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Defense Synchrotron Consortium (DSC) at Brookhaven National Laboratory

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Introduction

The Defense Synchrotron Consortium (DSC) at Brookhaven National Laboratory, to be established in early 2020, has emerged from concerted efforts by the Defense Threat Reduction Agency (DTRA) of the U.S. Department of Defense to advance structural and functional analysis of materials critical to national defense. The DSC will provide outreach, training, provision of specialized sample-handling capabilities, designing and assisting with multimodal operando experiments, and provide hands-on beamline experimental support and expert assistance for data analysis. DSC will specifically emphasize the applications of in-situ and operando X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), and pair distribution function (PDF), as well as multimodal applications of these methods in correlation with Raman and infrared vibrational spectroscopies for developing an atomic-level understanding of structure-function relationships for next-generation materials that support DTRA's mission. Specific aims of the DSC are:

- Advance DTRA research priorities in chemical/materials research by exploiting operando synchrotron characterization of novel materials. The DSC-supported staff will accelerate progress by providing technical expertise and/or collaborating with DTRA-funded investigators to access and apply synchrotron methods to their research challenges. They will provide outreach, training, support for user-proposal development, hands-on support at the National Synchrotron Light Source (NSLS-II) beamlines and other synchrotrons when needed, and expert scientific support for data analysis. They will also develop specialized in-situ and/or operando sample-handling capabilities for chemical samples at beamlines to meet specialized DTRA needs.
- Apply X-ray spectroscopy and diffraction for characterization of multi-functional materials under operational conditions to decipher the atomic and molecular chemistry of catalysts and filtration materials. The overall impact of this effort will be to develop property-function relationships that guide the design of advanced materials for the DTRA mission.

A brief history

A brief history of the events preceding the decision to establish the DSC is similar to the stories told in this special issue by other scientific communities worldwide. Namely, synchrotron methods were not being widely utilized by DTRA-funded researchers until early in 2016, but the advancement of novel materials for filtration, catalysis, and other applications called for the use of appropriate tools, such as synchrotron radiation sources, which are only available at comprehensive user facilities. That year, a group of principal investigators from academia (Virginia Tech, Emory, Kennesaw State, and Stony Brook Universities) and a national laboratory (Brookhaven) joined forces with the CCDC Chemical Biological Center to adapt synchrotron methods to the task of developing a mechanistic understanding of capture and decomposition of chemical warfare agents (CWAs) by novel metal organic frameworks (MOFs) and polyoxometalates (POMs). The focus of the team on the use of multimodal methods is reflected in its name: Multidisciplinary Research for Agent Destruction (MultiRAD) and in its *modus operandi*: correlative studies of agents and simulants conducted in parallel; agents were studied at the U.S. Army Command Capabilities Development Command (CCDC Chemical Biological Center (CBC), while simulants were investigated within the laboratories of co-PIs, using similar in-situ techniques designed to enable direct comparison of results across laboratories. Those POM and MOF materials that showed potential for capture and decomposition of both agents and simulants were selected for synchrotron studies and concomitant theoretical modeling. The high scientific impact of such experiments on DTRA mission needs is illustrated by recent DTRA-funded research that leveraged synchrotron-enabled studies to discover the working mechanisms of novel filtration materials to combat chemical agents.

In the first example [1], we highlight the results of ambient pressure, multimodal in-situ spectroscopic and scattering techniques, which have been combined to illuminate atomic-level details of bond breaking and formation during the hydrolysis of a chemical warfare nerve agent simulant over a polyoxometalate catalyst. Specifically, a $Cs_8[Nb_6O_{19}]$ polyoxoniobate catalyst has been shown to react readily with dimethyl methylphosphonate (DMMP, a low-toxicity general-use surrogate for the agent sarin). The atomic-level transforma-

tions of all reactant moieties, the $[Nb_6O_{19}]_8^-$ polyanion, its Cs^+ counterions, and the DMMP substrate, were tracked under ambient conditions by a combination of X-ray absorption fine structure spectroscopy, Raman spectroscopy, and X-ray diffraction. Results revealed that the reaction mechanism follows general base hydrolysis. Together with computational results, the work demonstrates that the ultimate fate of DMMP hydrolysis at the $Cs_8[Nb_6O_{19}]$ catalyst is strong binding of the (methyl) methylphosphonic acid product to the polyanions.

Although the previous example highlighted a material capable of strongly sequestering agents, further benefit to chemical defense would come from a material that functions as a catalyst. For rational design of such a catalyst, the follow-up work [2] focused studies on the decomposition of the nerve agent sarin and the simulant dimethyl chlorophosphate (DMCP) by a zirconium polytungstate at the solid-gas interface. Using a multimodal approach (Figure 1), combining synchrotron-based X-ray absorption spectroscopy, X-ray diffraction, Raman and infrared spectroscopies with analysis of decomposition

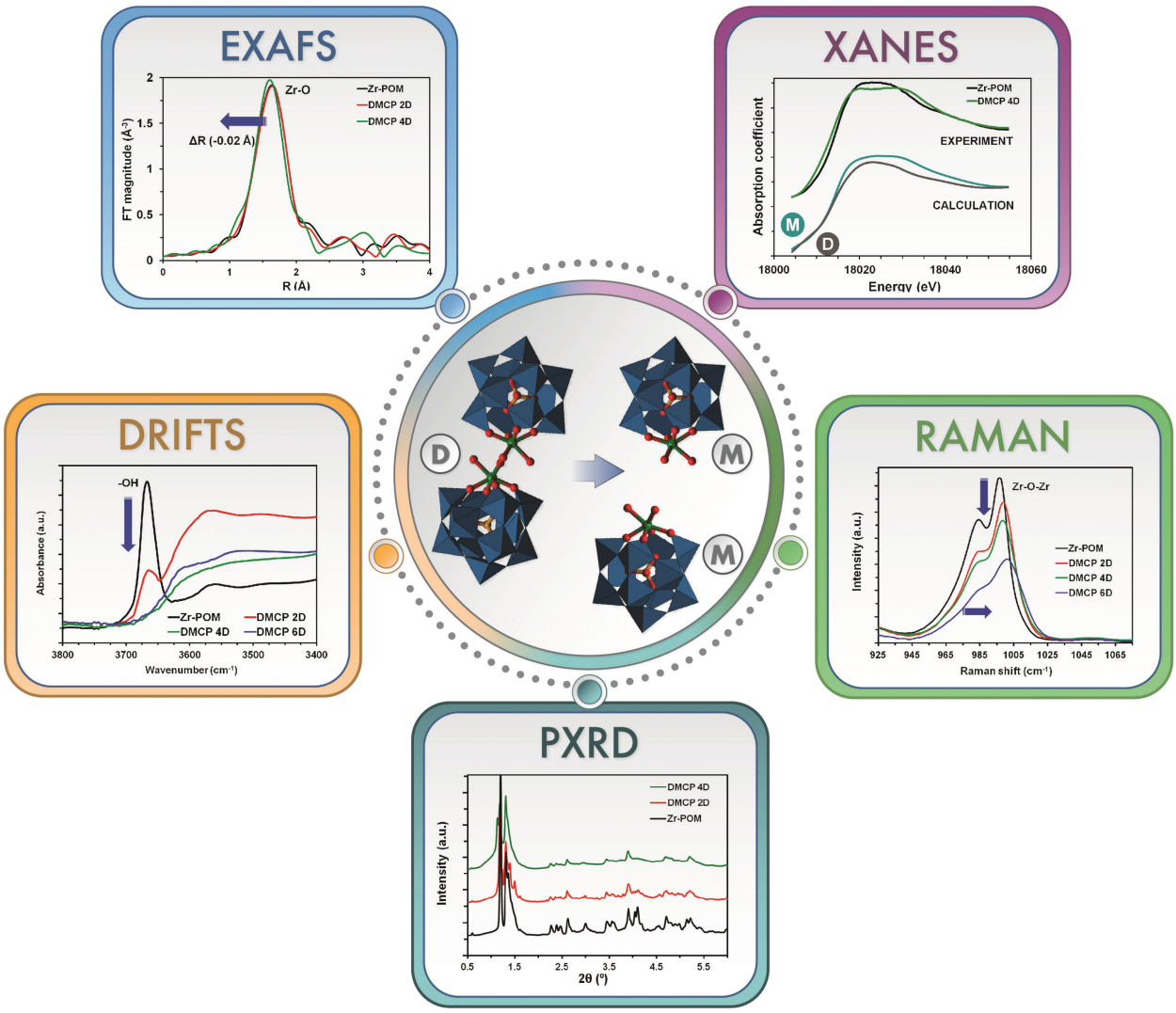

Figure 1: Combination of data from multiple probes obtained during the prolonged exposure (two days, four days, and six days) of Zr-POM to DMCP vapors reveals dissociation of Zr-POM dimers (D) to monomers (M), as shown schematically in the center. The results are shown clockwise from the top left: (1) Fourier-transform magnitudes of the Zr K-edge EXAFS spectra in Zr POM shift to lower Zr-O distances upon DMCP exposure; (2) behaviors of experimental (before and after DMCP exposure) and calculated (dimers vs monomers) Zr K-edge XANES spectra are similar; (3) Raman spectra in the Zr-O-Zr region indicate progressive decrease of these dimer-specific linkages; (4) X-ray powder diffraction (PXRD) pattern become more disordered upon exposure of Zr POM to DMCP; and (5) DRIFTS spectra in bridging O-H region demonstrate progressive decrease in the number of O-H species in the Zr POM dimer.

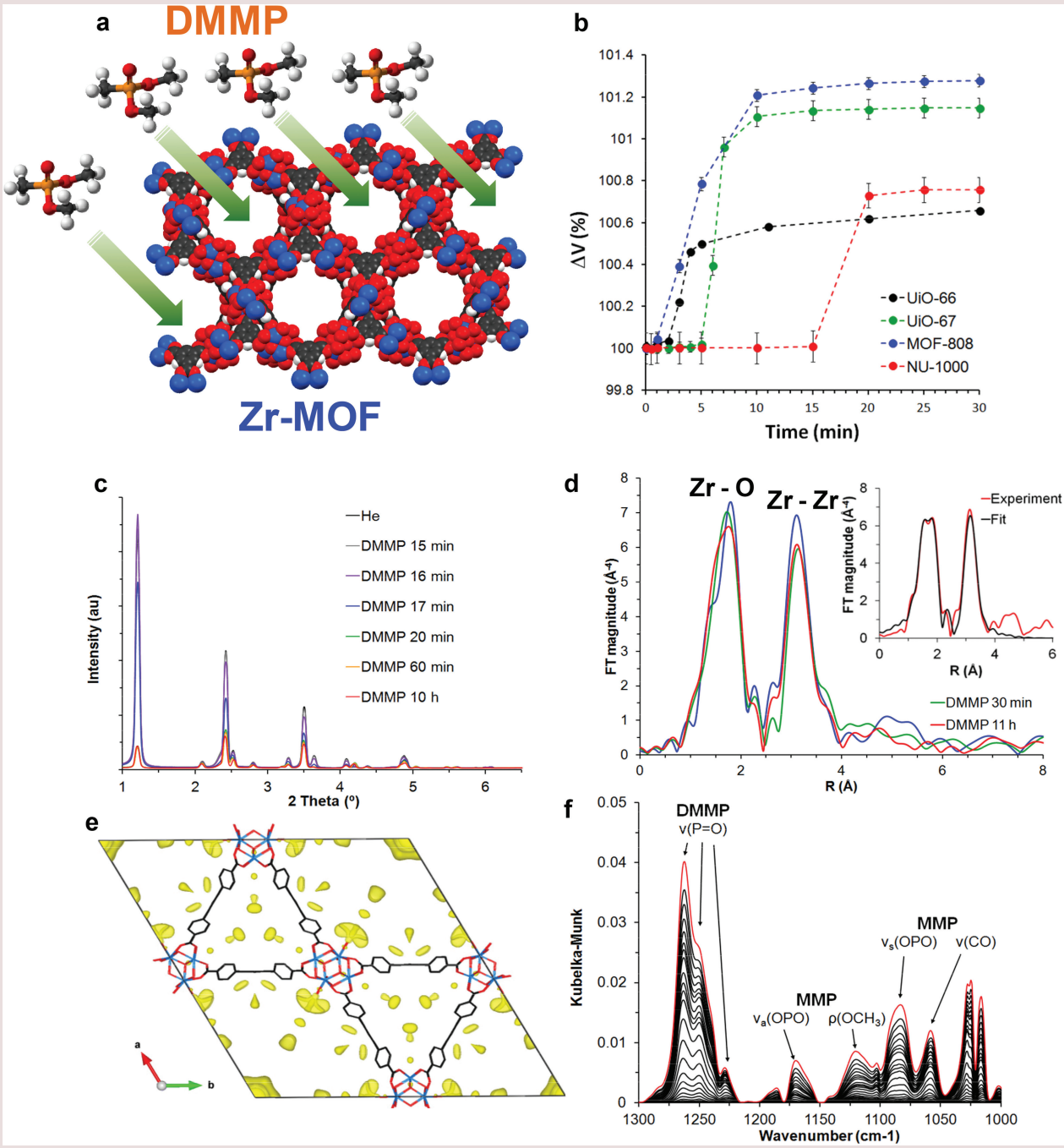

Figure 2: (a) Schematic of DMMP molecules entering the pore space of Zr-MOF; (b) evolution of UiO-66, UiO-67, MOF-808, and NU-100 unit cell volumes with the dosing of DMMP; (c) in-situ PXRD data of NU-1000 collected during exposure to DMMP; (d) in-situ EXAFS data of NU-1000 collected during exposure to DMMP. Inserts show experimental and fitted curves for the last DMMP dataset. (e) Difference Fourier electron density map of DMMP-treated NU-1000 after 10 h. Zr shown in blue, C in black, and O in red. Hydrogen atoms were removed for clarity. Electron density isosurface drawn at 0.3 ē/Å^3 in yellow. (f) Fingerprint region of DRIFTS data for DMMP-treated NU-1000. Red line shows the last dataset collected after 213 min.

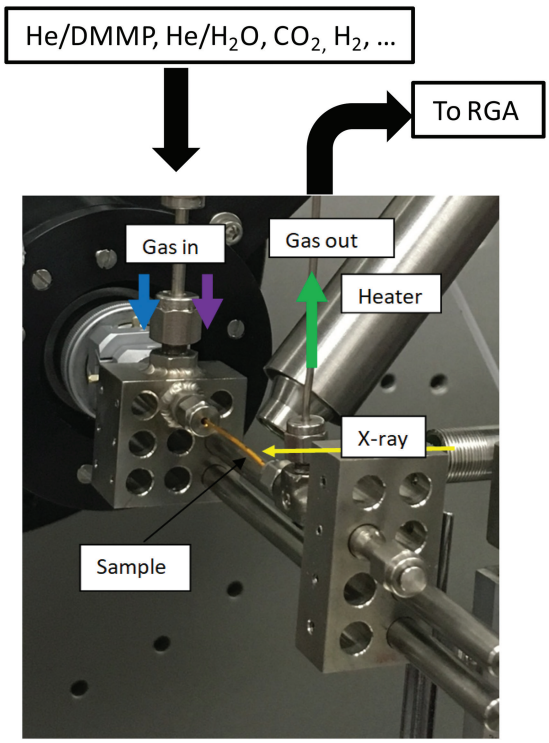

Figure 3: Flow reactor setup for in-operando X-ray scattering experiments.

products and theoretical calculations, they showed that, upon DMCP and sarin exposure, the dimeric tungstate undergoes monomerization, which opens coordinatively unsaturated Zr(IV)-centers. These centers are a key component to a potential catalyst because they bind nerve agents for activated decomposition via a nucleophilic (general base) hydrolysis mechanism. The isolation of one Zr atom in the Zr-POM of this work ameliorates product inhibition because the strong product binding is averted. This work revealed a strong similarity in the surface chemistry of DMCP and GB by direct comparison of several spectroscopic probes. As such, DMCP was proposed as a model system in the development of catalysts for CWA deactivation under relevant battlefield conditions.

In another correlative, multimodal study [3] of adsorption and decomposition of DMMP on several Zr-based metal organic frameworks (MOFs), key aspects of the reaction mechanism were revealed via synchrotron-based X-ray powder diffraction, X-ray absorption, and infrared spectroscopy. The diffraction measurements indicated that all MOFs adsorb DMMP vapors (introduced at atmospheric pressures to imitate real battlefield conditions) within the pore space (Figure 2). In addition, the combination of X-ray absorption and infrared spectra suggests direct coordination of DMMP to the Zr_6 cores of all MOFs, which ultimately leads to DMMP decomposition. The unique combination of synchrotron-based and complementary experimental probes provided important guidance for development of post-exposure treatments to regenerate the MOF-based sorbent materials.

Table 1: DTRA research problems addressing chemical threats and DSC-supported techniques that will address them.

Research problems	Technique	Details
Photocatalysis, nanocatalysis (including single atom catalysts), mechanistic studies of novel materials for CWA destruction, battlefield conditions	Synchrotron X-ray absorption spectroscopy (XAS)	Structural, dynamic, and electronic properties of nearest environment of selected atomic species (at the sub-nm scale)
Mechanistic studies of uptake and regeneration of novel filtration materials for CWA destruction, transport properties, battlefield conditions	Synchrotron X-ray diffraction	Structural properties of porous materials, phase speciation (at the > 1 nm scale); can be combined with XAS in the same in-situ/operando experiments to investigate changes that occur simultaneously at different length scales
Interaction of agents/simulants with filtration materials, battlefield conditions	Synchrotron high-energy X-ray diffraction/pair distribution function analysis	Provides radial distribution function information of multi-component materials (at the sub-nm to >1 nm scale)
Uptake and decontamination of agents/simulants using novel filtration materials, such as MOFs and POMs, in realistic battlefield conditions	Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)	Vibrational and electronic properties in agents and filtration materials; surface composition of agents/simulants on novel filtration materials and catalysts; complementary to the structural studies of the filtration materials and catalysts; complementary to Raman spectroscopy; can be combined with XAS in the same in-situ/operando experiments
	Raman spectroscopy	Vibrational and electronic properties in filtration materials; complementary to DRIFTS; can be combined with XAS or XRD in the same in-situ/operando experiments

Synchrotron experiments required access to X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) beamlines. XAS experiments were initially conducted at the NSLS-I beamlines X18B and X19A, equipped for in-situ/operando experiments with the help of the Synchrotron Catalysis Consortium (another article in this issue details the SCC operations), and then expanded to SSRL beamline BL2-2, APS beamline 9-BM, and NSLS-II beamlines TES, QAS, and ISS. XRD experiments were conducted at the APS beamline 17-BM and, from 2016, at the NSLS-II XPD beamlines. Figure 3 shows a typical in-situ setup (here, the XPD beamline was used at NSLS-II) demonstrating gas delivery into a reactor that contains an MOF sample, to be studied by XRD. The same setup was used for experiments at the hard X-ray spectroscopy beamlines.

During the four years of the MultiRAD team operations (from 2016 through 2019), the PIs and their group members spent approximately 3,000 hours running synchrotron experiments. These experiments and the results obtained were central for productivity of the team: approximately 12 publications released by the team from 2016 through 2019 used results of the synchrotron measurements.

Transition to a consortium

Successful efforts by the DTRA-supported MultiRAD team in establishing new methods for studying novel decontamination materials for civilian and soldier protection will be used as a model for the DSC, which will expand these resources to larger number of groups and other types of materials for research towards chemical agent destruction. In the near term (beginning, tentatively, in early 2020), several new DTRA-supported efforts will include materials related to atomically dispersed metal catalysts. The DSC intends to further expand operations over the long term. A summary of the future projects and the relevant techniques that will be used at DSC-supported facilities is provided in Table 1.

The operations of DSC will be led by a principal investigator and a staff scientist, stationed at Brookhaven National Laboratory (BNL). In discussions with each DTRA team, DSC will develop a plan of experiments that will be matched with the best synchrotron spectroscopy and/or scattering facilities available in the U.S. DSC staff will assist with the experiments and lead data analysis and modeling efforts, as required by the project. In addition to supporting experiments at the synchrotron facilities, DSC will operate a staging laboratory at the BNL Chemistry

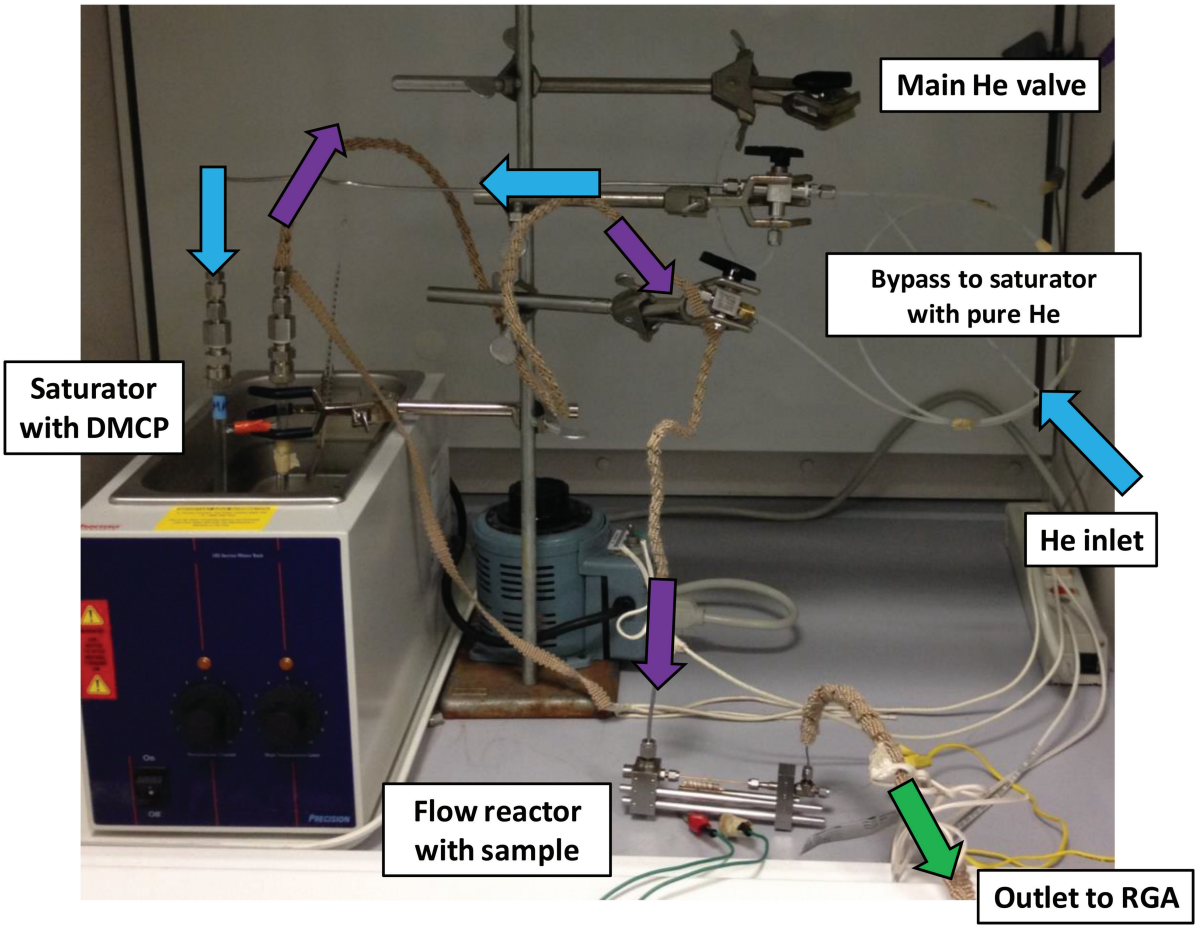

Figure 4: Vapor delivery system at the staging lab in BNL. Blue arrows show the direction of pure He flow; purple: He + DMCP; green: outlet of the reactor with products.

Division. The staging lab will be used to provide complementary characterization of the filtration and decontamination materials and simulants by Raman spectroscopy and infrared spectroscopy (DRIFTS). The simulant vapor delivery system located in the staging lab (Figure 4) is similar to the one used for agent studies in CBC, and to the portable system used at the beamlines. Additional capabilities at BNL include ambient pressure X-ray photoelectron spectroscopy, similar to one that will soon be used at the CBC for agent studies. In addition, the CBC facilities also include a multifunctional ultra-high vacuum surface science chamber, a wide pressure range high vacuum chamber for aerosol and solid studies, and vibrational spectroscopy characterization, thus providing correlations in the properties of simulants and agents that are required for successful implementation of the multimodal approach.

For research at the beamlines, the same gas delivery system and same reactors used for simulant testing in the staging lab will be available. The flow reactors are composed of small tube reactors (made of quartz, Kapton, or glassy carbon). Different tube materials and thicknesses are available for optimal signal in both transmission and fluorescence modes. Tubes are heated by resistive heating in the temperature range of 25–300°C for Kapton tubes and 25–600°C for quartz and glassy carbon tubes.

In summary, the DSC-supported capabilities will be vital for accelerating the use of powerful synchrotron methods by DTRA-funded investigators across university and Department of Defense (DoD) laboratories. These powerful experimental tools will enable scientists to address DTRA research challenges associated with the characterization of multifunctional materials that sense and respond to chemical or biological threats.

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