DTIC FILE COPY

(2)

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b.

4.

AD-A214 920

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release;
distribution unlimited.

5. MONITORING ORGANIZATION REPORT NUMBER(S)
1398
AFOSR-TR- 89-13[illegible]

6a. NAME OF PERFORMING ORGANIZATION
State University of
New York at Buffalo

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION
AFOSR

6c. ADDRESS (City, State, and ZIP Code)
Department of Chemistry,
Buffalo, NY 14260

7b. ADDRESS (City, State, and ZIP Code)
BLDG 410
BAFB DC 20332-6448

8a. NAME OF FUNDING/SPONSORING ORGANIZATION
AFOSR

8b. OFFICE SYMBOL (If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
AFOSR-78-3676

8c. ADDRESS (City, State, and ZIP Code)
BLDG 410
BAFB DC 20332-6448

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO.
61102F	2303	A3	

11. TITLE (Include Security Classification)
RAMAN STUDY OF SOLID STATE REACTIONS

12. PERSONAL AUTHOR(S)
Dr. Paras N. Prasad

13a. TYPE OF REPORT
Final

13b. TIME COVERED
FROM 9/1/78 TO 8/31/79

14. DATE OF REPORT (Year, Month, Day)

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

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

DTIC
ELECTE
NOV 28 1989
S B D

89 11 2[illegible] [illegible]13

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL

22b. TELEPHONE (Include Area Code)
767-4960

22c. OFFICE SYMBOL
NC

DD Form 1473, JUN 86 Previous editions are obsolete. SECURITY CLASSIFICATION OF THIS PAGE

FINAL REPORT

AFOSR-TR- 89-1398

PROJECT: RAMAN STUDY OF SOLID STATE REACTIONS

SPONSOR: USAFOSR

PERIOD: September 1, 1978 to August 31, 1979

GRANT #: AFOSR-78-3676

PRINCIPAL INVESTIGATOR: Dr. Paras N. Prasad
Associate Professor
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

During the period 9/1/78 to 8/31/79, a considerable amount of work was done towards understanding the nature of reactions in solids. The first step in the investigation of the solid state reactions was the synthesis and the characterization of the materials. Methyl-p-dimethylaminobenzenesulfonate, p-trimethylammoniumbenzene sulfonate, tri-o-thymotide were synthesized and characterized by their Raman spectra. Other compounds proposed for study were, trans-cinnamic acid and p-nitrophenol, the phonon spectra and the internal vibration spectra of which in two crystalline modifications were studied. Another matrix which we proposed for study was cyclodextrin whose Raman spectra were also studied.

Solid state photodimerization of two modifications of trans-cinnamic acids in pure crystals was investigated. The Raman spectra of both the phonon region and the internal vibration region were studied as a function of photodimerization. Figure 1 shows the Raman spectra was shown in phonon region of the trans-cinnamic acids and their respective dimers. ~~In~~ this photodimerization we investigated using the phonon spectra, the mechanism of the product lattice formation, i.e. whether the reaction proceeds by a homogeneous mechanism with the formation of a solid solution between the reactant and the product or by a heterogeneous reaction where the product forms its own lattice.

As was suggested in the proposal, phonon spectra proved to be conclusive and it was found that the photodimerization proceeds by a heterogeneous mechanism, i.e. no solid solution forms between the reactnat and the product. The major thrust of the research has been to derive a dynamical concept of reactivity by considering the role of phonon motions of the lattice in determining reactivity. Large amplitude phonon motions

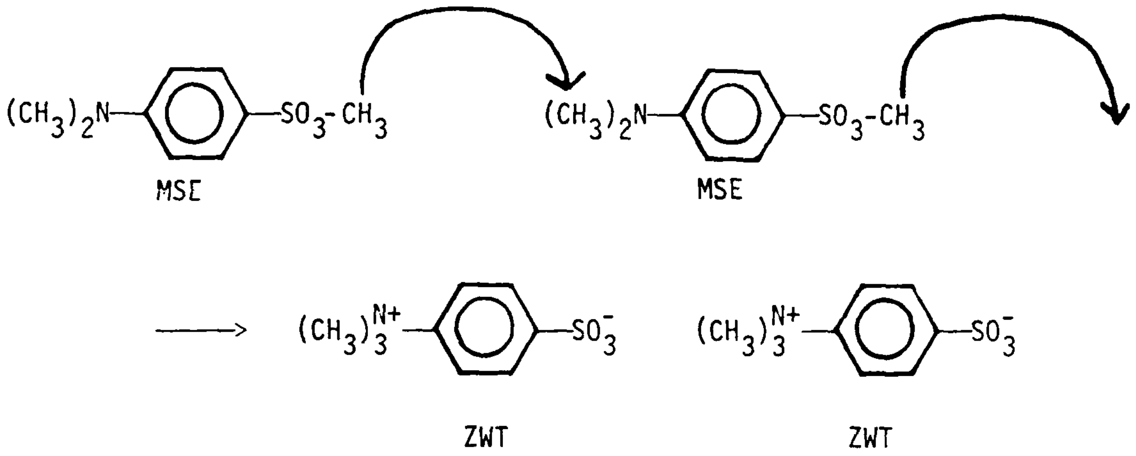
☑
☐
☐

on/
Availability Codes

Dist	Avail and/or Special
A-1	

are the analogs of molecular collisions in the gas phase. The two crystalline modifications of trans-cinnamic acid differ in the degree of reactivity. The β-form is more reactive than the α-form. It can be seen from figure 1 that the β-form has a very low lying phonon transition ($\sim$27 cm^{-1}) where as for the α-form the lowest phonon transition is at $\sim$52 cm^{-1}. In the 27 cm^{-1} motion the molecules execute large amplitude oscillations which may account for enhanced reactivity. These findings on trans-cinnamic acid were presented at the American Chemical Society Symposium on April 2, 1979 in Honolulu.

The thermal rearrangement reaction of methyl-p-dimethylaminobenzene sulfonate (MSE) in pure crystal to form the product p-trimethylammonium benzene sulfonate Zwitterion (ZWT) was also investigated during this period. Detailed studies of the phonon spectra as well as the internal vibration spectra were made as a function of the percentage rearrangement using polycrystalline samples as well as single crystals in different orientations. Figure 2 shows the spectra for the reactant (top Spectrum), the 40% conversion sample (middle spectrum) and the product (bottom spectrum) for the phonon region. Except for the spectral intensity changes due to a difference in orientation, the spectra of the 40% conversion sample can be explained as consisting of unperturbed bands of both the reactant and the product. The same is true for samples of other percentage conversion. From this result we conclude than no solid solution between the reactant and the product is formed when the reaction proceeds. In other words the reaction proceeds by a heterogeneous mechanism. This observation is consistent with the following mechanism:



This mechanism involves an intermolecular transfer of methyl group and, thus, a cooperative rearrangement. When the reaction is induced, it has to occur cooperatively over a large domain, and not just locally.

A temperature dependence study of phonons in MSE reveals that phonon transitions broaden rapidly as the temperature is raised from 120°K. There is a low lying phonon at $\sim 30 cm^{-1}$ ($\sim$120°K value). As the sample is warmed from 120°K, this phonon shifts to lower frequencies and rapidly broadens. By 200°K, this transition cannot be distinguished from the Rayleigh background. From this result we conclude that the low lying phonon of MSE represents an over-damped soft mode which,by executing very large oscillations,may be responsible for inducing the thermal rearrangement reaction. This result, again, lends support to a model based on phonon participation in solid state reactions. Our findings on MSE rearrangement reaction were presented at two conferences: (a) American Chemical Society Symposium on April 2, 1979 in Honolulu; (b) Molecular Spectroscopy Symposium in June 1979 at Columbus, Ohio.

An important aspect of a dynamical model is to determine specificity in phonon induction of solid state reactions. In order that a large population of selective and coherent vibrational excitation can be achieved to study its effect on reactivity it is necessary that vibrational relaxation be slow. For this reason it is important to investigate and characterize vibrational relaxation and dephasing in organic solids. This study was undertake during the tenure of the Air Force grant. Two proto systems were investigated. The dephasing of a localized internal vibration of the naphthalence crystal was investigated by studying the temperature dependence of the line width, the line shape and the line frequency. It was found that at liquid helium temperatures the contribution to dephasing due to physical processes which are of interest to us is almost negligible. The observed dephasing can entirely be explained due to inhomogeneities. Even at higher temperatures the T_1-relaxation time which is responsible for decay of the vibrational excitation is very long. This result is extremely encouraging from the point of view of being able to selectively pump a high degree of vibrational excitation of a given mode. Another system in which we have studied vibrational relaxation is p-bromochlorobenzene. This system in crystalline state exhibits orientational disorder and our motivation was to study phonon relaxation in a structurally disordered system. The work revealed that even in a structurally disordered system for which both anharmonic interactions and structural disorder provide scattering mechanisms, the study of temperature dependence of linewidths can be used to derive information on phonon relaxations. To discern the effect of disorder, the result on p-bromochlorobenzene was also compared with that on isomorphic p-dichlorobenzene crystal which exhibits no structural disorder. It was found that for both these p-dihalobenzenes the phonon relaxation at liquid helium temperatures is $>10^{-10}$ sec.

On the side of the instrumentation progress has also been made. An automation system has been introduced in which experiments are controlled by a MicroNova computer. The data are obtained and digitally processed. For larger computations the data can be transferred from MicroNova to the University computing facility through a modem. MicroNova will also control the multichannel detection system acquired through the Air Force grant. This system is in the process of being used for time resolved study of solid state reactions so that a large spectral region can be sampled in milliseconds. To improve the signal to noise ratio in this multichannel detection we are making several modifications. An iodine filter is being assembled which can be used with the 5145Å laser excitation to reduce the background. We are also in the process of building a background rejection optical-filter for cases where we need to use other excitation wavelengths. This filter consists of two gratings which are put together is a subtractive mode. The first grating disperses the scattered radiation. A stopper in the path of the dispersed beam blocks the laser light and the shorter wavelengths, but passes all the longer wavelengths which then are combined by the second grating and focused on the slit of the 14018 double monochromator.

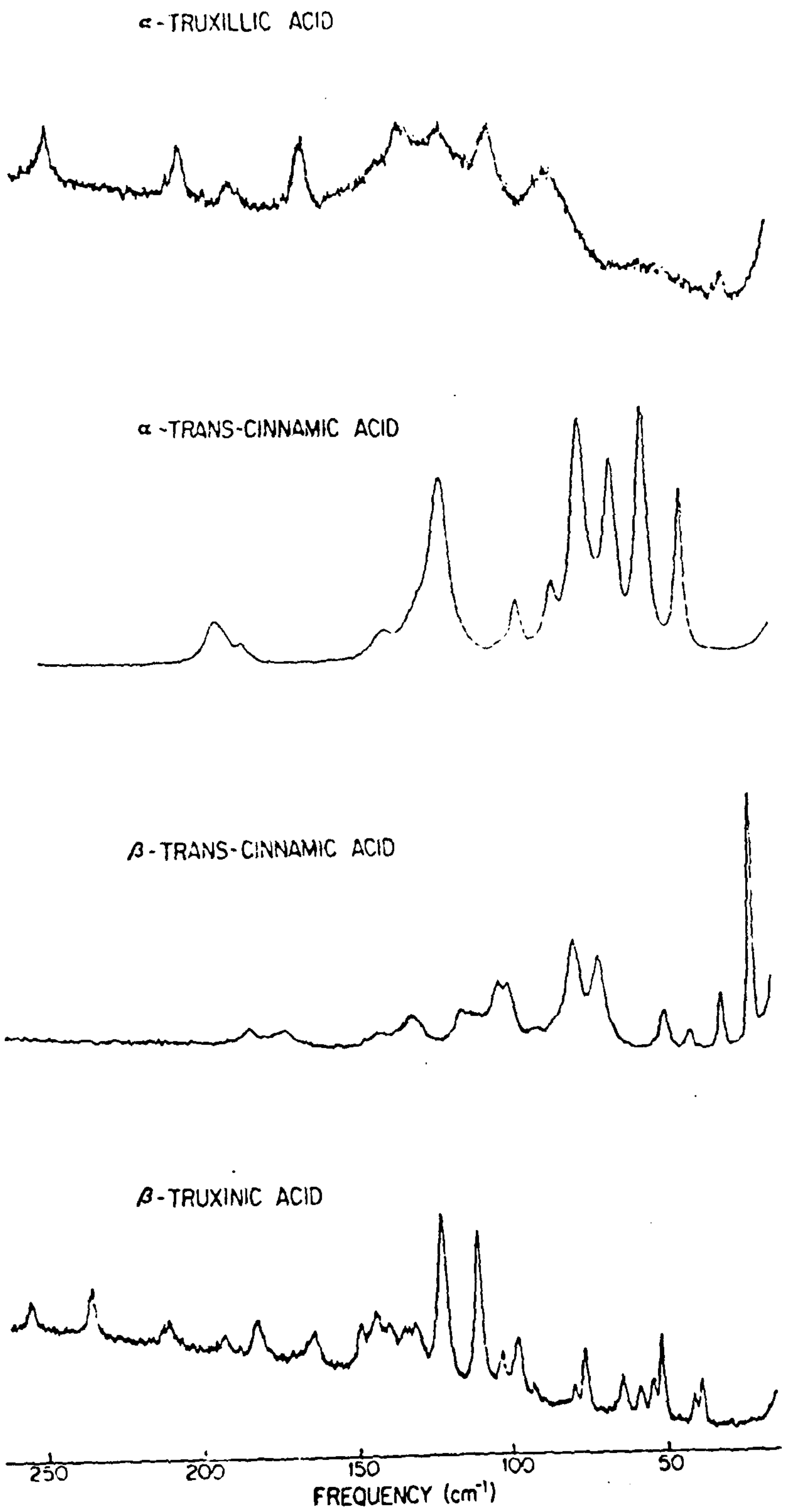

α-TRUXILLIC ACID
α-TRANS-CINNAMIC ACID
β-TRANS-CINNAMIC ACID
β-TRUXINIC ACID
250
200
150
100
50
FREQUENCY (cm⁻¹)

Figure 1

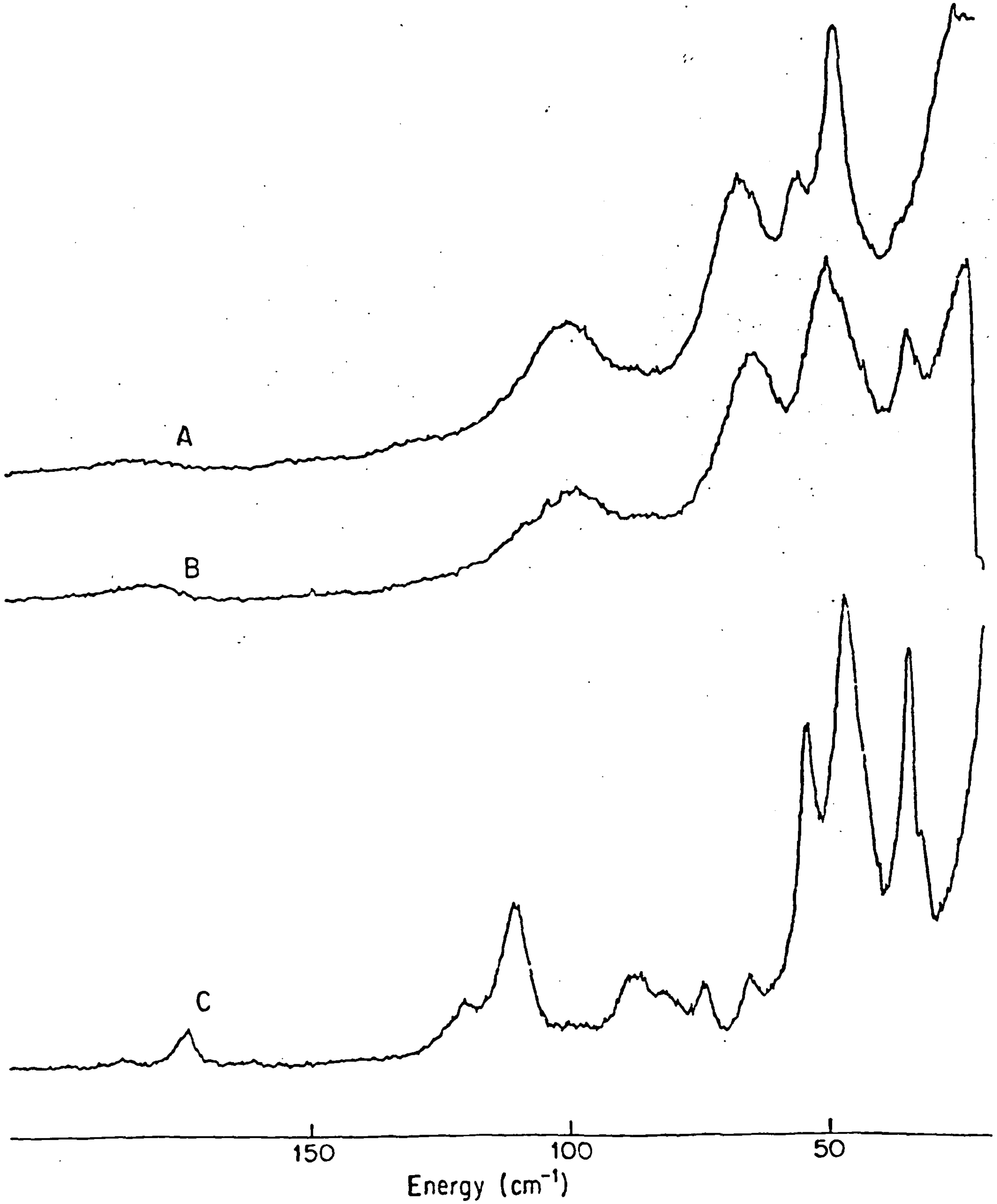


Figure 2

SUMMARY OF THE ACCOMPLISHED RESEARCH UNDER AFOSR-78-3676

(Period 9/1/78 - 8/31/79)

PUBLICATIONS

1. "Vibrational Relaxation in a Structurally Disordered Solid: Temperature Dependence of Raman Active Phonons in p-Bromochlorobenzene and p-Dichlorobenzene", P. N. Prasad, and R. V. Smith, J. Chem. Phys. 71, 4646 (1979).

2. "Vibrational Dephasing in Organic Solids: Temperature Dependence of a Localized Raman Active Internal Mode of Naphthalene", L. A. Hess and P. N. Prasad, J. Chem. Phys. Jan. 1, 1980 (scheduled publication date).

3. "Vibrational Relaxations and Dephasing in Organic Solids", P. N. Prasad. Mol. Cryst. Liq. Cryst. (in Press).

4. "Raman Phonon Spectroscopy of Solid State Reactions: Thermal Rearrangement of Methyl-p-Dimethylaminobenzene Sulfonate in Solid State", K. Dwarakanath and P. N. Prasad, Submitted for publication in J. Am. Chem. Soc.

ORAL PRESENTATIONS:

1. "Laser Raman Study of Solid State Reactions", P. N. Prasad. Presentation on April 2, 1979 at the American Chemical Society Symposium in Honolulu.

2. "Laser Raman Study of the Thermal Rearrangement of Methyl p-Dimethyl-Aminobenzene Sulfonate in Solid State", K. Dwarakanath, R. V. Smith and P. N. Prasad, Molecular Spectroscopy Symposium, June 12, 1979 at Columbus, Ohio.

3. "Vibrational Relaxation and Dephasing of Raman Active Modes in Molecular Solids and Crystalline Molecular Complexes", L. A. Hess and P. N. Prasad, Molecular Spectroscopy Symposium, June 12, 1979 at Columbus, Ohio.