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REPLY TO  
ATTENTION OF

DEPARTMENT OF THE ARMY  
U.S. ARMY CHEMICAL AND BIOLOGICAL DEFENSE COMMAND  
5232 FLEMING ROAD  
ABERDEEN PROVING GROUND, MARYLAND 21010-5423

June 24, 1998

Freedom of Information and Privacy Act Office

Mr. John Greenewald, Jr.  
[REDACTED]

Dear Mr. Greenewald, Jr.:

In response to your June 8, 1998, Freedom of Information Act (FOIA) request, I have enclosed a copy of "Raman Spectroscopy of Chemical Agents and Simulants, II. GA, DIMP, and HD".

Fees in the amount of \$10.15, incurred while processing your request, have been waived.

Sincerely,

Cheryl S. Fields  
Freedom of Information and  
Privacy Act Officer

Enclosure

\*ADP 200588 001\*

RAMAN SPECTROSCOPY OF CHEMICAL AGENTS AND SIMULANTS. II.  
GA, DIMP, AND HD

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Attn: SMCCR-RSL, Aberdeen Proving Ground, MD 21010-5423

The analysis of detection concepts based on Raman scattering requires a knowledge of the frequency dependence of the Raman cross sections (Raman excitation profiles). Last year, data on the chemical agent simulant dimethyl methylphosphonate (DMMP) and the chemical agent isopropyl methylphosphonofluoridate (GB) were presented. The Raman excitation profiles for diisopropyl methylphosphonate (DIMP) and ethyl N,N-dimethyl phosphoroamidocyanidate (GA) have been measured recently. Excitation wavelengths ranging from 363.8 to 514.5 nm from an argon ion laser were utilized in the measurements.

## INTRODUCTION

Concepts based on Raman scattering have frequently been proposed for chemical agent remote, or stand-off detection.<sup>1,2</sup> Early investigations sought to exploit the normal Raman effect while more recent efforts have centered on the use of coherent Raman techniques for remote sensing.<sup>3</sup> Sensitivity analyses of these concepts have been hampered by an incomplete knowledge of the strength of the Raman scattering (magnitude of the Raman cross section) for the chemical agents. Ordinary Raman scattering increases as the frequency of the excitation to the fourth power. As the excitation approaches resonance with an electronic transition, however, the Raman scattering can increase by orders of magnitude over what would be expected from the <sup>4</sup> dependence. For this reason, the Raman cross sections should be measured at shorter wavelengths and not calculated from values obtained with visible excitation.

## PREVIOUS WORK

Results from Raman excitation profile measurements for GB and DMMP (dimethyl methylphosphonate) were reported at this conference last year.<sup>4</sup> Only minor pre-resonance enhancement was observed for these compounds with excitation wavelengths down to 363.8 nm. Pre-resonance enhancement occurs with excitation that is close, but does not overlap an electronic absorption band of

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the molecule. Raman excitation profiles for GA (ethyl N,N-dimethyl phosphoramidocyanidate) and DIMP (diisopropyl methylphosphonate) have recently been obtained and are reported here. The Raman spectrum of HD or mustard (bis(2-chloroethyl)sulfide) has also been obtained with excitation at 514.5 nm.

#### EXPERIMENTAL METHODS AND RESULTS

Raman spectra were recorded at approximately  $1 \text{ cm}^{-1}$  resolution on a Spex Ramalog spectrometer equipped with a Datamate computer, photon counting electronics, and RCA 31034A photomultiplier tube. The Raman excitation wavelengths of 514.5, 488.0, 457.9, and 363.8 nm were provided by a Coherent Innova 12 argon ion laser. Because of their toxicity and the requirement to have the samples double contained, the liquid agents were first placed in a quartz cell and then sealed in an airtight containment cell. Quartz windows in the containment cell allowed the laser beam to enter and strike the sample and the scattered radiation at  $90^\circ$  to exit and enter the spectrometer. The containment cell was not utilized with the simulant DIMP.

FIGURE 1  
Raman Spectrum of GA with 363.8 nm Excitation.

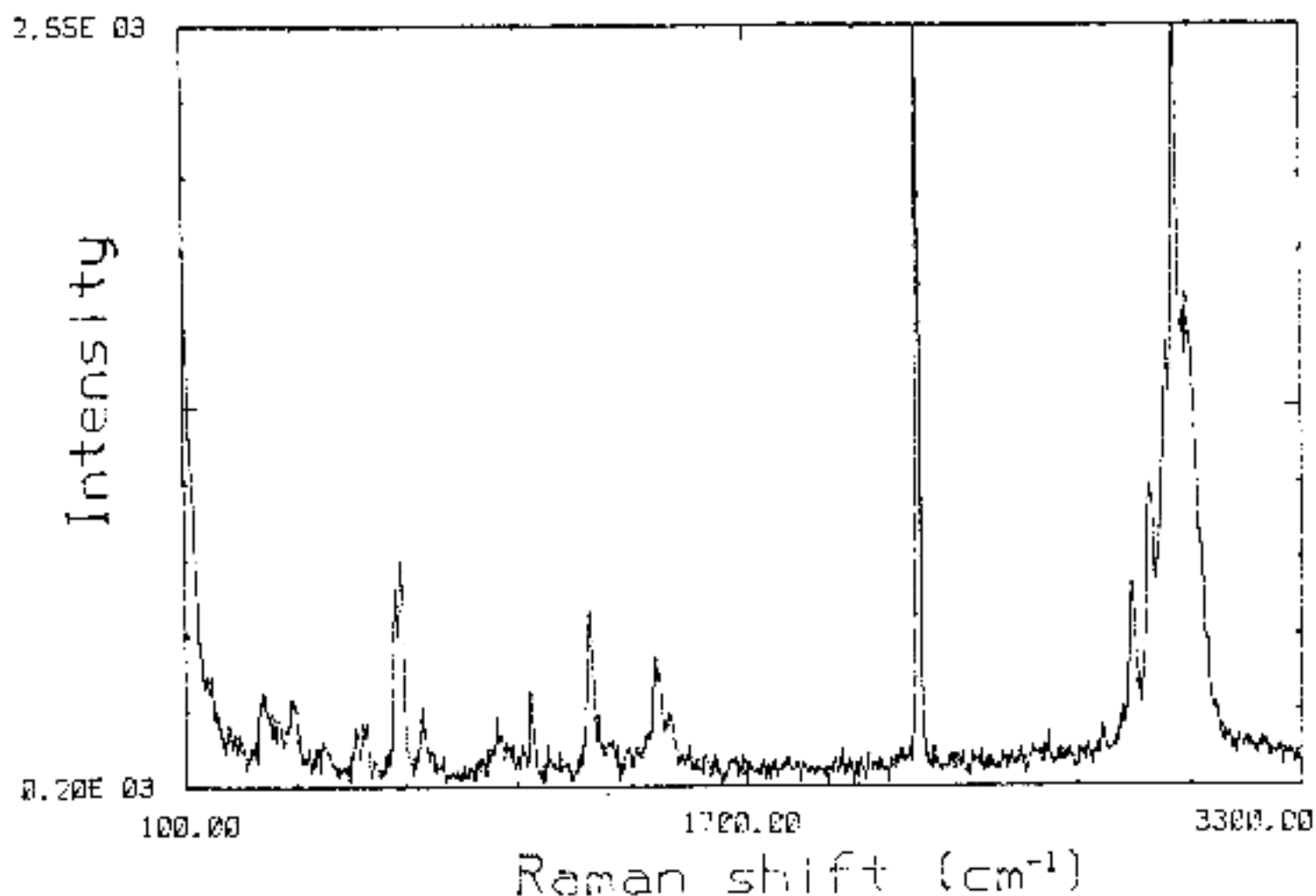


FIGURE 2  
Raman Spectrum of DIMP with 363.8 nm excitation.

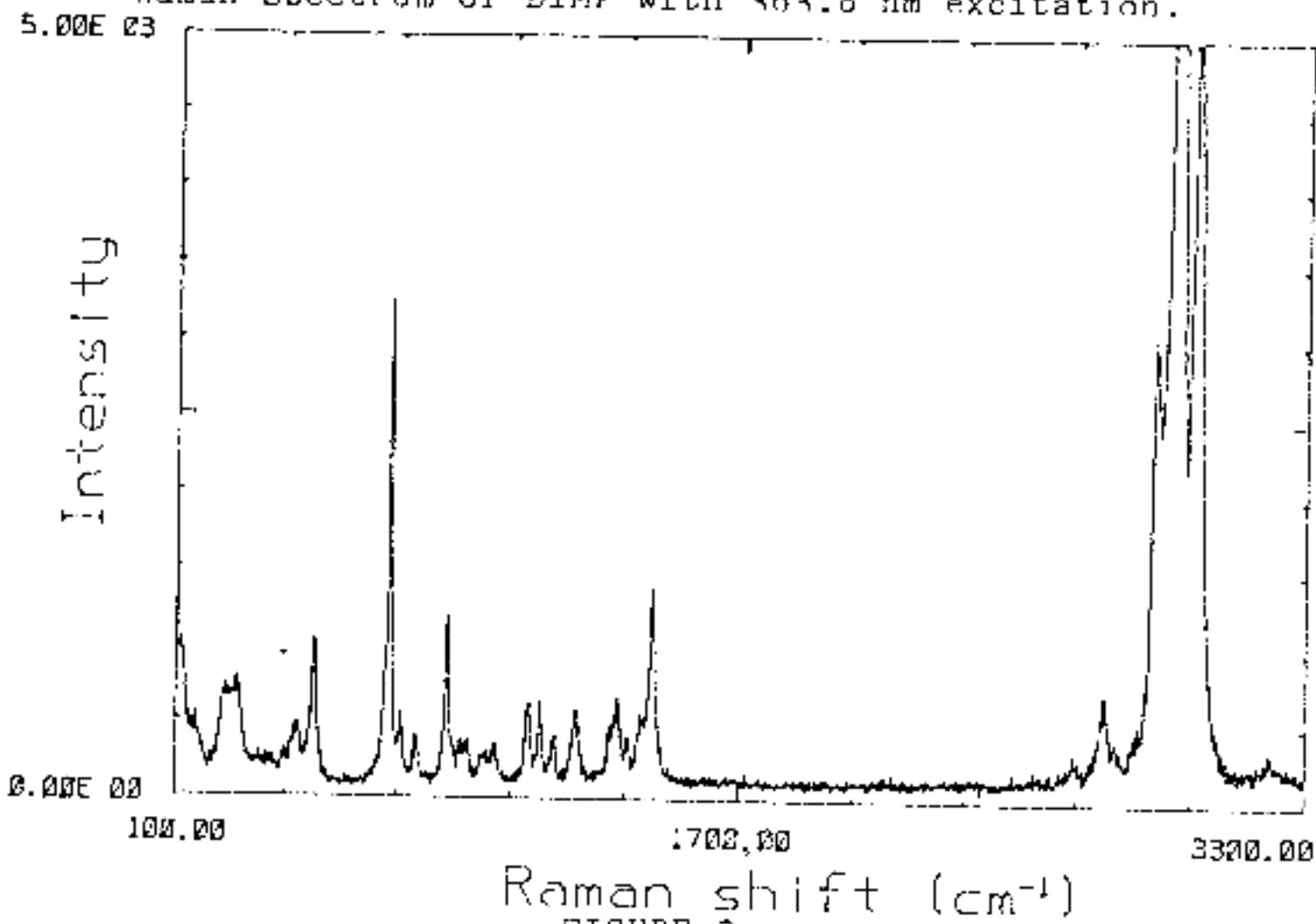
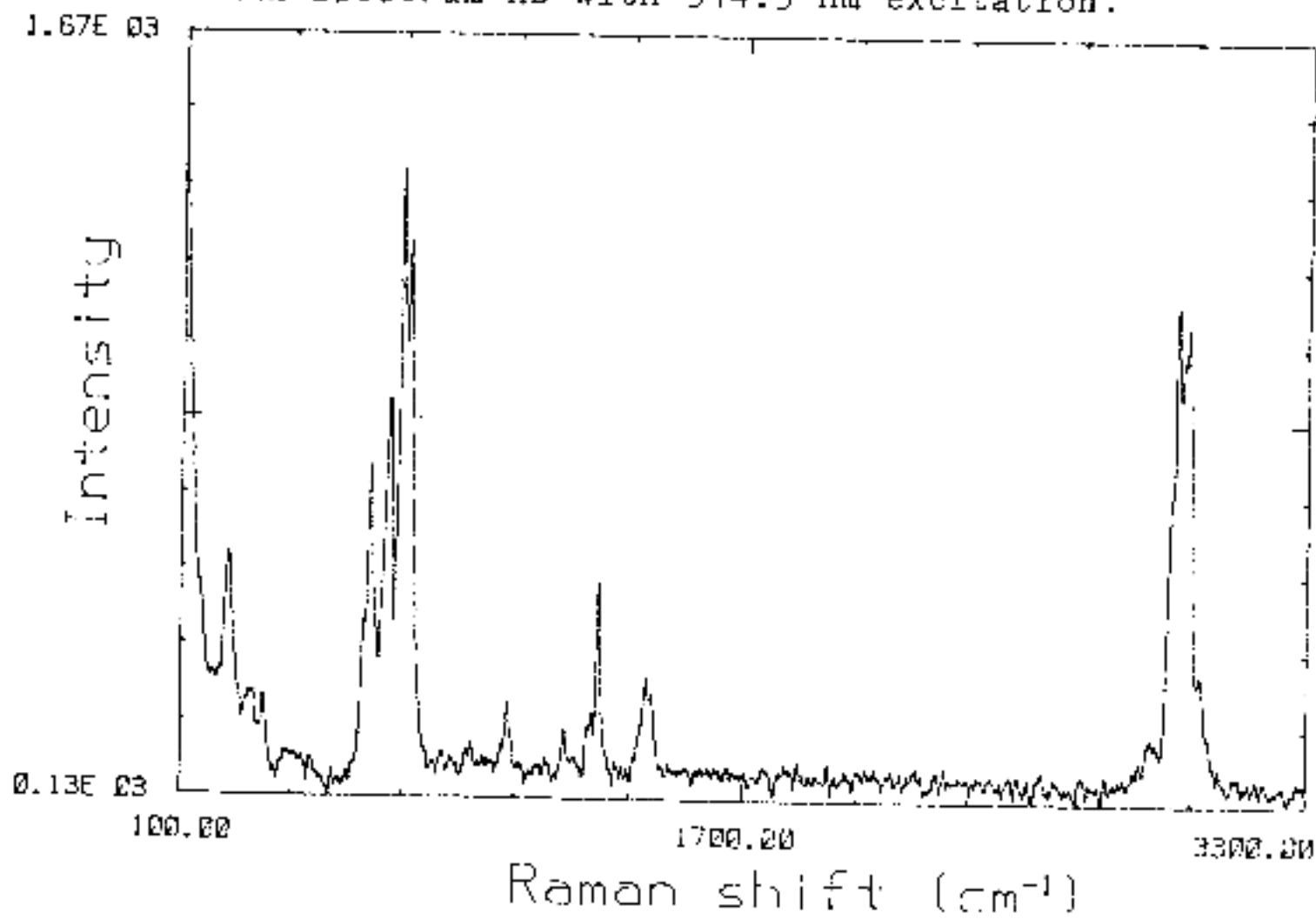


FIGURE 3  
Raman Spectrum HD with 514.5 nm excitation.



Cross sections of DIMP and GA were determined by comparing the integrated line intensity of a single Raman band of the sample to that of the  $992\text{ cm}^{-1}$  line of benzene and the  $459\text{ cm}^{-1}$  line of carbon tetrachloride. Benzene and carbon tetrachloride were used as references because they have well established values for the Raman cross sections at the excitation wavelengths employed. Corrections were made to account for the differences in the sample and reference molecular volumes, indices of refraction, and Raman transition frequencies.

GA, DIMP, and HD spectra are presented in Figures 1 through 3. The strongest line in the GA spectrum is the CN stretch at  $2198\text{ cm}^{-1}$ . As with GB and DMMP, the strongest line in the DIMP spectrum is around  $720\text{ cm}^{-1}$  and corresponds to a stretching mode involving the phosphorus atom. A cross section of  $1.2 \times 10^{-30}\text{ cm}^2/\text{Sr}$  was measured for the S-CH<sub>2</sub> deformation ( $1296\text{ cm}^{-1}$ ) in mustard (HD) with  $514.5\text{ nm}$  excitation. The set of lines corresponding to C-Cl and C-S stretches at around  $700\text{ cm}^{-1}$  are much stronger but are not well resolved.

Cross sections for the strongest lines of GA and DIMP are presented in Table 1 and are plotted vs. wavelength in Figure 4. Uncertainties in the cross sections are estimated to be + or - 20% and result predominantly from uncertainties in the reference cross section values and in the measurement of the peak areas. The cross sections are corrected for the inherent<sup>4</sup> frequency dependence in Table 2. The relatively small increase in the cross sections at shorter wavelengths evident in the data in Table 4 is due solely to pre-resonance enhancement of the Raman intensity. Absorption spectra of GA and DIMP show no appreciable absorption above  $250\text{ nm}$  and the small enhancement is not surprising. The CN stretch in GA, however, is a strong Raman band and has a cross section comparable to the  $992\text{ cm}^{-1}$  line of benzene.

TABLE 1

Wavelength dependence of the Raman cross sections for GA and DIMP.

Wavelength (nm)	Cross Section ( $\times 10^{-30}\text{ cm}^2/\text{Sr}$ )	
	GA (2198)	DIMP (719)
514.5	26	6.0
488.0	44	9.2
457.9	62	12.5
363.8	182	42.4

#### CONCLUSIONS

The wavelength dependence of the Raman scattering cross sections of GA and DIMP have been measured for excitation wavelengths from  $520$  to  $360\text{ nm}$ . Only slight pre-resonance enhancement is observed for these compounds. The CN stretch of GA

FIGURE 4  
Wavelength Dependence of the Raman Cross Sections  
for the Strongest Lines of GA and DIMP.

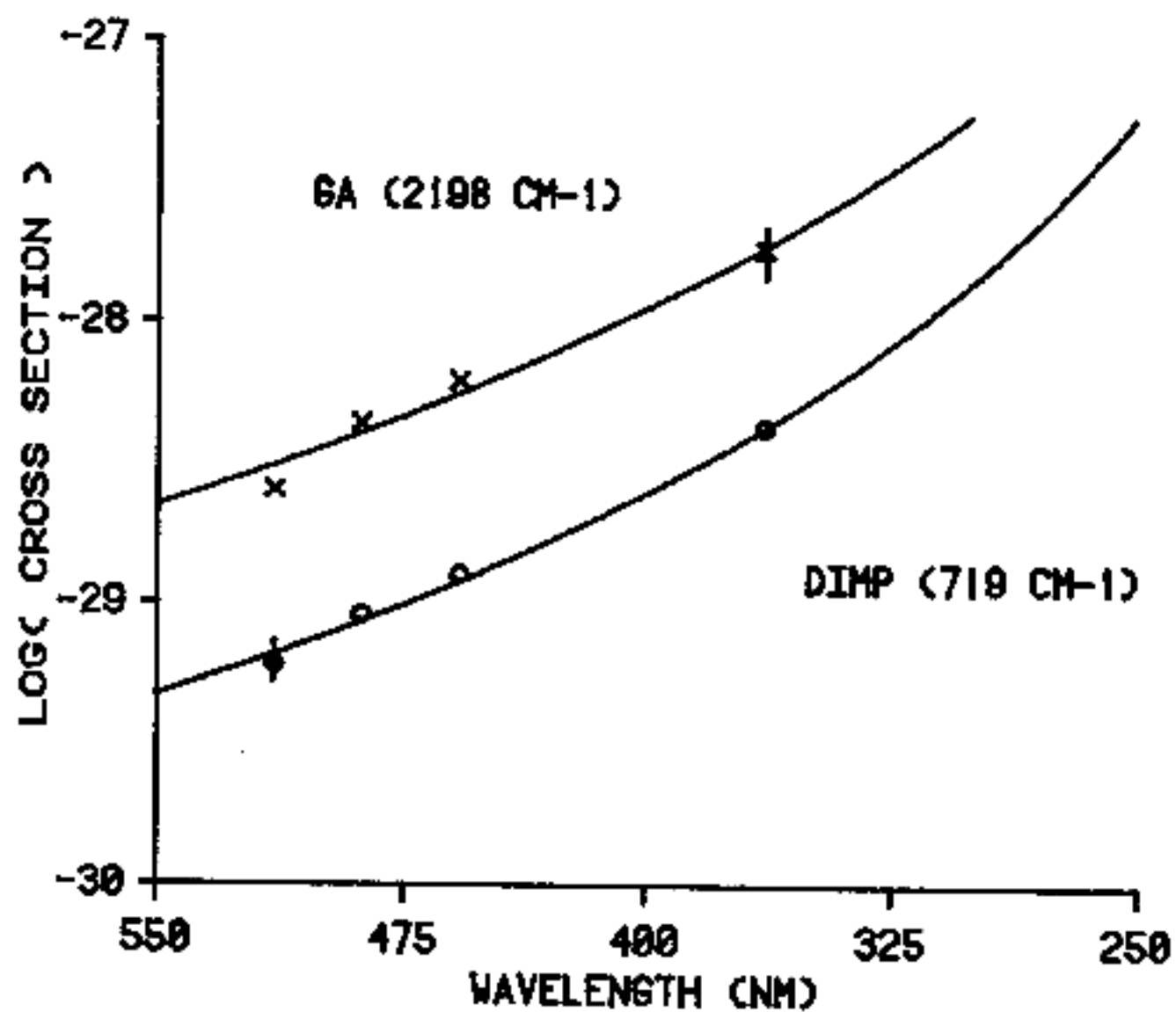


TABLE 2

Raman cross sections of GA and DIMP corrected for the fourth power frequency dependence.

Wavelength (nm)	$\times 10^{-48}$ Cross Section ( $\times 10^{-48}$ cm <sup>6</sup> /Sr)	
	GA (2198)	DIMP (719)
514.5	294	48.9
488.0	393	60.2
457.9	417	62.8
363.8	445	82.6

exhibits very strong Raman scattering and the cross section for this line is 4 times larger than that of any other agent or simulant studied. A Raman spectrum of HD has also been obtained with 514.5 nm excitation, and the cross section of the S-CH<sub>2</sub> deformation at 1296 cm<sup>-1</sup> was measured to be 1.2 x 10<sup>-30</sup> cm<sup>2</sup>/sr. Raman scattering cross sections have now been measured for the chemical agents GB, GA, VX, and HD, and the simulants DMMP and DIMP.

#### REFERENCES

1. Block Engineering. Final Report ED-CD-73007. Remote Raman Detection Study Instrument. Contract No. DAAA15-70-C-0418. October, 1979. UNCLASSIFIED Report.
2. Block Engineering. Final Report BEI-70-184. Remote Raman Detection Studies. Contract No. DAAA15-69-C-0328. December, 1970. UNCLASSIFIED Report.
3. SRI, International. Exploratory Development of a Remote NBC Detector Using Ultraviolet Technology. CRDC-CR-84102, November, 1984. UNCLASSIFIED Report.
4. Christesen, S. D. and Heyl, M. J., "Raman Spectroscopy of Chemical Agents and Simulants," Proceedings of the 1985 CRDC Scientific Conference on Chemical Defense Research. CRDC-SP-86007, April 1986.