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Virtual Issue on Chiroptical Spectroscopy

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Chiroptical spectroscopy, defined broadly as the discrimination of chiral structures and processes through the agency of electromagnetic radiation, has a long and venerable history in the molecular sciences, starting with the essential roles that it played in establishing the foundations of stereochemistry at the dawn of the 19th century.[1,2] The well-known linear chiroptical effects of circular birefringence (CB) and circular dichroism (CD) respectively impart a characteristic differential retardation and attenuation on right-circular and left-circular states of polarization, the origins of which can be traced to concerted electric-dipole (E1) and magnetic-dipole (M1) interactions that occur in an isotropic chiral medium.[3] The resulting spectral signatures take the form of a dispersive rotation (via nonresonant CB) and an absorptive elliptization (via resonant CD) for a traversing beam of plane-polarized light, which commonly are measured in either the ultraviolet/visible or infrared regions to access features attributable to electronic or vibrational transitions. Underlying the many applications of chiroptical spectroscopy is the ability to distinguish enantiomers (which display identical physicochemical properties in the absence of a chiral-discriminating agent like polarized light) by the opposite sign, yet equal magnitude, of their wavelength-resolved optical activities (i.e., a term referring to chiroptical phenomena collectively), with complementary circular-differential methods based on Raman-scattering (Raman optical activity or ROA) and spontaneous-emission (circularly polarized luminescence or CPL) detection schemes offering additional advantages in terms of sensitivity and selectivity.[4] Ongoing advances in experimental and theoretical methods have greatly expanded the complexity of systems amendable to detailed chiroptical investigations and have enhanced the scope of information gleaned from such studies, thus empowering a variety of new research efforts such as those designed to probe oriented/crystalline materials (where higher-order multipole interactions must be considered), to extend quantitative measurements of chirality to new spectral regions and sample environments (e.g., cryogenic molecular beams), and to implement coherent/nonlinear forms of chiro-specific spectroscopy that promise to bestow unique capabilities.

The 33 papers composing this Virtual Issue on chiroptical spectroscopy have been curated primarily from the pages of *The Journal of Physical Chemistry A* over the past 2−3 years, with a smaller number of publications drawn from *The Journal of Physical Chemistry Letters* during the same time period. Although the selected contributions have been separated into five (5) thematic categories to highlight the broad range of fundamental and applied activities encompassed by this vibrant area of research, it must be emphasized that the imposed segregation of topics is neither absolute nor rigorous, with the innovations emerging from one category inevitably serving to guide, interpret, and/or validate the findings made in others.

THEORETICAL ADVANCES

The advent of robust, yet accessible, theoretical paradigms for predicting and interpreting the signatures of optical activity from first-principles has led to a veritable renaissance in chiroptical spectroscopy, empowering the quantitative application of such discriminatory probes to diverse problems of fundamental and practical significance. Aside from ongoing efforts to improve the efficiency and reliability of established computational protocols based primarily on variants of density-functional theory (DFT) and coupled-cluster (CC) theory, a variety of technical and conceptual advancements designed to enhance the nature and scope of structural/dynamical information extracted from chiral targets have been reported.

Among notable advances in theory are continuing efforts to incorporate the effects of anharmonicity (mechanical, electrical, and magnetic), energy resonances, and large-amplitude motions into treatments of vibrational optical activity (VOA), thus enabling the locations and signed intensities of spectral features to be predicted quantitatively in a semiautonomous fashion that does not rely on *ad hoc* assumptions. Such endeavors are epitomized by the work of Paoloni et al.[5] which combined spectroscopic measurements and computational analyses to interpret the complex solution-phase vibrational absorption (VA) and vibrational circular dichroism (VCD) spectra displayed by chiral diols over the mid-IR and near-IR regions. Parallel efforts by Jähnigen and co-workers[6] reported a new theoretical framework for predicting solid-state VCD spectra directly from first-principles (DFT) molecular-dynamics simulations. In particular, these authors addressed long-standing issues related to the coordinate-origin dependence of the magnetic (transition) moment pseudovector, with the resulting gauge freedom enabling requisite rotational strengths for VOA to be calculated uniformly in the presence of periodic boundary conditions. To address recent controversies[7,8] surrounding the interpretation of resonance Raman optical activity (RROA) spectroscopy, the Bouř group[9] elaborated and tested computational protocols for extracting reliable RROA

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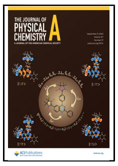

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signatures in the presence of significant ECD-Raman contamination, the latter of which arises from resonant circular-differential absorption of unpolarized incident light by the chiral solute and subsequent nonresonant circular-differential scattering by the achiral solvent.

Scott and co-workers[10] reported the first *ab initio* calculations of excited-state chiroptical properties performed at correlated-wavefunction levels of theory by exploiting a novel algebraic-diagrammatic construction of the polarization propagator, thereby extending robust predictions of ground-state electronic circular dichroism (ECD) to their excited-state counterparts (ES-ECD) and establishing a theoretical framework for interpreting transient pump−probe experiments capable of chiral discrimination. The unique ability of theory to dissect complex phenomena into discrete contributions that reveal the origins of observed behavior was illustrated by Balduf and Caricato[11] in a comprehensive assessment of their $\tilde{S}$ approach for decomposing predictions of dispersive optical activity across a chemically meaningful configuration space. In particular, novel insights into key structure−property relationships were obtained by projecting the E1-M1 rotatory strengths responsible for electronic circular birefringence (ECB) onto the coupled pairs of occupied and virtual molecular orbitals that constitute each participating excited-state configuration.

The ability of theory to open entirely new vistas in the realm of chiroptical spectroscopy was highlighted by Vu et al.[12] in their development of a cavity quantum-electrodynamics generalization of time-dependent DFT (TDDFT) that included provisions for the relaxation of ground-state Kohn−Sham orbitals in the presence of an optical cavity. Building on recent experimental demonstrations of selective photochemical enrichment for diastereomers of BINOL (1,1′-bi-2-naphthol) in which one hydroxyl moiety had been functionalized by a chiral directing group,[13] these authors systematically explored the intriguing possibility of altering the operative excited-state proton-transfer mechanism for isomerization though selective strong matter-field coupling, thereby controlling the chirality and the diastereomeric purity of resulting photoproducts.

NATURE OF CHIRAL INTERACTIONS

Chiroptical signatures, in general, exhibit sensitivity not only to the inherent structures of chiral molecules but also to the resulting favored conformations, which arise from intricate intra- and intermolecular interactions among chiral entities. The ensuing interplay of enantiospecific hetero/homochiral interactions may lead to some fascinating observations. For example, Favereau et al.[14] harnessed the distinct molecular packing of enantiomers as opposed to racemic mixtures to investigate persistent metal-free room-temperature phosphorescence (RTP) materials in a study that combined X-ray diffraction with photophysical and ECD analyses. This work demonstrated the pivotal role played by binary heterochiral and homochiral interactions in stabilizing the triplet excited state, resulting in RTP efficiencies for enantiopure systems higher than those of their racemic counterparts and highlighting the potency of subtle intermolecular forces in influencing supramolecular properties. Similarly, a study of circularly polarized luminescence materials by Yao and colleagues[15] showcased an interesting phenomenon wherein CPL signals experience amplification due to the highly ordered spiral arrangement of dyes within a well-organized liquid-crystal motif, the formation of which was facilitated by self-aggregation. Such organized assembly offers an ingenious and promising strategy for engineering high g_{lum} materials, where the dissymmetry ratio or *g*-factor is a common optical-activity metric that quantifies the magnitude of circular-differential chiroptical response relative to the total strength of absorption (for ECD and VCD) or emission (for CPL). The identification of a distinct ROA feature in green-light-absorbing proteorhodopsin enabled Unno and co-workers[16] to pinpoint the conformation of the associated retinal Schiff-base chromophore, revealing that the polyene chain on the beta-ionone ring side was bent out-of-plane.

To delve deeper into the homo/heterochiral interactions between pairs of chiral molecules, researchers have combined detailed gas-phase spectroscopic investigations with DFT calculations. For example, Andersson et al.[17] engaged infrared multiphoton dissociation (IRMPD) spectroscopy to elucidate disparities in the intermolecular interactions exhibited by homochiral and heterochiral protonated asparagine dimers. Similarly, Blodgett et al.[18] applied IR-UV double-resonance probes to corroborate enantiospecific interactions influencing the conformational preferences of chiral helices in the gas phase. In both of these studies, DFT calculations and energy-decomposition schemes like symmetry adapted perturbation theory (SAPT), as explored extensively by Korona,[19] Rong,[20] and their respective co-workers, were instrumental in unraveling the nature of intramolecular and intermolecular noncovalent interactions.

SOLVATION PHENOMENA

Because chiroptical spectroscopy is exquisitely sensitive to the details of molecular structure, the geometrical relaxation and differential stabilization of individual conformations that take place in the presence of a solvent medium can radically alter the magnitude and the sign of observed spectral features. This characteristic behavior was exploited by Matsu and Gekko[21] to probe the aqueous dynamics of monosaccharides, where the use of vacuum-ultraviolet radiation in a synchrotron-based ECD spectrometer afforded access to high-energy $\sigma^* \leftarrow n$ transitions of oxygen-bearing moieties (e.g., hydroxyl groups and acetyl bonds) that facilitated a conformer-specific decomposition of chiroptical signatures and allowed the opposing effects of intramolecular hydrogen bonding and intermolecular hydration events to be distinguished. Hartweg et al.[22] explored the molecular-level changes accompanying the onset of condensation by comparing angle-resolved valence photoelectron spectra recorded for isolated proteinogenic amino-acid molecules with those obtained for their amorphous homochiral and racemic aerosol particles. These authors found the chiro-specific forward/backward asymmetry imprinted onto the spatial distribution of electrons when an isotropic ensemble of chiral species is photoionized by circularly polarized radiation (a chiroptical effect known as photoelectron circular dichroism or PECD) is retained to a surprising extent in condensed-phase environments.

To elucidate the impact of solvation on dispersive electronic optical activity, Craft et al.[23] examined the optical rotatory dispersion (ORD or wavelength-resolved ECB) for two saturated cyclic amines under solvated and isolated conditions. The latter vapor-phase work exploited the long-pathlength (>1 km) sensitivity of cavity ring-down polarimetry to measure intrinsic (solvent-free) benchmarks for specific rotation, thus permitting the extent and direction of solvent-induced effects to be determined unambiguously while simultaneously assessing the reliability of various theoretical approaches to model the ensemble-averaged properties of conformationally flexible species. D'Cunha and Crawford[24] undertook a systematic investigation of quantum-chemical protocols for evaluating the nonadditive contributions to ORD induced by interactions between solute and solvent degrees of freedom, with atomistic molecular-dynamics (MD) simulations of explicit solute−solvent coupling being performed on rigid epoxide and episulfide derivatives. In addition to exploring complex phenomena such as "chiral imprinting" whereby the handedness of a chiral solute is transcribed onto the surrounding achiral solvent, the inherent structural sensitivity of chiroptical spectroscopy was manifest in the magnitude and the sign of computed response, which varied markedly as the spatial arrangement of the solvent and the vibrational displacement of the solute evolved. The ability of theory to guide the rationale design of chiral systems possessing desired absorptive (ECD) and emissive (CPL) properties that may be affected strongly by their interactions with the surrounding environment was examined in detail by Hillers-Bendtsen et al.[25] for a series of azaoxahelicenes by combining MD simulations of explicit solute−solvent coupling with a polarizable-embedding treatment for long-range (bulk) electrostatic interactions.

Underlying the above efforts is the need to understand the structural/dynamical consequences of chiral solute−solvent coupling, as exemplified by the incipient-solvation studies of Carlson and co-workers.[26] These authors combined high-resolution microwave spectroscopy conducted in a cryogenic molecular beam with extensive computational analyses to interrogate the nascent steps of hydration in binary adducts formed between a chiral fluoroalcohol and water. The identification of dynamical-averaging processes, whereby large-amplitude motion of the water solvent induces a tunneling-mediated exchange of its bound and free hydrogen atoms that permitted a computed minimum of the potential-energy surface to be bridged in a barrierless fashion, offers a note of caution for the unchecked reliance on theoretical predictions of equilibrium geometries.

INTERPRETATION OF CHIROPTICAL SPECTROSCOPY

Building on remarkable theoretical advancements, Johnson and Polavarapu[27] demonstrated the ability to deduce the three-dimensional structures of small chiral molecules solely from their chemical formulas by directly comparing measured and simulated chiroptical data sets through quantitative similarity analyses. For more intricate and flexible cyclic peptides, Ruud and collaborators[28] devised a computational strategy built upon the Conformer-Rotamer Ensemble Sampling Tool (CREST) developed by Grimme and associates.[29,30] This comprehensive approach facilitated the precise identification of all significant conformers/stereoisomers, enabling the assignment of complex VCD spectra and the extraction of stereochemical information for the targeted peptides. One of the primary objectives for such computational efforts is to provide user-friendly, "black-box" packages that cater to applied spectroscopists, empowering them to deduce stereospecific structural information accurately and efficiently from experimental chiroptical spectra. Toward this goal, Autschbach and his team[31] introduced VROA36, a new database offering simulated ROA spectra for 36 chiral molecules that encompass a total of 93 conformers, some of which are in (near) resonance. This repository of DFT predictions has employed multiple combinations of functionals and basis sets, allowing it to serve as a valuable resource for researchers engaged in chiroptical spectroscopy. The CH stretching region often proves especially challenging to interpret in VOA measurements due to the dominating influence of anharmonicity. Hope and colleagues[32] formulated a streamlined model to effectively address the issue of anharmonicity and extract the rich structural information typically hidden in peptide CH-stretching ROA bands. Factors such as aggregation, lateral extensions, helical structures, and other special properties also can influence chiroptical response. Mahato et al.[33] and Sharma et al.[34] delved into these crucial effects through their ECD and CPL studies of pentacene and helicene, respectively. Finally, the intricate dynamics of vibrational excitation and nuclear motion taking place in the multiphoton PECD of fenchone were investigated by Powis and co-workers.[35] Detailed analyses of the resulting photoelectron angular distributions unveiled substantial differences between the forward/backward chiral-asymmetry parameters determined for $\Delta\nu = 0$ and $\Delta\nu > 0$ vibronic transitions.

NOVEL TECHNIQUES

Over the past few decades, chiroptical spectroscopic techniques have undergone a remarkable evolution, characterized by dynamic advances on multiple fronts. Researchers not only have refined the technical aspects of existing tools but also have ventured into novel territory, employing innovative sample-preparation methodologies such as supersonic free-jet expansions and electrospray ionization assemblies. Moreover, they have extended the scope of chiroptical measurements into the realm of stereochemical imaging and have explored other frontiers that previously were uncharted.

One particularly impactful development has been the emergence of chiral induced spin selectivity (CISS), as extensively reviewed by Naaman and collaborators.[36] Recent experiments have delved into uncovering the CISS mechanism, as well as its manifestation in electronic and magnetic properties of chiral molecules and materials. Naaman and his team suggested a simplified model wherein the spin polarization of a chiral system is enhanced by a spin blockade effect, resulting in substantial spin filtering. More recently, Ye et al.[37] proposed a novel concept, termed "quantum chiral spectroscopy," which leverages the entanglement of two-photon pairs to serve as a coherent probe for generating background-free chiroptical signals. Their theoretical framework elucidates how the quantum spectra of left-handed and right-handed molecules can be differentiated through tailored configurations of such frequency-entangled two-photon pairs. In a notable contribution, Lightner et al.[38] reported an award-winning achievement in the field of ROA spectroscopy.[39] These authors integrated high-frequency polarization modulation into a specially constructed polarimeter, achieving performance on par with existing ROA instruments while reducing opto-mechanical complexity and polarization artifacts. Cho and co-workers[40] utilized vibrational sum-frequency generation, a variant of nonlinear-optical spectroscopy possessing interfacial (surface) specificity, to explore the possibility of realizing background-free chiroptical characterization with enhanced spectral resolution.

Although supersonic free-jet expansions predominantly have been employed in rotational, vibrational, and electronic spectroscopic studies of molecules and clusters, their application to chiroptical measurements has been extremely limited. A noteworthy breakthrough by Kim and his team[41] successfully coupled jet-cooled chiral molecules with conformation-specific ECD spectroscopy. To overcome the inherently weak nature of CD effects and the low density of gas-phase molecules, these authors implemented a dual-beam technique where pulsed photoionization by both circularly and linearly polarized light was exploited to improve sensitivity. To probe the chirality of large biomolecular systems (e.g., gramicidin anions consisting of 15 amino-acid residues), Weitzel and co-workers[42] developed a novel sample introduction method based on electrospray ionization, which was coupled with a PECD detection scheme to create a promising approach for studying the stereochemistry and secondary structures of biopolymers. The field of VCD spectroscopy also has made significant strides, including the transition to an imaging modality. In particular, Sato et al.[43] employed VCD to capture protein spatial distributions and to examine supramolecular structures in the wings of insects, showcasing its ability to reveal complex molecular arrangements.

The guest editors hope that the brief survey of recent developments contained in this Virtual Issue has served to highlight the vibrancy, synergism, and innovation that permeates the burgeoning field of chiroptical spectroscopy. Building on the strong interplay forged between experiment and theory, the ability to unravel and interpret complex chiral phenomena *in situ* through their discriminatory interactions with electromagnetic radiation continues to expand and evolve, leading to new applications of fundamental and practical importance in diverse research endeavors that span the entire gamut of modern-day molecular science.

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Notes

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REFERENCES

(1) Lowry, T. M. *Optical Rotatory Power*; Longmans, Green, and Co. Ltd.: London, 1935.

(2) Eliel, E. L.; Wilen, S. H.; Doyle, M. P. *Basic Organic Stereochemistry*; John Wiley and Sons, Inc.: New York, 2001.

(3) Barron, L. D. *Molecular Light Scattering and Optical Activity*, 2nd ed.; Cambridge University Press: Cambridge, 2004.

(4) Berova, N.; Polavarapu, P. L.; Nakanishi, K.; Woody, R. W. *Comprehensive Chiroptical Spectroscopy*; John Wiley & Sons, Inc.: Hoboken, NJ, 2012.

(5) Paoloni, L.; Mazzeo, G.; Longhi, G.; Abbate, S.; Fusè, M.; Bloino, J.; Barone, V. Toward Fully Unsupervised Anharmonic Computations Complementing Experiment for Robust Assignment and Interpretation of IR and VCD Spectra from Mid-IR to NIR: The Case of 2,3-Butanediol and *trans*-1,2,-Cyclohexanediol. *J. Phys. Chem. A* **2020**, *124*, 1011−1024.

(6) Jähnigen, S.; Zehnacker, A.; Vuilleumier, R. Computation of Solid-State Vibrational Circular Dichroism in the Periodic Gauge. *J. Phys. Chem. Lett.* **2021**, *12*, 7213−7220.

(7) Machalska, E.; Zajac, G.; Wierzba, A. J.; Kapitan, J.; Andruniow, T.; Spiegel, M.; Gryko, D.; Bour, P.; Baranska, M. Recognition of True and False Resonance Raman Optical Activity. *Angew. Chem., Int. Ed.* **2021**, *60*, 21205−21210.

(8) Li, G.; Alshalalfeh, M.; Yang, Y.; Cheeseman, J. R.; Bouř, P.; Xu, Y. Can One Measure Resonance Raman Optical Activity? *Angew. Chem., Int. Ed.* **2021**, *60*, 22004−22009.

(9) Wu, T.; Kapitán, J.; Bouř, P. Resolving Resonant Electronic States in Chiral Metal Complexes by Raman Optical Activity Spectroscopy. *J. Phys. Chem. Lett.* **2022**, *13*, 3873−3877.

(10) Scott, M.; Rehn, D. R.; Norman, P.; Dreuw, A. *Ab Initio* Excited-State Electronic Circular Dichroism Spectra Exploiting the Third-Order Algebraic-Diagrammatic Construction Scheme for the Polarization Propagator. *J. Phys. Chem. Lett.* **2021**, *12*, 5132−5137.

(11) Balduf, T.; Caricato, M. Gauge Dependence of the $\tilde{S}$ Molecular Orbital Space Decomposition of Optical Rotation. *J. Phys. Chem. A* **2021**, *125*, 4976−4985.

(12) Vu, N.; McLeod, G. M.; Hanson, K.; DePrince, A. E., III Enhanced Diastereocontrol via Strong Light-Matter Interactions in an Optical Cavity. *J. Phys. Chem. A* **2022**, *126*, 9303−9312.

(13) Ayad, S.; Posey, V.; Das, A.; Montgomery, J. M.; Hanson, K. Enantioenrichment of Racemic BINOL by Way of Excited-State Proton Transfer. *Chem. Commun.* **2019**, *55*, 1263−1266.

(14) Favereau, L.; Quinton, C.; Poriel, C.; Roisnel, T.; Jacquemin, D.; Crassous, J. Persistent Organic Room-Temperature Phosphorescence in Cyclohexane-*trans*-1,2-Bisphthalimide Derivatives: The Dramatic Impact of Heterochiral vs Homochiral Interactions. *J. Phys. Chem. Lett.* **2020**, *11*, 6426−6434.

(15) Yao, K.; Shen, Y.; Li, Y.; Li, X.; Quan, Y.; Cheng, Y. Ultrastrong Red Circularly Polarized Luminescence Promoted from Chiral Transfer and Intermolecular Forster Resonance Energy Transfer in Ternary Chiral Emissive Nematic Liquid Crystals. *J. Phys. Chem. Lett.* **2021**, *12*, 598−603.

(16) Fujisawa, T.; Nishikawa, K.; Tamogami, J.; Unno, M. Conformational Analysis of a Retinal Schiff Base Chromophore in Proteorhodopsin by Raman Optical Activity. *J. Phys. Chem. Lett.* **2021**, *12*, 9564−9568.

(17) Andersson, Å.; Poline, M.; Houthuijs, K. J.; van Outersterp, R. E.; Berden, G.; Oomens, J.; Zhaunerchyk, V. IRMPD Spectroscopy of Homo- and Heterochiral Asparagine Proton-Bound Dimers in the Gas Phase. *J. Phys. Chem. A* **2021**, *125*, 7449−7456.

(18) Blodgett, K. N.; Jang, G.; Kim, S.; Kim, M. K.; Choi, S. H.; Zwier, T. S. Coexistence of Left- and Right-Handed 12/10-Mixed Helices in Cyclically Constrained beta-Peptides and Directed Formation of Single-Handed Helices upon Site-Specific Methylation. *J. Phys. Chem. A* **2020**, *124*, 5856−5870.

(19) Chojecki, M.; Rutkowska-Zbik; Korona, T. Description of Chiral Complexes within Functional-Group Symmetry-Adapted Perturbation Theory − The Case of (*S*/*R*)-Carvone with Derivatives of (−)-Menthol. *J. Phys. Chem. A* **2020**, *124*, 7735−7748.

(20) Li, M.; He, X.; Chen, J.; Wang, B.; Liu, S.; Rong, C. Density Functional Theory and Information-Theoretic Approach Study on the Origin of Homochirality in Helical Structures. *J. Phys. Chem. A* **2021**, *125*, 1269−1278.

(21) Matsuo, K.; Gekko, K. Vacuum Ultraviolet Electronic Circular Dichroism Study of D-Glucose in Aqueous Solution. *J. Phys. Chem. A* **2020**, *124*, 642−651.

(22) Hartweg, S.; Garcia, G. A.; Božanić, D. K.; Nahon, L. Condensation Effects on Electron Chiral Asymmetries in the Photoionization of Serine: From Free Molecules to Nanoparticles. *J. Phys. Chem. Lett.* **2021**, *12*, 2385−2393.

(23) Craft, C. L.; Lemler, P. M.; Vaccaro, P. H. Optical Activity in Saturated Cyclic Amines: Untangling the Roles of Nitrogen-Inversion and Ring-Puckering Dynamics. *J. Phys. Chem. A* **2021**, *125*, 5562−5584.

(24) D'Cunha, R.; Crawford, T. D. Modeling Complex Solvent Effects on the Optical Rotation of Chiral Molecules: A Combined Molecular Dynamics and Density Functional Theory Study. *J. Phys. Chem. A* **2021**, *125*, 3095−3108.

(25) Hillers-Bendtsen, A. E.; Todarwal, Y.; Pittelkow, M.; Norman, P.; Mikkelsen, K. V. Modeling Absorption and Emission Spectros-

copies of Symmetric and Asymmetric Azaoxahelicenes in Vacuum and Solution. *J. Phys. Chem. A* **2022**, *126*, 6467−6472.

(26) Carlson, C. D.; Hazrah, A. S.; Mason, D.; Yang, Q.; Seifert, N. A.; Xu, Y. Alternating 1-Phenyl-2,2,2-Trifluoroethanol Conformational Landscape With the Addition of One Water: Conformations and Large Amplitude Motions. *J. Phys. Chem. A* **2022**, *126*, 7250−7260.

(27) Johnson, J. L.; Polavarapu, P. L. Chiral Molecular Structure Determination for a Desired Compound Just from Its Molecular Formula and Vibrational Optical Activity Spectra. *J. Phys. Chem. A* **2021**, *125*, 8000−8013.

(28) Eikås, K. D. R.; Beerepoot, M. T. P.; Ruud, K. A Computational Protocol for Vibrational Circular Dichroism Spectra of Cyclic Oligopeptides. *J. Phys. Chem. A* **2022**, *126*, 5458−5471.

(29) Pracht, P.; Bohle, F.; Grimme, S. Automated Exploration of the Low-Energy Chemical Space with Fast Quantum Chemical Methods. *Phys. Chem. Chem. Phys.* **2020**, *22*, 7169−7192.

(30) Plett, C.; Grimme, S. Automated and Efficient Generation of General Molecular Aggregate Structures. *Angew. Chem., Int. Ed.* **2023**, *62*, e202214477.

(31) Morgante, P.; Ludowieg, H. D.; Autschbach, J. Comparative Study of Vibrational Raman Optical Activity with Different Time-Dependent Density Functional Approximations: The VROA36 Database. *J. Phys. Chem. A* **2022**, *126*, 2909−2927.

(32) Hope, M.; Šebestik, J.; Kapitán, J.; Bouř, P. Understanding CH-Stretching Raman Optical Activity in Ala-Ala Dipeptides. *J. Phys. Chem. A* **2020**, *124*, 674−683.

(33) Mahato, B.; Panda, A. N. Effects of Heterocyclic Ring Fusion and Chain Elongation on Chiroptical Properties of Polyaza[9]-helicene: A Computational Study. *J. Phys. Chem. A* **2022**, *126*, 1412−1421.

(34) Sharma, A.; Athanasopoulos, S.; Kumarasamy, E.; Phansa, C.; Asadpoordarvish, A.; Sabatini, P.; Pandya, R.; Parenti, K. R.; Sanders, S. N.; McCamey, D. T.; et al. Pentacene-Bridge Interactions in an Axially Chiral Binaphthyl Pentacene Dimer. *J. Phys. Chem. A* **2021**, *125*, 7226−7234.

(35) Singh, D. P.; Thompson, J. O. F.; Reid, K. L.; Powis, I. Influence of Vibrational Excitation and Nuclear Dynamics in Multiphoton Photoelectron Circular Dichroism of Fenchone. *J. Phys. Chem. Lett.* **2021**, *12*, 11438−11443.

(36) Naaman, R.; Paltiel, Y.; Waldeck, D. H. Chiral Molecules and the Spin Selectivity Effect. *J. Phys. Chem. Lett.* **2020**, *11*, 3660−3666.

(37) Ye, C.; Sun, Y.; Zhang, X. Entanglement-Assisted Quantum Chiral Spectroscopy. *J. Phys. Chem. Lett.* **2021**, *12*, 8591−8597.

(38) Lightner, C. R.; Gisler, D.; Meyer, S. A.; Niese, H.; Keitel, R. C.; Norris, D. J. Measurement of Raman Optical Activity with High-Frequency Polarization Modulation. *J. Phys. Chem. A* **2021**, *125*, 8132−8139.

(39) This article received the 2022 Philip J. Stephens Award, which is bestowed at the biennial Vibrational Optical Activity (VOA) conference in recognition of a research paper published in the prior two years that makes a significant and creative development in the VOA field.

(40) Lee, T.; Oh, J.; Nah, S.; Choi, D. S.; Rhee, H.; Cho, M. Time-Variable Chiroptical Vibrational Sum-Frequency Generation Spectroscopy of Chiral Chemical Solution. *J. Phys. Chem. Lett.* **2021**, *12*, 10218−20224.

(41) Jeong, C.; Eun, H. J.; Yun, J.; Kim, N. J. Dual-Beam Circular Dichroism Spectroscopy of Jet-Cooled Chiral Molecules. *J. Phys. Chem. A* **2022**, *126*, 4295−4299.

(42) Krüger, P.; Both, J. H.; Linne, U.; Chirot, F.; Weitzel, K.-M. Photoelectron Circular Dichroism of Electrosprayed Gramicidin Anions. *J. Phys. Chem. Lett.* **2022**, *13*, 6110−6116.

(43) Sato, H.; Yamagishi, A.; Shimizu, M.; Watanabe, K.; Koshoubu, J.; Yoshida, J.; Kawamura, I. Mapping of Supramolecular Chirality in Insect Wings by Microscopic Vibrational Circular Dichroism Spectroscopy: Heterogeneity in Protein Distribution. *J. Phys. Chem. Lett.* **2021**, *12*, 7733−7737.

https://doi.org/10.1021/acs.jpca.3c05566
J. Phys. Chem. A 2023, 127, 7677−7681