Classical trajectory simulation of the CO_2 collision-induced band profile in the far IR spectral range

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Introduction

There is a growing demand to improve existing methods of collision-induced absorption (CIA) spectra simulation [1]. From the one hand, the impetus to refine presently available theories is due to anticipation of future observations concerning a multitude of exoplanetary atmospheres. From the other hand, there is a remarkable progress in computer facilities that opens access to unprecedented computational performance.

The use of computationally heavy pure quantum [2] and molecular dynamics [3, 4] methods of CIA simulation is still infrequent and can hardly satisfy near future practical requirements in terms of variety of molecular constituents and range of temperature. In contrast, the method based on consideration of classical trajectories seems to have good perspective for extensive CIA simulation. Recent analysis [5] of the classical dynamics in laboratory frame of reference permitted satisfactory simulation of the CO_2-Rg (Rg = Ar, Xe) rototranslational CIA band profiles.

An alternative trajectory based approach is being developed in our research group. Salient features and some preliminary results of it were recently reported elsewhere [6]. Excellent agreement was demonstrated among our calculated trajectory based rototranslational profiles in N_2-N_2 and those computed quantum mechanically in [2] or obtained experimentally (see [1] and references therein). We use body-fixed frame in which classical dynamics of a collision as well as quantum chemical electronic energy (PES) and induced dipole (IDS) surfaces are rigorously examined. Present paper shows results concerning CO_2-Ar and CO_2-CO_2 systems.

Trajectory-based CIA spectra simulation
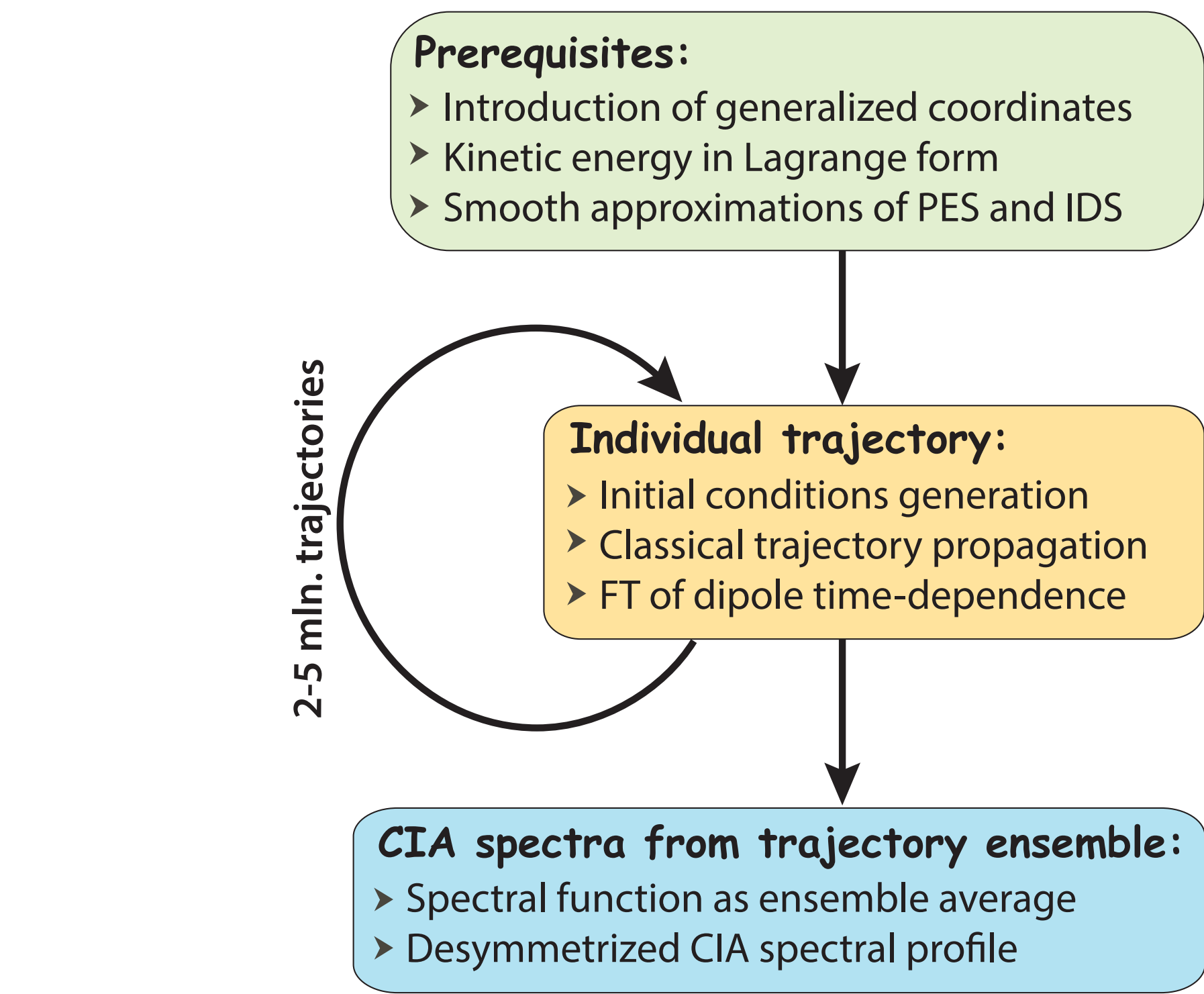
Absorption coefficient α normalized to the product of densities is known to be written as

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

Classical spectral function $J_{class}(\nu,T)$ can be found as Fourier transform of the dipole autocorrelation function

$$J_{class}(\nu,T) = \frac{1}{4\pi\varepsilon_0}\frac{1}{2\pi}\int_{-\infty}^{+\infty}\langle\mathbf{d}(0)\cdot\mathbf{d}(t)\rangle e^{-2\pi ic\nu t}dt.$$

As a result of the change of variables that greatly improves the convergence properties of the integral for the free states, we obtained the following expression for classical spectral function

$$J_{class}(\nu,T) = \frac{1}{4\pi\varepsilon_0}\frac{1}{2\pi\Gamma_0}\int\cdots\int\frac{p_R}{\mu}dp_R\exp\left(-\frac{H}{k_BT}\right)d\mathbf{q}'d\mathbf{p}'\left|\int_{-\infty}^{+\infty}\mathbf{d}(t;\mathbf{q}',p_R,\mathbf{p}')e^{-2\pi ic\nu t}dt\right|^2.$$

Here μ is the reduced mass of a molecule pair, $\Gamma_0 = \int\cdots\int\exp\left(-\frac{H}{k_BT}\right)d\mathbf{q}\,d\mathbf{p}$ is the normalization factor, $d\mathbf{q}'$ relates to angular degrees of freedom of each of the monomers and the complex as a whole.
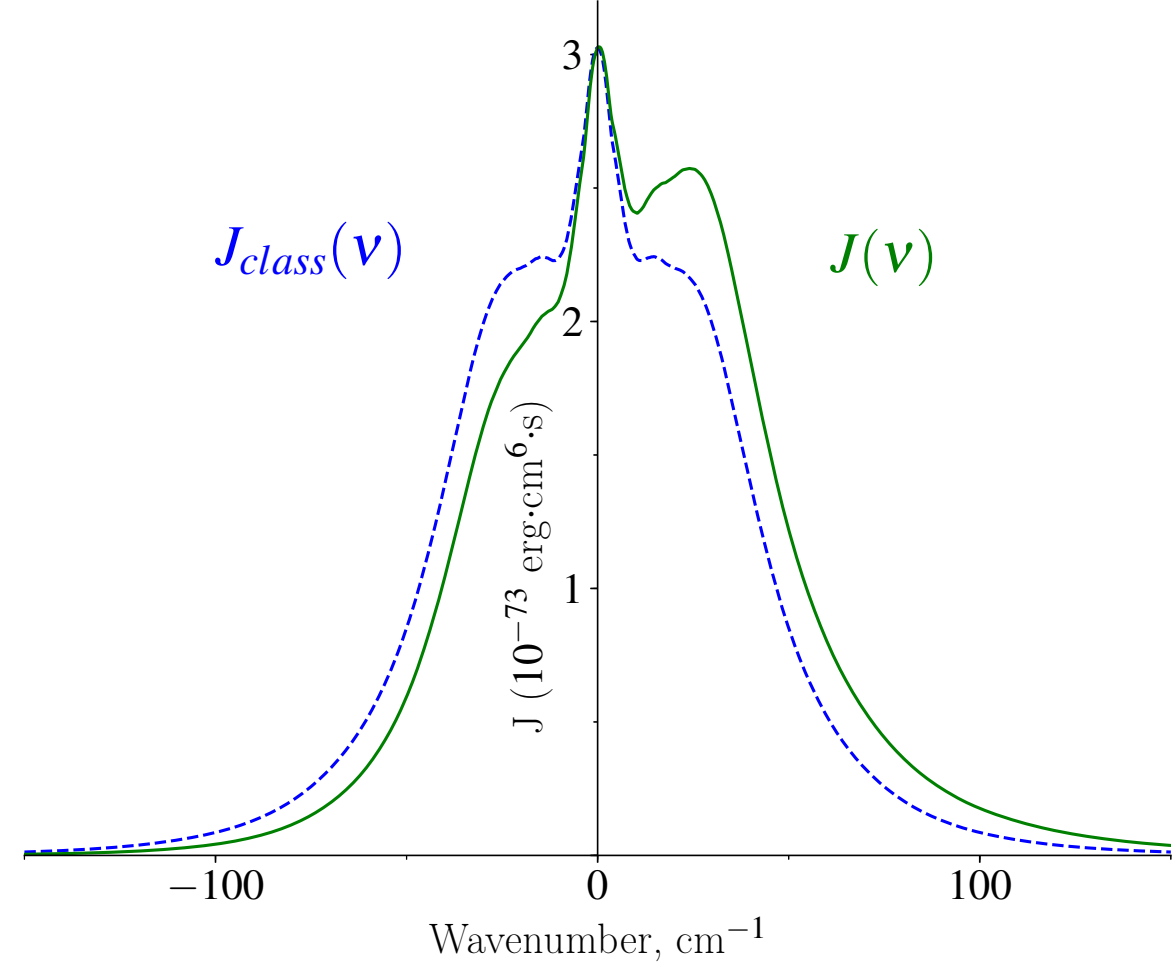
Simple procedure to account for quantum interaction with EM field:

$$J(\nu) = \exp\left(\frac{hc\nu}{k_BT}\right)J_{class}(\nu)$$

Desymmetrized spectral function satisfies quantum "detailed balance" principle:

$$J(-\nu) = \exp\left(\frac{hc\nu}{k_BT}\right)J(\nu)$$

Spectral moments

Spectral moments are integral values, which are widely used to characterise CIA spectra. The use of spectral moments is justified by the possibility to represent them either in terms of integrals over experimentally measured spectral profiles or in terms of Boltzmann weighted functions of induced dipole.
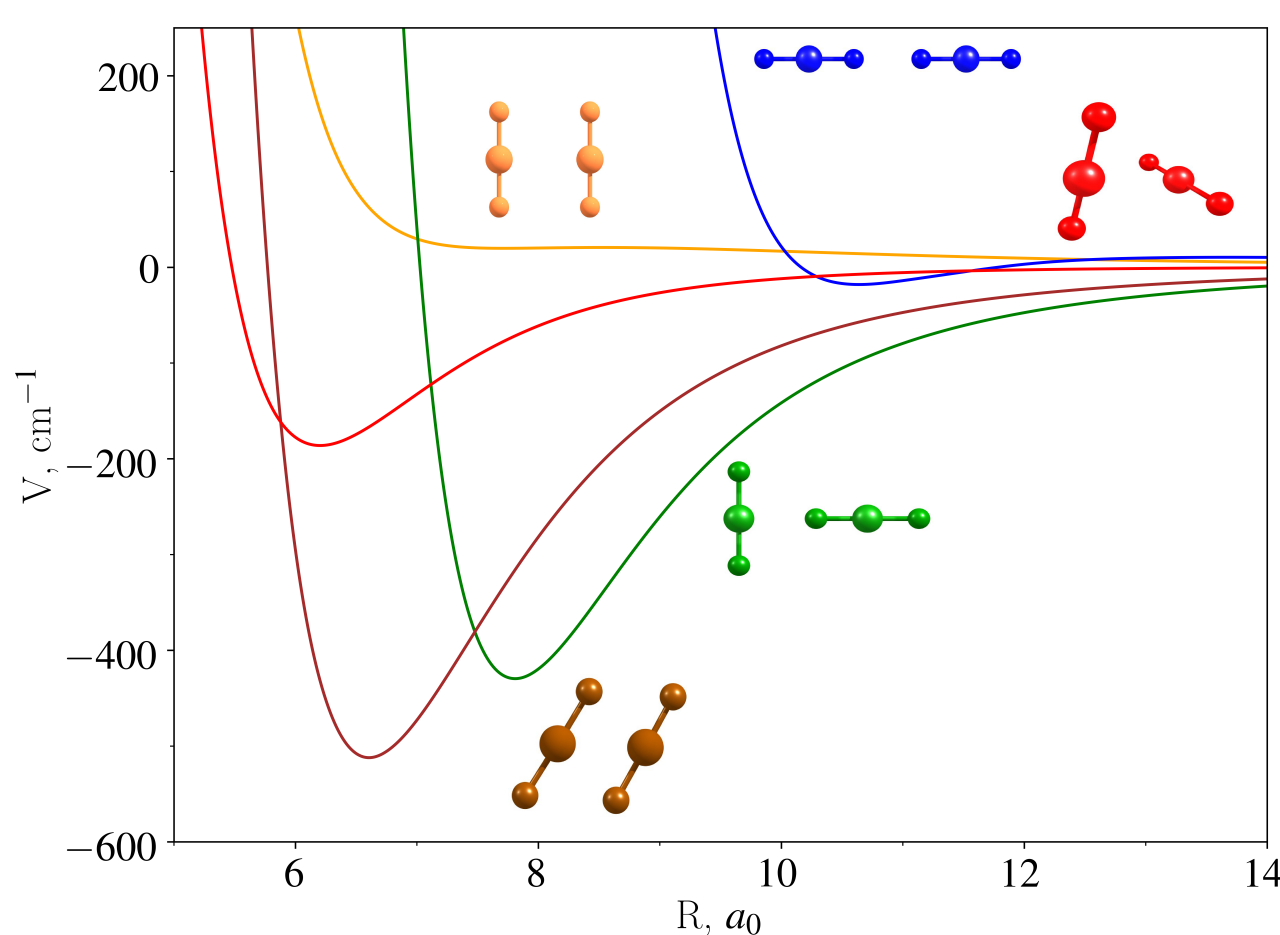
Calculation of spectral moments as phase space integrals

$$M_0 = \frac{\int\mathbf{d}^2\exp\left[-H(\mathbf{q},\mathbf{p},\mathbf{J})/k_BT\right]d\mathbf{q}\,d\mathbf{p}\,d\mathbf{J}}{\int\exp\left[-H(\mathbf{q},\mathbf{p},\mathbf{J})/k_BT\right]d\mathbf{q}\,d\mathbf{p}\,d\mathbf{J}} \qquad M_2 = \frac{\int\dot{\mathbf{d}}^2\exp\left[-H(\mathbf{q},\mathbf{p},\mathbf{J})/k_BT\right]d\mathbf{q}\,d\mathbf{p}\,d\mathbf{J}}{\int\exp\left[-H(\mathbf{q},\mathbf{p},\mathbf{J})/k_BT\right]d\mathbf{q}\,d\mathbf{p}\,d\mathbf{J}}$$

Calculation of spectral moments from spectral profile
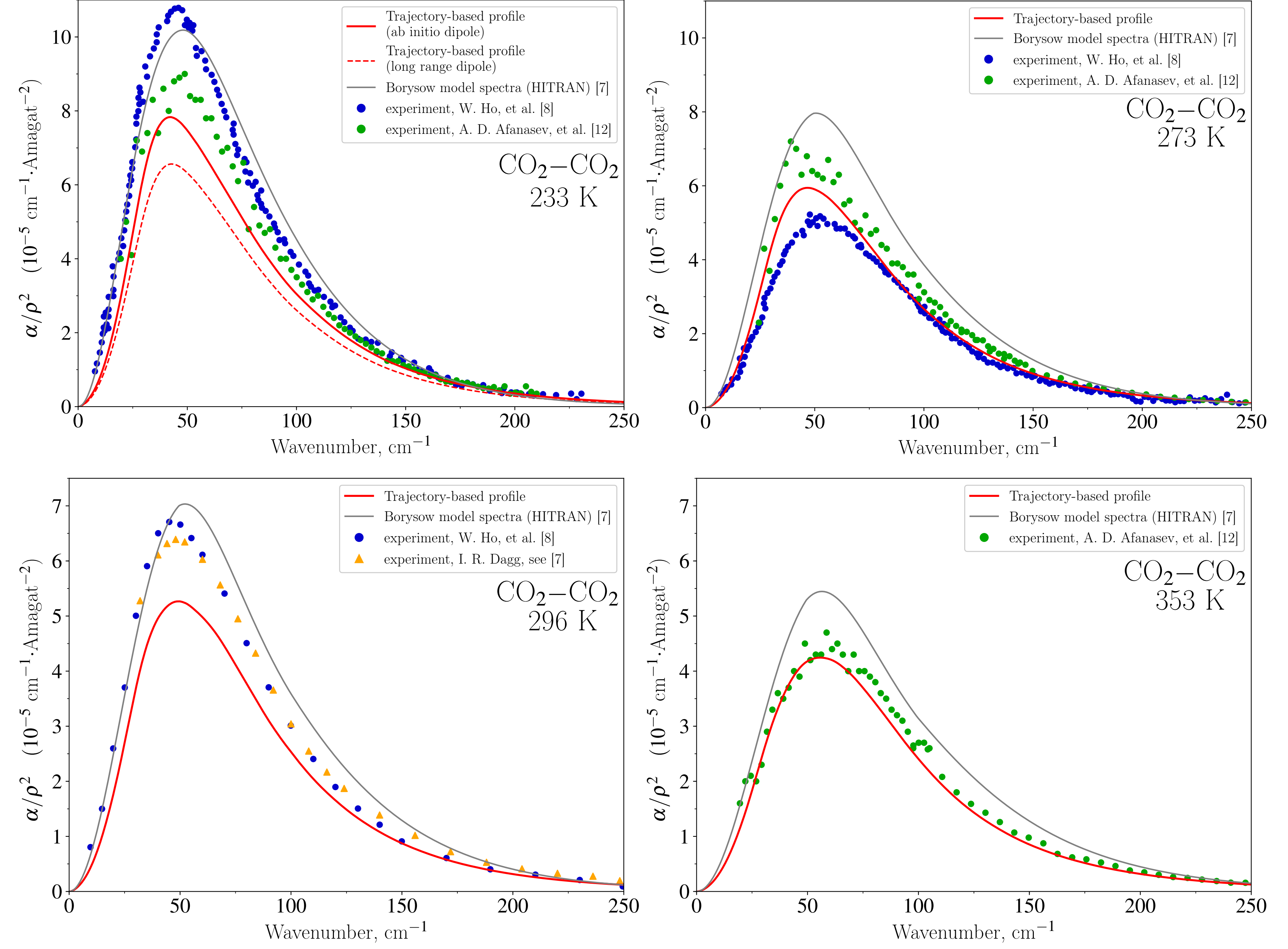
$$M_0 = 2\int_0^\infty\left[1-\exp\left(-\frac{hc\nu}{k_BT}\right)\right]^{-1}\frac{\alpha(\nu)}{\nu}d\nu \qquad M_2 = 2\int_0^\infty\left[1-\exp\left(-\frac{hc\nu}{k_BT}\right)\right]^{-1}\nu\,\alpha(\nu)\,d\nu$$
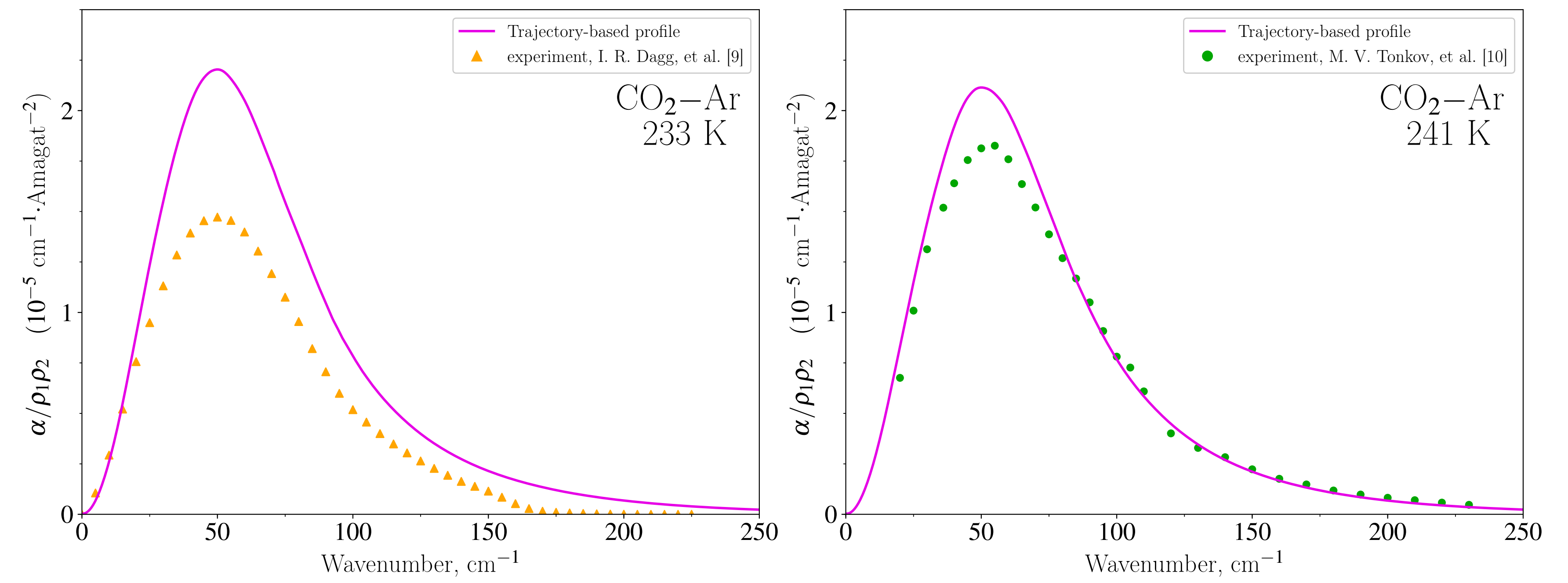
Ab initio PES and IDS computation

- CO_2-Ar PES and IDS: CCSD(T)/*aug*-cc-pVQZ and CCSD(T)/*aug*-cc-pVTZ, both supplemented with midbond functions
- CO_2-CO_2 PES and IDS: CCSD(T)-F12/aug-cc-pVTZ supplemented with midbond functions
- BSSE correction
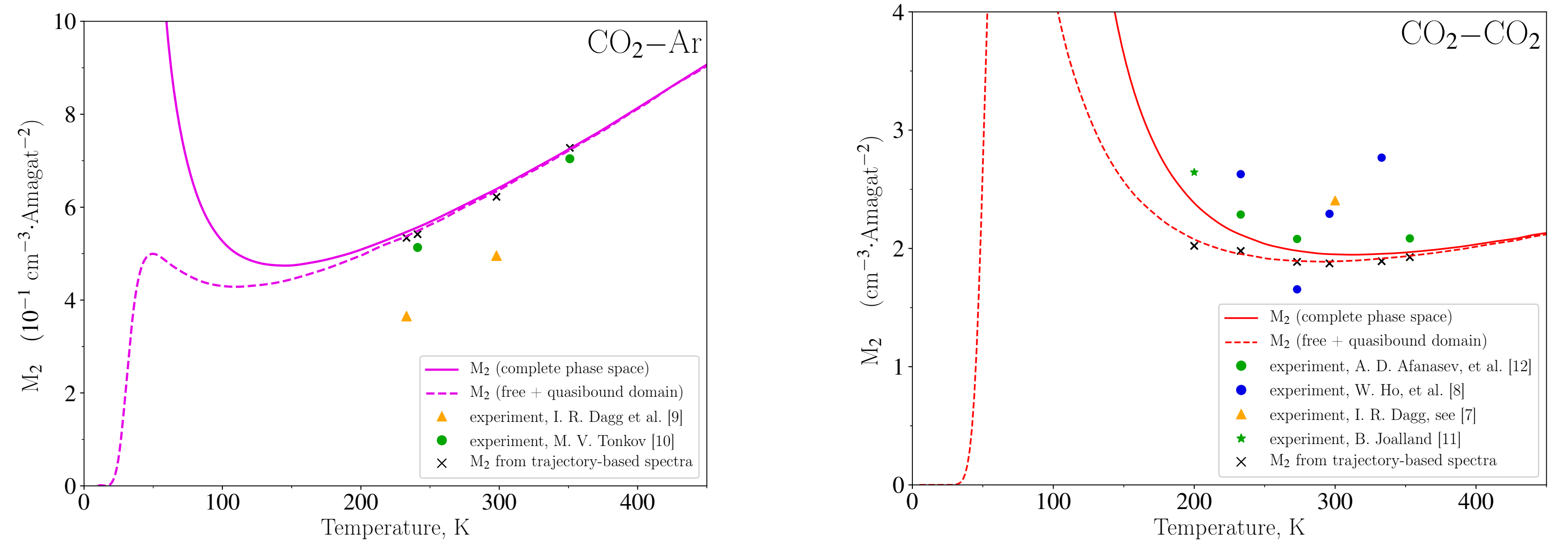- PES and IDS fit using the basis of spherical functions and cubic splines

CO_2-CO_2 rototranslational band

CO_2-Ar rototranslational band

Experimental vs. calculated CIA intensities

Conclusions

The results reported here show encouraging perspective for our trajectory based method to be employed in extensive CIA simulation. To the best of our knowledge, trajectory based calculation of CIA spectra for various pairs of linear molecules is performed for the first time. Moreover, we extended calculations to CO_2-CO_2 pair which is known to possess strong anisotropy of intermolecular interaction. We admit that ensemble of available experimental data for CO_2-CO_2 is yet not perfectly reproduced by our trajectory based calculations. Nevertheless, overall agreement is quite reasonable bearing in mind an appreciable uncertainty, which characteristic to experimental data issuing from different laboratories. Moreover, in contrast to some series of experimental data our spectra vary reguarly as a function of temperature. These calculated variations are strongly supported by our independent computations of the zeroth and the second spectral moments as integrals over phase space.

Acknowledgements

References

1. T. Karman, I. E. Gordon, A. van der Avoird, *et al.* (2019) *Icarus* 328, 160-175.
2. T. Karman (2018) "Collision-induced absorption by oxygen and nitrogen molecules", PhD thesis, Radboud University.
3. J.-M. Hartmann, *et al.* (2011) *J. Chem. Phys.* 134 (9), 094316.
4. B. Bussery-Honvault, and J.-M. Hartmann (2014) *J. Chem. Phys.* 140 (5), 054309.
5. D. Oparin, N. N. Filippov, I. M. Grigoriev, *et al.* (2017) *J. Quant. Spectr. Radiat. Transf.* 196, 87-93.
6. D. N. Chistikov, A. A. Finenko, Y. N. Kalugina, *et al.* (2018) *Classical trajectory simulation of collision-induced absorption spectra*. HRMS, Bilbao, Spain.
7. M. Gruszka, and A. Borysow (1997) *Icarus* 129, 172-177.
8. W. Ho, G. Birnbaum, and A. Rosenberg (1971) *J. Chem. Phys.* 55 (3), 1028-1038.
9. I. R. Dagg, A. Anderson, S. Yan, *et al.* (1986) *Can. J. Phys.* 64 (11), 1475-1481.
10. M. V. Tonkov (1995) In: *Collision- and Interaction-Induced Spectroscopy.* Kluwer AP.
11. B. Joalland, M. Goubet, R. Georges (2016) "Far-infrared collision-induced absorption in CO2 at T = 200 K". 13th ASA Conference, Reims.
12. A. D. Afanasev, N. M. Grigorovich, and M. V. Tonkov (1985) *Opt. Spectrosc.* 58, 772-774.