Journal of Quantitative Spectroscopy & Radiative Transfer 103 (2007) 168–174

Journal of Quantitative Spectroscopy & Radiative Transfer

www.elsevier.com/locate/jqsrt

Note

On the line parameters for the $X^1\Sigma_g^+$ (1–0) infrared quadrupolar transitions of $^{14}N_2$

A. Goldman[a,*], R.H. Tipping[b], Q. Ma[c], C.D. Boone[d], P.F. Bernath[d], P. Demoulin[e], F. Hase[f], M. Schneider[f], J.W. Hannigan[g], M.T. Coffey[g], C.P. Rinsland[h]

[a]*Department of Physics, University of Denver, Denver, CO 80208-2238, USA*

[b]*Department of Physics and Astronomy, University of Alabama, Tuscaloosa, AL 35487-0324, USA*

[c]*NASA Goddard Institute for Space Studies and Department of Applied Physics and Applied Mathematics, Columbia University, 2880 Broadway, New York, NY 10025, USA*

[d]*Department of Chemistry, University of Waterloo, Waterloo, Ont. N2L3G1, Canada*

[e]*Institut d'Astrophysique et de Géophysique, allée du VI août, 17, bâtiment B5a, B-4000 Liège, Belgium*

[f]*Institut für Meteorologie und Klimaforschung, Forschungszentrum Karlsruhe, Postfach 3640, D-76021 Karlsruhe, Germany*

[g]*Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, CO 80303, USA*

[h]*NASA Langley Research Center, Atmospheric Sciences Competency, Mail Stop 401A, Hampton, VA 23681-2199, USA*

Received 19 April 2006; received in revised form 22 May 2006; accepted 24 May 2006

Abstract

Re-examination of the $^{14}N_2$ $X^1\Sigma_g^+$ (1–0) line parameters in the HITRAN database showed that the vibration–rotation interaction effect on the line intensities has been neglected, and that the halfwidths are not compatible with experimental and theoretical studies. New line parameters have been generated, which improve the consistency and accuracy in individual N_2 line retrievals from atmospheric spectra. Unresolved line shape issues require further studies.

Keywords: N_2 quadrupole lines; Infrared atmospheric spectra

1. Introduction

The $^{14}N_2$ $X^1\Sigma_g^+$ (1–0) quadrupole lines in the atmospheric infrared spectrum were first detected by Goldman et al. [1], along with the $X^3\Sigma_g^-$ (1–0) O_2 quadrupole lines. A more detailed study of the N_2 lines followed by Camy-Peyret et al. [2] and calculated line parameters were included in the HITRAN 1982 edition [3]. The N_2 line parameters have become an integral part of retrievals from atmospheric infrared spectra recorded by ground-based, balloon-borne and satellite instruments. However, despite subsequent improvements in the line parameters, difficulties persist in quantitative analysis of the spectra.

In the atmospheric spectrum, both the O and Q branches of the N_2 lines are masked by the strong CO_2 4.3-μm band. In ground-based spectra, only lines from the range of $S(7)$–$S(21)$ are observable without

*Corresponding author. Tel.: +1 303 871 2897; fax: +1 303 871 4405.
E-mail addresses: agoldman@du.edu, goldman@acd.ucar.edu (A. Goldman).

0022-4073/$ - see front matter
doi:10.1016/j.jqsrt.2006.05.010

significant interferences, above 2395 cm^{-1}, superimposed on the high wavenumber wings of continuum created by the CO_2 sub-Lorentzian lines of the band head and the N_2 collision-induced absorption. Figure 1 in Rinsland et al. [4] shows the region in a series of ATMOS spectra. The lines $S(11)$, $S(13)$ are less isolated than others, $S(14)$, $S(17)$, $S(18)$ and $S(19)$ are masked, and $S(20)$ and $S(21)$ are very weak. The range of observable lines extends from $S(4)$ to $S(21)$ and also includes the partially isolated $O(7)$ and $O(14)$ lines in occultation spectra recorded with balloon-borne and satellite instruments. The observed N_2 lines exhibit the expected intensity alternation, which makes the odd J lines significantly weaker (see Eqs. (2), (3)). The $S(8)$–$S(10)$ lines have been the prime choice for atmospheric retrievals. However, it was found that the mixing ratios obtained from the total column are several percent higher than the expected 0.781 value and the columns retrieved from the individual lines are inconsistent [5,6]. Even larger inconsistencies are found in the individual line analysis of $S(7)$–$S(16)$ performed on ACE satellite-borne occultation spectra [7,8].

In what follows, we will review the development of the N_2 line parameters since 1982, and present new improvements which lead to more reliable atmospheric retrievals.

2. Spectroscopic parameters for N_2

Following the publication of the initial N_2 line parameters [3], laboratory measurements and analysis by Reuter et al. [9] provided improved energy levels and line positions, as well as values for Lorentz halfwidths and the derivative of the molecular quadrupole moment.

Reuter et al. [9] analyzed the energy levels according to the Dunham formulation [10]

$$E(v,J) = \sum_{ij} Y_{ij}\left(v+\frac{1}{2}\right)^i [J(J+1)]^j, \tag{1}$$

with Y_{ij} as the Dunham coefficients.

Improved Dunham coefficients were derived from the analysis of high-resolution stratospheric spectra by Rinsland et al. [11], and these were adopted for the line positions and lower state energies in the 1992 edition of the HITRAN database [12].

The N_2 quadrupole line intensities [cm^{-1}/(molecule cm^{-2})] at temperature T (K) are given by [13]

$$S_{vJ}^{v'J'}(T) = I_a \frac{8\pi^5}{15hc} v^3 g_J \frac{(2J+1)}{Z(T)} \exp\left(\frac{-hcE}{kT}\right)\left[1-\exp\left(\frac{-hcv}{kT}\right)\right] \times (2J'+1)\begin{pmatrix} J & 2 & J' \\ 0 & 0 & 0 \end{pmatrix}^2 |\langle vJ|Q|v'J'\rangle|^2, \tag{2}$$

where

$$(2J'+1)\begin{pmatrix} J & 2 & J' \\ 0 & 0 & 0 \end{pmatrix}^2 = \begin{cases} \dfrac{3J(J-1)}{2(2J-1)(2J+1)}, & J' = J-2 \text{ (}O\text{ branch)}, \\ \dfrac{J(J+1)}{(2J-1)(2J+3)}, & J' = J \text{ (}Q\text{ branch)}, \\ \dfrac{3(J+1)(J+2)}{2(2J+1)(2J+3)}, & J' = J+2 \text{ (}S\text{ branch)}. \end{cases} \tag{3}$$

I_a is the natural terrestrial isotopic abundance. v and E are in units of cm^{-1}. $Z(T)$ is the total internal partition function. g_J is the nuclear spin statistical weight (3 or 6 for J odd or even).

The $3j$ symbol is related to the Clebsch–Gordan coefficient, so that

$$(2j_3+1)\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}^2 = |\langle j_1 m_1 j_2 m_2 | j_1 j_2 j_3 m_3\rangle|^2. \tag{4}$$

The allowed branches in Eq. (3) are determined by the triangle relations $\Delta(j_1 j_2 j_3)$, with $j_2 = 2$ the electric quadrupole tensorial rank.

$\langle vJ \mid Q \mid v'J' \rangle$ are the radial vibration–rotation quadrupole matrix elements. In the approximation used in Refs. [2,9] and adopted for HITRAN, it was assumed [14] that

$$\langle v, J|Q|v+1, J'\rangle = \left(\frac{\partial Q}{\partial r}\right)_{\mathrm{e}} r_{\mathrm{e}} \left(\frac{B_{\mathrm{e}}}{\omega_{\mathrm{e}}}\right)^{1/2} \sqrt{v+1}, \tag{5}$$

in which the parameters are equilibrium constants, and $\sqrt{v+1}$ is from the harmonic oscillator matrix elements.

For the HITRAN 1992 edition [12] the 1982 intensities were scaled by a uniform factor of 1.049, based on the analysis of the lines $S(7)$–$S(10)$ in high-resolution ground-based spectra, as described by Demoulin et al. [15]. J-dependent halfwidths were introduced into HITRAN 1992 on the basis of solar fits and Raman measurements, as described by Rinsland et al. [16]. The constant n value of 0.5 has been retained for the temperature dependence. No changes were introduced in the 2004 HITRAN edition for N_2 [17].

Using Eqs. (1)–(5) with the spectroscopic constants given in Refs. [2,11] for a re-calculation of the HITRAN 1982 and 1992 N_2 lines, duplicates well the energy levels and line positions, but not the intensities. The calculated intensities are smaller than those in HITRAN 1982 by a constant factor of about 4%, and thus about 9% smaller than the HITRAN 1992–2004 values. No explanation was found for this discrepancy, which is probably due to using different constants than reported. However, this does not affect the present study, as the HITRAN 2004 line intensities will be individually modified, and then re-normalized by observed spectra.

The formulation in Eq. (5) does not take into account the effect of vibration–rotation interaction on the line intensities. It is customary to model this effect using the Herman–Wallis F-factor formulation

$$|\langle v, J|Q|v', J'\rangle|^2 = |\langle v, 0|Q|v', 0\rangle|^2 F_{v,J}^{v',J'}, \tag{6}$$

and represent the F-factors by the series

$$F_{vJ}^{v'J'} = 1 + C_v^{v'} m + D_v^{v'} m^2 + \cdots, \tag{7}$$

with m definitions appropriate to the multipolar type of transitions and vibration–rotation branches.

Detailed algebraic expressions of the F-factors for quadrupolar transitions in $^1\Sigma$ diatomic molecules O, Q and S branches have been derived by Tipping and Ogilvie [18]. Individual molecule parameters in these expressions are spectroscopic constants, Dunham potential constants, and quadrupole moment matrix elements. Following their results one can obtain the following approximate expression for the (1–0) quadrupolar S (and O) transitions $(1, J') \leftarrow (0, J)$ as

$$F_{0J}^{1J'} = \left[1 + \gamma \frac{(\beta' - \beta)}{2} \left\{\frac{-2Q_0}{(\gamma/2)^{-1/2}\langle 00|Q|10\rangle}\right\}\right]^2, \tag{8}$$

where $\gamma = 2B_{\mathrm{e}}/\omega_{\mathrm{e}}$, $\beta' = J'(J'+1)$, $\beta = J(J+1)$. Q_0 is the permanent quadrupole moment, and $\langle v = 0|Q(r)|v = 1\rangle$ is the rotationless fundamental matrix element.

Following Boissoles et al. [19], we use $B_{\mathrm{e}} = 1.99824\,\mathrm{cm}^{-1}$, $\omega_{\mathrm{e}} = 2358.6\,\mathrm{cm}^{-1}$, $Q_0 = -1.09ea_0^2$, $\langle 00|Q|10\rangle = 5.63 \times 10^{-2} ea_0^2$, and find that

$$F_{0J}^{1J'} = \left[1 + 1.91 \times 10^{-3}(\beta' - \beta)/2\right]^2. \tag{9}$$

Applying this factor to the individual lines shows that the F-factor increases by about 7% from $S(7)$ to $S(17)$. (A corresponding intensity decrease occurs in the O-branch lines).

A more accurate Herman–Wallis factor can be calculated from Ref. [18] by using spectroscopic constants to find the reduced displacement coefficients a_1 and a_2 for the Dunham constants and the average of the two second order derivatives of the quadrupole moment from Lawson and Harrison [20] as

$$F_{0J}^{1J'} = [1 + 1.9067 \times 10^{-3}(\beta' - \beta)/2 + 4.1 \times 10^{-6}(\beta' + \beta)/2]^2. \tag{10}$$

This introduces insignificant changes for the O and S branches compared to Eq. (9), but also allows the calculation of the effect on Q-branch lines (which is smaller by a factor γ than that in the O and S branches).

It is interesting to note that the Herman–Wallis factor for O_2 is smaller than that of N_2 by a factor of 6.9, and it should also be incorporated into the HITRAN database.

Examination of the N_2 halfwidths listed in the HITRAN database [17] shows that their *J*-dependence is independent of the branch type (*O*, *Q* or *S*) and is decreasing linearly over the entire *J* range. However, the *O*-, *Q*-, and *S*-branch lines should have different halfwidths and *J*-dependence, due to the type of polarizabilities involved, as discussed by Bruet et al. [21]. Furthermore, the self- and air-broadened halfwidths of N_2 in HITRAN were taken to be the same, while the quadrupole moment of N_2 is approximately a factor of 4 larger than that of O_2. The rate of decrease in HITRAN values with *J* is not as large as shown in experimental studies, such as those by Lavorel et al. [22] and by Fanjoux et al. [23], as well as in the recent theoretical studies by Bruet et al. [21] and by Ma et al. [24]. The latter are based on a corrected Robert–Bonamy formalism and more accurate interaction potentials, and will be extended in the future for a more complete set of N_2–N_2 and N_2–air halfwidths, line shifts, line-mixing parameters and the temperature dependence coefficient *n* (assumed 0.5 in HITRAN).

In the present study, we implemented the *F*-factors from Eq. (10), and adapted the experimental halfwidths of the *Q* lines in Table 2 of Lavorel et al. [22] and the *S* lines in Table 4 of Fanjoux et al. [23]. (Note, however, the oscillatory *J*-dependence of the halfwidths in Ref. [22] vs. the linear dependence in Ref. [23].) The modified halfwidths are similar to the HITRAN values at low *J* but decrease faster with increasing *J*. Initially, these modifications were applied only to the *S*(6)–*S*(20) lines, normalizing the *F*-factor modified intensities to the *S*(8) HITRAN intensity. Approximate temperature dependence coefficients for these lines were taken from preliminary calculations for the *Q*-branch by one of the authors (Ma). These decrease with *J*, unlike the constant 0.5 value used in HITRAN.

3. Tests with atmospheric spectra

The modified line parameters were tested in retrievals from four sets of atmospheric spectra, the ACE occultation spectra [8] and ground-based spectra from the Jungfraujoch (46.5°N, 8°E, 3580 m a.s.l.) [6], Izaña (28°N, 16°W, 2370 m a.s.l.) [25] and Thule, Greenland (76.5°N, 68.8°W, 220 m a.s.l.). The retrievals, for vertical profiles or column amounts, are based on optimal spectral fitting of an *a priori* model to observed data in pre-selected spectral regions for the individual N_2 lines.

ACE retrievals of N_2 volume mixing ratio (VMR) profiles were performed for a selection of occultation measurements from the period 27 December 2004 to 8 August 2005, over 1300 occultations in total. At this time, only a limited altitude range of the retrievals will be considered for the intensity normalization of the N_2 lines. In the 25–35 km range, the average retrieved profile was approximately constant, as expected. However, below 25 km, the average profile decreased with decreasing altitude. This unexpected behavior is not understood at this time, but could be related to the presence of the N_2 collision-induced absorption, which continue to be the subject of intensive experimental and theoretical studies [26]. For unknown reasons, the average profile above 35 km increased with increasing altitude. The results for *S*(13)–*S*(20) showed discrepancies with the results for lower-*J* lines, but there was no clear trend to the discrepancies. These unresolved issues, each reaching a magnitude of several percent, are under further study. We therefore only consider here the ACE N_2 retrieval results from 25 to 35 km for *S*(7)–*S*(12). In this altitude range, the effect of new line parameters is mostly from the intensities, as the influence of the collision halfwidths is significantly reduced.

Although the cause of the discrepancies above 35 km is not known, they are not believed to be the result of non-LTE effects. The energy levels population changes in non-LTE can have a dramatic impact in emission measurements, but with absorption-based measurements (such as with ACE) the impact is typically small. Also, non-LTE effects in N_2 should be small to negligible near 40 km.

As expected, the individual line ACE retrievals using the new line parameters resulted in significantly improved internal consistency compared to that obtained with the HITRAN line parameters (over the complete altitude range), but the retrieved VMR value is too high. Based on the *S*(7)–*S*(12) lines, the new intensities (of the *F*-factor corrected lines, normalized to the *S*(8) HITRAN line intensity) should be increased by $(3.9 \pm 1.3)\%$.

Several versions of N_2 retrievals from the Jungfraujoch spectra, all for the *S*(8)–*S*(10) lines, have been described in previous studies [5,6], with improved consistency achieved in the 2005 results, but no clear *J*-dependence of the N_2 columns. Column retrievals with the new line parameters were performed for 358 spectra of year 2002 and extended to the $S(7)$–$S(20)$ lines. Using the HITRAN N_2 line parameters showed a gradual increase of the retrieved N_2 column vs. J, with a magnitude of about 40% from $S(7)$ to $S(20)$. This dependence on J is strongly reduced with the new line parameters, with a remaining 3% increase of the N_2 column from $S(7)$ to $S(20)$. The F-factors increase only by 10% from $S(7)$–$S(20)$, and the modified halfwidth parameters are responsible for the rest. The mean N_2 column retrieved is 1.06 higher than the expected value, suggesting that the new intensities should be increased by $(6 \pm 2)\%$. The quality of the fits improves greatly with the new parameters, except for the lines $S(8)$–$S(10)$ that show a small degradation.

N_2 retrievals from the Izaña spectra were conducted with the $S(7)$–$S(16)$ lines for column retrievals, and the $S(7)$–$S(13)$ for profile retrievals. A set of 98 spectra measured between January and October 2005 were used in the analysis. Using the HITRAN individual line parameters in column retrievals showed the need of gradual increase in the line intensities of more than 15% (for a proper N_2 column). The new line parameters significantly improved the internal consistency for both the column and profile retrievals, with the more consistent improvements being due to the intensity corrections. The column retrievals show that the new intensities should be increased by $(6 \pm 2)\%$. However, the quality of the spectral fittings is not uniformly improved with the new line shape parameters. In particular, the fitting residuals using the new lines are larger for $S(8)$–$S(10)$, but much smaller for higher-J lines. The retrieved profiles show unexplained curvatures, which are probably also related to the halfwidths and their temperature dependence. The retrieved profiles imply an intensity increase of $(4 \pm 2)\%$, in agreement with ACE scaling factor.

Observations in the 4.1-μm region are routinely made as part of the normal operation of the Network for the Detection of Stratospheric Change (NDSC; http://www.ndsc.ws/) solar viewing high-resolution IR-FTS ($250\,cm^{-1}$ OPD) at the high-arctic site at Thule. Measurements of N_2 are limited by the large absorption of CO_2 due to the low altitude of the site and the low solar zenith angles that persist for much of the available observation time. During mid-summer measurements can be made at higher solar zenith angles which reveal N_2 lines in the $S(7)$–$S(20)$ range, but the still low 100% transmission level tends to reduce the SNR. Observations made on 10 July 2004 at a solar zenith angle of 54.7° with an RMS SNR of 100 were used for individual total column scaling retrievals performed on the strongest of these lines, $S(7)$–$S(13)$. The retrievals were performed using the SFIT2 v3.91 code [27] and the new N_2 lines substituted into the HITRAN 2004 [17] line listing. Atmospheric paths were calculated using the FASCATM v2.08 code (an updated version, 2006) [27]. The NCEP temperature profile was used [28] with the actual observation site pressure. The mean profile scaling factor (from the *a priori* constant VMR of 0.781) for the retrievals is 1.06 ± 0.02, consistent with measurements from the high-altitude sites.

Subsequently, the complete set of the HITRAN N_2 (1–0) line parameters was revised. In principle, the total band intensity should not change, so the modified intensities would be normalized to the HITRAN band intensity. Previously, the HITRAN intensities were scaled on the basis of measurements of the $S(7)$–$S(10)$ lines [12,15]. Instead, in the present study, we combine the ACE profile results for $S(7)$–$S(12)$ [$(3.9 \pm 1.3)\%$], the new Jungfraujoch column results for $S(7)$–$S(20)$ [$(6 \pm 2)\%$], the Izaña column results for $S(7)$–$S(16)$ [$(6 \pm 2)\%$] and the Thule column results for $S(7)$–$S(13)$ [$(6 \pm 2)\%$], for a $(5.5 \pm 2)\%$ increase in the F-factor modified line intensities. For the complete band, the Q-branch J:1–18 halfwidths of Ref. [22] were extrapolated to $J = 40$. The S-branch halfwidths from Ref. [23] were adapted, with linear interpolation for the missing values in the published J:0–18 range, and quadratic, bounded below, extrapolation to $J = 40$. The O-branch halfwidths values were set to the S-branch values. The new line parameters are available upon request from Goldman.

4. Conclusions

Significant corrections have been made to both line intensities and halfwidths on the $^{14}N_2$ (1–0) line parameters in the HITRAN database. A new line parameters set has been generated which improves consistency and accuracy of individual line retrievals from atmospheric spectra. Unresolved issues in profile retrievals indicate the need for further studies of the N_2 line shape parameters in the infrared atmospheric spectrum.

Acknowledgments

Research at the University of Denver was supported in part by NSF and in part by NASA. Acknowledgment is made to the National Center for Atmospheric Research, which is sponsored by the National Science Foundation, for computer time used in this project. Two of the authors (R.H. Tipping and Q. Ma) acknowledge financial support from NASA under Grants NAG5-13337 and FCCS-547. Q. Ma wishes to also acknowledge financial support from the Biological and Environmental Research Program (BER), US Department of Energy, Interagency Agreement No. DE-A102-93ER61744. Funding for ACE was provided by the Canadian Space Agency and the Natural Sciences and Engineering Research Council (NSERC) of Canada. Acknowledgment is made to the Jungfraujoch Stiftungsrat, for hosting the University of Liège laboratory.

References

[1] Goldman A, Reid J, Rothman LS. Identification of electrical quadrupole O_2 and N_2 lines in the infrared atmospheric absorption spectrum due to the vibration–rotation fundamentals. Geophys Res Lett 1981;8:77–8.

[2] Camy-Peyret C, Flaud J-M, Delbouille L, Roland G, Brault JW, Testerman L. Quadrupole transitions of the $1 \leftarrow 0$ band of N_2 observed in a high resolution atmospheric spectrum. J Phys Lett 1981;42:L279–83.

[3] Rothman LS, Goldman A, Gillis JR, Gamache RR, Pickett HM, Poynter RL, et al. AFGL trace gas compilation: 1982 version. Appl Opt 1983;22:1616–27.

[4] Rinsland CP, McHugh MJ, Irion FW. Lower stratospheric densities from solar occultation measurements of continuum absorption near 2400 cm^{-1}. J Geophys Res 2003;108. doi:10.1029/2003JD003803.

[5] Griffith D. N_2 intercomparison exercise. NDSC infrared working group meeting, Bordeaux Observatory, France; 20–21 September 2001.

[6] Demoulin P. N_2 exercise-Jungfraujoch. NDSC infrared working group meeting, Queenstown, New Zealand; 9–12 November 2004; NDSC infrared working group meeting, Toronto, Canada; 13–15 June 2005.

[7] Bernath PF, McElroy CT, Abrams MC, Boone CD, Butler M, Camy-Peyret C, et al. Atmospheric chemistry experiment (ACE): mission overview. Geophys Res Lett 2005;32:L15S01. doi:10.1029/2005GL022386.

[8] Boone CD, Nassar R, Walker KA, Rochon Y, McLeod SD, Rinsland CP, et al. Retrievals for the atmospheric chemistry experiment Fourier-transform spectrometer. Appl Opt 2005;44:7218–31.

[9] Reuter D, Jennings DE, Brault JW. The $v = 1 \leftarrow 0$ quadrupole spectrum of N_2. J Mol Spectrosc 1986;115:294–304.

[10] Dunham JL. The energy levels of a rotating vibrator. Phys Rev 1932;41:721–31.

[11] Rinsland CP, Zander R, Goldman A, Murcray FJ, Murcray DG, Gunson MR, et al. The fundamental quadrupole band of $^{14}N_2$: line positions from high-resolution stratospheric solar absorption spectra. J Mol Spectrosc 1991;148:274–9.

[12] Rothman LS, Gamache RR, Tipping RH, Rinsland CP, Smith MAH, Benner DC, et al. The HITRAN molecular database: editions of 1991 and 1992. JQSRT 1992;48:469–507.

[13] Penner SS. Quantitative molecular spectroscopy and gas emissivities. Reading, MA: Addison-Wesley; 1959;
Judd BR. Angular momentum theory for diatomic molecules. New York: Academic Press; 1975.

[14] Karl G, Poll JD. On the quadrupole moment of the hydrogen molecule. J Chem Phys 1967;46:2944–50.

[15] Demoulin P, Farmer CB, Rinsland CP, Zander R. Determination of absolute strengths of N_2 quadrupole lines from high-resolution ground-based IR solar observations. J Geophys Res 1991;96:13003–8.

[16] Rinsland CP, Goldman A, Flaud J-M. Infrared spectroscopic parameters of COF_2, SF_6, ClO, N_2 and O_2. JQSRT 1992;48:693–9.

[17] Rothman LS, Jacquemart D, Barbe A, Benner Chris D, Birk M, Brown LR, et al. The HITRAN 2004 molecular spectroscopic database. JQSRT 2005;96:139–204.

[18] Tipping RH, Ogilvie JF. Herman–Wallis factors for Raman transitions of $^1\Sigma$-state diatomic molecules. J Raman Spectrosc 1984;16:38–40.

[19] Boissoles J, Tipping RH, Boulet C. Theoretical study of the collision-induced fundamental absorption spectra of N_2–N_2 pairs for temperatures between 77 and 297 K. JQSRT 1994;51:615–27.

[20] Lawson DB, Harrison JF. Distance dependence and spatial distribution of the molecular quadrupole moments of H_2, N_2, O_2, and F_2. J Phys Chem A 1997;101:4781–92.

[21] Bruet X, Bonamy L, Bonamy J. Extension of the energy-corrected sudden model to anisotropic Raman lines: application to pure N_2. Phys Rev A 2000;62:062702-1-6.

[22] Lavorel B, Millot B, Saint-Loup R, Wenger C, Berger H, Sala JP, et al. Rotational collisional line broadening at high temperatures in the N_2 fundamental Q-branch studied with stimulated Raman spectroscopy. J Phys 1986;47:417–25.

[23] Fanjoux G, Millot G, Lavorel B. Collisional shifting and broadening coefficients for the rovibrational anistropic $S(J)$ lines of nitrogen studied by inverse Raman spectroscopy. J Raman Spectrosc 1996;27:475–83.

[24] Ma Q, Tipping RH, Boulet C. Irreducible correlation functions of the $\hat{S}$ matrix in the coordinate representation: application in calculating Lorentzian half-widths and shifts. J Chem Phys 2006;124. doi:10.1063/1.2139671.

[25] Schneider M, Blumenstock T, Chipperfield MP, Hase F, Kouker W, Reddmann T, et al. Subtropical trace gas profiles determined by ground-based FTIR spectroscopy at Izaña (28°N, 16°W): five-year record, error analysis, and comparison with 3-D CTMs. Atmos Chem Phys 2005;5:153–67.

[26] Boissoles J, Boulet C, Tipping RH, Brown A, Ma Q. Theoretical calculation of the translation–rotation collision-induced absorption in N_2–N_2, O_2–O_2, and N_2–O_2 pairs. JQSRT 2003;82:505–16.

[27] Hase F, Hannigan JW, Coffey MT, Goldman A, Höpfner M, Jones NB, et al. Intercomparison of retrieval codes used for the analysis of high-resolution, ground-based FTIR measurements. JQSRT 2004;87:25–52.

[28] Lait L, Newman P, Schoeberl R. Using the Goddard Automailer, ⟨http://code916.gsfc.nasa.gov/Data_services/⟩; 2005.