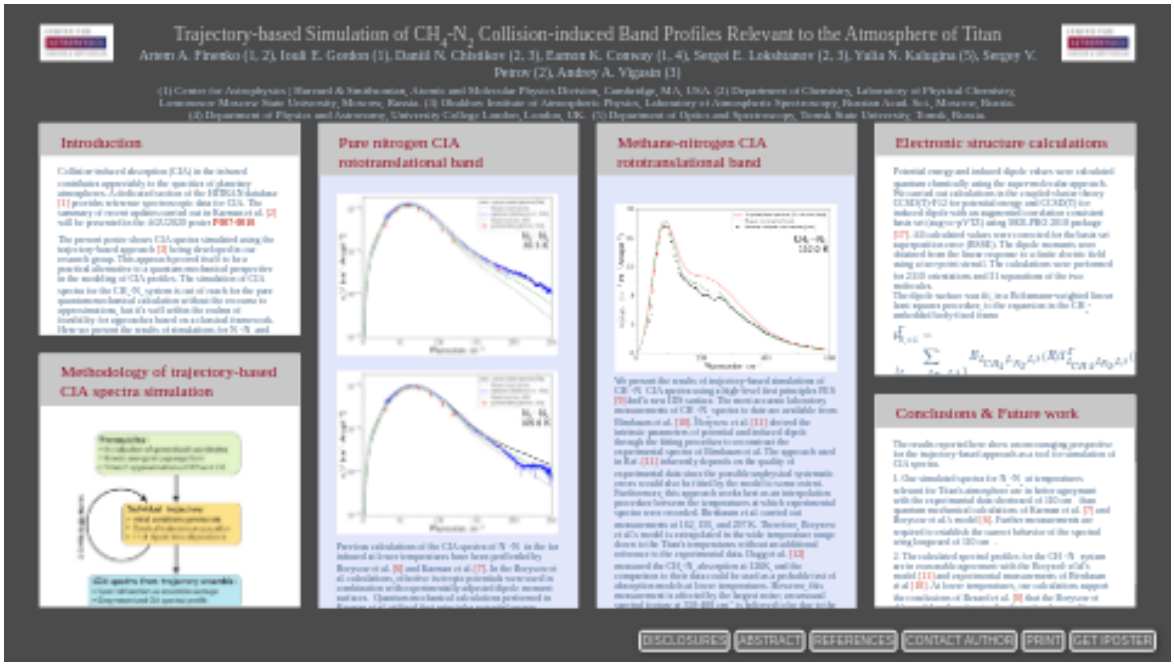
Trajectory-based Simulation of CH_4-N_2 Collision-induced Band Profiles Relevant to the Atmosphere of Titan



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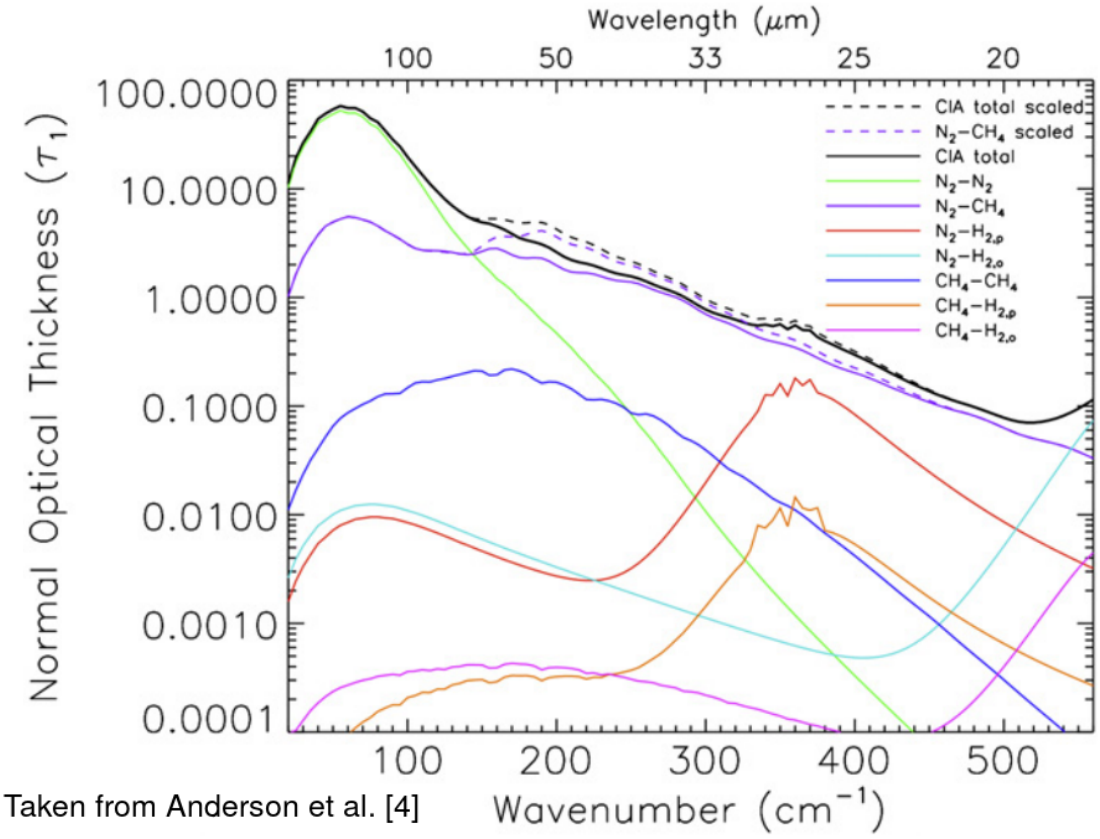
INTRODUCTION

Collision-induced absorption (CIA) in the infrared contributes appreciably to the opacities of planetary atmospheres. A dedicated section of the HITRAN database [1] provides reference spectroscopic data for CIA. The summary of recent updates carried out in Karman et al. [2] will be presented in the AGU2020 poster **P007-0010**.
(https://agu.confex.com/agu/fm20/meetingapp.cgi/Paper/694071)

The present poster shows CIA spectra simulated using the trajectory-based approach [3] being developed in our research group. This approach proved itself to be a practical alternative to a quantum mechanical perspective in the modeling of CIA profiles. The simulation of CIA spectra for the CH_4-N_2 system is out of reach for the pure quantum mechanical calculation without the recourse to approximations, but it's well within the realms of feasibility for approaches based on a classical framework. Here we present the results of simulations for N_2-N_2 and CH_4-N_2 applicable to the Titan's atmosphere.

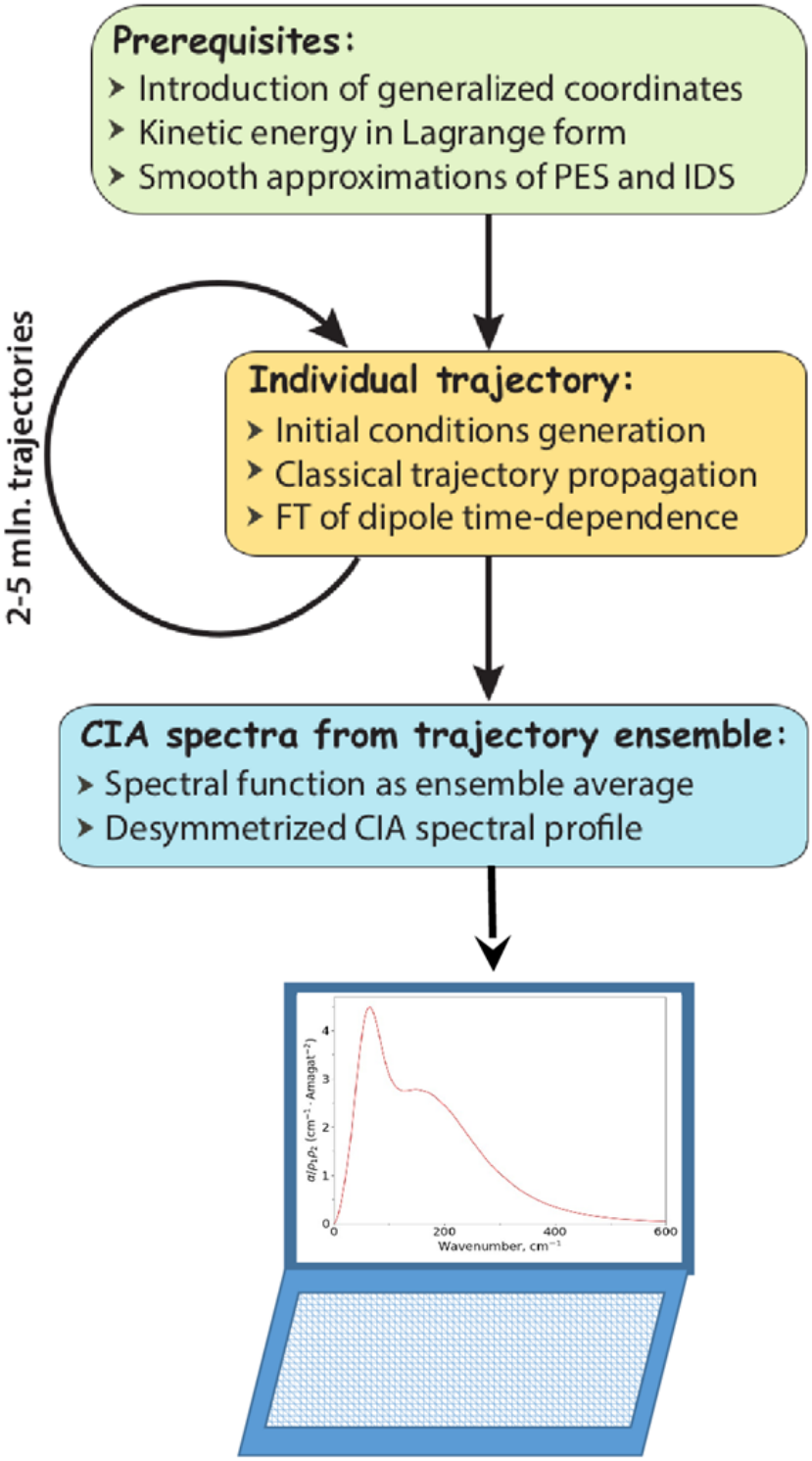
The following picture demonstrates normal optical thicknesses of Titan's atmosphere at 15°S due to different sources of CIA.



Taken from Anderson et al. [4]

Based on the analysis of Titan's opacity data, empirical corrections to the models of CIA absorption for N_2-N_2 and CH_4-N_2 were suggested. In the following, we are using the results of our simulations to evaluate these corrections.

METHODOLOGY OF TRAJECTORY-BASED CIA SPECTRA SIMULATION



Absorption coefficient normalized to the product of densities of constituent gases is known to be written as [5]

$$\frac{\alpha(\nu,T)}{\rho_1\rho_2} = \frac{(2\pi)^2 N_L^2}{3\hbar}\nu\left[1-\exp\left(-\frac{hc\nu}{k_{\mathrm{B}}T}\right)\right]VJ(\nu,T).$$

In the classical framework, the spectral function $J_{\mathrm{class}}(\nu,T)$ is given by the Fourier transform of the dipole moment autocorrelation function

$$J_{\text{class}}(\nu, T) = \frac{1}{2\pi} \int\limits_{-\infty}^{\infty} \langle \boldsymbol{d}(0) \cdot \boldsymbol{d}(t) \rangle e^{-2\pi i c \nu t} \mathrm{d}t,$$

where the angular brackets denote Boltzmann averaging over the corresponding phase space. In the case of short-lived free and quasibound states, the Wiener-Khintchine theorem can be applied to obtain an alternative integral representation for the corresponding spectral function [3]

$$J_{\text{class}}(\nu, T) = \frac{1}{2\pi Q} \int\limits_{-\infty}^{0} \frac{-p_R}{\mu} \mathrm{d}p_R \int \cdots \int_{H>0} \exp\left(-\frac{H}{k_{\text{B}} T}\right) \mathrm{d}\mathbf{q}^* \mathrm{d}\mathbf{p}^* \left| \int\limits_{-\infty}^{\infty} \mathbf{d}(t) e^{-2\pi i c \nu t} \mathrm{d}t \right|.$$

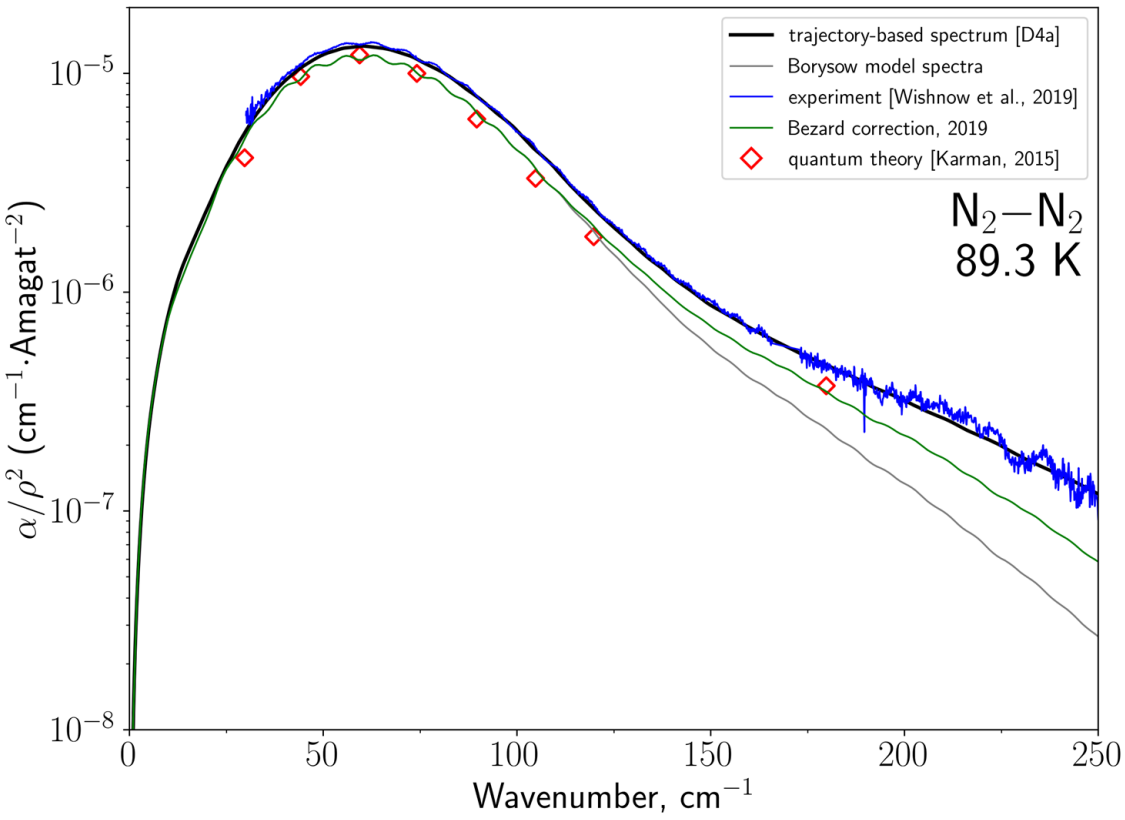
Here

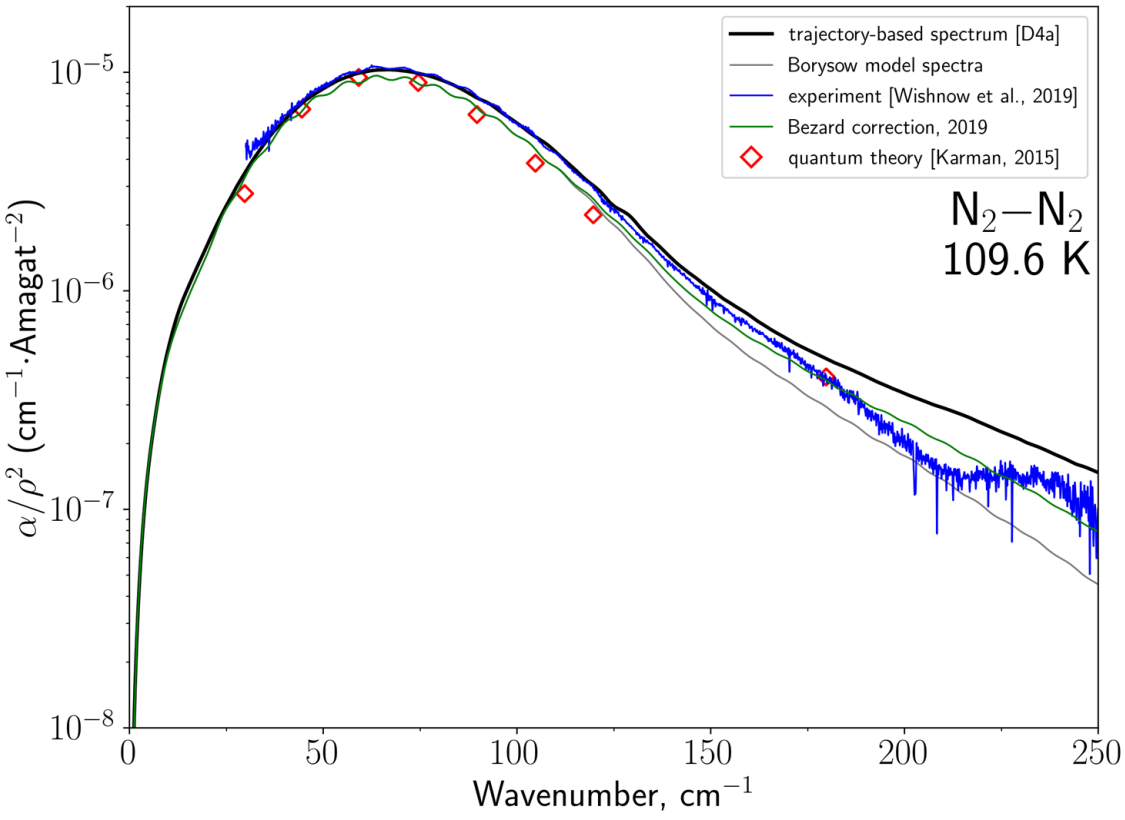
$$Q = \int \cdots \int \exp\left(-\tfrac{H}{k_{\text{B}} T}\right) \mathrm{d}\mathbf{q}\, \mathrm{d}\mathbf{p}$$

is the normalization factor, and $\mathrm{d}\mathbf{q}^*$ and $\mathrm{d}\mathbf{p}^*$ relate to the vectors of generalized coordinates and momenta obtained upon exclusion of the radial coordinate R and the conjugated momenta p_R from $\mathbf{q}$ and $\mathbf{p}$, respectively.

In the final steps of the calculation, the classical spectral function is corrected through the use of the desymmetrization procedure to account for quantum interaction with the EM field [5]. The profiles desymmetrized using two different procedures are referred to as D3 or D4a in the Figures (see [5] for more details).

PURE NITROGEN CIA ROTOTRANSLATIONAL BAND



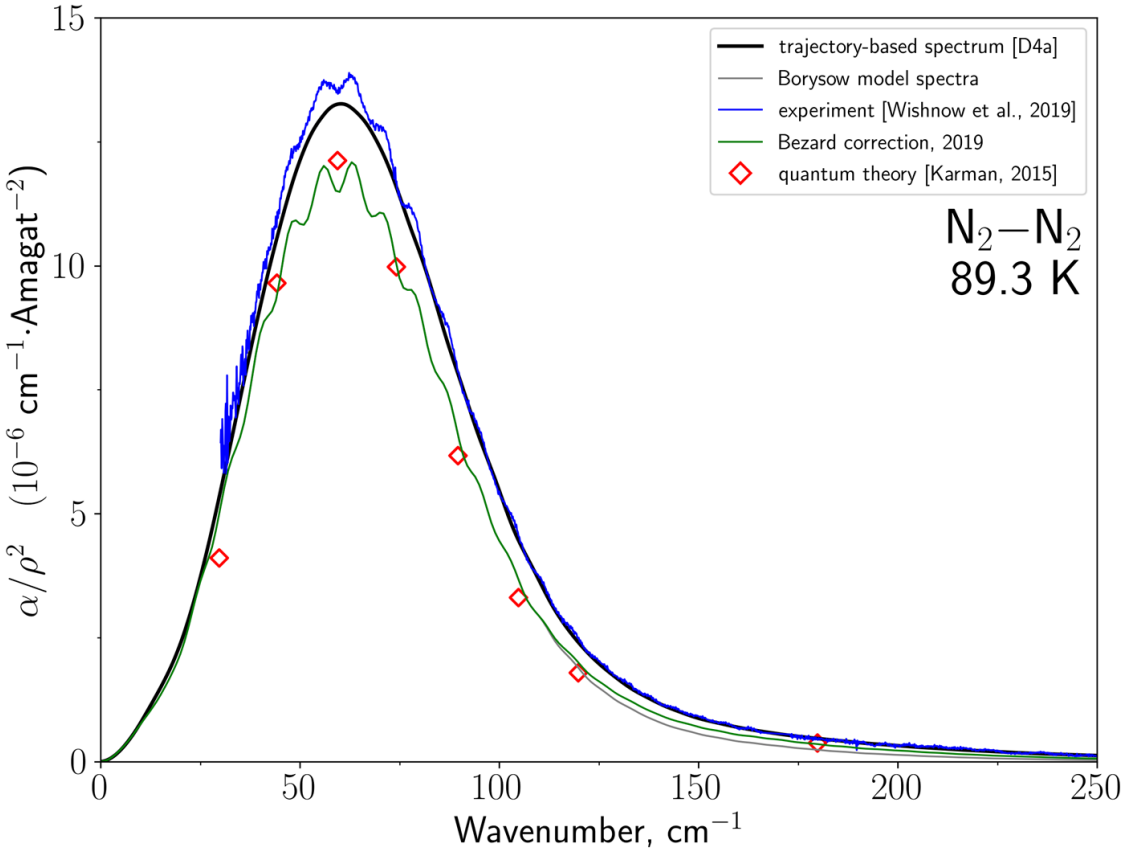


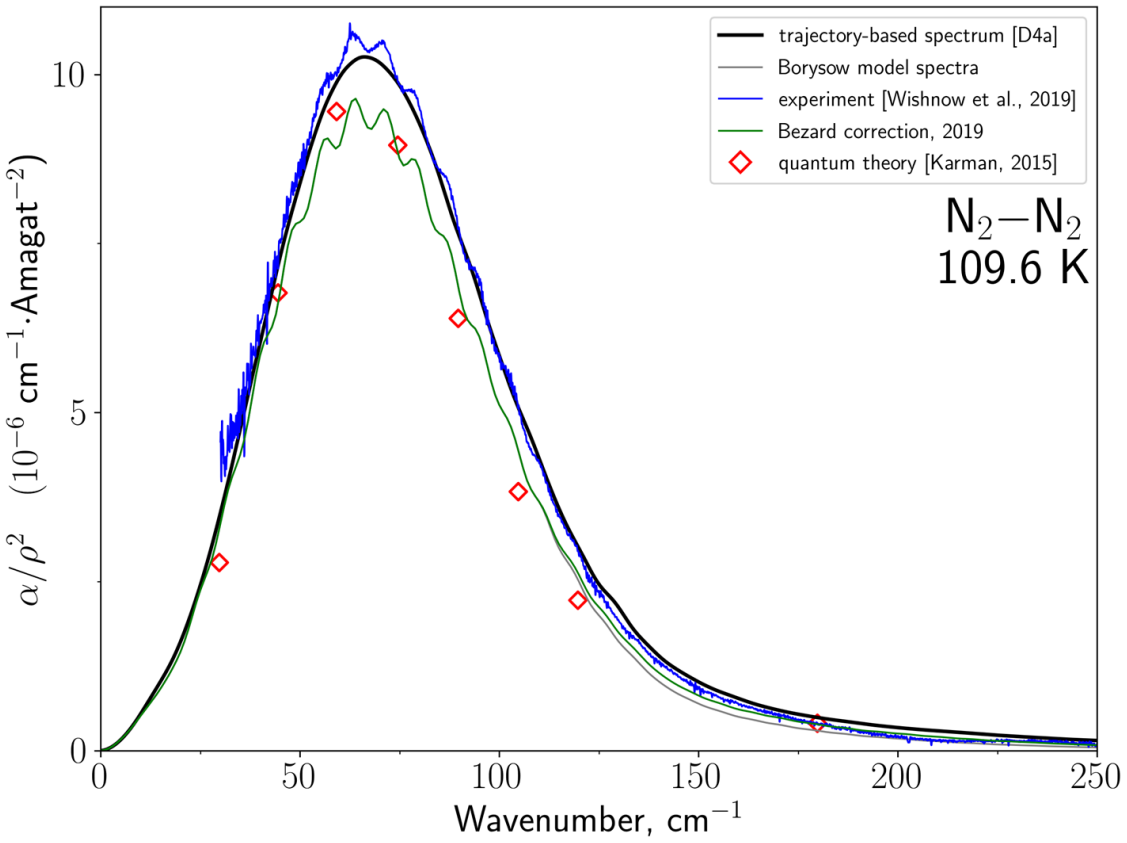
Previous calculations of the CIA spectra of N_2-N_2 in the far infrared at lower temperatures have been performed by Borysow et al. [6] (http://adsabs.harvard.edu/full/1986ApJ...311.1043B) and Karman et al. [7] (https://aip.scitation.org/doi/full/10.1063/1.4907917?casa_token=p6X_4jx-uykAAAAA%3AI_2oGNPMBxJZe3ZapkpQwILiJpjqluEAar8Ffb8BK0o07l7OoSlClQ0a1hskIfM5exiuqJI7RdU). In the

Borysow et al. calculations, effective isotropic potentials were used in combination with experimentally adjusted dipole moment surfaces. Quantum mechanical calculations performed in Karman et al. utilized first principles potential energy (PES) and induced dipole (IDS) surfaces. The time-independent close coupling equations for the collision system were considered in the coupled-states approximation. We present the simulated CIA spectra based on the semiclassical trajectory-based formalism [3] (https://aip.scitation.org/doi/full/10.1063/1.5125756?casa_token=WRT4AVSQRnYAAAAA%3AqEYWK1fhKfL1m_QMqWShvhI6yXSCnesuB7SRNO_15N8OjjDF_9noOiM8Ly6iJLa4C8cu1CMReP utilizing the ab initio PES and IDS surfaces of Karman et al. The dynamics of the collision system was considered in the classical framework without recourse to the approximations, and the spectra are modeled without the use of any adjustable parameters.

Based on the analysis of the spectra recorded between 50 and 650 cm^{-1} by the Composite Infrared Spectrometer (CIRS) aboard the Cassini spacecraft, Bezard et al. [8] (https://www.sciencedirect.com/science/article/pii/S0019103518307279?casa_token=5vaJNx3IKQ0AAAAA:hSkOJpKcir45frJQs6IDoGKsWl73jEmJqnxBNBHJkkW4GXBj3fw96YWTUNUUh0XeKNVayOtSKA) reported that Borysow et al.'s spectra underestimate the observed absorption between 110 and 250 cm^{-1}. They introduced a multiplicative corrective factor to the Borysow et al.'s data longward of 110 cm^{-1} to reproduce Karman et al. calculations at 180 cm^{-1}. Thus introduced an empirical increase in the N_2-N_2 CIA allowed them to significantly reduce the discrepancy between measured opacity in the troposphere and their model.

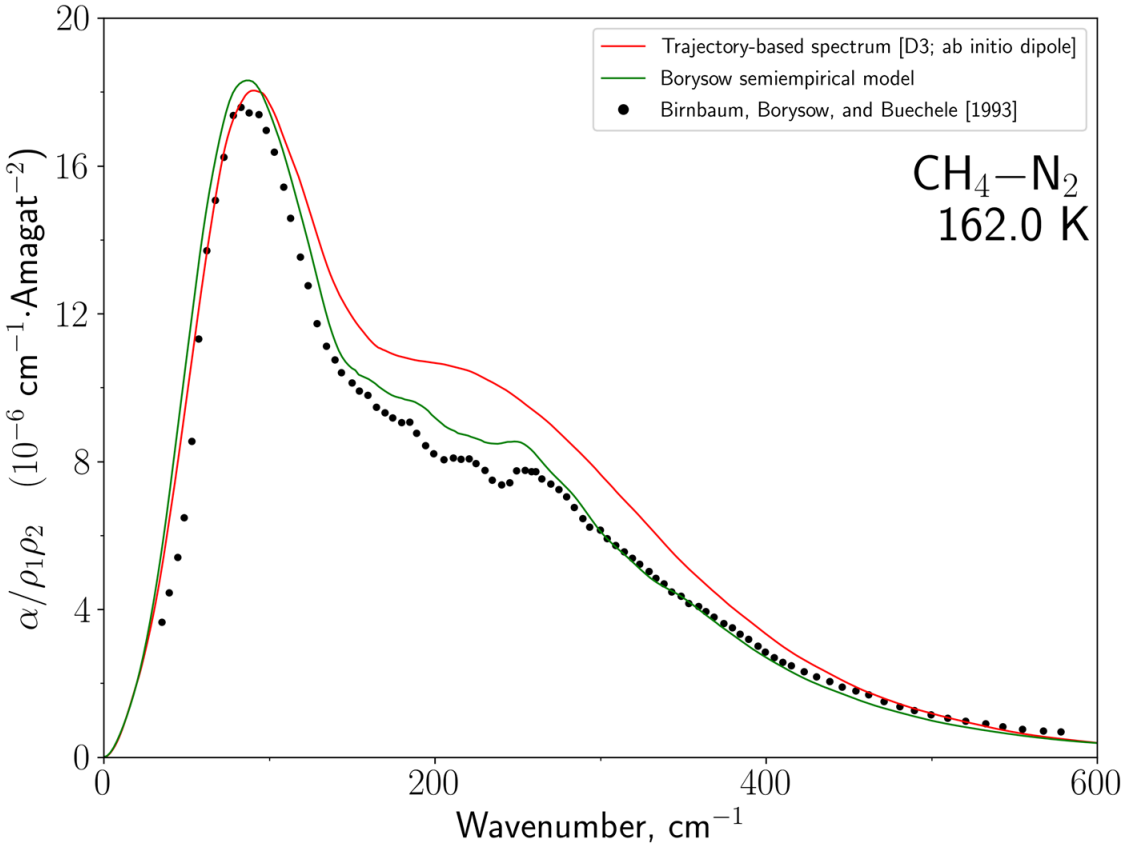
The Figures at the top contain the comparisons of the results of calculations with the measurements performed at the Jet Propulsion Laboratory by Wishnow et al. [2] (https://www.sciencedirect.com/science/article/pii/S0019103518306997?casa_token=s0eyC6Vb6fkAAAAA:TPqfN4JSN7axNJn0z9vBeW9_kls39tv8KaL9G9PrXd72haSQ3MdUJCvWpQsgVAa6Ue-ePSVqiQ). The conclusion of Bezard et al. that Borysow et al.'s model underestimates absorption longward of 110 cm-1 is supported by our calculations and experimental data. Nevertheless, current experimental results do not allow to determine whether the results of Karman et al. or trajectory-based spectra are more accurate in this spectral range.



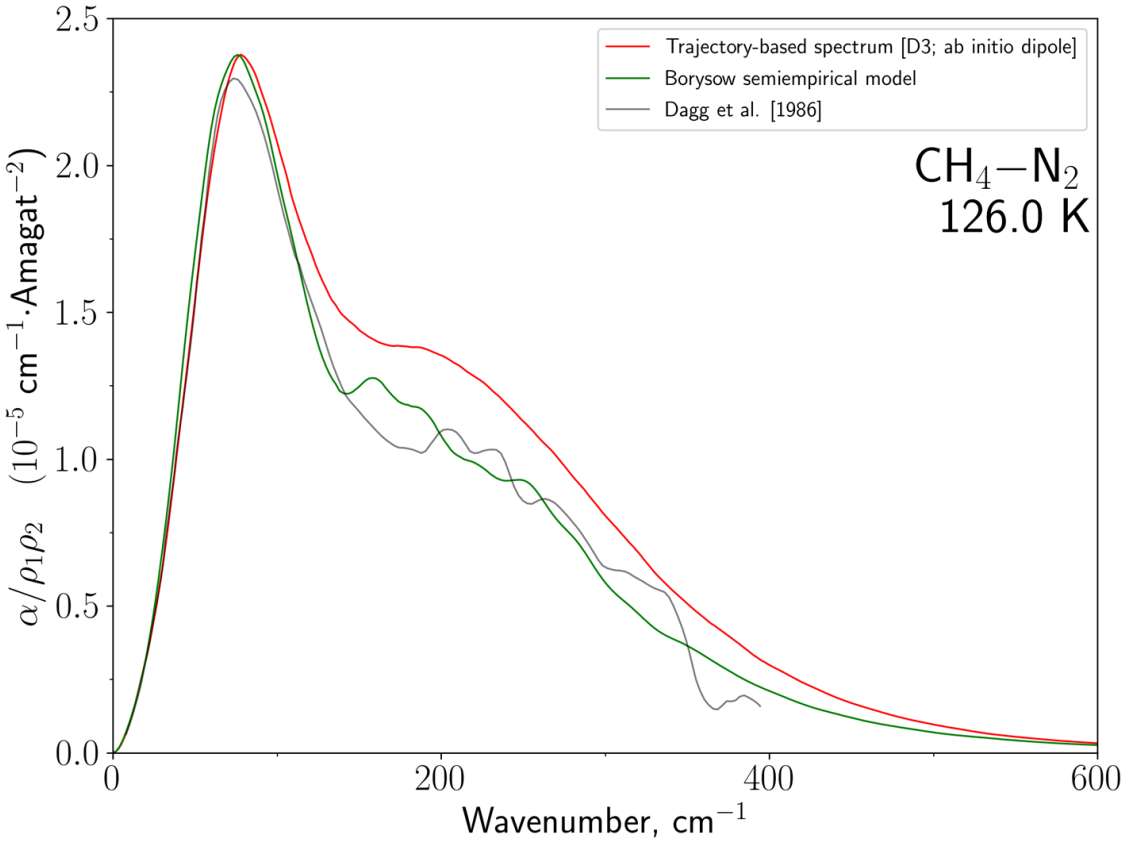


Note that trajectory-based results demonstrate better agreement with experimental data near the spectrum peak.

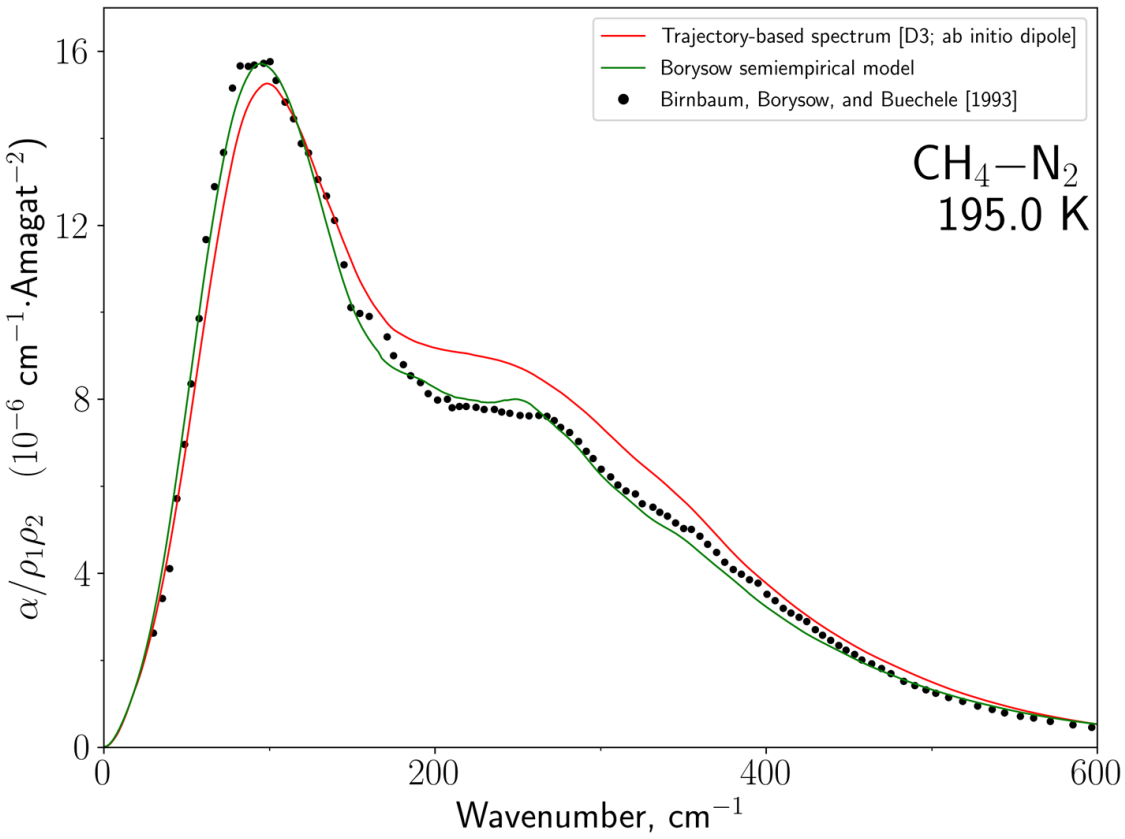
METHANE-NITROGEN CIA ROTOTRANSLATIONAL BAND



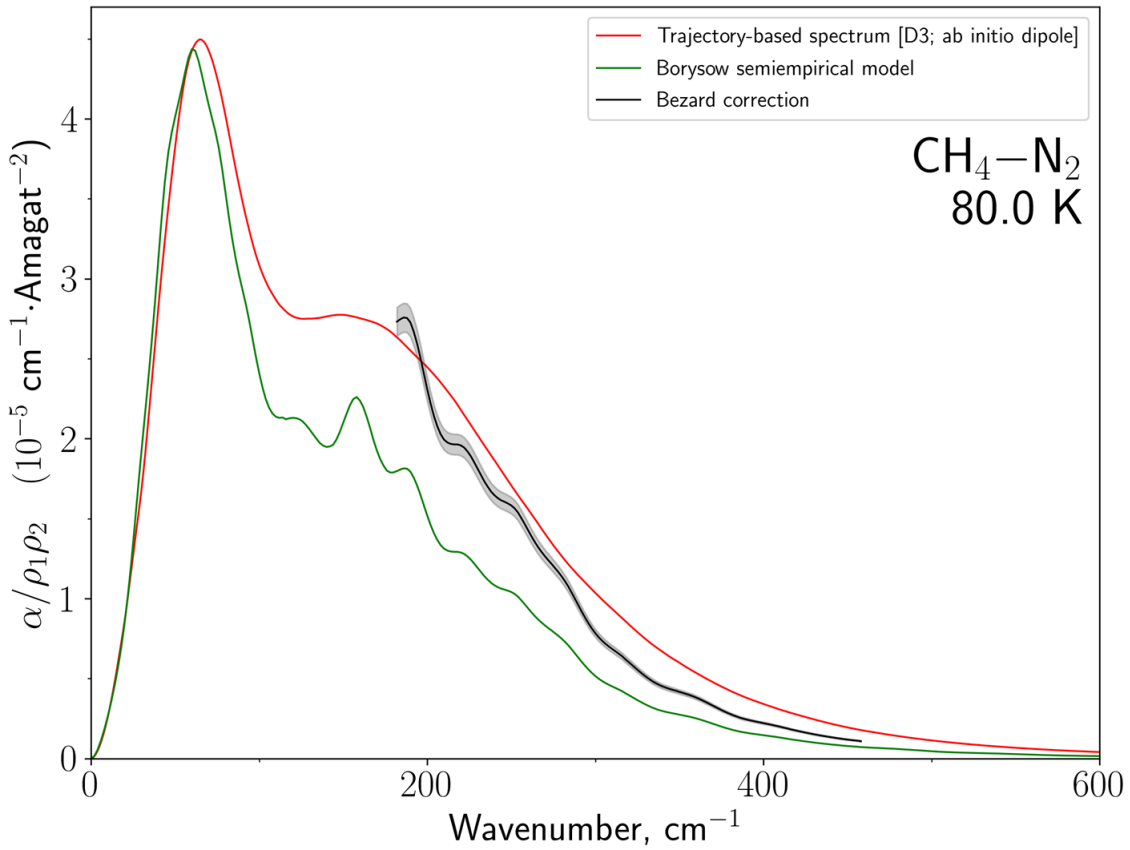
We present the results of trajectory-based simulations of CH_4-N_2 CIA spectra using a high-level first principles PES [9] and a new IDS surface. The most accurate laboratory measurements of CH_4-N_2 spectra to date are available from Birnbaum et al. [10]. Borysow et al. [11] derived the intrinsic parameters of potential and induced dipole through the fitting procedure to reconstruct the experimental spectra of Birnbaum et al. The approach used in Ref. [11] inherently depends on the quality of experimental data since the possible unphysical systematic errors would also be fitted by the model to some extent. Furthermore, this approach works best as an interpolation procedure between the temperatures at which experimental spectra were recorded. Birnbaum et al. carried out measurements at 162, 195, and 297 K. Therefore, Borysow et al.'s model is extrapolated in the wide temperature range down to the Titan's temperatures without an additional reference to the experimental data. Dagg et al. [12] measured the CH_4-N_2 absorption at 126K, and the comparison to their data could be used as a probable test of absorption models at lower temperatures. However, this measurement is affected by the largest noise; an unusual spectral feature at 350-400 cm^{-1} is believed to be due to the experimental noise.

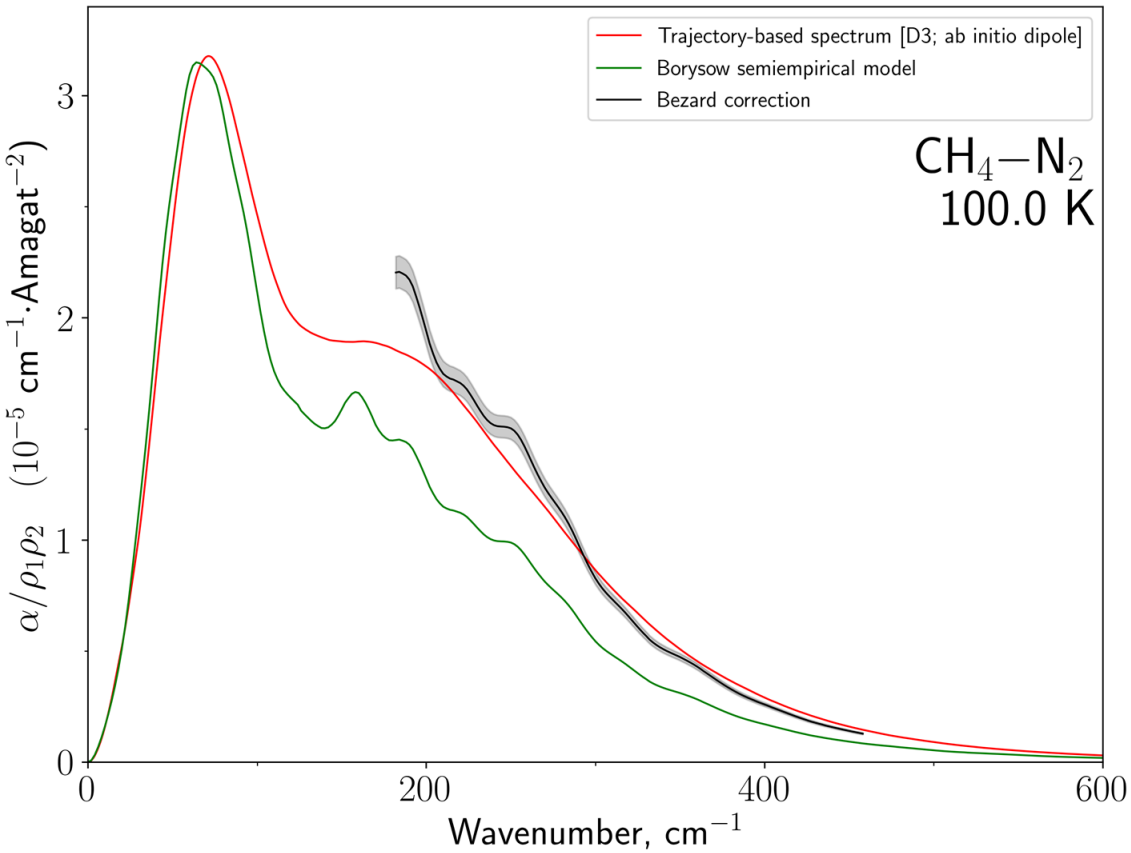


Results of trajectory-based simulations demonstrate reasonable agreement with experimental measurements at 162 and 195 K. An excess absorption compared to the experimental data is observed in the 200-400 cm^{-1} region.



The magnitude of the excess absorption in this spectral range compared to the Borysow model increases with the temperature decrease.





The CH_4-N_2 CIA absorption is known to dominate in the 150-450 cm^{-1} region of the Titan's tropospheric opacity. Several previous analyses [4, 13, 14] have concluded that the opacity could not be reproduced if Borysow et al.'s model [11] is used. In the papers by Courtin et al. [15] and Samuelson et al. [16], it was suggested that missing opacity could be attributed to a large supersaturation of methane in the troposphere. In the later studies by Tomasko et al. [13] and de Kok et al. [14], the supersaturation was not observed, and it was suggested that Borysow et al.'s CIA data is probably in error. Both studies derived

that a multiplicative factor of approximately 1.5 needed to be applied to obtain a satisfactory fit. Anderson et al. [4] proposed the wavenumber-dependent factor of the same magnitude. In the recent paper, Bezard et al. [8] estimated the value of multiplicative factor to be 1.52, with a typical uncertainty of 0.05. Also, Bezard et al. reported that the wavenumber-dependent correction of Anderson et al. produces too much absorption between 180 and 300 cm^{-1}, and its overall shape does not match the observations.

The results of trajectory-based simulations, by and large, support the findings of Bezard et al. Yet, it should be noted that the difference between trajectory-based results and Borysow et al.'s model is both wavenumber- and temperature-dependent.

ELECTRONIC STRUCTURE CALCULATIONS

Potential energy and induced dipole values were calculated quantum chemically using the super-molecular approach. We carried out calculations in the coupled-cluster theory CCSD(T)-F12 for potential energy and CCSD(T) for induced dipole with an augmented correlation consistent basis set (aug-cc-pVTZ) using MOLPRO 2010 package [17]. All calculated values were corrected for the basis set superposition error (BSSE). The dipole moments were obtained from the linear response to a finite electric field using a two-point stencil. The calculations were performed for 2310 orientations and 31 separations of the two molecules.

The dipole surface was fit, in a Boltzmann-weighted linear least squares procedure, to the expansion in the CH_4-embedded body-fixed frame

$$\mu^{\Gamma}_{0,\pm1} = \sum_{\left\{L_{CH_4},L_{N_2},L,\lambda\right\}} B_{L_{CH_4},L_{N_2},L,\lambda}(R) T^{\Gamma}_{L_{CH_4},L_{N_2},L,\lambda}(\zeta,\zeta_{N_2})$$

in symmetry-adapted rotational functions carrying the same representation Γ as dipole in the molecular symmetry group

$$T^{\Gamma}_{L_{CH_4},L_{N_2},L,\lambda}(\zeta,\zeta_{N_2}) = \sum_{\left\{K_{CH_4}\right\}} \mathcal{W}(L_{CH_4},L_{N_2},L,\lambda;K_{CH_4}) T_{L_{CH_4},L_{N_2},L,\lambda}(\zeta,\zeta_{N_2}),$$

where $\mathcal{W}$ are constant factors and the primitive basis functions $T_{L_{CH_4},L_{N_2},L,\lambda}(\zeta,\zeta_{N_2})$form the complete basis set in the respective space of rotational functions.

CONCLUSIONS & FUTURE WORK

The results reported here show an encouraging perspective for the trajectory-based approach as a tool for simulation of CIA spectra.

1. Our simulated spectra for N_2-N_2 at temperatures relevant for Titan's atmosphere are in better agreement with the experimental data shortward of 110 cm^{-1} than quantum mechanical calculations of Karman et al. [7] and Borysow et al.'s model [6]. Further measurements are required to establish the correct behavior of the spectral wing longward of 110 cm^{-1}.

2. The calculated spectral profiles for the CH_4-N_2 system are in reasonable agreement with the Borysow et al's model [11] and experimental measurements of Birnbaum et al [10]. At lower temperatures, our calculations support the conclusions of Bezard et al. [8] that the Borysow et al.'s model underestimates the absorption by roughly a factor of 1.5 in the spectral range between 180 and 460 cm^{-1}. Note that the ratio of our spectra to Borysow et al.'s model has a complicated temperature- and wavenumber-dependence and could not be approximated by a constant factor. We encourage performing experimental measurements at lower temperatures to validate our simulated results.

3. We will work with planetary scientists to evaluate the impact of calculated CH_4-N_2 opacities on the modeling of the atmosphere of Titan.

4. At temperatures below 80 K, the contribution of bound states to the total absorption in the CH_4-N_2 rototranslational band ceases to be negligible. We will carry out the trajectory-based calculations for the bound states and provide the aggregate spectra corresponding to the totality of pair states.

The reported trajectory-based results for N_2-N_2 and CH_4-N_2 systems will be included in the dedicated section of the HITRAN database.

DISCLOSURES

Acknowledgements.

The quantum chemical calculations were carried out using HPC resources of Smithsonian Institution High Performance Cluster (SI/HPC) and UCL Myriad High Throughput Computing Facilities.

This work is partially supported by NASA HITRAN grant and RFBR Grant 18-05-00119.

ABSTRACT

Collision-induced absorption (CIA) in the millimeter and far-infrared ranges contributes appreciably to the total absorption of radiation in planetary atmospheres. To aid atmospheric and planetary scientists reference spectroscopic data for CIA are provided in the dedicated section [1] of the HITRAN database [2].

Titan's atmosphere is composed mainly of nitrogen, with a small percentage of methane and hydrogen. Collision-induced absorption by molecular complexes involving N_2 and CH_4 contributes to a greenhouse effect in the Titan's atmosphere. The uncertainty of the CH_4-N_2 CIA in the far-infrared may have a severe impact on retrieval of the height profiles of minor atmospheric constituents. Recent opacity models utilized the semiempirical model [3] for the CH_4-N_2 CIA adjusted to existing experimental data. In [4], the correctness of models [3] is questioned, and a heuristic correction factor is adopted to fit limb-scan data.

The trajectory-based approach proved itself [5] to be a practical alternative to both quantum mechanical [6] and classical many-body [7] perspectives in the modeling of CIA band profiles. Note that up-to-now a fairly limited number of molecular pairs have been studied without recourse to the use of adjustable parameters. In this work, we extend the trajectory-based non-empirical approach to model CIA band profiles of methane-containing molecular pairs.

Our approach relies on the use of high-level quantum-chemically characterized potential energy and induced dipole surfaces. Classically exact equations of motion for colliding molecules are solved from a thermal distribution of initial conditions. The spectral profile is calculated as an averaged Fourier spectrum of the induced dipole moment.

We discuss the reliability of our calculated CIA profiles in light of their comparison with existing experimental and semiempirical data.

This work is partially supported by RFBR Grant 18-05-00119, Program 12 by Presidium of RAS and NASA HITRAN grant.

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