

The use of spectral moments to simulate rototranslational collision-induced bandshapes

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Introduction

Reliable knowledge of collision-induced absorption (CIA) is requested for a variety of atmospheric researches from remote sensing of Earth's atmosphere to exploration of exoplanetary atmospheres. Irrespective of the theoretical formalism chosen to simulate the spectral profile, the use of spectral moments helps to quantify dipole-forbidden absorbance. On the one hand, spectral moments are defined as integrals of properly weighted binary absorption coefficient. On the other hand, zeroth and second moments can be calculated directly via statistical averaging of either squared induced dipole or Poisson bracket composed of the dipole and Hamiltonian derivatives, respectively.

The aim of the present paper is to examine how the knowledge of the zeroth and second classical spectral moments can help in the modelling of the CIA spectral profiles (see also **Poster P1-33** which is devoted to precise CIA spectra modelling using classical trajectories). The topics covered below include:

- theoretical computation of spectral moments and their determination from the measured spectra;
- examination of how theoretical values should be compared with experimental ones;
- the use of spectral moments as trial values to check the quality of the potential energy and specifically induced dipole surfaces;
- the procedure for approximate and fast modelling of rototranslational CIA spectra based on *ab initio* classically calculated spectral moments – the procedure is applicable when some initial guess on the spectral shape is already available.

Spectral moments: definition and some properties

Binary absorption coefficient (measured experimentally) $\rightarrow \alpha(\nu) = \nu \left[1 - \exp\left(-\frac{h\nu}{kT}\right) \right] J(\nu) \leftarrow$ Spectral density function (convenient for theoretical consideration)

Classical interaction with EM field (detailed balance principle): $J(-\nu) = J(\nu)$

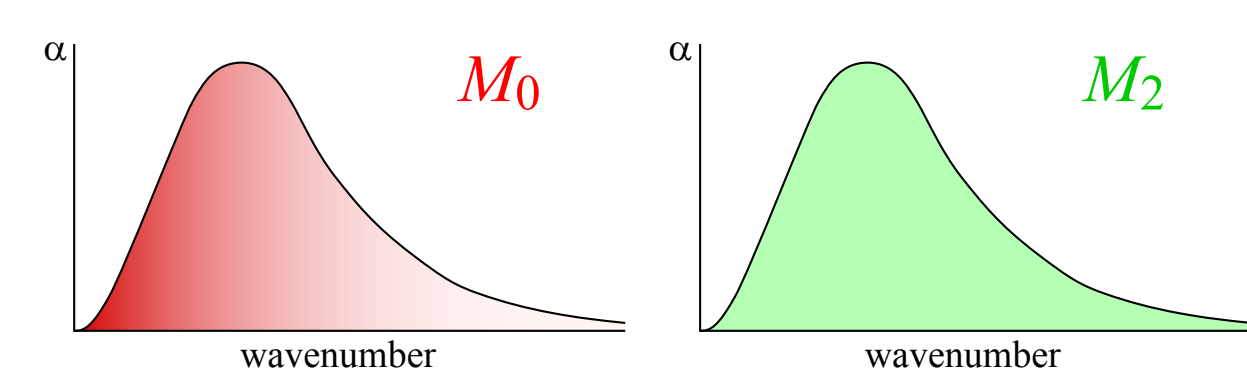
$$M_0 = 2 \int_0^\infty \left[1 - \exp\left(-\frac{h\nu}{kT}\right) \right]^{-1} \frac{\alpha(\nu)}{\nu} d\nu$$

$$M_2 = 2 \int_0^\infty \left[1 - \exp\left(-\frac{h\nu}{kT}\right) \right]^{-1} \nu \alpha(\nu) d\nu$$

Real interaction with EM field ('quantum detailed balance'): $J(-\nu) = \exp\left(-\frac{h\nu}{kT}\right) J(\nu)$

$$M_0 = \int_0^\infty \coth\left(\frac{h\nu}{2kT}\right) \frac{\alpha(\nu)}{\nu} d\nu$$

$$M_2 = \int_0^\infty \coth\left(\frac{h\nu}{2kT}\right) \nu \alpha(\nu) d\nu$$



Formally M_0 should be treated as integrated intensity of a rototranslational band, though it is the equation for M_2 that describes nearly uniform integration of $\alpha(\nu)$

Calculation of spectral moments as phase space integrals:

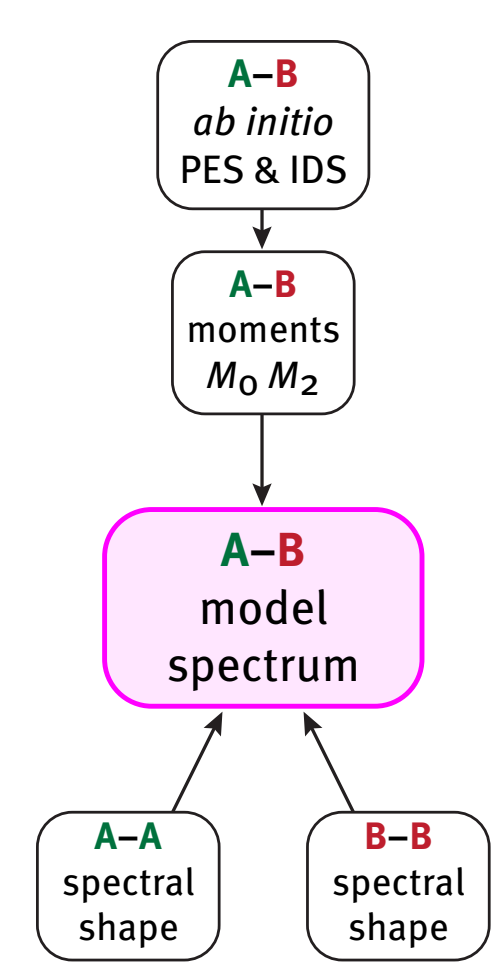
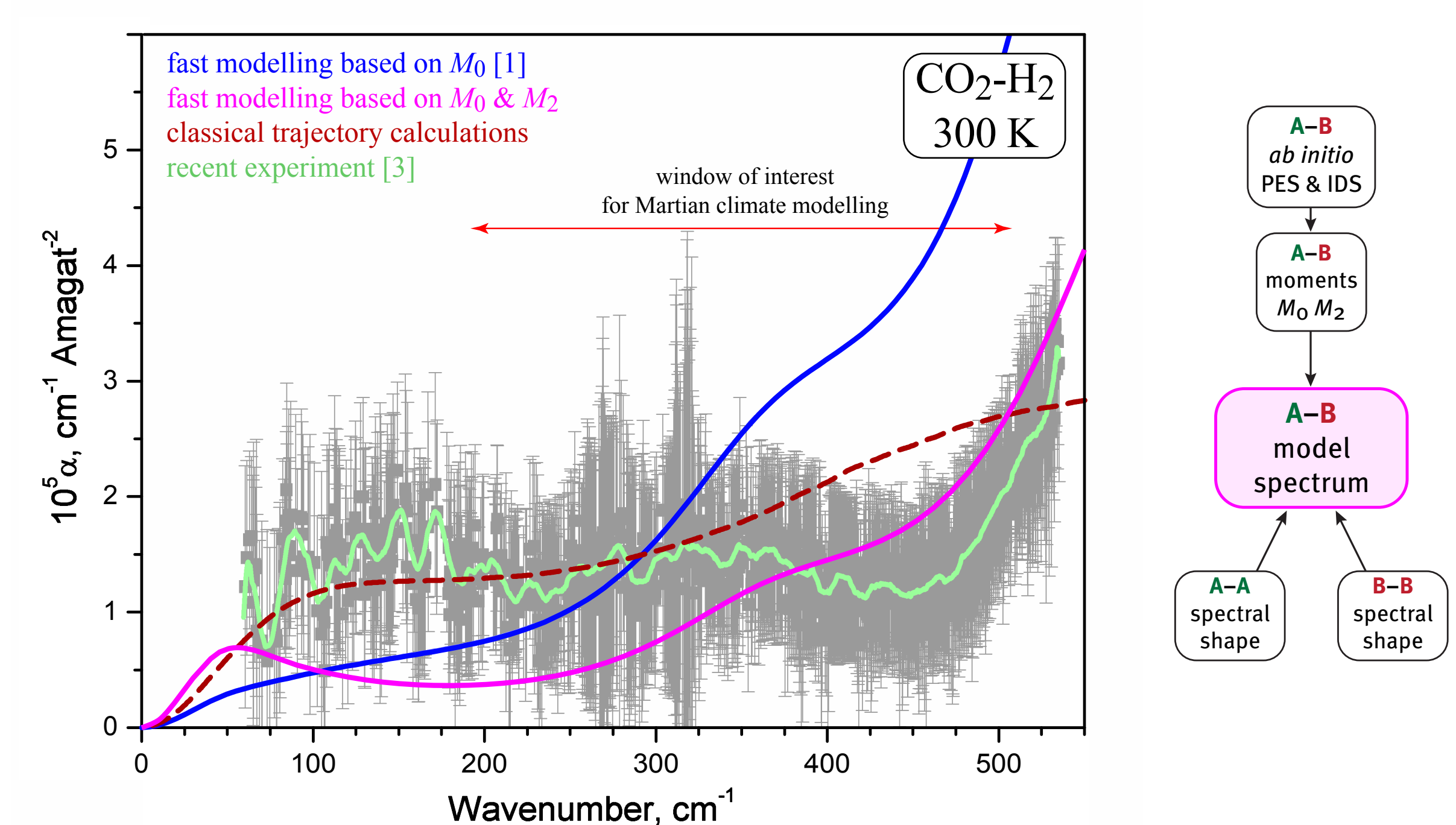
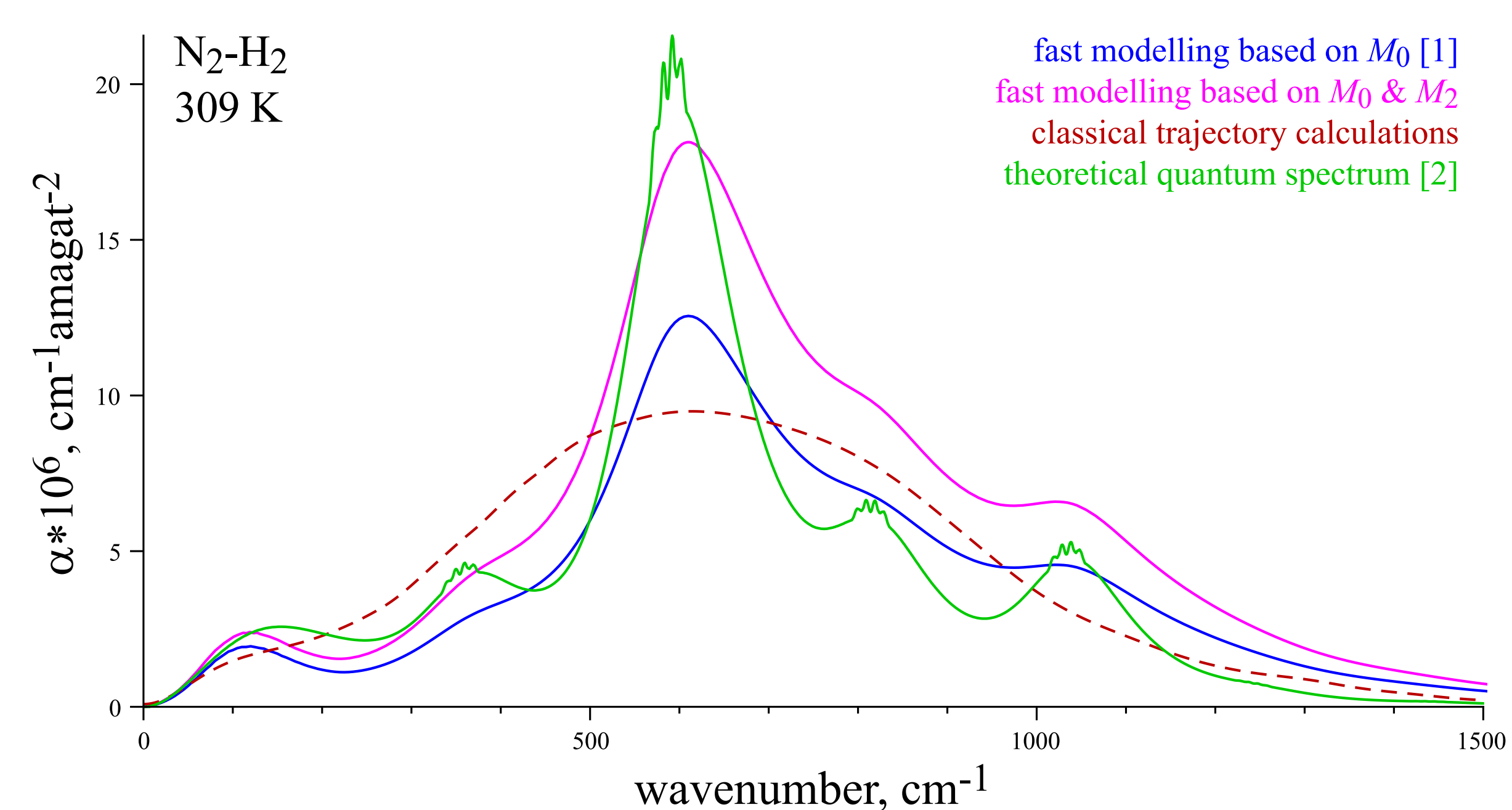
$$M_0 = \frac{\int \mu^2 \exp[-H(\mathbf{q}, \mathbf{p}, \mathbf{J})/kT] d\mathbf{q} d\mathbf{p} d\mathbf{J}}{\int \exp[-H(\mathbf{q}, \mathbf{p}, \mathbf{J})/kT] d\mathbf{q} d\mathbf{p} d\mathbf{J}} = \dots$$

$$M_2 = \frac{\int \dot{\mu}^2 \exp[-H(\mathbf{q}, \mathbf{p}, \mathbf{J})/kT] d\mathbf{q} d\mathbf{p} d\mathbf{J}}{\int \exp[-H(\mathbf{q}, \mathbf{p}, \mathbf{J})/kT] d\mathbf{q} d\mathbf{p} d\mathbf{J}} = \dots$$

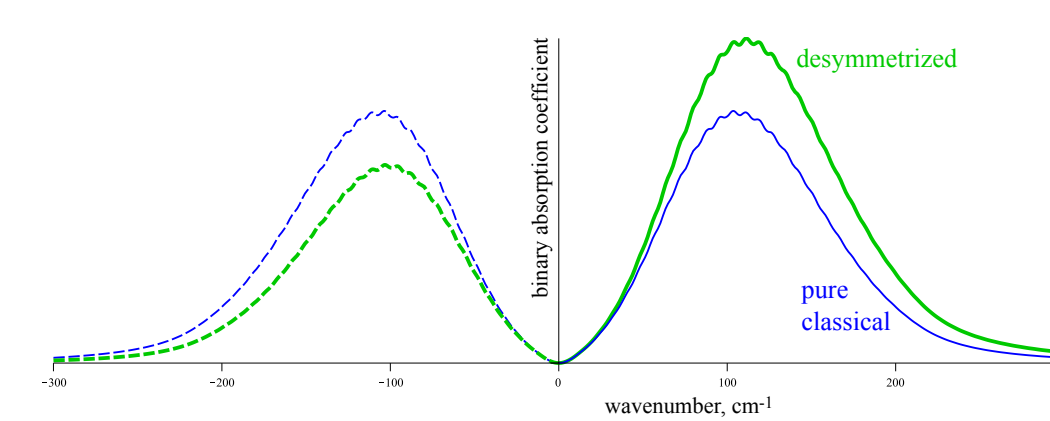
A procedure is developed to compute M_0 and M_2 integrals with the exact Hamiltonian of an arbitrary molecular pair.

$$\dot{\mu} = \frac{d\mu}{dt} = [\mu, H] = \sum_i \left(\frac{\partial \mu}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \mu}{\partial p_i} \frac{\partial H}{\partial q_i} \right) = \dots$$

Fast modelling of CIA spectra based on *ab initio* spectral moments

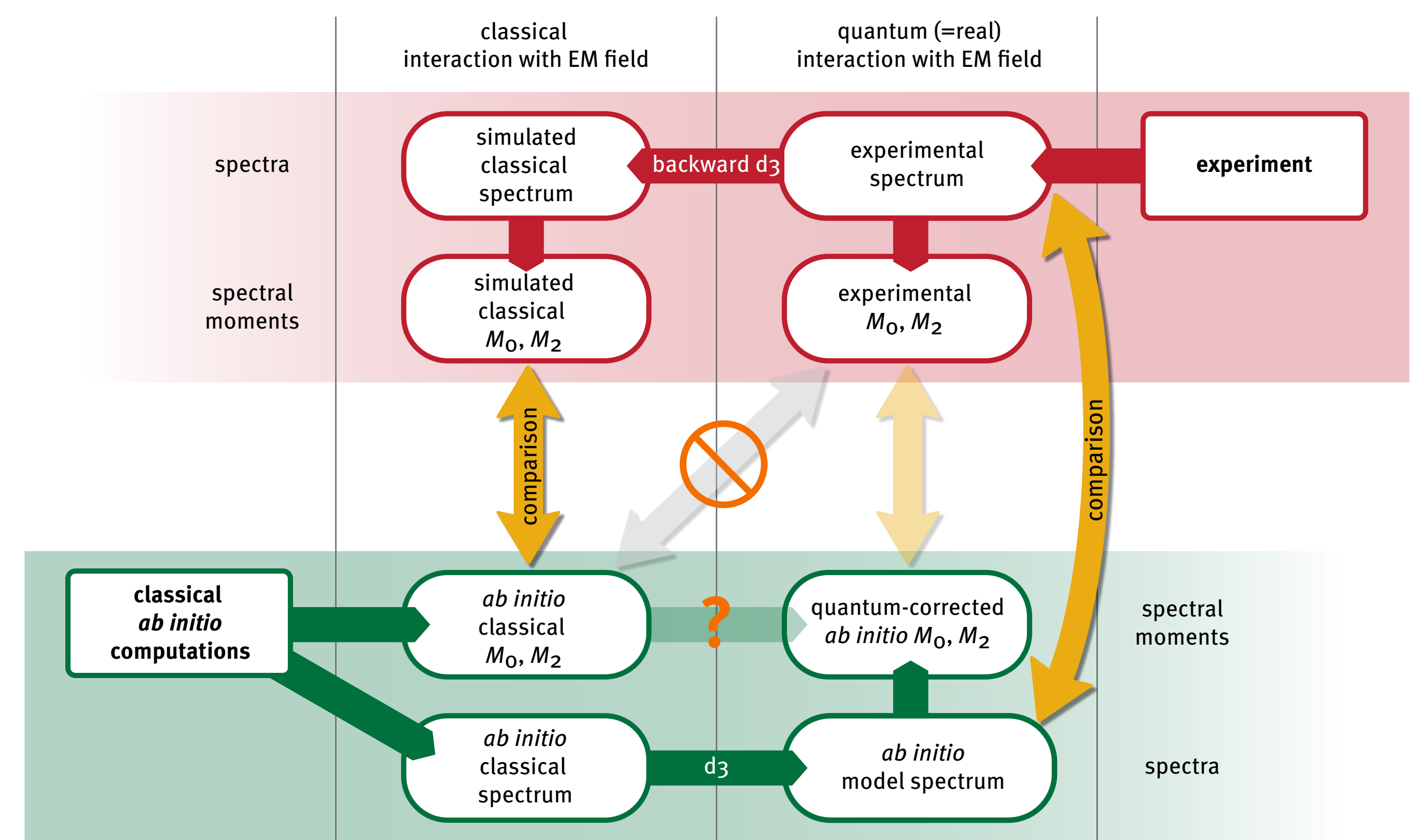


Spectral moments: relating theory to experiment

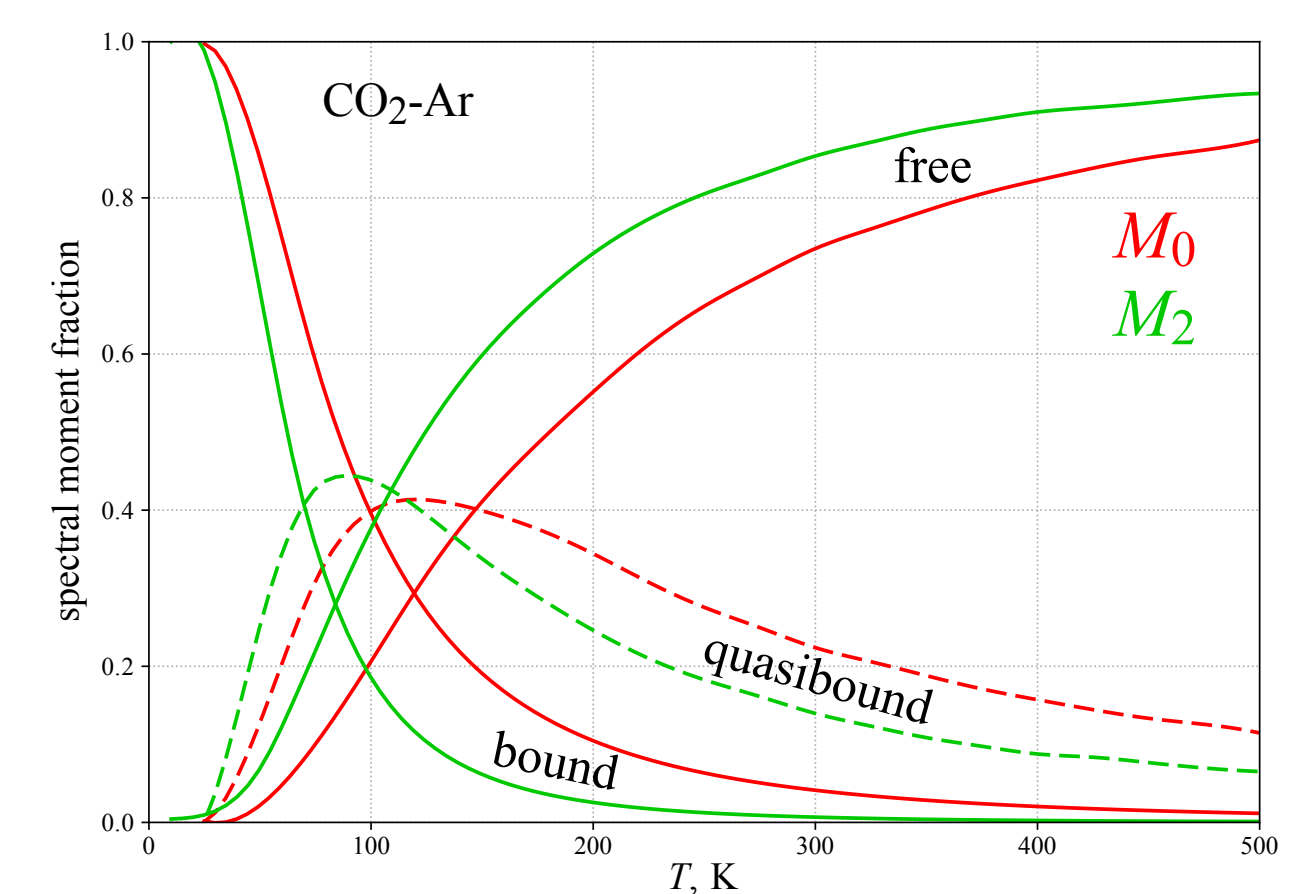
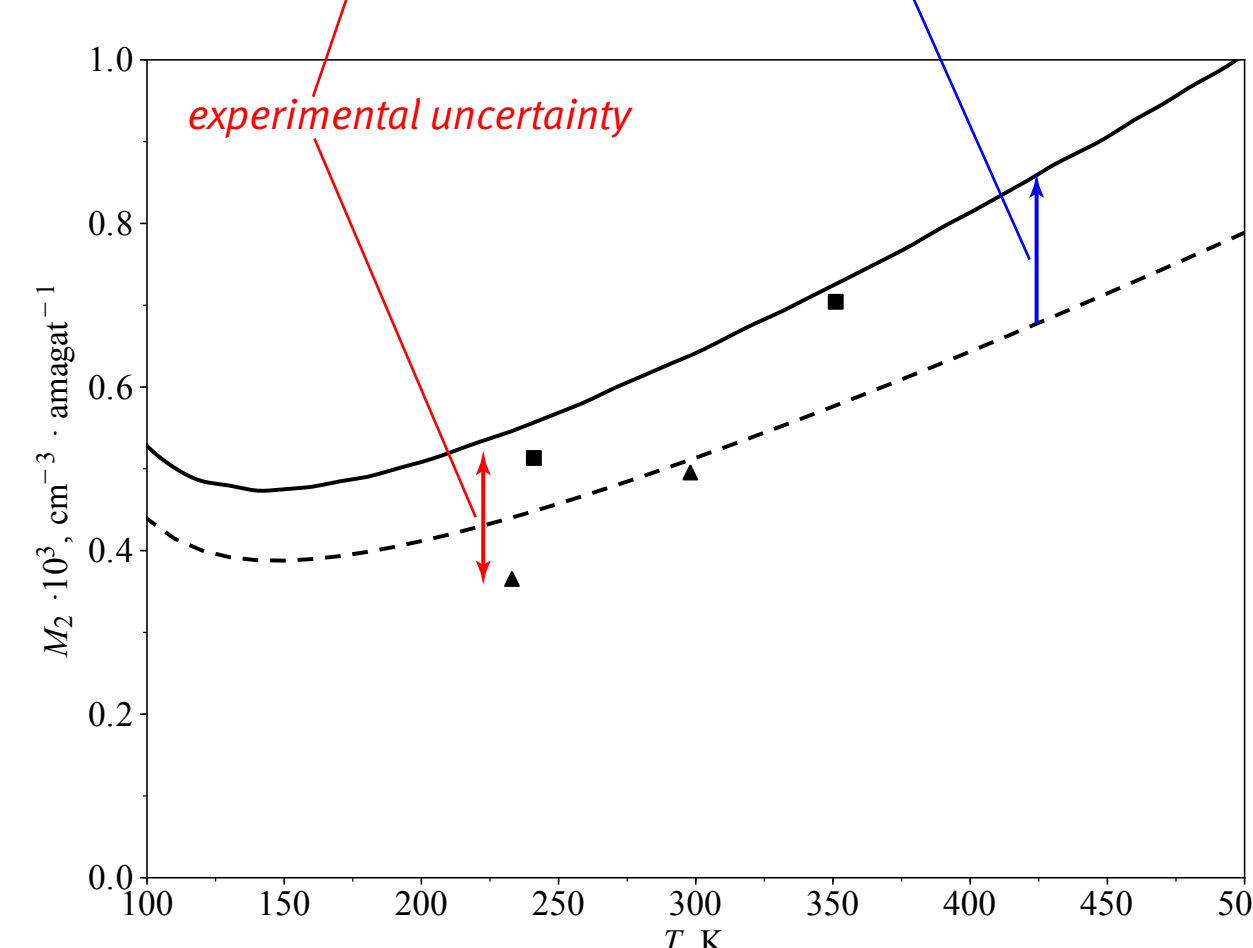
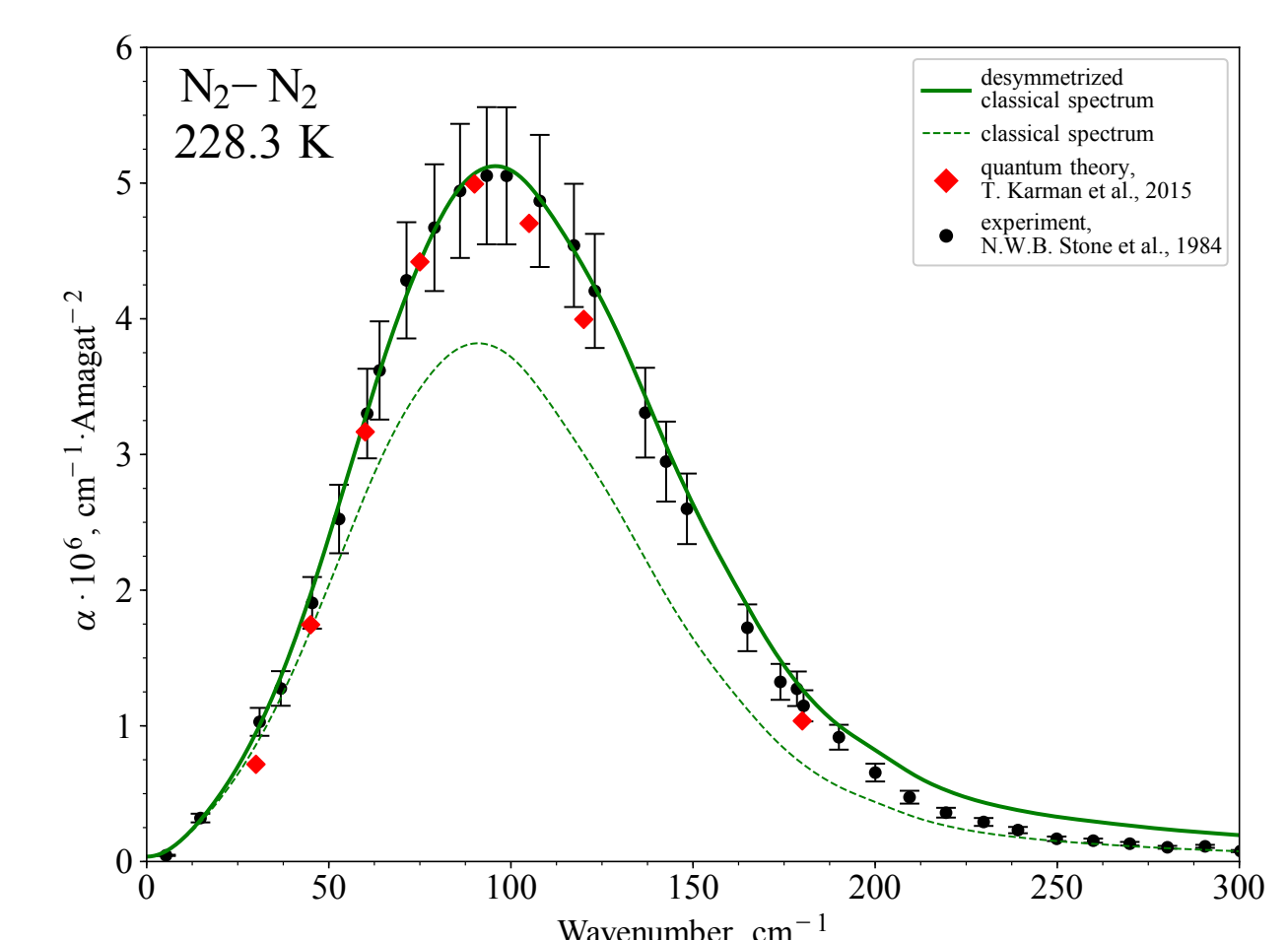
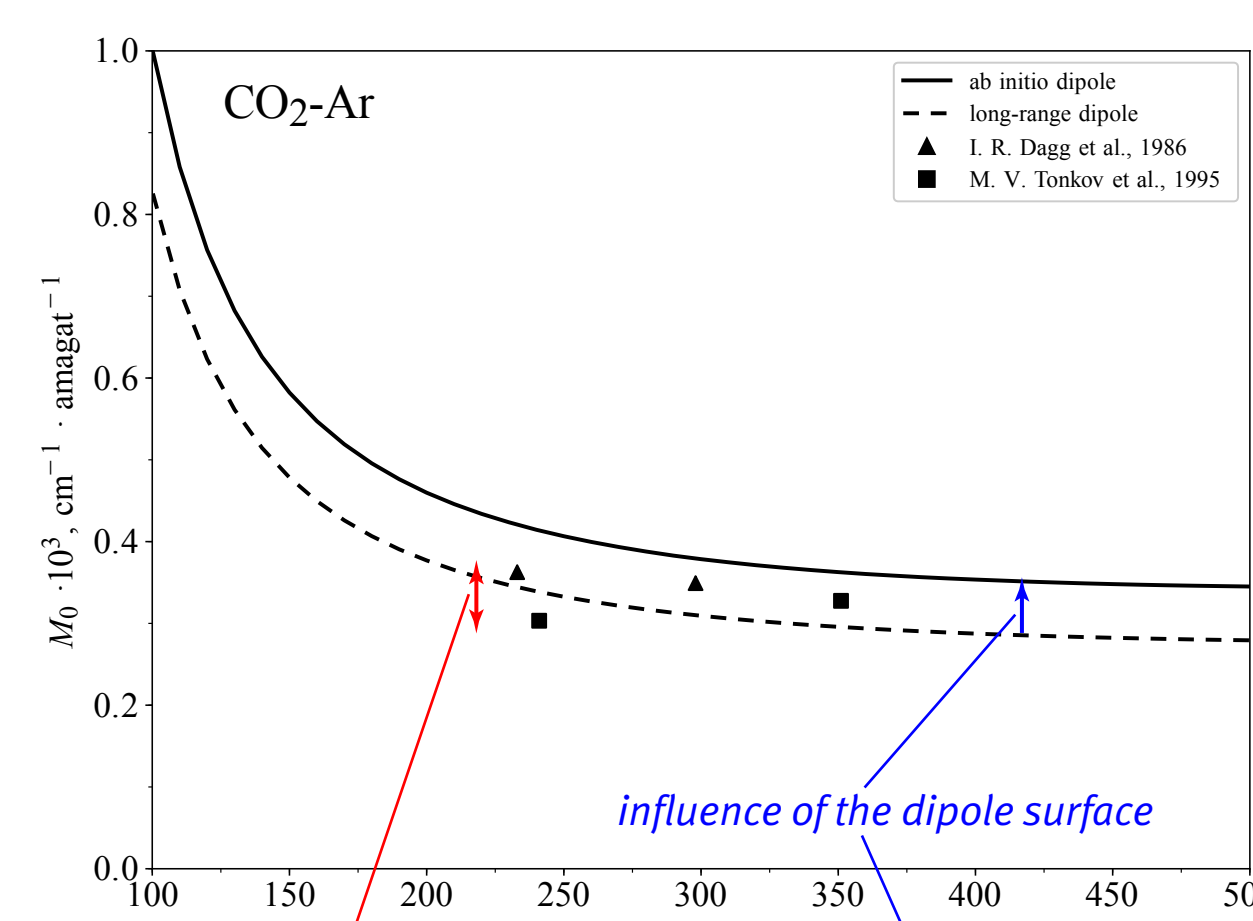


Desymmetrization procedure – a simple way to enhance a pure classical spectrum to account for quantum interaction with EM field:

$$J(\nu) = \exp\left(\frac{h\nu}{2kT}\right) J_0(\nu) \quad (d3)$$



Some examples (see poster P1-33 for more)



Conclusions

1. Rigorous calculation of classical spectral moments using statistical averaging procedure is shown to provide a powerful tool to verify the results of the spectral profiles simulation;
2. Quantum nature of the molecular system's interaction with electro-magnetic field cannot be ignored when classical trajectory-based approach is used to simulate CIA spectra at typical atmospheric temperatures. The use of desymmetrization procedure is crucial to adequately model CIA spectra and to reproduce experimental values of spectral moments.
3. Quantum chemically calculated *ab initio* potential energy and induced dipole surfaces are strongly preferable to be used for the modelling of CIA spectra. The use of long-range approximation for induced dipole results in underestimation of the first two spectral moments by up to 15%.
4. Fast modelling of rototranslational CIA spectra based on *ab initio* moments is justified, although reliability of such approach for an arbitrary molecular pair is questionable and requires independent verification.

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