magnitude and speed of changes in ocean environments caused by a rapidly warming climate. Whales were assumed to be largely buffered from environmental variation by their enormous size, mobility, and slow life histories. But from a variety of recent studies, it is clear that climate change is affecting the ecology of these animals in ways that can exacerbate existing conservation problems or create new ones (*4*).

The most immediate effects of a changing climate on whale populations are modifications to their patterns of distribution, which are typically driven by prey availability. These are also the most straightforward effects to document. For example, over the past decade, many North Atlantic right whales (*Eubalaena glacialis*) shifted their primary summer feeding grounds from the Gulf of Maine to the Gulf of St. Lawrence, resulting in an increase in mortality from ship strikes and entanglement in fishing gear in Canadian waters (*5*). Similarly, the marine heat wave that occurred from 2014 to 2016 off the US West Coast resulted in a shoreward shift in the distribution of humpback whales (*Megaptera novaeangliae*) and an increase in the number of entanglements in the Dungeness crab fishery (*6*).

Other populations of whales are benefiting from climate change, at least in the short term. For example, humpback whales feeding on krill along the western Antarctic Peninsula are taking advantage of longer feeding seasons that are due to reductions in sea ice, resulting in excellent body condition (*7*) and high rates of fecundity (*8*). But what will happen when the sea ice, on which the krill ultimately depend, disappears?

Stewart *et al.* describe two factors that may be responsible for the swings they observed in the Eastern Pacific gray whale population. The whales feed on amphipods, a low-trophic-level crustacean prey that is affected directly by environmental fluctuations. In addition, gray whales use a capital breeding strategy, in which they feed intensively during the summer and draw on stored energy reserves to fuel their long migrations and the costs of reproduction during the remainder of the year. Interannual variation in the duration of their feeding season, caused by the timing of sea ice formation and breakup, can thus affect their ability to store enough energy during the critical summer feeding period.

How applicable are the lessons from gray whales for other species of baleen whales? Some species, such as humpback whales, have relatively broad diets that include both crustaceans and fish and are adept at prey-switching when environmental conditions change (*9*). This behavior may allow humpback whales to be more buffered than gray whales from environmental variation. By contrast, blue whales (*Balaenoptera musculus*) feed almost entirely on krill and track their prey closely, even when its distribution changes (*10*). If Stewart *et al.* are correct, then species with a narrow dietary niche composed of low-trophic-level prey species should be expected to exhibit considerable variation in their demography as environmental conditions change. As more baleen whales recover from overhunting in the coming decades, these hypotheses can be tested.

Today, Eastern Pacific gray whales experience very limited levels of human-caused mortality. Stewart *et al.* included mortality from entanglements and ship strikes in their model and concluded that these factors could not have caused the changes in abundance that they observed. But what if this population is subjected to higher levels of anthropogenic mortality in the future? The paradigm used to manage whales and other marine mammals in US waters relies on biological reference points to establish limits on the number of whales that can be removed from each population by human activities. These reference points, known as potential biological removal levels, were developed by using simulation models that assume that populations will remain at relatively constant carrying capacity (*11*). The boom-and-bust cycles observed by Stewart *et al.* do not fit this paradigm, and it is unclear how human-caused mortality would be managed on top of such a large degree of climate-induced variation in abundance.

During the past century, commercial whaling removed almost 3 million large whales from the world's oceans (*12*). The era of unregulated hunting of whales is largely behind us, but the findings of Stewart *et al.* remind us that the recovery of these populations may not be as straightforward as expected in the era of a rapidly changing climate. ■

REFERENCES AND NOTES

1. T. Eguchi, A. R. Lang, D. W. Weller, NOAA technical memo NMFS-SWFSC-668 (2022).
2. A. E. Punt, C. Allison, G. Fay, *J. Cetacean Res. Manag.* **6**, 121 (2004).
3. J. D. Stewart *et al.*, *Science* **382**, 207 (2023).
4. F. M. D. Gulland *et al.*, *Clim. Change Ecol.* **3**, 100054 (2022).
5. E. Meyer-Gutbrod, C. Greene, K. Davies, D. Johns, *Oceanography* **34**, 22 (2021).
6. J. A. Santora *et al.*, *Nat. Commun.* **11**, 536 (2020).
7. K. C. Bierlich *et al.*, *Front. Mar. Sci.* **9**, 1036860 (2022).
8. L. J. Pallin *et al.*, *R. Soc. Open Sci.* **5**, 180017 (2018).
9. A. H. Fleming, C. T. Clark, J. Calambokidis, J. Barlow, *Glob. Change Biol.* **22**, 1214 (2016).
10. A. R. Szesciorka *et al.*, *Sci. Rep.* **10**, 7710 (2020).
11. P. Wade, *Mar. Mamm. Sci.* **14**, 1 (1998).
12. R. Rocha Jr., P. J. Clapham, Y. V. Ivashchenko, *Mar. Fish. Rev.* **76**, 37 (2014).

10.1126/science.adk4244

PHYSICAL CHEMISTRY

Chiral molecules to transmit electron spin

Electron transfer through chiral molecules displays a strong spin preference

By **Joseph E. Subotnik**

Understanding how electrons move through molecules and carry energy with them has been crucial for the development of multiple technologies, including photovoltaic cells and light-emitting diodes. The standard theory (*1*) establishes that electron transfer (ET) can be understood by considering energy conservation and the movement of electrons and nuclei. However, this view of ET has been challenged with the observation of chirality-induced spin selectivity (CISS), whereby electrons with one spin move differently through a material than do electrons of the other spin (*2*, *3*). On page 197 of this issue, Eckvahl *et al.* (*4*) report a CISS signal for an isolated chiral molecular system in a liquid crystal environment, after excitation with light. These results suggest that the standard ET theory should be modified to include both energy and total (orbital plus spin) angular momentum conservation, thereby opening the door to new CISS applications, including "green" hydrogen generation.

The spin of an electron is an internal rotation of the elementary particle that was historically considered peripheral for ET. Nevertheless, over the last 24 years, the CISS effect (*2, 3*) has been demonstrated directly through a range of photoemission experiments (*5*) and indirectly through a variety of measurements, including spin-valve devices in which magnetoconductance (electrical conductivity change that results from an applied magnetic field) was measured through chiral molecules (*6*) and magnetic-field dependent adsorption experiments. However, until now, the CISS effect has always been observed in the vicinity of a semiconductor or metal, where there are many mobile

Department of Chemistry, University of Pennsylvania, Philadelphia, PA, USA. Email: subotnik@sas.upenn.edu

electrons and a well-defined direction along which spin—like any angular momentum—can be measured. Remarkably, Eckvahl *et al.* demonstrate CISS in an environment without a solid or surface of any kind nearby.

To demonstrate a CISS effect far from a surface, Eckvahl *et al.* had to overcome some inherent experimental difficulties. For CISS, all spins are polarized in the molecular frame (that is, relative to a molecular bond direction), and molecules are oriented randomly in a disordered solution, which means that such spin signals cancel each other out in liquids. To that end, Eckvahl *et al.* employed a liquid crystal to achieve partial alignment of the molecules relative to a fixed known direction in space. Thereafter, as a probe, they used electron paramagnetic resonance (EPR), whereby a molecule with unpaired electrons is placed under a magnetic field and the resulting different spin alignments lead to a small splitting of spin energy levels in the microwave domain. The molecule is then excited with microwaves, which results in measurable transitions between the occupied and unoccupied spin energy states.

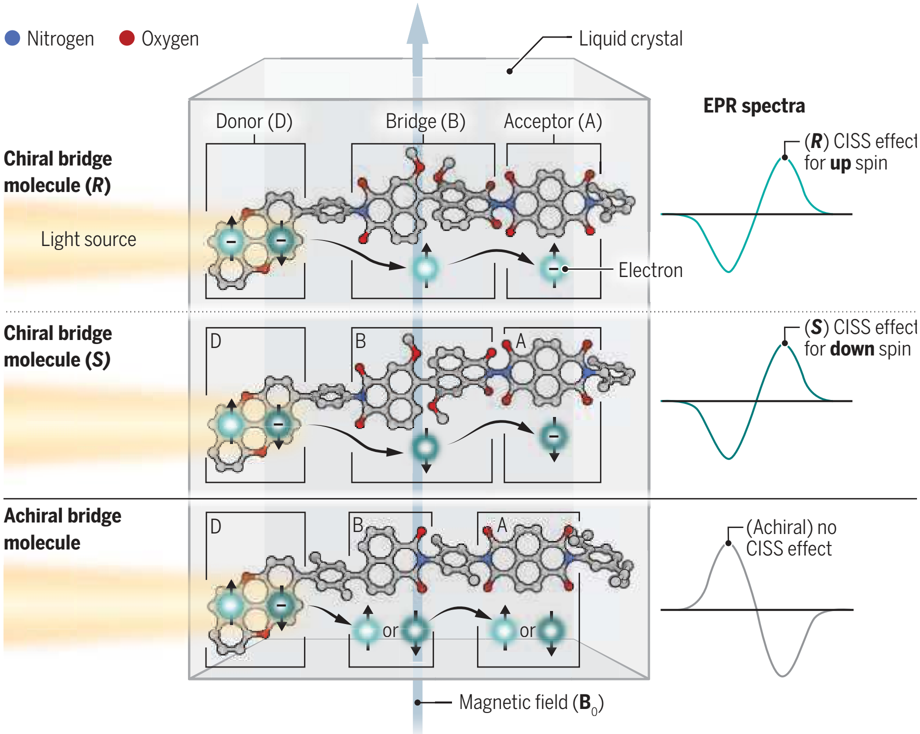
Eckvahl *et al.* studied molecules that comprise an electron donor (D), a bridge (B), and an electron acceptor (A) (see the figure). Chirality is introduced by B, which can be either *R* (right-handed) or *S* (left-handed), depending on the direction in which B polarizes light. Recognizing that the EPR spectra of molecules with *R* or *S* chirality can arise from a partial (rather than complete) spin preference for ET from D to A (*7*, *8*), Eckvahl *et al.* have fit the EPR absorption curves with standard rate equations and estimate that, for this molecular experiment, the probability for one electron with a specific spin to transfer from D to B to A is at least 40% greater than for the electrons with the other spin to transfer.

The underlying physical mechanism for CISS remains unknown; it is even unclear whether a single mechanism or multiple mechanisms underly the range of CISS observations. The leading source of confusion is that, for electrons in organic materials, the spin of an electron is coupled very weakly to the electron's overall orbital motion—known as spin-orbit coupling, SOC—such that for an electron traveling through a large organic molecule, there is simply no time for any meaningful change of spin (*9*). A leading hypothesis to explain CISS taking place on a surface even with a weak molecular SOC is that the CISS effect is caused by electron-electron interactions at the molecule–metal interface. According to that theory, the relevant SOC arises from the underlying inorganic metallic substrate (*9*–*11*).

For the experiment of Eckvahl *et al.*, there is no substrate from which to share SOC, and

Electron spin transfer depends on molecular chirality

Only electrons with a certain spin are efficiently transferred when the donor-bridge-acceptor (D-B-A) molecule has the appropriate chirality (*R*, *S*). This is determined by electron paramagnetic resonance (EPR) spectra (shown here for illustration purposes). This selection is the chirality-induced spin selectivity (CISS) effect (top and middle). Achiral molecules do not affect electron spin transfer (bottom).



so the underlying CISS mechanism must be different. A proposed explanation (*12*) is that nonequilibrium nuclear motion (*13, 14*) (i.e., phonons, a collective excitation of a network of atoms) may be responsible for imparting angular momentum to electronic spins. Nevertheless, this effect has never been directly observed by, for example, changing the nuclear mass of atoms (by using different isotopes). Interestingly, the EPR data in Eckvahl *et al.* imply that deuterating (replacing hydrogen for deuterium, a "heavier" isotope) the D-B-A system leads to a decrease in the CISS signal. However, the authors attribute this change to the difference in the nuclear spins of hydrogen versus deuterium, and not to any nuclear vibrational effects.

The field of spin-selective ET is ripe for future discovery. Eckvahl *et al.* have fashioned their study on the possibility of using CISS as a means of transmitting quantum information in the form of electronic spin (a candidate for a qubit, the basic unit of information in quantum computing), but equally important is the possibility of using the CISS effect for electrochemical and photochemical purposes. The strongest means by which spins interact with each other is through exchange and the Pauli exclusion principle, which forbids two electrons with the same spin to be at the same point in space at the same time. Thus, it can be expected that CISS dynamics will play a role in multi-electron transfer processes, for example, in water-splitting experiments where multiple redox steps take place to generate "green" hydrogen fuels (*15*). Moreover, because the CISS effect can take place away from a surface, it may be useful for magnetic-field detection, perhaps explaining the physics of bird navigation (*7*). ■

REFERENCES AND NOTES

1. M. Bixon, J. Jortner, *Adv. Chem. Phys*. **106**, 35 (1999).
2. K. Ray, S. P. Ananthavel, D. H. Waldeck, R. Naaman, *Science* **283**, 814 (1999).
3. R. Naaman, D. H. Waldeck, *J. Phys. Chem. Lett*. **3**, 2178 (2012).
4. H. J. Eckvahl *et al*., *Science* **382**, 197 (2023).
5. B. Göhler *et al*., *Science* **331**, 894 (2011).
6. T. Liu *et al*., *ACS Nano* **14**, 15983 (2020).
7. J. Luo, P. Hore, *New J. Phys*. **23**, 043032 (2021).
8. T. P. Fay, *J. Phys. Chem. Lett*. **12**, 1407 (2021).
9. J. Gersten, K. Kaasbjerg, A. Nitzan, *J. Chem. Phys*. **139**, 114111 (2013).
10. Y. Liu, J. Xiao, J. Koo, B. Yan, *Nat. Mater*. **20**, 638 (2021).
11. S. Alwan, Y. Dubi, *J. Am. Chem. Soc*. **143**, 14235 (2021).
12. S. S. Chandran, Y. Wu, J. E. Subotnik, *J. Phys. Chem. A* **126**, 9535 (2022).
13. J. Fransson, *Phys. Rev. B* **102**, 235416 (2020).
14. X. Bian *et al*., arXiv:2303.13787 (2023).
15. R. Naaman, Y. Paltiel, D. H. Waldeck, *Acc. Chem. Res*. **53**, 2659 (2020).

ACKNOWLEDGMENTS

J.E.S. thanks the National Science Foundation (grant no. CHE-2102402) for support.

10.1126/science.adk5634

GRAPHIC: N. BURGESS/SCIENCE