Erratum: Harmonic Models in Cartesian and Internal Coordinates to Simulate the Absorption Spectra of Carotenoids at Finite Temperatures

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Ⓢ *Supporting Information*

We found an error in the calculation of the normal mode displacements in internal coordinates that we used to compute the vibronic spectra of carotenoids with the Adiabatic Hessian (AH) model in the original paper.[1] The error derived
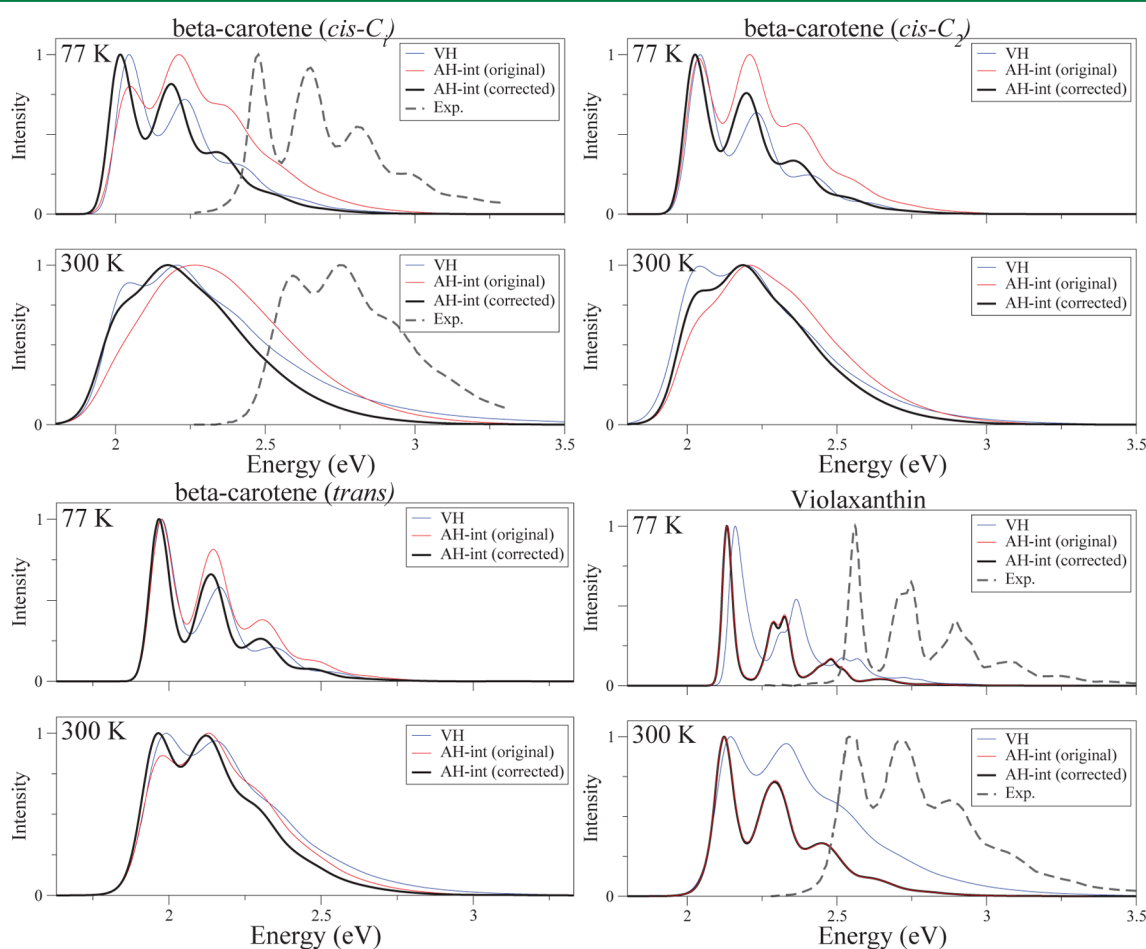

Figure 1. Corrected absorption spectra simulated with the AH model using internal coordinates (AH-int) are reported as black thick lines. The wrong AH-int spectra originally included in ref 1 are also shown (red lines). We also report the computed VH spectra (blue), and the experimental spectra (dashed) taken from the works by Jailaubekov et al.,[2] for *β*-carotene, and Cong et al.,[3] for violaxanthin.

from an inconsistency in the sign convention adopted for dihedrals in the calculation of the displacements and of the elements of the Wilson **B** matrix.

We fixed the error and recomputed all the spectra obtained in ref 1 with the AH-int model (AH model described in internal coordinates). Figure 1 compares the original and the corrected spectra. The spectra simulated with the Vertical Hessian (VH) model in Cartesian coordinates, not affected by the error, are also included along with the experimental ones.

For cis-C_i and cis-C_2 isomers of β-carotene, the corrected AH-int spectra are appreciably different from the original ones and are systematically closer to VH simulations and to the experimental results. For the cases where the dihedral displacements are smaller, that is, for the $trans$ isomer of β-carotene and for violaxanthin, minor changes are observed, with virtually no variations for violaxanthin. This behavior was expected since, clearly, the introduced error was larger for torsional normal modes (which are dominated by dihedral angles) and was more significant for systems, such as cis-C_i and cis-C_2 isomers of β-carotene, characterized by large dihedral displacements between the minima of the initial and final electronic states.

The new results indicate that AH-int model delivers spectra of comparable quality as those provided by the VH model, even in the cases of large dihedral angles differences between the minima of the initial and the final electronic states (namely, the cis isomers of β-carotene).

The reported error did not affect the evaluation of the Duschinsky matrix, which was central to our findings. Indeed, in ref 1, we found that the main cause of the overbroadened spectra computed with the AH model in Cartesian coordinates (AH-Cart), were the inaccuracies in the Duschinsky matrix rather than in the related normal mode displacements. This general conclusion remains valid (see also the updated figures in the Supporting Information). Furthermore, data in Supporting Information show that the corrected spectra exhibit a pattern of vibronic stick (computed with the Time-independent, TI, approach) similar to that of the original spectra in ref 1, since, actually, the same main progressions appear. The convergence of the TI calculations is, however, better (0.81 as opposed to 0.53 in ref 1). More generally, except for the description of the vibronic shape of AH-int simulated spectra, the whole discussion in ref 1 still holds.

In conclusion, in ref 1 we highlighted the advantages of AH-int and VH models showing that they remarkably improve the simulation of the spectra of the studied carotenoids, overcoming the limitations of the AH-Cart model. The latter delivers excessively broad spectra[1] due to the problems arising in the description of curvilinear normal modes with Cartesian coordinates. The corrected AH-int results compare even more favorably than the original ones to experiments, further highlighting the potentiality of the usage of the AH model in internal coordinates. In fact, even if for the investigated systems AH-int delivers results of very similar quality with respect to VH, it is noteworthy that, by definition, it allows to avoid the problems arising from imaginary frequencies in the final-state Hessian that usually occur in VH calculations.[4]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Corrected SI Table 1 and Figures 1−3. This material is available free of charge via the Internet at http://pubs.acs.org.

■ REFERENCES

(1) Cerezo, J.; Zúñiga, J.; Requena, A.; Ávila Ferrer, F. J.; Santoro, F. Harmonic Models in Cartesian and Internal Coordinates to Simulate the Absorption Spectra of Carotenoids at Finite Temperatures. *J. Chem. Theory Comput.* **2013**, *9*, 4947−4958.

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