# RELIABILITY AND RESONANCES IN VIBRATIONAL PERTURBATION THEORY

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The availability of integrated solutions in user-friendly computational packages coupled with capabilities of modern hardware have facilitated the inclusion of anharmonicity in the simulation of vibrational spectra over the recent years. Cost-effective methods such as the second-order vibrational perturbation theory (VPT2) can even be applied to molecular systems comprising dozens of atoms. However, the well-documented problem of resonances, their identification and correction remain a critical pitfall of perturbative methods. Recent works have highlighted the sensitivity of band intensities to even subtle resonance effects, underlying the importance of a correct treatment to predict accurate spectral band-shapes.[1] This aspect is even more critical with chiroptical spectroscopies whose signal is weak.

In this contribution, we analyze the impact of resonances and explore strategies to identify and correct them, not only in energy calculations, but also on the transition moments.[2] A selection of representative molecules of different sizes was used for the study. We show how resonances can affect the overall spectral band-shapes, especially on chiroptical spectroscopies, and the accuracy achievable once they are properly treated, even beyond the fingerprint region.[3,4]

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[2] Q. Yang, J. Bloino, *J. Phys. Chem. A* 2022, **126**, 9276-9302

[3] M. Fusè, G. Longhi, G. Mazzeo, S. Stranges, F. Leonelli, G. Aquila, E. Bodo, B. Brunetti, C. Bicchi, C. Cagliero, J. Bloino, S. Abbate, *J. Phys. Chem. A* 2022, **126**, 6719-6733

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