ULTRAFAST PHOTOINDUCED TERAHERTZ EMISSION PROPERTIES OF BULK AND FEW LAYER MoS_2

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JULY 2025

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by

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Department of Physics

submitted

in fulfilment of the requirements of the degree of

Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

July 2025

Dedicated

to

My Parents

Certificate

This is to certify that the thesis entitled “**Ultrafast photoinduced terahertz emission properties of bulk and few layer MoS_2,**” submitted by **Neetesh Dhakar** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in Physics, is a record of the original, bona fide research work carried out by her under my supervision and guidance. The thesis has reached the standards fulfilling the requirements of the regulations related to the award of the degree. The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma to the best of my knowledge.

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Acknowledgments

The past five years of my PhD journey at the Indian Institute of Technology (IIT) Delhi have been truly enriching, remarkable, and inspiring. Throughout this time, I have gained invaluable and unforgettable experiences in the field of terahertz research. As I reach the milestone of graduation, I would like to take this opportunity to express my heartfelt gratitude to all those who have supported and encouraged me throughout my PhD journey.

Firstly, I would like to express my deepest gratitude to my supervisor, Prof. Sunil Kumar, for his invaluable guidance, unwavering support, and insightful advice throughout my PhD journey. His expertise and encouragement have been instrumental in shaping this research and my academic growth. His patience and dedication in reviewing my work, providing thoughtful feedback, and encouraging critical thinking have significantly contributed to my research development. Beyond research, I am deeply grateful for his constant motivation and mentorship, which have helped me navigate challenges and grow as a researcher. I am truly fortunate to have had the opportunity to work under his supervision, and I will always be grateful for his guidance and support.

I sincerely appreciate the contributions of my collaborators, whose expertise and support have been invaluable in shaping part of the research. I am grateful to Prof. Brijesh Kumar, Prof. Sang-Woo Kim, Pin Zhao, and Hyeon Yeong Lee, for providing us with the interesting mono and multilayer TMDs which provided us the opportunity to learn new things about them using the THz emission spectroscopy. I am extremely grateful to my SRC committee members, Prof. Aloka Sinha, Prof. Rajendra Singh Dhaka, and Prof. Leena Nebhani, for their invaluable time and expertise that they have generously offered towards the betterment of my thesis work.

I would like to extend my sincere appreciation to my colleagues and lab mates at Femtosecond Spectroscopy and Nonlinear Photonics Laboratory for their support, insightful discussions, and the collaborative spirit that made this journey more enriching. Special thanks to my seniors Dr. Madhu Bochalya, Dr. Arvind Singh, Dr. Anand Nivedan, and Dr. Sandeep Kumar for their invaluable discussions, technical assistance, and shared enthusiasm for research. Their insights and suggestions have greatly contributed to the progress of this work. I am also thankful to my other lab members, including Ekta Yadav, Satakshi Gupta, Shiwangi Puri, Prateek Nautiyal, Akanksha Yadav, Sandeep Jakhar, Meera S, Rahul Joshi, Shivani,

Anjali, Pooja Pal, Bappa Karmakar, for creating a supportive and enjoyable working environment.

I am grateful to the Indian Institute of Technology Delhi, New Delhi, for providing me a home for me to be able to complete my PhD in a homely environment. Central Research Facility (CRF) and Nanoscale Research Facility (NRF) at IIT Delhi are acknowledged for providing some of the experimental facilities which were useful for my research. My research would not have been possible without the financial support from the Council of Scientific and Industrial Research (CSIR), the Government of India.

I am incredibly grateful to my friends, whose unwavering support and encouragement have been invaluable throughout this PhD journey. A heartfelt thank you to Dr. Sandeep Kumar, Himanshu Joshi, Sarita Mittal, and Rahul Joshi for always being there, whether to celebrate small victories, offer words of encouragement during challenging times or simply provide much-needed distractions from research. Your friendship has been a source of strength and joy. This PhD journey would not have been the same without your support, laughter, and companionship.

I deeply appreciate the support I have received from each of you, which has equipped me with invaluable skills and experiences. These will not only contribute to my growth as a professional but, more importantly, help me become a more open-minded and self-aware individual. I am grateful for every moment that has instilled in me the fundamental values one should uphold.

Last and most importantly, I would like to express my deepest gratitude to my parents, for their unconditional love, unwavering support, and endless encouragement throughout my life and academic journey. This achievement is as much theirs as it is mine, and I dedicate this thesis to them with all my love and gratitude.

NEETESH DHAKAR

Abstract

Transition metal dichalcogenides (TMDs) have attracted significant attention in recent years due to their remarkable and unique electrical, optical, and mechanical properties, making them promising candidates for next-generation electronic and optoelectronic devices. Among the various TMDs, the interest in molybdenum disulfide (MoS_2) has been primarily driven by its potential to enable groundbreaking advancements in fields such as valleytronics, spintronics, and quantum computing. Its most notable characteristics are tunable bandgap, strong spin-valley coupling, and strong excitonic effects, which are used in field effect transistors, photodetectors, energy storage devices, and sensors. To reveal how these materials respond to ultrafast excitations, ultrafast terahertz emission spectroscopy has emerged as a powerful tool to probe the fundamental charge, spin, and excitonic dynamics at femtosecond timescales. In this thesis, the main research focuses on investigating and understanding new physical phenomena occurring in the femtosecond optically excited bulk and few-layer MoS_2 crystals. Initially, we demonstrated the THz generation efficiency from single crystalline bulk MoS_2 by tuning excitation wavelength and sample temperature and gained insight into the fundamental processes governing the response. A key aspect of this investigation was the differentiation among the distinct mechanisms responsible for THz emission when MoS_2 is excited above and below its photonic bandgap energy. This distinction is crucial for understanding the interplay between different charge carrier dynamics contributing to THz radiation. Subsequently, by performing temperature-dependent THz emission studies, the presence of the excitonic shift current in the bulk MoS_2 at low temperatures has been investigated and the possible transition of the pure exciton-rich phase to an electron-hole liquid phase has been highlighted. Further, we have used the THz time domain emission spectroscopy for obtaining quantitative information about the THz radiation generation efficiency of thin films (monolayer and a few-layer) of MoS_2. Here, a significant enhancement in THz generation efficiency due to Nb-doping in thin film MoS_2 as compared to the pristine MoS_2 samples is observed. Finally, we have studied the role of interfacial effects in a heterostructure, for which, we choose a multilayer MoS_2-nanocrystalline graphene heterostructure. Here, the influence of the interfacial charge transfer and photon drag effect on the THz emission property have been investigated.

सारांश

हाल के वर्षों में, ट्रांज़िशन मेटल डाइकाल्कोजेनाइड्स (TMDs) ने अपनी असाधारण और विशिष्ट विद्युत, प्रकाशीय और यांत्रिक गुणों के कारण वैज्ञानिक समुदाय का काफी ध्यान आकर्षित किया है, जिससे वे अगली पीढ़ी के इलेक्ट्रॉनिक और ऑप्टोइलेक्ट्रॉनिक उपकरणों के लिए एक संभावनाशील सामग्री बन गए हैं। विभिन्न TMDs में से, मोलिब्डेनम डाइसल्फ़ाइड (MoS_2) विशेष रूप से अनुसंधानकर्ताओं के लिए आकर्षण का केंद्र बना हुआ है, मुख्य रूप से वैलीट्रॉनिक्स, स्पिनट्रॉनिक्स और क्वांटम कंप्यूटिंग जैसे क्षेत्रों में इसकी क्रांतिकारी प्रगति की संभावनाओं के कारण। MoS_2 की कुछ प्रमुख विशेषताएँ हैं: ट्यूनबल बैंडगैप, मजबूत स्पिन-वैली कपलिंग, और शक्तिशाली एक्साइटोनिक प्रभाव, जो इसे फील्ड-इफ़ेक्ट ट्रांज़िस्टर, फोटो-डिटेक्टर, ऊर्जा भंडारण उपकरणों और सेंसर में अनुप्रयोग के लिए उपयुक्त बनाते हैं। यह समझने के लिए कि ये सामग्री अल्ट्राफास्ट (अति-तीव्र) उत्तेजनाओं के प्रति कैसी प्रतिक्रिया देती हैं, अल्ट्राफास्ट टेराहर्ट्ज़ (THz) उत्सर्जन स्पेक्ट्रोस्कोपी एक महत्वपूर्ण उपकरण के रूप में उभरा है, जो फेमटोसेकंड टाइमस्केल पर मूलभूत चार्ज, स्पिन और एक्साइटोनिक गतिकी की जांच करने की क्षमता प्रदान करता है। इस शोध प्रबंध में, मुख्य रूप से फेमटोसेकंड ऑप्टिकल रूप से उत्तेजित बल्क और कुछ-परत वाले MoS_2 क्रिस्टलों में प्रकट होने वाली नई भौतिक घटनाओं की जांच और समझने पर ध्यान केंद्रित किया गया है। प्रारंभ में, हमने एकल-क्रिस्टलीय बल्क MoS_2 से THz उत्सर्जन दक्षता का अध्ययन किया, जिसमें हमने उत्तेजना तरंगदैर्घ्य और नमूना तापमान को नियंत्रित करके इस प्रक्रिया की गहरी अंतर्दृष्टि प्राप्त की। इस अध्ययन का एक महत्वपूर्ण पहलू यह था कि जब MoS_2 को इसके फोटोनिक बैंडगैप ऊर्जा से ऊपर और नीचे उत्तेजित किया जाता है, तो THz उत्सर्जन के लिए उत्तरदायी विभिन्न तंत्रों के बीच अंतर को स्पष्ट रूप से अलग किया जाए। यह अंतर THz विकिरण में योगदान देने वाले विभिन्न चार्ज कैरियर गतिकी के परस्पर प्रभाव को समझने के लिए अत्यंत महत्वपूर्ण है। इसके बाद, हमने तापमान-निर्भर THz उत्सर्जन अध्ययन करके यह जांच की कि कम तापमान पर MoS_2 में एक्साइटोनिक शिफ्ट करंट मौजूद है, और यह भी अध्ययन किया कि क्या शुद्ध एक्साइटॉन-समृद्ध अवस्था से इलेक्ट्रॉन-होल तरल अवस्था में संभावित रूपांतरण हो सकता है। आगे, हमने THz टाइम-डोमेन उत्सर्जन स्पेक्ट्रोस्कोपी का उपयोग करके MoS_2 की पतली फिल्मों (एकल-परत और कुछ-परत) से THz विकिरण उत्पन्न करने की दक्षता की मात्रात्मक जानकारी प्राप्त की। यहाँ, Nb-डोपिंग के कारण MoS_2 की पतली फिल्मों में THz उत्पादन दक्षता में उल्लेखनीय वृद्धि देखी गई, जो कि शुद्ध (प्रिस्टाइन) MoS_2 नमूनों की तुलना में अधिक थी। अंत में, हमने हेटरोस्ट्रक्चर में इंटरफेस प्रभावों की भूमिका का अध्ययन किया, जिसके लिए हमने बहु-परत MoS_2-नैनोक्रिस्टलाइन ग्राफीन हेटरोस्ट्रक्चर का चयन किया। यहाँ, हमने इंटरफेसियल चार्ज ट्रांसफर और फोटॉन ड्रैग प्रभाव के THz उत्सर्जन गुणधर्म पर प्रभावों की विस्तृत जाँच की।

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List of Abbreviations

BBO	Beta Barium Borate
DFG	Difference frequency generation
ExS	Excitonic shift current
EDS	Energy dispersive spectroscopy
HRTEM	High resolution transmission electron microscopy
HWP	Half wave plate
ICT	Interfacial charge transfer
NR-OR	Non-resonant optical rectification
NC	Nonlinear crystal
OPM	Optical parabolic mirrors
OPA	Optical parametric amplifier
OR	Optical rectification
PC	Pockels cell
PL	Photolumnisence
PGE	Photogalvanic effect
PD	Photodiode
PDE	Photon drag effect
QWP	Quarter wave plate
R-OR	Resonant optical rectification
SHG	Second harmonic generation
SFG	Sum frequency generation
TMD	Transition metal dichalcogenides
TPE	Transient photocurrent effect
THz	Terahertz
WP	Wollaston prism
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
ZnTe	Zinc telluride