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# LASER RAMAN SPECTRA OF DIMETHYLNITROSAMINE (DMNA) IN $H_2O$

Dwaine M. Thomas, Ph.D.

December 1977

Final Report for Period June 1976-September 1976

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USAF SCHOOL OF AEROSPACE MEDICINE
Aerospace Medical Division (AFSC)
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## NOTICES

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This technical report has been reviewed and is approved for publication.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The Raman spectra of a 1% solution of dimethylnitrosamine in $H_2O$ has been recorded over the region 550 - 1550 $cm^{-1}$. Polarization results indicate symmetry in solution phase to be $C_1$. Variation of laser excitation wavelength showed that the intensity of some of the vibrational modes was wavelength dependent.

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# LASER RAMAN SPECTRA OF DIMETHYLNITROSAMINE (DMNA) IN $H_2O$

## INTRODUCTION

Dimethylnitrosamine (DMNA) is an intermediate product in one synthetic route to the manufacture of the rocket fuel unsymmetrical dimethylhydrazine (UDMH). Since DMNA is highly toxic, U.S. Air Force operations which involve UDMH pose a personnel hazard (2). Recently, Thomas (4) has utilized laser Raman spectroscopy as a means of detecting and measuring trace amounts of DMNA in $H_2O$. The investigation presented here is a fallout from the laser Raman DMNA feasibility study.

Levin et al. (1) have previously reported the liquid and solid phase Raman spectra for DMNA, and Williams et al. (5) have studied DMNA dissolved in carbon tetrachloride and dibromomethane. A more recent study by Rademacher and Lüttke (3) included more solvents, but agreed with the work by Williams et al. (5). These three papers discuss the spectral properties of DMNA and assign its vibrational spectrum under various experimental conditions. With the present availability of high-power, variable-wavelength laser excitation sources, many unusual and informative results have been documented. It is the purpose of this study to examine the polarization effects of DMNA in $H_2O$ and to investigate the intensity distribution of the spectrum from 550 to 1550 $cm^{-1}$ of DMNA as a function of excitation wavelength and laser power.

## EXPERIMENTAL METHOD

Reagent grade dimethylnitrosamine was obtained commercially and used without purification. A 1% solution was made with distilled water under a $N_2$ atmosphere and stored in a light protective container. There is no indication in the literature to support any contention that DMNA is sensitive to visible radiation.

Raman spectra were recorded using a Cary model 82 Raman Spectrophotometer; a Spectra-Physics model 170-03 argon-ion laser was used as an excitation source. Figure 1 is a schematic of the entire Raman system. The laser beam is directed to the sampling area by a series of prisms and slits. The prisms serve two purposes: the first is to direct the beam from the laser head to the actual sampling area, and the second is to function as a secondary selector of the laser wavelength reaching the sample. The slits serve to isolate the particular excitation wavelength from nonlasing emission lines. At the sampling area the beam is focused down to a diffraction limited spot which is coincident with the image of the monochromator. Light scattered at 90° is collected by a series of lenses and is focused onto the entrance slit of the monochromator. The monochromator consists of three gratings: the first two act to disperse the incoming light, while the third grating acts as a rejection filter for stray light. Light from the exit slit is focused onto a cooled ITT FW-130 photomultiplier. The output from this is fed into a photon counting device, and eventually to a strip-chart recorder for display. A quartz cuvette was used as a sample container. Figure 2 shows the cuvette cell and its orientation with respect to the incident and collected, scattered light. The cuvette is quartz with optical flats on all four sides and bottom; the top has a Teflon stopper. The laser beam enters the bottom and exits at the top of the cuvette. Light scattered at 90° is collected by the transfer optical system leading to the entrance slit of the monochromator. The polarization of the incoming beam is directed perpendicular to the entrance of the monochromator; the polarization of the scattered light is controlled by an analyzer and polarization scrambler. The scrambler is used to compensate for the polarization characteristics of the gratings. Three laser excitation wavelengths were used: 5145, 4965, and 4880 Å. Laser power was variable, and levels at the sample were measured and adjusted between 0.5 and 2.0 watts using a Cary laser power meter. Each sample was used for several days of experimentation and monitored for spectral changes. No changes were detected even after 2 watts of exposure. It was thus assumed that sample integrity was maintained, and no decomposition had occurred.

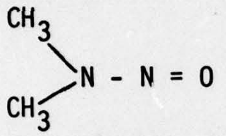
## RESULTS AND DISCUSSION

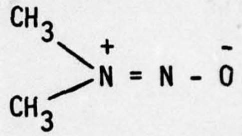
Figure 3 shows the background Raman spectrum for $H_2O$ for the region 0 to 4000 $cm^{-1}$. Only one prominent band appears in the region of interest; this is the deformation vibration at approximately 1650 $cm^{-1}$. However, at high gain levels there is considerable background scattering below 800 $cm^{-1}$ resulting from the librational modes of $H_2O$. Thus, for any weak solute band in this region, detection can prove to be quite difficult. Figure 4 shows the polarized Raman spectra of 1% DMNA in $H_2O$ for the region 500 to 1500 $cm^{-1}$. Table 1 summarizes the polarization results from this measurement. The depolarization ratios were obtained by standard methods. Peak height intensities were used; intensity in the perpendicular orientation ($I_\perp$) was divided by the intensity in the parallel orientation ($I_\parallel$) to give the depolarization, $\rho = I_\perp/I_\parallel$. The ($I_\parallel$) spectrum was obtained with the analyzer oriented so as to allow only light polarized in the same direction as the incident light polarization. The ($I_\perp$) spectrum was recorded with the analyzer rotated to allow only the perpendicular component to pass through to the monochromator. Figures 5, 6, and 7 show the Raman spectra of 1% DMNA in water at the excitation wavelengths of 5145, 4965, and 4880 Å, respectively.

Spectra of 1% DMNA in $H_2O$ were recorded at various laser power levels as a check on possible decomposition at high power levels and for the possibility of observing higher order effects on the vibrational frequencies. Laser power levels of 1, 2, 3, and 4 watts were used in recording these spectra; at the sample, this corresponded to approximately 0.5, 1, 1.5, and 2 watts, respectively. Under different excitation levels the spectral properties of DMNA remained unchanged. Decomposition would be characterized as new bands in the spectrum, shifted

DMNA bands, changes in band shape, and possibly disappearance of DMNA bands. None of these characteristics appeared even after several days of illuminating the same sample. Different (fresh) samples behaved in a similar fashion. These results ruled out the possibility of decomposition under laser irradiation at these wavelengths. This supports the fact that there is no literature reference relating to the decomposition of DMNA under visible radiation. Thus, even under 2 watts of illumination DMNA in $H_2O$ appears to be quite stable and exhibits its normal vibrational spectrum.

The polarized spectral results agree with the results for neat DMNA as reported by Levin et al. (1). All bands in this region seem to be polarized which supports a molecular symmetry of $C_1$ rather than the gas phase symmetry of $C_s$. This might be expected since in solution phase the gas phase structure is no longer present. In $H_2O$ two resonance structures are present:


(A)


(B)

These types of resonance forms would tend to give a linear N-N-O moiety. In solution there should exist considerable dipolar coupling (long-range ordering) which would lower the symmetry to $C_1$. Thus, the polarized spectra indicate that DMNA in $H_2O$ has lost its gas phase symmetry $C_s$ and now retains only the trivial symmetry of $C_1$.

Table 2 summarizes the relative peak intensities obtained for the four strongest bands in the region 550 - 1550 $cm^{-1}$. The bands are 1384, 1085, 847, and 688 $cm^{-1}$. These bands may be described as follows: 1384 ($CH_3$ symmetric deformation), 1085 (N-N stretch), 847 (C-N symmetric stretch), and 688 (O-N-N bend). The intensity ratios were calculated in the usual fashion. The intensity of the medium strong $H_2O$ band at 1650 $cm^{-1}$ is invariant under different excitation wavelengths and power levels, and thus was used as a reference band in comparing peak height intensities. For example, the peak height intensity for the 1384 $cm^{-1}$ band was measured for 5145 Å excitation and divided by the peak height intensity for the 1650 $cm^{-1}$ $H_2O$ band at 5145 Å. This gave ratios independent of DMNA with a more accurate representation of any change which might have occurred due to instrumental variation. In the spectrum there are essentially three scattering levels. Beyond 1850 $cm^{-1}$ toward higher $cm^{-1}$, scattering levels remain quite low. From 1850 to 1500 $cm^{-1}$ the scattering level increases slowly; it remains fairly constant between 1500 and 1000 $cm^{-1}$. Again there is a rise between 1000 and 550 $cm^{-1}$, and past 550 $cm^{-1}$ there is a dramatic rise in scattering. The main contributory cause of the scattering comes from the two bands for $H_2O$ at 1650 $cm^{-1}$ (a deformation mode), and at 470 $cm^{-1}$ (a librational mode). The scattering level here is independent of the excitation wavelength. The two bands at 1384 and 1085 $cm^{-1}$ did not change in intensity for the three excitation wavelengths used; however, the 847 and 688 $cm^{-1}$ bands did change. Although all experimental parameters were maintained constant except excitation wavelength, the intensities for these two bands decreased for the shorter wavelengths. The intensity change for 847 $cm^{-1}$ was 0.13 and for the 688 $cm^{-1}$ band was 0.25; this is well outside of experimental error. The other two bands were within 0.02 of their three values. Since scattering levels did not appreciably change, the results appear to indicate some intensity enhancement through a preresonance or resonance condition. In the free molecule DMNA does not possess any electronic absorption close to the visible region. However, because of the resonance structures and the reasonable possibility of dipolar coupling, structures could exist which might support a lower energy state. This could then lead to resonance enhancement of some of the vibrational modes of DMNA. Further explanations with more definitive answers are possible only after a complete identification of the various structures of DMNA in $H_2O$.

## CONCLUSION

Evidence from this experiment indicates that high laser energy levels will not noticeably alter the vibrational spectrum of DMNA dissolved in $H_2O$. However, the particular wavelength chosen for excitation could possibly yield intensity enhancement through resonance Raman or preresonance Raman for some vibrational modes. This must be considered when measuring intensity changes and especially for concentration measurements applied to analytical determinations.

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TABLE 1. DEPOLARIZATION RATIOS FOR THE FOUR PRINCIPAL BANDS OF 1% DMNA IN $H_2O$

| Vibrational frequency ($cm^{-1}$) | Depolarization ratios |
|---|---|
| 1384 | 0.23 |
| 1085 | 0.27 |
| 847 | 0.12 |
| 688 | 0.08 |

TABLE 2. INTENSITY RATIOS FOR THE FOUR PRINCIPAL BANDS OF 1% DMNA IN $H_2O$ FOR DIFFERENT EXCITATION WAVELENGTHS

| Vibrational frequency ($cm^{-1}$) | Laser excitation wavelength (Å) | | |
|---|---|---|---|
| | 5145 | 4965 | 4880 |
| 1384 | 2.50 | 2.50 | 2.48 |
| 1085 | 0.90 | 0.88 | 0.88 |
| 847 | 0.69 | 0.61 | 0.56 |
| 688 | 1.14 | 1.00 | 0.89 |

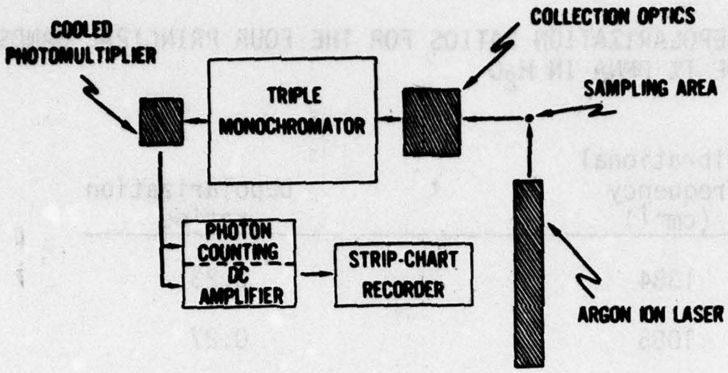

Figure 1. Schematic of laser Raman system.

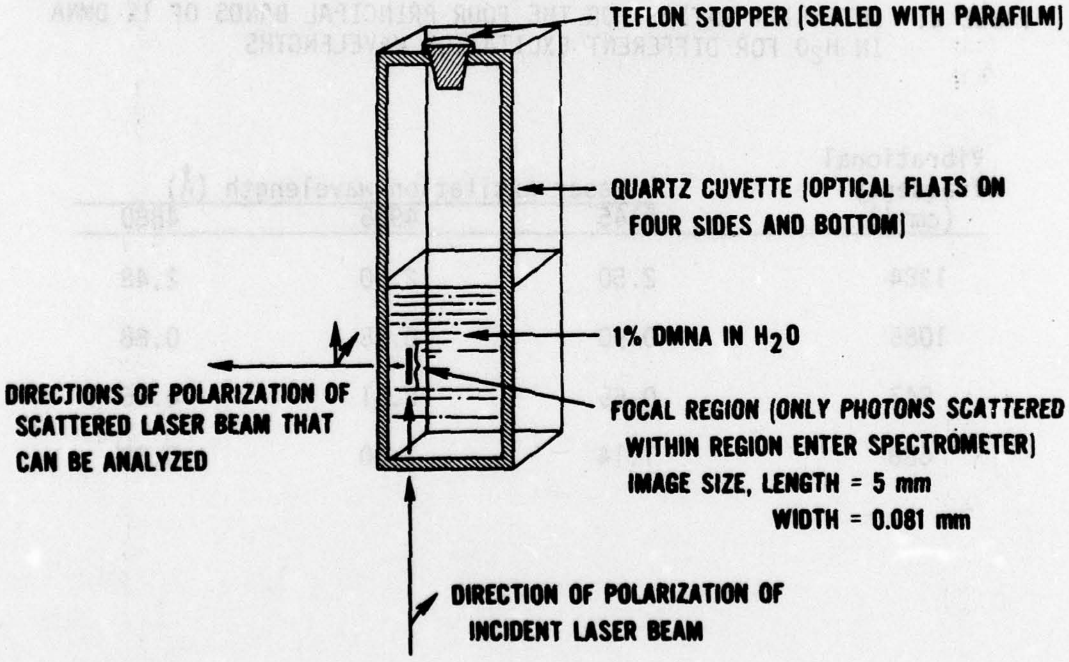

Figure 2. Cuvette cell used in measurements and its orientation with respect to the incident and scattered laser beam.

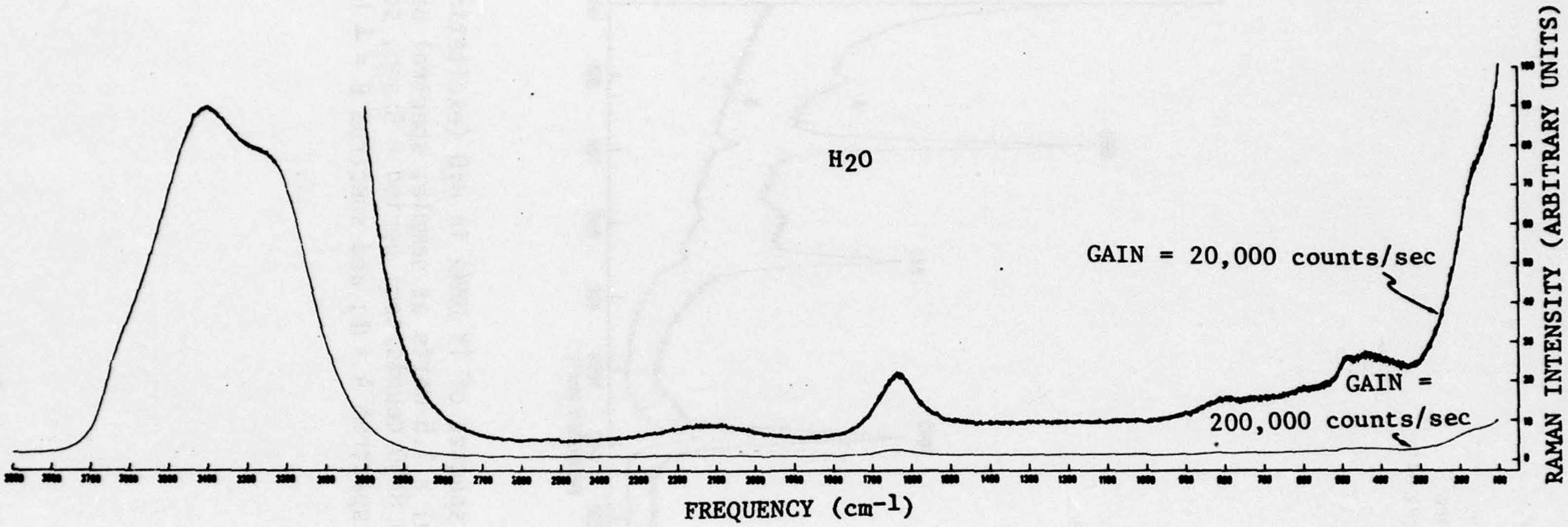

Figure 3. Background Raman spectrum of $H_2O$ (excitation = 5145 Å; laser power level = 0.5 watts at sample; spectral bandwidth = 3 $cm^{-1}$; gain = 200,000 and 20,000 counts/sec; period = 1 sec; scan speed = 1 $cm^{-1}$/sec).

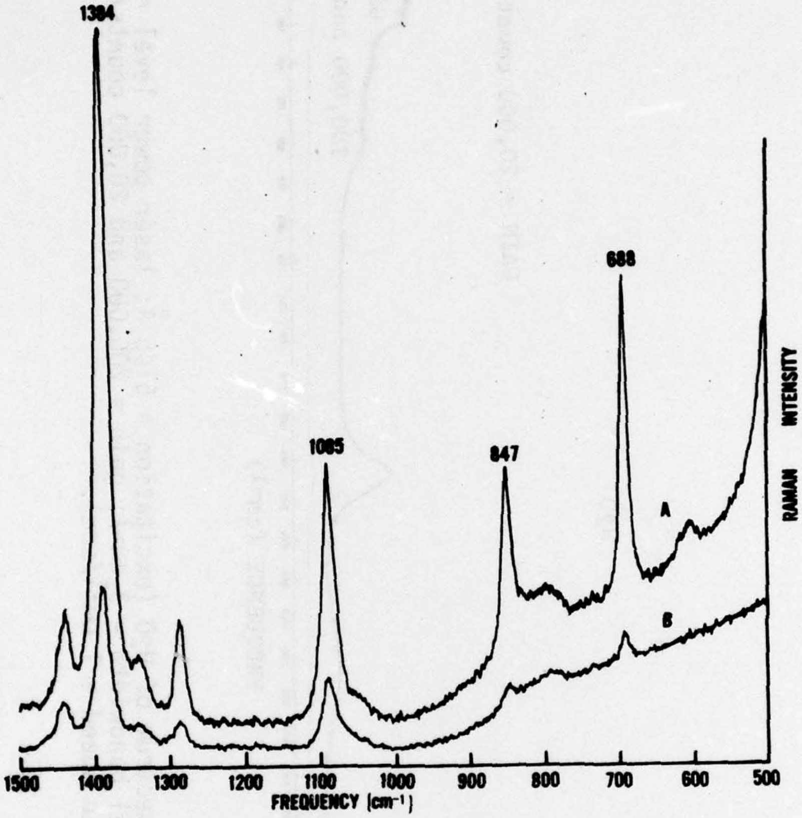

Figure 4. Polarized Raman spectra of 1% DMNA in $H_2O$ (excitation = 5145 Å; laser power level = 1.5 watts at sample; spectral bandwidth = 3 $cm^{-1}$; gain = 8500 counts/sec; period = 5 sec; scan speed = 0.6 $cm^{-1}$/sec; spectrum A = $\parallel$; and spectrum B = $\perp$ ).

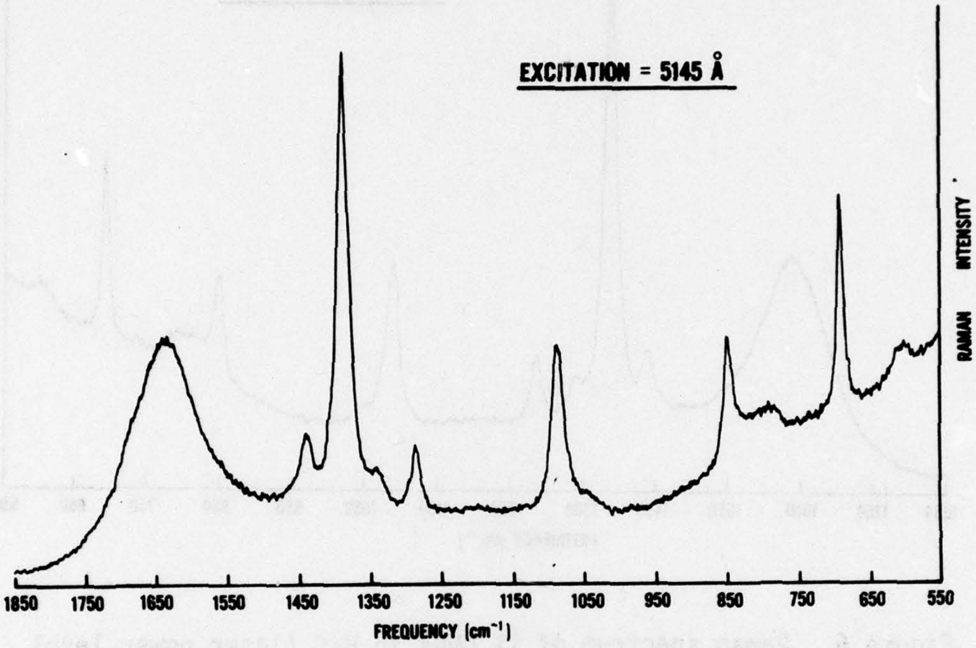

Figure 5. Raman spectrum of 1% DMNA in $H_2O$ (laser power level = 0.5 watts at sample; spectral bandwidth = 3 $cm^{-1}$; gain = 10,000 counts/sec; period = 2 sec; scan speed = 0.6 $cm^{-1}$/sec).

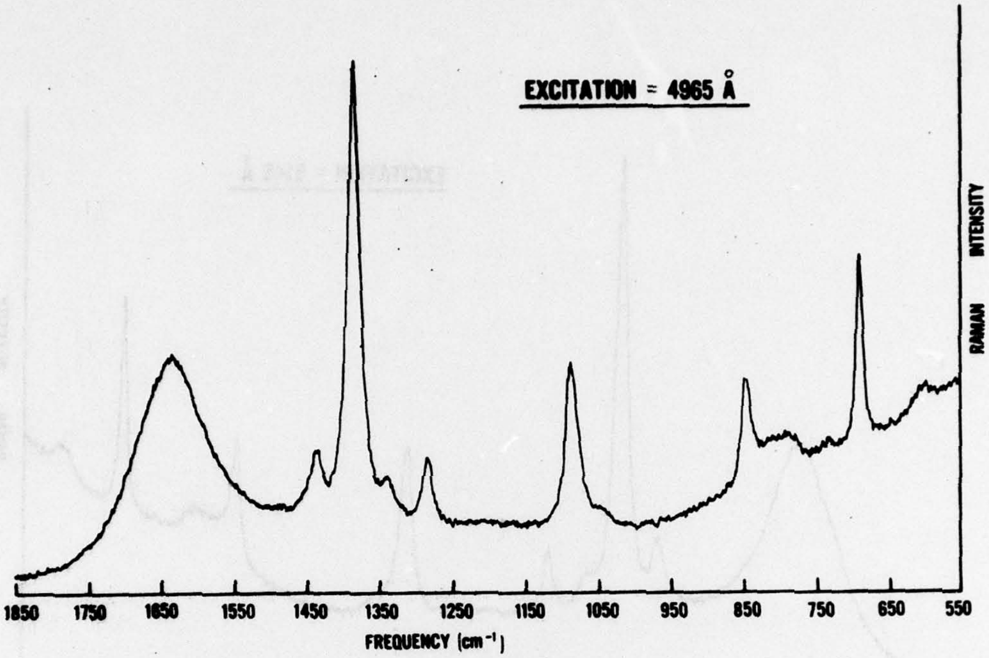

Figure 6. Raman spectrum of 1% DMNA in $H_2O$ (laser power level = 0.5 watts at sample; spectral bandwidth = 3 cm$^{-1}$; gain = 10,000 counts/sec; period = 2 sec; scan speed = 0.6 cm$^{-1}$/sec).

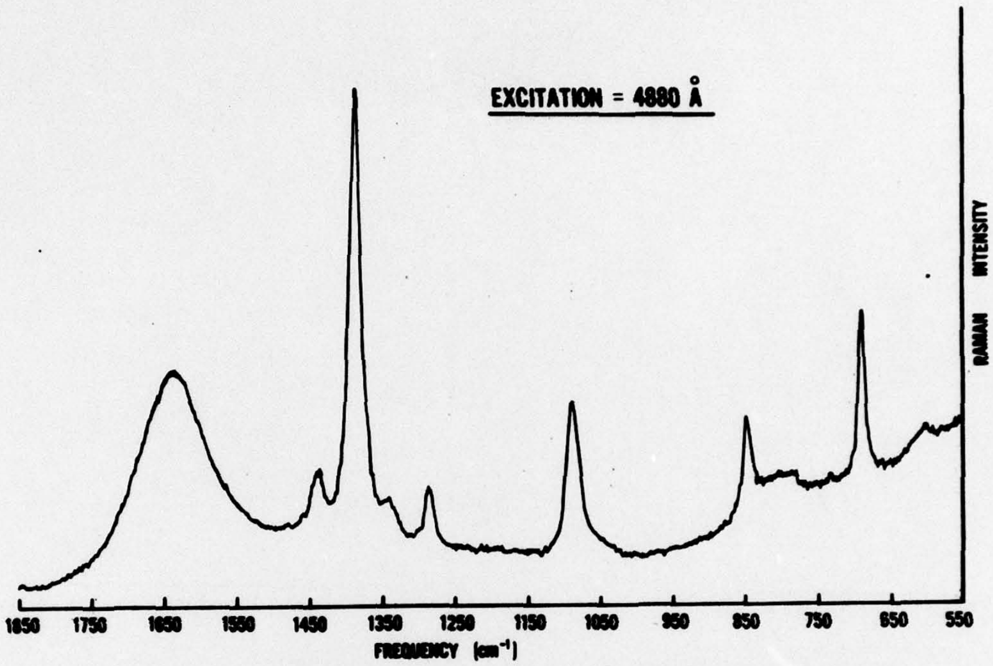

Figure 7. Raman spectrum of 1% DMNA in $H_2O$ (laser power level = 0.5 watts at sample; spectral bandwidth = 3 $cm^{-1}$; gain = 10,000 counts/sec; period = 2 sec; scan speed = 0.6 $cm^{-1}$/sec).