

Midinfrared Cavity-Enhanced Two-Photon Absorption Spectroscopy for Selective Detection of Trace Gases

Yu-Zhong Liu, Meng-Yi Yu, Yan-Dong Tan, Jin Wang, Cun-Feng Cheng,* Wei Jiang, and Shui-Ming Hu*



transition. The quantitative capability of the method is demonstrated by measuring ${}^{13}CO_2$ abundances in CO₂ samples. The method is promising for the quantitative measurement of extremely trace molecules or isotopologues in gas samples.

INTRODUCTION

Laser-based quantitative analysis of trace molecules is widely utilized due to its nondestructive characteristics and the capability for in situ and real-time measurements, such as tracking greenhouse gases and pollutants,¹⁻⁶ monitoring atmospheric reactions,^{7–9} controlling industrial processes,^{10–1} and analyzing clumped isotopes.^{13,14} These applications necessitate ultrahigh sensitivity and selectivity. After decades of development, particularly with the use of cavity-enhanced techniques, the detection sensitivity has been significantly improved, showing promise in overcoming these challenges.^{15–18} However, a major limitation in detection selectivity arises from the substantial overlap of absorption lines among different molecules and isotopologues due to Doppler broadening. For example, the ¹⁴CO₂ line at 2209.1077 cm^{-1} was proposed¹⁹ to determine the ¹⁴C/C abundances in atmospheric CO_2 samples. However, it is challenging to eliminate the interference^{20,21} from the ¹³CO₂ line at 2209.1159 cm⁻¹ and the N_2O line at 2209.1144 cm⁻¹, since abundances of $^{13}\rm{CO}_2$ and N_2O in the atmosphere exceed ¹⁴CO₂ by many orders of magnitude. While the resolving power can be improved by reducing the sample temperature^{19,20,22} or selecting molecules at a certain speed,²³⁻²⁵ these approaches can lead to a decrease in sensitivity, as fewer molecules interact with the probe laser. Multiphoton spectroscopy, as opposed to single-photon absorption (SPA), provides a means to significantly reduce the resonance line width and enhance selectivity.^{26–29} By employing counterpropagating laser beams, all molecules with varying velocities can, in

and compensates for the small cross-section of the two-photon

principle, contribute to a narrow, Doppler-free two-photon absorption (TPA) signal. Nevertheless, two primary drawbacks limit the effectiveness of multiphoton spectroscopy for trace detection: (i) the cross sections of multiphoton transitions between rovibrational states of molecules are extremely small, leading to a significant loss of sensitivity, and (ii) the reliance on laser power complicates quantitative measurements. In this study, we introduce a novel strategy based on cavity-enhanced two-photon absorption (CETPA) spectroscopy for quantitative trace gas measurements. The TPA cross-section is significantly enhanced by the presence of a near-resonance intermediate state (Figure 1A) and the use of high laser power intensity (Figure 1B). The Doppler-free nature of TPA results in a line width that is over 2 orders of magnitude narrower than that of SPA transitions. 30,31 The use of a high-finesse cavity not only amplifies the effective laser power within the cavity, meeting the demands for TPA, but also extends the effective optical path length for laser-molecule interactions, thereby increasing detection sensitivity. To verify the quantitative capability of the TPA method, we use a TPA transition of ${}^{13}\text{CO}_2$ at 2.78 μm to determine the ${}^{13}\text{CO}_2/\text{CO}_2$

Received:October 8, 2024Revised:December 22, 2024Accepted:December 29, 2024Published:January 3, 2025







Figure 1. (A) Energy diagram of a two-photon transition, with the initial, intermediate, and final states labeled as $|0\rangle$, $|1\rangle$, and $|2\rangle$, respectively. (B) Schematic representation of SPA and TPA spectra. The dashed box highlights a zoomed-in view of the TPA spectra, illustrating the increase in laser intensity. (C) Schematic of the CETPA experimental setup. The mid-infrared laser, generated by a continuous-wave optical parametric oscillator (OPO) source, is optically locked to a longitudinal mode of a high-finesse cavity. The frequencies of the OPO pump and signal lasers are monitored by a near-infrared optical frequency comb (OFC) for calibration of the idler laser frequency. The light transmitted through the cavity is detected by a HgCdTe photodetector (MCT). More details of the experimental setup are given in the Supporting Information.



Figure 2. (A) Absorption coefficients for the six most abundant isotopes of CO_2 within the range of 3600.0–3600.5 cm⁻¹ at 296 K. The pressure of CO_2 (with natural isotopic abundances) is set at 20 Pa, and different colors correspond to different isotopes. Parameters of the absorption lines are from the HITRAN database.³⁵ (B) The energy diagram of the resonance enhanced Q(36) two-photon transition of ¹³CO₂. (C) Simulated TPA spectra (red dashed lines) of ¹³C¹⁶O₂ under different laser powers and the SPA baseline (black solid line) around 3600.26 cm⁻¹ (107 933 GHz).

abundance in a series of samples and compare to conventional mass spectrometry measurements.

EXPERIMENTAL SECTION

The schematic of the CETPA system is shown in Figure 1C. A homemade continuous-wave optical parametric oscillator (OPO) laser system, pumped by a 1064 nm external-cavity diode laser (ECDL), generates mid-infrared idler light tunable within the range of 2.6–4.5 μ m, with the signal light enhanced by the OPO cavity.^{32,33} The idler light is stabilized by locking it to a 75-cm-long high-finesse cavity, which consists of a pair

of high-reflective (HR) mirrors ($R \approx 99.967\%$ at 2778 nm). Its frequency, determined by the difference between the nearinfrared pump and signal laser frequencies, is precisely measured using an optical frequency comb (OFC). The cavity is enclosed within a sample cell with a total volume of approximately 7.5 L, and the sample pressure is measured using a Baratron capacitance manometer. The entire cell is thermally stabilized, ensuring temperature fluctuations remain below 10 mK at 300 K.



Figure 3. (A) Experimental TPA spectra for samples with different ${}^{13}CO_2$ concentrations (scattering points), fitted using Voigt functions (solid lines). The residuals from the fitting are shown in the lower panel. Measurements were conducted at a sample pressure of 20 Pa and an input laser power of 17 mW. (B) TPA signals measured under different input laser powers at a constant sample pressure of 20 Pa. The solid curve represents a linear fit to the data. (C) TPA signals measured under different sample pressures, with the input power fixed at 17 mW. The solid curve illustrates the fitting results based on the TPA model described in the Supporting Information, while the dashed line indicates the high-pressure limit. (D) Comparison of the CETPA signal for each sample (at 20 Pa and 17 mW input laser power) with the corresponding ${}^{13}C/C$ ratio measured by IRMS. Circular points denote the measured data, and the red curve represents a linear fit. Fitting residuals are shown in the lower panel.

In the experiment, we measure the cavity's transmittance at the center frequency ν_0 of the two-photon transition, defined as

$$\kappa \equiv \frac{P_{\rm ic}(\nu_0)}{P_{\rm ic,0}} \tag{1}$$

where c and $P_{ic,0}$ represent the intracavity laser powers with and without the TPA, respectively. We further define the dimensionless TPA signal intensity as

$$S_{\rm TPA} \equiv \frac{1-\kappa}{\kappa^2} = \frac{\gamma_2 P_{\rm ic,0}}{\beta} \tag{2}$$

where γ_2 is the TPA rate proportional to the mole fraction of the analyte,²⁷ $\beta = c(1 - R)/L$ is the cavity loss rate without sample absorption, *R* is the reflectivity of the cavity mirror, and *L* is the cavity length. Enhancing the TPA signal can be achieved by using mirrors with higher reflectivity and lower loss, thereby reducing γ_0 , or by increasing the input laser power before the signal saturates, thus increasing $P_{ic,0}$ and improving the detection sensitivity. More details of the method and experimental setup are given in the Supporting Information.

RESULTS

To demonstrate the CETPA technique and verify its quantitative analysis capability, we prepared six CO_2 gas samples with varying ${}^{13}CO_2/CO_2$ and employed the TPA transition of ${}^{13}CO_2$ near 2778 nm (3600.26 cm⁻¹, 107 933 GHz) to measure the abundance of this isotopologue.

Figure 2A illustrates the simulated Doppler-limited SPA spectrum for a CO_2 gas sample at a pressure of 20 Pa. All of the isotopologues in natural abundances were considered in the simulation. Although the experimental detection limit (defined as the noise-equivalent absorption coefficient) can



Figure 4. Calculated TPA signal amplitudes of ${}^{13}\text{CO}_2$ at 3600.26 cm⁻¹ for natural isotopic abundances of 1.1×10^{-2} . The yellow dotdash lines denote conditions where the TPA line width is 1% and 10% of the SPA line width. The red star highlights the specific conditions of sample pressure and laser power employed in this study.

reach³⁴ the level of 10^{-13} cm⁻¹, quantitative measurement of ${}^{13}C^{16}O_2$ with its strong lines in this region is still difficult since transitions from other CO₂ isotopologues heavily overlap the lines. Figure 2B presents the energy diagram for the selected two-photon transition of ${}^{13}C^{16}O_2$, corresponding to the transition from the J = 36 level in the ground vibrational state (00001e) to the J = 36 level in the excited state (20021e), with a detuning of approximately 5 GHz from the intermediate J = 35 level (10011e).^{35,36} Below the saturation threshold of laser power, the SPA signal is independent of the laser power, while the TPA increases with laser power. Figure 2C presents

Table 1. Calculated TPA Signal Amplitudes of Trace Species at 296 K under a Sample Pressure of 1 kPa, with the	Laser Power
Set to the Saturation Level	

the effective absorption coefficients (see Supporting Information for the definition) near the TPA transition of ${}^{13}C_{16}O_{2}$ around 107 933 GHz at varying laser powers. The Doppler-free nature of TPA ensures high resolution with a line width narrower than 1% of those observed in SPA. This advantage, in comparison to the broader absorption contributions, provides excellent selectivity for molecular analysis.

Six carbon dioxide samples (purity >99.995%) with $^{13}\rm{CO}_2/\rm{CO}_2$ ratios ranging from 1% to 10% were analyzed using the CETPA method. Each measurement was conducted at a sample pressure of approximately 20 Pa. Example spectra are shown in Figure 3A. Each TPA spectrum was averaged over approximately 150 scans acquired over 38 min and fitted using a Voigt function. Note that the line width observed in this work is only 1/10 of that observed by Zhao et al.²⁹ The halfwidth at half-maximum (HWHM) was measured at about 280 kHz, primarily attributed to transit-time broadening ($\Gamma_{\rm t} \approx 56$ kHz)³⁷ and collision-induced broadening ($\Gamma_{\rm c} \approx 270$ kHz). The collision-induced broadening increases approximately linearly with the sample pressure.

The fluctuation in signal amplitude, which currently limits the quantitative determination of isotope abundance, is primarily due to laser power noise. This noise can be reduced by stabilizing the laser power using a feedback servo system that incorporates an acousto-optic modulator (AOM).³⁸ We also conducted spectral measurements at various laser powers and sample pressures by using a sample with a ${}^{13}C/C$ isotope abundance of 4.92%. The results are shown in Figure 3B and C. Under these experimental conditions, the TPA signal exhibits a linear dependence on the laser power and reduced sensitivity to sample pressure when moderately high pressures above 20 Pa are applied. These findings align with the model described in the Supporting Information. For subsequent measurements, an idler laser power of 17 mW was injected into the optical cavity, and the sample gas pressure was maintained at 20 Pa. The TPA signal amplitude was then determined by using eq 2.

The quantitative capability of the CETPA method was validated through comparison with measurements obtained via mass spectrometry. Six samples with varying ${}^{13}CO_2/CO_2$ ratios were analyzed using CETPA in Hefei and also sent to Wuhan Newradar Special Gas Co., Ltd. for mass spectrometric analysis. Three samples with concentrations below 2% were measured using an isotope ratio mass spectrometer (IRMS, Thermo Scientific Delta V Advantage), while the remaining three samples were analyzed with an isotope mass spectrometer (IMS, Nu Evolution). The results from CETPA spectroscopy conducted in Hefei and the mass spectrometry results from Wuhan are presented in Figure 3D. For each sample, the fractional uncertainty of the $R(^{13}C/C)$ ratio measured in Wuhan ranged from 0.02% to 0.4%. The uncertainty analysis of the CETPA data includes statistical uncertainties of the TPA signal and uncertainties related to the

laser power fluctuations. The ${}^{13}C/C$ ratios measured by both methods exhibit an excellent linear correlation, with a fractional deviation of the linear fit of 0.5%, primarily attributed to uncertainties in laser power during the TPA measurements.

Article

To evaluate the potential of the TPA approach, we computed ¹³CO₂ TPA signals at 2778 nm for natural samples under varying sample pressures and laser powers using the current experimental setup. The calculations employed an approximate formula, assuming that the laser-induced Rabi frequency is much smaller than the detuning $(\Delta \nu)$.²⁷ When the Rabi frequency approaches the detuning, the computed TPA signal is slightly lower than the numerical solution of the density matrix, with a deviation of less than 50%. This level of accuracy is sufficient to demonstrate the signal's potential. Previous experiments for quantitative ${}^{13}C/C$ measurements were performed under low sample pressure and laser power conditions (indicated by the red star in Figure 4). The yellow dotted-dash lines in the contour plot represent experimental conditions where the TPA line width is 1% and 10% of the SPA line width. A narrower line width corresponds to improved selectivity in the TPA method, offering significant opportunities for highly selective detection. We also observed that the TPA signal increases linearly with laser power until saturation with the saturation power scaling linearly with sample pressure. This suggests substantial potential for sensitivity improvement. Notably, two cavity mirrors with a reflectivity of 99.967% at 2778 nm were used in these experiments to enable quantitative measurements. A significant enhancement in intracavity laser power and the TPA signal could be achieved by using ultralow-loss, high-reflectivity mirrors.^{39,40} According to the contour plot (Figure 4), increasing both sample pressure and laser power could enhance the TPA signal by up to 3 orders of magnitude.

DISCUSSION AND PERSPECTIVE

In conclusion, we have presented a cavity-enhanced twophoton absorption (CETPA) spectroscopy strategy that offers both high selectivity and sensitivity. The capability for quantitative detection was demonstrated by measuring the 13 CO₂/CO₂ ratios in a series of gas samples with an accuracy of 0.5%, verified against isotope ratio mass spectrometry. The CETPA approach provides excellent selectivity, paving the way for trace gas detection. It is important to note that the sensitivity of the conventional single-photon detection is fundamentally limited by the transition strength, whereas the TPA signal scales with intracavity laser power. With advancements in coating technology, intracavity power could potentially exceed 10 kW,⁴¹ leading to a substantial increase in sensitivity without sacrificing selectivity. With stable control of the laser power, sample pressure, and gas flow rate, as well as by reduction of the cavity volume (potentially to about 50

mL), it is feasible to achieve fast measurements with a time resolution of a few seconds. The current CETPA technique can also be extended to detect other molecules in gas mixtures where exceptional selectivity is required, as shown in Table 1. This strategy is invaluable for the sensitive and selective detection of challenging molecules such as radioactive carbon dioxide, clumped isotopes, reactive radicals, and other rare species. These applications are likely to have broad impacts across chemistry, environmental science, geoscience, and biomedicine.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.analchem.4c05414.

Two-photon absorption coefficient, cavity-enhanced two-photon absorption spectroscopy, detailed experimental setup (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Cun-Feng Cheng State Key Laboratory of Molecular Reaction Dynamics and Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China; Hefei National Laboratory, University of Science and Technology of China, Hefei 230088, China; orcid.org/0000-0003-3637-0989; Email: cfcheng@ustc.edu.cn
- Shui-Ming Hu Hefei National Laboratory, University of Science and Technology of China, Hefei 230088, China; Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China; ● orcid.org/0000-0002-1565-8468; Email: smhu@ustc.edu.cn

Authors

- Yu-Zhong Liu School of Physical Sciences, University of Science and Technology of China, Hefei 230026, China
- Meng-Yi Yu State Key Laboratory of Molecular Reaction Dynamics, University of Science and Technology of China, Hefei 230026, China; Hefei National Laboratory, University of Science and Technology of China, Hefei 230088, China
- Yan-Dong Tan Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China
- Jin Wang Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China
- Wei Jiang School of Physical Sciences, University of Science and Technology of China, Hefei 230026, China; Hefei National Laboratory, University of Science and Technology of China, Hefei 230088, China; orcid.org/0000-0002-6355-7637

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.analchem.4c05414

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Z.-T. Lu for helpful discussions. This work was jointly supported by the Chinese Academy of Science

(Grant Nos.YSBR-055, XDB0970100), the Innovation Program for Quantum Science and Technology (Grant No. 2021ZD0303102, 2023ZD0301000), and the National Natural Science Foundation of China (Grant Nos. 22241302, 12393825).

REFERENCES

(1) Rieker, G. B.; Giorgetta, F. R.; Swann, W. C.; Kofler, J.; Zolot, A. M.; Sinclair, L. C.; Baumann, E.; Cromer, C.; Petron, G.; Sweeney, C.; et al. *Optica* **2014**, *1*, 290–298.

(2) Fleisher, A. J.; Yi, H.; Srivastava, A.; Polyansky, O. L.; Zobov, N. F.; Hodges, J. T. *Nat. Phys.* **2021**, *17*, 889–893.

(3) Sampaolo, A.; Patimisco, P.; Giglio, M.; Zifarelli, A.; Wu, H.; Dong, L.; Spagnolo, V. Anal. Chim. Acta **2022**, 1202, 338894.

(4) Kwaśny, M.; Bombalska, A. Sensors 2023, 23, 2834.

(5) Wang, M.; Varma, R.; Venables, D. S.; Zhou, W.; Chen, J. Anal. Chem. 2022, 94, 4286-4293.

(6) Cao, Y.; Liu, K.; Wang, R.; Gao, X.; Kang, R.; Fang, Y.; Chen, W. Anal. Chem. **2023**, 95, 1680–1685.

(7) Liu, Y.; Zhang, J. Anal. Chem. 2014, 86, 5391-5398.

(8) Bjork, B. J.; Bui, T. Q.; Heckl, O. H.; Changala, P. B.; Spaun, B.; Heu, P.; Follman, D.; Deutsch, C.; Cole, G. D.; Aspelmeyer, M.; et al. *Science* **2016**, 354, 444–448.

(9) Long, D. A.; Cich, M. J.; Mathurin, C.; Heiniger, A. T.; Mathews, G. C.; Frymire, A.; Rieker, G. B. *Nat. Photonics* **2024**, *18*, 127–131.

(10) Zhang, Z.; Pang, T.; Yang, Y.; Xia, H.; Cui, X.; Sun, P.; Wu, B.; Wang, Y.; Sigrist, M. W.; Dong, F. *Opt. Express* **2016**, *24*, A943– A955.

(11) Lewen, Z.; Zhirong, Z.; Qianjin, W.; Pengshuai, S.; Bian, W.;
Tao, P.; Hua, X.; Sigrist, M. W. Opt. Lasers Eng. 2022, 152, 106950.
(12) Yang, Q.-y.; Tan, Y.; Qu, Z.-h.; Sun, Y.; Liu, A.-w.; Hu, S.-m.
Anal. Chem. 2023, 95, 5652–5660.

(13) Ostrom, N. E.; Ostrom, P. H. Biogeochemistry 2017, 132, 359–372.

(14) Yanay, N.; Wang, Z.; Dettman, D. L.; Quade, J.; Huntington, K. W.; Schauer, A. J.; Nelson, D. D.; McManus, J. B.; Thirumalai, K.; Sakai, S.; Rebaza Morillo, A.; Mallik, A. *Sci. Adv.* **2022**, *8*, No. eabq0611.

(15) Giusfredi, G.; Bartalini, S.; Borri, S.; Cancio, P.; Galli, I.; Mazzotti, D.; De Natale, P. *Phys. Rev. Lett.* **2010**, *104*, 110801.

(16) Kassi, S.; Campargue, A. J. Chem. Phys. 2012, 137, 234201.

(17) Long, D.; Cygan, A.; van Zee, R.; Okumura, M.; Miller, C.; Lisak, D.; Hodges, J. Chem. Phys. Lett. **2012**, 536, 1–8.

(18) Maity, A.; Maithani, S.; Pradhan, M. Anal. Chem. 2021, 93, 388-416.

(19) Galli, I.; Bartalini, S.; Borri, S.; Cancio, P.; Mazzotti, D.; De Natale, P.; Giusfredi, G. *Phys. Rev. Lett.* **2011**, *107*, 270802.

(20) Fleisher, A. J.; Long, D. A.; Liu, Q.; Gameson, L.; Hodges, J. T. J. Phys. Chem. Lett. 2017, 8, 4550-4556.

(21) Galli, I.; Bartalini, S.; Ballerini, R.; Barucci, M.; Cancio, P.; De Pas, M.; Giusfredi, G.; Mazzotti, D.; Akikusa, N.; De Natale, P. *Optica* **2016**, 3, 385.

(22) Wu, H.; Stolarczyk, N.; Liu, Q.-H.; Cheng, C.-F.; Hua, T.-P.; Sun, Y. R.; Hu, S.-M. *Opt. Express* **2019**, *27*, 37559–37567.

(23) Jiang, J.; McCartt, A. D. J. Chem. Phys. 2021, 155, 104201.

(24) McCartt, A. D.; Jiang, J. ACS Sensors 2022, 7, 3258-3264.

(25) Jiang, J.; McCartt, A. D. Proc. Natl. Acad. Sci. U.S.A. 2024, 121, No. e2314441121.

(26) Lehmann, K. K. Appl. Phys. B: Laser Opt. 2014, 116, 147–155.

(27) Lehmann, K. K. J. Chem. Phys. 2019, 151, 144201.

(28) Lehmann, K. K. J. Opt. Soc. Am. B 2020, 37, 3055-3062.

(29) Zhao, G.; Bailey, D. M.; Fleisher, A. J.; Hodges, J. T.; Lehmann, K. K. *Phys. Rev. A* **2020**, *101*, 062509.

(30) Vasilenko, L. S.; Chebotaev, V. P.; Shishaev, A. V. JETP Lett. 1970, 12, 161.

(31) Biraben, F.; Cagnac, B.; Grynberg, G. Phys. Rev. Lett. 1974, 32, 643-645.

(32) Zhang, Z.-T.; Tan, Y.; Wang, J.; Cheng, C.-F.; Sun, Y. R.; Liu, A.-W.; Hu, S.-M. Opt. Lett. **2020**, 45, 1013–1016.

(33) Zhang, Z.-T.; Cheng, C.-F.; Sun, Y. R.; Liu, A.-W.; Hu, S.-M. Opt. Express 2020, 28, 27600-27607.

(34) Castrillo, A.; Khan, M. A.; Fasci, E.; D'Agostino, V.; Gravina, S.; Gianfrani, L. *Optica* **2024**, *11*, 1277–1284.

(35) Gordon, I. E.; Rothman, L. S.; Hargreaves, R. J.; Hashemi, R.; Karlovets, E. V.; Skinner, F. M.; Conway, E. K.; Hill, C.; Kochanov, R. V.; Tan, Y.; et al. *J. Quant. Spectrosc. Radiat. Transfer* **2022**, 277, 107949.

(36) Gamache, R. R.; Vispoel, B.; Rey, M.; Nikitin, A.; Tyuterev, V.; Egorov, O.; Gordon, I. E.; Boudon, V. J. Quant. Spectrosc. Radiat. Transfer **2021**, 271, 107713.

(37) Lehmann, K. K. J. Chem. Phys. 2021, 154, 104105.

(38) Tricot, F.; Phung, D. H.; Lours, M.; Guérandel, S.; de Clercq, E. *Rev. Sci. Instrum.* **2018**, *89*, 113112.

(39) Cole, G. D.; Zhang, W.; Bjork, B. J.; Follman, D.; Heu, P.; Deutsch, C.; Sonderhouse, L.; Robinson, J.; Franz, C.; Alexandrovski, A.; et al. *Optica* **2016**, *3*, 647–656.

(40) Truong, G.-W.; Perner, L. W.; Bailey, D. M.; Winkler, G.; Catano-Lopez, S. B.; Wittwer, V. J.; Sudmeyer, T.; Nguyen, C.; Follman, D.; Fleisher, A. J.; Heckl, O. H.; Cole, G. D. *Nat. Commun.* **2023**, *14*, 7846.

(41) Liu, Q. H.; Zhang, H.; Wen, L.; Xie, Y.; Yang, T.; Cheng, C. F.; Hu, S. M.; Yang, X. J. Phys. Chem. Lett. **2024**, 15, 9926–9931.