ALMD66044121163

MONSANTO RESEARCH CORPORA

From LOCATION : Research Department, Mound Laboratory

DATE : April 15, 1966

MOUND LABORATORY-MONSANTO
CENTRAL FILE NO. 66-4-412

SUBJECT : MAJOR WORK ORDER JUSTIFICATION

REFERENCE : MWO 318263-720

SECRET

DATE 4/18/66 INIT.

TO : Distribution

Distribution:
Copy 1A - Record Center
Copy 2A - Record Center
Copy 3A - Record Center
Copy 4A - R. E. Vallee
Copy 5A - F. C. Fushimi
Copy 6A - Warren Smith
Copy 7A - G. R. Grove

THIS DOCUMENT CONSIST OF 5 PAGES
THIS IS COPY 1 OF 7 SERIES A

1. Description: Purchase a Raman Spectrophotometer

2. Savings: Very small sample size (few milligrams) and sealed sample samples are used with this instrument. Therefore:

(1) This instrument can be used to perform studies on plutonium-238 containing samples, on tritium containing samples (or other radioactive samples), and on explosives as well as on non-radioactive samples.

(2) This instrument does not require a box line for radioactive containment or for protection against atmospheres, thus allowing use of existing facilities in the areas generating the materials for sample preparation.

Due to the above versatility, one Raman spectrophotometer can serve all areas whereas this type of equipment is normally required for each area.

The Raman spectrophotometer supplements existing equipment; and, in addition, information obtainable with this instrument can often not be obtained with other type spectrophotometers. This is especially true for aqueous and solid samples, the two most common types of samples encountered in problems at Mound Laboratory.

In addition to obtaining data on samples which cannot be obtained by other means, other data can be obtained directly and much quicker with a savings in manpower.

3. Alternate Course: Eliminate those investigations requiring the use of a Raman Spectrophotometer or design and construct an instrument at Mound. The latter course is being taken at LRL and the expenditure of time and manpower has been very costly and a functioning spectrophotometer has not been obtained.

4. <u>Remarks</u>: The following are examples of studies which have been performed or are most readily solved with the use of a Raman Spectrophotometer and some of the reasons that the Raman technique is superior from some applications to those now being used at Mound Laboratory.

(a) Raman studies would provide information required for the calculation of equilibrium constants and other thermodynamic properties, which are of extreme importance to the SM, SW, and explosives program. An example of this would be a paper recently published by O. D. Bonner, "The Determination of the Ionization Constants of Sulfonic Acids by Raman Measurements", J.P.C. <u>69</u>, 4109 (1965).

(b) Since the Raman effect is viewed in the visible region of the spectrum, water can be used as a solvent. Thus many studies can be performed that would be impossible using infrared spectrophotometry because of water absorption in the infrared region. These data obtained from the Raman effect would be directly applicable to the SM program, since most of the process involves reactions which are performed in aqueous media. Raman studies would also provide information on the species which are present in these aqueous solutions such as those which cause polymer formations and those which cause or inhibit corrosion.

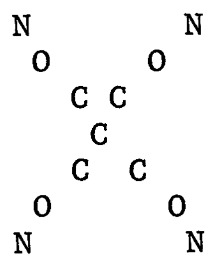
(c) The positions of substituent groups on organic and inorganic compounds can be determined, for example, ortho-, meta-, and para- substituted derivatives of benzene can be differentiated. This type of information is needed in the plastics and adhesives program.

(d) The height of Raman peaks varies linearly with concentration, therefore, the instrumental accuracy (the reciprocal of the relative error) is at least 2.3 times higher than in absorption spectroscopy where the absorption intensity varies exponentially with concentration. This behavior will allow the application of complimentary tristimulus colorimetry to the Raman effect. This colorimetric technique will provide a capability for completely characterizing chemical reactions with regards to kinetics, mechanisms

(d) (continued) and equilibria. These type data would directly support the SM program, while elucidation of explosive mechanisms could possibly result in an explanation of processes in explosive reactions.

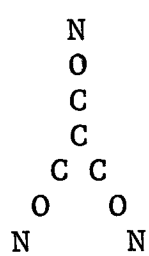
(e) With only a single source and detector, almost the entire range of molecular vibration frequencies, 60-5000 Δcm^{-1}, can be covered in a single continuous scan. This instrument, together with infrared and visible spectrophotometers, provides capabilities for doing studies in almost any portion of the energy spectrum. This type of information will support any existing and future programs at Mound Laboratory.

(f) In the SM, Explosives, Plastics, and SW salt programs, knowledge of the molecular structure of many of the materials employed would be extremely useful. For example, it is necessary to be able to distinguish between pentaerythritol tetranitrate(I), dipentaerythritol hexanitrate(II), and tripentaerythritol octanitrate(III). If we assume a tetrahedral symmetry T_d for (I) the number of infrared active (IR) and Raman active (R) fundamentals can be calculated. There are six IR and six R fundamentals. The model used for (I) is presented below.



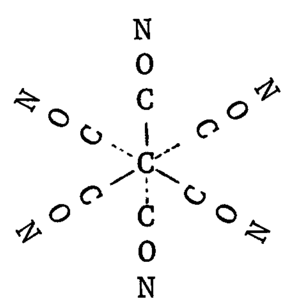
(I)

For (II) there are two possible symmetry types as shown below, which correspond to D_{3h} and D_{3d}.



(II)

D_{3h} (End View)



(II)

D_{3d}

End View

For D_{3h} there are 19 IR active and 30 R active fundamentals. In the case of D_{3d} there are 19 IR active and 18 R active fundamental vibrations. This result implies that Raman spectroscopy could tell in which form (II) exists. In the case of (III) two point groups are possible, one being C_{2v} the other C_{2h}. For C_{2v} there are 73 IR active and 91 R active fundamentals; with C_{2h}, 46 IR active and 46 R active vibrations are possible. If this type of work is pursued it is quite possible that Raman spectroscopy will be able to distinguish between (II) and (III).

This type of information provides for a better understanding of the chemistry involved, and therefore enables improvement of the materials and procedures used. The Raman spectrophotometer will facilitate the complete structural determination of these materials because of the following reasons.

1. Excitation with polarized light permits the determination of the depolarization ratios of individual lines. This parameter alone often suffices to exclude from consideration otherwise acceptable hypothetical molecular structures or vibrational assignments.

2. Overtone and combination effects are small in proportion to the strong Raman bands. This sometimes simplifies spectral interpretation.

3. Symmetrical vibrations of molecules can be studied by the Raman effect, whereas they are not observed in infrared spectroscopy.

(g) The addition of the Raman spectrophotometer would complete the spectrophotometric equipment needed for the investigation of inorganic reactions, including inorganic explosives.

(h) Oak Ridge National Laboratory has shown the feasibility of using powdered samples with the Raman spectrophotometer. Hence, the Raman effect can be applied to solid samples of radioactive material, which would greatly increase the applicability of the instrument.

(h) (continued)

An example of this work would be a paper published from the Bettis Atomic Power Laboratory on the "Raman Spectra of Zirconium Oxide". The reason for the study was to determine possible effects of neutron inelastic scattering on ZrO_2. In order to establish the vibrational energy levels from which inelastic scattering could occur, a knowledge of the infrared and Raman spectra of ZrO_2 is essential.

(i) The Cary Model 81 Raman Spectrophotometer is now available with a He-Ne laser source. The laser source has greatly increased the usefulness of the Raman. As an example of this, samples of uranyl nitrate were sent to the Applied Physics Corporation so that the Raman spectra of these samples could be obtained on their instrument. Up until this time it had not been possible to obtain a Raman spectra of solid uranyl nitrate. The spectra obtained were of excellent quality. The Raman spectra successfully showed the IR inactive symmetrical stretching band. This is the first experimental evidence that the postulated symmetrical vibrational frequency was correct.

A by-product of using this instrument due to it's small sample size is the inherent safety and economy associated with milligram size samples of explosives and radioactive samples.

GRGrove

G. Richard Grove

GRG:lg