1. Resonance Raman Optical Activity Shows Unusual Structural Sensitivity for Systems in Resonance with Multiple Excited States: Vitamin B12 Case

By Machalska, Ewa; Zajac, Grzegorz; Gruca, Anna; Zobi, Fabio; Baranska, Malgorzata; Kaczor, Agnieszka Justyna
From Journal of Physical Chemistry Letters (2020), Ahead of Print. Language: English, Database: CAPLUS, DOI:10.1021/acs.jpclett.0c01218

In this work cobalamins with different upper axial substituents and a cobalamin deriv. with a ring modification were studied using chiroptical spectroscopies, in particular resonance Raman Optical Activity (RROA) to shed light on influence of structural modifications on RROA spectra in these strongly chiral systems in resonance with multiple excited states at 532 nm excitation. We have demonstrated that for these unique systems RROA possesses augmented structural specificity, surpassing resonance Raman spectroscopy and enabling at the same time measurement of cobalamins at fairy low concns. of ca. 10-5 mol dm-3. The enhanced structural specificity of RROA is a result of bisignate spectra due to resonance via more than one electronic state. Observation of increased structural capability of RROA for cobalamins opens a new perspective for studying chiral properties of other biol. systems incorporating d-metal ions.

2. Binuclear Lanthanide(III) Complexes with Chiral Ligands: Dynamic Equilibria in Solution and Binding with Nucleotides Studied by Spectroscopic Methods

By Sahoo, Jashobanta; Wu, Tao; Klepetarova, Blanka; Valenta, Jan; Bour, Petr
From ChemPlusChem (2020), 85(4), 694-700. Language: English, Database: CAPLUS, DOI:10.1002/cplu.202000182

Binuclear lanthanide complexes of Eu(III) and Sm(III) were obtained in the presence of chiral ligand 1,2-(R,R+S,S)-N,N'-bis(2-pyridylmethylene),2-diamine. An unusual structure of the Eu(III) compd. with two lanthanide atoms connected through two chlorines was detd. by X-ray crystallog. In soln., the dimer coexists with a monomeric complex, and the stability of the binuclear form depends on the solvent and concn. The dimer-monomer equil. was monitored by circularly polarized luminescence (CPL) measured on a Raman optical activity (ROA) spectrometer, where both forms provided large CPL anisotropic ratios of up to 5.6×10^{-2}. Monomer formation was favored in water, whereas the dimer was stabilized in methanol. When mixed with adenosine phosphates, AMP gave much smaller CPL than ADP and ATP, indicating a high affinity of the Eu (III) complex for the phosphate group, which in connection with the ROA/CPL technique can be developed into a bioanal. probe.

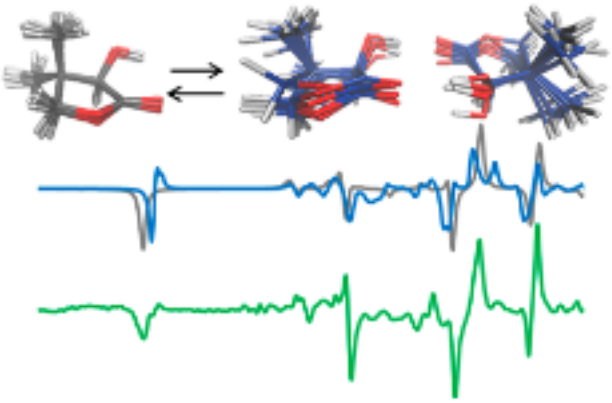
3. Raman Optical Activity of Glucose and Sorbose in Extended Wavenumber Range

By Palivec, Vladimir; Michal, Pavel; Kapitan, Josef; Martinez-Seara, Hector; Bour, Petr
From ChemPhysChem (2020), Ahead of Print. Language: English, Database: CAPLUS, DOI:10.1002/cphc.202000261

Raman optical activity (ROA) is pursued as a promising method for structural analyses of sugars in aq. solns. In the present study, exptl. Raman and ROA spectra of glucose and sorbose obtained in an extended range (50-4000 cm^{-1}) are interpreted using mol. dynamics and d. functional theory, with the emphasis on CH stretching modes. A reasonable theor. basis for spectral interpretation was obtained already at the harmonic level. Anharmonic corrections led to minor shifts of band positions (up to 25 cm^{-1}) below 2000 cm^{-1}, while the CH stretching bands shifted more, by ~180 cm^{-1}, and better reproduced the expt. However, the anharmonicities could be included on a relatively low approxn. level only, and they did not always improve the harmonic band shapes. The dependence on the structure and conformation shows that the CH stretching ROA spectral pattern is a sensitive marker useful in saccharide structure studies.

4. Solvent Effects and Aggregation Phenomena Studied by Vibrational Optical Activity and Molecular Dynamics: The Case of Pantolactone

By Ghidinelli, Simone; Abbate, Sergio; Koshoubu, Jun; Araki, Yasuyuki; Wada, Takehiko; Longhi, Giovanna
From Journal of Physical Chemistry B (2020), Ahead of Print. Language: English, Database: CAPLUS, DOI:10.1021/acs.jpcb.0c01483



Raman and Raman Optical Activity (ROA), IR and Vibrational CD (VCD) spectra of (R)- and (S)-pantolactone have been recorded in three solvents. ROA has been employed on water and DMSO solns., VCD on DMSO and CCl_4 solns. In the last solvent, monomer-dimer equil. is present. Due to the low conformational flexibility of the isolated mol. and to the possibility of aggregation, this compd. has been used here to test different protocols for computation of the spectroscopic responses taking into account solvent effects. Mol. Dynamics (MD) simulations have been employed together with statistical clustering methods based on collective variables to ext. the structures needed to calc. the spectra. Quantum Mech. DFT calcns. based on PCM are compared with approaches based on different representations of the solvent shell (MM or QM level). Appropriate treatment of the solvent permits to obtain good band-shapes, with the added advantage that the MD anal. allows one to take into account flexibility of dimeric structures justifying the broadness of obsd. bands and the absence of intense VCD couplets in the carbonyl and OH stretching regions.

5. TRAVIS - A free analyzer for trajectories from molecular simulation

By Brehm, M.; Thomas, M.; Gehrke, S.; Kirchner, B.
From Journal of Chemical Physics (2020), 152(16), 164105/1-164105/20. Language: English, Database: CAPLUS, DOI:10.1063/5.0005078

TRAVIS ("Trajectory Analyzer and Visualizer") is a program package for post-processing and analyzing trajectories from mol. dynamics and Monte Carlo simulations, mostly focused on mol. condensed phase systems. It is an open source free software licensed under the GNU GPL, is platform independent, and does not require any external libraries. Nine years after the original publication of TRAVIS, we highlight some of the recent new functions and features in this article. At the same time, we shortly present some of the underlying algorithms in TRAVIS, which contribute to make trajectory anal. more efficient. Some modern visualization techniques such as Sankey diagrams are also demonstrated. Many anal. functions are implemented, covering structural analyses, dynamical analyses, and functions for predicting vibrational spectra from mol. dynamics simulations. While some of the analyses are known since several decades, others are very recent. For example, TRAVIS has been used to compute the first ab initio predictions in the literature of bulk phase vibrational CD spectra, bulk phase Raman optical activity spectra, and bulk phase resonance Raman spectra within the last few years. (c) 2020 American Institute of Physics.

6. Raman Optical Activity (ROA) as a New Tool to Elucidate the Helical Structure of Poly(phenylacetylene)s

By Palomo, Luis; Rodriguez, Rafael; Medina, Samara; Quinoa, Emilio; Casado, Juan; Freire, Felix; Ramirez, Francisco J.
From Angewandte Chemie, International Edition (2020), 59(23), 9080-9087. Language: English, Database: CAPLUS, DOI:10.1002/anie.202000651

Poly(phenylacetylene)s are a family of helical polymers constituted by conjugated double bonds. Raman spectra of these polymers show a structural fingerprint of the polyene backbone which, in combination with its helical orientation, makes them good candidates to be studied by Raman optical activity (ROA). Four different well-known poly(phenylacetylene)s adopting different scaffolds and ten different helical senses have been prepd. Raman and ROA spectra were recorded and allowed to establish ROA-spectrum/helical-sense relationships: a left/right-handed orientation of the polyene backbone (Mhelix/Phelix) produces a triplet of pos./neg. ROA bands. Raman and ROA spectra of each polymer exhibited the same profile, and the sign of the ROA spectrum was opposite to the lowest-energy electronic CD (ECD) band, indicating a resonance effect. Resonance ROA appears then as an indicator of the helical sense of poly(phenylacetylene)s, esp. for those with an extra Cotton band in the ECD spectrum, where a wrong helical sense is assigned based on ECD, while ROA alerts of this misassignment.

7. Recent Trends in Chiroptical Spectroscopy: Theory and Applications of Vibrational Circular Dichroism and Raman Optical Activity

By Krupova, Monika; Kessler, Jiri; Bour, Petr
From ChemPlusChem (2020), 85(3), 561-575. Language: English, Database: CAPLUS, DOI:10.1002/cplu.202000014

Chiroptical spectroscopy exploring the interaction of matter with polarized light provides many tools for mol. structure and interaction studies. Here, some recent discoveries are reviewed, primarily in the field of vibrational optical activity. Technol. advances results in the development of more sensitive vibrational CD (VCD), Raman optical activity (ROA) or circular polarized luminescence (CPL) spectrometers. Significant contributions to the field also come from the light scattering and electronic structure theories, and their implementation in computer systems. Finally, new chiroptical phenomena have been obsd., such as enhanced CD of biopolymers (protein fibrils, nucleic acids), plasmonic and resonance chirality-transfer ROA expts. Some of them are not yet understood or attributed to instrumental artifacts so far. Nevertheless, these unknown territories also indicate the vast potential of the chiroptical spectroscopy, and their investigation is even more challenging.

8. Theoretical study of the Raman optical activity spectra of [M(en)3]3+ with M = Co, Rh

By Abella, Laura; Ludowieg, Herbert D.; Autschbach, Jochen
From Chirality (2020), 32(6), 741-752. Language: English, Database: CAPLUS, DOI:10.1002/chir.23194

Vibrational Raman optical activity (ROA) spectra were calcd. under off-resonance, near-resonance, and at-resonance conditions for [Co(en)3]3+ (A) and under off-resonance conditions for [Rh(en)3]3+ (B) using a new driver software for calcg. the ROA intensities from complex (damped) time-dependent linear response Kohn-Sham theory. The off-resonance spectra of A and B show many similarities. At an incident laser wavelength of 532 nm, used in com. ROA spectrometers, the spectrum of A is enhanced by near-resonance with the ligand-field transitions of the complex. The near-resonance spectrum exhibits many qual. differences compared with the off-resonance case, but it remains bi-signate. Even under full resonance with the ligand-field electronic transitions, the ROA spectrum of A remains bi-signate when the electronic transitions are broadened such as to yield absorption line widths that are comparable with those in the exptl. UV-vis absorption and electronic CD spectra.

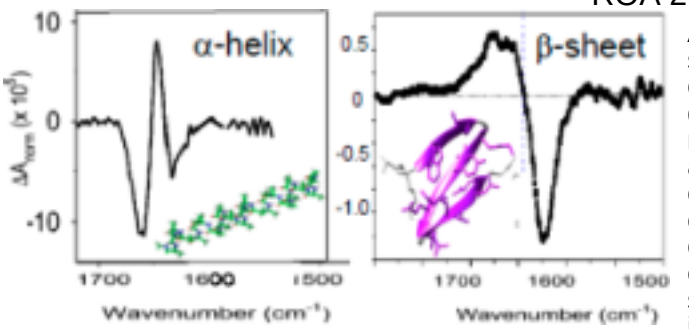
9. Pressure dependence of vibrational optical activity of model biomolecules. A computational study

By Plamitzer, Lubos; Bour, Petr
From Chirality (2020), 32(5), 710-721. Language: English, Database: CAPLUS, DOI:10.1002/chir.23216

Change of mol. properties with pressure is an attracting means to regulate mol. reactivity or biol. activity. However, the effect is usually small and so far explored rather scarcely. To obtain a deeper insight and est. the sensitivity of vibrational optical activity spectra to pressure-induced conformational changes, we investigate small model mols. The Ala-Ala dipeptide, isomaltose disaccharide and adenine-uracil dinucleotide were chosen to represent three different biomol. classes. The pressure effects were modeled by mol. dynamics and d. functional theory simulations. The dinucleotide was found to be the most sensitive to the pressure, whereas for the disaccharide the smallest changes are predicted. Pressure-induced relative intensity changes in vibrational CD and Raman optical activity spectra are predicted to be 2-3-times larger than for non-polarized IR and Raman techniques.

10. Structure of Condensed Phase Peptides: Insights from Vibrational Circular Dichroism and Raman Optical Activity Techniques

By Keiderling, Timothy A.
From Chemical Reviews (Washington, DC, United States) (2020), 120(7), 3381-3419. Language: English, Database: CAPLUS, DOI:10.1021/acs.chemrev.9b00636



A review. Peptides and proteins are naturally chiral mol. systems so that sensing their structure and conformation with chirality-based spectral methods is an obvious and long-used diagnostic application. Extending chiroptical techniques to measurement of vibrational transitions, as vibrational CD (VCD) and Raman optical activity (ROA), expands the no. and types of excitations available that might provide structural insight and can provide an alternate and, in some cases, a more distinctive conformational probe. Since the dominant repeating structural element in peptides is the locally achiral amide group, VCD senses the polymeric structure through amide coupling, which is directly dependent on secondary structure. Detn. of the type and relative contribution of these structural components through empirical correlation with spectral character has been the main application of VCD for peptides and proteins, although this is now reinforced by extensive theor. modeling. Monitoring structural and conformational change induced by environmental perturbations provides another important application. More recently, VCD has been used to detect morphol. variations in fibril states of aggregated peptides and proteins. ROA has parallel secondary structural sensitivities, with more applications for proteins than peptides, and has more sensitivity to local configuration and side chains. This review covers the range of peptide studies done with VCD and extends them to compare with example protein and ROA applications.

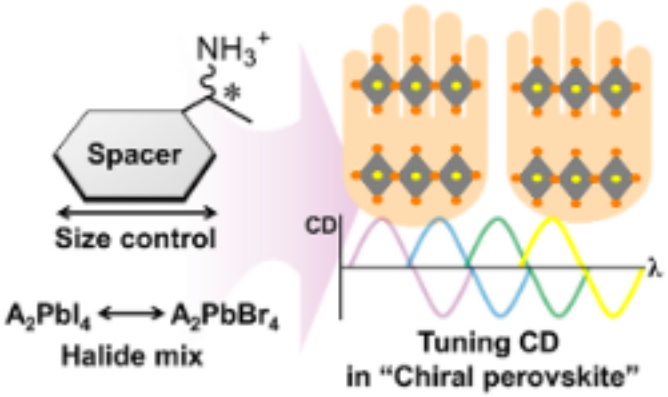
11. Vibrational optical activity: From discovery and development to future challenges

By Nafie, Laurence A.
From Chirality (2020), 32(5), 667-692. Language: English, Database: CAPLUS, DOI:10.1002/chir.23191

Vibrational optical activity (VOA) consisting of IR vibrational CD (VCD) and vibrational Raman optical activity (ROA) was predicted, discovered, and confirmed between 1971 and 1975. My path to VOA was mentored by three pioneers of chirality and vibrational spectroscopy: Professors Albert Moscowitz, Warner L. Peticolas, and Philip J. Stephens, and while they are no longer alive today, the Chirality Medal, my award address, and this paper are dedicated to each of them. Since the discovery of VOA, a no. of key advances have made possible the current era of widespread applications. The principal instrumental advances were Fourier-transform VCD (FT-VCD) and multichannel charge coupled detector (CCD) ROA. Computational advances include the first complete quantum chem. formulation of VCD leading to the magnetic field perturbation (MFP) and the nuclear velocity perturbation (NVP) theories. The strength of VOA is the comparison between measured and calcd. spectra that enables the detn. of abs. configuration and soln.-state conformations. More recently, VCD has uncovered supramol. chirality in amyloid fibrils and ROA to high-order protein structure. Future challenges for VOA include describing the effects of weak intermol. interactions, transfer of chirality, solvent effects, supramol. chirality, and the generation of nuclear velocity electron c.d.

12. Chiral 2D Organic Inorganic Hybrid Perovskite with Circular Dichroism Tunable Over Wide Wavelength Range

By Ahn, Jihoon; Ma, Sunihl; Kim, Ji-Young; Kyhm, Jihoon; Yang, Wooseok; Lim, Jung Ah; Kotov, Nicholas A.; Moon, Jooho
From Journal of the American Chemical Society (2020), 142(9), 4206-4212. Language: English, Database: CAPLUS, DOI:10.1021/jacs.9b11453



The effect of chem.-compn. modification on the chiroptical property of chiral org. NH_4^+ cation-contg. org. inorg. hybrid perovskite (chiral OIHP) is studied. Varying the mixing ratio of bromide and iodide anions in S- or $(R\text{-}C_6H_5CH_2MeNH_3)_2PbI_{4(1-x)}Br_{4x}$ modifies the band gap of chiral OIHP, leading to a shift of the CD signal from 495 to 474 nm. An abrupt cryst. structure transition occurs, and the CD signal is turned off when iodide-determinant phases are transformed into the bromide-determinant phase. To obtain CD in the wavelength range where the bromide-determinant phase is supposed to exhibit chiroptical activity, i.e., <474 nm, S- or $R\text{-}C_{12}H_7CH_2MeNH_3$ with a larger spacer group can be adopted; the CD signal can be further blue-shifted to ~375 nm. Here, chem.-compn. modification of chiral OIHP affects the chiroptical properties of chiral OIHP in 2 ways: (1) tuning the wavelength of CD by modulating the excitonic band structure and (2) switching the CD on and off by inducing a cryst.-structure change. These properties can be used for structural engineering of high-performance chiroptical materials for spin-polarized light-emitting devices and polarization-based optoelectronics.

13. Simulation of Raman and Raman optical activity of saccharides in solution

By Palivec, Vladimir; Kopecky, Vladimir, Jr.; Jungwirth, Pavel; Bour, Petr; Kaminsky, Jakub; Martinez-Seara, Hector
From Physical Chemistry Chemical Physics (2020), 22(4), 1983-1993. Language: English, Database: CAPLUS, DOI:10.1039/c9cp05682c

Structural studies of sugars in soln. are challenging for most of the traditional anal. techniques. Raman and Raman optical activity (ROA) spectroscopies were found to be extremely convenient for this purpose. However, Raman and ROA spectra of saccharides are challenging to interpret and model due to saccharides' flexibility and polarity. In this study, we present an optimized computational protocol that enables the simulation of the spectra efficiently. Our protocol, which results in good agreement with expts., combines mol. dynamics and d. functional theory calcns. It further uses a smart optimization procedure and a novel adaptable scaling function. The numerical stability and accuracy of individual computational steps are evaluated by comparing simulated and exptl. spectra of D-glucose, D-glucuronic acid, N-acetyl-D-glucosamine, Me β-D-glucopyranoside, Me β-D-glucuronide, and Me β-N-acetyl-D-glucosaminide. Overall, our Raman and ROA simulation protocol allows one to routinely and reliably calc. the spectra of small saccharides and opens the door to advanced applications, such as complete 3-dimensional structural detn. by direct interpretation of the exptl. spectra.

14. Vibrational Raman optical activity of camphor: The importance of electric-dipole-electric-quadrupole polarizability contribution

By Johnson, Jordan L.; Zajac, Grzegorz; Baranska, Malgorzata; Polavarapu, Prasad L.
From Journal of Raman Spectroscopy (2020), 51(4), 669-679. Language: English, Database: CAPLUS, DOI:10.1002/jrs.5829

The importance of the elec.-dipole-elec.-quadrupole polarizability contribution to the vibrational Raman optical activity (VROA) and dimensionless circular intensity difference spectra of (1S)-camphor is examd. The spectra are simulated with and without this tensor contribution using d. functional theory calcns., and similarity is evaluated for each against the exptl. spectra. Careful examn. of the comparison between exptl. and calcd. spectra reveals multiple vibrational bands, in the ~1,130-950 cm^{-1} region, originating from -C-H bending vibrations that are dominated by the elec.-dipole-elec.-quadrupole polarizability contributions. The similarity overlap anal. also reveals that the similarity overlap between exptl. and predicted spectra in the measured spectral range increases, by up to 12%, when elec.-dipole-elec.-quadrupole polarizability contributions are included. The neg. VROA band at 1,125 cm^{-1} in the exptl. spectrum of (1S)-(-)-camphor can only be reproduced in the predicted spectra when elec.-dipole-elec.-quadrupole polarizability contribution is included. Investigations on addnl. mols. indicated that (a) two exptl. VROA bands of (1S,4R)-(+)-fenchone at ~1,740 and 220 cm^{-1} originate from dominating elec.-dipole-elec.-quadrupole polarizability contribution and (b) the sym. and antisym. ring deformation modes of dimethyloxirane have dominating elec.-dipole-elec.-quadrupole polarizability contribution. These observations establish the importance of elec.-dipole-elec.-quadrupole polarizability contribution to VROA for the first time.

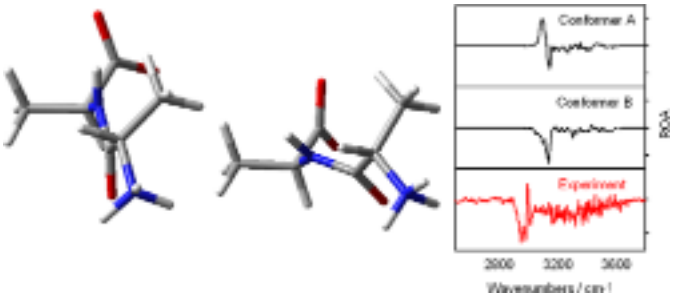
15. Recent advances in nano-photonic techniques for pharmaceutical drug monitoring with emphasis on Raman spectroscopy

By Frosch, Timea; Knebl, Andreas; Frosch, Torsten
From Nanophotonics (2020), 9(1), 19-37. Language: English, Database: CAPLUS, DOI:10.1515/nanoph-2019-0401

A review. Innovations in Raman spectroscopic techniques provide a potential soln. to current problems in pharmaceutical drug monitoring. This review aims to summarize the recent advances in the field. The developments of novel plasmonic nanoparticles continuously push the limits of Raman spectroscopic detection. In surface-enhanced Raman spectroscopy (SERS), these particles are used for the strong local enhancement of Raman signals from pharmaceutical drugs. SERS is increasingly applied for forensic trace detection and for therapeutic drug monitoring. In combination with spatially offset Raman spectroscopy, further application fields could be addressed, e.g. in situ pharmaceutical quality testing through the packaging. Raman optical activity, which enables the thorough anal. of specific chiral properties of drugs, can also be combined with SERS for signal enhancement. Besides SERS, micro- and nano-structured optical hollow fibers enable a versatile approach for Raman signal enhancement of pharmaceuticals. Within the fiber, the vol. of interaction between drug mols. and laser light is increased compared with conventional methods. Advances in fiber-enhanced Raman spectroscopy point at the high potential for continuous online drug monitoring in clin. therapeutic diagnosis. Furthermore, fiber-array based non-invasive Raman spectroscopic chem. imaging of tablets might find application in the detection of substandard and counterfeit drugs. The discussed techniques are promising and might soon find widespread application for the detection and monitoring of drugs in various fields.

16. Understanding CH-Stretching Raman Optical Activity in Ala-Ala Dipeptides

By Hope, Marius; Sebestik, Jaroslav; Kapitan, Josef; Bour, Petr
From Journal of Physical Chemistry A (2020), 124(4), 674-683. Language: English, Database: CAPLUS, DOI:10.1021/acs.jpca.9b10557



Raman optical activity (ROA) becomes a std. method to monitor peptide conformation. However, the signal in the CH-stretching region is particularly difficult to measure and interpret. In order to understand the structural information contained in this part of the spectrum, data obtained on a custom-made ROA spectrometer have been analyzed for the model Ala-Ala mol., with the help of mol. dynamics (MD) and d. functional theory computations. The Ala-Ala enantiomers provided the "mirror image" spectra, which proves that the signal can be reliably measured, in spite of a rather low ROA/Raman intensity ratio (~2 × 10^{-5}). The theor. modeling indicated that the most intense ROA bands can be attributed to locally asym. CH_3 and αCH vibrations, whereas sym. Me CH-stretching modes contribute less. A simplified model made it possible to est. the contribution of local chirality of the two alanine residues to the resultant ROA pattern. In spite of a significant frequency shift (over 100 cm^{-1}) because of the anharmonic corrections, the harmonic level was able to explain the main spectral features. The anharmonic corrections were treated by second-order perturbation and limited vibrational CI procedures. This allowed for assignment of some weaker spectral features because of the combination and overtone vibrations. The results show that the peptide CH-stretching ROA signal contains rich structural information, reflecting also the peptide environment. The exptl. data, however, need to be deciphered by relatively complex and time-consuming spectral simulations.

17. Optical properties of S2 and S3 excited states of protonated Schiff-base retinal chromophores in TPA, ECD and ROA

By Wang, Xinxin; Yan, Penji; Mu, Xijiao
From Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy (2020), 228, 117532. Language: English, Database: CAPLUS, DOI:10.1016/j.saa.2019.117532

The electronic transitions of the protonated Schiff base of 11-cis-retinal (PSB11) and protonated Schiff bases of all-trans retinal (PSBT) for the second or higher electronic excited states are hard to be obsd. exptl., due to weak intensities of electronic state excitations. In this paper, we propose visualizations method to investigate these weak electronic state transitions of PSB11 and PSBT, using two-photon absorption (TPA), electronic CD (ECD) and Raman optical activity (ROA) spectra. Because of the resonance excitations of PSB11 and PSBT in TPA, the transition intensity of the third electronic state is significantly enhanced, which are much larger than that of S_1 and S_2 electronic transitions. The charge transfer and electron-hole coherence of these electronic transitions in each step in TPA are visualized with charge difference d. and transition d. matrix. Also, the strong absorptions of S_1 and S_2 electronic excited states are obsd. with ECD spectra, and the phys. mechanism of elec. and magnetic interactions for these electronic transitions are revealed by visualization method. The large intensity of ROA at S_3 excited state results from transition elec. and magnetic dipole interactions, not from transition elec. dipole and transition elec. quadrupole interactions. Our results provide a new visualization method to study the optical properties of biol. system using TPA and ECD spectra.

18. Vibrational spectra and theoretical calculations of a natural pentacyclic triterpene alcool isolated from Mucuna pruriens

By Castaneda, Sandra M. B.; Alvarenga, Elson S.; Demuner, Antonio J.; Guimaraes, Luciano M.
From Structural Chemistry (2020), 31(2), 599-607. Language: English, Database: CAPLUS, DOI:10.1007/s11224-019-01431-9

Nematode control is a significant problem in agriculture industry all over the world. The control is often made with the use of toxic chems. which can bring detrimental effect to humans, animals, and the environment. Therefore, developing an alternative method of control has become an area of interest such as use of antagonistic plant. Among the variety of antagonist plant species, Mucuna genus are most commonly used. We have carried out a study of the secondary metabolites present on the aerial parts of Mucuna pruriens var. utilis, from which it was isolated and purified a pentacyclic triterpene alc., named glutinol. This is the first time the isolation of glutinol is described from this plant species. Identification of this natural product was carried out using IR, Raman, and NMR spectroscopies. The assignment of the vibrational frequencies was assisted by theor. calcns. using two functionals (HF and B3LYP). Raman optical activity (ROA) frequencies were calcd. to assist in te detailed identification of the broad band obsd. at 2926 cm^{-1} in the exptl. Raman spectrum. The calcd. ROA spectra for glutinol (S configuration for the carbon bonded to the hydroxyl group) and R-glutinol (R configuration for the carbon bonded to the hydroxyl group) are discussed to show the potential of this technique to det. the abs. configuration of natural products.

19. Solvent Effects and Aggregation Phenomena Studied by Vibrational Optical Activity and Molecular Dynamics: The Case of Pantolactone

By Ghidinelli Simone; Abbate Sergio; Longhi Giovanna; Abbate Sergio; Longhi Giovanna; Koshoubu Jun; Araki Yasuyuki; Wada Takehiko
From The journal of physical chemistry. B (2020), 124(22), 4512-4526, Language: English, Database: MEDLINE

Raman and Raman optical activity (ROA), IR, and vibrational circular dichroism (VCD) spectra of (R)- and (S)-pantolactone have been recorded in three solvents. ROA has been employed on water and DMSO solutions, VCD on DMSO and CCl4 solutions. In the last solvent, monomer-dimer equilibrium is present. Due to the low conformational flexibility of the isolated molecule and to the possibility of aggregation, this compound has been used here to test different protocols for computation of the spectroscopic responses taking into account solvent effects. Molecular dynamics (MD) simulations have been carried out together with statistical clustering methods based on collective variables to extract the structures needed to calculate the spectra. Quantum mechanical DFT calculations based on PCM are compared with approaches based on different representations of the solvent shell (MM or QM level). Appropriate treatment of the solvent permits obtaining of good band-shapes, with the added advantage that the MD analysis allows one to take into account flexibility of dimeric structures justifying the broadness of observed bands and the absence of intense VCD couplets in the carbonyl and OH stretching regions.