LEVEL II

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Proton Magnetic Resonance Spectroscopy Studies of Aluminum (III), Gallium (III), and Indium(III) in Methanol and Ethanol: Determination of Solvation Numbers and Exchange Rates.

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The objectives of this research endeavor are to determine the solvation numbers and rates of ligand exchange for selected aluminum, gallium, and indium salts in methanol and ethanol utilizing a Varian EM-390 Nuclear Magnetic Resonance Spectrometer.

Special sample preparation techniques were employed to make the anhydrous inorganic salts. These methods were similar to those used by Donoghue and Drago[1] to prepare anhydrous cobalt perchlorate. Anhydrous aluminum nitrate in ethanol, aluminum perchlorate in ethanol, gallium perchlorate in ethanol, indium chloride in methanol and ethanol, indium nitrate in methanol and ethanol and indium perchlorate in methanol and ethanol have prepared via the chemical dehydration of their respective hydrated salts with 2,2-dimethoxypropane. The order of addition of reactants is important. If the hydrated salt is first added to 2,2-dimethoxypropane or 2,2-diethoxypropane, a strong brown discoloration is produced. However, if the hydrated salt is added to "super-dry" methanol or ethanol, and then the 2,2-dialkoxypropane the discoloration is reduced. Nevertheless, in the case of indium salts some discoloration results regardless of the order of addition.

$$MX_3 \cdot nH_2O \;+\; n(CH_3)_2C(OR)_2 \;\rightarrow\; MX_3(\text{anhydrous}) \;+\; 2nROH \;+\; n(CH_3)_2CO$$

The "super dry" alcohols were prepared by treatment with magnesium turnings using iodine to initiate the reaction as described by Vogel[2]. The alcohols were stored over Linde 4A molecular sieve in a nitrogen environment.

All starting materials and other chemicals were reagent grade quality. Solutions for nmr measurements were prepared by adding a specific quantity of anhydrous alcohol to the appropriate anhydrous salt in a dry environment (glove bag under a nitrogen atmosphere). The measured anhydrous mixtures were accurately weighed. The samples were sealed in standard nmr tubes following freeze-thaw degassing, and stored in a dry ice-2-propanol mixture when not in use. Samples used for solvation number determinations were approximately 0.5 M, while those used for rate determinations were approximately 0.25 M.

Measurements for solvation numbers and exchange rates were recorded on a Varian EM-390 spectrometer equipped with a special temperature controller. Signal areas were integrated with an Alvin PL-655M planimeter.

Ligand-exchange rates were obtained by curve-fitting experimental OH slow-passage spectra with computer calculated spectra for several trial exchange rates, as well as by the Bloch equation for the region for which the slow exchange approximation is valid(Appendix A). Measurements of parameters required for rate calculations were made over a wide range of temperatures.

Consultations of methodologies described and interpretation of data obtained up-to-date were made with Dr. Terry D. Alger and Dr. Joseph Morse(Higher Board of Education of Utah and Utah State University respectively).

Spectra of $In(ClO_4)_3$ in ethanol were taken from -30°C to -70°C for solvation studies and spectra for rate studies were taken from -5°C to -95°C.

Spectra for $InCl_3$ in ethanol were taken from -65°C to -90°C for solvation studies and -60°c to -95°C for rate studies.

The rate studies and the solvation studies for $In(ClO_4)_3$ in ethanol proved to be of particular significance. The result of the rate studies is indicated in figure 1. The computer program has recently been debugged, therefore, the thermodynamic parameters sought have not as of yet been ascertained. An approximation of what is anticipated and what will be used to calculate the thermodynamic parameters(which will be used to predict the mechanism of ligand exchange) is indicated in figure 2.

The solvation number determination proved to be fantastically interesting(TableI). There is a definite change in the solvation number(never before observed in such a dramatic manner) as the temperature is lowered. Evidence strongly suggest that the solvation effects undergo a rather remarkable modification as the temperature is lowered for the indium system in ethanol. The spectra for this system will have to be photographed, therefore, they will be included in the final report. Nevertheless, such a system apparently exhibits a coordination complex of seven at lower temperatures and a coordination of six at higher temperatures. Further discussion of this will appear in the final report.

Additional spectra and other systems have not been interpreted or obtained since the EM-390 has been made fully operational only very recently.

Serious difficulties have been encountered with this research activity. The magnet to the EM-390 was dropped by individuals employed to move it to a specified location. The magnet had to undergo extensive repairs. This unforturnate accident set the project back several months. The instrument has recently been properly installed and is functioning at peak efficiency.

Considerable problems were encountered in preparing $In(ClO_4)_3$ in methanol. The samples gave rather broard nmr peaks which were not ideal for solvation number determinations.

Problems were also obtained in debugging the many site nmr Line Shape Program.

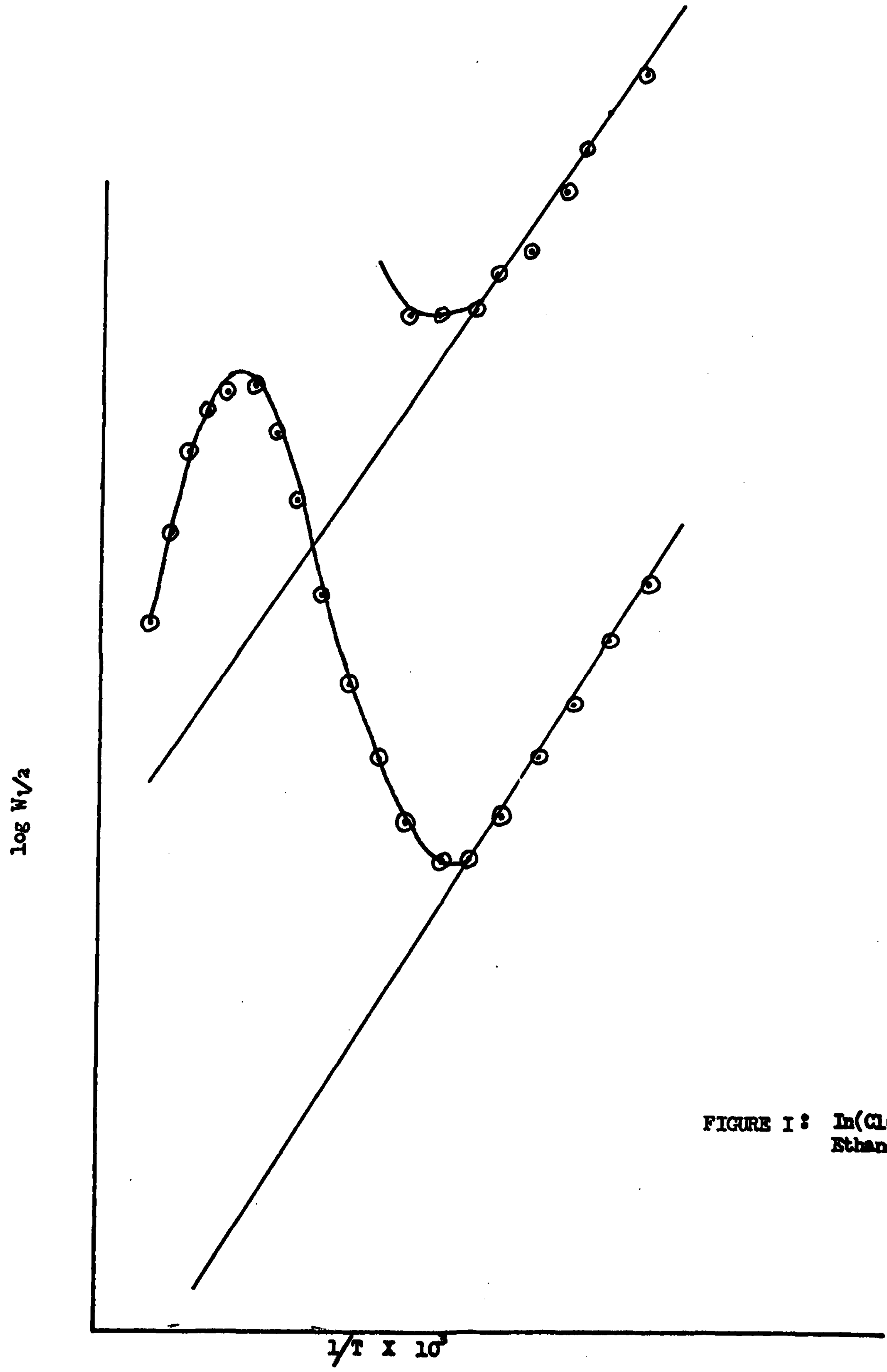

FIGURE I: $In(ClO_4)_3$ in Ethanol

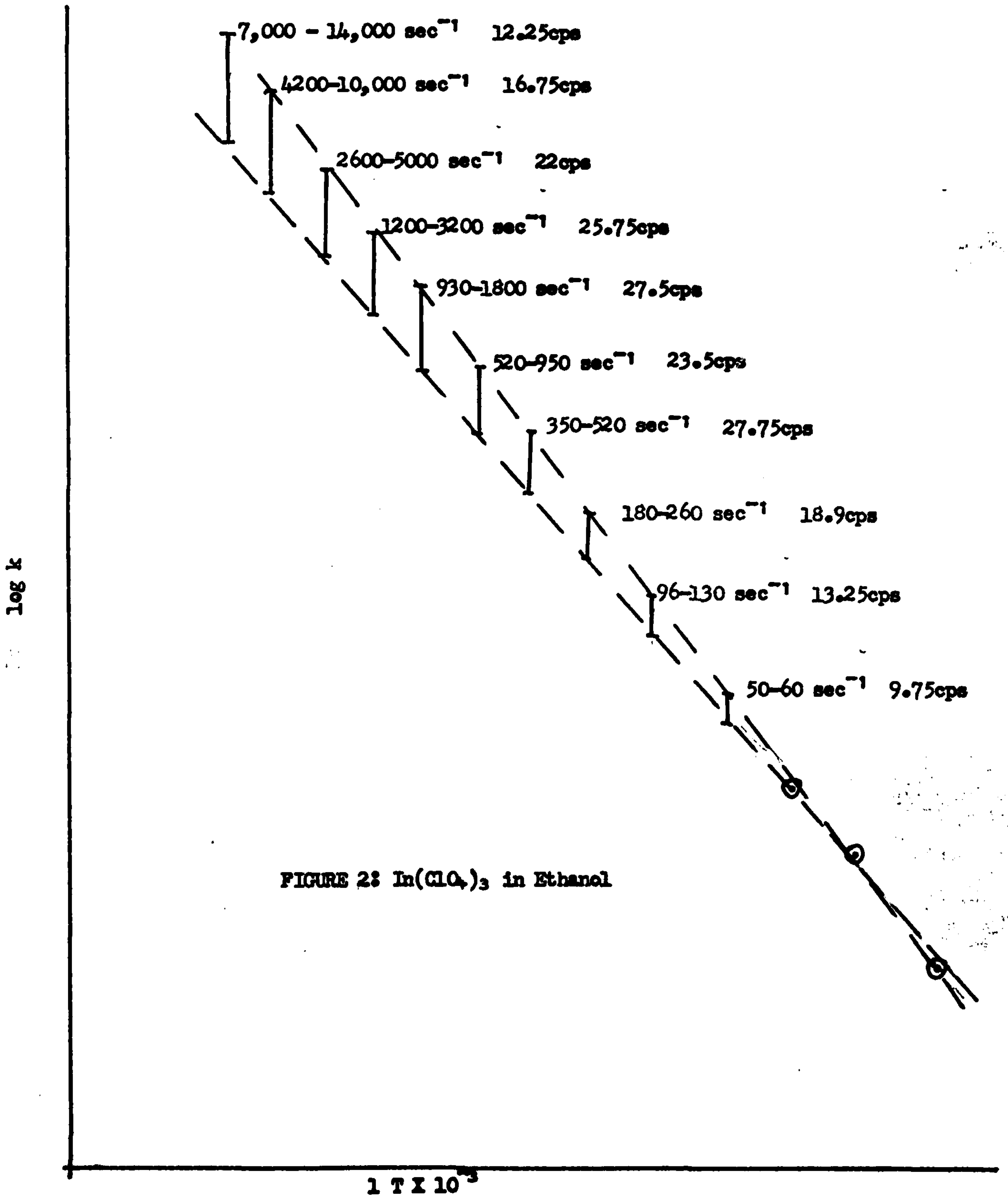

FIGURE 2: $In(ClO_4)_3$ in Ethanol

Table I: Determination of the Solvation Number — In(III) in Ethanol

Temp °C	moles of Indium Perchlorate X 10^3	Molar Ratio M/M	Solvation OH A_s	Area under Bulk OH peak	Solvation Number
-40	5.1	33.33	0.057	0.131	5.9
-40	5.1	33.33	0.049	0.220	6.07
-45	5.1	33.33	0.040	0.196	5.64
-50	5.1	33.33	0.030	0.116	6.8
-50	5.1	33.33	0.034	0.131	6.9
-55	5.1	33.33	0.026	0.1053	6.6
-60	5.1	33.33	0.026	0.0985	6.96
-70	5.1	33.33	0.026	0.095	7.2

Reference

1. J. T. Donoghue and R. S. Drago, Inorg. Chem., 1, 866(1962)

2. Arthur I. Vogel: A Textbook of Practical Organic Chemistry, third edition, page 166. Longman

APPENDIX A

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              SAUNDERS MANY SITE NMR LINE-SHAPE PROGRAM
PROGRAM FOR CALCULATING NMR LINE SHAPES FOR CASES INVOLVING UP TO 25
LINES.  ANY PROBABILITIES FOR TRANSITIONS BETWEEN THE VARIOUS SITES
MAY BE INCLUDED,  BUT SPIN-SPIN COUPLING SHOULD BE ABSENT UNLESS IT IS
FIRST ORDER IN WHICH CASE IT MAY BE CONSIDERED TO PRODUCE ADDITIONAL SITES
IF DESIRED,  THE SYSTEM PRINTER MAY BE USED TO PLOT THE LINE-SHAPE.
    THE PROGRAM FIRST READS A CONTROL CARD WITH THE FOLLOWING INFORMATION
    N(1) # ORDER OF MATRIX (THE NUMBER OF SITES)
    N(2) WHEN POSITIVE CALLS PLOT WHICH DRAWS A GRAPH ON THE SYSTEM PRINTE
    N(3) POSITIVE SUPPRESSES PRINTING OF SPECTRUM
    N(4) WHEN POSITIVE PROGRAM OMITS READING NEW PROBABILITY MATRIX AND
         GOES ON TO READ A NEW RATE CARD.
    N(5) WHEN EQUAL TO 1, CHECKS TRANSITION PROBABILITY MATRIX AGAINST
         EQUILLIBRIUM PROBABILITIES AND EXITS IF AN ERROR IS FOUND.
    N(7) WHEN POISITVE ADDS SPECTRUM TO PREVIOUS ONE. NO RATE CARD IS NEEDE
    THEN A CARD WITH THE FREQUENCIES (IN CPS), THE RELATIVE EQUILLIBRIUM
    POPULATIONS, THE HALF WIDTHS OF THE LINES IN THE ABSENCE OF EXCHANGE,
    THE RELATIVE EQUILLIBRIUM POPULATIONS, AND THE NUMBER OF SITES TO WHICH
    THE PARTICULAR LINE IN QUESTION CAN GO IS READ.
    THE PROGRAM THEN READS CARDS WITH THE RELATIVE PROBABILITIES FOR GOING
    FROM THE I'TH SITE TO THE M'TH SITE.
    AFTER THE COMPLETE PROBABILITY MATRIX IS READ, THE PROGRAM READS A
    CARD WITH THE RATE CONSTANT(PSEUDO FIRST ORDER IN 1/SEC),THE FIRST
    AND LAST FREQUENCIES AT WHICH THE INTENSITY IS TO BE CALCULATED AND THE
    INTERVAL FOR THIS CALCULATION.
    ONE CAN CONTINUE WITH A CONTROL CARD WITH A ONE IN COLUMN 20 FOLLOWED
    BY ANOTHER RATE CARD ETC. IN ORDER TO REPEAT THE CALCULATION AT DIFFER
   RATES.
   DIMENSION N(7), W(25),P(25),TR(25),SR(2000),A(25,25),Q(25)
   DIMENSION T2(25), B(25,25), FG(2000)
   DIMENSION C(25,25),D(25,25)
   COMMON N
                                      READ CONTROL CARD
 1 READ  (5,5)N
 5 FORMAT(14I5)
   WRITE (6,8)N
   FORMAT (1H1, 5X, 14I7)
   IF(N(7).GE.1) GO TO9
   DO 11 NN = 1,2000
11 SR(NN) = 0.
   NA = N(1)
   IF(NA.GT.25.OR.NA.LE.0) GO TO 1
 6 IF(N(4)-1)2,27,1
                                      CLEAR PROBABILITY MATRIX
   DO 30 I = 1, NA
   DO 30 J = 1, NA
   B(I, J) = 0.
                                      READ FREQUENCIES, POPULATIONS, WIDTHS
 9 DO 10 J = 1,NA
   READ (5, 15) W(J), P(J), T2W, K
   FORMAT (3F10.3, I10)
   IF (T2W .LE. 0.) T2W = .001
   T2(J) = T2W*3.14159
14 WRITE (6,15)W(J),P(J),      T2W,K
                                      READ RELATIVE TRANSITION PROBABILITIES
   IF(K) 10,10,16
16 DO 20 L= 1,K
   READ  (5,25)I,M,PL
25 FORMAT(2I10,F10.7)
   WRITE (6,26)I,M,PL
26 FORMAT(35X,2I10,F15.8)
20 B(I,M) = -PL
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      IF(N(5)) 27,27,25
      DO 24 I = 1, NA
 24   Q(I) = P(I)
      CALL MARKOV(A,B,P)
      IF(N(5).GT.2) GO TO 27
      DO 28 I = 1,NA
      IF((ABS(Q(I)-P(I))/Q(I)).GT..005) CALL EXIT
 28   CONTINUE
                                          READ RATE CONSTANTS  ETC.          000004
 27   IF(N(7).GE.1) GO TO 34
      READ  (5,35)R,FI,FF,STEP
 35   FORMAT(4F10.4)
        TRACE
 34   WRITE (6,36) R,FI,FF,STEP
 36   FORMAT(// 13X,4F15.5 //)
      IF(STEP)380,1,380
 .80  IF((FF-FI)/STEP)1,1,383
 .83  IF((FF-FI)/STEP-1800.)38,38,1
 38   NO = 0
      DO 82 I = 1,NA
      TR(I) = 0.0
      DO 82 J = 1,NA
 82   TR(I) = TR(I) - B(I,J)
      DO 70 I = 1,NA
      DO 70 J = 1,NA
      D(I,J) = 0.
]       C(I,J) = B(I,J)*R
      DO 49 I = 1,NA
 49   C(I,I) = TR(I)*R + T2(I)
      AMAX = 0.0
                                          STEP FREQUENCY                     000006
 43   NO = NO + 1
      ANO = NO-1
      F = FI +ANO*STEP
      IF(F-FF) 41,41,90
 41   G = F*6.283185
      DO 40 I = 1,NA
 40   D(I,I) = -G + W(I)*6.283185
      CALLINVC(NA,A,C,D)
      S = 0.0
      DO 50 I = 1,NA
      DO 50 J = 1,NA
 50   S = S + A(I,J) * P(I)
      SR(NO) = ABS(S) +SR(NO)
      IF(ABS(SR(NO)).GT.AMAX) AMAX = ABS(SR(NO))
 55   IF(N(3)) 59,59,43
 59   WRITE (6,51) F,SR(NO)
 51   FORMAT(20X,F10.3,F25.9)
      FG(NO) = F
      GO TO 43
0     NO = NO - 1
      FS = FS - STEP
 89   IF(N(2)) 1,1,57
7     CONTINUE
2     CONTINUE
      GO TO 1
      END

>ERROR COUNT: 0000, PSECT SIZE: 1282, DSECT SIZE: 3289; REV. 5
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      SUBROUTINE INVC (N, A, C, D)
C INVERSION OF COMPLEX MATRIX WITHOUT COMPLEX ARITHMETIC
C USES  A # %C & DC-1D<-1
      DIMENSION A(25,25),C(25,25),D(25,25),E(25,25)
      DO 10 I = 1,N
      DO 10 J = 1,N
   10 E(I,J) = C(I,J)
      CALL INV(N,E)
      DO 20 I = 1,N
      DO 20 J = 1,N
      A(I,J) =0.
      DO 20 K = 1,N
   20 A(I,J) = A(I,J) + D(I,K)*E(K,J)
      DO 30 I = 1,N
      DO 30 J = 1,N
      E(I,J) = 0.
      DO 30 K = 1,N
   30 E(I,J) = E(I,J) + A(I,K)*D(K,J)
      DO 40 I = 1,N
      DO 40 J = 1,N
   40 A(I,J) = C(I,J) +E(I,J)
      CALL INV(N,A)
      RETURN
      END

>EPROR COUNT: 0000, PSECT SIZE: 0359, DSECT SIZE: 1271; REV. 5
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      SUBROUTINE INV(N,A)
    SINGLE PRECISION REAL MATRIX INVERSION
     DIMENSION A(25,25)
     DIMENSION IPIVOT(25),INDEX(25,2)
     EQUIVALENCE (N1,IROW,JROW),(ICOLUM,JCOLUM,JCOLUM,K1)
15   DO 20 J=1,N
 20  IPIVOT(J)=0
 30  DO 550 I=1,N
.0   AMAX = 0.
,5   DO 105 J=1,N
;0   IF (IPIVOT(J) - 1) 60, 105, 60
 60  DO 100 K=1,N
'0   IF(IPIVOT(K)-1)80,100,790
:0    IF(ABS(AMAX)-ABS(A(J,K))) 85,100,100
35   IROW=J
 90  ICOLUM=K
)5   AMAX=A(J,K)
100  CONTINUE
105  CONTINUE
110  IPIVOT(ICOLUM)=IPIVOT(ICOLUM)+1
130  IF(IROW-ICOLUM) 150,260,150
150  DO 200 L=1,N
160  SWAP=A(IROW,L)
170  A(IROW,L)=A(ICOLUM,L)
?00  A(ICOLUM,L)=SWAP
?60  INDEX(I,1)=IROW
?70  INDEX(I,2)=ICOLUM
510  PIVOT=A(ICOLUM,ICOLUM)
530  A(ICOLUM,ICOLUM)= 1.
540  DO 350 L=1,N
550  A(ICOLUM,L)=A(ICOLUM,L)/PIVOT
580  DO550 L1=1,N
590  IF(L1-ICOLUM) 400,550,400
,00  T=A(L1,ICOLUM)
,20  A(L1,ICOLUM)= 0.
,30  DO 450 L=1,N
,50  A(L1,L)=A(L1,L)-A(ICOLUM,L)*T
;50  CONTINUE
;00  DO710 I=1,N
;10  L=N+1-I
;20  IF(INDEX(L,1)-INDEX(L,2)) 630,710,630
,30  JROW=INDEX(L,1)
,40  JCOLUM = INDEX(L,2)
,50  DO 705 K=1,N
.60  SWAP=A(K,JROW)
.70  A(K,JROW)=A(K,JCOLUM)
 00  A(K,JCOLUM)=SWAP
 05  CONTINUE
 710 CONTINUE
 90  CONTINUE
     RETURN
     END

>ERROR COUNT: 0000, PSECT SIZE: 0554, DSECT SIZE: 0107; REV. 5
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      SUBROUTINE MARKOV (A, B, P)
      DIMENSION A(25,25), B(25,25), P(25), N(5)
      COMMON N
      NA = N(1)
      DO 50 I = 1, NA
      TR = 0.
      DO 51 J = 1, NA
 1    TR = TR - B(I,J)
 0    B(I, I) = TR
      DO 10 I = 1, NA
      DO 10 J = 1, NA
 0    A(I,J) = -B(I,J)
      DO 20 I = 1, NA
 0    A(I, NA) = 1.
      CALL INV(NA,A)
      DO 30 I = 1, NA
 0    P(I) = A(NA, I)
      WRITE (6, 35) (P(I), I=1,NA)
 5    FORMAT (5X, 10F12.8)
      NM = NA - 1
      DO 40 I = 1, NM
      IP = I + 1
      DO 40 J = IP, NA
      IF (ABS ((B(I,J) * P(I)) - (B(J,I) * P(J)))
     1 + (B(I,J) * P(I)) + (B(J,I) * P(J)) * .02 ) 40, 40, 41
 1    WRITE (6, 42) I, J, P(I), P(J), B(I,J), B(J,I)
 2    FORMAT (12H ERROR IN K          , 2I10, 4F12.6)
      IF (N(6) - 2) 43, 40, 43
 3    CALL EXIT
 0    CONTINUE
      DO 60 I = 1, NA
 0    B(I, I) = 0.
      RETURN
      END

>>ERROR COUNT: 0000, PSECT SIZE: 0420, DSECT SIZE: 0034; REV. 5

6=LP
NMR
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