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Synthesis of *ab initio* and effective Hamiltonian line lists for ozone

David Jacquemart[1]

Sorbonne Université, CNRS, De la MOlécule aux NAno-objets : Réactivité, Interactions et Spectroscopies, MONARIS, 75005 Paris, France

Vladimir Yu. Makhnev, Nikolai F. Zobov

Institute of Applied Physics, Russian Academy of Science, Ulyanov Street 46, Nizhny Novgorod, Russia 603950

Jonathan Tennyson

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom

Oleg L. Polyansky[2]

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom; Institute of Applied Physics, Russian Academy of Science, Ulyanov Street 46, Nizhny Novgorod, Russia 603950

Abstract

A synthetic line list for the ozone molecule is presented. Variational calculation using the semi-empirical potential energy surface (PES) and *ab initio* dipole moment surface (DMS) produce very accurate values of line intensities, but give line positions far away from their experimental values. Furthermore assignment of approximate rotational and vibrational quantum numbers are missing from variationally calculated line list. Effective Hamiltonian calculations are complimentary to *ab initio* line lists in these properties giving excellent value of line positions, close to experimental ones, and a full set of

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quantum numbers assignment. The synthesis of both these qualities in one line list is highly desirable. Here a synthetic line list for $^{16}O_3$ is presented. The method of corrections of distorted intensities in variational linelist with *ab initio* DMS due to the artificial intensity stealing is developed and applied. Comparison of the synthetic line list with all major published line lists and available experimental data is given. The calculated line intensities agree to within experimental error for most bands for which accurate measurements are available.
Keywords:
ozone, potential energy surface, dipole moment surfaces, IR spectra, line intensities, HITRAN database

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1. Introduction

Ozone, O_3, is a much discussed component of our atmosphere. While at low altitudes it is considered an unwanted pollutant which is detrimental to human health, at high altitudes the so-called ozone layer provides essential protection against the harmful effects of solar UV radiation. Atmospheric ozone is therefore regularly monitored [1] with, for example, a number of ground-based and space-borne experiments dedicated to monitoring atmospheric ozone concentrations using spectroscopy [2, 3]. As a result a number of databases of ozone spectroscopic parameters have been compiled for infrared (IR) [4, 5, 6, 7, 8, 9, 10] and ultraviolet (UV) studies [9, 11] which feed into general atmospheric databases such as HITRAN [12] and GEISA [13]. However, monitoring requires high accuracy, in particular intensities for all key bands are needed to better than 1%, so small relative changes can

be determined with low uncertainty. In this work we concentrate on the IR spectrum of ozone for which there are well-documented difficulties in determining transition intensities with the accuracy and consistency required for atmospheric studies [14, 9, 15]. This issue has led to a series of recent studies both experimental [16, 17, 18] and, in a new development for the field, *ab initio* [19, 20, 21].

Recent experimental studies [22, 23] have been performed in LERMA using a special H shaped cell designed to record most intense transitions of ozone at 5 μm and 10 μm regions. Spectra at 5 and 10 μm were recorded simultaneously from the same ozone samples allowing consistent measurements in both spectral regions. Intensities accurate of 1% or better were measured for around 800 lines. Because of the very good agreement obtained between LERMA measurements and the variational calculation reported in this work, we decided to construct a line list based on assignments and line positions from effective Hamiltonian (EH) calculations but using variational intensities.

In this paper we concentrate on the IR spectrum of $^{16}O_3$. Section 2 describes the calculation of the first principles ozone line list using our previously published semi-empirical potential energy surface (PES) [20] and *ab initio* the dipole moment surface (DMS), produced by Tyuterev and co-authors [21]. Program DVR3D [24] is used to solve nuclear-motion Schrödinger equation to produce ro-vibrational wavefunctions and to compute line positions and line intensities. Details of the line list calculations are given in this section. Section 3 describes the synthesis of the *ab initio* line list and the HITRAN2016 [12] line positions obtained from EH calculations. The details

of line-by-line matching of these two line lists is described. The resulting synthetic line list consists of the EH line positions and the first principles variationally calculated intensities. Section 4 describes the corrections to the *ab initio* intensities, obtained by comparison with the EH line lists. Since the EH line positions are more accurate, the information on EH intensities helps to correct outliers, which appear due to intensity stealing between lines affected by resonances [25]. Section 5 presents the results of comparisons of the synthetic line list with all available theoretical calculations and experimental measurements; it demonstrates the significant advantages of the present line list over other available ones. We conclude this paper in the section 6.

2. Calculation of the *ab initio* line list

The theoretical rotation-vibration line list of any molecule consists of the line position and line intensity, which are calculated as a result of solution of ro-vibrational Schrödinger equation. In order to calculate line positions and line intensities accurately, high precision knowledge of the PES of the molecule and its DMS is necessary. When these two surfaces are available, their use for the calculation of line lists is described elsewhere [26, 27]. Here we will briefly discuss the two surfaces used for our ozone *ab initio* line list calculation. The ozone PES we have obtained in the [20] as follows. First an *ab initio* PES was calculated using the MOLPRO package [28] at the multi-reference configuration interaction (MRCI) level of theory and aug-cc-pwcVQZ basis set [20]. The accuracy of rovibrational energy levels calculation using this *ab initio* PES was a few cm^{-1}. A much higher accuracy PES is required to obtain high precision wavefunctions for the calculation of

intensities [29]. In order to improve the accuracy of the PES the procedure of fitting the starting *ab initio* PES to the experimental energy levels was used. A very accurate semi-empirical PES was obtained with a standard deviation of the fitted energy levels of only 0.027 cm^{-1} [20].

The PES describes vibrational levels up to 6000 cm^{-1}. The convergence of energy levels variational calculations was tested up to this limit during its PES [20]. Since the convergence obtained was significantly better than the above mentioned standard deviation of 0.027 cm^{-1}, it was not described in [20]. Tests were performed on the size of the discrete variable representation (DVR) grid, effectively the basis set size, and size of the final Hamiltonian which demonstrated convergence of about 0.002 cm^{-1} below 6000 cm^{-1} with the parameters described below. The rotational energies are converged to better than 0.001 cm^{-1} for J=5.

Intensity calculations for lines belonging to the several ozone bands, measured experimentally were also presented in [20]. These calculations used two different DMSs. One *ab initio* DMS, calculated in [20] and another calculated *ab initio* by Tyuterev and coworkers [21] at a higher level of theory. The intensities computed these two DMSs differ by a few percent. At the time of the publication of the paper [20] it was unclear which DMS gave the more accurate results. The recent LERMA intensity measurements [22, 23] are very interesting since sub-percent accuracy is obtained in both 5 and 10 μm spectral regions thus providing a stringent test of theoretical predictions. As shown below, excellent agreement is obtained with the variational intensities using the DMS of Ref. [21]. For the ν_3 and ν_1+ν_3 bands at 10 μm and 5 μm respectively, the LERMA measured intensities and variational

intensities agree with a standard deviation (SD) of around 0.5% (see section 5). The LERMA intensity measurement of around 800 of $^{16}O_3$ lines allows a clear choice to be made in favor of the DMS of paper [21]. In the present variational line list calculation this DMS has been used.

For the line positions and intensities calculation we used the program suite DVR3D [24], making use of an exact kinetic energy operator. Radau coordinates and Morse-like oscillators with parameters $r_e = 2.8$ a$_0$, $D_e = 0.1$ E$_h$, $\omega_e = 0.0024$ a.u. were used in the calculations. 20 DVR radial grid points and 70 angular grid points were used with the final vibrational matrices of dimension 1500. Rotational problem was solved using matrices of dimension $500(J + 1 - p)$, where p is the rotationless parity. Atomic masses were used allowing approximately account for non-adiabatic effects. Calculations considered all transitions with $J \leq 60$. Lines with frequencies between 0 cm^{-1} and 4930 cm^{-1} are retained. The resulting line list consists of 78 024 lines with intensities stronger than 10^{-24} in HITRAN units (cm/molecule) at 296 K. Partition function for ozone molecule was taken from work of Gamache *et al.* [30]. All $^{16}O_3$ intensities given in the present manuscript and supplementary materials are in natural abundance (scaled by 0.9929). Previously the calculations of the lines down to 10^{-32} intensities were retained and we saved these lines for wavenumbers below 2024 cm^{-1} . This second line list will be used in the section 4 for taking into account resonances between levels affecting line intensities in the main line list.

Variational calculation results in the energy levels, line positions and line intensities. Every energy level is labelled by the rotational quantum number J, its parity p, and the number within each (J, p) block. For spectroscopic

and database purposes, however, labelling of the energy levels by asymmetric top rotational quantum numbers J, K_a and K_c as well as normal-mode vibrational quantum numbers v_1,v_2 and v_3 is important. Such labelling is performed in the following section.

3. Matching of effective Hamiltonian and variational line lists

Variational line lists, such as the ones described in the previous section, have been shown to give excellent predicted transition intensities, in some cases with the accuracy better than the experimental one [31, 32, 33]; however they have two major drawbacks. The accuracy of the line positions are at best an order of magnitude worse than the experimental value. Secondly - there is no automatic line assignment with quantum numbers K_a, K_c, v_1, v_2 and v_3. EHs solve both these problems, but generally do not predict intensities with the required accuracy. A natural development is therefore lines lists synthesized using the two approaches, as has been done for CO_2 [34, 35, 36]. However, while for CO_2 combining the two approaches proved reasonably straightforward, for $^{16}O_3$ a procedure based only on direct line-by-line matching is not sufficient. In the next two sections we develop a method for producing a synthesis of variational and EH line lists. This method results in a line list which combines the advantages and removes disadvantages of both its parents.

An effective Hamiltonian (EH) model is required to assign transitions from variational calculations but also to correct line intensities of transitions involving levels in resonance (see section 4). In the present work the HITRAN2016 database [12] has been used to assign all transitions from vari-

ational line list except for 19 not found in HITRAN2016 but present in the JPL catalog [37].

Variational line list includes for each transition, upper and lower J quantum numbers, line positions and intensities as well as energy of upper and lower states. In order to perform an accurate match with EH line list, several sets of criteria have been used. The primary criterion is based on identical upper and lower J quantum numbers in both line lists. The second criterion is relative to lower energy states and line positions differences between transitions from the two line lists. Because of the presence of many nearby transitions, a third criterion based on intensities was included. For each transition from the variational line list, the corresponding transition is first searched in the EH line list using for second and third criterion low values for maximum differences on positions and lower energy state and close line intensities respectively. If not found, the line is searched again with less severe limit values for second or third criterion. By implementing eight different sets of various limits for second and third criteria, the corresponding transition is searched up to eight times in the EH line list. The main problem of such algorithm is that cases always exists where the selected sets of criteria will not lead to correct assignments due to resonance between levels involved in nearby transitions. As a consequences two different codes based on different sets of criteria were used, and assignments were compared and manually corrected in a few cases. Transitions can be particularly difficult to assign when they involve levels involved in a resonance. Indeed, in such cases variational calculation lead to erroneous intensities (see section 4) making assignments more difficult. For example, let us consider the two transitions (110–000;

J, K_a, K_c = 39 2 38 - 40 5 35) and (011-000, 39 5 34 - 40 5 35) located in HITRAN [12] at 1681.8382 and 1682.0075 cm^{-1} with intensity equal to 7.750×10^{-24} and 8.192×10^{-24} cm/molecule respectively. Both transitions have same lower states and close upper states in resonance (with identical J quantum numbers). In the variational line list the two corresponding transitions can be identified at 1682.0389 and 1682.2739 cm^{-1} with intensities equal to 1.996×10^{-24} and 1.279×10^{-23} cm/molecule, respectively. In such situations automatic assignments are hazardous and manual operations are required.

The main goal in this step is to assign most of the transitions from the variational line list. When transitions involve levels under resonance (as in example above), the variational calculations may lead to large intensity errors. This situation has been observed for the water [25] and carbon dioxide molecules [34] and arises because the variational-computed eigenfunctions are not precise even when the PES is refined using the observed line positions. Artificially strong transitions can be generated by stealing intensity from real transition. In general, it is only the distribution of intensity between transitions involving levels in resonance that is badly calculated, while the sum of intensities is not affected. This is the case for the example given above; the sum of intensities of the 2 lines in HITRAN is equal to 1.594×10^{-23} cm/molecule, close to the sum of *ab initio* intensities equal to 1.479×10^{-23} cm/molecule.

Two variational line lists, used in the present study, were calculated using PES from Polyansky *et al.* [20] and DMS from Tyuterev *et al.* [21]. First one from 0 to 4930 cm^{-1} with an intensity cutoff of 10^{-24} cm/molecule, and

another from 0 – 2024 cm^{-1} with an intensity cutoff of 10^{-32} cm/molecule. The first one has been completely assigned whereas the second one has been assigned only partially to improve corrections (see section 4). Since a line list from 0 to 4930 cm^{-1}, including 5 μm and 3 μm regions, is of more interest even with higher intensity cutoff, the focus of the present work is on calculations between 0 and 4930 cm^{-1}. Assignments were found for the 78 028 transitions from 0 to 4930 cm^{-1} with the exception of 171 lines with intensities ranging from 10^{-23} to 10^{-24} cm/molecule. 19 out of these 171 lines could be found in the JPL line list [37]. Note that variational line lists (with both intensity cutoff) are limited to J values below 60. Some transitions with $J > 60$ and with intensities greater than 10^{-24} cm/molecule can be found in HITRAN [12]; these are not included in the present line list.

4. Transitions involving levels in resonance

Due to resonance between levels, outliers appear in the variational calculations caused by the wrong intensity distribution between transitions involving levels in resonance. The case of transitions with artificially high intensity stealing in variational calculation is an extreme case of erroneous intensity distribution from variational calculation. Since levels in resonance can be easily predicted, the intensity of variational calculation can be corrected using EH calculations tuned to better reproduce intensity perturbations for transitions involving levels in resonance. The first step of the corrections applied to variational calculation is to select transitions involving levels in resonance, meaning levels of same symmetry, same J and close energy (< 3 cm^{-1}). In most cases, only 2 transitions (involving levels in resonance for upper or lower

state) are stealing intensity from each other. These two transitions belongs to different bands as in example from section 3 with (110-000, 39 2 38 - 40 5 35) and (011-000, 39 5 34 - 40 5 35) transitions located in HITRAN [12] at 1681.8382 and 1682.0075 cm^{-1} with intensity equal to 7.750×10^{-24} and 8.192×10^{-24} cm/molecule respectively. In this example, upper levels of these transitions are in resonance. Correction of intensities is based on using the EH intensity distribution to rebalance the intensities from the variational calculation. In the case of the two lines cited as example above, the HITRAN intensity of the (110-000, 39 2 38 - 40 5 35) and (011-000, 39 5 34 - 40 5 35) transitions corresponds to 48.6 % and 51.4 % of the HITRAN summed intensities. By using the sum of intensities of corresponding transitions in variational line list (1.479×10^{-23} cm/molecule) and the distribution from HITRAN, the (110-000, 39 2 38 - 40 5 35) and (011-000, 39 5 34 - 40 5 35) transitions have corrected intensities equal to 7.188×10^{-24} and 7.602×10^{-24} cm/molecule, respectively. The originally calculated intensities were 1.996×10^{-24} and 1.279×10^{-23} cm/molecule, respectively, for these two transitions.

It may happen that four transitions are coupled together through levels in resonance in both upper and lower states. Two examples are given in Table 1 with four transitions involving levels in resonance both for upper and lower states. Such cases are rare (concerning less than 200 transitions) and have been partially corrected by hand as shown in Table 1. The first example involves 4 transitions involving 2 different levels in the upper and lower states. The correction is based on the transfer of intensity distribution from EH calculation to variational calculation, using the sum of intensities

from variational calculation. It is particularly difficult to perform corrections when the correspondence is not complete between EH and variational calculations. As shown in Table 1 for second set of "coupled" transitions, the 110-010 transition is missing in HITRAN2016. Moreover, the intensity from variational calculation for this transition is 3×10^{-28} cm/molecule, compared to a few 10^{-24} cm/molecule for the other "connected" transitions. In such case, the distribution of intensities inside the three HITRAN transitions is applied to the three corresponding transitions using the sum of intensities of these transitions. The complete selection of transitions (involving levels in resonance) is not possible because the variational and EH line list are generated using an intensity cutoff. As a consequence, some weak transitions may be missing inside the resonance configuration. To illustrate this effect, we first performed corrections based on the variational line list with 10^{-24} cm/molecule intensity cutoff. These corrections, called "first-order corrections", allowed us to correct most of the intensities where the variational line list gave outliers. However, when among 2 coupled transitions involving levels in resonance, one transition is missing in the variational line list because the intensity cutoff, no correction can be performed. "Second-order corrections" are then performed using variational line list (from 0 to 2024 cm^{-1}) with an intensity cutoff equal to 10^{-32} cm/molecule. As shown in Table 1 for the first set of "connected" transitions, (030-001, 19 3 17 - 18 5 14), a transition calculated with an intensity of 2.55×10^{-25} completed the scheme of 4 connected transitions and allows a more rigorous correction for transitions below 2024 cm^{-1} .

Table 1: Correction of intensity distribution within four transitions involving levels in resonance in both upper and lower state. Positions are given in cm^{-1}, and intensities (S) are for natural abundance (0.9929) in cm/molecule. Number 1 corresponds to HITRAN2016 parameters, 2 to the variational calculation, and 3 refers to the corrected intensity. .

Band	$J'K'_aK'_c$ - $J''K''_aK''_c$	ω_1/cm^{-1}	S_1	ω_2/cm^{-1}	S_2	S_3
101-001	19 2 17 - 18 5 14	1021.5008	2.020(-23)	1021.487041	2.001(-23)	1.961(-23)
101-100	19 2 17 - 18 2 16	1021.5782	1.370(-22)	1021.563043	1.392(-22)	1.330(-22)
030-001	19 3 17 - 18 5 14	1021.5989	1.123(-24)	1021.877708	2.551(-25)	1.090(-24)
030-100	19 3 17 - 18 2 16	1021.6763	7.523(-24)	1021.953711	1.554(-24)	7.304(-24)
011-010	49 11 38 - 50 11 39	964.3651	5.221(-24)	964.277996	5.314(-24)	5.401(-24)
101-001	49 1 48 - 50 4 47	961.6807	3.275(-24)	961.530441	2.648(-24)	3.388(-24)
002-001	49 4 46 - 50 4 47	963.2390	7.839(-24)	963.153542	8.937(-24)	8.110(-24)
110-010	49 ? ? - 50 11 39	N.A	N.A	962.213352	3.140(-28)	N.A

In order to observe the effects of the corrections on the line intensities, ratios of line intensities (HITRAN2016 divided by variational calculation) before and after correction can be plotted. Figures 1 and 2 correspond to comparisons with HITRAN2016 respectively for 110-000 and 101-000 bands using various symbols according to cases: black symbols are used when no correc-

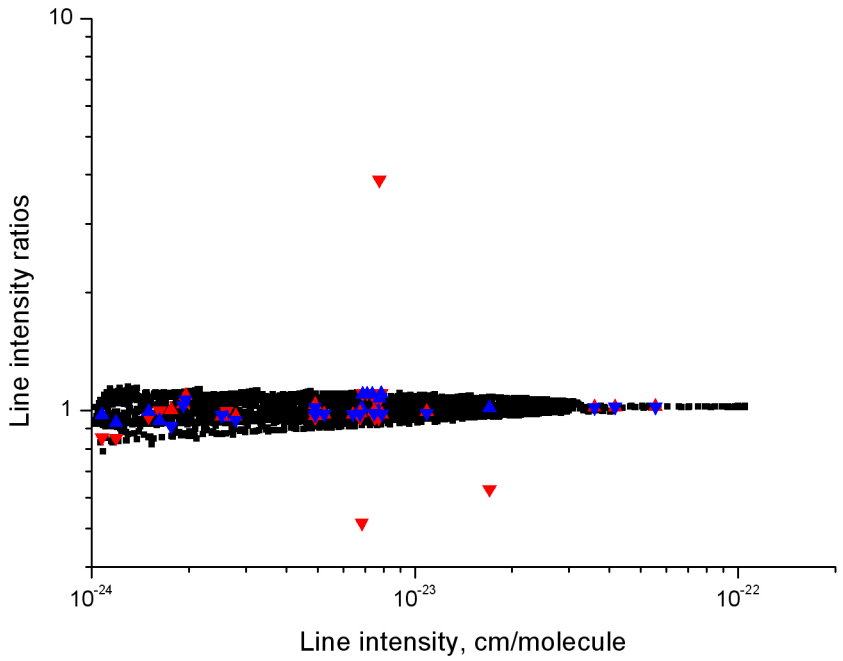

Figure 1: Ratios of line intensities (HITRAN2016/ab-initio) for 110-000 band obtained with and without corrections of line intensities: ■ uncorrected; ▲ first-order correction; ▲ second-order correction; ▼ uncorrected transition in resonance.

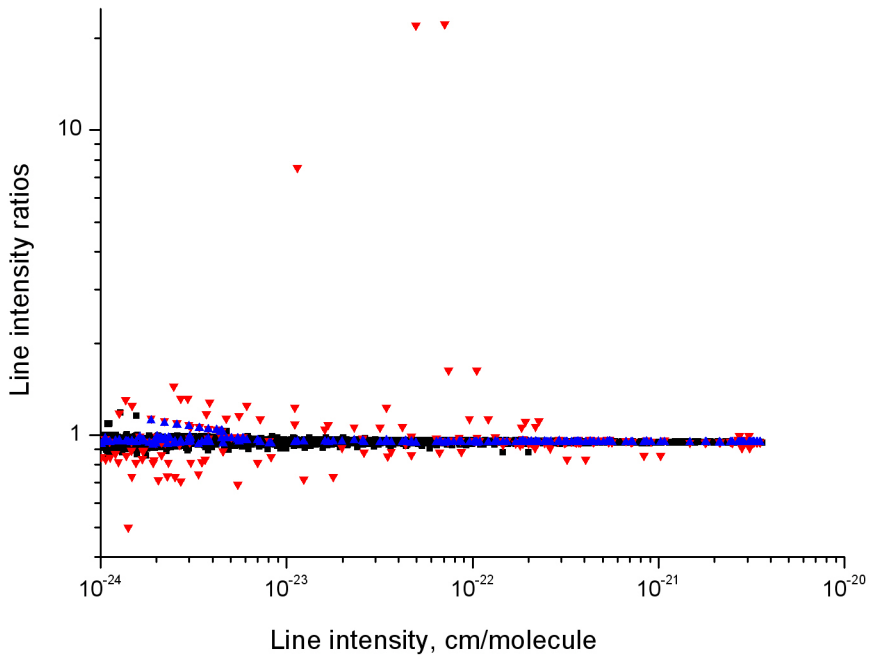

Figure 2: Ratios of line intensities (HITRAN2016/ab-initio) for 101-000 band obtained with and without corrections of line intensities: ■ uncorrected; ▲ first-order correction; ▲ second-order correction; ▼ uncorrected transition in resonance.

tion is performed (because transition involves no level in resonance), blue up triangles show when "first-order corrections" are applied (red down triangles are corresponding uncorrected variational intensities), and blue down triangles when "second-order corrections" are applied (in red up triangles when variational intensities are not corrected). As can be observed in Fig. 1 for 110-000 band, the red symbol corresponding to ratio of about 3.9 is clearly an outlier. It corresponds to the (110-000, 39 2 38 - 40 5 35) transition for which upper level is in resonance with upper level of (011-001, 39 5 34 - 40 5 35) transition. After correction based on the transfer of intensity distribution among these two transitions from EH to variational calculation, the corresponding blue up triangle symbol for (110-000, 39 2 38 - 40 5 35) transition corresponds to a ratio equal to 1.08 instead of 3.6. In the same way the correction for 011-001, 39 5 34 - 40 5 35) transition lead to a ratio of 1.08 instead of 0.64 (when using *ab initio* intensity without correction). As can be seen in Figs. 1 and 2, the several red symbols that looked like outliers correspond to blue symbols closer to average ratio. For bands located above 2024 cm^{-1} no "second order correction" was performed since no variational calculation were available with intensity cutoff lower than 10^{-24} cm/molecule. An example for the 111-010 band is given in Fig. 3 where several black symbols still appear to be outliers. Only a few lines have been corrected using "second-order corrections", and all the black symbols looking as outliers correspond to transition with wavenumbers higher than 2024 cm^{-1}. By using variational calculation with low intensity cutoff on the whole 0-5000 cm^{-1} spectral region, we believe new resonances between levels will be identified and will allow improved intensities for weak transitions ($< 10^{-22}$)

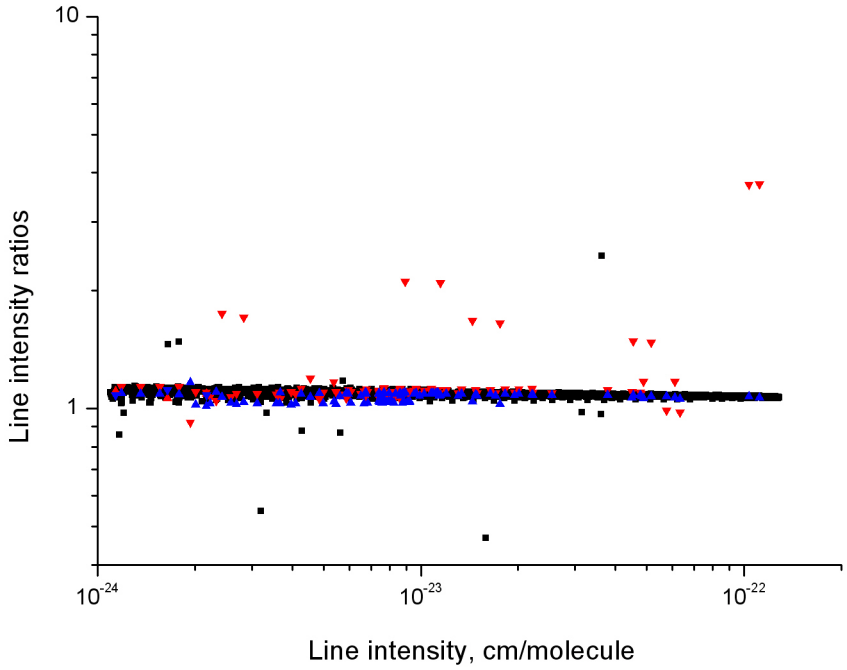

Figure 3: Ratios of line intensities (HITRAN2016/ab-initio) for 111-010 band obtained with and without corrections of line intensities ■ uncorrected; ▲ first-order correction; ▲ second-order correction; ▼ uncorrected transition in resonance.

above 2024 cm^{-1}.

The whole variational line list both without correction and with "first- and second-order corrections" is given as supplementary material. This file also contains full vibrational and rotational assignments.

5. Comparison of the resulting line list with experimental observations and effective Hamiltonian calculations

Systematic comparisons of variational line intensities (with the corrections of section 4) with recent calculated and measured line intensities have been performed in order to better understand issues concerning ozone line intensities. Ratios of variational line intensities to intensities from the literature have been plotted band by band and are available in supplementary material. For each band, ratios using measurements or calculations from literature have been distinguished. The comparisons for 001-band are presented in Figs. 4 and 5. For calculations from literature, following data have been used: EH calculations present in HITRAN2016 [12], in JPL catalog [37], and performed recently by Flaud [38] (denoted JMF hereafter) and by Barbe and Tyuterev (denoted URCA-ESA) [10], as well as *ab initio* calculations from Tyuterev *et al.* [21]. As for experimental measurements, recent studies from LERMA [22, 23], DLR [10], and Barbe and De Backer [39] (noted GSMA hereafter) have been selected to be compared with present variational calculations and synthetic line list. A sample of average ratios and associated SDs are presented in Table 2 for various bands in the microwave, 14 μm, 10 μm and 5 μm spectral regions. The whole set of average ratios for around 100 bands between 0 and 5000 cm^{-1} is given in supplementary material.

For rotational bands, comparisons between our variational (synthetic) line list and HITRAN2016 [12] from one side and JPL [37, 18] from other side lead to a general trend (see Table 2) where variational intensities are closer to JPL than to HITRAN2016. Agreement between variational line list and JPL catalog is excellent for the 2 most intense 000-000 and 010-

010 bands. The average discrepancy is sub-percent with a SD of around 0.5% (see Table 2). For these two bands, HITRAN2016 line intensities are systematically lower by 4% as compared to variational and JPL line lists. For other bands, when HITRAN 2016 line intensities are systematically lower by around 5% as compared to variational line list whereas JPL line intensities are systematically higher than variational intensities by 1-5% depending on the bands. For those bands variational intensities are between HITRAN2016 and JPL intensities.

In the 14 μm spectral region, revisited intensities from Birk *et al.*[40] led to systematic scaling intensities in this region by 1.4% as compared to HITRAN [12]. This correction lead to closer intensities but are still lower than variational intensities by around 4-5% for the two strongest bands presented in Table 2.

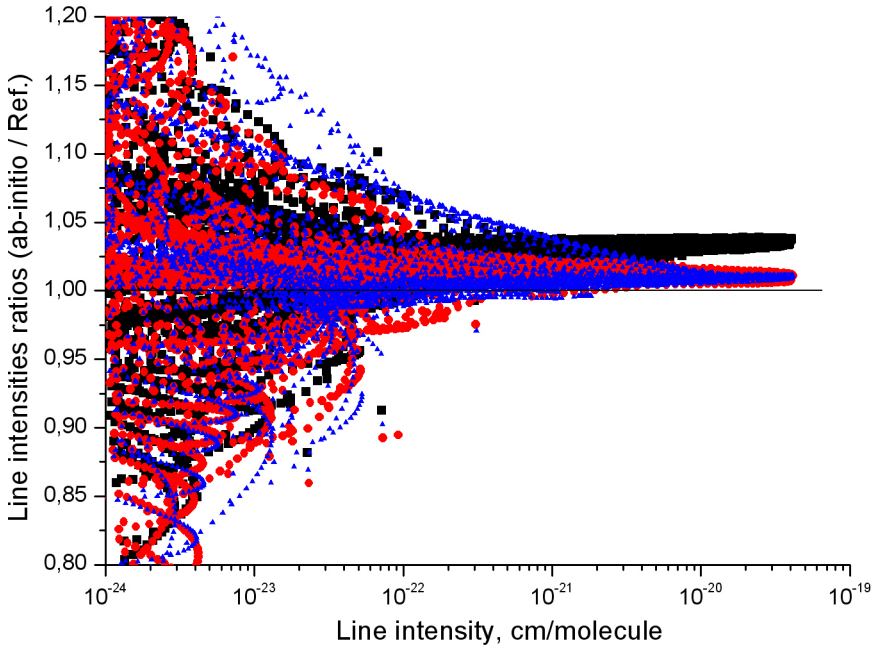

Figure 4: Ratios of variational intensities to effective Hamiltonian intensities from HITRAN2016 [12] (■), JMF [38] (●), and URCA-ESA [10] (▲). The ratios are plotted versus line intensity in a log scale.

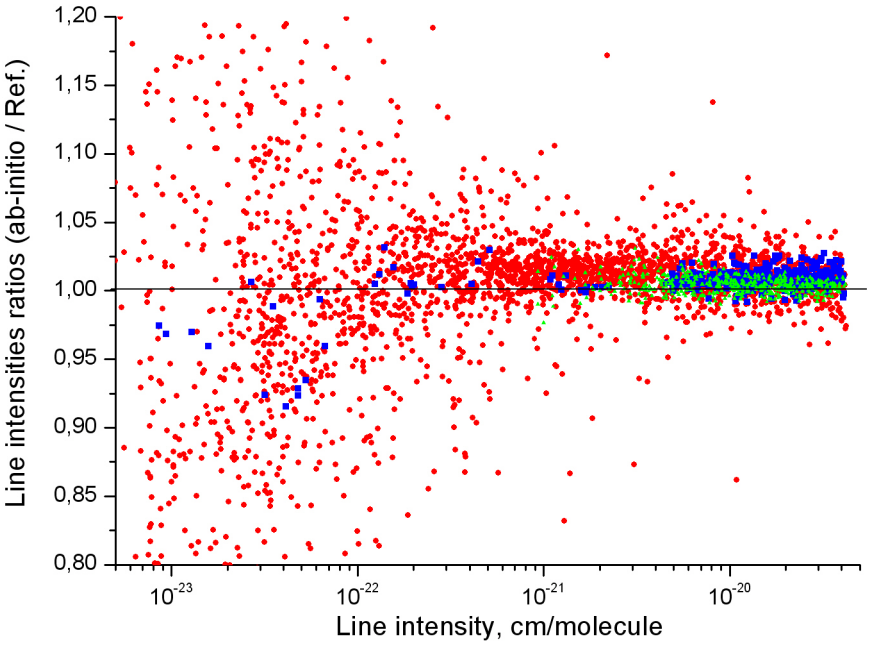

Figure 5: Ratios of variational intensities to measured intensities from DLR [10] (●), GSMA [39] (■), and LERMA [22, 23] (▲). The ratios are plotted versus line intensity in a log scale.

Table 2: Extract of average comparisons between intensities from variational calculation and intensities from literature for various bands in the microwave, 14 μm, 10 μmand 5 μm regions. R_1 (ab-initio/HITRAN) and R_2 (ab-initio/Ref) are average ratios of line intensities. Digits between parentheses correspond to the standard deviation of the average in units of the last digit. $\sigma_{\min}$ and $\sigma_{\max}$ correspond the range of positions in cm^{-1}, $S_{\max}$ is the maximum line intensity (given with powers of 10 in parenthesis) in the band (cm/molecule). Common transitions between variational calculation and HITRAN (N_1) and between variational calculation and reference (N_2) are given.

$\sigma_{\min}$	$\sigma_{\max}$	$S_{\max}$	Band	N_1	R_1	N_2	R_2	Ref
2.5	176.4	1.43(-21)	000-000	3088	1.0399(54)	3075	1.0013(57)	JPL
5.6	146.2	4.65(-23)	010-010	1460	1.0404(41)	1460	1.0051(29)	JPL
14.8	121.5	6.44(-24)	100-100	601	1.0482(158)	598	0.9724(43)	JPL
12.5	125.1	8.78(-24)	001-001	723	1.0471(172)	722	0.9892(341)	JPL
43.9	94.5	1.52(-24)	020-020	125	1.0558(100)	105	0.9531(9)	JPL
24.2	103.3	3.80(-24)	100-001	66	1.0444(224)	40	0.9508(1208)	JPL
22.6	103.9	4.10(-24)	001-100	69	1.0462(166)	38	0.9858(467)	JPL

Continued on next page

$\sigma_{\min}$	$\sigma_{\max}$	$S_{\max}$	Band	N_1	R_1	N_2	R_2	Ref
574.2	873.6	1.66(-21)	010-000	4840	1.0687(225)	4592	1.0545(247)	BirkPC
592.8	832.0	1.10(-22)	020-010	2794	1.0525(139)	2770	1.0385(148)	BirkPC
961.7	1226.0	4.06(-20)	001-000	4877	1.0244(613)	476	1.0041(63)	LERMA
975.5	1213.8	2.13(-23)	200-001	1082	1.2817(346)	1068	1.0335(213)	JMF
1960.7	2244.0	3.60(-21)	101-000	3180	1.0510(166)	316	1.0059(42)	LERMA
1983.5	2066.3	4.76(-23)	102-001	1286	0.8898(498)			
2011.0	2108.2	1.28(-22)	111-010	1634	0.9186(491)			
1915.2	2104.1	4.86(-23)	012-010	682	0.8445(748)			
2052.3	2133.3	1.70(-22)	030-000	25	1.0919(1610)			

In the 10 μm spectral region, two bands have been given as example in Table 2, the strong 001-000 band and a weaker band, namely the 200-001 band, for which a large dispersion is observed when comparing variational and HITRAN2016 intensities. For the 001-000 band a deviation of around 2.5% is observed between variational and HITRAN intensities, whereas an average sub-percent agreement is observed between LERMA measurements (476 strong transitions) and variational calculation with a SD of 0.6%. For the weak 200-001 band plotted in Fig. 6, the average deviation between variational and HITRAN intensities reaches 28%. Let us recall that in this region HITRAN2016 is based on EH from Ref. [41] where no measurements were available for this band. With recent measurements from Birk *et al.*[10], Flaud's calculation [38] leads to intensities in better agreement with varia-

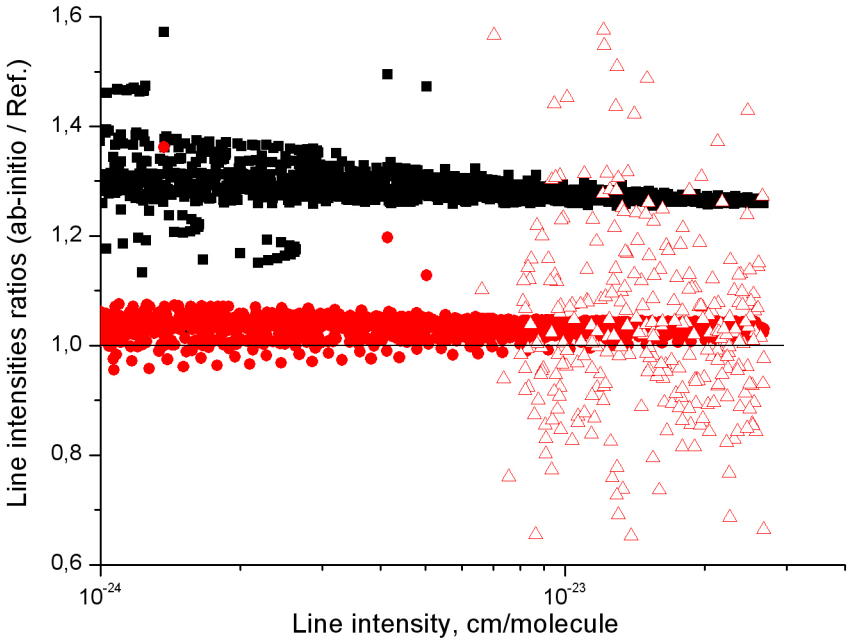

Figure 6: Ratios of variational intensities to effective Hamiltonian calculated intensities from HITRAN2016 (black squares) and from Flaud [38] (solid red circles) as well as to measured intensities from DLR [10] (open red triangles) for the 200-001 band.

tional calculation (deviation of 3.3%). Without experimental measurements Hamiltonian calculated intensities can deviate by up to 30% whereas variational calculation (that does not require measurements) lead to intensities quite close (3.3%) to those obtained from EH using new measurements for this band.

In the 5 μm spectral region, for the strongest 101-000 band, the average agreement between LERMA measurements and variational line list is equal to 0.6% for 316 intense common transitions with a SD of 0.4%. However,

a systematic deviation between HITRAN2016 and variational intensities of around 5% is observed with a SD of 1.7% for 3180 common transitions.The other four bands at 5 μm presented in Table 2 are bands which present average deviation up to 15 % when comparing HITRAN2016 and variational intensities. Those bands were calculated from Hamiltonian calculation without fitting any measurements for these bands from literature. It would be very interesting to measure (even with accuracy of 2-3% which is more realistic accuracy for the weak bands, than the sub-percent accuracy) transitions of these bands in order to check the variational calculation. The case of 200-001 band, where the disagreement between HITRAN2016 and variational linelist is about 28 % and the agreement between variational calculations and EH calculations based on the fitting to the experimental data is only 3 % is very promising in this respect. This case indicates, that the reason of very serious disagreement between HITRAN16 and variational calculations for certain bands might point to the problems with the present HITRAN2016 version.

6. Conclusions

Very accurate intensity calculations from the first principles and determination of the line positions with the accuracy of experiment by effective Hamiltonian calculations do not provide necessary final result for the spectroscopic databases in their separate essences. The variational calculations provide the line centers with the accuracy far from the experimental values. The intensities computed using an effective Hamiltonian (EH) do not provide accurate values beyond the ones included in the empirical determination of

the effective dipole constants.

A method for constructing a synthetic line list is developed. Matching lines between the variationally-calculated and EH line lists is combined with the removal of outliers of such a line list due to the distorting effects of resonances in the variational calculations which can be associated with the imperfect accuracy of its line positions and its underlying potential energy surface. This method could be useful in cases when the synthesis of variational and EH linelists is required due to complimentary advantages and disadvantages of both of them. We are now considering other molecules where this approach may be useful.

Our newly constructed synthetic line list gives line positions with the accuracy of experiment. Comparison of the *ab initio* calculated intensities with the experimentally available data also demonstrates the accuracy of the line intensities which are predicted within the experimental error for most of the bands. The most stunning difference in accuracy of the calculated intensity arises for the 200–001 band. The line intensities of this band was calculated using both EHs and variational calculations before the experimentally adjusted EH become available. The EH predictions deviated from EH calculations adjusted to the measurements by 28 % while the predictions of the variational calculations deviated by only 3 %, which seems a realistic estimation of the measurement uncertainty. The synthesis of the EH and variational calculations presented here provides the information required to represent the $^{16}O_3$ spectrum in atmospheric databases such as HITRAN and GEISA.

Further work is required to calculate the lines with higher rotational quan-

tum numbers J. However, before this further improvement in the accuracy of the fitted semi-empirical PES should result in better line intensities and fewer outliers. Isotopologues of ozone also require the similar type calculations for the completeness of the natural abundance ozone linelist. All these improvements are under way.

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