



Editorial Symmetry and Molecular Spectroscopy

Pier Remigio Salvi * and Cristina Gellini 🔎

Dipartimento di Chimica Ugo Schiff, Università di Firenze, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy * Correspondence: piero.salvi@unifi.it

Symmetry plays a fundamental role in molecular spectroscopy [1–3]. The symmetry of molecules provides the basic information required for the classification of molecular states and determines the selection and intensity rules of several types of spectroscopies. Furthermore, the ultrashort pulses generated for experimental investigations [4] and improved computational methods [5] have increased the scope of spectroscopic research and have strengthened the use of symmetry. Therefore, to highlight the relevance of this concept, this Special Issue, titled "Symmetry and Molecular Spectroscopy", was announced in 2019. The issue, which consists of five research papers, was completed in 2021 and aims to address current aspects of interest in the field of molecular spectroscopy, reporting both experimental and theoretical studies.

Ragnoni et al. report on the IR spectrum of penicillin G sodium salt in D_2O and DMSO solutions measured in steady-state and pump–probe experiments [6]. Nonlinear experiments were performed by exciting the sample with broadband infrared femtosecond pulses. Transient absorption spectra were then measured with a pump–probe arrangement. According to their measurements, the authors describe how to evaluate the anharmonic coupling constants between the different CO bonds present in the molecule. The interaction of β -lactam CO with the carboxylate CO oscillator gives origin to the strongest coupling. This was attributed to the structural pseudo-parallel configuration of the two oscillators.

The study of Al-Majid et al. is focused on the crystal structures of interesting molecular systems, such as gem-aminals based on morpholine and pyrrolidine moieties, that have been employed as building blocks for the synthesis of ionic liquids [7]. The authors report on the synthesis and single-crystal X-ray diffraction studies of the gem-aminals 1,2-dimorpholinoethane (1) and 1-morpholino-3-morpholinium bromide propane (2). Compound 1 was found to crystallize in the monoclinic crystal system, with the molecule having a center of symmetry. The less symmetric analogue 2, while also belonging to the monoclinic crystal system, lost its inversion center. Considerations about molecular packing in the two crystals were proposed based on Hirshfeld analysis, and it was determined that N \dots H, O \dots H, H \dots H, and Br \dots H (in the case of compound 2) weak interactions are responsible for packing.

A comprehensive study of the lowest 17 excited states of ethylene was undertaken by Tao et al. using the time-dependent density functional theory (TDDFT) [8]. All 17 states were assigned to irreducible representations of the D_{2h} symmetry of ground-state ethylene and the vertical energies determined at the CAM-B3LYP/aug-cc-pVTZ calculation level. The authors were able to calculate the optimized geometries of 11 excited states and found symmetry lowering from D_{2h} to D₂, C_{2h} and C_{2v} for some of them. For the latter symmetry configuration (C_{2v}), the two carbon atoms are no longer equivalent. The local stretching force constants of the C=C and C-H oscillators were determined for the 11 optimized excited states. A good correlation between the C=C force constants and C=C equilibrium bond lengths was found; the correlation was weaker in the case of C-H.

An alternative scheme to classify the highly excited rovibrational states of linear molecules was proposed by Mellor et al. in [9]. The authors note that for well-bent molecules such as H_2S , a standard zero-order Hamiltonian system is expressed in terms of



Citation: Salvi, P.R.; Gellini, C. Symmetry and Molecular Spectroscopy. *Symmetry* 2022, 14, 2012. https://doi.org/10.3390/ sym14102012

Received: 23 July 2022 Accepted: 4 August 2022 Published: 25 September 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). three vibrational and three rotational degrees of freedom. This is not the case for a linear (CO_2) or even a bent molecule whose potential energy surface would allow a linear configuration. A new theoretical framework is proposed based on the use of non-degenerate irreps of bent molecules. To this purpose advantage is taken of the symmetry group algebra and of the introduction of an artificial symmetry group. The theory was applied to calculate the rovibrational levels of CO_2 .

The Auger spectrum of ozone is the object of the paper by Taioli and Simonucci [10]. The authors present a first-principles method to calculate and interpret core-electron spectra and then apply the theoretical results to the K-LL Auger and autoionization spectra of ozone, whose role in our atmosphere is well known. A good comparison is shown between the Auger experimental spectrum K-LL (K = $1a_1$) and the theoretical simulation after the convolution of the line shape was considered to account for the experimental broadening. The authors point out that the calculation method may be applied to other molecular systems due to the polycentric nature of their basis functions.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Herzberg, G. Electronic Spectra and Electronic Structure of Poly-atomic Molecules. In *Molecular Spectra and Molecular Structure;* Van Nostrand Reinhold: New York, NY, USA, 1966.
- 2. Califano, S. Vibrational States; Wiley: New York, NY, USA, 1976.
- 3. McWeeny, R. Symmetry. An Introduction to Group Theory and Its Applications; Dover: New York, NY, USA, 2002.
- 4. Zewail, A.H. Femtochemistry: Ultrafast Dynamics of the Chemical Bond; World Scientific: London, UK, 1994.
- 5. Szabo, A.; Ostlund, N.S. *Modern Quantum Chemistry. Introduction to Advanced Electronic Structure Theory;* Dover: New York, NY, USA, 1966.
- 6. Ragnoni, E.; Catalini, S.; Becucci, M.; Lapini, A.; Foggi, P. Linear and non-linear middle infrared spectra of Penicillin G in the CO stretching mode region. *Symmetry* **2021**, *13*, 106. [CrossRef]
- 7. Al-Majid, A.M.; Haukka, M.; Soliman, S.M.; Alamary, A.S.; Alshahrani, S.; Ali, M.; Islam, M.S.; Barakat, A. X-ray Crystal Structure and Hirshfeld Analysis of Gem-Aminals Based Morpholine and Pyrrolidine Moieties. *Symmetry* **2021**, *13*, 20. [CrossRef]
- Tao, Y.; Zhang, L.; Zou, W.; Kraka, E. Equilibrium Geometries, Adiabatic Excitation Energies and In-trinsic C=C/C-H Bond Strengths of Ethylene in Lowest Singlet Excited States Described by TDDFT. Symmetry 2020, 12, 1545. [CrossRef]
- 9. Mellor, T.M.; Yurchenko, S.N.; Jensen, P. Artificial Symmetry for Calculating Vibrational Energies of Linear Molecules. *Symmetry* **2021**, *13*, 548. [CrossRef]
- 10. Taioli, S.; Simonucci, S. The Resonant and Normal Auger spectra of Ozone. Symmetry 2021, 13, 516. [CrossRef]