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Report No. 5

on

Contract No. N6onr 22517 NR 017 408

Jih-Heng Hu and P. M. Harris
September 1953

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

RF Project 355

Report No. 5

TECHNICAL
R E P O R T

by

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

Columbus 10, Ohio

To: OFFICE OF NAVAL RESEARCH, NAVY DEPARTMENT
N6onr 22517 NR 017 408

On: ORDER-DISORDER TRANSFORMATIONS IN CRYSTALS
LOW TEMPERATURE HEAT CAPACITY AND THE SOLID I-
SOLID II TRANSITION IN TETRANITROMETHANE

For the period: September 1953

Submitted by: Jih-Heng Hu and P. M. Harris
Department of Chemistry

Date: September 1953

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LOW TEMPERATURE HEAT CAPACITY AND THE SOLID I-
SOLID II TRANSITION IN TETRANITROMETHANE

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Navy Department, Office of Naval Research
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Ohio State University Research Foundation
Columbus 10, Ohio

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PREFACE

Previous work on the structure and solid-solid transition of tetranitromethane made the determination of its heat capacity desirable. Since most of the work carried out on $C(NO_2)_4$ in this laboratory has been associated with support from ONR Contract N6onr 225-17 NR 017 408, which is presently being transferred, it has seemed desirable for the sake of completeness to present these results in a technical report. For want of detailed consideration, the experimental results appear with a minimum of discussion.

INTRODUCTION

The structure of tetranitromethane has been investigated in this laboratory by Mabis⁽¹⁾ and Lindenmeyer⁽²⁾ and elsewhere by Oda, Nitta and co-workers⁽³⁾. Mabis found evidence of solid-solid transition but investigated only the structure of solid I, the solid which is in equilibrium with the liquid at the normal melting point (13.8°C.), as did the Japanese investigators. Lindenmeyer found the transition, solid I to solid II, to be at approximately -99°C by a cooling curve investigation, and by differentiation of the cooling curve obtained a "relative" heat capacity as a function of the temperature, which suggested that the transition might have second order characteristics superimposed on the first order transition.

Above the transition temperature Solid I is clearly disordered, the disordering being one of molecular orientation in a body-centered, 2-molecule cubic cell⁽²⁾. This conclusion is reached both from the x-ray investigations of Mabis and Oda et al. and from the infrared absorption spectra analysis of Lindenmeyer on Solid I, Solid II, liquid, and vapor.

In the light of these results an investigation of the low temperature heat capacity of tetranitromethane was undertaken over the range from liquid nitrogen temperature to room temperature.

EXPERIMENTAL

PREPARATION OF THE SAMPLE

About three pounds of tetranitromethane was obtained from Dr. Harold Shechter of The Ohio State University, Department of Chemistry. It was purified by melting at room temperature and then recrystallizing at ice temperature until about half of the material was solidified. The process was repeated for the solid part, and approximately 300 g of purified tetranitromethane was thus obtained. This substance was further purified by fractional distillation in an all-glass still essentially as described by Nicholson⁽⁴⁾. Distillations were carried out under a pressure of 19-20 mm of Hg at 36-40°C. A 10-ml sample was used to minimize dangers of explosion and was separated into four approximate equal fractions. The process was continued, equal numbered fractions being combined until approximately 150 g of fractions 2 and 3 was obtained.

THE COOLING CURVE MEASUREMENTS

The cooling curve was taken in a double-walled glass tube immersed in a dewar which was filled with water and was maintained at approximately constant temperature (9°C in most cases, and 0°C in a few cases). The temperature was measured by a Beckmann thermometer which had been calibrated against a standard thermocouple in the Cryogenic Laboratory of The Ohio State University, Chemistry Department. The cooling curve

shows a clear-cut break at 13.8°C , but the cooling persists, though at much slower rate, at considerably lower temperatures. This situation will be more clearly shown in the heat capacity curve.

THE LOW TEMPERATURE HEAT MEASUREMENTS

The calorimeter used in this research was of the Nernst vacuum type described by Johnston and Kerr.⁽⁵⁾ It was filled with 109.465 g. (0.5584 moles) of pure tetranitromethane. The dead space left was (~ 1 cc). Since the highest temperature reached in the heat capacity measurements was 30°C , at which the vapor pressure is reported by Nicholson to be 19 mm of Hg, the correction for the appearance of the vapor phase over the liquid is negligible. The actual heat capacity measurements are reported in Table 1 and shown in Figure 1. The heat capacity curve shows a transition at -98.21°C . The width of the peak is of the order of $0.3\text{-}0.6^{\circ}\text{C}$. Two determinations of transition heat were taken, and their values were almost coincident as reported in Table 2. The transition temperature was determined from a heating curve. A known amount of energy was supplied by a heater-resistance thermometer wire wound around the calorimeter. By properly adjusting the temperature of its surroundings (upper and lower blocks), the heat exchange of the calorimeter with its surroundings could be held to a negligible amount. The temperature of the calorimeter was recorded after its drift rate was less than 0.0005°C per minute. The data on the transition temperature determination are recorded in Table 3, and shown in Figure 2. The

TABLE 1. LOW TEMPERATURE HEAT CAPACITIES
OF TETRANITROMETHANE

Average temp., °K, Solid II	Temp. interval, °K	Heat capacity, cal. deg. ⁻¹ mol. ⁻¹
58.05	3.298	17.19
62.86	6.356	18.12
69.85	7.699	19.59
77.01	6.633	21.06
83.81	6.974	22.36
86.96	3.022	22.92
90.81	7.107	23.55
98.03	7.415	24.83
103.54	6.971	25.83
111.09	8.153	27.08
118.44	7.396	28.25
126.32	8.490	29.51
134.52	7.752	30.80
141.91	7.151	31.98
148.29	6.701	32.93
160.29	8.858	34.84
168.89	8.280	36.20
172.01	1.932	36.72
172.90	1.872	37.24
173.93	1.735	43.41
174.38	1.062	74.07
174.97	0.043	~ 6000
174.97	0.206	~ 1000
175.00	0.117	~ 2500
175.91	1.870	77.49

Transition Temperature 174.95°K

Solid I

175.98	1.652	45.36
180.95	7.151	46.56
181.54	5.278	46.60
188.83	9.619	48.00
198.24	8.955	49.52
209.87	10.774	50.99
221.05	11.381	51.99
232.13	10.733	52.86

Table I. (Cont'd)

Average temp., °K, Solid II	Temp. interval, °K	Heat capacity cal. deg. ⁻¹ mol. ⁻¹
Solid I starts to melt at 233.2°K		
242.84	10.105	53.70
252.87	9.507	55.16
262.48	10.049	56.49
272.84	9.185	59.83
278.64	4.469	63.36
280.25	4.043	66.56
282.95	2.196	76.15
283.15	4.437	88.38
285.95	1.395	307.9
Melting complete at 13.81°C		
Liquid		
292.27	6.516	57.36
299.01	6.249	58.19

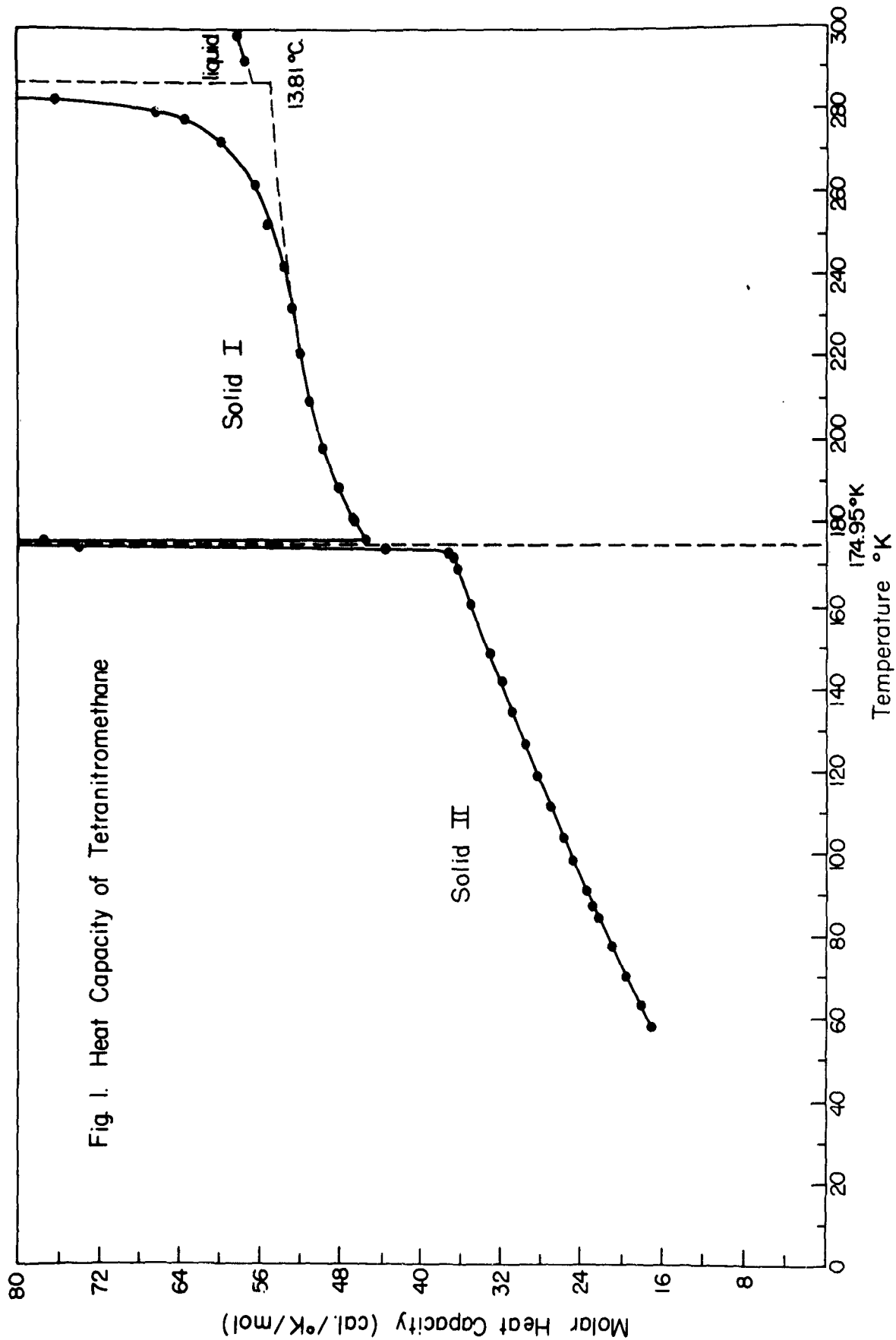


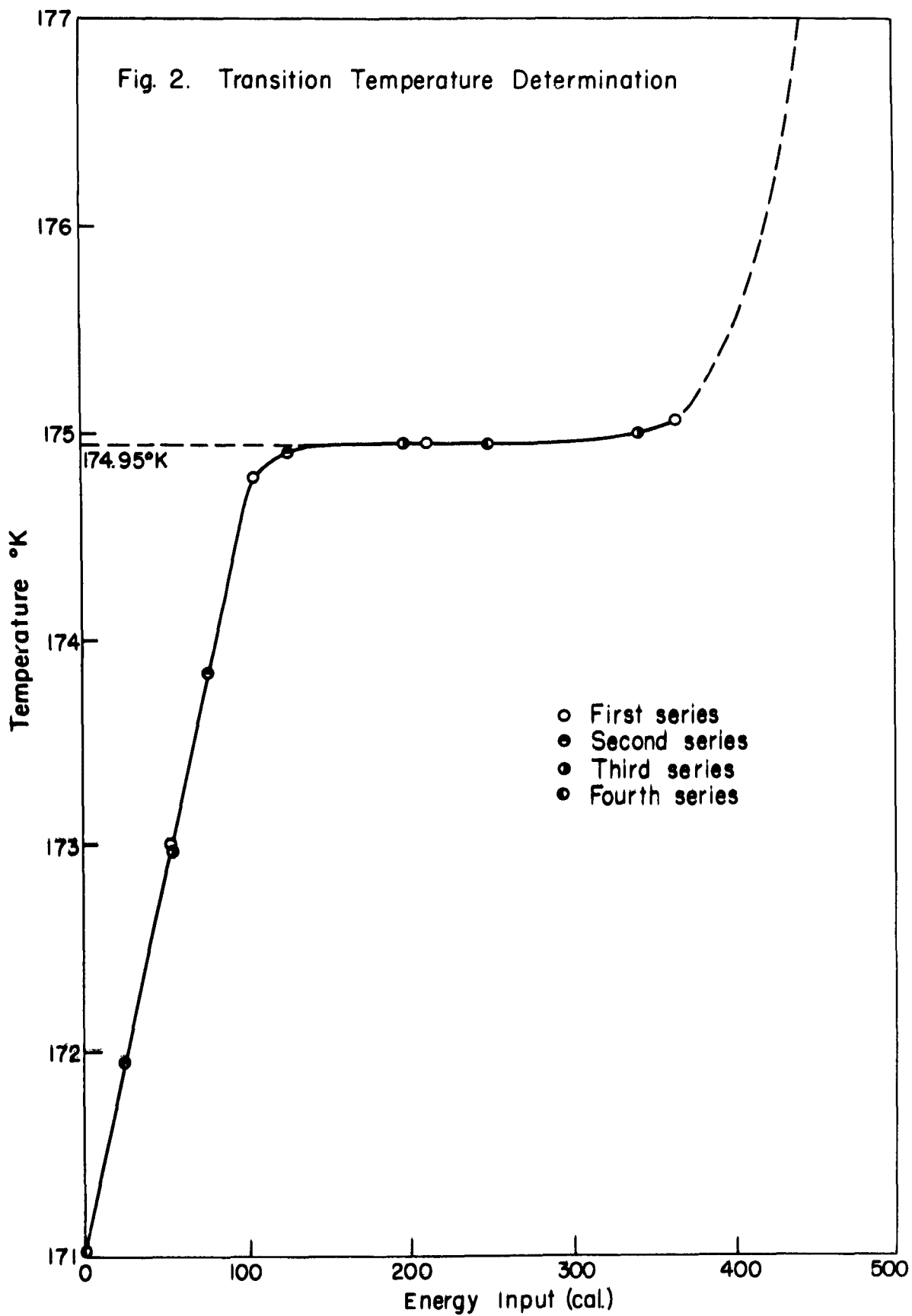
TABLE 2

(a) Heat of Transition	
First Run	$\Delta H_T = 472.4 \text{ cal.}$
Second Run	$\Delta H_T = 472.7 \text{ cal.}$
Average Run	$\Delta H_T = 472.6 \pm 0.3 \text{ cal.}$
(b) Heat of Fusion	
First Run	$\Delta H_F = 2250.5 \text{ cal.}$
Second Run	$\Delta H_F = 2250.7 \text{ cal.}$
Third Run	$\Delta H_F = 2241.7 \text{ cal.}$
Average Value	$\Delta H_F = 2250.6 \pm 3 \text{ cal.}$

TABLE 3. DETERMINATION OF TRANSITION TEMPERATURE OF TETRANITROMETHANE

Energy input, cal.	Temperature, °K	Series No.
0	171.042	1
25.01	171.964	2
52.79	172.005	1
55.40	172.977	3
76.73	173.841	2
106.65	174.791	1
127.95	174.897	2
199.51	174.948	3
213.66	174.949	1
251.50	174.936	4
343.18	174.995	3
366.64	175.062	1
444.41	177.149	4

Transition Temperature = $174.95 \pm .05^\circ\text{K}$ (-98.21°C)



heat capacity curve also shows that incipient melting starts as low as 233.2°K, with the complete melting at 13-13.8°C. Three determinations of heat of fusion were carried out. The premelting part was obtained by extrapolating the trend of the heat capacity curve below 233.2°K, at which point the melting starts, to 13.8°C. The area between the actual heat capacity curve and the extrapolated curve was obtained by numerical integration. Two values of heat of fusion determined were almost equal. The third value differed from the other two by 9 cal., which is about 0.4%. This difference is explainable, however, because in order to minimize the possible error in the estimation of the premelting part of the heat of fusion, the third run was started at a considerably lower temperature than the other two, and the blocks had to be heated during the run. In the absence of a knowledge of the temperature of the blocks during the heating (about 5 min. against 75 min. for the complete run of the heat of fusion), it was assumed in the heat leakage corrections that the temperature of the blocks increased linearly, which was probably not true because of the lag in establishing equilibrium between the upper and lower blocks. The values of heat of fusion are reported in Table 2. The average value of the heat of fusion has been obtained from the first and second determinations without regard to the third one.

DISCUSSION

A plot of the heat capacity as a function of the temperature (Figure 1) exhibits several interesting features. First, the transition at 174.95°K is clearly first order. It is believed that the sample used was of high purity, and the sharpness of this transition indicates that the transforming solid phase is quite pure. However, just above the transition temperature the heat capacity of Solid I is more than eight calories per degree per mol greater than that for Solid II just below the transition point. Since it is a fact that the molecules in Solid I are disordered, then the lattice transformation from Solid II to Solid I is probably accompanied by an isothermal disordering process.

The entropy increase, as a result of the transformation from Solid I to Solid II, amounts to $2.70 \text{ e.u.} (\approx 2 R \ln 2)$.

In the Solid I range ($T_{Tr} < T < T_F$), the heat capacity starts to rise rather rapidly with increasing temperature, passes through an inflection point, and then exhibits a marked "premelting" character. Using the freezing point as a criterion of purity, there is certainly not sufficient impurity present to account for such pronounced premelting. Further, just above the melting point the heat capacity of the liquid is less than the extrapolated heat capacity of Solid I just below the melting point.

These observations suggest that additional modes of vibration become excited in Solid I just above the transition temperature and that certain of these become translational modes (i.e., shear with

little or no restoring force) after melting, with the resultant decrease in heat capacity. (Most of the "entropy of fusion" is acquired by Solid I prior to fusion).

Comparison of the heat capacity of $C(NO_2)_4$ with that of similar molecules, such as CCl_4 ⁽⁶⁾ and $C(CH_3)_4$ ⁽⁷⁾, is of interest. All three exhibit Solid-Solid transitions. The transition in CCl_4 at 225.5°K is apparently accompanied or followed by an order-disorder transformation⁽⁸⁾. That in $C(CH_3)_4$ occurs at 140.0°K. With both substances the heat capacity extrapolated through the transition appears to be a continuous function, in contrast to $C(NO_2)_4$. Further, the excess heat capacity in Solid I of $C(NO_2)_4$ is probably not due to onset of rotational disorder in the usual sense, since torsional vibration modes have been identified from the infrared spectra. Presumably a dynamic disorder of orientation does exist, accompanied by violent torsional oscillations. It is possible that these modes go over into actual rotations just below the melting point.

Since a frequency assignment has been made for the modes of vibration of $C(NO_2)_4$ ⁽²⁾, permitting a calculation of the entropy of the gas, it is desirable that the experimental measurement of the heat capacity of the solid be carried to lower temperatures to permit a judgment regarding frozen-in disorder in Solid II (and/or the existence of a barrier to rotation of the nitro groups).

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