

LINE OSCILLATOR STRENGTHS FOR THE  $c_4'1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(0-7)$  ABSORPTION  
BANDS OF  $N_2$

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## ABSTRACT

Theoretical absorption oscillator strengths for rotational lines of the  $c_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(0-7)$  bands of  $N_2$ , which are relevant to analyze the spectra of the atmospheres of the Earth, Titan, and Mars, are reported. The known interaction between the  $c_4^1\Sigma_u^+(4)$  and  $c_3^1\Pi_u^+(4)$  Rydberg states and the  $b^1\Sigma_u^+(13)$  valence state has been dealt with through an appropriate rovibronic energy matrix. Deviations in the intensity distribution of the rotational lines from considerations based on Hönl-London factors have been found for each one of the studied bands. Emission branching ratios for the above bands and lifetimes of the rotational levels of the  $v=4$  level of the  $c_4^1\Sigma_u^+$  state are also reported.

*Key words:* molecular data – ultraviolet: planetary systems

## 1. INTRODUCTION

The  $N_2$  Carroll-Yoshino bands, which corresponds to excitations from the ground state  $X^1\Sigma_g^+$  to the Rydberg state  $c_4^1\Sigma_u^+$ , have long been of interest in the analysis of the molecular emission observations in the extreme ultraviolet (EUV) spectral region of nitrogen-rich planetary atmospheres. In particular, several bands belonging to the  $c_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(v'')$  progression, which are the object of the present study, has been seen in the EUV spectra from Titan and Earth atmospheres, where molecular nitrogen is the main component. In the Rocket observations of the dayglow spectrum of the terrestrial atmosphere, Morrison et al. (1990) have identified the  $c_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(3)$  band of  $N_2$  at 944 Å. Feldman et al. (2001) by using the Far Ultraviolet spectroscopic explorer (FUSE), have observed the  $c_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(3,4,5,6)$  bands in the terrestrial day airglow spectra. The  $c_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(0)$  band is present in Titan's EUV emission spectra obtained by Voyager 1 spacecraft (Strobel & Shemansky, 1982). Later, from an analysis of the airglow observations of Titan's atmosphere made with the Ultraviolet Imaging Spectrograph (UVIS) on Cassini, Ajello et al. (2007) associated some of the strong emission features found in the EUV spectra with the  $c_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(1,3,4,5,6)$  bands of  $N_2$ . Most recently, from an analysis of higher resolution Titan airglow data also obtained with the UVIS, Stevens et al. (2011) identified the  $c_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(v'')$  progression with  $v''=1-7$  in the

EUV spectrum. The  $c_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(3,4,5)$  bands were also found in a spectrum of Mars obtained by Krasnopolsky & Feldman (2002) using FUSE. As has been claimed by Heays et al. (2009), the interpretation of the Titan, Mars and Earth's atmosphere observations as well as the modeling of many photochemical processes requires a detailed knowledge of the EUV spectrum of  $N_2$ . Line positions, line oscillator strengths and radiative branching ratios are some of the database required to understanding the EUV photoabsorption spectrum of  $N_2$  (Stark et al. 2000, 2005a).

Regarding to the  $c_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(0-7)$  bands, there are numerous high resolution studies of the emission spectra where these bands have been observed (Roncin et al. 1987, 1998, Ajello et al. 1989, 1998, Heays et al. 2014). Other reported studies on the  $c_4^1\Sigma_u^+(4)$  Rydberg state include measurements of linewidth of some individual rotational levels (Helm et al. 1993). Predissociation yields for several rotational levels of the  $c_4^1\Sigma_u^+(v'=4)$  state, which follow a strong rotational dependence, have been measured by Walter et al. 1994, using a fast beam technique, and by Ajello et al. (1998), from an analysis of the high-resolution optically thin emission spectrum of the  $c_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(3)$  band by electron impact excitation at 100 eV. Ajello et al. (1998) have also estimated impact emission cross sections for the  $c_4^1\Sigma_u^+(v'=4)$  level. The rotational energies of the  $c_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(0-7)$  bands are well known (Roncin et al. 1998). However, the rotational structure of the spectrum corresponding to the  $c_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(0-7)$  bands is poorly understood, even though these bands are observed in emissions from Mars and in the atmospheres of Earth and Titan, as we have mentioned above. So, for the  $v'=4$  progression of the  $c_4^1\Sigma_u^+(v')$ - $X^1\Sigma_g^+(v')$  system, only have been reported, as far as we know, the absorption oscillator strengths for rotational lines of the  $c_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(0)$  band measured by Heays et al. (2009).

Recently, we have carried out a theoretical study of the dipole-allowed photoabsorption spectrum of molecular nitrogen, which covered the  $c_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(0-7)$  bands of  $N_2$  (Lavin & Velasco, 2016). We supplied, for the first time, transition intensities that have vibrational resolution in the form of absorption oscillator strengths for bands other than the  $c_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(0)$ . In our calculations we took into account the electronic interactions between the excited Rydberg  $c_4^1\Sigma_u^+$  state and the valence states of  $^1\Sigma_u^+$  symmetry. In particular, we showed that the Rydberg  $c_4^1\Sigma_u^+(4)$  level is strongly mixed with the valence  $b^1\Sigma_u^+(13)$  level, according to what had already been predicted (Lavin & Velasco, 2016).

The rotational structure of bands where the  $c_4^{-1}\Sigma_u^+(4)$  Rydberg state is involved will also be affected by these interactions. The present work has been raised as an extension of this previous study with the addition of rotational resolution. The molecular quantum defect orbital (MQDO) method, which have been previously used for dealing with rovibronic transitions of Carroll-Yoshino band systems of  $N_2$  (Lavín & Velasco, 2011, Lavín et al. 2010) has been employed to calculate electronic transition moment for Rydberg transitions. The homogeneous and heterogenous interactions between the  $c_4^{-1}\Sigma_u^+(4)$ ,  $c_3^1\Pi_u^+(4)$ , and  $b^1\Sigma_u^+(13)$  levels have been taken into account in the present calculations through an interaction matrix. Oscillator strengths (or f-values) for rotational lines in the P and R branches have been calculated. The studied bands show anomalous P and R branch intensity patterns. In this work, we have also estimate the rotational dependence of the emission branching ratios from the  $c_4^{-1}\Sigma_u^+(4)$  state to  $X^1\Sigma_g^+(1-7)$  states and the lifetimes of rotational levels of the  $c_4^{-1}\Sigma_u^+(4)$  state.

## 2. METHOD OF CALCULATION

The MQDO approach formulated to deal with molecular Rydberg transitions has been described in detail elsewhere (Martín et al. 1996). In this method the radial wavefunctions are the analytical solutions of a one-electron Schrödinger equation that contains an effective potential of the following form:

$$V(r) = \frac{(c-\delta)(2l+c-\delta+1)}{2r^2} - \frac{1}{r} \quad (1)$$

where  $\delta$  is the quantum defect that is related to the energy eigenvalue through the well-known Rydberg formula and  $c$  is an integer within a narrow range of values that ensures the normalizability of the molecular orbitals and their right nodal pattern. The angular part of the molecular Rydberg wave functions is a symmetry-adapted linear combination of spherical harmonics. In this way, the transition integrals happen to be analytical expressions. This feature of the MQDO formalism offers, in our view, an important computational advantage compared to *ab initio* methods.

For a diatomic molecule the dimensionless absorption oscillator strength can be defined as follows:

$$f_{v'J',v''J''} = \frac{8\pi^2 m c a_0^2}{3h} \nu_{v'J',v''J''} \frac{S_{J'J''}}{2J''+1}, \quad (2)$$

where the line frequency,  $\nu_{v'J',v''J''}$  is introduced in  $\text{cm}^{-1}$  and  $S_{J'J''}$  is the rotational line strength, expressed in atomic units.

The Einstein emission coefficient,  $A_{v'J',v''J''}$  (in  $\text{s}^{-1}$ ), for a rovibronic transition is given by (Morton & Noreau 1994)

$$A_{v'J',v''J''} = \frac{64\pi^4}{4\pi\epsilon_0 3h} \frac{1}{\lambda_{v'J',v''J''}^3} \frac{S_{J'J''}}{2J'+1} \quad (3)$$

where  $\lambda_{v'J',v''J''}$  is the wavelength of the radiation.

If the Born-Oppenheimer approximation is taken into account together with the fact that the nuclear factor of the wavefunction can be closely approximated by the product of vibrational and rotational wave functions, the rotational line strength can be written as follows (Whiting & Nicholls, 1974):

$$S_{J'J''} = q_{v'v''} R_e^2 \mathfrak{S}_{J'J''} \quad , \quad (4)$$

where  $q_{v'v''}$  is the Franck-Condon (FC) factor,  $R_e$  is the electronic transition moment expressed in atomic units and  $\mathfrak{S}_{J'J''}$  is the Hönl-London factor which accounts for the rotational dependence of the line rotational intensity within an electronic-vibrational band.

If rotational perturbation is present, equation 4 is no longer appropriate. As we have mentioned above, the Rydberg  $c_4^1\Sigma_u^+(4)$  state is mainly perturbed by the valence  $b^1\Sigma_u^+(13)$  state. Thus, to adequately model the intensity distribution of the rovibronic transitions studied in the present work, the interactions between the rotational excited states will need to be considered. To this aim, each perturbed electronic state of a rovibrational level turns out to be an appropriate linear combination of diabatic unperturbed basis states (Walter et al. 2000). In this way, the line strength acquires the following expression:

$$S_{J'J''} = \left| \sum_k C_k \langle v'_k | v'' \rangle R_e^k (\mathfrak{S}_{J'J''})^{1/2} \right|^2 \quad (5)$$

where  $C_k$ 's are the coefficients of the  $k$ th bases states,  $\langle v'_k | v'' \rangle$  is the vibrational overlap integral and  $R_e^k$  is the electronic moment for the transition from the electronic lower state to the upper  $k$ th diabatic state.

The eigenvector components,  $C_k$ , have been determined by diagonalization of an interaction matrix for each  $J$  value, where the diagonal elements are the unperturbed

rotational energies of the states, and the off-diagonal elements are the interaction parameters. The overlapping integrals had been calculated with the Rydberg Klein Rees (RKR) approach. The Hönl London factors have been obtained from the equations reported by Kovacks (1969).

### 3. RESULTS AND DISCUSSION

The  $c_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(0-7)$  absorption bands are originated by transitions from the  $v''=0-7$  vibrational levels of the ground state  $X^1\Sigma_g^+$  to the vibrational level  $v=4$  of the excited state  $c_4^1\Sigma_u^+$ , which happens to be the lowest member of the  $n\rho\sigma$  Rydberg series (with  $n=3$ ) that converges into the ground state of the cationic core  $N_2^+$ . It is well known that the  $c_4^1\Sigma_u^+$  state is strongest mixing with the  $b^1\Sigma_u^+$  valence state (Yoshino et al. 1975, 1979, Stahel et al. 1983). In a previous work (Lavín & Velasco 2016), we have made a quantitative analysis of the homogeneous Rydberg-valence interaction between states of  $^1\Sigma_u^+$  symmetry of  $N_2$ , through an interaction matrix that contains vibrational coupling. According to our calculations, a substantial mixing of the Rydberg  $c_4^1\Sigma_u^+(4)$  and valence  $b^1\Sigma_u^+(13)$  states occurs. In particular, we found that the electronic character of the  $c_4^1\Sigma_u^+(4)$  state is about 72% of  $c_4^1\Sigma_u^+(4)$ , 20% of  $b^1\Sigma_u^+(13)$ , 2% of  $b^1\Sigma_u^+(14)$ , 1% of  $b^1\Sigma_u^+(15)$ , and 1% of  $c_5^1\Sigma_u^+(1)$ . An analysis, including homogeneous and heterogeneous interactions between Rydberg and valence states performed by Helm et al. (1993) showed that the rotational levels of  $c_4^1\Sigma_u^+(4)$  are strongly mixed with the  $b^1\Sigma_u^+$  valence state, predominantly  $b^1\Sigma_u^+(13)$ , with a small contribution from the  $c_3^1\Pi_u$  Rydberg state, mainly  $c_3^1\Pi_u(4)$ . The heterogeneous interaction only involves the  $c_3^1\Pi_u^+$  levels of the  $c_3^1\Pi_u(4)$  state. So, in order to calculate oscillator strengths, we have taking into account the coupling between  $c_4^1\Sigma_u^+(4)$ ,  $c_3^1\Pi_u^+(4)$ , and  $b^1\Sigma_u^+(13)$  states.

The eigenvector components, for the three interacting diabatic states are obtained by diagonalizing of the  $3\times 3$  symmetric Hamiltonian matrix for each  $J$  value. Diagonal elements are the unperturbed rotational energies of the three states involved in the perturbation. To estimate the unperturbed energies, we have followed the procedure described by Yoshino et al. (1975). To this end, we have used the experimental rovibronic energies reported by Roncin et al. (1998), Stark et al. (2005b), and Helm et al. (1993). The off-diagonal elements represent the homogeneous coupling between the  $^1\Sigma_u^+$  levels and the

heterogeneous  ${}^1\Sigma_u^+ - {}^1\Pi_u^+$  interaction. The homogeneous rotational coupling parameter is presently determined by using the expression given by Kovacs (p. 207) for singlet states. From the obtained value,  $57.4\text{ cm}^{-1}$ , the estimated value of the electronic interaction parameter is  $1100\text{ cm}^{-1}$ , which is between the values  $900$  and  $1200\text{ cm}^{-1}$  reported by Stahel et al. (1983) and Dressler (1969), respectively. The heterogeneous coupling parameters, which are dependent of the rotational quantum number, are obtained by a fit of eigenvalues of the  $3\times 3$  Hamiltonian matrix to the experimental term values for the rotational levels of  $c_4'{}^1\Sigma_u^+(4)$ ,  $b'{}^1\Sigma_u^+(13)$  and  $c_3'{}^1\Pi_u^+(4)$  states. In order to check the accuracy of the deperturbation scheme used, experimentally determined term values (Roncin et al. 1998; Helm et al. 1993; Stark et al. 2005b) for the rotational levels of  $c_4'{}^1\Sigma_u^+(4)$ ,  $b'{}^1\Sigma_u^+(13)$  and  $c_3'{}^1\Pi_u^+(4)$  states have been compared with the calculated ones. At high  $J$  values, measured term values from different experiments can differ by as much as  $51\text{ cm}^{-1}$  for the  $J=17$  and  $19$ , and even  $79\text{ cm}^{-1}$  for the  $J=18$  rotational levels of  $c_4'{}^1\Sigma_u^+(4)$  state. So, in the comparison with the experiment data, we have included term values for the  $c_4'{}^1\Sigma_u^+(4)$ ,  $c'{}^1\Pi_u^+(4)$ , and  $b'{}^1\Sigma_u^+(13)$  states up to  $J = 16$ ,  $J = 8$  and  $J = 8$ , respectively, for which the discrepancies from different experiments is less than  $1\text{ cm}^{-1}$ . The mean absolute deviation was found to be  $1.5\text{ cm}^{-1}$ .

The eigenvector components for the  $c_4'{}^1\Sigma_u^+(4)$  state are listed in Table 1. Our calculations reveal that the Rydberg valence mixing is strongly  $J$  rotational level dependent and that the percentage of  $b'{}^1\Sigma_u^+(13)$  character in the  $c_4'{}^1\Sigma_u^+(4)$  state increases with  $J$ . So, the named  $c_4'{}^1\Sigma_u^+(4)$  state is predominantly of  $c_4'$  electronic character at low values of  $J$  but it becomes mainly of  $b'$  character for high  $J$  according to previous predictions (Walter et al. 2000).

In tables 2-5 line oscillator strengths, calculated with perturbed transition moments, corresponding to each of the  $c_4'{}^1\Sigma_u^+(4) - X'{}^1\Sigma_g^+(0-7)$  bands of  $N_2$  are collected. Except for the  $c_4'{}^1\Sigma_u^+(4) - X'{}^1\Sigma_g^+(0)$  band, no comparative data for these rovibronic transitions are available in the literature, as far as we known. In order to analyse the mixing effects, the oscillator strengths determined with the unperturbed transition moments are also included in the tables. The  $c_4'{}^1\Sigma_u^+ - X'{}^1\Sigma_g^+$  and  $c_3'{}^1\Pi_u^+ - X'{}^1\Sigma_g^+$  transition electronic moments required to calculate the oscillator strengths has been obtained with the MQDO method. The MQDO method required as an input the values of the ionization energy of  $N_2$  and the electronic energy of the  $c_4'{}^1\Sigma_u^+$  and  $c_3'{}^1\Pi_u^+$  states. In this work, we have used the data given by Huber

& Jungen (1990). The rotational line positions were taken from the experimental rotational energies reported by Edwards et al. (1993) for the ground state and by Roncin et al. (1998) for the  $c_4^1\Sigma_u^+$  and  $c_3^1\Pi_u^+$ -states. For the  $b^1\Sigma_u^+ - X^1\Sigma_g^+$  transition we have used the electronic moment given by Spelsberg & Meyer (2001).

If the perturbation is not considered, the  $c_4^1\Sigma_u^+(4) - X^1\Sigma_g^+(5)$  band should be the strongest band in the  $v'=4$  progression, because this transition has the highest Franck-Condon factor (Lavin & Velasco 2016). However, when the interaction  $c_4^1\Sigma_u^+(4) - b^1\Sigma_u^+(13) - c_3^1\Pi_u^+(4)$  is included in the model, the  $c_4^1\Sigma_u^+(4) - X^1\Sigma_g^+(3)$  is the most intense band in agreement with emission measurements from the  $v'=4$  level reported by Ajello et al. (1998). As a consequence of the Rydberg-valence interaction, perturbed f-values for both branches of the  $c_4^1\Sigma_u^+(4) - X^1\Sigma_g^+(5)$  are lower than the corresponding unperturbed ones, particularly for high values of J. This is due to the vibrational overlap between  $X^1\Sigma_g^+(5)$  and  $b^1\Sigma_u^+(13)$  state (-0.016) is much smaller than for the  $c_4^1\Sigma_u^+(4)$  state (-0.575) and, therefore, the loss of  $c_4^1\Sigma_u^+$  character in the interaction with  $b^1\Sigma_u^+(13)$  with increasing rotational level results in a weakening of the intensity of the lines. So, our calculations predict the lines of the  $c_4^1\Sigma_u^+(4) - X^1\Sigma_g^+(3)$  band to be the most intense, followed by those of the  $c_4^1\Sigma_u^+(4) - X^1\Sigma_g^+(5)$  band. Stevens et al. (2011) analyzed the Titan's airglow EUV spectra obtained with UVIS on Cassini, and found the blended (3,2)+(4,3) and (3,4)+(4,5) bands to be the most prominent bands of  $c_4^1\Sigma_u^+(3,4,6) - X^1\Sigma_g^+(v')$  progressions. This result is consistent with the present calculations concerning the  $v'=4$  progression.

The unperturbed oscillator strengths for rotational lines of the  $c_4^1\Sigma_u^+(4) - X^1\Sigma_g^+(0)$  band are extremely weak due to its Franck-Condon factor is very low,  $1.2 \times 10^{-5}$ . However, with the perturbation, lines of both R and P branches have measurable intensities owing they borrow their intensities mainly from the  $b^1\Sigma_u^+(13) - X^1\Sigma_g^+(0)$  band. Indeed, the  $b^1\Sigma_u^+(13) - X^1\Sigma_g^+(0)$  contribution to the rovibronic transition moment completely dominates the line f-values for this band. As already mentioned, the only data on line oscillator strengths found in the literature for the  $v'=4$  progression are those obtained by Heays et al. (2009) from photoabsorption measurements for the  $c_4^1\Sigma_u^+(4) - X^1\Sigma_g^+(0)$  band with uncertainty range from 10% to 20%. They are included in Table 2 for comparative purposes. Our results calculated with mixed transition moments are in a global good agreement with high resolution measurements. For R- and P-branches with  $J' \geq 7$  (25 lines) the differences between our results and the experimental data are, on average, of about 22%. It should be



notice that the usual differences between high resolution photoabsorption measurements and theoretical calculations are of  $\approx 20\%$  or  $\approx 25\%$  (Heays et al. 2009). However, at low-J in the P branch (5 lines), present f-values are, on average, of about 54% lower than measurements. To assess the reliability of the electronic transition moments, overlap integrals, and eigenvector components obtained in this work, we have also calculated the oscillator strength for the  $c_4^1\Sigma_u^+(4)-X^1\Sigma_g^+(0)$  band. From the calculated line oscillator strengths, we have derived integrated absorption cross sections for the individual rotational lines of the  $c_4^1\Sigma_u^+(4)-X^1\Sigma_g^+(0)$  band through the expression reported by Nicholls (1969). By adding up the integrated absorption cross section contribution for all the rotational lines we have estimated the band oscillator strength through the following equation (Morton & Noreau 1994):

$$f_{v'v''} = \frac{mc^2}{\pi e^2} \int \sigma(v) dv \quad (6)$$

The calculated oscillator strength for the  $c_4^1\Sigma_u^+(4)-X^1\Sigma_g^+(0)$  band results to be equal to 0.016, which conforms well with the high-resolution photoabsorption measurement of Heays et al. (2009),  $f_{v'v''} = 0.018 \pm 0.002$ ; therefore, the parameters used in our calculations seem to be correct.

Regarding the  $c_4^1\Sigma_u^+(4)-X^1\Sigma_g^+(1,7)$  bands, the unfavorable Franck-Condon factors between the  $c_4^1\Sigma_u^+(4)$  vibronic state and the  $X^1\Sigma_g^+(1)$ , and  $X^1\Sigma_g^+(7)$  states, 0.001 and 0.004, respectively, renders the unperturbed line f-values of such bands to be very weak. Nevertheless, when perturbation is taken into account for, the intensity of lines belonging to the mentioned bands increase notably owing to the better Franck-Condon overlap between the  $b^1\Sigma_u^+(13)$  state and the  $v''=1$  and  $v''=7$  vibrationals levels of the ground state, 0.041 and 0.018 respectively. In fact, for the rotational lines of  $c_4^1\Sigma_u^+(4)-X^1\Sigma_g^+(1)$  and  $c_4^1\Sigma_u^+(4)-X^1\Sigma_g^+(7)$  bands, the largest contribution to the rovibronic transition moment comes from the  $b^1\Sigma_u^+(13)$  state. Thereby, the observation of the  $c_4^1\Sigma_u^+(4)-X^1\Sigma_g^+(1)$  band in the terrestrial day airglow and in the atmosphere of Titan could be explained by coupling between the  $c_4^1\Sigma_u^+(4)$  and  $b^1\Sigma_u^+(13)$  states. The present calculations show that the intensities of the lines of the  $c_4^1\Sigma_u^+(4)-X^1\Sigma_g^+(1)$  and  $c_4^1\Sigma_u^+(4)-X^1\Sigma_g^+(7)$  bands are similar in magnitude and, thus, the latter should also be detected in the atmospheres of the Earth and Titan.

It can be noticed in tables 2-5 that the unperturbed line oscillator strengths for R and P branches of each band shown a regular pattern, based on Hönl-London factors, as the rotational quantum number increases. That is, a decreasing in the R branch and an increasing in the P branch, followed by flat behavior at high J values. Significant deviations of this behavior are exhibited by our results with mixed transition moments due to the J variability of the  $b^1\Sigma_u^+(13)$ - $X^1\Sigma_g^+(v')$  transition moment contribution to the line strength.

We have also calculated the emission branching ratios for the rotational lines of all the bands studied in the present work. To this end, we have employed the expression given by Ajello et al. (1998) for the emission branching ratio of a rotational line:

$$w = \frac{A(v'J',v''J'')}{A(v',J')} \quad (7)$$

where  $A(v'J',v''J'')$  is the line spontaneous transition probability, which is defined by equation 3.  $A(v',J')$  is the total transition probability of the upper level. When predissociation is considered,  $A(v',J')$  is the sum of the radiative contribution and that due to predissociation.

The emission yield, can be expressed as:

$$\eta_E(v'J') = \frac{A_{em}(v'J')}{A(v',J')} \quad (8)$$

where  $A_{em}(v'J')$  is the radiative contribution.

By combination of equation (7) and (6), the branching ratio adopts the form:

$$w = \frac{A(v'J',v''J'')\eta_E(v'J')}{A_{em}(v'J')} \quad (9)$$

In the calculation of both the line and total spontaneous emission transition probabilities, the perturbation between the  $c_4^1\Sigma_u^+(4)$ ,  $c_3^1\Pi_u^+(4)$ , and  $b^1\Sigma_u^+(13)$  states have been considered. The emission yield for each rovibronic level has been derived from the predissociation yields,  $\eta_P(v'J')$ , reported by Ajello et al. (1998) by means of the relation  $\eta_E(v'J') = 1 - \eta_P(v'J')$ . These authors have measured the predissociation yields for the  $J'=0-13$  rotational states of the  $c_4^1\Sigma_u^+(4)$  level and normalized to the  $J'=9$  predissociation yield given by Walter et al. (1994).

Dipole allowed radiative decay can occur energetically, not only to the rotational levels of the ground state  $X^1\Sigma_g^+(v'')$ , but also to those of the  $a'^1\Sigma_g^+$  state. Thus, in the calculations of  $A_{em}(v'J')$ , we have also included the line emission coefficients of the  $c_4'^1\Sigma_u^+(4)$ - $a'^1\Sigma_g^+(v'')$  bands. It should be mentioned that as Einstein emission coefficients are inversely proportional to the square of the transition wavelengths, the contribution of the rotational lines of the  $c_4'^1\Sigma_u^+(4)$ - $a'^1\Sigma_g^+(v'')$  system results to be significant smaller than those of the  $c_4'^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(v'')$  bands. The present emission branching ratios for the rotational levels  $J=0-13$  of the  $c_4'^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(0-7)$  bands are listed in Table 6. The experimental emission branching ratios measured by Ajello et al. (1998) for the  $c_4'^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(0-6)$  bands have also been included in the table. The emission branching ratios for each one of the bands studied here decrease as the rotational quantum number increases due to increasing amount of  $b^1\Sigma_u^+(13)$  character in the  $c_4'^1\Sigma_u^+(4)$  state. The  $b^1\Sigma_u^+$  state is affected by strong predissociation via continuum states of triplet symmetry (Helm et al. 1993). Our calculations reveals that, the emission from the  $c_4'^1\Sigma_u^+(4)$  Rydberg state is mainly due to the  $c_4'^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(3)$  band followed by the  $c_4'^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(5)$  and  $c_4'^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(4)$  bands in accord with measurements of Ajello et al. (1998).

Finally, we have calculated the lifetimes ( $\tau$ ) for individual rotational levels of the  $c_4'^1\Sigma_u^+(4)$  excited state by using the relation given by Walter et al. (1994):

$$1 - \eta_p = \tau A_{em}(v'J') \quad (10)$$

Lifetimes for  $J'= 0-13$  rotational levels together with those derived from absorption linewidth measurements (Helm et al. 1993) are given in Table 7. The present calculations and experiment are in the same order of magnitude and our results predict the correct trend of the lifetimes for the  $c_4'^1\Sigma_u^+(4)$  state as  $J$  increases. This agreement makes us feel confident in the correctness of our model formulation.

In summary, in the present study, oscillator strengths of rovibronic transitions belong to the  $c_4'^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(0-7)$  bands of molecular nitrogen are calculated using a model that includes the homogeneous and heterogeneous perturbations between the rotational levels of  $c_4'^1\Sigma_u^+(4)$ ,  $b^1\Sigma_u^+(13)$ , and  $c_3^1\Pi_u^+(4)$  states. The perturbation leads to changes in the electronic character of the rotational levels within the  $c_4'^1\Sigma_u^+(4)$  state, occasioning considerable deviations from normal rovibronic intensity distributions. In addition, we

have calculated lifetimes of rotational levels of the  $c_4^1\Sigma_u^+(4)$  state, which are consistent with experimental measurements of Helm et al. (1993). Line oscillator strengths, reported here for the first time as far as we know for the  $c_4^1\Sigma_u^+(4)$ -  $X^1\Sigma_g^+(1-7)$  bands, are of relevance in order to interpret the EUV spectra of Mars, Titan, and Earth atmospheres. On the other hand, very recently the (0,0) and (1,0) bands of the  $c_4^1\Sigma_u^+$ -  $X^1\Sigma_g^+$  system have been observed, in the EUV spectrum of Venusian airglow obtained by the HISAKI spacecraft (Nara et al. 2018). The bands studied in the present work are in the spectroscopic window covered by Extreme Ultraviolet Spectroscope for Exospheric Dynamics (EXCEED) aboard HISAKI and some of them show a similar intensity to the identified  $c_4^1\Sigma_u^+(0)$ -  $X^1\Sigma_g^+(1)$  band. Thus, we are hopeful the present results provide also a guide to the analysis of the spectroscopic data of Venusian airglow. Finally, from our study, we conclude that the electronic interactions play an important role in modifying the contribution to the emission from the  $c_4^1\Sigma_u^+(4)$  state, highlighting the need to include such considerations if to be truly simulation of the emission spectra.

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Table 1. Eigenvector components for the  $c_4^1\Sigma_u^+(4)$  rovibronic states of  $N_2$ .

$J'$	$C_k^2$	$C_k^2$	$C_k^2$
	$c_4^1\Sigma_u^+(4)$ character	$b^1\Sigma_u^+(13)$ character	$c_3^1\Pi_u^+(4)$ character
0	0.786	0.214	0.000
1	0.781	0.218	0.000
2	0.772	0.227	0.001
3	0.757	0.240	0.003
4	0.736	0.258	0.006
5	0.706	0.282	0.012
6	0.668	0.311	0.021
7	0.617	0.346	0.037
8	0.554	0.388	0.058
9	0.479	0.442	0.078
10	0.398	0.519	0.084
11	0.316	0.615	0.070
12	0.242	0.711	0.047
13	0.180	0.790	0.030
14	0.131	0.848	0.021
15	0.095	0.889	0.016
16	0.066	0.919	0.016
17	0.040	0.945	0.016
18	0.032	0.951	0.017
19	0.032	0.965	0.003
20	0.027	0.972	0.001

Table 2. Absorption oscillator strengths for the  $R$  and  $P$  branches of the  $c'_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(v''=0,1)$  bands of  $N_2$ .

$J''$	$c'_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(0)$						$c'_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(1)$			
	$R(J'')$ <sup>a</sup>	$R(J'')$ <sup>b</sup>	$R(J'')$ <sup>c</sup>	$P(J'')$ <sup>a</sup>	$P(J'')$ <sup>b</sup>	$P(J'')$ <sup>c</sup>	$R(J'')$ <sup>a</sup>	$R(J'')$ <sup>b</sup>	$P(J'')$ <sup>a</sup>	$P(J'')$ <sup>b</sup>
0	1.8E-06	0.0076					1.5E-04	0.0051		
1	1.2E-06	0.0052		6.0E-07	0.0025		1.0E-04	0.0035	5.0E-05	0.0017
2	1.1E-06	0.0050		7.2E-07	0.0030	0.007	9.0E-05	0.0033	6.0E-05	0.0020
3	1.0E-06	0.0051		7.8E-07	0.0034	0.009	9.0E-05	0.0034	7.0E-05	0.0023
4	1.0E-06	0.0054		8.0E-07	0.0037	0.0078	8.0E-05	0.0035	7.0E-05	0.0025
5	9.9E-07	0.0059		8.2E-07	0.0041	0.0082	8.0E-05	0.0038	7.0E-05	0.0027
6	9.8E-07	0.0064		8.4E-07	0.0045	0.0084	8.0E-05	0.0041	7.0E-05	0.0029
7	9.7E-07	0.0071		8.4E-07	0.0050	0.0088	8.0E-05	0.0044	7.0E-05	0.0032
8	9.6E-07	0.0081	0.011	8.5E-07	0.0056	0.0091	8.0E-05	0.0049	7.0E-05	0.0035
9	9.5E-07	0.0094	0.012	8.6E-07	0.0063	0.011	8.0E-05	0.0055	7.0E-05	0.0039
10	9.5E-07	0.0110	0.012	8.6E-07	0.0073	0.01	8.0E-05	0.0063	7.0E-05	0.0044
11	9.4E-07	0.0127	0.014	8.7E-07	0.0085	0.01	8.0E-05	0.0071	7.0E-05	0.0050
12	9.4E-07	0.0140	0.013	8.7E-07	0.0101	0.012	8.0E-05	0.0077	7.0E-05	0.0058
13	9.4E-07	0.0149	0.013	8.7E-07	0.0117	0.012	8.0E-05	0.0080	7.0E-05	0.0065
14	9.4E-07	0.0156	0.013	8.7E-07	0.0130	0.013	8.0E-05	0.0083	7.0E-05	0.0071
15	9.3E-07	0.0161	0.014	8.8E-07	0.0139	0.013	8.0E-05	0.0085	7.0E-05	0.0075
16	9.3E-07	0.0165	0.014	8.8E-07	0.0146	0.013	8.0E-05	0.0086	7.0E-05	0.0078
17	9.3E-07	0.0165	0.014	8.8E-07	0.0151	0.011	8.0E-05	0.0086	7.0E-05	0.0079
18	9.3E-07	0.0167	0.011	8.8E-07	0.0155	0.014	8.0E-05	0.0086	7.0E-05	0.0081
19	9.3E-07	0.0169	0.012	8.8E-07	0.0156	0.011	8.0E-05	0.0087	7.0E-05	0.0081

<sup>a</sup>This work, with unperturbed transition moment.

<sup>b</sup>This work, with perturbed transition moment.

<sup>c</sup>Heays et al. (2009).



Table 3. Absorption oscillator strengths for the  $R$  and  $P$  branches of the  $c'_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(v''=2,3)$  bands of  $N_2$ .

$J''$	$c'_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(2)$				$c'_4^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(3)$			
	$R(J'')^a$	$R(J'')^b$	$P(J'')^a$	$P(J'')^b$	$R(J'')^a$	$R(J'')^b$	$P(J'')^a$	$P(J'')^b$
0	0.0041	0.0040			0.0367	0.0502		
1	0.0028	0.0027	0.0014	0.0013	0.0244	0.0341	0.0122	0.0162
2	0.0025	0.0024	0.0017	0.0016	0.0220	0.0313	0.0147	0.0198
3	0.0024	0.0023	0.0018	0.0017	0.0209	0.0305	0.0157	0.0215
4	0.0023	0.0022	0.0018	0.0018	0.0204	0.0304	0.0163	0.0228
5	0.0023	0.0022	0.0019	0.0018	0.0200	0.0306	0.0167	0.0238
6	0.0022	0.0021	0.0019	0.0018	0.0197	0.0310	0.0169	0.0247
7	0.0022	0.0020	0.0019	0.0018	0.0196	0.0313	0.0171	0.0256
8	0.0022	0.0019	0.0020	0.0018	0.0194	0.0309	0.0172	0.0264
9	0.0022	0.0017	0.0020	0.0018	0.0193	0.0296	0.0174	0.0270
10	0.0022	0.0014	0.0020	0.0017	0.0192	0.0271	0.0174	0.0270
11	0.0022	0.0012	0.0020	0.0015	0.0191	0.0240	0.0175	0.0261
12	0.0022	0.0009	0.0020	0.0013	0.0191	0.0210	0.0176	0.0242
13	0.0022	0.0008	0.0020	0.0011	0.0190	0.0185	0.0176	0.0217
14	0.0021	0.0006	0.0020	0.0009	0.0190	0.0165	0.0177	0.0192
15	0.0021	0.0005	0.0020	0.0007	0.0189	0.0149	0.0177	0.0170
16	0.0021	0.0004	0.0020	0.0006	0.0189	0.0133	0.0177	0.0152
17	0.0021	0.0004	0.0020	0.0005	0.0188	0.0128	0.0178	0.0139
18	0.0021	0.0003	0.0020	0.0004	0.0188	0.0114	0.0178	0.0124
19	0.0021	0.0003	0.0020	0.0003	0.0188	0.0105	0.0178	0.0120

<sup>a</sup>This work, with unperturbed transition moment.

<sup>b</sup>This work, with perturbed transition moment.

Table 4. Absorption oscillator strengths for the  $R$  and  $P$  branches of the  $c'_4{}^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(v''=4,5)$  bands of  $N_2$ .

$J''$	$c'_4{}^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(4)$				$c'_4{}^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(5)$			
	$R(J'')$ <sup>a</sup>	$R(J'')$ <sup>b</sup>	$P(J'')$ <sup>a</sup>	$P(J'')$ <sup>b</sup>	$R(J'')$ <sup>a</sup>	$R(J'')$ <sup>b</sup>	$P(J'')$ <sup>a</sup>	$P(J'')$ <sup>b</sup>
0	0.0424	0.0207			0.0439	0.0376		
1	0.0283	0.0139	0.0141	0.0066	0.0293	0.0254	0.0146	0.0121
2	0.0254	0.0125	0.0170	0.0080	0.0264	0.0232	0.0176	0.0147
3	0.0242	0.0118	0.0182	0.0087	0.0251	0.0223	0.0188	0.0160
4	0.0235	0.0113	0.0188	0.0090	0.0244	0.0219	0.0195	0.0167
5	0.0231	0.0109	0.0193	0.0091	0.0240	0.0216	0.0200	0.0173
6	0.0228	0.0104	0.0196	0.0090	0.0237	0.0215	0.0203	0.0176
7	0.0226	0.0097	0.0198	0.0089	0.0234	0.0211	0.0205	0.0179
8	0.0224	0.0085	0.0199	0.0086	0.0233	0.0199	0.0207	0.0181
9	0.0223	0.0064	0.0201	0.0081	0.0231	0.0176	0.0208	0.0179
10	0.0222	0.0039	0.0202	0.0071	0.0230	0.0142	0.0209	0.0171
11	0.0221	0.0018	0.0203	0.0054	0.0229	0.0108	0.0210	0.0153
12	0.0220	0.0006	0.0203	0.0033	0.0228	0.0079	0.0211	0.0125
13	0.0220	0.0001	0.0204	0.0015	0.0228	0.0058	0.0211	0.0096
14	0.0219	0.00001	0.0204	0.0005	0.0227	0.0044	0.0212	0.0071
15	0.0219	0.0001	0.0205	0.0001	0.0227	0.0034	0.0212	0.0053
16	0.0218	0.0004	0.0205	0.00001	0.0226	0.0025	0.0213	0.0040
17	0.0218	0.0005	0.0205	0.0001	0.0226	0.0022	0.0213	0.0031
18	0.0217	0.0010	0.0206	0.0004	0.0225	0.0016	0.0213	0.0023
19	0.0217	0.0014	0.0206	0.0005	0.0225	0.0012	0.0214	0.0021

<sup>a</sup>This work, with unperturbed transition moment.

<sup>b</sup>This work, with perturbed transition moment.

Table 5. Absorption oscillator strengths for the  $R$  and  $P$  branches of the  $c'_4{}^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(v''=6,7)$  bands of  $N_2$ .

$J''$	$c'_4{}^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(6)$				$c'_4{}^1\Sigma_u^+(4)$ - $X^1\Sigma_g^+(7)$			
	$R(J'')$ <sup>a</sup>	$R(J'')$ <sup>b</sup>	$P(J'')$ <sup>a</sup>	$P(J'')$ <sup>b</sup>	$R(J'')$ <sup>a</sup>	$R(J'')$ <sup>b</sup>	$P(J'')$ <sup>a</sup>	$P(J'')$ <sup>b</sup>
0	0.0076	0.0146			0.0005	0.0034		
1	0.0050	0.0099	0.0025	0.0047	0.0004	0.0023	0.0002	0.0011
2	0.0045	0.0092	0.0030	0.0058	0.0003	0.0022	0.0002	0.0013
3	0.0043	0.0090	0.0032	0.0063	0.0003	0.0022	0.0002	0.0015
4	0.0042	0.0091	0.0034	0.0067	0.0003	0.0023	0.0002	0.0016
5	0.0041	0.0093	0.0034	0.0071	0.0003	0.0025	0.0002	0.0017
6	0.0041	0.0096	0.0035	0.0074	0.0003	0.0027	0.0002	0.0019
7	0.0040	0.0098	0.0035	0.0078	0.0003	0.0029	0.0002	0.0021
8	0.0040	0.0100	0.0036	0.0082	0.0003	0.0032	0.0003	0.0023
9	0.0040	0.0099	0.0036	0.0085	0.0003	0.0035	0.0003	0.0026
10	0.0040	0.0096	0.0036	0.0087	0.0003	0.0037	0.0003	0.0028
11	0.0039	0.0091	0.0036	0.0088	0.0003	0.0038	0.0003	0.0031
12	0.0039	0.0085	0.0036	0.0086	0.0003	0.0038	0.0003	0.0033
13	0.0039	0.0079	0.0036	0.0083	0.0003	0.0038	0.0003	0.0034
14	0.0039	0.0074	0.0036	0.0078	0.0003	0.0038	0.0003	0.0035
15	0.0039	0.0070	0.0037	0.0073	0.0003	0.0038	0.0003	0.0035
16	0.0039	0.0065	0.0037	0.0069	0.0003	0.0037	0.0003	0.0035
17	0.0039	0.0064	0.0037	0.0065	0.0003	0.0037	0.0003	0.0035
18	0.0039	0.0060	0.0037	0.0061	0.0003	0.0036	0.0003	0.0035
19	0.0039	0.0057	0.0037	0.0060	0.0003	0.0035	0.0003	0.0035

<sup>a</sup>This work, with unperturbed transition moment.

<sup>b</sup>This work, with perturbed transition moment.

Table 6. Emission branching ratios ( $w$ ), as a function of  $J$ , for the  $c'4^1\Sigma_u^+(4)$ -  
 $X^1\Sigma_g^+(v''=0-7)$  bands of  $N_2$

$J'$	(4,0)	(4,1)	(4,2)	(4,3)	(4,4)	(4,5)	(4,6)	(4,7)
0	0.052	0.034	0.025	0.298	0.116	0.203	0.076	0.017
1	0.051	0.033	0.025	0.297	0.116	0.204	0.076	0.017
2	0.049	0.032	0.023	0.279	0.108	0.191	0.072	0.016
3	0.042	0.027	0.019	0.232	0.088	0.157	0.060	0.014
4	0.038	0.024	0.016	0.196	0.072	0.131	0.051	0.012
5	0.037	0.023	0.014	0.182	0.064	0.120	0.048	0.012
6	0.044	0.027	0.015	0.200	0.067	0.129	0.053	0.014
7	0.038	0.023	0.011	0.160	0.051	0.101	0.043	0.012
8	0.039	0.023	0.010	0.149	0.044	0.091	0.041	0.012
9	0.041	0.024	0.009	0.138	0.035	0.081	0.039	0.012
10	0.044	0.025	0.007	0.119	0.024	0.064	0.035	0.012
11	0.048	0.026	0.006	0.103	0.014	0.049	0.032	0.012
12	0.037	0.020	0.003	0.062	0.004	0.025	0.021	0.008
13	0.044	0.023	0.003	0.058	0.002	0.020	0.021	0.009
$w^a$	<i>0.17</i>	<i>0.083</i>	<i>0.01</i>	<i>0.33</i>	<i>0.14</i>	<i>0.23</i>	<i>0.039</i>	

<sup>a</sup>Emission branching ratios for the band (Ajello et al. 1998).

Table 7. Radiative lifetimes (in s) as a function of  $J$ , for the  $c'4^1\Sigma_u^+(4)$  state of  $N_2$

$J'$	$\tau^a$	$\tau^b$
0	8.20E-10	
1	8.01E-10	3.40E-10
2	7.38E-10	
3	6.02E-10	
4	4.98E-10	
5	4.51E-10	2.50E-10
6	4.83E-10	
7	3.77E-10	2.10E-10
8	3.45E-10	
9	3.21E-10	2.30E-10
10	2.88E-10	
11	2.70E-10	1.80E-10
12	1.81E-10	1.50E-10
13	1.95E-10	1.00E-10

<sup>a</sup>This work.

<sup>b</sup>Helm et al. (1993)