

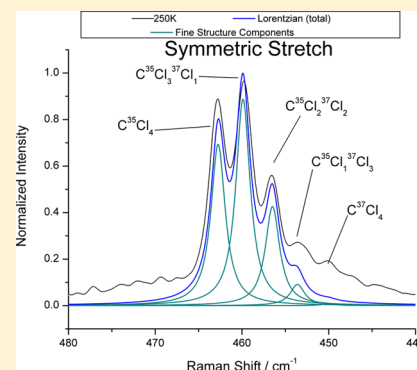
# Vibrational Spectroscopy of the $\text{CCl}_4$ $\nu_1$ Mode: Theoretical Prediction of Isotopic Effects

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## S Supporting Information

**ABSTRACT:** Raman spectroscopy is a powerful experimental technique, yet it is often missing from the undergraduate physical chemistry laboratory curriculum. Tetrachloromethane ( $\text{CCl}_4$ ) is the ideal molecule for an introductory vibrational spectroscopy experiment and the symmetric stretch vibration contains fine structure due to isotopic variations of the molecule according to  $\text{C}^{35}\text{Cl}_x\text{C}^{37}\text{Cl}_{4-x}$ . We report simple theoretical predictions of the fine structure, calculation of Raman differential scattering cross sections, and discussion of the inherent asymmetry in the  $\nu_1$  mode resulting from the different isotopes of chlorine. All calculations and discussion are appropriate for an undergraduate physical chemistry laboratory as either an independent dry lab or a supplement to a pre-existing vibrational spectroscopy lab.



**KEYWORDS:** Physical Chemistry, Upper-Division Undergraduate, Curriculum, Raman Spectroscopy, Quantum Chemistry, Hands-On Learning/Manipulatives, Laboratory Instruction

Raman spectroscopy is an important spectroscopic technique and is often missing from the undergraduate chemistry laboratory curriculum. Tetrachloromethane ( $\text{CCl}_4$ ) or carbon tetrachloride as it is more commonly known, is the ideal molecule to study because its symmetry allows only two infrared (IR) active modes (though one remains unseen due to its frequency resonating lower than the range of most IR spectrometers) and four Raman active modes below  $1000\text{ cm}^{-1}$ . Furthermore, carbon tetrachloride will be familiar to undergraduates as a common tetrahedral molecule in the organic chemistry curriculum.<sup>1</sup> Moreover, the peaks are well defined which avoids undue confusion during analysis. Resources exist that detail the undergraduate physical chemistry experiment with Raman spectroscopy; however, they are relatively few.<sup>2</sup> Understandably, many undergraduate chemistry departments may not have access to Raman spectrometers due to their cost or may not have a Raman expert on the faculty. This Journal has made available several Raman spectroscopy dry laboratories<sup>3–5</sup> and less-expensive, home-built spectrometer alternatives<sup>6</sup> to overcome this educational gap. To our knowledge, this paper is the first to extensively detail the isotopic effect and contributions due to hot bands in  $\text{CCl}_4$  observable in the high resolution ( $<2\text{ cm}^{-1}$ ) symmetric stretch peak for the undergraduate laboratory. The experiment can easily be used as an independent dry lab or a supplement to a developed Raman spectroscopy laboratory. It is suitable for a regular three or four hour laboratory period and can be performed individually or with lab partners. The insight gained by studying the isotopic effect in the symmetric stretch demonstrates specific spectroscopic details, such as the Raman differential scattering cross section, which are not standard

topics in undergraduate chemistry curricula. Symmetry considerations that are often introduced in either organic or inorganic curricula are re-emphasized and can be developed further by using this laboratory experiment.

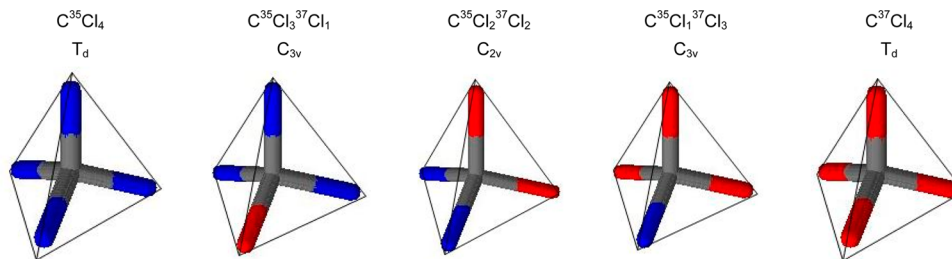
The fine structure in the Raman lines of  $\text{CCl}_4$  was first reported by Langseth<sup>7</sup> in 1931. Although isotopic effects could not account for fine structure in the degenerate vibrational modes, he concluded that the two chlorine isotopes account for the symmetric stretch fine structure because of the five  $\text{CCl}_4$  molecules present:  $\text{C}^{35}\text{Cl}_4$ ,  $\text{C}^{35}\text{Cl}_3\text{C}^{37}\text{Cl}_1$ ,  $\text{C}^{35}\text{Cl}_2\text{C}^{37}\text{Cl}_2$ ,  $\text{C}^{35}\text{Cl}_1\text{C}^{37}\text{Cl}_3$ , and  $\text{C}^{37}\text{Cl}_4$ . Discussions of crystal field splitting, isotopic effects,<sup>8–10</sup> and symmetry<sup>8,11,12</sup> considerations to resolve the discrepancy between predicted and observed splittings in other fundamental vibrations of  $\text{CCl}_4$  followed Langseth's work. This paper allows the undergraduate physical chemistry student to participate in the discussion by predicting the peak intensities of the  $\text{CCl}_4$  symmetric stretch and consider both quantum mechanical and classical mechanical descriptions of this vibration.

## THEORY

### Symmetry of $\text{CCl}_4$

The infrared and Raman spectra of a molecule are explained by the symmetry of the vibrational modes of the molecule. For example, the totally symmetric vibration of a molecule with tetrahedral,  $T_d$ , symmetry will not give rise to an oscillating dipole in the molecule causing it to be infrared inactive but the shift in electron density will give rise to a change in the

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Table 1. Symmetry Variation Owing to Cl Isotopes in CCl<sub>4</sub><sup>a</sup>

<sup>35</sup>Cl (blue), <sup>37</sup>Cl (red).

polarizability causing it to be Raman active. Carbon tetrachloride is a penta-atomic molecule and, thus, has nine vibrational modes but its tetrahedral symmetry leads to degeneracies resulting in just four unique frequencies. Conventionally, the four fundamental vibrations are denoted  $\nu_1$  (symmetric stretch),  $\nu_2$  (symmetric bend),  $\nu_3$  (antisymmetric stretch), and  $\nu_4$  (antisymmetric bend) with degeneracies of 1, 2, 3, and 3, respectively.<sup>2</sup> The  $\nu_1$  vibration is of specific interest in this paper because the direction of bond polarization lies along the C–Cl bond, which maximizes the change in polarizability during the symmetric stretch, thereby, allowing for the resolution of the isotopic fine structure. In the other vibrational modes, the isotopic effect is not so easily resolved, nor is it the only contributor to fine structure—crystal splitting effects also account for the differences in fine structure splitting in the  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$  fundamentals.<sup>10</sup>

The relative abundances of the two chlorine isotopes results in five isotopomers of CCl<sub>4</sub> according to the ratios of <sup>35</sup>Cl:<sup>37</sup>Cl present. Therefore, although the CCl<sub>4</sub> molecule is of *T<sub>d</sub>* symmetry, these isotopomers are not as symmetric as *T<sub>d</sub>*; in fact, only C<sup>35</sup>Cl<sub>4</sub> and C<sup>37</sup>Cl<sub>4</sub> are truly of *T<sub>d</sub>* symmetry. Table 1 summarizes the symmetries for all isotopic variants of the CCl<sub>4</sub> molecule. The isotopic variants of CCl<sub>4</sub> give rise to slightly different  $\nu_1$  peak positions (offset by  $\sim 3$  cm<sup>-1</sup>) and the intensities of each peak must be scaled by their respective relative abundance. The totally symmetric modes of the *T<sub>d</sub>*, *C<sub>3v</sub>*, and *C<sub>2v</sub>* point groups are all Raman active and the corresponding Raman shifted frequencies will be slightly different for each molecule.<sup>1</sup> Although the totally symmetric modes of *C<sub>3v</sub>* and *C<sub>2v</sub>* are infrared active, the change in the dipole moment for the isotopic variants of CCl<sub>4</sub> would be negligible; therefore, one would not expect to see any absorbance in the infrared spectrum due to these vibrations.

### Quantum Mechanical Considerations

At high optical frequencies (10<sup>15</sup> Hz), the oscillation of the electron density over the molecule occurs so rapidly that the motion of the heavy nuclei is effectively static by comparison. According to the Franck–Condon Principle the electronic excitations can be considered a vertical transition, indicating independence of internuclear spacing, when plotting a Morse Potential to model vibronic transitions within a molecule because molecular vibrations ( $\sim 10^{12}$  Hz) are orders of magnitude slower than an electronic transition ( $\sim 10^{15}$  Hz).<sup>13</sup> In vibrational Raman spectroscopy, the Raman lines are present due to a change in the molecular polarizability. The following relation is the induced dipole moment,  $\mu_{\text{induced}}$  (see Shoemaker et al.<sup>2</sup> for a thorough treatment)

$$\mu_{\text{induced}} = \alpha E_0 \cos(2\pi\nu_0 t) + \frac{1}{2} \left( \frac{\partial \alpha}{\partial Q} \right)_0 A E_0 [\cos 2\pi(\nu_0 - \nu_i)t + \cos 2\pi(\nu_0 + \nu_i)t] \quad (1)$$

where  $\alpha$  is the molecular polarizability,  $E_0$  is the incident electromagnetic field,  $A$  is the molecular vibrational amplitude, and  $Q$  is the vibrational coordinate. This expression accounts for Rayleigh scattering in the first term and Raman scattering in the second term. Specifically, the difference between incident frequency,  $\nu_0$ , and scattered frequency,  $\nu_s$ , accounts for Stokes ( $\nu_0 - \nu_i$ ) and anti-Stokes ( $\nu_0 + \nu_i$ ) Raman scattering. The resulting Raman line intensities are dependent on the Raman differential scattering cross section,  $\sigma$ ,

$$\sigma \propto \sigma_0 (\nu_0 - \nu_i)^4 \quad (2)$$

where  $\sigma_0$  is the frequency independent cross section.<sup>14</sup> With sufficiently resolved  $\nu_i$  for each isotopic variant, the relative differential scattering cross sections can be calculated to reflect the probability of Raman scattering for each molecule.

### Classical Mechanical Considerations

Quantum chemical computational programs such as Gaussian can be used to predict the peak positions of the  $\nu_1$  fine structure and this would provide students with a connection to the tools used by theoretical physical chemists. Alternatively, it is fairly straightforward to use Lagrangian mechanics to predict the peak positions.<sup>15</sup> Though Lagrangian mechanics are fairly calculation-intensive for the undergraduate laboratory, the equations used to describe the atomic coordinates within the molecule can be used to calculate the motion of the carbon atom relative to the center of mass for each isotopic variant fairly easily. The Supporting Information includes an Excel workbook that outlines these center of mass calculations, useful as a teaching aid in lecture or a physical chemistry laboratory supplement for both dry and wet laboratories.

Considering each C–Cl bond in CCl<sub>4</sub> to be modeled as a mass-spring system with anharmonic oscillations, a Taylor series expansion of the Morse potential can be used to obtain the quadratic potential energy of an anharmonic oscillator

$$V(x) = \frac{1}{2}(2a^2D)x^2 - (a^3D)x^3 \dots \quad (3)$$

The first term is used to approximate the potential energy of a mass-spring system with the spring constant equal to  $2a^2D$  where  $D$  is the dissociation energy and  $a$  gives the curvature of the potential. Both constants are specific to the molecule. Note that the frequency of oscillation changes when different masses are placed on the end of a spring with a given spring constant. Specifically, the vibrational frequencies are inversely proportional to the mass on the spring, and the symmetric stretch fine

Table 2. Comparison of Predicted Peak Intensities to Measured Values

Molecule	Arrangements, Count	Nominal Probability	Relative Intensity	Normalized to C <sup>35</sup> Cl <sub>4</sub>	Peak Intensities Normalized Measured Data (250 K)	Difference (Measured – Theoretical)
C <sup>35</sup> Cl <sub>4</sub>	1	(0.76) <sup>4</sup>	0.33	1	1	
C <sup>35</sup> Cl <sub>3</sub> <sup>37</sup> Cl <sub>1</sub>	4	(0.76) <sup>3</sup> (0.24) <sup>1</sup>	0.42	1.3	1.1	–0.2
C <sup>35</sup> Cl <sub>2</sub> <sup>37</sup> Cl <sub>2</sub>	6	(0.76) <sup>2</sup> (0.24) <sup>2</sup>	0.20	0.60	0.62	0.02
C <sup>35</sup> Cl <sub>1</sub> <sup>37</sup> Cl <sub>3</sub>	4	(0.76) <sup>1</sup> (0.24) <sup>3</sup>	0.042	0.13	0.30	0.17
C <sup>37</sup> Cl <sub>4</sub>	1	(0.24) <sup>4</sup>	0.0033	0.0099	<sup>a</sup>	<sup>a</sup>

<sup>a</sup>Although hot bands were reduced at 250 K, the peak intensity for C<sup>37</sup>Cl<sub>4</sub> was not easily discernible.

structure will reflect this in the peak positions for each CCl<sub>4</sub> isotopic variant. Equations of motion detailing the molecule's motion relative to its center of mass can be derived using Lagrangian mechanics. The Lagrangian summarizes the dynamics of the five-body system with its center of mass as the origin.<sup>16,17</sup> The Morse potential is used as the potential energy term,  $V$ , in the Lagrangian function

$$L = T - V \quad (4)$$

where  $T$  is the kinetic energy of each atom in the molecule.

## EXPERIMENT

### Chemicals

Carbon tetrachloride was used as obtained in the liquid phase from Spectrum Chemical (reagent grade). Sample preparation included the use of a fume hood and full protective laboratory equipment. Minimal CCl<sub>4</sub> is needed; ~1 mL sealed into a sample vial is sufficient. The sample cell may vary depending on the spectrometer used (a standard NMR tube works well for our Raman spectrometer stage). It is best to avoid using large sample cells, such as standard 3.0 mL cuvettes, to minimize use and exposure to CCl<sub>4</sub>. If the department has the resources, it is preferable to permanently seal the CCl<sub>4</sub> in the sample cell, minimizing exposure to a toxic solvent and substantially reducing the CCl<sub>4</sub> waste because a permanently sealed sample will last for many years.

### Spectrometer

A Thermo Scientific Nicolet 6700 FT-IR/NXR FT-Raman Module is available in our physical chemistry laboratory. The Raman Module uses a separate 1064 nm light source, an interferometric detection geometry housed in the FT-IR optical bench, an InGaAs detector and is operated by Thermo Scientific OMNIC Software Suite (Version 8). Spectra are averaged over 32 scans and the high resolution spectrum of the symmetric stretch vibrational mode at 459 cm<sup>-1</sup> requires at least 2 cm<sup>-1</sup> resolution for adequate identification of the isotopic fine structure at room temperature. The CCl<sub>4</sub> sample is arranged in the 180° backscattering geometry and a separate temperature control unit is employed to cool out the vibrational hot bands. Many Raman spectrometer set-ups are feasible for this experiment, to include home-built and other commercial-grade instruments.<sup>3,6</sup> Arranging the sample in a 90° scattering geometry is possible, although the scattering signal may be weaker. For the undergraduate laboratory lacking in instrumental resources the theoretical prediction of the  $\nu_1$  fine structure and the discussion that follows is achievable, instructive, and only requires reference to the spectra included in this paper and Supporting Information.

## HAZARDS

### CCl<sub>4</sub>

Extreme caution should be exercised in CCl<sub>4</sub> sample preparation as CCl<sub>4</sub> is very toxic and a known carcinogen. It is preferable for the professor or a trained laboratory assistant to appropriately prepare the CCl<sub>4</sub> in an NMR tube (or equivalent) with the full protection of lab coat, gloves, and goggles under a laboratory fume hood. Once the sample is prepared and sealed the same sample is easily used for multiple laboratory periods.

### Laser Safety

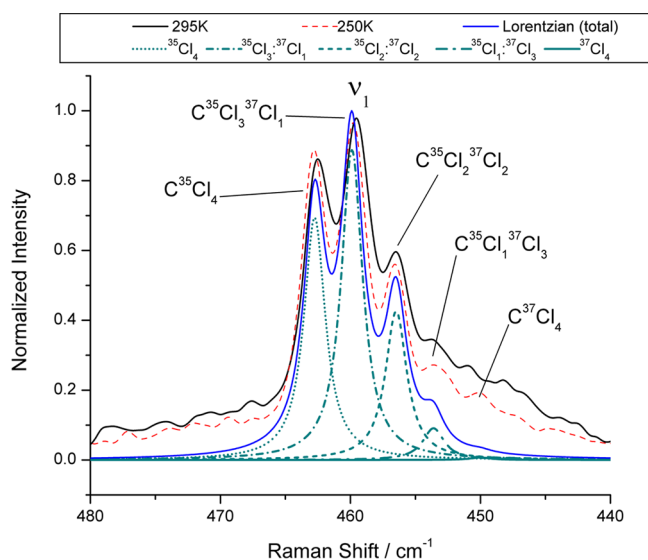
Laser safety should be incorporated into the laboratory session as suitable for the spectrometer in use. Regardless of available instrumentation general laser safety should be reviewed with the students. A review of safety mechanisms (shutters, etc.) incorporated into various instrumental designs allows students to become more familiar with new optical configurations used in chemical analysis.

## RESULTS

### Theoretical Prediction of the Isotopic Fine Structure of the CCl<sub>4</sub> Symmetric Stretch

The fine structure of the CCl<sub>4</sub> symmetric stretch is observed with sufficient resolution (~1 cm<sup>-1</sup>). Often, obtaining spectra with such resolution requires expensive equipment that is usually unavailable to the undergraduate physical chemistry laboratory. However, an instructive dry lab is possible with the results and methodology herein reported. Students can easily calculate theoretical peak intensities of the  $\nu_1$  fine structure as shown in Table 2 and then compare these to the measured results. Lorentzian deconvolution of the theoretical peaks is possible (see Supporting Information) using the intensity predictions from Table 2, which can be plotted as shown in Figure 1. The relative peak positions can be reasoned out by considering that the frequency of oscillation, and thus the energy, is lower for heavier masses. Calculations indicate isotopic peak separation of 3.2 cm<sup>-1</sup>; measured separation values are commonly in the range of 3.2–3.6 cm<sup>-1</sup>.<sup>10</sup>

For simplicity, the natural abundance of the <sup>35</sup>Cl and <sup>37</sup>Cl isotopes can be approximated to be 0.76 and 0.24, respectively. Because the  $\nu_1$  fundamental mode is the symmetric stretching motion of the four chlorine atoms about the carbon center, we chose to normalize the theoretical predictions and the measured data to the peak due to the C<sup>35</sup>Cl<sub>4</sub> molecule because it possess  $T_d$  symmetry, exhibits an excellent signal-to-noise ratio, and is least affected by the underlying hot bands. Although the theoretical peak intensities reflect the same overall trend in peak heights observed experimentally they are not a perfect match. We attribute this discrepancy to the underlying hot bands and baseline correction.



**Figure 1.** Symmetric stretch isotopic fine structure. Colder temperatures reduce the excited state population and reduce the intensity of hot band transitions that allows the less abundant  $C^{37}Cl_4$  symmetric stretch ( $\nu = 0$  to  $\nu = 1$  transition) to become visible. Comparison of measured data at 250 K with the Lorentzian model shows that hot bands still contribute significantly to the experimental intensities.

### Quantum Mechanical Perspective: Raman Differential Scattering Cross Section

Quantum mechanical considerations largely concern the Raman differential scattering cross section of  $CCl_4$  because it reflects the molecule's electronic polarizability. The differential scattering cross section generally reflects the strength of a scatterer in the sample.<sup>14</sup> From eq 2, the relative Raman differential scattering cross sections can be calculated and the strength of each isotopic variant determined (Table 3).

**Table 3.** Relative Raman Differential Scattering Cross Sections of  $CCl_4$   $\sigma \propto (\nu_0 - \nu_1)^4$

Molecule	Peak Positions ( $\nu_1$ )/ $cm^{-1}$	$(\nu_0 - \nu_1)^4$ / $(cm^{-1})^4$	Normalized Cross Section
$C^{35}Cl_4$	462.75	$6.375 \times 10^{15}$	1
$C^{35}Cl_3^{37}Cl_1$	459.88	$6.384 \times 10^{15}$	1.0013
$C^{35}Cl_2^{37}Cl_2$	456.48	$6.394 \times 10^{15}$	1.0028
$C^{35}Cl_1^{37}Cl_3$	453.61	$6.402 \times 10^{15}$	1.0041

Few citations of calculated Raman scattering cross sections exist in the literature. Therefore, the simplified comparison of Raman differential scattering cross sections is reported as only proportional to  $(\nu_0 - \nu_1)^4$ , which is suitable for this work. Ideally, a difference in scattering strength among isotopic variants of  $CCl_4$  would help explain the discrepancy in relative intensities between the theoretical and the measured results. However, Table 3 clearly shows that the Raman differential scattering cross section contributes very little to the difference in scattering intensities among the isotopic fine structure, as evidenced by the similarity of the normalized differential scattering cross sections. The data suggest that they are effectively equal in scattering strength. It turns out that hot bands underlying the low frequency side of the  $\nu_1$  peak cause the lower frequency fine structure to exhibit a greater intensity than is predicted. The treatment of the data to compensate for this phenomenon will be described in a follow-up to this

experiment. Also, the peak due to  $C^{35}Cl_4$  is  $\sim 10\%$  more intense than predicted. We proposed that this extra intensity is due to the  $\nu_3 - \nu_4$  difference band, and at this writing, the article reporting this work is in press at the Journal of Raman Spectroscopy.<sup>18</sup>

### Classical Mechanical Perspective: Center of Mass of Four Coupled Morse Oscillators

The slight asymmetries of the symmetric stretches of the isotopic variants can be interpreted as resulting from the displacement of each molecule's carbon atom relative to the center of mass of the molecule (Table 4).

**Table 4.** Displacement of Carbon Atom Relative to the Center of Mass

Molecule	Displacement/pm
$C^{35}Cl_4$	0
$C^{35}Cl_3^{37}Cl_1$	2.271
$C^{35}Cl_2^{37}Cl_2$	2.589
$C^{35}Cl_1^{37}Cl_3$	2.214
$C^{37}Cl_4$	0

The molecules with completely symmetric stretches ( $C^{35}Cl_4$ ,  $C^{37}Cl_4$ ) have stationary carbon atoms because all chlorine substituents are of equal mass. Because the  $\nu_1$  vibrational frequency is dependent on the mass of chlorine, the  $^{37}Cl$  will "pull" the carbon atom in the direction of its vibration. Therefore,  $C^{35}Cl_3^{37}Cl_1$  displaces the carbon atom along the  $C-^{37}Cl$  bond, whereas  $C^{35}Cl_1^{37}Cl_3$  does so equally split among the spatial components of the three  $C-^{37}Cl$  bonds. Accordingly, the carbon atom in  $C^{35}Cl_2^{37}Cl_2$  moves in the direction of the two  $C-^{37}Cl$  bonds with a magnitude proportional to the angle between the bonds and the vector describing the carbon atom's motion. It is important to note here that we did not consider the contribution of  $^{13}C$  to the  $\nu_1$  vibration because of its small relative abundance ( $\sim 1\%$ ) and small relative displacement from the center of mass ( $\sim 0.6\%$  different from  $^{12}C$ ).

## CONCLUSION

This experiment, whether conducted in the laboratory or as a dry lab, allows students to study the fine structure in the symmetric stretch mode of  $CCl_4$ , which arises due to the natural abundance of chlorine isotopes. In addition to providing high resolution ( $1\text{ cm}^{-1}$ ) measured data, this experiment guides students to theoretically predict the relative intensities of the fine structure peaks, generate a Lorentzian model to fit the measured data, consider quantum mechanical aspects (such as the Raman differential scattering cross sections) of the isotopic variants of  $C^{35}Cl_x^{37}Cl_{4-x}$ , and discuss classical mechanical aspects of the symmetric stretch through the motion of the carbon atom relative to the center of mass for each isotopic molecule.

## ASSOCIATED CONTENT

### Supporting Information

Excel workbooks for Lorentzian modeling and calculating the motion of the center of mass of each isotopic variant. These are available online through the American Chemical Society. This material is available via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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