15}N_2{}^{16}O$.

Table 6. Experimental data and statistics of the global fit of $^{15}N_2{}^{16}O$ line positions.

Table 7. Effective Hamiltonian parameters for the $^{15}N_2{}^{16}O$ isotopologue.

Captions of figures

Fig. 1. Average values ε_j (full squares) versus the total pressure of spectrum j. The solid line represents the linear fit of the ε_j values versus the pressure.

Fig. 2. Experimental (full squares) and calculated (solid line) values of the transition dipole moment squared of the $5\nu_1$I band of $^{15}N_2{}^{16}O$. The calculated values of $|R|^2$ are obtained using the parameters given in Table 6 and Eqs. [5-6].

Fig. 3. Experimental (full squares) and calculated (solid line) values of the transition dipole moment squared of the $5\nu_1$III band of $^{15}N_2{}^{16}O$. The calculated values of $|R|^2$ are obtained using the parameters given in Table 6 and Eqs. [5-6].

Fig. 4. Residuals of the global fit of $^{15}N_2{}^{16}O$ line positions.

Table 1. Experimental conditions and characteristics of the recorded spectra.

Unapodized apparatus function	
Maximum optical path difference	90 cm
Resolution	~ 0.0056 cm^{-1}
Effective iris radius	0.59 – 0.72 mm
Collimator focal length	418 mm

Absorbing sample					
Percentages of the total pressure for the various molecules:					
$^{15}N\ ^{15}N\ ^{16}$	97.2%	$^{15}N\ ^{15}N\ ^{18}$	1.6%	others N_2O isotopologues	~ 0.1%
$^{15}N\ ^{15}N\ ^{17}$	~ 0.1%	$^{15}N\ ^{14}N\ ^{16}$	~ 0.1%	impurities (N_2, O_2 H_2O, C_2H_2 ...)	0.9%

Experimental conditions	
SNR	~ 100
Absorption path	2015 cm

	Total pressure ($\times 10^{-2}$atm)[a]	Temperature (K)	Partial pressure C_2H_2($\times 10^{-6}$atm)	Partial pressure H_2O($\times 10^{-5}$atm)	ε_j [b] ($\times 10^{-6}$)	~~Reff~~[c] ~~(mm)~~
1	0.828	298.0	2.8	1.6	1.17(1)	~~0.72(4)~~
2	1.35	298.2	4.1	1.8	1.19(2)	~~0.69(4)~~
3	2.30	298.4	6.4	2.1	1.27(3)	~~0.68(3)~~
4	3.21	298.1	8.3	2.4	1.28(4)	~~0.61(2)~~
5	4.31	298.6	6.3	2.6	1.31(6)	~~0.59(1)~~

[a] 1 atm = 1013 mbar = 1013 hPa.
[b] Wavenumber calibration factor for spectrum *j* (see text in Section 3).
[c] ~~Average effective radius of the aperture for spectrum *j* (see text in Section 3).~~

Table 2. Line parameters obtained for the $3\nu_3$ band of $^{15}N_2{}^{16}O$[a].

Line	Position	S_{obs}	S_{calc}	%	$\|R\|^2_{obs}$
P42	6329.11794	2.60E-24	2.62E-24	-0.54	1.937E-06
P41	6330.72321	3.01E-24	3.01E-24	-0.13	1.943E-06
P39	6333.87577	3.94E-24	3.93E-24	0.13	1.944E-06
P38	6335.42302	4.48E-24	4.46E-24	0.41	1.947E-06
P37	6336.95100	5.02E-24	5.04E-24	-0.45	1.929E-06
P36	6338.45970	5.66E-24	5.67E-24	-0.23	1.931E-06
P35	6339.94900	6.36E-24	6.35E-24	0.15	1.936E-06
P34	6341.41897	7.07E-24	7.07E-24	0.08	1.933E-06
P33	6342.86962	7.84E-24	7.84E-24	0.08	1.931E-06
P32	6344.30094	8.64E-24	8.64E-24	-0.06	1.927E-06
P31	6345.71288	9.52E-24	9.49E-24	0.26	1.931E-06
P29	6348.47871	1.13E-23	1.13E-23	0.10	1.924E-06
P27	6351.16700	1.32E-23	1.31E-23	0.77	1.933E-06
P26	6352.48215	1.40E-23	1.40E-23	-0.19	1.913E-06
P23	6356.31118	1.66E-23	1.66E-23	0.12	1.914E-06
P22	6357.54874	1.74E-23	1.74E-23	0.28	1.915E-06
P21	6358.76694	1.82E-23	1.81E-23	0.34	1.914E-06
P20	6359.96568	1.87E-23	1.87E-23	0.11	1.908E-06
P19	6361.14503	1.92E-23	1.92E-23	0.13	1.907E-06
P17	6363.44545	1.99E-23	1.99E-23	0.11	1.903E-06
P16	6364.56654	2.00E-23	2.00E-23	0.05	1.900E-06
P15	6365.66820	1.99E-23	1.99E-23	0.03	1.898E-06
P14	6366.75042	1.97E-23	1.97E-23	-0.06	1.895E-06
P13	6367.81316	1.94E-23	1.93E-23	0.63	1.906E-06
P12	6368.85656	1.88E-23	1.88E-23	0.08	1.894E-06
P11	6369.88045	1.80E-23	1.80E-23	-0.22	1.887E-06
P10	6370.88487	1.71E-23	1.71E-23	-0.27	1.885E-06
P 8	6372.83544	1.48E-23	1.47E-23	0.28	1.892E-06
P 6	6374.70805	1.16E-23	1.17E-23	-0.38	1.876E-06
P 5	6375.61519	9.94E-24	9.97E-24	-0.35	1.875E-06
P 4	6376.50287	8.12E-24	8.13E-24	-0.12	1.878E-06
P 3	6377.37097	6.16E-24	6.19E-24	-0.43	1.871E-06
P 2	6378.21962	4.15E-24	4.17E-24	-0.59	1.867E-06
P 1	6379.04881	2.09E-24	2.10E-24	-0.42	1.868E-06
R 0	6380.64883	2.10E-24	2.11E-24	-0.30	1.868E-06
R 1	6381.41950	4.17E-24	4.20E-24	-0.66	1.860E-06
R 2	6382.17082	6.19E-24	6.24E-24	-0.79	1.856E-06
R 3	6382.90251	8.20E-24	8.22E-24	-0.20	1.865E-06
R 4	6383.61478	1.01E-23	1.01E-23	-0.34	1.861E-06
R 5	6384.30746	1.19E-23	1.19E-23	-0.27	1.861E-06
R 6	6384.98064	1.35E-23	1.35E-23	0.14	1.868E-06
R 7	6385.63431	1.50E-23	1.50E-23	-0.09	1.862E-06
R 8	6386.26843	1.64E-23	1.64E-23	-0.06	1.861E-06
R 9	6386.88302	1.76E-23	1.76E-23	0.03	1.861E-06
R10	6387.47809	1.85E-23	1.86E-23	-0.18	1.856E-06
R11	6388.05361	1.94E-23	1.94E-23	0.04	1.859E-06
R12	6388.60962	2.00E-23	2.00E-23	0.22	1.861E-06
R13	6389.14607	2.05E-23	2.05E-23	0.45	1.864E-06
R14	6389.66298	2.08E-23	2.07E-23	0.42	1.862E-06
R15	6390.16034	2.09E-23	2.08E-23	0.41	1.861E-06
R16	6390.63811	2.09E-23	2.08E-23	0.36	1.859E-06
R17	6391.09634	2.06E-23	2.06E-23	0.14	1.854E-06
R18	6391.53500	2.02E-23	2.02E-23	-0.09	1.848E-06
R19	6391.95410	1.97E-23	1.97E-23	-0.14	1.846E-06
R20	6392.35369	1.91E-23	1.91E-23	-0.09	1.846E-06
R21	6392.73366	1.85E-23	1.84E-23	0.12	1.849E-06
R22	6393.09407	1.77E-23	1.77E-23	0.13	1.848E-06
R23	6393.43493	1.69E-23	1.68E-23	0.59	1.855E-06
R24	6393.75622	1.61E-23	1.60E-23	0.79	1.858E-06
R25	6394.05786	1.51E-23	1.50E-23	0.67	1.854E-06
R26	6394.33996	1.42E-23	1.41E-23	0.62	1.852E-06
R27	6394.60245	1.32E-23	1.31E-23	0.87	1.856E-06

Table 2. (continued)

Line	Position	S_{obs}	S_{calc}	%	$\|R\|^2_{obs}$
R28	6394.84534	1.23E-23	1.22E-23	0.82	1.854E-06
R29	6395.06869	1.13E-23	1.12E-23	0.39	1.845E-06
R30	6395.27235	1.03E-23	1.03E-23	-0.43	1.829E-06
R31	6395.45645	9.37E-24	9.41E-24	-0.46	1.827E-06
R32	6395.62097	8.51E-24	8.55E-24	-0.53	1.825E-06
R33	6395.76585	7.66E-24	7.74E-24	-0.96	1.816E-06
R34	6395.89127	6.95E-24	6.96E-24	-0.22	1.829E-06
R35	6395.99695	6.18E-24	6.24E-24	-0.97	1.814E-06

[a] The position column contains the measured line position in cm^{-1}. S_{obs} is the measured line intensity in $cm \cdot molecule^{-1}$, for pure $^{15}N_2{}^{16}O$ at 296 K, and S_{calc} is that calculated with Herman-Wallis coefficients from Table 5. % is the percentage ratio $100 \times (S_{obs} - S_{calc}) / S_{obs}$. $|R|^2_{obs}$ is the transition dipole moment squared in D^2 (1 D = 3.33546×10^{-30} C·m).

Table 3. Line parameters obtained for the $3\nu_1 + \nu_3$ band of $^{15}N_2{}^{16}O$[a].

Line	Position	S_{obs}	S_{calc}	%	$\lvert R\rvert^2_{obs}$
P29	5819.33288	1.08E-23	1.08E-23	-0.47	2.004E-06
P28	5820.60055	1.17E-23	1.17E-23	-0.16	2.013E-06
P27	5821.85155	1.26E-23	1.26E-23	-0.37	2.012E-06
P25	5824.30513	1.44E-23	1.45E-23	-0.55	2.014E-06
P21	5829.01720	1.79E-23	1.77E-23	0.99	2.055E-06
P17	5833.46918	1.96E-23	1.96E-23	0.21	2.048E-06
P16	5834.54130	2.00E-23	1.97E-23	1.62	2.079E-06
P15	5835.59718	1.97E-23	1.97E-23	-0.09	2.046E-06
P14	5836.63647	1.96E-23	1.95E-23	0.54	2.061E-06
P13	5837.65955	1.93E-23	1.92E-23	0.63	2.065E-06
P12	5838.66634	1.89E-23	1.87E-23	1.11	2.076E-06
P11	5839.65682	1.80E-23	1.80E-23	0.05	2.056E-06
P10	5840.63022	1.69E-23	1.71E-23	-1.12	2.034E-06
P 9	5841.58818	1.60E-23	1.60E-23	-0.15	2.055E-06
P 8	5842.52940	1.48E-23	1.47E-23	0.44	2.069E-06
P 7	5843.45388	1.33E-23	1.33E-23	-0.36	2.054E-06
P 6	5844.36247	1.16E-23	1.17E-23	-0.80	2.047E-06
P 5	5845.25414	9.88E-24	1.00E-23	-1.52	2.033E-06
P 4	5846.12991	8.17E-24	8.19E-24	-0.19	2.062E-06
P 3	5846.98855	6.19E-24	6.24E-24	-0.81	2.051E-06
R 1	5851.03745	4.28E-24	4.26E-24	0.44	2.082E-06
R 2	5851.79756	6.31E-24	6.34E-24	-0.47	2.064E-06
R 3	5852.54155	8.44E-24	8.36E-24	0.87	2.092E-06
R 5	5853.97983	1.22E-23	1.21E-23	1.00	2.097E-06
R 6	5854.67468	1.39E-23	1.38E-23	0.55	2.088E-06
R 7	5855.35273	1.53E-23	1.54E-23	-0.35	2.070E-06
R 8	5856.01427	1.66E-23	1.68E-23	-0.75	2.062E-06
R 9	5856.65899	1.78E-23	1.80E-23	-1.03	2.057E-06
R11	5857.90008	1.97E-23	1.99E-23	-0.76	2.063E-06
R12	5858.49586	2.05E-23	2.05E-23	0.07	2.080E-06
R13	5859.07507	2.10E-23	2.10E-23	0.06	2.080E-06
R14	5859.63772	2.14E-23	2.13E-23	0.54	2.090E-06
R15	5860.18389	2.16E-23	2.14E-23	0.81	2.096E-06
R18	5861.72408	2.09E-23	2.08E-23	0.19	2.083E-06
R19	5862.20459	2.03E-23	2.03E-23	-0.03	2.078E-06
R20	5862.66861	1.97E-23	1.97E-23	-0.08	2.077E-06
R23	5863.96202	1.74E-23	1.74E-23	0.29	2.083E-06
R24	5864.36051	1.65E-23	1.65E-23	0.25	2.082E-06
R27	5865.45686	1.36E-23	1.36E-23	-0.14	2.072E-06
R29	5866.10579	1.16E-23	1.16E-23	0.01	2.074E-06
R30	5866.40565	1.06E-23	1.07E-23	-0.24	2.067E-06
R31	5866.68946	9.75E-24	9.74E-24	0.03	2.072E-06
R34	5867.44211	7.20E-24	7.21E-24	-0.07	2.067E-06

[a] See footnote of Table 2 for the meaning of column headings.

Table 4. Line parameters obtained for the $5\nu_1$ I band of $^{15}N_2{}^{16}O$[a].

Line	Position	S_{obs}	S_{calc}	%	$\|R\|^2_{obs}$
P42	6136.21128	2.07E-25	2.07E-25	0.07	1.589E-07
P41	6137.52969	2.34E-25	2.38E-25	-1.71	1.557E-07
P40	6138.83637	2.77E-25	2.72E-25	1.81	1.609E-07
P39	6140.12915	3.09E-25	3.09E-25	-0.26	1.571E-07
P38	6141.40987	3.48E-25	3.51E-25	-0.61	1.562E-07
P37	6142.67639	3.91E-25	3.96E-25	-1.13	1.550E-07
P36	6143.93185	4.48E-25	4.44E-25	0.79	1.577E-07
P35	6145.17410	4.96E-25	4.97E-25	-0.02	1.560E-07
P34	6146.40252	5.47E-25	5.52E-25	-0.99	1.542E-07
P33	6147.61883	6.12E-25	6.12E-25	0.11	1.556E-07
P32	6148.82243	6.70E-25	6.74E-25	-0.57	1.543E-07
P31	6150.01297	7.37E-25	7.39E-25	-0.38	1.543E-07
P30	6151.19161	8.12E-25	8.07E-25	0.60	1.555E-07
P29	6152.35793	8.80E-25	8.77E-25	0.37	1.549E-07
P28	6153.51049	9.52E-25	9.47E-25	0.46	1.548E-07
P27	6154.65106	1.02E-24	1.02E-24	0.35	1.544E-07
P26	6155.77930	1.09E-24	1.09E-24	0.25	1.540E-07
P25	6156.89500	1.16E-24	1.16E-24	0.19	1.537E-07
P24	6157.99819	1.24E-24	1.23E-24	1.21	1.551E-07
P23	6159.08887	1.30E-24	1.29E-24	0.69	1.541E-07
P22	6160.16695	1.35E-24	1.35E-24	0.33	1.533E-07
P20	6162.28676	1.46E-24	1.45E-24	0.71	1.536E-07
P19	6163.32806	1.49E-24	1.49E-24	0.27	1.528E-07
P18	6164.35672	1.52E-24	1.52E-24	0.18	1.526E-07
P17	6165.37367	1.54E-24	1.54E-24	0.11	1.524E-07
P16	6166.37785	1.56E-24	1.55E-24	0.62	1.531E-07
P15	6167.37009	1.55E-24	1.55E-24	0.23	1.524E-07
P14	6168.35007	1.54E-24	1.53E-24	0.41	1.526E-07
P13	6169.31797	1.52E-24	1.50E-24	0.95	1.534E-07
P12	6170.27310	1.45E-24	1.46E-24	-0.61	1.510E-07
P11	6171.21673	1.41E-24	1.40E-24	0.29	1.523E-07
P 9	6173.06649	1.24E-24	1.25E-24	-0.58	1.510E-07
P 8	6173.97388	1.15E-24	1.15E-24	0.35	1.524E-07
P 6	6175.75046	9.03E-25	9.14E-25	-1.23	1.501E-07
P 5	6176.62094	7.69E-25	7.80E-25	-1.53	1.497E-07
P 4	6177.47912	6.39E-25	6.37E-25	0.23	1.524E-07
P 3	6178.32557	4.82E-25	4.86E-25	-0.85	1.509E-07
P 2	6179.15964	3.23E-25	3.28E-25	-1.64	1.498E-07
R 2	6183.14772	4.90E-25	4.94E-25	-0.87	1.516E-07
R 3	6183.90806	6.49E-25	6.52E-25	-0.48	1.524E-07
R 4	6184.65772	7.98E-25	8.04E-25	-0.71	1.522E-07
R 5	6185.39464	9.30E-25	9.47E-25	-1.82	1.508E-07
R 6	6186.11895	1.08E-24	1.08E-24	-0.34	1.532E-07
R 7	6186.83132	1.21E-24	1.20E-24	0.30	1.544E-07
R 8	6187.53132	1.32E-24	1.31E-24	0.45	1.549E-07
R 9	6188.21906	1.42E-24	1.41E-24	0.79	1.557E-07
R10	6188.89487	1.50E-24	1.50E-24	0.54	1.556E-07
R11	6189.55829	1.56E-24	1.57E-24	-0.05	1.549E-07
R12	6190.20951	1.64E-24	1.62E-24	1.08	1.570E-07
R15	6192.08811	1.70E-24	1.70E-24	-0.21	1.560E-07
R16	6192.68996	1.70E-24	1.70E-24	-0.10	1.565E-07
R17	6193.27912	1.70E-24	1.69E-24	0.52	1.578E-07
R18	6193.85571	1.68E-24	1.67E-24	0.75	1.586E-07
R19	6194.42030	1.64E-24	1.63E-24	0.25	1.582E-07
R20	6194.97190	1.60E-24	1.59E-24	0.43	1.589E-07
R21	6195.51142	1.55E-24	1.54E-24	0.65	1.597E-07
R22	6196.03760	1.47E-24	1.48E-24	-0.67	1.580E-07
R23	6196.55181	1.42E-24	1.41E-24	0.22	1.599E-07
R24	6197.05341	1.34E-24	1.34E-24	0.13	1.602E-07
R25	6197.54154	1.26E-24	1.27E-24	-0.80	1.592E-07
R26	6198.01791	1.19E-24	1.19E-24	-0.21	1.606E-07

Table 4. (continued)

Line	Position	S_{obs}	S_{calc}	%	$\|R\|^2_{obs}$
R27	6198.48118	1.13E-24	1.12E-24	1.01	1.631E-07
R28	6198.93171	1.03E-24	1.04E-24	-0.80	1.607E-07
R29	6199.36904	9.74E-25	9.62E-25	1.13	1.644E-07
R30	6199.79386	8.83E-25	8.87E-25	-0.41	1.624E-07
R31	6200.20577	8.19E-25	8.13E-25	0.69	1.648E-07
R33	6200.99083	6.80E-25	6.74E-25	0.82	1.662E-07
R34	6201.36359	6.16E-25	6.09E-25	1.12	1.673E-07
R35	6201.72304	5.50E-25	5.48E-25	0.26	1.665E-07
R36	6202.07025	4.95E-25	4.91E-25	0.83	1.681E-07
R37	6202.40357	4.30E-25	4.38E-25	-1.92	1.642E-07
R40	6203.32450	2.97E-25	3.02E-25	-1.60	1.667E-07

[a] See footnote of Table 2 for the meaning of column headings.

Table 5. The spectroscopic constant of the observed in this work vibration energy levels.

State	Vibrational symmetry	G[a]	B	D ($\times 10^7$)	H ($\times 10^{12}$)
Ground	Σ^+	0.	0.4048599(3)[b]	1.635(2)	
ν_2	Π^+	-	0.40497(3)	1.2(4)	
ν_2	Π^-	-	0.40574(3)	1.3(5)	
$3\nu_3$	Σ^+	6379.858640(9)	0.39511266(7)	1.625(1)	0.18(4)
$\nu_2+3\nu_3$	Π^+	6339.4670(6)[c]	0.39535(2)	1.2(4)	
$\nu_2+3\nu_3$	Π^-	6339.4674(5)[c]	0.39607(3)	1.2(5)	
$\nu_1+3\nu_3$	Σ^+	7568.25825(7)	0.3933787(3)	1.596(3)	
$2\nu_1+2\nu_3$	Σ^+	6700.4416(1)	0.3949532(8)	1.556(9)	
$3\nu_1+\nu_3$	Σ^+	5849.46732(4)	0.3966341(2)	1.463(2)	
$4\nu_1+\nu_3$I	Σ^+	6980.937(1)	0.397466(6)	2.35(8)	
$4\nu_1+\nu_3$II	Σ^+	7066.5216(1)	0.3952271(7)	1.237(7)	
$5\nu_1$I	Σ^+	6180.79113(7)	0.3987898(5)	2.241(7)	2.5(3)
$5\nu_1$III	Σ^+	6259.03542(7)	0.3973491(5)	0.979(7)	3.9(3)

[a] The values of spectroscopic constants and band centres are given in cm^{-1}.
[b] Confidence intervals (1 SD, in unit of the last quoted digit) are given between parenthesis.
[c] For two states $\nu_2+3\nu_3$ the centers of the bands $\nu_2+3\nu_3-\nu_2$ are reported instead of G constant.

Table 5. Summary of vibrational transition dipole moments squared and Herman-Wallis coefficients obtained for the 9 bands of $^{15}N_2{}^{16}O$.

Center[a]	Band	Vibrational symmetry	Number of transitions	$\|R_0\|^2$ (in 10^{-6} D^2)[b]	A_1^{RP} (in 10^{-4})	A_2^{RP} (in 10^{-5})
6379.86	$3\nu_3$	$\Sigma^+ \leftarrow \Sigma^+$	70	1.875(1)[c]	-3.8(1)	0.18(5)
6339.47	$\nu_2+3\nu_3-\nu_2$	$\Pi^+ \leftarrow \Pi^+$	19	3.97(1)	–2.4(8)	0
6339.47	$\nu_2+3\nu_3-\nu_2$	$\Pi^- \leftarrow \Pi^-$	14	3.956(7)	–2.2(4)	0.8(2)
7568.26	$\nu_1+3\nu_3$	$\Sigma^+ \leftarrow \Sigma^+$	51	0.2418(1)	-1.3(1)	0
6700.44	$2\nu_1+2\nu_3$	$\Sigma^+ \leftarrow \Sigma^+$	42	0.0716(1)	2.7(3)	-0.7(2)
5849.47	$3\nu_1+\nu_3$	$\Sigma^+ \leftarrow \Sigma^+$	43	2.071(3)	2.5(3)	-0.8(2)
6980.94	$4\nu_1+\nu_3$I	$\Sigma^+ \leftarrow \Sigma^+$	16	0.0388(1)	5.4(8)	0
7066.52	$4\nu_1+\nu_3$II	$\Sigma^+ \leftarrow \Sigma^+$	42	0.0784(2)	4.4(4)	-1.7(3)
6180.79	$5\nu_1$I	$\Sigma^+ \leftarrow \Sigma^+$	72	0.1525(2)	4.3(2)	2.2(1)
6259.04	$5\nu_1$III	$\Sigma^+ \leftarrow \Sigma^+$	66	0.1570(2)	3.6(2)	-2.31(8)

[a] Rough values of band centers (in cm^{-1}) are reported only as a guide.
[b] 1 debye = 3.33546×10^{-30} C·m.
[c] Confidence intervals (1 SD, in unit of the last quoted digit) are given between parenthesis.

Table 6. Experimental data and statistics of the global fit of $^{15}N_2{}^{16}O$ line positions.

Reference	Spectral domain in cm^{-1}	Calibration factor [a]	Accuracy (10^{-3} cm^{-1})	N_{fit} [b]	RMS [c] (10^{-3} cm^{-1})
Amiot and Guelachvili [1]	3631-6396	0.999999983	2.0	1277	1.50
Toth [2]	1227-3415	1.000000000	0.1	374	0.08
This work	5814-7582	1.000000000	0.5	435	0.51

[a] Calibration factors are taken from Ref. [16] where they were derived in the result of the term values analysis performed for the principal isotopic species of nitrous oxide molecule.
[b] N_{fit} is the number of the lines included in the fit.
[c] A root mean squares of residuals for a given experimental source.

Table 7. Effective Hamiltonian parameters for the $^{15}N_2\,^{16}O$ isotopologue.

Diagonal vibrational parameters

N	Parameter	Value (cm^{-1})	Order	N	Parameter	Value (cm^{-1})	Order
1	ω_1	1280.527(25)		16	y_{133}	11.78(70)	10^{-2}
2	ω_2	580.845(27)		17	y_{222}	4.236(79)	10^{-2}
3	ω_3	2209.544(16)		18	y_{223}	11.94(66)	10^{-2}
4	x_{11}	-4.387(15)		19	y_{233}	0.161(78)	10^{-2}
5	x_{12}	-4.270(35)		20	y_{333}	-0.117(33)	10^{-2}
6	x_{13}	-24.238(88)		21	$y_{1\ell\ell}$	9.97(53)	10^{-2}
7	x_{22}	0.204(15)		22	$y_{2\ell\ell}$	-2.328(47)	10^{-2}
8	x_{23}	- 14.329(15)		23	$y_{3\ell\ell}$	17.84(68)	10^{-2}
9	x_{33}	- 14.1060(30)		24	z_{1113}	-1.239(24)	10^{-2}
10	$x_{\square}$ *	-0.5611535980		25	z_{1123}	-7.96(62)	10^{-2}
11	y_{111} **	0.0264922656	10^{-2}	26	z_{1133}	4.72(16)	10^{-2}
12	y_{112}	2.82(57)	10^{-2}	27	z_{1222}	-1.479(19)	10^{-2}
13	y_{113}	-35.82(59)	10^{-2}	28	z_{1223}	-1.03(56)	10^{-2}
14	y_{122} **	0.507836011	10^{-2}	29	z_{1333}	0.692(38)	10^{-2}
15	y_{123}	67.7(26)	10^{-2}	30	z_{2333}	0.079(19)	10^{-2}

Diagonal rotational and vibrational-rotational parameters

N	Parameter	Value (cm^{-1})	Order	N	Parameter	Value (cm^{-1})	Order
31	B_e	0.40683211(46)		39	γ_{23}	0.3438(17)	10^{-4}
32	α_1	0.179982(37)	10^{-2}	40	γ_{33}	-0.03804(63)	10^{-4}
33	α_2	-0.055123(42)	10^{-2}	41	$\gamma_{\ell\ell}$*	0.04477235290	10^{-4}
34	α_3	0.326540(17)	10^{-2}	42	D_e	0.16288(12)	10^{-6}
35	γ_{11}	-0.0634(36)	10^{-4}	43	β_1	0.1411(47)	10^{-8}
36	γ_{12}	0.616(11)	10^{-4}	44	β_2	0.0395(96)	10^{-8}
37	γ_{13}	-0.311(14)	10^{-4}	45	β_3	-0.0546(15)	10^{-8}
38	γ_{22}	-0.2837(22)	10^{-4}				

Parameters of ℓ - doubling matrix elements

N	Parameter	Value (cm^{-1})	Order	N	Parameter	Value (cm^{-1})	Order
46	L_e	-0.19086(31)	10^{-3}	49	L_3	0.3706(10)	10^{-5}
47	L_1	2.08(17)	10^{-5}	50	L_J	1.43(98)	10^{-10}
48	L_2	-0.567(33)	10^{-5}				

Parameters of Fermi interaction matrix element $\langle V_1 V_2\ \ell_2 V_3\ J \left| H^{eff} \right| V_1 - 1\ V_2 + 2\ \ell_2 + \Delta\ell_2\ V_3 J \rangle$

N	Parameter	Value (cm^{-1})	Order	N	Parameter	Value (cm^{-1})	Order
51	F_e	-17.982(54)		57	F_{13}	1.55(43)	10^{-2}
52	F_1	0.2411(71)		58	F_{23}	0.50(36)	10^{-2}
53	F_2	0.1578(29)		59	F_{33}	2.76(53)	10^{-2}
54	F_3	0.345(26)		60	F_j	1.430(13)	10^{-4}
55	F_{11}	-0.406(94)	10^{-2}	61	F_e^L	0.113(14)	10^{-4}
56	F_{12}	0.139(27)	10^{-2}				

Table 7 (continued)

Parameters of Fermi interaction matrix element $\langle V_1 V_2 \ell_2 V_3 J | H^{eff} | V_1 - 2\ V_2\ \ell_2 V_3 + 1\ J \rangle$

N	Parameter	Value (cm^{-1})	Order	N	Parameter	Value (cm^{-1})	Order
62	$F_e^{(2)}$	-10.66(36)		63	$F_j^{(2)}$	1.002(48)	10^{-4}

Parameters of anharmonic interaction matrix element $\langle V_1 V_2 \ell_2 V_3 J | H^{eff} | V_1 - 1 V_2 - 2\ \ell_2 V_3 + 1 J \rangle$

N	Parameter	Value (cm^{-1})	Order	N	Parameter	Value (cm^{-1})	Order
64	$F_e^{(3)}$	0.50(12)		65	$F_j^{(3)}$	-0.472(48)	10^{-4}

[a)] Uncertainties in parentheses represent one standard deviation in units of the last quoted digit; * fixed to the value given in Ref.[15], ** fixed.