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Ab initio predictions and laboratory validation for consistent ozone intensities in the MW, 10 and 5 micron ranges [#]

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ABSTRACT

Reliable ozone spectral data consistent over several spectral ranges is a challenge for both experiment and theory. We present *ab initio* calculations for strong lines that lead to consistent results from the microwave to mid-infrared regions. The results agree well with established microwave line lists and our new measurements in the fundamental and first overtone regions of ozone at 5 and 10 µm. The calculations and their agreement to within 1% with measurements provide an important step towards consistent and accurate spectroscopic ozone data. The results imply that actual data bases need to be corrected by about 3% in the corresponding mid-infrared spectral intervals. Appropriate recommendations for the consistency of strong line intensities of the ozone molecule in microwave, 10 and 5 micron ranges in HITRAN and GEISA databases are suggested.

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1. Introduction

Ozone (O_3) is a key molecule in the Earth's atmosphere and could play an important role in the detection of biotic signatures in extrasolar planets [1,2]. Its existence makes oxygen the first element in the periodic table with more than one relatively long-lived gaseous allotrope under terrestrial conditions. O_3 has a low binding energy of about 1 eV and a rich electronic structure [3-5], which implies strong reactivity and photochemical activity, combined with absorption features that range from the microwave (MW) and infrared (IR) to the ultraviolet (UV). Its chemistry is tightly linked to air quality as well as to atmospheric composition and climate change [6] explaining the urgent need to determine its abundance very accurately. Atmospheric and remote sensing measurements of ozone in particular, require therefore high quality spectroscopic data. With this incentive in mind, the World Meteorological Organization, the International Ozone Commission and the Integrated Global Atmospheric Chemistry Observations activity have created the ACSO (Atmospheric Cross Sections of Ozone) initiative, with the mandate to critically compare and evaluate existing data and possibly recommend most suited data for atmospheric retrieval in the UV and VIS spectral ranges[7]. The resulting report and a recommendation based on new data have been published recently[7], but these new recommendations are still inconsistent with IR and MW spectral data in atmospheric data bases, such as HITRAN[8] and GEISA[9]. Subsequent to an update of the HITRAN database in 2004, a series of laboratory[10] and atmospheric studies[11] have indicated a seemingly discrepancy of about 4 to 5 % in ozone abundance data when results from the IR region (around 10 µm) were compared with UV based measurements (around 300 nm). In the meanwhile, a series of laboratory measurements have been performed, leading to the above mentioned newly recommended UV-VIS data [10,11] for atmospheric remote sensing, but these data neither remove the UV-IR discrepancy problem [7,10], nor do they provide the required accuracy.

A very recent absorption cross section measurement at 325 nm actually indicates that even after the new recommendations a discrepancy of about 2%-3% remains when measurements in this wavelength region are compared to results from the 10 µm range[12]. Other comparisons, between the 10 and 5 µm ranges [13,14] show that relative discrepancies at the 1 to 2 % level exist between some data sets. It should also be noted that European and US air quality legislation is linked to the UV absorption cross section at 254 nm [15]. The need for improving the accuracy of absolute spectroscopic data that is consistent over several spectral domains all from the UV to the MW is therefore evident. After the recent update in the UV-VIS domain [15], it seems particularly important to revisit the MW and mid-IR ranges while targeting a relative uncertainty level of 1% or better.

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Another incentive for highly accurate quantum calculations of ozone comes from the quest of resolving the long standing puzzle of the isotope anomaly, first observed in balloon measurements of stratospheric ozone [16]. Current quantitative modeling [17] of the unusually large symmetry selection in the formation of the ozone molecule from the $O + O_2 + M \rightarrow O_3 + M$ reaction [18] always requires the introduction of ad-hoc factors or fitting to the experimental data. This unresolved puzzle has motivated many spectroscopic studies of ozone at high vibrational energies [19-21], and a recent combination of first-principal calculations with spectra analyses helped understanding the shape of the transition state towards the dissociation threshold [22]. Yet, these new spectroscopic studies did not resolve the issue of line intensities at the per cent level of accuracy.

In this work, we report advanced line-by-line ab initio intensity calculations for strong transitions in MW, and in 10 µm and 5 µm ranges which are the most important for atmospheric applications in IR. These calculations are fully consistent with empirical line lists [23,24] based on previous Stark-effect measurements [25-27] as well as with new accurate FTS measurements in 10 and 5 µm ranges [28,29] revealing the way to resolve actually existing discrepancies in ozone databases.

2. Ab initio dipole moment surfaces and intensities

Ab initio ozone intensities have been discussed previously [30-33], but they did not provide representative strong line sets in all considered ranges to treat the related controversies. A key issue is the evaluation of uncertainties. To this end, we used on the theoretical side several versions of the dipole moment surfaces (DMS) computed by external electric field approach [34] utilizing the multireference configuration interaction MRCI-SD method ([4,5,35] and references therein) in an "internally contracted" version as implemented in the MOLPRO code of electronic structure calculations [34]. The MRCI-SD electronic wave functions were built on the top of the CASSCF (18,12) full valence active space involving the 2*s* and 2*p* atomic orbitals of oxygen as described in [36] including relativistic corrections. The correlation consistent quintuple atomic basis set of Dunning [37], augmented by diffuse functions aug-cc-pV5z was employed [36], as it provided a large scale qualitatively correct picture for ozone band intensities [32]. Technical aspects of electronic structure calculations were reported in a recent paper [32]. Slightly different calculations were obtained using relaxed or fixed reference Davidson size-consistency corrections [34,35,38]. To certain extent, the predicted intensities also depend on the DMS model used to fit *ab initio* dipole moment values.

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A. *"Charge-function" Schwenke-type DMS model*

The first analytical DMS representation that we have employed was the "charge-function model" similar to that proposed by Schwenke and Partrigde [39] for the water molecule. The Schwenke-type DMS model [32,39] contains a Gaussian damping factor β that slightly affects dipole moment derivatives and could result in a re-distribution of strengths amongst fundamental and overtone bands. We have computed the intensities for mean (β = 1), strong (β = 2) and intermediate (β = 1.5) damping. The adjusted C_{ijk} parameters (eqs. (2), (3) of Ref. [32]) correlate with the damping factor in a way that the quality of the *ab initio* fit remains almost the same near the open state equilibrium. We consider that a comparison of the β = 1 and β = 2 versions of the fits provides acceptable margins for the variation of the DMS in the energy range associated to the upper states of the considered bands and will help evaluating possible errors of ab initio intensity predictions.

Damping tests beyond this range (β >> 2 or β << 1) deteriorated the quality of the global DMS fit on the full grid of 1850 geometries [32] up to $(E - E_{min}) / hc = 8200$ cm^{-1}. The difference in these models mainly affects the rate of the asymptotic behavior of the DMS towards zero at the dissociation limit and could have an impact on intensities of very high overtone bands [32]. For the fundamental (ΔV = 1) and the ΔV = 2, 3 bands the variations in calculated intensities were found quite small (typically in the range ~0.1% - 1%). An intermediate damping model (with β = 1.5) gave values for line and band intensities in general between the β = 1 and β = 2 results, as expected.

As was discussed in [32], the use of lower orders of expansions in the DMS models does not provide satisfactory root-mean-squares (RMS) deviations of the fit of *ab initio* dipole moment values on large grids of the nuclear configurations. For example, in case of the mean damping, the order o3 increases the RMS deviation by a factor of 7.5 for the symmetric component and by a factor of 21 for the anti-symmetric component with respect to the order o5. For the order o4, the RMS deviation is larger by a factor of 2.5 for symmetric component and by a factor of 4 for the anti-symmetric component with respect to the order o5. On the contrary, by using higher orders we risk to introduce too many parameters, which could be poorly defined in the fit. For the order o6, the N_{points} / $N_{parameters}$ ratio fell down from 30 to 20 and a part of the *ab initio* DMS parameters was poorly determined in the fit. For this reason, the o5 model was selected as an optimum order of the DMS expansion in the "charge function" model.

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B. Polynomial/cosine DMS model

A simpler power series expansion in bond length displacement and in cosines of the apex angle introduced by Jensen[40] was also tested. It is well known that a purely polynomial DMS model expansion on nuclear displacements does not respect the asymptotic behavior of the dipole moment at large distances (figure 1 of Ref [32]). However, this simple model has quite often been used [30,31,33] for calculations of transitions between the states for which vibrational wave-functions span a volume near the equilibrium configuration. A somewhat improved version of this model has been proposed by Jensen [40] by replacing the (θ -θ_e) power series by a cosine-type angular expansion. In these notations, for a molecule having the C_{2v} point group, the symmetric *Q*-component of the dipole moment vector corresponds to the bisector axis and the anti-symmetric *P*-component is the orthogonal one in the molecular plane as defined in [40]. The *P*-component would be oriented parallel to the linear configuration if $\theta \to \pi$.

$$\begin{aligned} \mu^P(r_1,r_2,\theta) &= \sum_{ijk} P_{ijk}(r_1-r_e)^i(r_2-r_e)^j(t)^k \\ \mu^Q(r_1,r_2,\theta) &= \sin(\rho)\sum_{ijk} Q_{ijk}(r_1-r_e)^i(r_2-r_e)^j(t)^k \end{aligned} \tag{1}$$

Here the θ - coordinate is expressed in terms of the apex angle supplement ρ with the following properties

$$\begin{aligned} t &= \cos(\rho_e)-\cos(\rho) \\ \rho &= \pi-\theta \\ P_{ijk} &= -P_{jik} \\ Q_{ijk} &= Q_{jik} \end{aligned} \tag{2}$$

With this modification, the DMS expansion (1), (2) has a correct behavior at a linear nuclear configuration for the vanishing bisector dipole moment component. In this work, we have also tested the DMS fits using this model by limiting the *ab initio* grid to (E - E_{min}) / hc = 4000 cm^{-1} because the RMS deviation was rapidly deteriorating for larger (r-r_e) nuclear displacements. However, within the considered energy range a very small RMS deviation for the *ab initio* dipole moments similar to that of the "charge function" was obtained. An optimal compromise for the ratio N_{points} / $N_{parameters}$ = 27 corresponded to the DMS expansion of the order o4 for symmetric and o5 for anti-symmetric components with the RMS deviation of 0.00005 a.u. for the symmetric and

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0.00002 a.u. for the anti-symmetric DMS components at the grid of 1170 geometries. Under these conditions, the DMS model can be safely used for rotational transitions in the vibrational ground state at least.

C. Variational intensity calculations

Energy levels and wavefunctions were computed by variational methods using the exact kinetic energy (EKE) operator of the nuclear motion in the frame of the Born-Oppenheimer scheme as described in [41, 36]. Various issues related to *ab initio* calculations of the potential energy surface (PES) of the ozone molecule have been discussed in [3-5, 30-33, 36] where the reader can find more details and a complementary list of references. In this study, we used the electronic ground state NR_PES of [36], which to our knowledge is currently the most accurate *ab initio* ozone PES for spectroscopy (predictions for band centers and vibrational dependence of rotational constants [21,42]), for the descriptions of the shape of the transition state towards the dissociation [22] and for modeling the dynamics of isotopic exchange reactions [43]. Similarly to recent work [32] we also used an empirically optimized PES_2 [44,32], which had been employed for many analyses of spectra [21, 45]. The latter PES was initially computed with the same *ab initio* ansatz [36] followed by an adjustment of low order parameters as discussed in [44] for a better account of vibrational inter-mode coupling.

Line intensities I_{ij} for rovibrational transitions ν_{ij} at a temperature T are defined by

$$I_{ij} = \frac{8\pi^3 10^{-36}}{3hcQ(T)} I_0 g_c \nu_{ij} \exp(-c_2 E_i / T)\left[1-\exp(-c_2 \nu_{ij} / T)\right] R_{ij} \qquad (3)$$

in units of cm^{-1}/(molecule×cm^{-2}). Here $c_2 = hc / k$ with k the Boltzmann constant, g_c and E_i are the nuclear spin statistical weight and the energy of the lower state. $Q(T)$ stands for the partition function, which was computed using direct summation of *ab initio* born vibration-rotation energy levels weighted with the Boltzmann exponents. The line strength of a dipole-allowed ro-vibrational transition is defined as $R_{ij} = \sum_{MM'} \langle i | \mu | j \rangle^2$, where the sum extends over all magnetic sublevels of both initial and final states and $|i\rangle$, $|j\rangle$ are vibration-rotational wave functions of the initial and final states of the transition. The dipole moment components (μ_x, μ_z) of $\boldsymbol{\mu}$ in the laboratory-fixed frame (LFF) are related to the *ab initio* DMS computed in the molecular fixed frame via the standard

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direction cosines transformation. The theoretical intensities of this work were computed with our *ab initio* partition sum value Q(276 K) = 3473 for the main isotopologue $^{16}O_3$ using atomic masses (m_{at} (^{16}O) = 29156.9455997 m_e) for the nuclear motion.

For the spectral intervals considered in this work, the differences between intensities of the strongest lines obtained with the *ab initio* NR_PES and with the empirical PES_2 were found negligible - on average about ~0.1% and much below experimental uncertainty. Several dimensions of the Hamiltonian matrix that varied between 20000 and 50000 were tested for the stability of line strengths. By these comparisons we consider that the basis set convergence was achieved to 0.1% - 0.2% for most of the intensities of strong lines in our three spectral ranges, except for few of them (marked by (*) in Tables of Supplementary Information files), for which individual line intensities could fluctuate by up to 0.3% - 0.5%, possibly due to numerical precision issues.

An evaluation of the uncertainties in *ab initio* intensity calculations is an important and challenging issue, which is rarely studied in the literature. We consider that a comparison of intensities obtained using different DMSs models is a useful indicator of prediction errors. It was found that line-by-line intensities in the considered spectral ranges depend to some extent on the damping factor in eq. (2) of Ref [32], on the analytical model used for the fit, and on the type of the size consistency Davidson "Q-corrections" [34,38]. We used both the relaxed reference scheme ("R-version") and the fixed reference scheme ("F-version") of Davidson corrections as specified in more detail in [32]. In general, the scatter in strong line intensities for various combinations of the calculation ansätze was found to stay in a relatively limited range between 0.1% and ~1%.

In each of the considered ranges, we quote two *ab initio* intensity values for the DMS versions denoted below as (a), (a'), (a"), (a#) with the dipole moment parameters given in Supplementary Information files. They basically correspond to the upper and lower "edges" (Tables 1 – 2) of the scatter among our calculations, depending on the spectral intervals considered in the present work.

The DMS versions (a), (a'), (a") were built with the "charge function" o5 model. The version (a) corresponds to the relaxed-reference Davidson corrections with the medium damping (β = 1). The versions (a') and (a") correspond to the fixed-reference and relaxed-reference Davidson corrections with the strong damping (β = 2).

The (a#) DMS version was built from separate fits of the symmetric (μ^Q) and anti-symmetric (μ^P) components of a combined polynomial/cosine Jensen-type model (Eqs. (1), (2)), which has not been used for the ozone dipole moment in previous publications. As argued above, it is well appropriate for the modeling of the surface in a limited (r-r_e) interval and is thus employed for the study of purely rotational spectra in the MW range (Table 1).

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3. Comparison with empirical line lists

On the experimental side, uncertainties depend on various factors [21,28,29,46,47]. These include acquisition parameters (variation of the ozone pressure during spectra records, temperature fluctuations, ….), apparatus function, and line shape model [48]. For an unstable molecule, acquisition related parameters (*purity, pressure and temperature*) are much harder to control than for stable species like CO, water or CO_2. Among atmospheric species, ozone is a relatively heavy asymmetric top molecule having quite crowded spectra [21] with many blended features: weaker lines due to high-J or high-K_a transitions, hot bands or isotopic species are often on the wings or under a stronger line. Therefore, the direct high precision intensity measurement of some important lines is not feasible. A common way to reduce hazardous intensity fluctuations from one line to another is performing least-squares-fits on the measurements using well established effective models for vibrational polyads [21,49]. These provide well representative values of positions and strengths over all branches and have been used to generate the JPL, HITRAN, GEISA, and S&MPO compilations [24,50,51,45]. Here we use the same approach for comparing theoretical and empirical lists.

A. Rotational band

It was recently noted [52,53] that line intensities of rotational transitions included in the last releases of HITRAN [50], JPL [24] and S&MPO [45] databases were not sufficiently consistent: the discrepancies in the strongest lines amounted up to 3% - 4% that was much more than a targeted accuracy for atmospheric applications of 0.5% - 1%. In the microwave (MW) range, the line lists for the rotational band included in commonly used spectroscopic compilations are based on Stark effect measurements of Lichtenstein et al [25], Mack and Muenter [26], and Meerts et al [27]. The latter measurements have covered limited intervals of quantum numbers (below J_{max} = 4 and J_{max} = 6 only), but permitted accurate determination of an average effective dipole moment for the vibrational ground state. Using these data, Flaud et al [23] have constructed J, K - dependent transition moment parameters (Table VIII of Ref [23]) for rotational ozone lines. In a similar work, Pickett et al derived in a somewhat different manner (unpublished work) a MW line list for ozone included in the JPL catalogue at T = 300 K (see also related comments in [58]). Empirical effective

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Hamiltonians (EH) [49] fitted to observed line positions have been used in both of these works to generate energies and wave functions.

In Table 1 we compare *ab initio* calculations of the strongest lines based on (a) and (a#) DMS models with the empirical list obtained from effective Stark-effect transition moments. The latter one has been generated from the empirical parameters of Table VIII of Flaud et al [23] using energies and wavefunctions of the empirical EH of ref. [54] and the standard empirically based value [55] for the partition function *Q*. An average discrepancy between both our *ab initio* data and these empirical intensities is at the level of 0.1% to 0.4%. Figure 1a shows a very good overall qualitative agreement for the rotational intensity patterns on the logarithmic scale. The *ab initio* calculations are also consistent with the JPL catalogue, whose strong intensities are slightly higher by 0.5% to 1% (Table 1). Concerning the strong lines, the HITRAN-2016 database is too low by 2.5% to 3.5% with respect to our *ab initio* predictions and also with respect to the MW lists based on Stark effect measurements.

Table 1. Ab initio intensities for the strongest rotational lines of ozone and comparison with values, generated from empirical dipole transition moment parameters [23] derived from Stark-effect experiments, and with JPL database [24]

J	Ka	J	Ka	WN	I *ab initio*		I Stark_d	I JPL	Stark_d – *abinitio* δI (%)		JPL – *abinitio* δI (%)	
up		low		cm^{-1}	(a)	(a#)			(a)	(a#)	(a)	(a#)
10	10	9	9	67.2338	1.482	1.488	1.489	1.496	0.5	0.1	0.9	0.5
11	10	10	9	68.0744	1.462	1.468	1.469	1.475	0.5	0.1	0.9	0.5
9	9	8	8	60.3241	1.449	1.455	1.458	1.463	0.6	0.2	1.0	0.5
10	9	9	8	61.1646	1.443	1.449	1.450	1.456	0.5	0.1	0.9	0.5
12	10	11	9	68.9148	1.443	1.449	1.449	1.455	0.4	0.0	0.8	0.4
11	9	10	8	62.0050	1.434	1.440	1.442	1.448	0.6	0.1	1.0	0.6
12	9	11	8	62.8453	1.425	1.431	1.432	1.438	0.5	0.1	0.9	0.5
13	10	12	9	69.7552	1.420	1.426	1.426	1.433	0.4	0.0	0.9	0.5
11	11	10	10	74.0992	1.416	1.422	1.422	1.429	0.4	0.0	0.9	0.5
13	9	12	8	63.6855	1.411	1.417	1.418	1.424	0.5	0.1	0.9	0.5
14	9	13	8	64.5256	1.395	1.401	1.401	1.407	0.4	0.0	0.9	0.4
14	10	13	9	70.5954	1.395	1.401	1.400	1.407	0.4	-0.1	0.9	0.4
12	11	11	10	74.9398	1.389	1.395	1.393	1.401	0.3	-0.1	0.9	0.4
15	9	14	8	65.3654	1.373	1.379	1.379	1.386	0.4	0.0	0.9	0.5
15	10	14	9	71.4355	1.366	1.372	1.371	1.378	0.4	-0.1	0.9	0.4
		S(100) =			118.30	118.70	118.80	119.30	0.38	0.06	0.83	0.50

Note: WN = wavenumber; I = line intensity [E-21 cm/molec]; *ab initio* DMSs (a,a#) are given in Supplementary Material; Stark_d - obtained with empirical dipole parameters of Flaud[23] derived from Stark-effect measurements [25-27], using empirical TIPS [55] value Q(296) = 3484; δI (%)= relative intensity difference = *100*((emp-theo)/emp);* S(100) = sum of 100 strongest line intensities; all values correspond to pure $^{16}O_3$ at 296 K.

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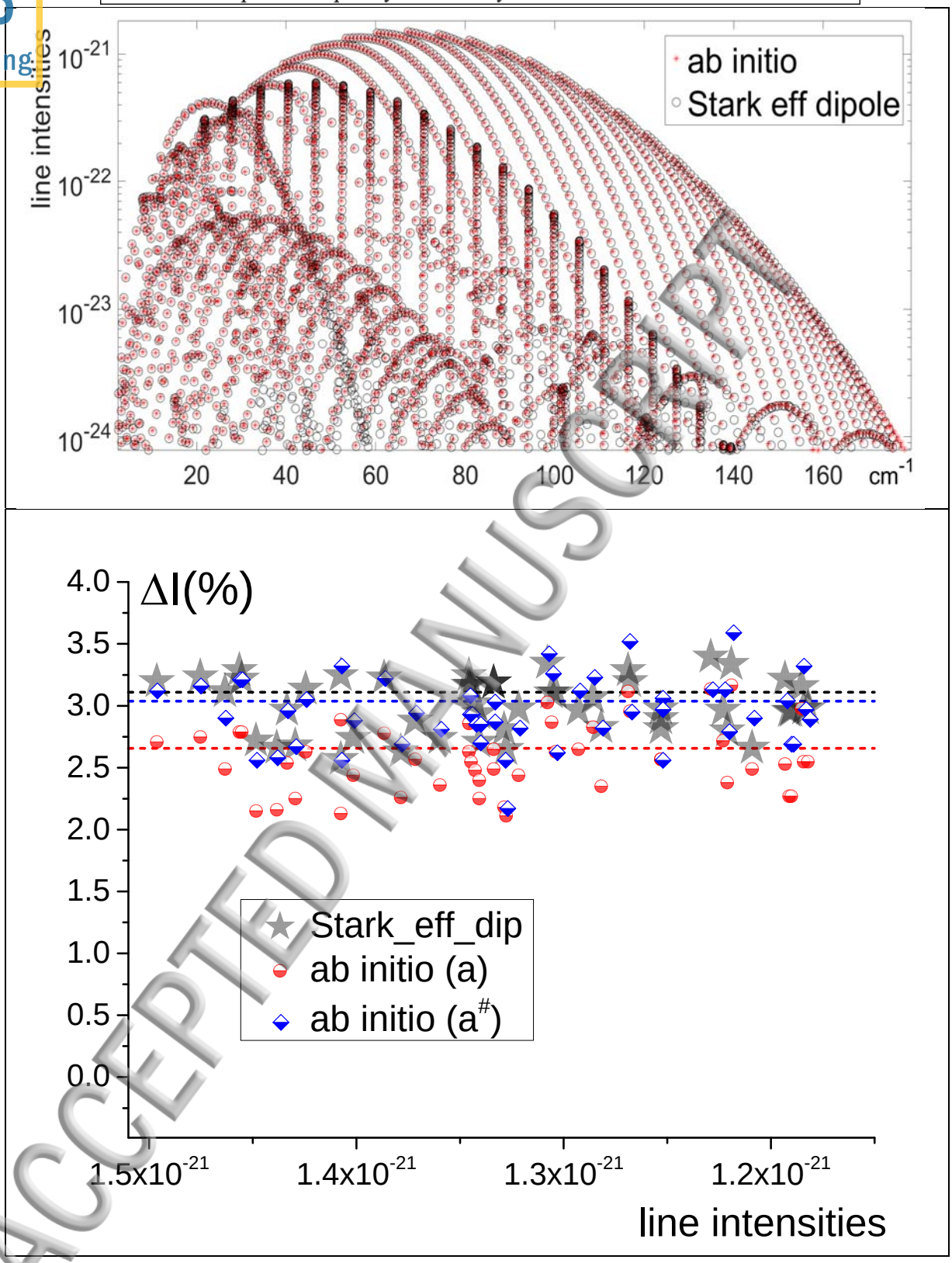

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Figure 1. Upper panel: a*b initio* rotational line intensities [cm/molec] of ozone $^{16}O_3$ versus wavenumber / cm^{-1} and comparison with intensities computed from effective dipole transition moment parameters [23] derived from Stark-effect experiments [23-25]. Lower panel: intensity deviations from HITRAN2016 database [50] with average values plotted as dashed horizontal lines. All values correspond to pure $^{16}O_3$ at 296 K.

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The rotational band intensities included in the S&MPO database [45] have been generated using empirical transition moment parameters of Birk et al [56] derived from the analyses of far infrared observed spectra, independently of Stark effect measurements. For the strongest rotational lines, the S&MPO intensities are consistent with our *ab initio* calculations and with the JPL line list, based on dipole moments derived from Stark effect measurements. The agreement is within about 1 %. The intensity scatter in medium and weak lines from different sources [24,50,51,45,56,57] needs further investigation. During preparation of the revised version of the manuscript we became aware of the publication of Birk et al [58] who also discuss discrepancies in available databases for the rotational transitions. These authors also conclude that HITRAN underestimates intensities of strong MW lines by about 3% due to some inadvertent scaling in the past. Our results are thus consistent with their conclusions.

B. Infrared 10 and 5 micron ranges

Previous experiments at 10 µm disagree by about 4%, the quest of precision being discussed by Flaud et al [59] and Smith et al [60]. Very recently, three groups [28,29,47] have reported independent new observations around 10 µm at the HITRAN 2018 Workshop. Two of the groups [28,29] also reported new measurements at 5 µm, but final results have not been published yet. For the validation of our *ab initio* intensities we use empirical lists obtained from fitting to the new spectra observed by GSMA laboratory in Reims [28] and LERMA laboratory in Paris [29]. The experimental data and measurement conditions will be published in full detail elsewhere.

GSMA spectra were recorded by a home-made FTS spectrometer [61]. It works on stepping mode, has 3 meters path difference, uses He/Ne laser stabilized on iodine. The ozone ν_3 transition (J = 24,Ka = 11) $\rightarrow$ (J = 23,Ka = 11), which had been observed by saturated absorption spectroscopy, permitted to calibrate positions with 6×10^{-5} cm^{-1} precision for best isolated lines. In the 10 microns range, pressures varied from some fractions of Torr to 40 Torr and optical path lengths from 5 to 3600 cm. In total, 3735 line positions were measured, the derived spectroscopic parameters, presented in HITRAN/ASA meeting [28] reproduce these data with the RMS deviation of 0.12×10^{-3} cm^{-1}. The data reduction, using these spectroscopic parameters show some improvements amounting to 4×10^{-3} cm^{-1} for Ka = 22 with respect to the last version of HITRAN database [50]. Line intensities were derived from Voigt profiles using the MULTIFIT code [62]. In 10 µm range, 547 absolute intensities were determined in a cell with a crossing ultraviolet path (3.100

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cm) using the reference UV cross-section at 253.65 nm. At 5 µm, over 1000 relative and 40 absolute intensities were measured and scaled with respect to the 10 µm range.

A new experimental setup at LERMA [29] using a commercial Bruker IFS-125 [64] instrument permitted almost simultaneous recording at 10 µm and 5 µm, using an H-shaped absorption cell with two light absorption path lengths of 5 and 20 cm, respectively. The ozone pressure has been continuously monitored by UV absorption at 253.65 nm. A multispectrum fitting procedure [66] using a speed-dependent line profile model [67] was used to retrieve around 650 and 350 line parameters at 10 µm and 5 µm, respectively, based on the analysis of 4 different spectra at ozone pressures between 0.14 and 1.16 Torr. The all glass setup allowed for long acquisition times (~14 h) at very low degree of decomposition (< 1%). Typical signal-to-noise ratios in individual spectra were between 0.2% and 0.7%.

Note that initially, in a preliminary presentation of experimental results[28,29], the IR intensities had been evaluated independently using UV cross-sections of Viallon et al.[63] for GSMA and of Mauersberger et al.[70] for LERMA. For this work, we have re-scaled our empirical GSMA and LERMA data both in 10 and in 5 microns ranges to be consistent with the most recent and presently most carefully evaluated UV reference at 253.65 nm from Hodges et al [65].

As it had been done in previous analyses for a construction of empirical line lists, we fitted an effective Hamiltonian model to individually measured line intensities in order to smooth instrumental errors. The application of this data reduction procedure to upper and lower states of the observed transitions [28,29], led to standard deviations for the new spectra close to the experimental precision. Though these results are yet preliminary and the uncertainty analysis incomplete, extensive tests show that various fit versions of measured spectra aimed at producing the empirical line lists are very robust with respect to the number of adjusted parameters and to the data weighting: the estimated fluctuations due to the model fit are within about 0.1% – 0.3%.

This work focuses on the strongest line intensities for the following reasons. Strong lines dominate the overall band intensities and play the most important role in the consistency of the absorption measurements in different spectral intervals. At the same time, they suffer less from line blending effects and reduced signal-to-noise ratios than weaker transitions. This applies to both, atmospheric observations and laboratory experiments. Moreover, line strengths of many medium and weak lines can be strongly perturbed by sharp accidental resonances. The corresponding lines appear to be extremely sensitive to resonant mixing of basis wavefunctions and to much lesser extent to the quality of the DMS. In *ab initio* calculations, these lines are often considered as “unstable” or “sensitive” ones [68,69,32]. Caution should therefore be taken to exclude

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such outliers from tests of the validity of dipole moment surfaces. We plan to investigate the corresponding fine details in future studies.

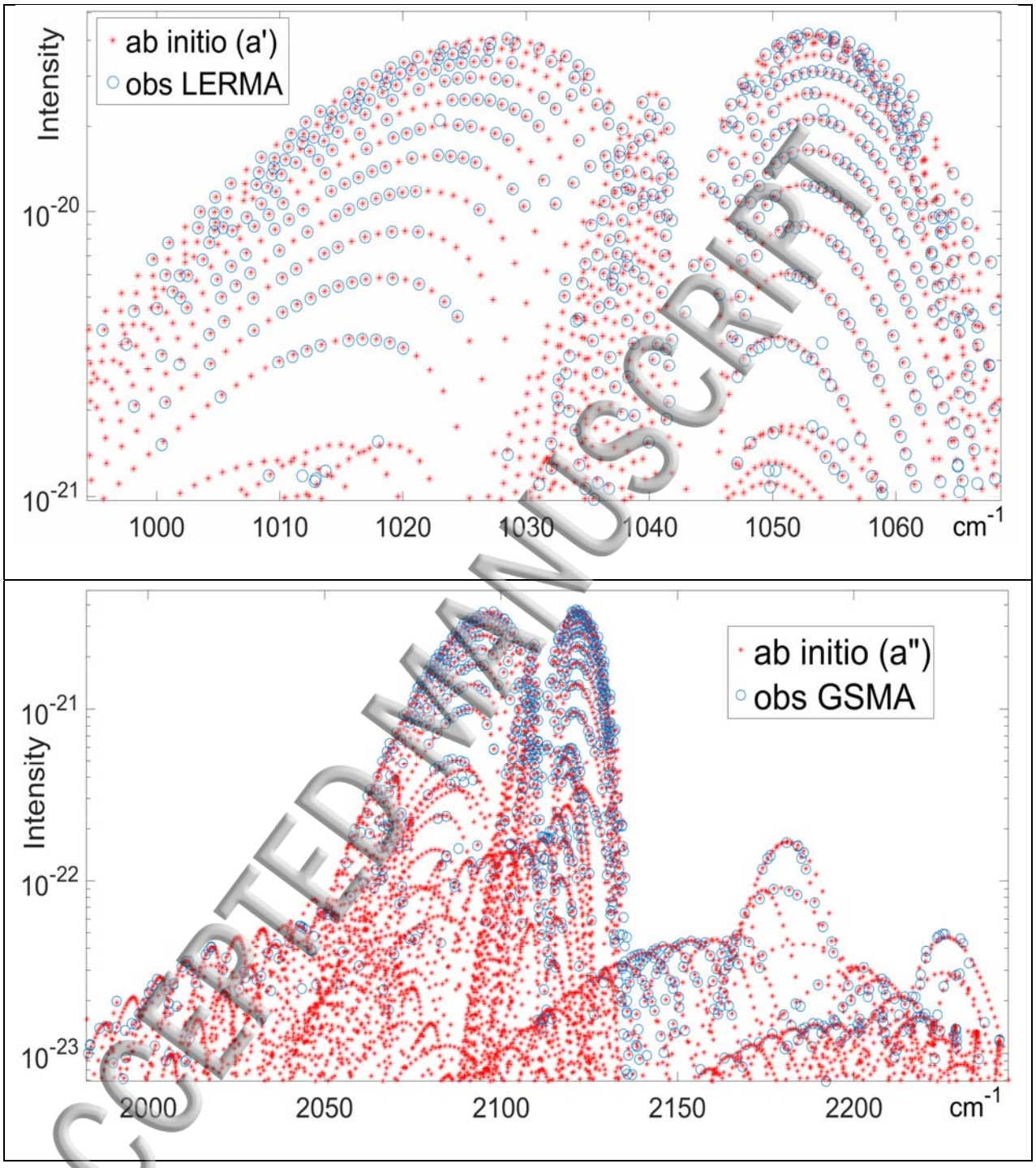

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Figure 2. Examples of *ab initio* line intensities (red asterisks) of the ozone molecule versus wavenumber / cm^{-1} and comparison with new experimental LERMA and GSMA intensities (blue cycles) in 10 µm (upper panel) and in 5 µm (lower panel) ranges. All values correspond to pure $^{16}O_3$ at 296 K.

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The comparison of strong lines in Figs 2, 3, Tables 2 and 3 and extended ones in the Supplementary Information files show excellent agreement between *ab initio* and new empirical line lists. Deviations are within 1%, corresponding to uncertainty estimates for both theoretical and experimental results.

Table 2. Ab initio intensities for the strongest lines of ozone in 10 μm and comparison with preliminary empirical lists fitted to new FTS experiments

ν_3 band				WN	I *ab initio*		I empirical		Differences δI *(%)*			
J	K_a up	J	K_a low	cm^{-1}	a	a'	L	G	L - a	L – a'	G - a	G – a'
15	0	14	0	1052.8484	42.26	42.00	41.99	42.18	-0.7	0.0	-0.2	0.4
17	0	16	0	1053.9658	42.10	41.82	41.76	41.97	-0.8	-0.2	-0.3	0.4
16	1	15	1	1053.1679	41.95	41.67	41.61	41.82	-0.8	-0.2	-0.3	0.4
15	1	14	1	1053.6918	41.50	41.25	41.27	41.48	-0.6	0.0	-0.1	0.5
14	1	13	1	1051.9849	41.30	41.04	41.01	41.20	-0.7	-0.1	-0.2	0.4
17	1	16	1	1055.0063	41.25	41.00	40.99	41.20	-0.6	0.0	-0.1	0.5
18	1	17	1	1054.2895	41.25	40.97	40.88	41.08	-0.9	-0.2	-0.4	0.3
13	0	12	0	1051.6568	41.04	40.79	40.79	40.99	-0.6	0.0	-0.1	0.5
15	0	16	0	1027.4559	40.96	40.71	40.81	40.91	-0.4	0.2	-0.1	0.5
14	1	15	1	1028.4951	40.59	40.36	40.49	40.60	-0.2	0.3	0.0	0.6
13	0	14	0	1029.4327	40.55	40.32	40.43	40.54	-0.3	0.3	0.0	0.5
19	0	18	0	1055.0164	40.68	40.42	40.33	40.54	-0.9	-0.2	-0.3	0.3
16	1	17	1	1026.4763	40.43	40.18	40.30	40.41	-0.3	0.3	0.0	0.6
13	1	12	1	1052.3084	40.30	40.06	40.10	40.29	-0.5	0.1	0.0	0.6
17	0	18	0	1025.4262	40.08	39.83	39.92	40.02	-0.4	0.2	-0.2	0.5
19	1	18	1	1056.2440	39.73	39.49	39.44	39.66	-0.7	-0.1	-0.2	0.4
12	1	13	1	1030.4630	39.40	39.17	39.30	39.42	-0.2	0.3	0.0	0.6
16	2	15	2	1053.6805	39.46	39.21	39.15	39.37	-0.8	-0.1	-0.2	0.4
15	2	14	2	1053.5199	39.36	39.12	39.11	39.32	-0.6	0.0	-0.1	0.5
17	2	16	2	1054.9679	39.38	39.12	39.09	39.30	-0.7	-0.1	-0.2	0.5
S(100)=					3620	3598	3598	3613	-0.61	0.00	-0.19	0.42

Note: WN = wavenumber (obs); I = line intensity [10^{-21} cm/molec]; *ab initio* DMSs (a, a') are given in Supplementary Information files; L = empirical fit to LERMA measurements; G = empirical fit to GSMA measurements; δI *(%)*= relative intensity difference = *100*((emp-theo)/emp);* S(100) = sum of 100 strongest line intensities; all values correspond to pure $^{16}O_3$ at 296 K.

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Table 3. *Ab initio* intensities for the strongest lines of ozone in 5 µm and comparison with preliminary empirical lists fitted to new FTS experiments

$\nu_1+\nu_3$ band				WN	*ab initio*		empirical		Differences δI *(%)*			
J	K_a up	J	K_a low	cm^{-1}	a	a"	L	G	L - a	L – a"	G - a	G – a"
15	0	14	0	2121.2486	3.766	3.731	3.767	3.743	0.0	0.9	-0.6	0.3
15	1	14	1	2121.8935	3.736	3.701	3.735	3.710	0.0	0.9	-0.7	0.2
17	0	16	0	2122.3081	3.714	3.687	3.722	3.698	0.2	0.9	-0.4	0.3
17	1	16	1	2123.0866	3.700	3.666	3.697	3.674	-0.1	0.8	-0.7	0.2
13	0	12	0	2120.1134	3.679	3.645	3.681	3.657	0.1	1.0	-0.6	0.3
14	1	13	1	2120.4649	3.676	3.641	3.677	3.654	0.0	1.0	-0.6	0.4
15	0	16	0	2095.8561	3.670	3.644	3.678	3.650	0.2	0.9	-0.6	0.2
13	0	14	0	2097.8893	3.661	3.627	3.662	3.635	0.0	1.0	-0.7	0.2
14	1	15	1	2096.9750	3.651	3.617	3.650	3.622	0.0	0.9	-0.8	0.1
13	1	12	1	2120.6233	3.638	3.604	3.639	3.615	0.0	1.0	-0.6	0.3
18	1	17	1	2122.6468	3.609	3.583	3.615	3.593	0.2	0.9	-0.4	0.3
17	0	18	0	2093.7685	3.571	3.546	3.577	3.550	0.2	0.9	-0.6	0.1
19	0	18	0	2123.2985	3.570	3.536	3.566	3.544	-0.1	0.8	-0.7	0.2
12	1	13	1	2098.9966	3.559	3.525	3.560	3.533	0.0	1.0	-0.7	0.2
15	1	16	1	2095.3051	3.552	3.519	3.552	3.525	0.0	0.9	-0.8	0.2
19	1	18	1	2124.1979	3.549	3.516	3.543	3.521	-0.2	0.8	-0.8	0.1
13	1	14	1	2097.4103	3.542	3.509	3.543	3.516	0.0	1.0	-0.7	0.2
15	2	14	2	2121.7368	3.539	3.506	3.536	3.514	-0.1	0.9	-0.7	0.2
17	2	16	2	2123.0316	3.518	3.493	3.524	3.502	0.2	0.9	-0.5	0.3
16	2	15	2	2121.9596	3.516	3.483	3.512	3.491	-0.1	0.8	-0.7	0.2
S(100)=					322.5	320.1	322.9	320.8	0.12	0.87	-0.54	0.20

Note: WN = wavenumber (obs); I = line intensity [10^{-21} cm/molec]; *ab initio* DMSs (a, a") are given in Supplementary Material; "unstable" lines excluded (§ in Supplementary files); L = empirical fit to LERMA measurements; G = empirical fit to GSMA measurements; δI *(%)*= relative intensity difference = *100*((emp-theo)/emp);* S(100) = sum of 100 strongest line intensities; all values correspond to pure $^{16}O_3$ at 296 K.

1. Conclusions

To summarize, our *ab initio* results suggest that HITRAN2016 intensities are to be augmented by (+3 ± 0.5)% in MW, by (+3 ± 0.7)% at 10 µm and by (+3.3 ± 0.7)% at 5µm as clearly seen at the lower panel of Figure 1 and in Figure 3. In this way, overall consistency of all data is achieved: including the lists generated from empirical parameters [23] and the JPL catalog [24] (both based on Stark-effect measurements [25-27]) in the MW as well as the new infrared measurements by GSMA and LERMA/MONARIS.

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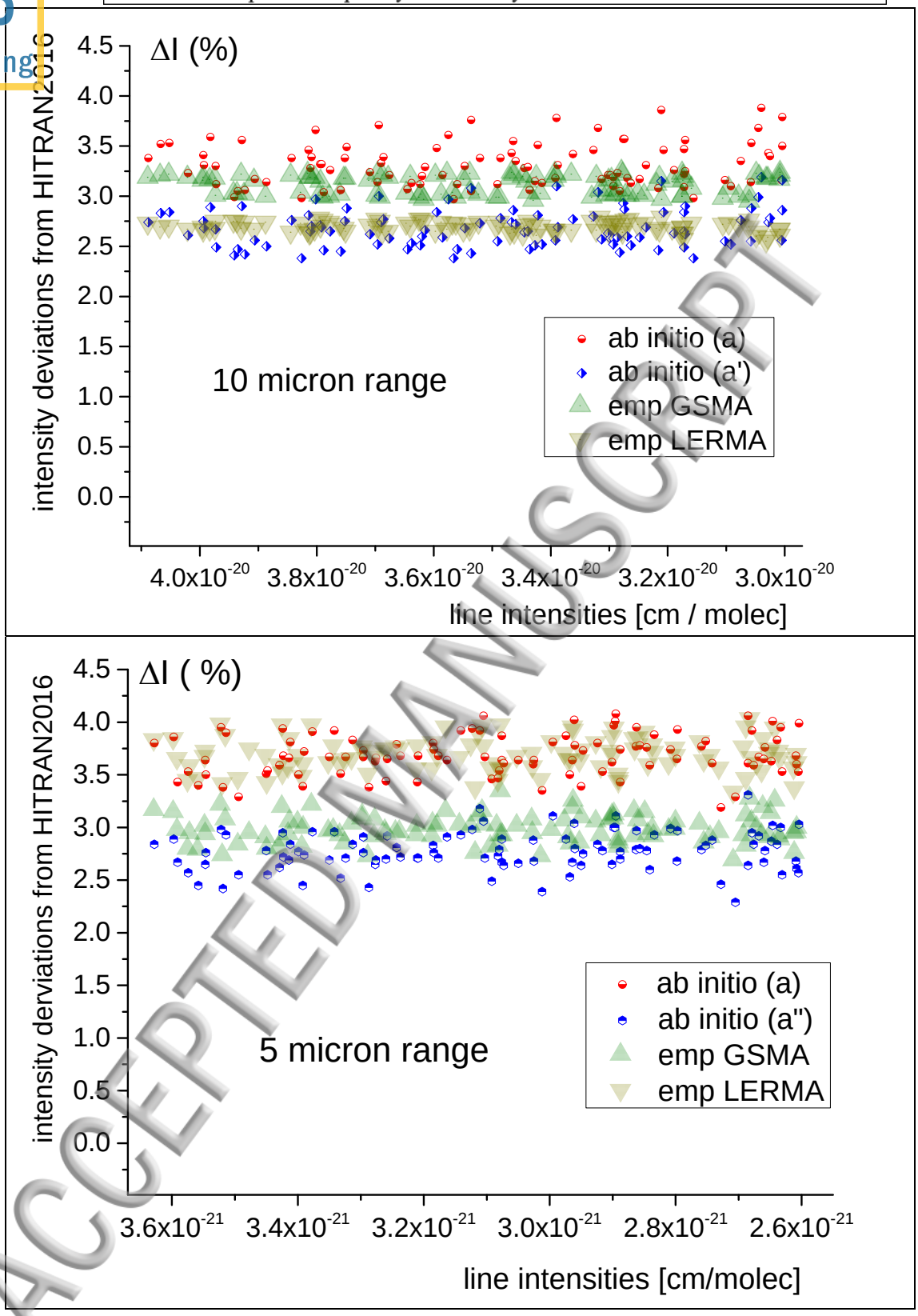

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Figure 3. Comparison of *ab initio* calculations (see text) and preliminary empirical GSMA and LERMA line lists with HITRAN2016 database [50] for the strongest transitions in 10 µm and 5 µm ranges for absorption intensities of the $^{16}O_3$ molecule at 296 K.

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The results of recently reported measurements in Oberpfaffenhofen DRL laboratory by Wagner et al.[47] support the necessity of stronger intensity values at 10 µm and this correction also establishes full consistency with the simultaneous MW and MIR measurements of Drouin et al [57]. A similar scaling of S&MPO data at 5 and 10 µm will maintain the consistency between these two ranges, demonstrated *via* atmospheric column observations as discussed by Janssen et al. [13]. Together with a recent high accuracy measurement of ozone at 325 nm [12], these new revised sets of strong line intensities should provide a decisive step forward to solving the long-standing UV-IR discrepancy problem. The evaluation of uncertainties for a new line list is subject of a HITRAN Work group including the teams of [50,28,29,47,57]. Note that a cumulated effect of many weaker features could also contribute to a correct interpretation of atmospheric measurements though to a lesser extent than the strong lines. More detailed discussions and analyses including medium strength and weak lines will be presented elsewhere in papers focused on the experimental measurements.

Supplementary Material

See supplementary information text file containing parameters of (a), (a'), (a''), (a#) DMSs used in this work and extended comparison between ab initio and empirical line intensities.

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Figure Caption

Figure 1. Upper panel: a*b initio* rotational line intensities [cm/molec] of ozone $^{16}O_3$ versus wavenumber / cm^{-1} and comparison with intensities computed from effective dipole transition moment parameters [23] derived from Stark-effect experiments [23-25]. Lower panel: intensity deviations from HITRAN2016 database [50] with average values plotted as dashed horizontal lines. All values correspond to pure $^{16}O_3$ at 296 K.

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Figure 2. Examples of *ab initio* line intensities (red asterisks) of the ozone molecule versus wavenumber / cm^{-1} and comparison with new experimental LERMA and GSMA intensities (blue cycles) in 10 µm (upper panel) and in 5 µm (lower panel) ranges. All values correspond to pure $^{16}O_3$ at 296 K.

Figure 3. Comparison of *ab initio* calculations (see text) and preliminary empirical GSMA and LERMA line lists with HITRAN2016 database [50] for the strongest transitions in 10 µm and 5 µm ranges for absorption intensities of the $^{16}O_3$ molecule at 296 K.

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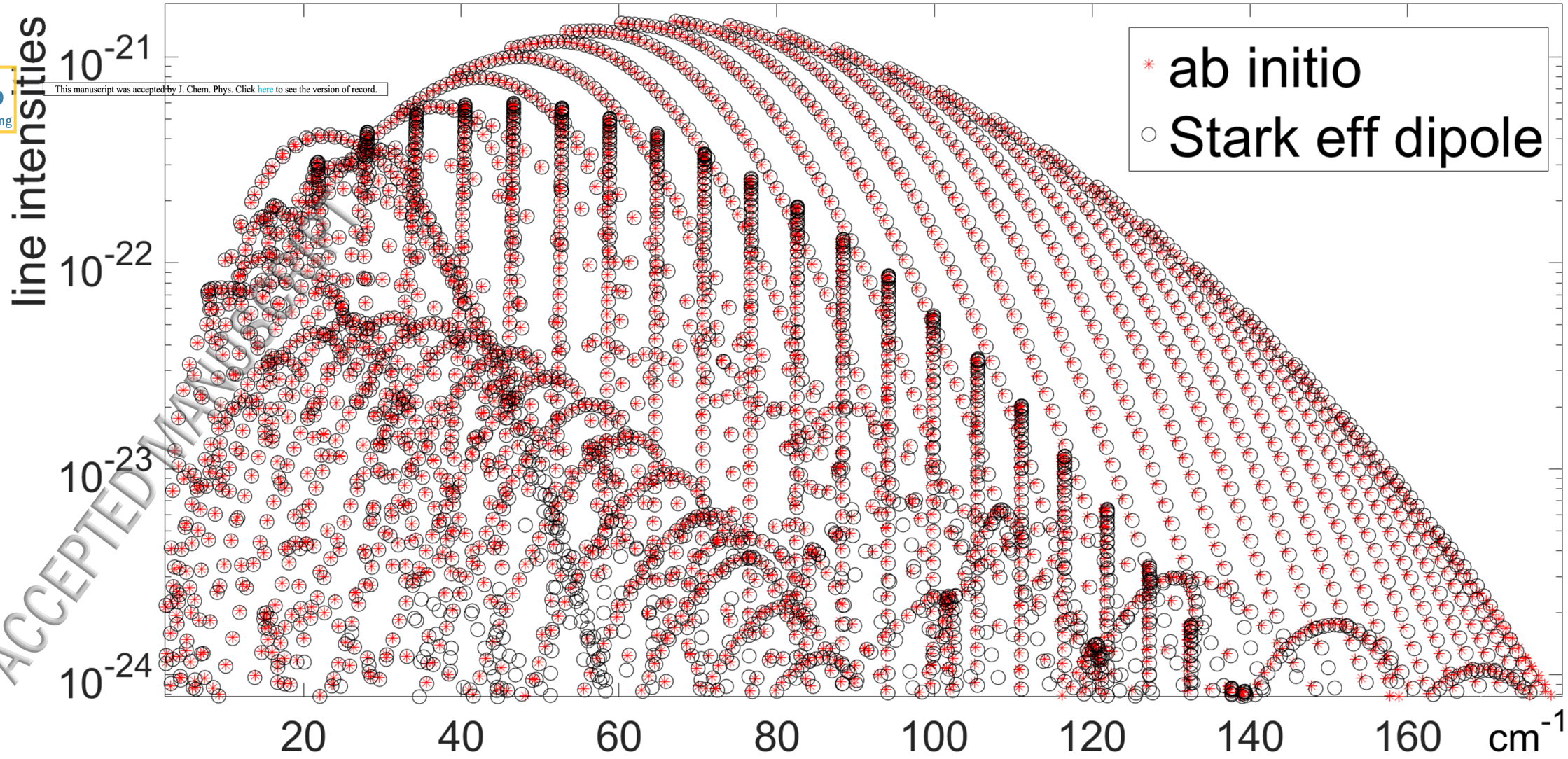

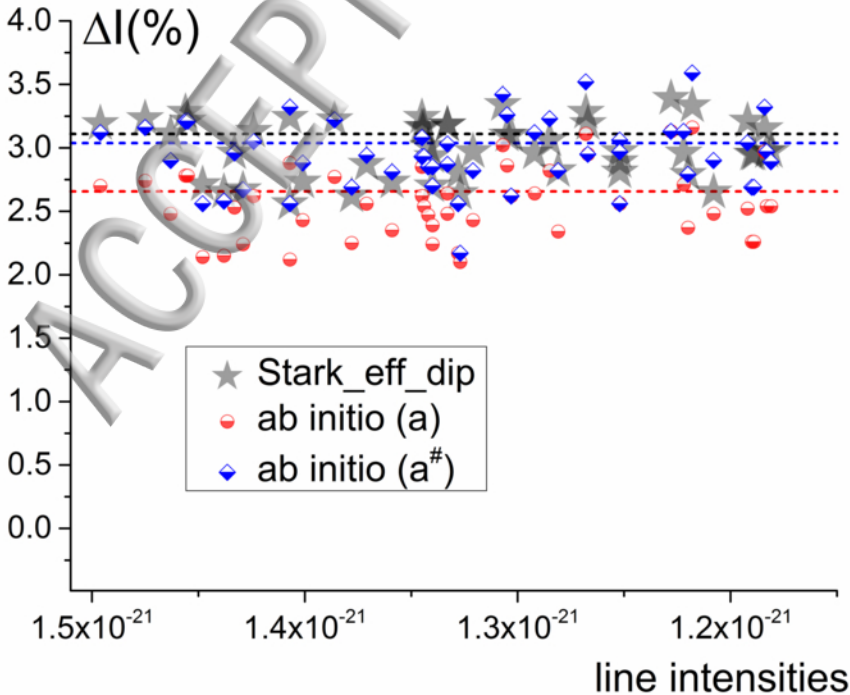
ΔI(%)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Stark_eff_dip
ab initio (a)
ab initio (a#)
1.5x10-21
1.4x10-21
1.3x10-21
1.2x10-21
line intensities

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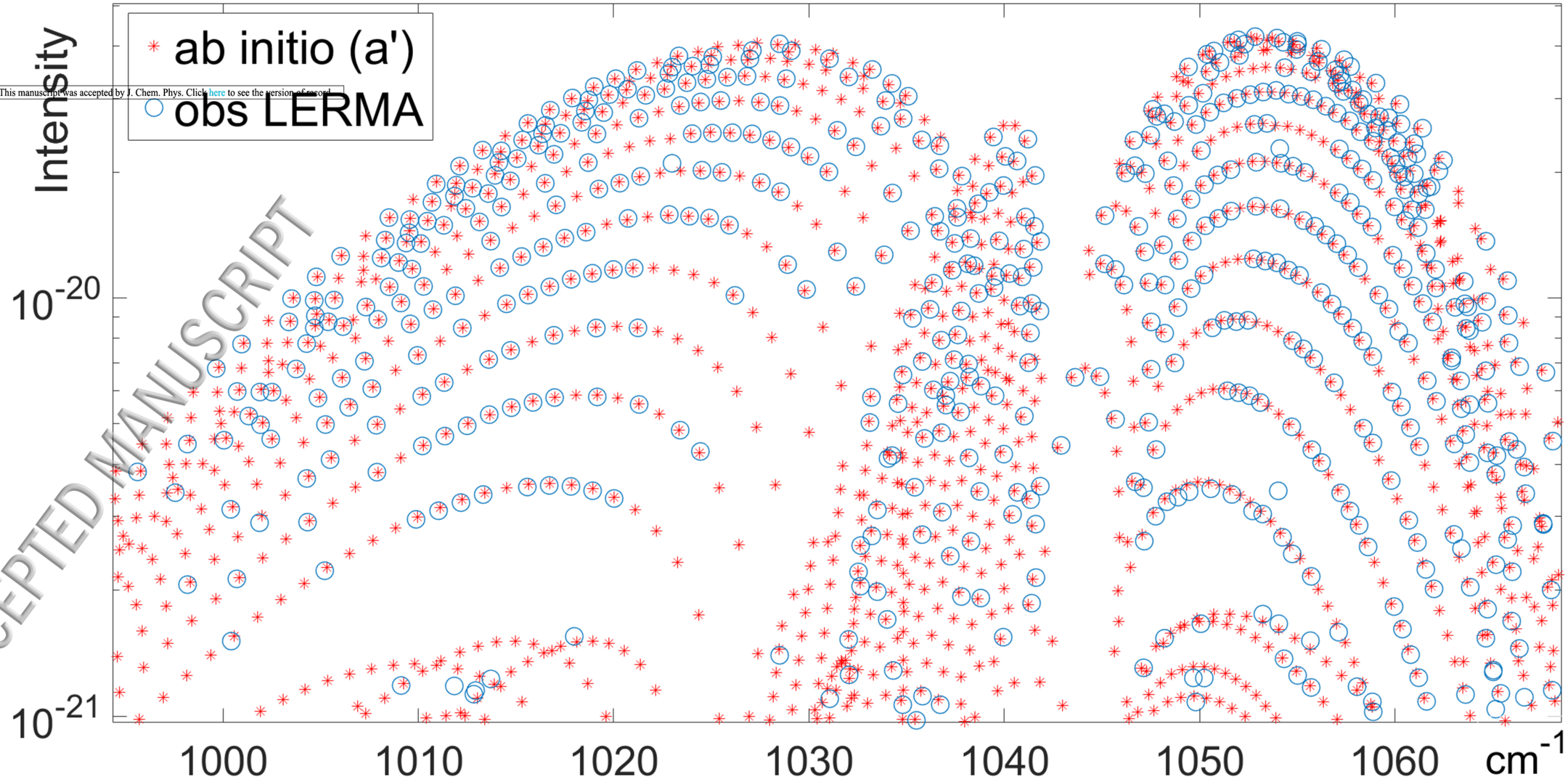

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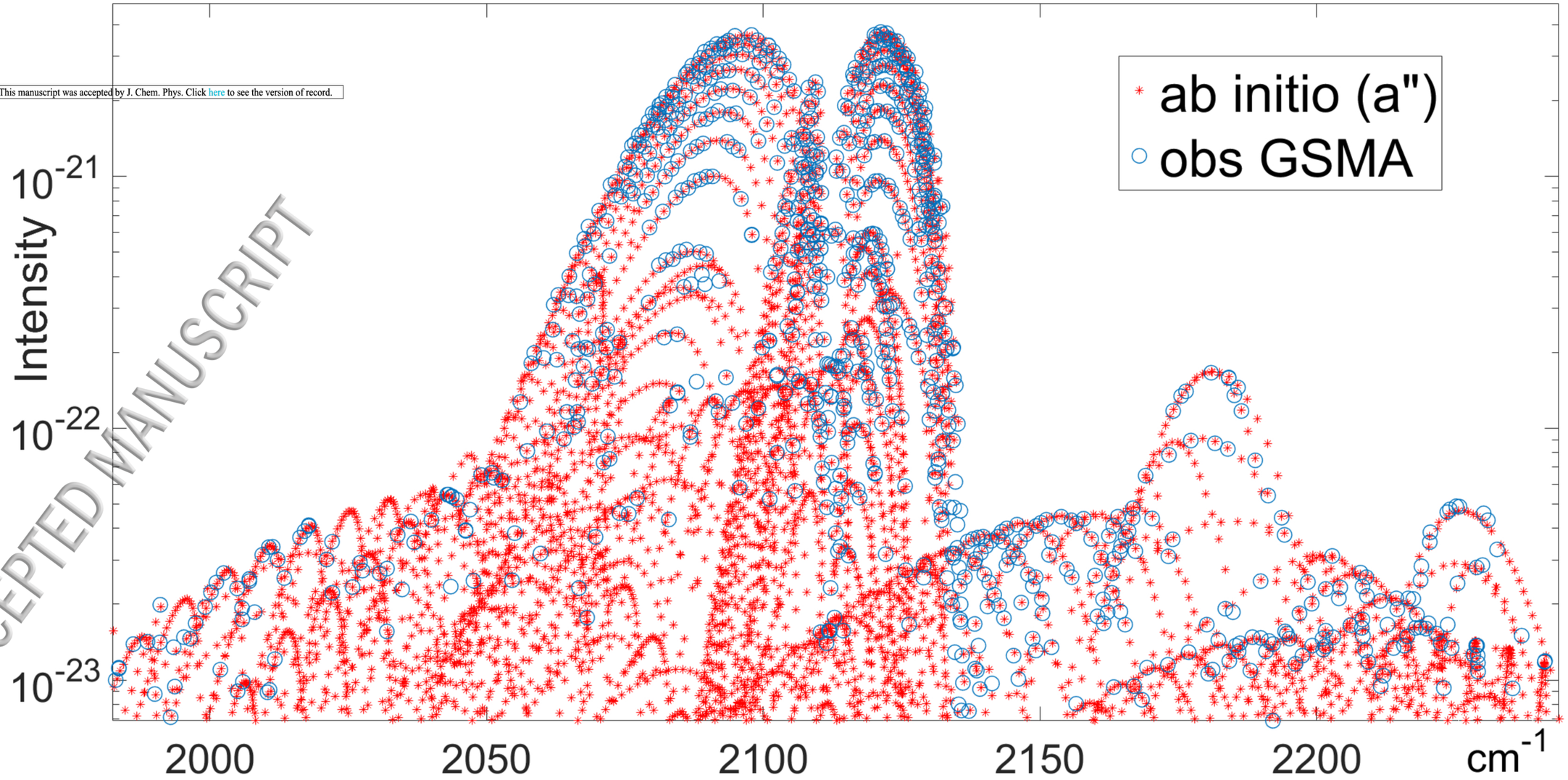

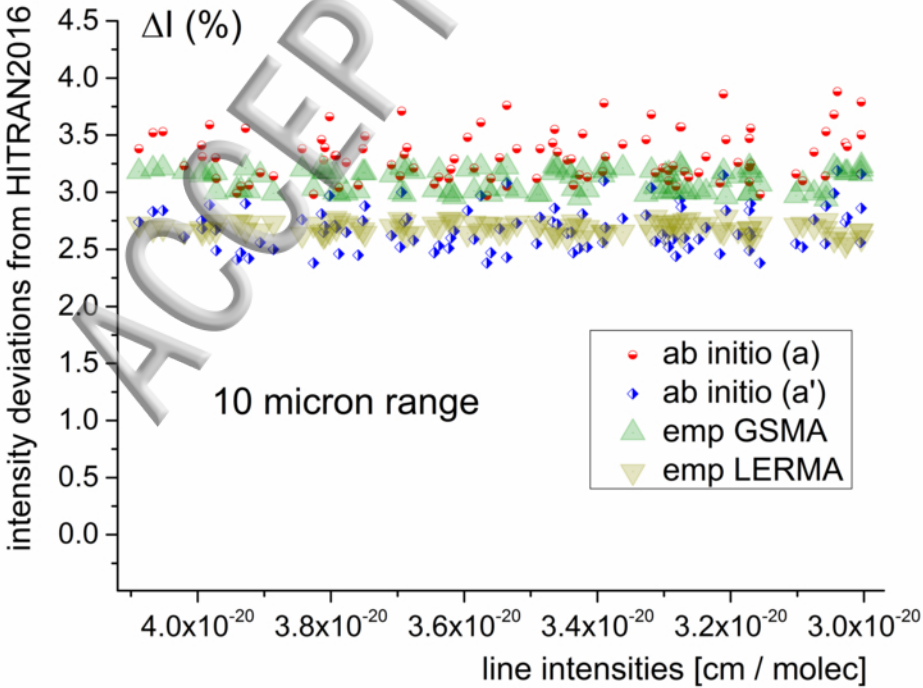
ΔI (%)
intensity deviations from HITRAN2016
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
10 micron range
ab initio (a)
ab initio (a')
emp GSMA
emp LERMA
4.0x10-20
3.8x10-20
3.6x10-20
3.4x10-20
3.2x10-20
3.0x10-20
line intensities [cm / molec]

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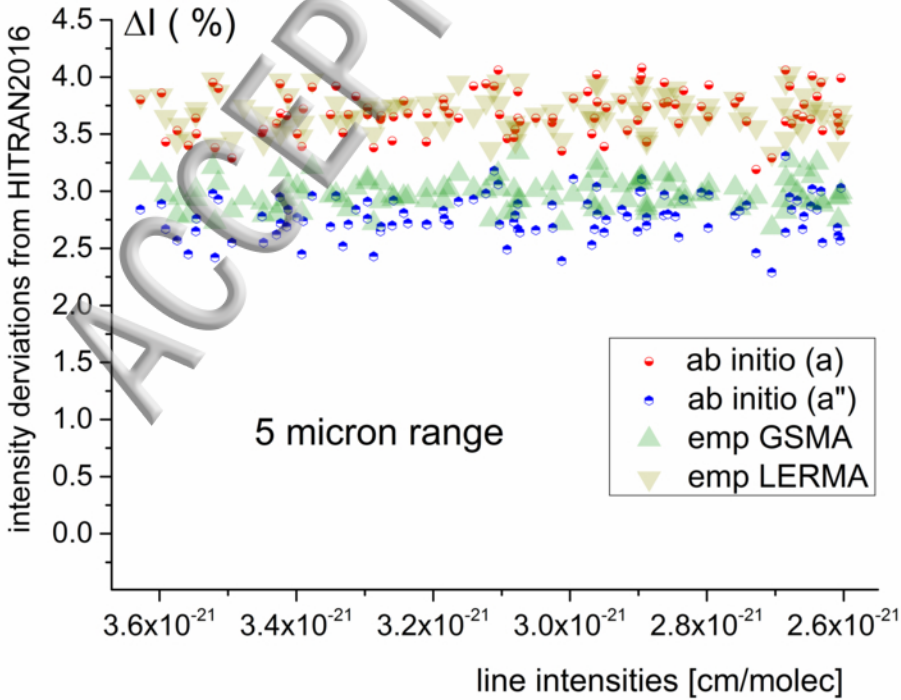
ΔI (%)
intensity derviations from HITRAN2016
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
5 micron range
ab initio (a)
ab initio (a")
emp GSMA
emp LERMA
3.6x10-21
3.4x10-21
3.2x10-21
3.0x10-21
2.8x10-21
2.6x10-21
line intensities [cm/molec]

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