APPROXIMATION METHODS
FOR
THE PARTITION FUNCTIONS OF ANHARMONIC SYSTEMS **MASTER**
by
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ABSTRACT

The analytical approximations for the classical , quantum mechanical and reduced partition functions of the diatomic molecule oscillating internally under the influence of the Morse potential have been derived and their convergences have been tested numerically . This successful analytical method is used in the treatment of anharmonic systems . Using Schwinger perturbation method in the framework of second quantization formulism , the reduced partition function of polyatomic systems can be put into an expression which consists separately of contributions from the harmonic terms , Morse potential correction terms and interaction terms due to the off-diagonal potential coefficients . The calculated results of the reduced partition function from the approximation method on the 2-D and 3-D model systems agree well with the numerical exact calculations .

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CHAPTER I

INTRODUCTION

The main objective of this thesis research is to find a new method in accounting for the anharmonicity in the reduced partition functions of polyatomic molecules, one that utilizes the Morse potential as has been successfully applied to the diatomic molecule. The reduced partition function represents the theoretical basis for equilibrium isotope effects as well as the isotope effect on the population of transition states, which is a major factor in kinetic isotope effects. Various methods of approximation for the reduced partition function of a pair of isotopic molecules within the framework of harmonic oscillator approximation have been developed in the last two decades, some of them primarily designed to permit quick and accurate numerical evaluation of the function, and others are particularly suited to give insight into the understanding of isotope effect, to give explicit relationships between the isotope separation factor and molecular structure and molecular forces. For the present status of accounting for the anharmonicity, one can refer to Chapter II A for a brief discussion of Wolfsberg's result. The advantage of this new approach to be discussed later is that one can readily calculate the contributions due

to the quadratic and cubic diagonal terms which are later identified with the Morse potential terms, and due to off-diagonal cubic terms separately. In case the contribution from the off-diagonal terms is negligible, we can justify to employ the diagonal terms alone in accounting for the anharmonicity involved and thus gain more insight in understanding the role of different diagonal terms in affecting the anharmonicity.

Part II of the thesis deals with the pertinent theories upon which the present research has been built, that is, with a discussion of the vibrational reduced partition function of the Morse oscillator and the second quantization formalism with operator technique for Schwinger's perturbation theory.

Part III is the research results of this study on the approximations for partition functions of diatomic systems. Results on approximations for the classical quantum-mechanical and reduced partition functions will be presented.

Part IV deals with the approximations for partition functions of polyatomic systems. Due to the complexity of the problem involved, a model system which simulates the two stretching modes of carbon dioxide is investigated with the exact numerical results compared to the approximate and the harmonic results. Then the results of a successful approximation on a linear triatomic system are presented.

In the Appendix, some results of other approximation methods which have been attempted during the course of

this research are presented. Padé Approximant method has been applied to the diatomic partition function. Orthogonal polynomial methods have also been explored. Nielsen's formulae and some essential details leading to simplified perturbation results of quantum partition function Eqs. (90) and (91) are also given. Listings of computer programs used for numerical evaluation of 2-D model systems and 3-D systems are also included.

CHAPTER II

BACKGROUND THEORY

A. VIBRATION REDUCED PARTITION FUNCTION OF THE MORSE OSCILLATOR

a. Introduction

The Born-Oppenheimer (BO) approximation is the underlying basic principle in most theoretical works on isotope effect. The isotope effect is a quantum mechanical effect and is most often described in terms of the reduced partition function ratio $\frac{s}{s'} f$, whereas

$$\frac{s}{s'} f = \frac{(Q/Q')_{qm}}{(Q/Q')_{cl}} = \frac{(Q_{qm}/Q_{cl})}{(Q'_{qm}/Q'_{cl})} = \frac{Q_r}{Q'_r} \quad (1)$$

with s and s' as the symmetry numbers of a pair of isotopic molecules. Q and Q' are the partition functions of the heavier and the lighter isotopic molecules, and the subscripts qm , cl , and r refer to the quantum mechanical, classical, and the reduced partition functions, respectively. Note that the validity of Eq. (1) does not depend on BO.

Under the harmonic oscillator treatment, and to the extent that the molecular translational and rotational motions are classical and separable from the internal

vibrational motions, the reduced partition function ratio is expressed as

$$\frac{S}{S'} f = \prod_i \frac{u_i e^{\frac{-u_i}{2}} (1 - e^{-u_i})}{u_i' e^{\frac{-u_i'}{2}} (1 - e^{-u_i'})} = \prod_i \frac{b(u_i)}{b(u_i')} \quad (2)$$

where each product is taken over all degrees of freedom, u is the energy of a normal vibration $h\nu_e$ in the units of kT , and $b(u)$ is the reduced partition function of a single harmonic oscillator,

$$b(u) = \frac{e^{\frac{-u}{2}}}{1 - e^{-u}} \quad (2a)$$

One usually accounts for the anharmonicity of vibration of a polyatomic molecule by a correction term $\prod_i \exp(u_i \chi_i / 4)$ to the zero-point energy term $\prod_i e^{-u_i/2}$ in Eq. (2) and ignores any effect of anharmonicity to the vibrational excitation. In 1969 Wolfsberg pointed out the presence of a mass dependent G_0 term in the energy terms of a diatomic molecule

$$\frac{E_v}{hc} = G_0 + w_e \left(v + \frac{1}{2}\right) - w_e x_e \left(v + \frac{1}{2}\right)^2 \quad (3)$$

In extending to simple polyatomic molecules, the G_0 term

which comes from non-rotating anharmonic terms and interaction between rotation and vibration terms was found to make significant contribution to the zero-point energy of isotopic water and ammonia and its inclusion in the calculation of the equilibrium constant yields good agreement between experimental and theoretical values. G_0 exactly vanishes for the Morse potential. Also the effect of anharmonicity due to its interaction with the rotational motions of a real molecule is generally significant but dealing with this effect would be out of the scope of this present study.

b. Formulations

The potential parameters of the Morse oscillator

$$U(q) = D(1 - e^{-\alpha q})^2 \quad (4)$$

are related⁶ to the parameters of the vibrational energy levels by

$$\omega_e = \alpha \sqrt{\frac{D}{2\pi^2 c^2 \mu}} \quad (5)$$

and

$$\omega_e x_e = \frac{h\alpha^2}{8\pi^2 c\mu} \quad (6)$$

where μ is the reduced mass. The classical partition function Q_{cl} of the bound state of the oscillator is given by

$$Q_{cl} = \frac{1}{u_e} \frac{1}{\sqrt{\pi}} \int_{-\rho \ln 2}^{\infty} \exp\left[-\rho^2 (1 - e^{-z/\rho})^2\right] \operatorname{erf} y_2 dz, \quad (7)$$

where ρ is a dimensionless quantity defined as

$$\rho = \sqrt{\frac{D}{kT}} = \frac{1}{2} \sqrt{\frac{u_e}{\chi_e}}, \quad (8)$$

erf is the error function,

$$\operatorname{erf} y_2 = \frac{2}{\sqrt{\pi}} \int_0^{y_2} e^{-t^2} dt, \quad (9)$$

and z and y_2 are dimensionless functions given by

$$z = apq \quad (10)$$

$$\text{and } y_2 = \rho [1 - (1 - e^{-z/\rho})^2]^{\frac{1}{2}} \quad (11)$$

The anharmonicity correction factor γ_{cl} for the classical partition function is expressed as

$$\gamma_{cl} = \frac{Q_{cl}}{Q_{cl}^0} = \frac{1}{\sqrt{\pi}} \int_{-\rho \ln 2}^{\infty} \exp[-\rho^2 (1 - e^{-z/\rho})^2] \operatorname{erf} y_2 dz, \quad (12)$$

where Q_{cl} and Q_{cl}^0 are the partition functions of the anharmonic and harmonic systems respectively. Note that γ_{cl} is a function of ρ only and does not depend on u_e and χ_e separately.

The quantum mechanical partition function is exactly given by

$$Q_{qm} = S \exp \left[-\frac{u_e}{2} + \frac{u\chi}{4} \right], \quad (13)$$

with

$$S = \sum_{v=0}^{V_D} \exp [-u_e v + u\chi(v + v^2)] \quad (14)$$

where V_D is the largest integer not exceeding c ,

$$c \equiv \frac{\omega_0}{2\omega_0\chi_0} = \frac{\omega_e - \omega\chi}{2\omega\chi} = \frac{u_e - u\chi}{2u\chi} = \frac{1 - \chi_e}{2\chi_e} \quad (15)$$

Eq. (13) gives the exact value of Q_{qm} for the allowed vibrational energy of the Morse oscillator expressed as

$$\frac{E_v}{hc} = \omega_e \left(v + \frac{1}{2} \right) - \omega_e \chi_e \left(v + \frac{1}{2} \right)^2 \quad (16)$$

The sum S can be equivalently expressed in terms of u or u_0 by using relations $u_e \chi_e = u_0 \chi_0 = u\chi$ and $u = u_0 - u\chi = u_e - 2u\chi$.

Then γ_{qm} , the anharmonic correction factor for the quantum mechanical partition function is

$$\gamma_{qm} = \frac{Q_{qm}}{Q_0} = \text{se}^{uX/4} [1 - \exp(-u_e)] \quad (17)$$

which depends on u_e and X_e individually.

γ_r , the anharmonicity correction factor for the reduced partition function follows

$$\gamma_r = \frac{Q_r}{Q_0} = \frac{Q_{qm}/Q_{cl}}{Q_{qm}/Q_{cl}} = \frac{\gamma_{qm}}{\gamma_{cl}} \quad (18)$$

c. Discussion

What I have attempted in this research is an improvement of the classical partition function Q_{cl} and quantum partition function Q_{qm} over the above presentation of the vibrational reduced partition function of the Morse oscillator. An approximation of partition functions for a system of anharmonic oscillators will help solve various thermodynamic problems that are currently being thwarted partly due to the lack of adequate ways to account for the anharmonicities in thermodynamic functions. Wolfsberg and his group have calculated the equilibrium constants of hydrogen isotope exchange reactions involving several simple

molecules, such as water and ammonia. Their calculations were based on a quartic potential function and included all other nonideal effects such as interactions of the anharmonic part of internal vibration with rotational motions, coriolis forces and are exact but tedious. It is hoped that a suitable approximation for the anharmonicity effect may provide some simplification of such calculations.

Partly to facilitate calculation of exact values to which one can compare any approximation, exact effects of anharmonicity of a single Morse oscillator to the classical, quantum mechanical, and reduced partition functions were calculated numerically. The anharmonicity correction factor for the classical partition function depends on a single parameter rather than on two potential parameters and temperature.¹ Several approximation methods have been investigated for the classical, quantum partition functions of a Morse oscillator. Only the method adopted will be presented in the main text and some other methods of interest will be relegated to the appendix.

B. SECOND QUANTIZATION WITH OPERATOR TECHNIQUE

a. General Formulation of the Schwinger Perturbation Theory^{8,9}

The problem is to derive an expression for $e^{-H_0+H_1}$ in which H_0 is regarded as a large operator and H_1 a small one. Let

$$\phi(t) = e^{-(H_0+H_1)t} \quad (19)$$

and forming $\phi(1)$ from Eq. (21) we find

$$\begin{aligned}
 \phi(1) &= e^{-(H_0+H_1)} = e^{-H_0} + (-1) \int_0^1 dt_1 e^{-(1-t_1)H_0} H_1 e^{-t_1 H_0} \\
 &+ (-1)^2 \int_0^1 t_1 dt_1 \int_0^1 dt_2 e^{-(1-t_1)H_0} H_1 e^{-t_1(1-t_2)H_0} H_1 e^{-t_1 t_2 H_0} \\
 &+ \dots + (-1)^n \int_0^1 t_1^{n-1} dt_1 \int_0^1 t_2^{n-2} dt_2 \dots \\
 &\int_0^1 dt_n e^{-(1-t_1)H_0} H_1 e^{-t_1(1-t_2)H_0} H_1 \\
 &\dots H_1 e^{-t_1 t_2 \dots t_{n-1}(1-t_n)H_0} H_1 e^{-t_1 t_2 \dots t_n H_0} \\
 &+ \dots
 \end{aligned} \tag{25}$$

If one is faced with the problem of taking the trace or the average value of $\phi(1)$, a further simplification can be made by virtue of the fundamental property of a trace, viz.,

$$\text{Tr}(AB \dots YZ) + \text{Tr}(ZAB \dots Y) = \text{Tr}(B \dots YZA), \text{ etc.} \tag{26}$$

Using Eq. (26) one may easily verify the following equation

$$\text{Tr} \left[e^{-(H_0+H_1)t} \right] - \text{Tr} \left[e^{-H_0 t} \right] = -t \int_0^1 d\alpha \text{Tr} \left[H_1 e^{-(H_0+\alpha H_1)t} \right] \tag{27}$$

Substituting the series of Eq. (25) for $e^{-(H_0+H_1)\alpha}t$.

we find

$$\begin{aligned} \text{Tr} \left[e^{-(H_0+H_1)} \right] &= \text{Tr} \left[e^{-H_0} \right] + (-1) \text{Tr} \left[H_1 e^{-H_0} \right] \\ &+ \frac{(-1)^2}{2} \int_0^1 dt_1 \text{Tr} \left[H_1 e^{-(1-t_1)H_0} H_1 e^{-t_1 H_0} \right] \\ &+ \dots + \frac{(-1)^{n+1}}{n+1} \int_0^1 t_1^{n-1} dt_1 \int_0^1 t_2^{n-2} dt_2 \\ &\dots \int_0^1 dt_n \text{Tr} \left[H_1 e^{-(1-t_1)H_0} H_1 e^{-t_1(1-t_2)H_0} \right. \\ &\left. \dots H_1 e^{-t_1 t_2 \dots t_n H_0} \right] + \dots \end{aligned} \quad (28)$$

Later on, the above result will be set in the framework of second quantization, and the reduced partition function of polyatomic system can be put into an expression which consists of contributions from the harmonic terms, Morse potential correction terms, and interaction terms due to off-diagonal cubic coefficients.

b. Occupation Number Formalism for Harmonic Oscillators

The Hamiltonian operator for a harmonic oscillator is¹⁰

$$\hat{H} = \frac{1}{2m} (\hat{p}^2 + m^2 \hat{q}^2), \quad (29)$$

with $\hat{p}$ and $\hat{q}$ as the momentum and coordinate operators

obeying the commutator rule.

$$[\hat{p}, \hat{q}]_- = -i\hbar \quad (30)$$

where

$$\hat{p} = i \left(\frac{m\hbar\omega}{2} \right)^{1/2} (a^\dagger - a) \quad (31a)$$

and

$$\hat{q} = \left(\frac{\hbar}{2m\omega} \right)^{1/2} (a^\dagger + a) . \quad (31b)$$

With the introduction of the creation and destruction operators $a^\dagger$ and a , the Hamiltonian operator becomes

$$\hat{H} = \hbar\omega (a^\dagger a + 1/2) \quad (32)$$

The $a^\dagger$, a are boson creation and destruction operators fulfilling the commutation relations

$$[a_i, a_j^\dagger]_- = \delta_{ij} . \quad (33)$$

For a multidimensional harmonic oscillator, the Hamiltonian H is

$$\hat{H} = \sum_{i=1}^n \hat{H}_i . \quad (34)$$

with

$$\hat{H}_i = \frac{1}{2m} (\hat{p}_i^2 + m\omega^2 \hat{q}_i^2) \quad (35)$$

Although, as Pauli has observed, all results derived from the occupation number formalism can also be obtained by the wave mechanical calculation, the advantage of the occupation number formalism lies in the simplicity of the algebraic manipulation of the destruction and creation operators. In a later section we will see the unfolding of the occupation number formalism in the framework of Schwinger's perturbation theory.

CHAPTER III

APPROXIMATIONS FOR PARTITION FUNCTIONS
OF DIATOMIC SYSTEMS

A. APPROXIMATION FOR CLASSICAL PARTITION FUNCTIONS

a. Classical Partition Function of Oscillator
in Finite Harmonic Well

The Hamiltonian of a harmonic oscillator in an infinitely deep harmonic well is given by

$$H = \frac{p_{\xi}^2}{2\mu} + \frac{1}{2} a\xi^2 \quad (36)$$

where ξ is the displacement coordinate, μ the reduced mass and a the force constant. As for the classical partition function Q_{cl}^{harm} , we have

$$\begin{aligned} Q_{cl}^{harm} &= \frac{1}{h} \int_{-\infty}^{\infty} dp_{\xi} \int_{-\infty}^{\infty} e^{-H/kT} d\xi \\ &= \frac{1}{h} \int_{-\infty}^{\infty} e^{-\frac{a\xi^2}{2kT}} d\xi \int_{-\infty}^{\infty} e^{-\frac{p_{\xi}^2}{2\mu kT}} dp_{\xi} \\ &= \frac{1}{h} \sqrt{\frac{2\pi kT}{a}} \sqrt{2\pi\mu kT} \\ &= \frac{2\pi kT}{h} \frac{1}{2\pi\nu_e} = \frac{kT}{h\nu_e} = \frac{1}{u_e} \end{aligned}$$

with

$$v_e = \frac{1}{2\pi} \sqrt{\frac{a}{\mu}} .$$

One is interested in developing a formula for the finite harmonic oscillator because it may exhibit features that are characteristic of a bound oscillator system. For an oscillator in a harmonic well of a finite depth, we have,

$$Q_{cl} = \frac{2}{h} \int_{-\sqrt{\frac{2D}{a}}}^{\sqrt{\frac{2D}{a}}} d\xi e^{-\frac{1}{2} \frac{a\xi^2}{kT}} \int_0^{\sqrt{2\mu(D - \frac{a\xi^2}{2})}} \frac{p^2}{e^{\frac{p^2}{2\mu kT}}} dp . \quad (38)$$

By setting

$$\frac{p^2}{2\mu kT} \equiv y^2 , \quad \frac{a\xi^2}{2kT} \equiv x^2 \quad (39)$$

we obtain

$$Q_{cl} = \frac{1}{u_e} \frac{2}{\pi} \int_{-\sqrt{\frac{D}{kT}}}^{\sqrt{\frac{D}{kT}}} e^{-x^2} dx \int_0^{\sqrt{\frac{D}{kT}(1 - \frac{a\xi^2}{2D})}} e^{-y^2} dy . \quad (40)$$

Integrating by parts (IBP), it can be shown that

$$\int_0^x e^{-t^2} dt = e^{-x^2} \left[x + \frac{2}{3} x^3 + \frac{2}{3} \frac{2}{5} x^5 + \dots \right. \\ \left. \left(\frac{2}{3} \frac{2}{5} \dots \frac{2}{2n-1} \right) x^{2n-1} \right] + E_n(x) \quad (41)$$

where

$$E_n(x) = \left[\frac{2}{1} \frac{2}{3} \frac{2}{5} \dots \frac{2}{2n-1} \right] \int_0^x e^{-t^2} t^{2n} dt. \quad (42)$$

It can easily be verified from Eq.(42) that the infinite series obtained above converges for all x .

An application of the series expansion, IBP, above to the harmonic oscillator problem of Eq.(40) leads to a very simple and exact result, which is the following closed form:

$$Q_{cl} = \frac{1}{u_e} (1 - e^{-\rho^2}) \quad (43)$$

where $\rho^2 = \frac{D}{kT}$.

The Q_{cl} of Eq.(43) tends to $\frac{1}{u_e}$ as $\rho \rightarrow \infty$, as expected. What we need is a modification of Eq.(41), or its equivalent, which would account for the anharmonicity. Since the finite harmonic oscillator is the simplest of its kind, the next bound oscillator to look into is the Morse oscillator.

b. Approximation for the Vibrational Classical Partition Function of the Morse Oscillator

For a small x value, Eq. (41) converges well, but in general x is not small and most of the results based on an expansion like Eq. (41) will not yield satisfactory results for real diatomic molecules. Further investigation leads to another expansion of the error function:¹¹

$$\begin{aligned} \operatorname{erf} x = 1 - \frac{e^{-x^2}}{\sqrt{\pi}} & \left(\frac{1}{x} - \frac{1}{2} \frac{1}{x^3} + \frac{1}{2} \frac{3}{2} \frac{1}{x^5} - \dots \right. \\ & \left. + (-1)^n \left(\frac{1}{2} \frac{3}{2} \dots \frac{2n-1}{2} \right) \frac{1}{x^{2n+1}} \right) + E_n(x) , \quad (44) \end{aligned}$$

where

$$E_n(x) = (-1)^n \left(\frac{2}{\sqrt{\pi}} \right) \left(\frac{1}{2} \frac{3}{2} \dots \frac{2^{n+1}}{2} \right) \int_x^\infty e^{-t^2} \frac{dt}{t^{2n+2}} , \quad (45)$$

and values of $E_n(x)$ have been tabulated in Table 1.

Difficulties arise in using Eq. (44) for the inner integral of Eq. (12) in the following manner. The outer integral of Eq. (12) obtained by substituting Eq. (44) for $\operatorname{erf} y_2$ in it is found to be unbound at both limits of integration, i.e., at $z = -\rho \ln 2$ and $z = \infty$. Schematically the exact integrand of the outer integral of Eq. (12) looks like Figure 1. It is seen that the value of the integrand is very small near the limits of the integral. It is

Table 1 : Remainder $E_n(x)$ for Eqn.(45)

	<u>x=1</u>	<u>x=2</u>	<u>x=3</u>	<u>x=4</u>	<u>x=5</u>
<u>n=1</u>	1.411×10^{-1}	2.204×10^{-3}	1.935×10^{-4}	3.444×10^{-5}	9.027×10^{-5}
<u>n=2</u>	2.645×10^{-1}	1.033×10^{-3}	4.031×10^{-5}	4.035×10^{-6}	6.770×10^{-7}
<u>n=3</u>	7.405×10^{-1}	7.231×10^{-4}	1.254×10^{-5}	7.062×10^{-7}	7.583×10^{-8}
<u>n=4</u>	2.777×10^0	6.780×10^{-4}	5.225×10^{-5}	1.655×10^{-7}	1.137×10^{-8}
<u>n=5</u>	1.309×10^1	7.990×10^{-4}	2.737×10^{-6}	4.877×10^{-8}	7.238×10^{-9}

feasible to conduct a study of chopping off both extremities of the range of the integral. The more one moves away from the end points, the more one reduces the error of integration due to the singularity. However, the more one moves away from the true limits of the integral, the more error one acquires due to the increase in the neglected area. There must be an optimum set of points z_1 and z_2 to be used in place of $-\rho \ln 2$ and ∞ , respectively.

One chooses to let z_1 and z_2 depend on each other as follows: choose a value for the ratio, R , of the level of y_2 called $y_{2,\min}$ and the maximum possible value of y_2 , which is ρ ;

$$R \equiv \frac{y_{2,\min}}{\rho} \quad (46)$$

Referring to Figure 1B, one obtains z_1 and z_2 as two real solutions of

$$R = \sqrt{1 - (1 - e^{-z/\rho})^2} \quad (47)$$

They are:

$$\begin{aligned} z_1 &= -\rho \ln \left(2 - \frac{R^2}{2} \right) \\ z_2 &= \rho \ln \left(\frac{2}{R^2} \right) \end{aligned} \quad (48)$$

As can be seen in Figure 2, the log-off error is negligible even at as large a value of R as 0.3 when ρ is 2 or larger. This plot has been obtained by approximating the integrand of Eq. (12) by using Eq. (41) for $\text{erf } y_2$ in the log-off regions of the integral.

Substituting Eq. (44) into Eq. (12), one obtains

$$\gamma_{c1} = \gamma_{c1}^0 - \Delta_1 \gamma_{c1} + \Delta_2 \gamma_{c1} - \dots, \quad (49)$$

where

$$\gamma_{c1}^0 = \frac{1}{\sqrt{\pi}} \int_{-\rho \ln 2}^{\infty} e^{-\rho^2 (1-e^{-z/\rho})^2} dz, \quad (50)$$

$$\Delta_1 \gamma_{c1} = \frac{1}{\pi} \int_{-\rho \ln 2}^{\infty} \frac{e^{-y_2^2} \exp[-\rho^2 (1-e^{-z/\rho})^2]}{y_2} dy_2 \quad (51)$$

and

$$\Delta_2 \gamma_{c1} = \frac{1}{2\pi} \int_{-\rho \ln 2}^{\infty} \frac{e^{-y_2^2} \exp[-\rho^2 (1-e^{-z/\rho})^2]}{y_2^3} dy_2 \quad (52)$$

It has been found that γ_{c1}^0 is the dominant term. A transformation of Eq. (50) leads to

$$\gamma_{c1}^0 = \frac{\rho}{\sqrt{\pi}} \int_{y_1}^{y_2} \frac{e^{-\rho^2 y^2} dy}{1-y^2}, \quad (53)$$

Integrand of Outer Integral
of Classical Partition Function

FIGURE 1A

FIGURE 1B

FIGURE 2 LOP-OFF ERROR

where

$$y \equiv e^{-z/\rho} - 1 \quad (54)$$

The Taylor expansion of $1/(1-y^2)$ in Eq. (53) further leads to

$$\gamma_{cl_0}^0(m) = 1 + \gamma_{cl_0}^0(m) + \frac{2\rho}{\sqrt{\pi}} \sum_{k=1}^m \Delta f_k \quad (55)$$

where

$$\gamma_{cl_0}^0(m) = \sum_{k=1}^m R_k(\rho) = \sum_{k=1}^m \frac{1}{2^{k-1} (2\rho^2)^k} \frac{(2k-1)!}{(k-1)!} \quad (56)$$

$$\begin{aligned} \Delta f_k &= \frac{-e^{-\rho^2 x^2}}{2\rho^2} \frac{(2k-1)!}{(k-1)!} \sum_{j=1}^k \frac{(j-1)!}{(2j-1)!} \frac{x^{2j-1}}{(4\rho^2)^{k-j}} \\ &+ \frac{2(2k-1)!}{(4\rho^2)^k (k-1)!} \Delta f_0 \quad (57) \end{aligned}$$

in which

$$\Delta f_0 = - \int_x^\infty e^{-\rho^2 y^2} dy \quad (58)$$

and

$$x = 1 - \frac{R^2}{2} \quad (59)$$

In Figure 3 I compare various approximations represented by Eq. (55) with the exact value of γ_{cl} obtained from Ref. (1). In this Figure,

$$cl_0^0(1) = 1 + \gamma_{cl_0^0}(1) = 1 + \frac{1}{2\rho^2} \quad (60)$$

and the curves labelled as $cl^0(1)$, $cl^0(2)$, $cl^0(3)$ are given by Eq. (55), including the terms of Δf_k , with $m = 1, 2$, and 3 , respectively. Figure 4 is a plot of relative errors obtained by

$$\gamma_{cl^0}(m) = 1 + \gamma_{cl_0^0}(m) \quad (61)$$

Figure 5 is a similar plot obtained by including terms of Δf_k as well. The $cl^0(3)$ approximation, or Eq. (55) with $m = 3$, seems to give a generally satisfactory approximation. The apparently strange behavior of the $cl^0(4)$ approximation is a consequence of the log-off procedure forced in obtaining Eq. (53).

Figure 6 shows the effects of inclusion of higher terms of Eq. (49). These higher terms come from the higher order terms of small anharmonicity approximation for the error function, Eq. (44). The behavior of these plots are

FIGURE 4 $\gamma_{Cl_0^0}$ -APPROXIMATION WITH $R=0.3$

FIGURE 5 $\gamma_{cl}^0(m)$ -APPROXIMATION WITH $R=0.3$

FIGURE 6 APPROXIMATION BY $\gamma_{Cl^0(m)} + \sum_n \Delta_n \gamma_{Cl}$

the results of the divergent nature of the series of Eq. (44).

B. APPROXIMATION FOR THE QUANTUM MECHANICAL VIBRATIONAL PARTITION FUNCTION OF THE MORSE-OSCILLATOR

For a Morse oscillator, the quantum mechanical partition function is exactly expressed as

$$Q_{qm} = S \exp \left[-\frac{ue}{2} + \frac{ux}{4} \right] \quad (62)$$

as it has been shown by Eqs. (13)-(16).

The best approximation obtained for S is by extending the upper limit of summation of Eq. (14) from the finite value V_D to ∞ and by grouping of exponents as $e^{-uv} e^{uxv^2}$ rather than as $e^{-ue^v} e^{ux(v+v^2)}$. The orthogonal polynomial expansion method has been tried besides the usual series type of expansion, but no improvement has been found.

Let $b = ux$. Then,

$$S = \frac{1}{1-e^{-u}} \left[1 + \frac{2b}{(e^u-1)^2} + \frac{b^2}{2} \left[\frac{e^{-u}}{(1-e^{-u})} + \frac{2e^{-2u}}{(1-e^{-u})^2} \right] \right] \quad (63)$$

The anharmonicity correction factor for the quantum mechanical partition function γ_{qm} is

$$\gamma_{qm} = \frac{Q_{qm}}{Q_{qm}^0} = S e^{\frac{ux}{4}} \left[1 - e^{-u} \right] \quad (64)$$

In Figures 7 and 8 we compare γ_{qm} calculated by using Eqs. (63) and (64), which are denoted by $\gamma_{qm}(3)$ with $\gamma_{qm}^*(3)$ calculated by using Eqs. (64) and (65), which are denoted by $\gamma_{qm}^*(3)$:

$$S = \frac{1}{1 - e^{-u_e}} + b \frac{e^{-u_e}}{(1 - e^{-u_e})^2} + (b + \frac{b^2}{2}) \left(\frac{e^{-u_e}}{(1 - e^{-u_e})^2} + \frac{2e^{-2u_e}}{(1 - e^{-u_e})^3} \right) \quad (65)$$

Figure 7 is for $x = 0.02$, and Figure 8 is for $x = 0.05$. It should be recalled¹ that γ_{qm} depends on the frequency and anharmonicity constant x individually, whereas the classical anharmonicity depends only on the ratio of frequency and anharmonicity constant, i.e., ρ .

C. THE REDUCED PARTITION FUNCTION FOR A NON-ROTATING DIATOMIC OSCILLATOR IN THE MORSE POTENTIAL

The reduced partition function ratio for a pair of isotopic molecules, $\frac{S}{S'}$, is a ratio of Q_{qm}/Q_{cl} of the heavier molecule to Q'_{qm}/Q'_{cl} of the lighter one. Using the $\gamma_{cl}^{(3)}$ approximation for Q_{cl} and Q'_{cl} and Eqs. (63) and (64) for Q_{qm} and Q'_{qm} , I obtain, for the Morse oscillator,

$$\ln \frac{S}{S'} = \sum_i \ln \frac{u_i e^{-u_i/2} (1 - e^{-u_i})}{u_i' e^{-u_i'/2} (1 - e^{-u_i'})}$$

$$+ \sum_i \ln \frac{e^{u_i \chi_i / 4} (1 - e^{-u_i}) (1 - e^{-u_i'}) (1 + 1/2 \rho'^2) A(u_i)}{e^{u_i' \chi_i' / 4} (1 - e^{-u_i'}) (1 - e^{-u_i}) (1 + 1/2 \rho^2) A(u_i')} \quad (66)$$

where $b = u\chi$ and

$$A(u) = 1 + \frac{2b}{(e^u - 1)^2} + \frac{b^2}{2} \left[\frac{e^{-u} + e^{-2u}}{(1 - e^{-u})^2} \right]. \quad (67)$$

The harmonic terms have been studied extensively by Bigeleisen and Ishida^{12,13,14}. Here our interest is to examine the anharmonic terms. For a small anharmonicity, $b \ll u$,

$$\begin{aligned} \ln \frac{S}{S'} f &= (\ln \frac{S}{S'} f)_{\text{harmonic}} \\ &+ \sum_i \left[\frac{1}{4} (b_i - b_i') + \left(\frac{2b_i}{(e^{u_i} - 1)} - \frac{2b_i'}{(e^{u_i'} - 1)} \right) \right. \\ &\quad \left. + \left(\frac{2b_i}{(e^{u_i} - e)^2} - \frac{2b_i'}{(e^{u_i'} - 1)^2} \right) + \left(\frac{1}{2\rho'^2} - \frac{1}{2\rho^2} \right) \right] \quad (68) \end{aligned}$$

The terms under the summation sign in Eq. (68) represent contributions of anharmonicity. Its first term, $\sum \frac{1}{4} (b_i - b_i')$, is the commonly used anharmonicity correction

on the zero point energy. The terms inside the bracket after $\sum_i$ in Eq.(68) have been used to account for the anharmonicity in each oscillator of the 2-D and 3-D problems in later chapters.

CHAPTER IV
APPROXIMATIONS FOR THE PARTITION FUNCTIONS
OF POLYATOMIC SYSTEMS

As stated earlier, the purpose of this research has been to develop a good approximation method in accounting for anharmonicity in calculations of the molecular vibrational partition functions. The simplest problem, i.e., that of the diatomic molecule with one degree of freedom, has been presented in the preceding chapter. When one attempts to apply an approximation method to a polyatomic molecule, the major problem is in evaluating the exact partition functions, either classical or quantum-mechanical, and in accounting for the off-diagonal terms in the Hamiltonian.

A. MODEL 2-D SYSTEM

Due to the complexity of the general polyatomic problem involved, I first worked with a model 2-D system with two degrees of freedom which simulates the two stretching modes of carbon dioxide and its associated isotopes.

a.i. Exact Solution for the Classical Partition
Function of a Model System with Two Degrees
of Freedom

The classical partition function Q_{cl}^{anh} of the bound

state of the model 2-D anharmonic oscillator in the potential given by

$$U(z_1, z_2) = kT \left[\rho_1 (1 - e^{-z_1/\rho_1})^2 + \rho_2 (1 - e^{-z_2/\rho_2})^2 + \gamma_{112} z_1^2 z_2 + \gamma_{122} z_1 z_2^2 \right] \quad (68)$$

is evaluated by using the following equation:

$$Q_{cl}^{anh} = \frac{1}{u_{e_1}} \frac{1}{u_{e_2}} \left(\frac{2}{\pi} \right)^2 \int_{-\rho_1 \ln 2}^{\infty} e^{-\rho_1^2 (1 - e^{-z_1/\rho_1})^2} \int_0^{\rho_1 \sqrt{2e^{-z_1/\rho_1} - e^{-2z_1/\rho_1}}} e^{-y_1^2} x \int_{-\rho_2 \ln 2}^{L_2(z_1)} e^{-\rho_2^2 (1 - e^{-z_2/\rho_2})^2} - \gamma_{112} z_1^2 z_2 - \gamma_{122} z_1 z_2^2 \int_0^{y_2+} dy_2 dz_2 dy_1 dz_1 \quad (69)$$

where ρ , z , y are defined analogous to those in the 1-D Morse oscillator problem and $\gamma_{112} = \frac{1}{2\sqrt{2}} \frac{1}{\alpha_1^2 \alpha_2 kT} \frac{1}{\rho_2 \rho_1^2} f_{112}$,

etc. One finds y_{2+} , the upper limit of the variable y_2 , appearing in Eq. (69) as

$$y_{2+} = \sqrt{\rho_2^2 (1 - (1 - e^{-z_2/\rho_2})^2 - \gamma_{122} z_1 z_2^2 - \gamma_{133} z_1 z_3^2)} \quad (70)$$

Care is taken in the calculations of the upper limits of z_1 , $L_2(z_1)$, to avoid inclusion of contributions from the unstable states corresponding to the repulsive forces that fictitiously arise from the truncation of the polynomial potential function. If the anharmonic term of the highest order of polynomial with respect to z_2 is positive, then $L_2(z_1) \rightarrow \infty$.

a.ii. Exact Solution for the Quantum Partition Function of a Model System with Two Degrees of Freedom

The quantum mechanical partition function is exactly expressed as

$$Q_{qm}^{anh} = \sum_{n_2=0}^{V_{D_2}} \sum_{n_1=0}^{V_{D_1}} e^{-\epsilon(1,2)/kT} \quad (71)$$

where

$$\begin{aligned} G(v_1, v_2) &= \frac{\epsilon(1,2)}{hc} = \omega_{e_1} (n_1 + \frac{1}{2}) + \omega_{e_2} (n_2 + \frac{1}{2}) \\ &\quad - \omega_{e_1} \chi_{e_1} (n_1 + \frac{1}{2})^2 + - \omega_{e_2} \chi_{e_2} (n_2 + \frac{1}{2})^2 \\ &\quad + \chi_{12} (n_1 + \frac{1}{2}) (n_2 + \frac{1}{2}) \end{aligned} \quad (72)$$

One observes that there are two upper limits, V_{D1} and V_{D2} , to be solved for. First I chose to define n_2 as the outer loop and n_1 as the inner loop. To obtain the value V_D for the inner loop, set

$$\frac{\partial G(V_1, V_2)}{\partial V_1} = 0 \quad (73)$$

and we obtain

$$V_{1D} = \frac{\omega_{e1} - \omega_{e1} \chi_{e1} + \chi_{12}(n_2 + \frac{1}{2})}{2\chi_{e1}\omega_{e1}} \quad (74)$$

For the outer loop, solving

$$\frac{\partial G(V_1=0, V_2)}{\partial V_2} = 0 \quad (75)$$

will yield V_{D2} for V_2 as

$$V_{D2} = \frac{\omega_{e2} - \chi_{e2}\omega_{e2}}{2\chi_{e2}\omega_{e2}} \quad (76)$$

Once Q_{cl}^{anh} and Q_{qm}^{anh} have been set up, the exact value of the logarithm of the reduced partition function can be calculated.

b. Approximations for the Partition Functions of the Polyatomic System

In this section I describe an approximation method I developed to account for the off-diagonal terms in the potential energy surface of a polyatomic molecule. Schwinger's perturbation theory is utilized to evaluate the vibrational partition functions. The basis coordinate system chosen was the normal coordinates of the given molecule. The Hamiltonian is, thus,

$$H = \frac{1}{2} \sum_i \lambda_{ii} Q_i^2 + \frac{1}{2} \sum_i \dot{Q}_i^2 + \sum_{ijk} f_{ijk} Q_i Q_j Q_k, \quad (77)$$

with the unperturbed Hamiltonian operator

$$H_0 = \frac{1}{2} \sum_i \lambda_{ii} Q_i^2 + \frac{1}{2} \sum_i \dot{Q}_i^2 + \sum_i f_{iii} Q_i^3 \quad (78)$$

and the perturbation

$$H_1 = \sum_{i \neq j \neq k} f_{ijk} Q_i Q_j Q_k + \sum_{i \neq j} f_{iij} Q_i Q_i Q_j \quad (79)$$

where the Q 's are normal coordinates. Analytical expression for the perturbation terms of the vibrational partition functions are obtained up to the second order.

In Schwinger's perturbation method for partition functions, the Hamiltonian operator H is divided into an

unperturbed H_0 and a perturbation H_1 . The diagonal density matrix is taken with respect to the eigenfunctions of H_0 . This perturbation method was developed by Schwinger^{8,9} to solve problems involving partition functions and exponential expressions in field theory.

From the development of the Schwinger perturbation theory, the final formula for the partition function is

$$\begin{aligned}
 Q &= \text{Tr} e^{-\beta(H_0+H_1)} = Q_0 + Q_1 + Q_2 + \dots + Q_{n+1} + \dots \\
 &= \text{Tr} e^{-\beta H_0} - \text{Tr} H_1 e^{-\beta H_0} \\
 &+ \frac{\beta^2}{2} \text{Tr} \int_0^1 dt_1 H_1 e^{-\beta H_0(1-t_1)} H_1 e^{-\beta H_0 t_1} + \dots \\
 &+ \frac{(-1)^{n+1}}{n+1} \beta^{n+1} \text{Tr} \int_0^1 t_1^{n-1} dt_1 \int_0^1 t_2^{n-2} dt_2 \dots \\
 &\int_0^1 dt_n \left[H_1 e^{-\beta H_0(1-t_1)} H_1 e^{-\beta H_0 t_1(1-t_2)} \right. \\
 &\left. H_1 e^{-\beta H_0 t_1 t_2(1-t_3)} \dots H_1 e^{-\beta H_0 t_1 t_2 \dots t_n} \right] + \dots
 \end{aligned} \tag{80}$$

The first term in the perturbation formula is just the partition function for the unperturbed Hamiltonian--the zeroeth order harmonic approximation. Successive terms contain higher powers of the perturbation H_1 . Employing the second quantization method with the raising and lowering

operators $a^\dagger$ and a which obey the commutation rules,

$$[a_i, a_i^\dagger] = \delta_{ij}$$

and

$$[a_i, a_j] = [a_i^\dagger, a_j^\dagger] = 0 \quad (81)$$

we can express¹⁵

$$\begin{aligned} Q_i &= \left(\frac{\hbar}{2\omega_i} \right)^{1/2} (a_i + a_i^\dagger) \\ P_i &= i \left(\frac{\hbar\omega_i}{2} \right)^{1/2} (a_i^\dagger - a_i) \end{aligned} \quad (82)$$

In terms of these operators, one obtains, after casting the conjugated momenta and coordinates in a form suitable for second quantization method,^{16,17}

$$H_0 = \frac{\hbar}{2} \sum \lambda_i^{1/2} \left[\left(\frac{P_i}{\hbar} \right)^2 + Q_i^2 \right] + \hbar c \sum_i f_{iii} Q_i^3, \quad (83a)$$

$$H_1 = \hbar c \sum_i \sum_j f_{ijj} Q_i Q_j^2 + \hbar c \sum_i \sum_j \sum_k f_{ijk} Q_i Q_j Q_k, \quad (83b)$$

where

$$p_i = \frac{i\hbar}{2} \sqrt{2} (a_i^\dagger - a_i), \quad (84a)$$

and

$$q_i = \frac{1}{2} \sqrt{2} (a_i^\dagger + a_i) . \quad (84b)$$

Now

$$\begin{aligned} Q_0 &= \text{Tr} e^{-\beta H_0} = \sum_{n_1, n_2, \dots} \langle | e^{-\beta E_{n_1, n_2, \dots}} | \rangle \\ &= \sum_{n_i} e^{-\beta \hbar E_{n_i}^{\text{anh}}} , \end{aligned} \quad (85)$$

where

$$\begin{aligned} E_{n_i}^{\text{anh}} &= \omega_{e_i} (n_i + \frac{1}{2}) + \omega_{e_i} \chi_{e_i} (n_i + \frac{1}{2})^2 , \\ | \rangle &= | n_1 n_2 \dots \rangle , \end{aligned} \quad (86)$$

and for this zeroeth order partition function, eigenfunctions for the Morse oscillator have been utilized.

The previous results that I obtained for the diatomic molecules employ the internal valence coordinates. However, since the internal coordinate and the normal coordinate are identical for diatomic molecules, all the equations derived for the one-dimensional case can be said to be in terms of the normal coordinate. If the normal coordinates for polyatomic molecules were uncoupled under the anharmonic forces,

then the partition functions of such polyatomic molecules would have been expressible simply as the products of the diatomic functions. Thus, we make use of Schwinger's perturbation method in the following way. The unperturbed problem consists of an assembly of independent Morse-type potential,

$$U_i = D_i (1 - e^{-\alpha_i Q_i})^2 \quad (87)$$

where Q_i is the i -th normal coordinate. For each such oscillator, the mass is unity, and the force constant is λ_i , the i -th eigenvalue of the corresponding harmonic oscillator problem. The perturbation is represented by the cubic off-diagonal terms, $f_{ijj}Q_iQ_jQ_j$ and $f_{ijk}Q_iQ_jQ_k$.

The association of the energy levels of H_0 to that of the Morse potential is based on the assumption that for small anharmonicity,

$$\begin{aligned} U_i &= D_i (1 - e^{-\alpha_i Q_i})^2 \\ &\approx D_i \alpha_i^2 Q_i^2 - D_i \alpha_i^3 Q_i^3 \\ &= \frac{1}{2} \lambda_{ii} Q_i^2 + \frac{1}{2} f_{iii} Q_i^3. \end{aligned} \quad (88)$$

The relationship between the Morse potential parameter D_i, α_i and quadratic and cubic coefficients λ_{ii} and f_{iii} will

enable one to calculate ω_{ei} and χ_{ei} in terms of known λ_{ii} and f_{iii} . Physically this represents the picture in which the eigenfunctions of the unperturbed Hamiltonian are products of uncoupled Morse-type oscillators, corresponding to the various frequencies ω_{ei} and not to complicate the situation any further, $|n\rangle$ is taken to be the same as in the harmonic case.

Q_1 and Q_2 terms in Eq. (80) are evaluated as follows.

$$Q_1 = -\beta \text{Tr} \left[H_1 e^{-\beta H_0} \right] = 0 \quad (89)$$

$$\begin{aligned}
 Q_2 = \frac{1}{2} \beta^2 \text{Tr} & \left[\sum_{i \neq j} \int_0^1 dt F_{ij}^2 [a_i a_i (a_j + a_j^\dagger) \right. \\
 & + a_i^\dagger a_i^\dagger (a_j + a_j^\dagger) + 2a_i^\dagger a_i (a_j + a_j^\dagger) + (a_j + a_j^\dagger)] \\
 & e^{-\beta H_0} [a_i a_i e^{-2\beta \omega_{ei} \hbar t} (a_j e^{-\beta \hbar \omega_{ej} t} + a_j^\dagger e^{\beta \hbar \omega_{ej} t}) \\
 & + a_i^\dagger a_i^\dagger e^{2\beta \hbar \omega_{ei} t} (a_j e^{-\beta \hbar \omega_{ej} t} + a_j^\dagger e^{\beta \hbar \omega_{ej} t}) \\
 & + 2a_i^\dagger a_i (a_j e^{-\beta \hbar \omega_{ej} t} + a_j^\dagger e^{\beta \hbar \omega_{ej} t}) \\
 & \left. + (a_j e^{-\beta \hbar \omega_{ej} t} + a_j^\dagger e^{\beta \hbar \omega_{ej} t})] \right] \\
 & + \sum_{i \neq j \neq k} \int_0^1 dt F_{ijk}^2 [a_i a_j a_k + a_i a_j a_k^\dagger + a_i a_j^\dagger a_k \\
 & + a_i a_j^\dagger a_k^\dagger + a_i^\dagger a_j a_k + a_i^\dagger a_j a_k^\dagger + a_i^\dagger a_j^\dagger a_k + a_i^\dagger a_j^\dagger a_k^\dagger]
 \end{aligned}$$

$$\begin{aligned}
& e^{-\beta H_0} [a_i a_j a_k^\dagger e^{-\beta \hbar (\omega_{e_i} + \omega_{e_j} + \omega_{e_k}) t} \\
& + a_i a_j a_k^\dagger e^{-\beta \hbar (\omega_{e_i} + \omega_{e_j} - \omega_{e_k}) t} \\
& + a_i a_j^\dagger a_k e^{-\beta \hbar (\omega_{e_i} + \omega_{e_k} - \omega_{e_j}) t} \\
& + a_i a_j^\dagger a_k^\dagger e^{-\beta \hbar (\omega_{e_i} - \omega_{e_j} - \omega_{e_k}) t} \\
& + a_i^\dagger a_j a_k e^{-\beta \hbar (\omega_{e_j} + \omega_{e_k} - \omega_{e_i}) t} \\
& + a_i^\dagger a_j a_k^\dagger e^{-\beta \hbar (\omega_{e_j} - \omega_{e_k} - \omega_{e_i}) t} \\
& + a_i^\dagger a_j^\dagger a_k e^{-\beta \hbar (\omega_{e_k} - \omega_{e_i} - \omega_{e_j}) t} \\
& + a_i^\dagger a_j^\dagger a_k^\dagger e^{\beta \hbar (\omega_{e_k} + \omega_{e_i} + \omega_{e_j}) t}] \quad (90)
\end{aligned}$$

where

$$F_{ijk} = \left(\frac{1}{\sqrt{2}} \right)^3 f_{ijk}^{hc} ,$$

Q_2 can be simplified further. Details of the simplification will be given in Appendix D. The final result is

$$Q_2 = \frac{\beta^2}{2} \left(\sum_i^{3N-6} e^{-\beta \hbar \omega_i / 2} \right) \prod_l z_{0l} \sum_i \sum_j \sum_k \left(F_{ijk}^2 \right)$$

$$\left. \begin{aligned} & (U_{ijk} + U_{i-jk} + U_{ij-k} + U_{-ijk} + U_{i-j-k} + U_{-ijk} \\ & + U_{-i-jk} + U_{-i-j-k}) \end{aligned} \right\} \quad (91)$$

where

$$U_{ijk} = z_{1i} z_{1j} z_{1k} \frac{Y(i+j+k)-1}{\beta \hbar (\omega_{e_i} + \omega_{e_j} + \omega_{e_k})}, \quad (92a)$$

$$U_{i-jk} = z_{1i} (z_{1j} + z_{0j}) z_{1k} \frac{Y(i-j+k)-1}{\beta \hbar (\omega_{e_i} - \omega_{e_j} + \omega_{e_k})}, \quad (92b)$$

$$U_{i-j-k} = z_{1i} (z_{1j} + z_{0j}) (z_{1k} + z_{0k}) \frac{Y(i-j-k)-1}{\beta \hbar (\omega_{e_i} - \omega_{e_j} - \omega_{e_k})}, \quad (92c)$$

$$U_{-i-j-k} = (z_{0i} + z_{0i}) (z_{1k} + z_{0j}) (z_{1k} + z_{0k}) \frac{1 - Y^{-1}(i+j+k)}{\beta \hbar (\omega_{e_i} + \omega_{e_j} + \omega_{e_k})}. \quad (92d)$$

with

$$z_0 = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega_{e_n}} = e^{\frac{v}{e}} (e^{\frac{v}{e}} - 1)^{-1}, \quad (93a)$$

$$z_1 = \sum_{n=0}^{\infty} n e^{-\beta \hbar \omega_{e_n}} = e^{\frac{v}{e}} (e^{\frac{v}{e}} - 1)^{-2}, \quad (93b)$$

$$z_2 = \sum_{n=0}^{\infty} n^2 e^{-\beta \hbar \omega_{e_n}} = e^{\frac{v}{e}} (e^{\frac{v}{e}} + 1) (e^{\frac{v}{e}} - 1)^{-3}, \quad (93c)$$

$$Y(i \pm j \dots) = e^{\beta \hbar (\omega_{e_i} \pm \omega_{e_j} \pm \dots)}, \quad (94a)$$

$$Y^{-1}(i \pm j \pm \dots) = e^{-\beta \hbar (\omega_{e_i} \pm \omega_{e_j} \pm \dots)}, \quad (94b)$$

in which $v_e = \beta \hbar \omega_e$.

In Eq. (91) the product over ℓ is taken over 1 to $3N-6$, excluding i, j, k , and the summations are taken over each of i, j, k from 1 to $3N-6$, excluding the cases when $i=j=k$.

The preceding solution was applied to a model 2-D system with two degrees of freedom. In the expansion of $\frac{s}{s'} f = \frac{Qr}{Q'r'}$, the final expression of $\ln \frac{s}{s'} f$ for our model system is

$$\ln \frac{s}{s'} f = (\ln \frac{s}{s'} f)_{\text{harm}} + \sum_i^2 \ln A_i + (D-D') + (E'-E), \quad (95)$$

where

$$(\ln \frac{s}{s'} f)_{\text{harm}} = \ln \prod_{i=1}^2 \frac{v_{e_i} e^{-\frac{v_{e_i}}{2}} (1 - e^{-v_{e_i}'})}{v_{e_i}' e^{-\frac{v_{e_i}'}{2}} (1 - e^{-v_{e_i}})}, \quad (96)$$

and A_i is the same as in Eq. (66) with the proper identification of variables.

$$D = \frac{Q_2^{\text{quant}}}{\sum_{n_i} e^{-\beta E_{n_i}^{\text{anh}}}} \quad (97a)$$

$$E = \frac{Q_2^{\text{class}}}{\prod_{i=1}^2 \frac{1}{v_{e_i}} \prod_{i=1}^2 (1 + \frac{1}{2\rho_i^2})} \quad (97b)$$

and D' and E' are D and E of the lighter isotopic molecule.

In Eqs. (97a, 97b),

$$\begin{aligned} Q_2^{\text{quant}} = & \frac{\beta^2}{2} e^{-\frac{v_{e_1}}{2}} e^{-\frac{v_{e_2}}{2}} \left[F_{112}^2 ((z_{21} - z_{11})^2 - \right. \\ & z_{12} U(2v_{e_1} + v_{e_2})) + [(4z_{21} + 4z_{11} + z_{01}) z_{12} U(v_{e_2})] \\ & + [(z_{21} - z_{11})(z_{12} + z_{02}) U(2v_{e_1} - v_{e_2})] \\ & + [(z_{21} + 3z_{11} + 2z_{12})(z_{12} + z_{02}) U(-2v_{e_1} + v_{e_2})] \\ & + [(4z_{21} + 4z_{11} + z_{01})(z_{12} + z_{02}) U(-v_{e_1})] \\ & + [(z_{21} + 2z_{11} + z_{01})(z_{12} + z_{02}) U(-2v_{e_1} - v_{e_2})] \\ & \left. + F_{122}^2 ([\text{with } 1 \text{ \& } 2 \text{ interchanged}]) \right] , \quad (98) \end{aligned}$$

with

$$U(v_{e_i} + v_{e_i} - v_{e_j}) = \frac{e^{v_{e_i} + v_{e_i} - v_{e_j} - 1}}{v_{e_i} + v_{e_i} - v_{e_j}}, \quad (99a)$$

$$U(-v_{e_i}) = \frac{e^{-v_{e_i} - 1}}{-v_{e_i}}, \quad (99b)$$

$$Q_2^{\text{class}} = \frac{\beta^2}{2} \sum_{i,j=1}^2 24F_{ij}^2 \frac{1}{v_{e_i}^2 v_{e_j}^2}. \quad (100)$$

The expression of Eq. (100) for the classical vibrational partition function Q_2^{class} was obtained in the limit of $T \rightarrow \infty$ from Q_2^{quant} for the 2-D system.

c. Numerical Results for the Model System

Numerical results of the 2-D cases are first presented with a discussion following right after this section. Equation (94) is used to calculate the $\ln \frac{S}{S_T} f$ (anharm). Equation (95) is used to calculate $\ln \frac{S}{S_T} f$ (harm). To calculate $\ln \frac{S}{S_T} f$ (exact), the numerical integration method is employed for the classical partition function and numerical summation is used for the quantum partition function of the model system. The program for the actual calculation of the 2-D case is listed in the appendix.

Inputs for the program are the temperature, the symmetric stretching frequency ω_1 , the antisymmetric stretching

frequency ω_2 , anharmonicity constants χ_1, χ_2 . From Nielsen's result of the relationship between anharmonicity constants χ_i and cubic coefficients F_{ijk} , one can calculate F_{122}, F_{111} by knowing the values of F_{112}, F_{222} (which equal zero in this model case due to symmetry), χ_i , and ω_i .

In the following tables, first values of χ_1, χ_2 are tabulated. The values of the exact, harmonic, anharmonic $\ln \frac{s}{s'} f$ are presented in columns 3,4,5. Columns 6,7 yield the percent error of the harmonic $\ln \frac{s}{s'} f$ vs exact and that of the anharmonic $\ln \frac{s}{s'} f$ vs exact respectively. In columns 8,9,10, A stands for $\sum_{i=1}^2 \ln A_i$; E stands for $E'-E$; D stands for $D-D'$. The last two entries are the calculated values of $F_{122}, F_{122}', F_{111}$ and F_{111}' .

Table 2 . $\ln(s/s')$ for model 2-D system #1 at 100° K

T = 100.000 WE(1) = 500.00 WE(1) = 475.00 WE(2) = 600.00 WE(2) = 760.00

		LN(S/S')F			% ERROR								
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')		
0.002	0.002	0.364130	0.365352	0.364511	0.326	0.105	-0.000507	-0.000028	-0.000307	(-39.1, -41.1)	(-11.0, -11.5)		
	0.005	0.363064	0.365352	0.363571	0.620	0.140	-0.000765	-0.000068	-0.000747	(-61.8, -65.0)	(-11.0, -11.5)		
	0.010	0.361446	0.365352	0.362057	1.081	0.169	-0.001729	-0.000135	-0.001431	(-87.4, -92.0)	(-11.0, -11.5)		53
0.005	0.002	0.363533	0.365352	0.364213	0.500	0.187	-0.000888	-0.000027	-0.000304	(-39.1, -41.1)	(-17.3, -18.3)		
	0.005	0.362297	0.365352	0.363279	0.843	0.271	-0.001267	-0.000067	-0.000739	(-61.8, -65.0)	(-17.3, -18.3)		
	0.010	0.360487	0.365352	0.361772	1.350	0.356	-0.002031	-0.000138	-0.001416	(-87.4, -92.0)	(-17.3, -18.3)		
0.010	0.002	0.362699	0.365352	0.363718	0.731	0.281	-0.001309	-0.000027	-0.000298	(-39.1, -41.1)	(-24.5, -25.8)		
	0.005	0.361271	0.365352	0.362792	1.130	0.421	-0.001767	-0.000066	-0.000727	(-61.8, -65.0)	(-24.5, -25.8)		
	0.010	0.359295	0.365352	0.361298	1.700	0.572	-0.002531	-0.000131	-0.001392	(-87.4, -92.0)	(-24.5, -25.8)		

T IS IN ° K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS

Table 3. $\ln(s/s')$ for model 2-D system #2 at 100° K

$T = 100.000$ $WE(1) = 500.00$ $WE(1) = 475.00$ $WE(2) = 1600.00$ $WE(2) = 1520.00$

LN(S/S') F				% ERROR							
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')
0.002	0.002	0.651429	0.653102	0.651808	0.257	0.058	-0.000786	-0.000013	-0.000494	-54.1, -56.9	-11.0, -11.5
	0.005	0.649066	0.653102	0.650228	0.498	0.055	-0.001663	-0.000033	-0.001178	-85.5, -90.0	-11.0, -11.5
	0.010	0.647485	0.653102	0.647737	0.867	0.039	-0.003124	-0.000066	-0.002175	-120.9, -127.3	-11.0, -11.5
0.004	0.002	0.650720	0.653102	0.651512	0.366	0.122	-0.001887	-0.000013	-0.000489	-54.1, -56.9	-17.3, -18.3
	0.005	0.648922	0.653102	0.649940	0.444	0.157	-0.001964	-0.000033	-0.001166	-85.5, -90.0	-17.3, -18.3
	0.010	0.646274	0.653102	0.647459	1.027	0.183	-0.003426	-0.000065	-0.002152	-120.9, -127.3	-17.3, -18.3
0.010	0.002	0.649759	0.653102	0.651020	0.514	0.194	-0.001588	-0.000013	-0.000481	-54.1, -56.9	-24.5, -25.8
	0.005	0.647696	0.653102	0.649460	0.835	0.272	-0.002465	-0.000032	-0.001145	-85.5, -90.0	-24.5, -25.8
	0.010	0.644748	0.653102	0.646927	1.296	0.349	-0.003926	-0.000064	-0.002115	-120.9, -127.3	-24.5, -25.8

T IS IN O K; WE'S AND F'S IN CM-1; THE REST ARE DIMENSIONLESS

Table 4. $\ln(s/s')f$ for model 2-D system at 100° K #3

$T = 100.000$ $WE(1) = 500.00$ $WE(1) = 475.00$ $WE(12) = 2400.00$ $WE(12) = 2260.00$

$\ln(s/s')f$

% ERROR

X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	O	(F122,F122')	(F111,F111')
0.002	0.002	0.936751	0.940859	0.939143	0.225	0.042	-0.001071	-0.000009	-0.000637	(-66.0, -69.5)	(-11.0, -11.5)
	0.005	0.936679	0.940859	0.936982	0.446	0.032	-0.002375	-0.000022	-0.001481	(-104.4, -109.8)	(-11.0, -11.5)
	0.010	0.934993	0.940859	0.933639	0.789	0.016	-0.004548	-0.000044	-0.002628	(-147.6, -155.3)	(-11.0, -11.5)
0.004	0.002	0.937953	0.940859	0.938649	0.310	0.096	-0.001372	-0.000009	-0.000630	(-66.0, -69.5)	(-17.3, -18.3)
	0.005	0.935592	0.940859	0.936697	0.563	0.110	-0.002676	-0.000022	-0.001465	(-104.4, -109.8)	(-17.3, -18.3)
	0.010	0.932002	0.940859	0.933367	0.992	0.130	-0.004849	-0.000043	-0.002600	(-147.6, -155.3)	(-17.3, -18.3)
0.010	0.002	0.937199	0.940859	0.938359	0.390	0.124	-0.001872	-0.000009	-0.000619	(-66.0, -69.5)	(-24.5, -25.8)
	0.005	0.934206	0.940859	0.936223	0.712	0.216	-0.003176	-0.000021	-0.001439	(-104.4, -109.8)	(-24.5, -25.8)
	0.010	0.930331	0.940859	0.932914	1.132	0.278	-0.005350	-0.000042	-0.002553	(-147.6, -155.3)	(-24.5, -25.8)

T IS IN ° K, WE'S AND F'S (IN CM-1). THE REST ARE DIMENSIONLESS

Table 5. $\ln(s/s')$ for model 2-D system #4 at 1000 K

$T = 100.000$ $WE(11) = 500.00$ $WE(11) = 475.00$ $WE(12) = 3200.00$ $WE(12) = 3140.00$

LNIS/S*IF			% ERROR							
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122*) (F111,F111*)
0.002	0.002	0.540094	0.541588	0.540638	0.277	0.101	-0.000634	-0.000002	-0.000314	(-77.4, -80.1)(-11.0, -11.5)
	0.005	0.538777	0.541588	0.539981	0.522	0.149	-0.001284	-0.000006	-0.000717	(-122.3, -126.7)(-11.0, -11.5)
	0.010	0.536796	0.541588	0.537971	0.893	0.219	-0.002368	-0.000012	-0.001238	(-173.0, -179.2)(-11.0, -11.5)
0.005	0.002	0.539246	0.541588	0.540342	0.474	0.203	-0.000936	-0.000002	-0.000300	(-77.4, -80.1)(-17.3, -18.3)
	0.005	0.537853	0.541588	0.539293	0.894	0.268	-0.001586	-0.000006	-0.000709	(-122.3, -126.7)(-17.3, -18.3)
	0.010	0.535616	0.541588	0.537694	1.315	0.388	-0.002669	-0.000011	-0.001214	(-173.0, -179.2)(-17.3, -18.3)
0.010	0.002	0.531178	0.541588	0.539851	1.940	1.633	-0.001436	-0.000002	-0.000299	(-77.4, -80.1)(-24.5, -25.8)
	0.005	0.536652	0.541588	0.538814	0.920	0.403	-0.002086	-0.000006	-0.000682	(-122.3, -126.7)(-24.5, -25.8)
	0.010	0.534127	0.541588	0.537232	1.357	0.581	-0.003169	-0.000011	-0.001176	(-173.0, -179.2)(-24.5, -25.8)

T IS IN 0 K; WE'S AND F'S IN CM-1; THE REST ARE DIMENSIONLESS

Table 6 . $\ln(s/s')$ for model 2-D system #5 at 100°K

$T = 100.000$ $WE(1) = 1000.00$ $WE(1) = 950.00$ $WE(2) = 800.00$ $WE(2) = 760.00$

$\ln(S/S')F$

% ERROR

X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')
0.002	0.002	0.542472	0.544876	0.543692	0.443	0.216	-0.000680	-0.000039	-0.000515	(-65.2, -68.6)	(-21.9, -23.1)
	0.005	0.540213	0.544876	0.542394	0.063	0.404	-0.001139	-0.000096	-0.001247	(-103.1, -108.5)	(-21.9, -23.1)
	0.010	0.536717	0.544876	0.540416	1.520	0.689	-0.001903	-0.000189	-0.002368	(-145.8, -153.5)	(-21.9, -23.1)
0.004	0.002	0.541413	0.544876	0.543091	0.640	0.310	-0.001241	-0.000038	-0.000504	(-65.2, -68.6)	(-34.7, -36.5)
	0.005	0.538866	0.544876	0.541859	1.115	0.556	-0.001700	-0.000095	-0.001221	(-103.1, -108.5)	(-34.7, -36.5)
	0.010	0.535044	0.544876	0.539906	1.877	0.909	-0.002464	-0.000187	-0.002319	(-145.8, -153.5)	(-34.7, -36.5)
0.010	0.002	0.539917	0.544876	0.542174	0.913	0.410	-0.002177	-0.000038	-0.000487	(-65.2, -68.6)	(-49.1, -51.6)
	0.005	0.537044	0.544876	0.540967	1.453	0.731	-0.002636	-0.000094	-0.001179	(-103.1, -108.5)	(-49.1, -51.6)
	0.010	0.532866	0.544876	0.539853	2.276	1.163	-0.003400	-0.000185	-0.002238	(-145.8, -153.5)	(-49.1, -51.6)

T IS IN O K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS

Table 7 . $\ln(s/s')f$ for model 2-D system #6 at 100° K

$T = 100.000$

$WE(1) = 1000.00$

$WF(1) = 950.00$

$WE(2) = 1600.00$

$WE(2) = 1520.00$

		LN(S/S')F		% ERROR							
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')
0.002	0.002	0.830219	0.832625	0.831049	0.290	0.100	-0.000952	-0.000014	-0.000603	(-78.1, -82.3)	(-21.9, -23.1)
	0.005	0.828114	0.832625	0.829527	0.545	0.146	-0.001036	-0.000035	-0.001433	(-123.6, -130.1)	(-21.9, -23.1)
	0.010	0.824928	0.832625	0.826626	0.933	0.206	-0.003298	-0.000069	-0.002633	(-174.7, -183.9)	(-21.9, -23.1)
0.005	0.002	0.829062	0.832625	0.830500	0.410	0.173	-0.001520	-0.000014	-0.000591	(-78.1, -82.3)	(-34.7, -36.5)
	0.005	0.826611	0.832625	0.828791	0.728	0.264	-0.002397	-0.000034	-0.001403	(-123.6, -130.1)	(-34.7, -36.5)
	0.010	0.823034	0.832625	0.826120	1.165	0.375	-0.003859	-0.000068	-0.002578	(-174.7, -183.9)	(-34.7, -36.5)
0.010	0.002	0.827454	0.832625	0.829585	0.625	0.258	-0.002456	-0.000014	-0.000570	(-78.1, -82.3)	(-49.1, -51.6)
	0.005	0.824613	0.832625	0.827905	0.972	0.399	-0.003333	-0.000034	-0.001354	(-123.6, -130.1)	(-49.1, -51.6)
	0.010	0.820596	0.832625	0.825276	1.466	0.570	-0.004795	-0.000067	-0.002487	(-174.7, -183.9)	(-49.1, -51.6)

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T IS IN O K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS

Table 8 . $\ln(s/s')$ for model 2-D system #7 at 100° K

T = 100.000 WE(1) = 1000.00 WC(1) = 950.00 WE(12) = 2400.00 WE(2) = 2280.00

		LN(S/S')F			% ERROR						
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	IF122,F122'	(F111,F111')
0.002	0.002	1.117519	1.120382	1.118421	0.256	0.081	-0.001244	-0.000009	-0.000708	(-94.2, -99.1)	(-21.9, -23.1)
	0.005	1.114920	1.120382	1.116171	0.490	0.112	-0.002548	-0.000023	-0.001641	(-148.9, -156.7)	(-21.9, -23.1)
	0.010	1.110975	1.120382	1.112722	0.897	0.157	-0.004721	-0.000045	-0.002895	(-210.5, -221.6)	(-21.9, -23.1)
0.005	0.002	1.116237	1.120382	1.117876	0.371	0.147	-0.001805	-0.000009	-0.000693	(-94.2, -99.1)	(-34.7, -36.5)
	0.005	1.113223	1.120382	1.115646	0.643	0.218	-0.003109	-0.000022	-0.001605	(-148.9, -156.7)	(-34.7, -36.5)
	0.010	1.108809	1.120382	1.112226	1.044	0.308	-0.005283	-0.000044	-0.002830	(-210.5, -221.6)	(-34.7, -36.5)
0.010	0.002	1.114494	1.120382	1.116965	0.528	0.222	-0.002741	-0.000009	-0.000667	(-94.2, -99.1)	(-49.1, -51.6)
	0.005	1.111008	1.120382	1.114770	0.844	0.339	-0.004045	-0.000022	-0.001545	(-148.9, -156.7)	(-49.1, -51.6)
	0.010	1.106064	1.120382	1.111327	1.295	0.482	-0.006216	-0.000044	-0.002724	(-210.5, -221.6)	(-49.1, -51.6)

T IS IN ° K. WE'S AND F'S IN CM-1. THE REST ARE DIMENSIONLESS

Table 9 . $\ln(s/s')f$ for model 2-D system #8 at 100°K

$T = 100.000$

$WE'(1) = 1000.00$

$WF(1) = 950.00$

$WE'(2) = 3200.00$

$WE(2) = 3140.00$

		LN(S/S')F			% ERROR						
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	O	(F122,F122')	(F111,F111')
0.002	0.002	0.718951	0.721112	0.719947	0.303	0.141	-0.000608	-0.000002	-0.000355	(-109.9,-113.9)	(-21.9,-23.1)
	0.005	0.717113	0.721112	0.710637	0.554	0.240	-0.001458	-0.000006	-0.000812	(-173.7,-180.0)	(-21.9,-23.1)
	0.010	0.714406	0.721112	0.717154	0.939	0.385	-0.002541	-0.000011	-0.001405	(-245.7,-254.6)	(-21.9,-23.1)
0.005	0.002	0.717707	0.721112	0.719394	0.463	0.225	-0.001369	-0.000002	-0.000342	(-109.9,-113.9)	(-34.7,-36.5)
	0.005	0.715642	0.721112	0.718304	0.764	0.372	-0.002019	-0.000006	-0.000783	(-173.7,-180.0)	(-34.7,-36.5)
	0.010	0.712550	0.721112	0.716645	1.200	0.574	-0.003102	-0.000011	-0.001353	(-245.7,-254.6)	(-34.7,-36.5)
0.010	0.002	0.716009	0.721112	0.718483	0.713	0.346	-0.002305	-0.000002	-0.000322	(-109.9,-113.9)	(-49.1,-51.6)
	0.005	0.713680	0.721112	0.717416	1.041	0.523	-0.002955	-0.000006	-0.000735	(-173.7,-180.0)	(-49.1,-51.6)
	0.010	0.710171	0.721112	0.715794	1.541	0.792	-0.004034	-0.000011	-0.001262	(-245.7,-254.6)	(-49.1,-51.6)

T IS IN O K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS

Table 10. $\ln(s/s^*)F$ for model 2-D system #9 at $100^\circ K$

$T = 100.000$ $WE(1) = 1500.00$ $WE(1) = 1425.00$ $WE(12) = 1600.00$ $WE(2) = 1520.00$

LN(S/S*)F			% ERROR								
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	O	(F122,F122')	(F111,F111')
0.002	0.002	1.009217	1.012473	1.010509	0.323	0.136	-0.001134	-0.000016	-0.000735	(-100.4,-105.7)	(-32.9,-34.6)
	0.005	1.006367	1.012473	1.008686	0.607	0.230	-0.002011	-0.000038	-0.001738	(-158.8,-167.1)	(-32.9,-34.6)
	0.010	1.002030	1.012473	1.005750	1.042	0.371	-0.003473	-0.000076	-0.003175	(-224.5,-236.4)	(-32.9,-34.6)
0.005	0.002	1.007627	1.012473	1.009788	0.441	0.214	-0.001958	-0.000015	-0.000712	(-100.4,-105.7)	(-52.0,-54.8)
	0.005	1.004332	1.012473	1.007917	0.811	0.357	-0.002035	-0.000038	-0.001683	(-158.8,-167.1)	(-52.0,-54.8)
	0.010	0.999494	1.012473	1.005026	1.299	0.553	-0.004256	-0.000075	-0.003075	(-224.5,-236.4)	(-52.0,-54.8)
0.010	0.002	1.005391	1.012473	1.008452	0.704	0.304	-0.003331	-0.000015	-0.000674	(-100.4,-105.7)	(-73.6,-77.5)
	0.005	1.001595	1.012473	1.006632	1.086	0.503	-0.004204	-0.000038	-0.001595	(-158.8,-167.1)	(-73.6,-77.5)
	0.010	0.996191	1.012473	1.003814	1.634	0.765	-0.005670	-0.000075	-0.002915	(-224.5,-236.4)	(-73.6,-77.5)

T IS IN O K, WE'S AND F'S IN CM-1. THE REST ARE DIMENSIONLESS

Table 11. $\ln(s/s')$ for model 2-D system #10 at 100°K

$T = 100.000$ $WE(1) = 1500.00$ $WE(1) = 1425.00$ $WE(2) = 2400.00$ $WE(2) = 2280.00$

LN(S/S')F			R ERROR								
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	O	(F122,F122')	(F111,F111')
0.002	0.002	1.296642	1.300230	1.296022	0.277	0.106	-0.001419	-0.000009	-0.000780	(-117.2,-123.4)	(-32.9,-34.6)
	0.005	1.293496	1.300230	1.295684	0.521	0.169	-0.002723	-0.000023	-0.001800	(-185.3,-195.1)	(-32.9,-34.6)
	0.010	1.288735	1.300230	1.292130	0.892	0.263	-0.004896	-0.000046	-0.003157	(-262.1,-275.9)	(-32.9,-34.6)
0.005	0.002	1.294924	1.300230	1.297224	0.410	0.170	-0.002243	-0.000009	-0.000754	(-117.2,-123.4)	(-52.0,-54.8)
	0.005	1.291259	1.300230	1.294920	0.695	0.284	-0.003547	-0.000023	-0.001740	(-185.3,-195.1)	(-52.0,-54.8)
	0.010	1.285913	1.300230	1.291414	1.113	0.428	-0.005720	-0.000046	-0.003050	(-262.1,-275.9)	(-52.0,-54.8)
0.010	0.002	1.292544	1.300230	1.295893	0.595	0.259	-0.003616	-0.000009	-0.000712	(-117.2,-123.4)	(-73.6,-77.5)
	0.005	1.288293	1.300230	1.293645	0.927	0.415	-0.004920	-0.000023	-0.001642	(-185.3,-195.1)	(-73.6,-77.5)
	0.010	1.282787	1.300230	1.290215	1.399	0.618	-0.007093	-0.000046	-0.002676	(-262.1,-275.9)	(-73.6,-77.5)

T IS IN O K. WE'S AND F'S IN CM-1. THE REST ARE DIMENSIONLESS

Table 12 -- $\ln(s/s^*)F$ for model 2-D system #11 at 100°K

$T = 100.000$ $WE(11) = 1500.00$ $WE(11) = 1425.00$ $WE(12) = 3200.00$ $WE(12) = 3140.00$

		LN(S/S*)F			% ERROR								
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')		
0.002	0.002	0.898085	0.900960	0.899974	0.320	0.166	-0.000903	-0.000002	-0.000401	(-135.6,-140.6)	(-32.9,-34.6)		
	0.005	0.895736	0.900960	0.898403	0.583	0.298	-0.001633	-0.000006	-0.000918	(-214.5,-222.3)	(-32.9,-34.6)		
	0.010	0.892212	0.900960	0.896639	0.980	0.496	-0.002716	-0.000011	-0.001593	(-303.3,-314.4)	(-32.9,-34.6)		
0.005	0.002	0.896538	0.900960	0.898770	0.493	0.249	-0.001807	-0.000002	-0.000381	(-135.6,-140.6)	(-52.0,-54.8)		
	0.005	0.893770	0.900960	0.897624	0.804	0.931	-0.002456	-0.000005	-0.000872	(-214.5,-222.3)	(-52.0,-54.8)		
	0.010	0.889774	0.900960	0.895898	1.257	0.608	-0.003540	-0.000011	-0.001511	(-303.3,-314.4)	(-52.0,-54.8)		
0.010	0.002	0.894350	0.900960	0.897429	0.739	0.344	-0.003180	-0.000002	-0.000348	(-135.6,-140.6)	(-73.6,-77.5)		
	0.005	0.891110	0.900960	0.896327	1.105	0.586	-0.003830	-0.000005	-0.000797	(-214.5,-222.3)	(-73.6,-77.5)		
	0.010	0.886581	0.900960	0.894650	1.622	0.911	-0.004913	-0.000011	-0.001370	(-303.3,-314.4)	(-73.6,-77.5)		

T IS IN D K. WE'S AND F'S IN CM-1. THE REST ARE DIMENSIONLESS

Table 13. $\ln(s/s')$ for model 2-D system #1 at 300° K

T = 300.000 WE(1) = 500.00 WE(1) = 475.00 WE(2) = 800.00 WE(2) = 760.00

LN(S/S')F			% ERROR									
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')	
0.002	0.002	0.070522	0.070772	0.070487	0.356	-0.049	-0.000144	-0.000080	-0.000061	-39.1	-41.114	-11.0, -11.5)
	0.005	0.070287	0.070772	0.070141	0.690	-0.209	-0.000284	-0.000197	-0.000151	-61.8	-65.011	-11.0, -11.5)
	0.010	0.069928	0.070772	0.069579	1.207	-0.499	-0.000513	-0.000383	-0.000297	-87.4	-92.011	-11.0, -11.5)
0.004	0.002	0.070412	0.070772	0.070418	0.511	0.007	-0.000215	-0.000076	-0.000061	-39.1	-41.114	-17.3, -16.3)
	0.005	0.070155	0.070772	0.070074	0.894	-0.115	-0.000355	-0.000197	-0.000151	-61.8	-65.011	-17.3, -16.3)
	0.010	0.069772	0.070772	0.069517	1.434	-0.365	-0.000584	-0.000374	-0.000297	-87.4	-92.011	-17.3, -16.3)
0.010	0.002	0.070259	0.070772	0.070308	0.731	0.069	-0.000328	-0.000076	-0.000061	-39.1	-41.114	-24.5, -25.8)
	0.005	0.069977	0.070772	0.069967	1.136	-0.014	-0.000468	-0.000187	-0.000151	-61.8	-65.011	-24.5, -25.8)
	0.010	0.069572	0.070772	0.069415	1.726	-0.225	-0.000696	-0.000364	-0.000297	-87.4	-92.011	-24.5, -25.8)

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T IS IN O K. WE'S AND F'S IN CM-1. THE REST ARE DIMENSIONLESS

Table 14 $\ln(s/s^*)f$ for model 2-D system #2 at 300° K

$T = 300.000$ $WE(1) = 500.00$ $WE(2) = 475.00$ $WE(2) = 1600.00$ $WE(2) = 1520.00$

		LN(S/S*)F			% ERROR						
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')
0.002	0.002	0.161766	0.162238	0.161792	0.279	0.004	-0.000263	-0.000039	-0.000144	(-54.1, -56.9)	(-11.0, -11.5)
	0.005	0.161316	0.162238	0.161205	0.571	-0.069	-0.000583	-0.000096	-0.000354	(-85.5, -90.0)	(-11.0, -11.5)
	0.010	0.160582	0.162238	0.160244	1.031	-0.208	-0.001115	-0.000188	-0.000686	(-120.9, -127.3)	(-11.0, -11.5)
0.004	0.002	0.161634	0.162238	0.161722	0.374	0.054	-0.000334	-0.000038	-0.000144	(-54.1, -56.9)	(-17.3, -18.3)
	0.005	0.161114	0.162238	0.161137	0.697	0.014	-0.000654	-0.000094	-0.000353	(-85.5, -90.0)	(-17.3, -18.3)
	0.010	0.160326	0.162238	0.160183	1.193	-0.089	-0.001186	-0.000184	-0.000685	(-120.9, -127.3)	(-17.3, -18.3)
0.010	0.002	0.161432	0.162238	0.161611	0.499	0.111	-0.000447	-0.000037	-0.000143	(-54.1, -56.9)	(-24.5, -25.8)
	0.005	0.160859	0.162238	0.161028	0.857	0.105	-0.000766	-0.000091	-0.000352	(-85.5, -90.0)	(-24.5, -25.8)
	0.010	0.160013	0.162238	0.160077	1.391	0.040	-0.001298	-0.000179	-0.000683	(-120.9, -127.3)	(-24.5, -25.8)

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T IS IN O K. WE'S AND F'S IN CM-1. THE REST ARE DIMENSIONLESS

Table 15. $\ln(s/s')$ for model 2-D system #3 at 300° K

$T = 300.000$ $WE(11) = 500.00$ $WE(11) = 975.00$ $WE(12) = 2400.00$ $WE(12) = 2260.00$

		LN(S/S')F			% ERROR						
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')
0.002	0.002	0.257367	0.257947	0.257459	0.225	-0.103	-0.000355	-0.000026	-0.000207	(-66.0, -69.5)	(-11.0, -11.5)
	0.005	0.256738	0.257947	0.256564	0.471	-0.068	-0.000814	-0.000064	-0.000505	(-104.4, -109.8)	(-11.0, -11.5)
	0.010	0.255751	0.257947	0.255275	0.049	-0.186	-0.001578	-0.000126	-0.000968	(-147.6, -155.3)	(-11.0, -11.5)
0.005	0.002	0.257195	0.257947	0.257284	0.292	0.036	-0.000426	-0.000025	-0.000207	(-66.0, -69.5)	(-17.3, -18.3)
	0.005	0.256505	0.257947	0.256495	0.562	-0.009	-0.000885	-0.000062	-0.000504	(-104.4, -109.8)	(-17.3, -18.3)
	0.010	0.255440	0.257947	0.255209	0.978	-0.094	-0.001649	-0.000123	-0.000966	(-147.6, -155.3)	(-17.3, -18.3)
0.010	0.002	0.256971	0.257947	0.257177	0.340	0.080	-0.000539	-0.000025	-0.000206	(-66.0, -69.5)	(-24.5, -25.8)
	0.005	0.256215	0.257947	0.256386	0.676	0.067	-0.000997	-0.000061	-0.000503	(-104.4, -109.8)	(-24.5, -25.8)
	0.010	0.255084	0.257947	0.255103	1.121	0.006	-0.001761	-0.000120	-0.000963	(-147.6, -155.3)	(-24.5, -25.8)

T IS IN °K, WE'S AND F'S IN CM-1. THE REST ARE DIMENSIONLESS

Table 16. $\ln(s/s^*)f$ for model 2-D system #4 at 300°K

$T = 300.000$ $WE(1) = 500.00$ $WE(1) = 475.00$ $WE(12) = 3200.00$ $WE(12) = 3140.00$

		LN(S/S*)F			X ERROR							
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')	
0.002	0.002	0.146101	0.146426	0.146118	0.223	0.012	-0.000198	-0.000007	-0.000103	(-77.4, -80.1)	(-11.0, -11.5)	
	0.005	0.145764	0.146426	0.145740	0.454	-0.017	-0.000421	-0.000017	-0.000248	(-122.3, -126.7)	(-11.0, -11.5)	
	0.010	0.145233	0.146426	0.145131	0.821	-0.071	-0.000794	-0.000033	-0.000468	(-173.0, -179.2)	(-11.0, -11.5)	
0.005	0.002	0.145967	0.146426	0.146047	0.301	0.041	-0.000270	-0.000007	-0.000103	(-77.4, -80.1)	(-17.3, -18.3)	
	0.005	0.145629	0.146426	0.145669	0.551	0.031	-0.000493	-0.000016	-0.000248	(-122.3, -126.7)	(-17.3, -18.3)	
	0.010	0.145064	0.146426	0.145060	0.959	-0.003	-0.000865	-0.000032	-0.000469	(-173.0, -179.2)	(-17.3, -18.3)	
0.010	0.002	0.145831	0.146426	0.145938	0.409	0.071	-0.000382	-0.000006	-0.000103	(-77.4, -80.1)	(-24.5, -25.8)	
	0.005	0.145444	0.146426	0.145557	0.675	0.078	-0.000605	-0.000015	-0.000248	(-122.3, -126.7)	(-24.5, -25.8)	
	0.010	0.144860	0.146426	0.144949	1.001	0.061	-0.000977	-0.000031	-0.000469	(-173.0, -179.2)	(-24.5, -25.8)	

T IS IN O K; WE'S AND F'S IN CH-1. THE REST ARE DIMENSIONLESS

Table 17 . $\ln(s/s')$ for model 2-D system #5 at 300° K

T = 300.000

WE*(1) = 1000.00

WE(1) = 950.00

WE*(2) = 800.00

WE(2) = 750.00

$\ln(S/S')$

% ERROR

X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')
0.002	0.002	0.117482	0.120163	0.119695	0.365	0.172	-0.000229	-0.000113	-0.000132	(-65.2, -68.6)	(-21.9, -23.1)
	0.005	0.118883	0.120163	0.119197	1.077	0.264	-0.000364	-0.000277	-0.000326	(-103.1, -108.5)	(-21.9, -23.1)
	0.010	0.117958	0.120163	0.118392	1.870	0.360	-0.000592	-0.000539	-0.000640	(-145.8, -153.5)	(-21.9, -23.1)
0.005	0.002	0.119166	0.120163	0.119505	0.837	0.284	-0.000416	-0.000111	-0.000131	(-65.2, -68.6)	(-34.7, -36.5)
	0.005	0.118489	0.120163	0.119012	1.413	0.442	-0.000556	-0.000272	-0.000323	(-103.1, -108.5)	(-34.7, -36.5)
	0.010	0.117486	0.120163	0.118214	2.279	0.620	-0.000785	-0.000529	-0.000635	(-145.8, -153.5)	(-34.7, -36.5)
0.010	0.002	0.118701	0.120163	0.117192	1.232	0.414	-0.000733	-0.000109	-0.000129	(-65.2, -68.6)	(-49.1, -51.6)
	0.005	0.117944	0.120163	0.118704	1.882	0.645	-0.000873	-0.000267	-0.000319	(-103.1, -108.5)	(-49.1, -51.6)
	0.010	0.116856	0.120163	0.117915	2.830	0.906	-0.001102	-0.000519	-0.000628	(-145.8, -153.5)	(-49.1, -51.6)

T IS IN ° K. WE'S AND F'S IN CM-1. THE REST ARE DIMENSIONLESS

Table 18. $\ln(s/s')$ for model 2-D system #6 at 300° K

$T = 300.000$

$WE(11) = 1000.00$

$WE(1) = 950.00$

$WE(12) = 1600.00$

$WE(2) = 1520.00$

LN(S/S')F			% ERROR								
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')
0.002	0.002	0.210040	0.211628	0.211048	0.374	0.099	-0.000343	-0.000041	-0.000196	(-78.1, -82.3)	(-21.9, -23.1)
	0.005	0.210143	0.211628	0.210343	0.707	0.114	-0.000663	-0.000101	-0.000482	(-123.6, -130.1)	(-21.9, -23.1)
	0.010	0.209081	0.211628	0.209298	1.218	0.104	-0.001195	-0.000199	-0.000936	(-174.7, -183.9)	(-21.9, -23.1)
0.004	0.002	0.210444	0.211628	0.210858	0.553	0.187	-0.000535	-0.000040	-0.000195	(-78.1, -82.3)	(-34.7, -36.5)
	0.005	0.209667	0.211628	0.210195	0.978	0.254	-0.000855	-0.000100	-0.000479	(-123.6, -130.1)	(-34.7, -36.5)
	0.010	0.208482	0.211628	0.209116	1.509	0.304	-0.001367	-0.000196	-0.000930	(-174.7, -183.9)	(-34.7, -36.5)
0.010	0.002	0.209939	0.211628	0.210544	0.003	0.288	-0.000852	-0.000040	-0.000193	(-78.1, -82.3)	(-49.1, -51.6)
	0.005	0.209019	0.211628	0.209805	1.249	0.415	-0.001172	-0.000098	-0.000474	(-123.6, -130.1)	(-49.1, -51.6)
	0.010	0.207700	0.211628	0.208812	1.855	0.532	-0.001704	-0.000192	-0.000920	(-174.7, -183.9)	(-49.1, -51.6)

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T IS IN O K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS

Table 19 . $\ln(s/s')$ for model 2-D system #7 at 300° K

T = 300.000 WE(1) = 1000.00 WE(1) = 950.00 WE(12) = 2400.00 WE(12) = 2280.00

$\ln(s/s')$

% ERROR

X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')
0.002	0.002	0.306401	0.307338	0.306614	0.304	0.070	-0.000435	-0.000027	-0.000262	(-94.2, -99.1)	(-21.9, -23.1)
	0.005	0.305541	0.307338	0.305740	0.599	0.065	-0.000693	-0.000066	-0.000638	(-148.9, -156.7)	(-21.9, -23.1)
	0.010	0.304229	0.307338	0.304326	1.022	0.032	-0.001657	-0.000130	-0.001224	(-210.5, -221.6)	(-21.9, -23.1)
0.004	0.002	0.305906	0.307338	0.306424	0.442	0.143	-0.000627	-0.000026	-0.000260	(-94.2, -99.1)	(-34.7, -36.5)
	0.005	0.304990	0.307338	0.305553	0.767	0.182	-0.001086	-0.000065	-0.000634	(-148.9, -156.7)	(-34.7, -36.5)
	0.010	0.303543	0.307338	0.304144	1.250	0.198	-0.001850	-0.000128	-0.001217	(-210.5, -221.6)	(-34.7, -36.5)
0.010	0.002	0.305416	0.307338	0.306111	0.629	0.227	-0.000944	-0.000026	-0.000257	(-94.2, -99.1)	(-49.1, -51.6)
	0.004	0.304206	0.307338	0.305244	1.003	0.315	-0.001403	-0.000063	-0.000628	(-148.9, -156.7)	(-49.1, -51.6)
	0.010	0.302671	0.307338	0.303842	1.542	0.307	-0.002167	-0.000125	-0.001204	(-210.5, -221.6)	(-49.1, -51.6)

T IS IN D K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS

Table 20 . $\ln(s/s')f$ for model 2-D system #8 at 300° K

$T = 300.000$

$WE(1) = 1000.00$

$WE(1) = 950.00$

$WE(12) = 3200.00$

$WE(2) = 3140.00$

		LN(S/S')F			% ERROR						
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')
0.002	0.002	0.195124	0.195817	0.195370	0.355	0.126	-0.000278	-0.000007	-0.000162	(-109.9,-113.9)	(-21.9,-23.1)
	0.005	0.194548	0.195817	0.194905	0.652	0.183	-0.000501	-0.000017	-0.000394	(-173.7,-180.0)	(-21.9,-23.1)
	0.010	0.193682	0.195817	0.194161	1.102	0.247	-0.000873	-0.000033	-0.000750	(-245.7,-254.6)	(-21.9,-23.1)
0.004	0.002	0.194761	0.195817	0.195179	0.542	0.214	-0.000470	-0.000007	-0.000161	(-109.9,-113.9)	(-34.7,-36.5)
	0.005	0.194089	0.195817	0.194716	0.890	0.323	-0.000694	-0.000016	-0.000390	(-173.7,-180.0)	(-34.7,-36.5)
	0.010	0.193114	0.195817	0.193976	1.400	0.446	-0.001066	-0.000032	-0.000743	(-245.7,-254.6)	(-34.7,-36.5)
0.010	0.002	0.194252	0.195817	0.194865	0.806	0.316	-0.000707	-0.000006	-0.000159	(-109.9,-113.9)	(-49.1,-51.6)
	0.005	0.193472	0.195817	0.194406	1.212	0.483	-0.001010	-0.000016	-0.000385	(-173.7,-180.0)	(-49.1,-51.6)
	0.010	0.192377	0.195817	0.193671	1.788	0.673	-0.001383	-0.000031	-0.000732	(-245.7,-254.6)	(-49.1,-51.6)

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T IS IN O K. WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS

Table 21. $\ln(s/s')$ for model 2-D system #9 at 300° K

$T = 300.000$ $WE(1) = 1500.00$ $WE(1) = 1425.00$ $WE(12) = 1600.00$ $WE(2) = 1520.00$

		LN(S/S')F			% ERROR						
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')
0.002	0.002	0.268533	0.269643	0.268933	0.413	0.149	-0.000415	-0.000046	-0.000250	(-100.4,-105.7)	(-52.9,-54.6)
	0.005	0.267560	0.269643	0.269103	0.776	0.230	-0.000735	-0.000112	-0.000613	(-158.0,-167.1)	(-52.9,-54.6)
	0.010	0.266095	0.269643	0.266966	1.333	0.327	-0.001267	-0.000220	-0.001190	(-224.5,-236.4)	(-52.9,-54.6)
0.005	0.002	0.267981	0.269643	0.268635	0.620	0.244	-0.000716	-0.000045	-0.000247	(-100.4,-105.7)	(-52.0,-54.8)
	0.005	0.266870	0.269643	0.267890	1.079	0.382	-0.001036	-0.000111	-0.000607	(-158.0,-167.1)	(-52.0,-54.8)
	0.010	0.265235	0.269643	0.266601	1.662	0.545	-0.001568	-0.000217	-0.001177	(-224.5,-236.4)	(-52.0,-54.8)
0.010	0.002	0.267196	0.269643	0.268139	0.916	0.353	-0.001216	-0.000048	-0.000243	(-100.4,-105.7)	(-73.6,-77.5)
	0.005	0.265922	0.269643	0.267401	1.399	0.556	-0.001536	-0.000109	-0.000597	(-158.0,-167.1)	(-73.6,-77.5)
	0.010	0.264104	0.269643	0.266204	2.057	0.795	-0.002068	-0.000214	-0.001157	(-224.5,-236.4)	(-73.6,-77.5)

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T IS IN O K. WE'S AND F'S IN CM-1. THE REST ARE DIMENSIONLESS

Table 22 . $\ln(s/s')$ for model 2-D system #10 at 300° K

$T = 300.000$ $WE(1) = 1500.00$ $WE(1) = 1425.00$ $WE(12) = 2400.00$ $WE(12) = 2280.00$

$\ln(s/s')$

% ERROR

X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')
0.002	0.002	0.364130	0.365352	0.364511	0.334	0.105	-0.000507	-0.000028	-0.000307	(-117.2,-123.4)	(-32.9,-34.6)
	0.005	0.363064	0.365352	0.363571	0.630	0.140	-0.000965	-0.000068	-0.000747	(-185.3,-195.1)	(-32.9,-34.6)
	0.010	0.361446	0.365352	0.362057	1.081	0.149	-0.001729	-0.000134	-0.001431	(-262.1,-275.9)	(-32.9,-34.6)
0.005	0.002	0.363533	0.365352	0.364213	0.500	0.187	-0.000408	-0.000027	-0.000304	(-117.2,-123.4)	(-52.0,-54.8)
	0.005	0.362297	0.365352	0.363279	0.893	0.271	-0.001267	-0.000067	-0.000739	(-185.3,-195.1)	(-52.0,-54.8)
	0.010	0.360487	0.365352	0.361772	1.350	0.356	-0.002031	-0.000133	-0.001416	(-262.1,-275.9)	(-52.0,-54.8)
0.010	0.002	0.362699	0.365352	0.363718	0.731	0.281	-0.001309	-0.000027	-0.000298	(-117.2,-123.4)	(-73.6,-77.5)
	0.005	0.361271	0.365352	0.362792	1.130	0.421	-0.001767	-0.000066	-0.000727	(-185.3,-195.1)	(-73.6,-77.5)
	0.010	0.359295	0.365352	0.361298	1.700	0.572	-0.002531	-0.000131	-0.001392	(-262.1,-275.9)	(-73.6,-77.5)

T IS IN O K, WE'S AND F'S IN CM-1, THE REST ARE DIMENSIONLESS

Table 23. $\ln(s/s')$ for model 2-D system #11 at 300° K.

T = 300.000 WE'(1) = 1500.00 WE(1) = 1425.00 WE'(2) = 3200.00 WE(2) = 3140.00

		LN(S/S')F			% ERROR								
X1	X2	EXACT	HARM.	ANHARM.	HARM.	ANHARM.	A	E	D	(F122,F122')	(F111,F111')		
0.002	0.002	0.252859	0.253831	0.253260	0.385	0.162	-0.000350	-0.000006	-0.000207	(-135.6,-140.6)	(-32.9,-34.6)	74	
	0.005	0.252077	0.253831	0.252740	0.696	0.263	-0.000573	-0.000016	-0.000502	(-214.5,-222.3)	(-32.9,-34.6)		
	0.010	0.250901	0.253831	0.251098	1.168	0.397	-0.000945	-0.000032	-0.000956	(-303.3,-314.4)	(-32.9,-34.6)		
0.005	0.002	0.252321	0.253831	0.252970	0.599	0.257	-0.000651	-0.000006	-0.000204	(-135.6,-140.6)	(-52.0,-54.8)		
	0.005	0.251401	0.253831	0.252496	0.967	0.416	-0.000874	-0.000016	-0.000495	(-214.5,-222.3)	(-52.0,-54.8)		
	0.010	0.250072	0.253831	0.251611	1.503	0.616	-0.001247	-0.000031	-0.000942	(-303.3,-314.4)	(-52.0,-54.8)		
0.010	0.002	0.251552	0.253831	0.252479	0.906	0.367	-0.001152	-0.000006	-0.000199	(-135.6,-140.6)	(-73.6,-77.5)		
	0.005	0.250479	0.253831	0.251958	1.339	0.590	-0.001375	-0.000015	-0.000483	(-214.5,-222.3)	(-73.6,-77.5)		
	0.010	0.248976	0.253831	0.251135	1.950	0.867	-0.001747	-0.000030	-0.000912	(-303.3,-314.4)	(-73.6,-77.5)		

T IS IN O K. WE'S AND F'S IN CM-1; THE REST ARE DIMENSIONLESS

d. Discussion

The numerical results in the previous section were obtained by my investigation of a model 2-D system that simulates the two stretching modes of a representative linear triatomic molecule. I chose to model the 2-D cases after CO_2 because this is one of the few triatomic molecules that have readily available data on anharmonicity constants and cubic coefficients.¹⁸ As can be seen from the previous section I varied the symmetric stretching frequency ω_1 from 500 cm^{-1} to 1500 cm^{-1} while the symmetric stretching frequency of $^{12}\text{C}^{16}\text{O}_2$ is 1349.97 cm^{-1} . The other stretching mode ω_2 is set to values ranging from 800 cm^{-1} to 3200 cm^{-1} while the antisymmetric stretching frequency of CO_2 is 2395.89 cm^{-1} .¹⁸ For the heavier isotopic pair I investigated, I decreased the corresponding ω_1 and ω_2 by 5%. Generally the values of ω_1 and ω_2 were selected to avoid resonance.

Under all circumstances, the new approximation gives substantially improved results over the harmonic oscillator treatment. It shows clearly the dominance of the diagonal Morse potential correction term when the anharmonicity constants χ_i are small but when χ_i values become larger, the off-diagonal quantum-mechanical perturbation terms, D and D', then play a more important role. The classical off-diagonal cubic correction terms, E and E', are generally much smaller in magnitude compared with the Morse potential correction terms and off-diagonal cubic quantum-mechanical perturbation

terms. Approximation results are represented for temperatures of both 100°K and 300°K.

One big contrast between the exact result and the approximation result is in the utilized computer time. The former takes about 200 seconds CPU time in the CUNY-UCC IBM 370/168 to execute while the approximate method program takes less than one second CPU time in execution. The more important advantage of the approximation over the exact calculation lies in the physical insight gained by observing the interplay of various factors that make up the reduced partition function so we know under what circumstances we can omit the off-diagonal contribution terms and still have a result within tolerable percentage error.

With the encouraging numerical results that we have obtained this far it was logical to look into the quasi-3-dimensional problem of the total CO_2 vibration.

B. APPROXIMATION FOR 3-D SYSTEM

a. Exact Calculation

i. Numerical Solution for the Phase Integral

The expression for the total energy E becomes quite involved in CO_2 for now we have two stretching modes and a degenerate bending mode to work with. With the designation of q_1 standing for symmetric stretching coordinate, q_2 for antisymmetric stretching coordinate, and q_3 and q_3' for the degenerate bending coordinate, the total energy E then becomes

$$\begin{aligned}
E = & \frac{P_1^2}{2} + D_1 (1 - e^{-\alpha_1 q_1})^2 + \frac{P_2^2}{2} + D_2 (1 - e^{-\alpha_2 q_2})^2 \\
& + \frac{P_3^2}{2} + D_3 (1 - e^{-\alpha_3 q_3})^2 + \frac{P_3'^2}{2} + D_3' (1 - e^{-\alpha_3 q_3'})^2 \\
& + \gamma_{122} q_1 q_2^2 + \gamma_{133} q_1 q_3^2 + \gamma_{133} q_1 q_3'^2
\end{aligned} \tag{101}$$

The classical partition function Q_{cl} is:

$$\begin{aligned}
Q_{cl} = & \int \int \int \int \int \int \int e^{-H/kT} dp dq \\
= & \int_{-\frac{\ln 2}{\alpha_1}}^{\infty} \left[\int_{P_1^-}^{P_1^+} \int_{-\frac{\ln 2}{\alpha_1}}^{L_2(q_1)} \left[\int_{P_2^-}^{P_2^+} \left[\int_{-\frac{\ln 2}{\alpha_3}}^{L_3(q_1, q_2)} \right. \right. \right. \\
& \left. \left. \int_{P_3^-}^{P_3^+} e^{-H(q_1, P_1, q_2, P_2, q_3, P_3)/kT} dp_3 \right. \right. \\
& \left. \left. dq_3 \right] dp_2 \right] dq_2 dp_1 \left. \right] dq_1,
\end{aligned} \tag{102}$$

whereas degeneracy q_3' is not explicitly included in the above equation for the sake of clarity but will be later on included in the actual computer calculation.

Since it is impossible to find all the integration limits by analytical methods, one has to utilize a numerical technique. By extending the formulation used in dealing with

the model 2-D system, recalling that one should recover the classical anharmonic partition function Q_{cl}^{anh} with no interaction as $\gamma_{ijj} \rightarrow 0$, we have

$$\begin{aligned}
 Q_{cl}^{anh} = & \frac{1}{u_{e_1}} \frac{1}{u_{e_2}} \frac{1}{u_{e_3}} \left(\frac{2}{\pi} \right)^3 \int_{-\rho_1}^{\infty} \ln 2 \, dz_1 \\
 & \int_0^{\rho_1} \sqrt{e^{-\frac{z_1}{\rho_1}} \left[2 - e^{-\frac{z_1}{\rho_1}} \right]^2} e^{-y_1^2} dy_1 \times \\
 & \int_{-\rho_2}^{\infty} \ln 2 \, dz_2 \int_0^{\rho_2} \sqrt{e^{-\frac{z_2}{\rho_2}} \left[2 - e^{-\frac{z_2}{\rho_2}} \right]^2} e^{-y_2^2} dy_2 \\
 & \int_{-\rho_3}^{\infty} \ln 2 \, e^{-\rho_1^2 \left[1 - e^{-\frac{z_1}{\rho_1}} \right]^2} - \rho_2^2 \left[1 - e^{-\frac{z_2}{\rho_2}} \right]^2 \\
 & - \rho_3^2 \left[1 - e^{-\frac{z_3}{\rho_3}} \right]^2 - \gamma_{122} z_1 z_2^2 - \gamma_{133} z_1 z_3^2 \, dz_3 \times \\
 & \int_0^{\rho_3} \sqrt{e^{-\frac{z_3}{\rho_3}} \left[2 - e^{-\frac{z_3}{\rho_3}} \right]^2} e^{-y_3^2} dy_3 , \tag{103}
 \end{aligned}$$

with the usual transformations

$$z_1 = \frac{u_1 q_1}{2} \sqrt{\frac{u_{e_1}}{\chi_{e_1}}} , \quad (104a)$$

$$\rho_1 = \frac{1}{2} \sqrt{\frac{u_{e_1}}{\chi_{e_1}}} , \quad (104b)$$

and

$$y_1 = \frac{p_1^2}{2kT} . \quad (104c)$$

Thus, with intercoordinate interactions,

$$Q_{cl}^{anh} = \frac{1}{u_{e_1}} \frac{1}{u_{e_2}} \frac{1}{u_{e_3}} \left(\frac{2}{\pi} \right)^3 \int_{-\rho_1}^{\infty} \ln 2 \, dz_1 \int_0^{\rho_1} \sqrt{e^{-\frac{z_1}{\rho_1}} \left[2 - e^{-\frac{z_1}{\rho_1}} \right]^2}$$

$$e^{-y_1^2} dy_1 \int_{-\rho_2}^{L_2(q_1)} \ln 2 \, dz_2$$

$$\int_0^{\rho_2} \sqrt{1 - \left[1 - e^{-\frac{z_2}{\rho_2}} \right]^2} - \gamma_{122} z_1 z_2^2 \, x$$

$$\begin{aligned}
& \int_{-\rho \ln 2}^{L_3(z_1, z_2)} dz_3 e^{-\rho_1^2 \left(1 - e^{-\frac{z_1^2}{\rho_1}}\right) - \rho_2^2 \left(1 - e^{-\frac{z_2^2}{\rho}}\right)} \times \\
& e^{-\rho_3^2 \left(1 - e^{-\frac{z_3^2}{\rho_3}}\right) - \gamma_{122} z_1 z_2^2 - \gamma_{133} z_1 z_3^2} \times \\
& \int_0^{\rho_3} \sqrt{1 - \left(1 - e^{-\frac{z_3^2}{\rho_3}}\right) - \gamma_{133} z_1 z_3^2} d^{-y_3^2} dy_3 \quad (105)
\end{aligned}$$

Care must be taken in the calculations of the upper limits z , L_2 , L_3 to avoid inclusion of contributions from the unstable states corresponding to the repulsive forces that fictitiously arise from the truncation of the polynomial potential functions, as in the 2-D model case.

ii. Numerical Solution for the Quantum Partition Function

The quantum mechanical partition function is exactly expressed as

$$Q_{qm}^{anh} = \sum_{n_1=0}^{v_{D_1}} \sum_{n_2=0}^{v_{D_2}} \sum_{n_3=0}^{v_{D_3}} \sum_{n_4=0}^{v_{D_4}} e^{-\epsilon(1,2,3,4)/kT}, \quad (106)$$

where

$$\begin{aligned}
G(n_1, n_2, n_3, n_4) &= \frac{e(1, 2, 3, 4)}{\hbar c} \\
&= [\omega_{e_1}(n_1 + \frac{1}{2}) - \omega_{e_1} \chi_{e_1}(n_1 + \frac{1}{2})^2] \\
&+ [\omega_{e_2}(n_2 + \frac{1}{2}) - \omega_{e_2} \chi_{e_2}(n_2 + \frac{1}{2})^2 + \\
&\chi_{12}(n_1 + \frac{1}{2})(n_2 + \frac{1}{2})] + [\omega_{e_3}(n_3 + \frac{1}{2}) - \\
&\omega_{e_3} \chi_{e_3}(n_3 + \frac{1}{2})^2 + \chi_{13}(n_1 + \frac{1}{2})(n_3 + \frac{1}{2}) + \\
&\chi_{23}(n_2 + \frac{1}{2})(n_3 + \frac{1}{2})] + [\omega_{e_3}(n_4 + \frac{1}{2}) - \\
&\omega_{e_3} \chi_{e_3}(n_4 + \frac{1}{2})^2 + \chi_{13}(n_1 + \frac{1}{2})(n_4 + \frac{1}{2}) + \\
&\chi_{23}(n_2 + \frac{1}{2})(n_4 + \frac{1}{2})] . \quad (107)
\end{aligned}$$

Note that the bending vibrational frequency ω_{e_3} is degenerate. By regarding n_1 as the variable for the outer summation, n_2 for the intermediate loop and n_3 and n_4 as the inner loops, one follows a similar approach as in solving Q_{qm}^{anh} in the 2-D numerically.

b. Numerical Results and Discussion

With all the above formulations, it is time now to put them to work. I now try to compare the results of the harmonic reduced partition function $\ln \frac{S}{S^T} f(\text{harm})$, and

$\ln \frac{S}{S_T} f(\text{harm})$ with the usual anharmonicity correction terms,

i.e., $\sum_i \frac{u_{e_i} \chi_{e_i} - u_{e_i}' \chi_{e_i}'}{4}$, and the newly developed approxima-

tion $\ln \frac{S}{S_T} f(\text{anharmonic})$ and the exact $\ln \frac{S}{S_T} f$ numerically evaluated by the methods described in the preceding section.

Evaluation of the sextuple integrals and four-fold summations turns out to be very time consuming. In particular, retention of the small χ_e value for the bending mode of CO_2 in the summation in Eq. (106) requires more computer CPU time than we can handle. For instance, a calculation of one value of $Q_{\text{qm}}^{\text{anh}}$ with $\chi_e(\text{bending}) = -0.23$ at $T = 300^\circ\text{K}$ would have taken 200 minutes of the IBM 370-168 CPU time.

Since the purpose of this phase of calculation is merely to show the precision of the newly developed approximation, I chose to use a value of the anharmonicity constants for the degenerate bending mode which is ten times larger than the reported real value, while I retained the real values for the anharmonicity constants of the symmetric and antisymmetric modes. For the temperature of 300°K , I obtain the results reported in Table 24.

The percentage error for anharmonic $\ln \frac{S}{S_T} f$ has been halved from 1.3%, the value obtained by the ordinary ZPE correction, to 0.6%, the value achieved by the present method. The value of 0.1751 consists of the contribution of the harmonic approximation = 0.1773, the Morse potential

TABLE 24. $\ln \frac{S}{S^*}$ f for a model 3-D system.

Exact	Harmonic	Anharmonic	Anharmonic with ordinary ZPE correction
0.1741	0.1773	0.1751	0.1763
Inputs:			
$\omega_1' = 1349.97,$	$\chi_{11}' = -2.38$		$\omega_1 = 1349.97, \chi_{11} = -2.38$
$\omega_2' = 2395.89,$	$\chi_{22}' = -12.4$		$\omega_2 = 2327.41, \chi_{22} = -11.64$
$\omega_3' = 674.85,$	$\chi_{33}' = -2.3$		$\omega_3 = 655.65, \chi_{33} = -2.2$
$F_{133}' = 69.84$			$F_{133} = 67.86$
$F_{122}' = -245.53$			$F_{122} = -238.54$
$\chi_{12}' = -18.5$			$\chi_{12} = -18.05$
$\chi_{13}' = 1.01$			$\chi_{13} = 0.99$
$\chi_{23}' = -12.61$			$\chi_{23} = -11.82$

All above units for inputs are in cm^{-1} .

correction terms = -0.0011, the quantum off-diagonal cubic terms = -0.0015, and the classical off-diagonal cubic terms = 0.0004. The ordinary anharmonicity correction is similar in magnitude to the Morse potential correction and it is -0.0010 in this case. The marked improvement of $\ln \frac{s}{s_r}$ (anharmonic) over $\ln \frac{s}{s_r}$ (harmonic) and $\ln \frac{s}{s_r} f$ (ordinary correction) is the consequence of the inclusion of off-diagonal cubic terms that are not always negligible.

CHAPTER V

POSSIBLE FURTHER STUDIES

My goal of obtaining a better approximation for the reduced partition function of polyatomic systems has been accomplished. As one can readily observe, to arrive at the exact $\ln \frac{S}{S^*} f$ requires lengthy computer calculation whereas to obtain the approximate $\ln \frac{S}{S^*} f$ takes much less CPU time. More important is the physical insight that one can obtain by using the approximation method. One can investigate the interplay of contributions of terms in $\ln \frac{S}{S^*} f$ derived from quadratic and cubic force constants. The extent to which the diagonal approximation is valid will be an interesting problem that one can investigate. Another area that deserves further studies is the relative importance of the off-diagonal cubic terms in contributing to $\ln \frac{S}{S^*} f$, which would pinpoint the important sources of anharmonicity correction for the thermodynamic functions.

Another important step forward is to re-examine the potential function of the anharmonic polyatomic systems and include the quartic terms in the framework of the perturbation theory. But this will be a big challenge due to the complexity of the calculation involved.

I am impressed by the interests of physicists in the

investigation of the anharmonic oscillator^{19,20} because the anharmonic oscillator is a simple model field theory in one-dimensional space-time and the properties exhibited by this model may give some indication of the analytic structure of a more realistic field theory. The same importance can be ascribed to a model anharmonic oscillator in understanding isotopic related studies.

VI APPENDIX

FOREWORD

In the course of doing this research I have looked into the possibilities of using the Padé Approximant and orthogonal series as the approximation methods. In the Appendix, Sections A and B, some results are reported. In Section C I present some key formulae from Nielsen's paper. In Section D the essential details for simplification of the second order perturbation terms are presented. Section E contains listings of computer programs. These programs take ω_i 's, X_{ij} 's, F_{ijk} , oK as input and calculate $\ln \frac{S}{S^*} f$ (exact), $\ln \frac{S}{S^*} f$ (anh), $\ln \frac{S}{S^*} f$ (harm) by using methods developed in the preceding chapters.

A. PADE APPROXIMANT

The classical partition function of a Morse oscillator, Q_{cl}^{anh} , is given by Eq. (7). Substitution of Eq. (41) into Eq. (7) yields

$$Q_{cl}^{anh} = \frac{2}{u_e} e^{-p^2} \sum_{k=0}^{\infty} \frac{p^{2k+2}}{(2k+1)k!} \quad (108)$$

It can be shown that this Q_{cl}^{anh} tends to Q_{cl}^{harm} as $p \rightarrow \infty$, as expected. A computer program is written to compare the series obtained in Eq. (107) with the exact value and Eq. (108)

converges to the exact values as expected.

The Padé approximant is originally intended to be used to effect a more rapid convergence. A function may be evaluated from a sequence of rational fractions, called the Padé approximant.²¹ This method often evaluates functions beyond the radius of convergence of the corresponding infinite series (if divergent).

Let

$$f(x) = \sum_{n=0}^{\infty} a_n x^n \quad [a_0 \neq 0] \quad (109)$$

Then, the Padé approximant is expressed as

$$f(x) = \frac{\sum_{n=0}^j \alpha_n x^n}{\sum_{n=0}^k \beta_n x^n} + O(x^{j+k+1}), \quad (110)$$

where the coefficients α_n and β_n can be defined by solving

$$f(x) \cdot \sum_{n=0}^k \beta_n x^n - \sum_{n=0}^j \alpha_n x^n = O(x^{j+k+1}), \quad (111)$$

in which the higher order terms have been neglected.

To generalize this process, a function may be evaluated as the root of a quadratic equation

$$f^2(x) \sum_{n=0}^{\ell} \gamma_n x^n + f(x) \sum_{n=0}^k \beta_n x^n + \sum_{n=0}^j \alpha_n x^n = 0 \quad (x^{j+k+\ell+2}) \quad (112)$$

where I again neglect the higher order terms. According to R. Shafer,²² the "quadratic" approximation is an attractive alternative to the Padé approximant if convergence of the Padé approximation is not rapid.

By applying the Padé approximant to our expansion of Eq.(108) with the objective of effecting a more rapid convergence, I have found that the Padé approximant outperforms the corresponding truncated series, Eq.(108), by a little, but not as fast as I would like it to be: Figures 9,10,11 show plots of the percent errors that the three-five-, and nine-term expansion of Eq.(108) will respectively yield as a function of ρ . Those figures also show plots of percent errors that the Padé approximants $P[1,1]$, $P[2,2]$, and $P[4,4]$ would respectively yield. A Padé approximant $P[n,n]$, which contains $2n+1$ adjustable parameters, should be compared to the $(2n+1)$ -term expansion of the type of Eq.(108). For a less than 0.01% accuracy, Padé $P[5,5]$ holds on until $\rho = 2.1$, while the corresponding eleven term series holds on until $\rho = 1.8$. Padé $[10,10]$ holds on until $\rho = 3.2$ as compared with $\rho = 2.9$ for the 21-term series. I also notice that the roll-off characteristic of Padé for this case is

very abrupt, compared to the smooth and slow roll-off of the truncated integration-by-parts series.

Since the diagonal Padé element is of more interest than the off-diagonal ones, no effort is made to calculate the off-diagonal Padé elements.

A computer program is written in which the quadratic approximation method is used in our problem in a rather simple case;

$$f^2(x)(\gamma_0 + \gamma_1 x + \gamma_2 x^2) + f(x)(\beta_0 + \beta_1 x) + (\alpha_0 + \alpha_1 x + \alpha_2 x^2) = O(x^7) \quad (113)$$

We find that no significant improvement can be obtained by the quadratic approach.

B. ORTHOGONAL POLYNOMIAL

Here I investigate further another method, the τ method, which is found to be satisfactory at large values of p .

In the τ -method,²³ one sets up a differential equation pertinent to a given approximation problem, and admits an error term to the differential equation. The error term is set to be proportional to an orthogonal polynomial. A series solution for such a modified differential equation, with the error term, is then obtained. The proportionality constant for the error term, τ , is undetermined a priori but is evaluated later in connection with certain boundary conditions. The net effect of the τ -method is to spread out

the error of approximation throughout a certain range of expansion, rather than achieving a high degree of accuracy near one point at the expense of poorer results from the center of expansion. The τ -method has been successfully applied to^{13,14} the problem of approximation of the reduced partition function ratio, $\ln \frac{S}{S^*} f$, for systems of harmonic oscillators. It is, therefore, a natural extension to attempt an application of τ -method to the present problem.

Our purpose here is to find an approximation for the inner integral of γ_{c1} , Eq.(12). Set

$$\int_0^{y_2} e^{-t^2} dt = e^{-y_2^2} f(y_2) = e^{-y_2^2} \sum_{i=1}^n a_i y_2^i \quad (114)$$

Since the left-hand side of Eq.(114) is an odd function of y_2 , we seek the right-hand side of Eq.(114) containing only odd i -terms. Eq.(114) can be rewritten as

$$f(x) = e^{\rho^2 x^2} \int_0^{\rho x} e^{-t^2} dt \quad (115)$$

where

$$x \equiv \frac{y_2}{\rho} \quad (116)$$

Then we have

$$0 \leq x \leq 1 \quad (117)$$

Differentiating Eq. (115) with respect to x , we get

$$\frac{df(x)}{dx} - 2\rho^2 x f(x) - \rho = 0 \quad (118)$$

Inserting the error term into Eq. (118),

$$f' - 2\rho^2 x f - \rho = \tau T_{n+1}(x) \quad (119)$$

where $T_{n+1}(x)$ is the Chebyshev polynomial of $(n+1)$ -th order, which is defined in $0 \leq x \leq 1$:

$$T_{n+1}(x) = \sum_{i=0}^{n+1} C_{n+1}^i x^i \quad (120)$$

Only odd n 's are employed in the above equation. A series solution of Eq. (119) in the form of

$$f(x) = \sum_{i=1}^n a_i x^i \quad (121)$$

leads to

$$\gamma_{cl} = \frac{2e^{-\rho^2} \sum_{k=0}^{\frac{n-1}{2}} \frac{\rho^{2k+2}}{(2k+1)k!} \sum_{i=k+1}^{\frac{n+1}{2}} J_n^i(\rho)}{C_{n+1}^0 + \sum_{i=1}^{\frac{n+1}{2}} J_n^i(\rho)} \quad (122)$$

where

$$J_n^i(\rho) \equiv \frac{(2i-1)!}{(i-1)! 2^{2i-1}} \rho^{-2i} C_{n+1}^{2i} \quad (123)$$

The error of the above approximation, Eq.(122), is found to oscillate as expected. However, the approximation of Eq.(122) has at least one singular point, due to the alternating signs of C_{n+1}^j . The approximation is, therefore, found unsatisfactory after the first such singular point, and such points are generally at values of ρ which are smaller than the corresponding values of ρ for the 1% accuracy quoted for the approximation of γ_{cl} .

C. NIELSEN'S RESULT

Nielsen has derived relationships, correct through second-order of approximation, relating the vibrational energies and rotational constants to the cubic and quartic terms in the potential energy expressed in normal coordinate space. In the absence of resonance, the vibrational frequencies are given, in the notation of Ref. 16, Eq.(34.12), by:

$$\begin{aligned} E_{\text{vib}}/hc &= E_0/hc + \sum_s \omega_s (v_s + \frac{1}{2} g_s) \\ &+ \sum_s \sum_{s'} \chi_{ss'} (v_s + \frac{1}{2} g_s) (v_{s'} + \frac{1}{2} g_{s'}) + \end{aligned}$$

$$+ \sum_{t, t'} \chi_{l_t l_{t'} l_t l_{t'}} \quad (124)$$

where

$$\chi_{ss} = \frac{1}{4} \left[6k_{ssss} - 15 \left(\frac{k_{sss}^2}{\omega_s} \right) - \sum_{s'} \left(\frac{k_{sss'}^2}{\omega_{s'}} \right) \frac{8\omega_s^2 - 3\omega_{s'}^2}{4\omega_s^2 - \omega_{s'}^2} \right], \quad (125)$$

$$\begin{aligned} \chi_{ss'} &= \frac{1}{2} \left[k_{ssss's'} - 6 \left(\frac{k_{sss} k_{ss's'}}{\omega_s} \right) - 4k_{ssss'}^2 \left(\frac{\omega_s}{4\omega_s^2 - \omega_{s'}^2} \right) - \sum_{s''} \left(\frac{k_{sss''} k_{s''s's'}}{\omega_{s''}} \right) \right. \\ &\quad \left. - \sum_{s''} \left(\frac{k_{ss's''}^2}{2(g_s + g_{s'} - 2)!} \right) \omega_{s''} \right. \\ &\quad \left. \left(\frac{\omega_{s''}^2 - \omega_s^2 - \omega_{s'}^2}{(\omega_s + \omega_{s'} + \omega_{s''})(\omega_s + \omega_{s'} - \omega_{s''})(\omega_s - \omega_{s'} + \omega_{s''})(\omega_s - \omega_{s'} - \omega_{s''})} \right) \right. \\ &\quad \left. + \left(\frac{2}{g_s g_{s'}} \right) \sum_{\alpha} \sum_{\sigma \sigma'} (\xi_{s\sigma s' \sigma'}^{(\alpha)})^2 B_{\sigma}(\alpha \alpha) \left(\frac{\omega_{s'}}{\omega_s} \right) \right]. \end{aligned}$$

(126)

$$\chi_{l_t l_t} = \frac{1}{4} \left\{ 2k_{tttt} + \sum_{s'} k_{tts'}^2 \left[\omega_{s'} / (4\omega_t^2 - \omega_{s'}^2) \right] \right\} \quad (127)$$

and

$$\begin{aligned} \chi_{l_t l_{t'}} = & \frac{1}{2} \sum_{s''} (k_{tt's''})^2 \\ & \frac{\omega_t \omega_{t'} \omega_{s''}}{(\omega_t + \omega_{t'} + \omega_{s''}) (\omega_t + \omega_{t'} - \omega_{s''}) (\omega_t - \omega_{t'} + \omega_{s''}) (\omega_t - \omega_{t'} - \omega_{s''})} \\ & + \sum \frac{1}{2} (Be^{(\alpha\alpha)}) (\xi_{t_1 t'_1}^{(\alpha)} \xi_{t_2 t'_2}^{(\alpha)} - \xi_{t_1 t'_2}^{(\alpha)} \xi_{t_2 t'_1}^{(\alpha)}) \end{aligned} \quad (128)$$

The sum over σ indicates a sum over the components of a degenerate vibration and the index t takes on those values of s corresponding to doubly degenerate vibrations. $\xi_{s\sigma s'\sigma'}^{(\alpha)}$ is the Coriolis coupling factor: l_s is the quantum number of total vibrational angular momentum associated with a two- or three-fold degenerate vibration; $Be^{(\alpha\alpha)}$ is reciprocal of inertia $(h/8\pi^2 I_{\alpha\alpha}^{(e)} c)$.

For calculation, all data for ω_2 are taken from Ref. 18.

D.

In evaluating Eq. (90) we have used the relationship¹⁰

$$e^a b e^{-a} = b + [a, b] + \frac{1}{2!} [a, [a, b]] + \dots \quad (129)$$

where a, b are operators.

For a simple illustration, let

$$\begin{aligned} a &= \frac{\beta t}{2} [\omega_i (a_i a_i^\dagger + a_i^\dagger a_i)] \\ &= \frac{\beta t}{2} [\omega_i (2a_i^\dagger a_i + 1)] \end{aligned} \quad (130)$$

$$b = a_i a_j \quad (131)$$

Then we have, by employing Eq. (129)

$$\begin{aligned} e^a b e^{-a} &= a_i a_j + \frac{\beta t}{2} [2\omega_i (a_i^\dagger a_i a_i a_j - a_i a_j a_i^\dagger a_i)] \\ &= a_i a_j + \frac{\beta t}{2} [2\omega_i (a_i^\dagger a_i a_i a_j - a_i a_i^\dagger a_i a_j)] \\ &= a_i a_j - \beta t \omega_i a_i a_j + \frac{(\beta t)^2}{2} \omega_i^2 a_i a_j + \dots \\ &= a_i a_j e^{-\beta t \omega_i} \end{aligned} \quad (132)$$

Likewise, it can be shown that if $b = a_i^\dagger a_j^\dagger$ instead of $b = a_i a_j$, then

$$e^a b e^{-a} = a_i^\dagger a_j^\dagger e^{\beta t \omega_i} \quad (133)$$

By applying the above method and recalling that all terms with uncompensated raising or lowering operators will give zero when averaged in a state $\langle n_1 n_2 \dots n_n |$, we arrive at Eq. (90).

From the relationship $a_i^\dagger a_i |n_i\rangle = n_i |n_i\rangle$ and $n_i = \frac{1}{e^{\beta \hbar \omega_i} - 1}$,²⁴ we can simplify Eq. (90) to Eq. (91) with the help of Eq. (93).

E. LISTINGS OF COMPUTER PROGRAMS

```

1. // JOB 'MMNMMN', REGION=140K, TIME=9
2. // *MAIN LINES=3
3. //PHOC EXEC FORTGCC
4. //FORT.SYSORINT NO DUMPT, DCB=(RECF=FB, LRECL=120, BLKSIZE=1920)
5. //FORT.SYSIN NO *
6. C PROGRAM FFXACT FOR 2-D SYSTEM
7. C Q-QM AND Q-CL WILL BE CALCULATED EXACTLY AND LN(S/S) IF
8. C EQUALS (Q-QM/Q-CL)/(Q-QM/Q-CL)
9.
10. IMPLICIT REAL*8(A-H,O-Z)
11. DIMENSION G122(20), G122P(20), W120(1), QM(20), QMPP(20), C1(20), C2(20)
12. 1) V(2,20), YP(12,20), ALPHA1(20), ALPHA2(20), FSU2(20), FSU2P(20)
13. DIMENSION YNP(12,20), X(2,20), WF(2,20), TNPUP(12,20), XP(12,20), WEP(12,20), QUOT(20), QUOP(20), EXACT(20)
14. DIMENSION FSUB(20), F11(20), F11P(20), F11PP(20), EHP(20),
15. X12(20), X2P(12,20), Y12(20), Y12P(12,20), EHQ(20), EHP(20), T(2,20), TP12(20), ALF1P(20), ALF2P(20), F122(20), F122P(20), PEN(20), PENP(20)
16. DIMENSION FPI(20), F(20), PERHAR(20), PFRANH(20), AT(20), ET(20), DT(20)
17. 1311 READ(5,300) INDEX, NP, F112, F222, TEMP
18. 300 FORMAT(12I3, 4F8.3)
19. HC=6.62559D-27*9979240-17
20. VALKT=1.36054D-16*TEMP
21. IF (INDEX+1) 200, 311, 200
22. 311 WRITE(6,313) INDEX, NP, F112, F222, TEMP
23. 313 FORMAT(11H1, ' INDEX= ', I3, ' NUMBER OF POINTS = ', I3, ' F112= ', F8.3,
24. 2' F222= ', F8.3, ' TEMP= ', F8.3)
25. DO 305 J=1, NP
26. READ(5,307) (WEP(I,J), XP(I,J), WE(I,J), X(J,I), J=1, 21)
27. 307 FORMAT(4F17.5)
28. 305 CONTINUE
29. DO 309 J=1, NP
30. PEN(1)=4.0*WE(1,1)+2*WE(1,1)+2)/10.0*WE(2,1)+2-3.0*WE(1,1)+2)
31. PENP(1)=(4.0*WEP(1,1)+2*WEP(1,1)+2)/10.0*WEP(12,1)+2-3.0*WEP(1,1)+2)
32. F122(1)=OSQRT(4.0*X(2,1)*WE(2,1)*WE(1,1)+PEN(1))
33. F122P(1)=OSQRT(4.0*XP(12,1)*WEP(2,1)*WEP(1,1)+PENP(1))
34. 309 CONTINUE
35. DO 601 J=1, NP
36. DO 601 J=1, 2
37. TNPUP(J,1)=WE(J,1)/VALKT/HC
38. YNPUP(J,1)=WEP(J,1)/VALKT/HC
39. Y1(J,1)=-X(J,1)*WF(J,1)+HC/VALKT
40. YP(J,1)=-70*Y(J,1)+WEP(J,1)*(HC/VALKT)
41. T(J,1)=-X(J,1)*WE(J,1)
42. TP(J,1)=YP(J,1)+FPI(J,1)
43. F122P(1)=F122*WEP(1,1)/WE(1,1)
44. 601 CONTINUE
45. CONST=8.0D0*(3.14159D0**2)*2.9979D10/6.6262D-27
46. CONST=OSQRT(CONST)
47. DO 512 I=1, NP
48. FSUB(1)=(F112**2/WE(2,1))+(8.0*WE(1,1)+2-3.0*WE(2,1)+2)/14.0*WE(1,1)+2*WF(2,1)+2)
49. FSUBP(1)=(F112P**2/UFPI(2,1))+(8.0*WEP(1,1)+2-3.0*WEP(12,1)+2)
50. 4)/14.0*WEP(1,1)+2*WEP(12,1)+2)
51. DU=WE(1,1)/15.0D0
52. HUP(1)=FPI(1,1)/15.0D0
53. F11(1)=OSQRT(4.0D0*TP(1,1)+DU-FSUB(1)+DU)
54. F11P(1)=OSQRT(4.0D0*TP(1,1)+DU-FSUBP(1)+DU)
55. FSU2(1)=F122(1)+2*WE(1,1)+(8.0*WE(2,1)+2-3.0*WE(1,1)+2)/(4.0*WE(2,1)+2*WF(1,1)+2)
56. FSU2P(1)=F122P(1)+2*WEP(1,1)+(8.0*WEP(12,1)+2-3.0*WEP(1,1)+2)/(4.0*WEP(12,1)+2*WEP(1,1)+2)
57. 512 CONTINUE
58. 512 CONTINUE

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63.      DUF=WF(2,1)/15.000
64.      DUFF1=LFPI(2,1)/15.000
65.      F222PI=0.000
66.      ALPHA1(1)=DSORT(4,0+3,14159+X(1,1))
67.      ALPHA2(1)=DSORT(4,0+3,14159+X(2,1))
68.      ALF1P(1)=XDSORT(4,0+3,14159+XPI(1,1))
69.      ALF2P(1)=DSORT(4,0+3,14159+XPI(2,1))
70.      C      WRITE(6,702) ALPHA1(1),ALPHA2(1),F111(1),F111P(1),F122(1),F122P(
71.      C      1111
72.      702      FORMAT(///,' ALPHA1(2), F111,PI, F122,PI ARE ',6F14,3)
73.      X12(1)=0.500+((-6.000+F111(1)+F122(1)/WE(1,1))-4.000*(F112+*2)*WE(
74.      S1,1)/4.000+WE(1,1)+*2-WE(2,1)+*2))
75.      1      +0.500+((-6.000+F222+F112/WE(2,1))-4.000*(F122(1)+*2)*WE(
76.      S2,1)/4.000+WE(2,1)+*2-WE(1,1)+*2))
77.      X12P(1)=0.500+((-6.000+F111P(1)+F122P(1)/WEPI(1,1))-4.000*(F112
78.      SP1+*2)*WEPI(1,1)/4.000+WEPI(1,1)+*2-WEPI(2,1)+*2))
79.      1      +0.500+((-6.000+F222P+F112P/WEPI(2,1))-4.000*(F122P(1)
80.      SP1+*2)*WEPI(2,1)/4.000+WEPI(2,1)+*2-WEPI(1,1)+*2))
81.      WRITE(6,713) 1,X12(1),X12P(1)
82.      713      FORMAT(//,' 1,X12,X12P ARE ',3F14,2E14,5)
83.      SUM=0.0
84.      C2(1)=1.000-X(2,1)/(2.000+X(2,1))
85.      NC2PI=11.000-XPI(2,1)/12.0+XPI(2,1)
86.      NC2=C2(1)
87.      V12(1)=X12(1)*(HC/VALKT)
88.      V12P(1)=X12P(1)*(HC/VALKT)
89.      DO 901 N2=1,NC2
90.      V22=V2+1.000+0.500-1.000
91.      C1(1)=WE(1,1)+X(1,1)*WE(1,1)+X12(1)+V22/(2.0+X(1,1))*WE(1,1)
92.      HC=C1(1)
93.      DO 901 N1=1,NC1
94.      V11=V1+1.000+0.500-1.000
95.      CH(1)=YHPU(1,1)+V1)+YHPU(2,1)+V22+Y(1,1)+V11+*2+Y(2,1)+V22+*2+V12(
96.      S1)+V11+V22
97.      CHECK=C1(1)
98.      IF(CHECK-70) 405,409,401
99.      405      SUM=SUM+DEXP(-CH(1))
100.      401      CONTINUE
101.      RH01=0.500+DSORT(YHPU(1,1)/X(1,1))
102.      RH02=0.500+DSORT(YHPU(2,1)/X(2,1))
103.      C      WRITE(6,703) VALKT,RH01,RH02
104.      703      FORMAT(///,' KT= ',E16,5,' RH01= ',E16,5,' RH02= ',E16,5)
105.      G112=HC+F112/(1+ALPHA1(1)+*2+ALPHA2(1)+VALKT+RH01)+*2+RH02)*DSORT(8
106.      1,000)
107.      G122(1)=HC+F122(1)/(1+ALPHA2(1)+*2+ALPHA1(1)+VALKT+RH02)+*2+RH01)*D
108.      SSORT(10,000)
109.      C708      WRITE(6,701) G112,G122(1)
110.      701      FORMAT(///,' G112= ',F15,5,' G122= ',E15,5)
111.      707      CALL QUAD(1,RH01,RH02,G112,G122,W)
112.      EHM(1)=0.500*(YHPU(1,1)+YHPU(2,1))+0.2500*(YHPU(1,1)+Y(1,1)/WE(1,1)
113.      1)+YHPU(2,1)+Y(2,1)/WE(2,1)+YHPU(1,1)+V12(1)/WE(1,1))
114.      GDM(1)=SUM
115.      QUO(1)=1(YHPU(1,1)+YHPU(2,1))+GDM(1)/W(1)
116.      SUM=0.0
117.      DO 507 N2=1,NC2PI
118.      V22=V2+1.000+0.500-1.000
119.      NC1P(1)=WEPI(1,1)+XPI(1,1)+WEPI(1,1)+X12P(1)+V22/(2.0+XPI(1,1))*WE
120.      1P(1,1)
121.      DO 507 N1=1,NC1PI
122.      V1)=V1+1.000+0.500-1.000
123.      EHP1(1)=YHPUPI(1,1)+V11+YHPUPI(2,1)+V22+YPI(1,1)+V11+*2+YPI(2,1)+V
124.      522+*2+V12P(1)+V11+V22
125.      CHECK2=EHPI(1)
126.      IF(CHECK2-70) 505,505,507
127.      505      SUM1=SUM1+DEXP(-EHPI(1))
128.      507      CONTINUE

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195. 6035 CONTINUE
196.  WRITF(6,6041)
197. 6041 FORMAT(1X,9(1,620) ' IS IN 0 N, 6E'S AND F'S IN CM-1. THE REST ARE
198. 1 DIMENSION(ESS)
199.  GO TO 131)
200. 200 CALL FIT
201.  END
202.  SUBROUTINE QUAD(I1,N,R2,G112,G122,W1
203. C SUPROUTINE TO INTEGRATE QUAD INTEGRAL
204. IMPLICIT REAL*8(A-H,O-Z)
205. C OCL : FOR COMPUTING THE ANHARMONICITY CORRECTION FACTOR FOR
206. C R(CL,FXACT), A FUNCTION OF RHO AND GAMMA - A 2-D SITUATION
207. DIMENSION G122(20),W(20),NUP(12),NDOWN(12)
208.  U=1.000
209.  P(=).772454851
210.  N=4
211.  NUP(1)=100
212.  NUP(2)=100
213.  NUP(3)=100
214.  NDOWN(1)=1000
215.  NDOWN(2)=200
216.  NDOWN(3)=200
217.  NUP(4)=2000
218. 60 CONTINUE
219.  IF(N-2,3) 2,2,3
220.  2 NDOWN(4)=500/100.0-3.0*R*R)
221.  GO TO 10
222.  3 NDOWN(4)=7.0+R
223.  WRITF(6,311) N,U,H,G112,G122(1),R2
224. 311 FORMAT(1/, ' N,U,R,G112,G122,N2 ARE ',13.5E12.3)
225.  10 CALL SUBCLP(1,N,U,R,G112,G122,R2,NUP,NDOWN,R,C1,C2)
226.  W(1)=C1
227.  WRITE(6,3002) I,W(1)
228. 3002 FORMAT(1H0,' I = ',13,' C1 = ',F16.7)
229.  RETURN
230.  END
231.  SUBROUTINE SUBCL2(11,N,U,H,G112,G122,R2,N1,N2,A,B,C)
232.  IMPLICIT REAL*8(A-H,O-Z)
233.  C INPUT: U=1, R=0.5*SQRT(U/X1) N=NO. OF SUBRANGES
234.  C IN EACH OF WHICH THE RANGE IS EQUALLY DIVIDED: N2(1)=NO. OF
235.  C EQUAL INTERVALS IN 1-TH RANGE;N2(1)=NO. INTO WHICH R*LN2
236.  C IS DIVIDED TO OBTAIN EQUAL INTERVALS IN 1-TH SUBRANGE
237.  C SUBCLS WILL BE CALLED TO EVALUATE THE INNER INTEGRALS .
238.  OBTAIN AN F(22(20),N1(12),N2(12)
239.  STOP*1.00-7
240.  N=4
241.  P(=).772453451
242.  CALL FRFH(R,TTMAX)
243.  TTSTOP =TVMAY*STOP
244.  S=0.000
245.  RR=R*OLOG(2.000)
246.  X=-RR
247.  C FOR EVERY SUBRANGE1
248.  DO 100 I=1,0
249.  DX=RR/ND(1)
250.  X=X+DX/2.000
251.  NR=N1(1)
252.  C FOR EVERY SUBDIVISION1
253.  DO 50 J=1,NR
254.  IF IX/R-100)2,1,1
255.  1 V=1.000
256.  Y=0.000
257.  GO TO 7
258.  2 V=1.000-(EXP(-X/X))**2
259.  Y=Y+V*P(1,ND0-V)
260.  50

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261.      IF(VAR-100) 3,3,7
262.      3 CX=DEXPI-VPR
263.      IF(Y-1.00+30/E) 7,4,4
264.      4 CALL FNFPI(Y,C)
265.      CALL SUBCLS(I,N,R,X,G112,G122,VPR,R2,M1,M2,A1,B1)
266.      YY=I+M1
267.      GO TO 10
268.      7 YY=0.000
269.      10 CONTINUE
270.      S=S+YY*CX
271.      X=X+CX
272.      IF(I-M) 50,20,200
273.      200 CALL FXIF
274.      20 IF(YY-YYSTOP) 150,150,50
275.      50 CONTINUE
276.      X=X+CX/2.000
277.      100 CONTINUE
278.      S=S+1.0010
279.      150 H=S/PI
280.      C WRITE(6,205) B,S
281.      205 FORMAT(7,' B AND S =',2E14,4)
282.      A=1.000/U
283.      C=1.000+0.500/(B+H)
284.      RETURN
285.      END
286.      SUBROUTINE SUBCLS(I,N,R,X1,G112,G122,VPR,R2,M1,M2,A1,B1)
287.      C SUBCLS TAKES CARE OF THE INNER INTEGRAL
288.      IMPLICIT REAL*8(A-H,O-Z)
289.      C INPUT: U=1, R=0.5*SQRT(U/X), N=NO. OF SUBRANGES
290.      C IN EACH OF WHICH THE RANGE IS EQUALLY DIVIDED; M1(I)=NO. OF
291.      C EQUAL INTERVALS IN 1-TH RANGE; R2(I)=NO. INTO WHICH R+LN2
292.      C IS DIVIDED TO OBTAIN EQUAL INTERVALS IN 1-TH SUBRANGE
293.      C SUBCLS WILL BE CALLED TO EVALUATE THE INNER INTEGRALS.
294.      DIMENSION G122(20),M1(12),M2(12)
295.      STOP=1.00-7
296.      N=N
297.      M1=1.772453851
298.      IF(R.F0,R2) GO TO 110
299.      IF(R2-2.3) 21,21,25
300.      21 M2(1)=500/(4A.0-3.0*R2+R2)
301.      GO TO 110
302.      25 M2(1)=7.0+R2
303.      110 CALL ERFN(R2,YYMAX)
304.      CALL NEWTON(I,N,X1,G112,G122,R2,RMAX)
305.      YYSTOP=YYMAX+STOP
306.      S=0.000
307.      RR=R2+LOG(2.000)
308.      X=-RR
309.      C FOR EVERY SUBRANGE
310.      DO 100 I=1,N
311.      IF(I-4) 30,35,35
312.      35 IC=G122(I)+X
313.      IF(IC-0.050) 37,30,30
314.      37 CONTINUE
315.      IF(HMAX.GT.200) GO TO 30
316.      DX=HMAX/0.111
317.      GO TO 32
318.      30 DX=RR/R2(1)
319.      32 X=X+DX/2.000
320.      H=M1(1)
321.      C FOR EVERY SUBDIVISION
322.      DO 50 J=1,H
323.      IF(X/R2-100) 2,2,1
324.      1 V=1.000
325.      Y=0.000

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327.      2 V=1.000-DEXP(-X/42)**2
328.      V1=1.000-DEXP(-X1/41)**2
329.      Y=DSQNTIP2*R2*(1.000-V)
330.      YH=R2*R2*(1.000-V)-G112*X*X1*X1-G122(11)*X*X1
331.      YR=R2*R2*(1.000-V)
332.      IF(YH.GE.YR) GO TO 300
333.      IF(YH.LE.1.00-30) GO TO 300
334.      YL=R2*R2*(1.000-11.000-DEXP(-RMAX/R2)**2)-G112*X1*X1-RMAX-G122(11)
335.      Z1=RMAX+RMAX*X1
336.      IF(V1.LE.0.0) GO TO 300
337.      Y=DSQNT(YL)
338. 300 CONTINUE
339.      VHR2=V+92*R2
340.      CHEK=VHR+VHR2+G112*X*X1+X1+G122(11)*X*X1
341.      IF(CHEK-100) 3.3.7
342.      3 YJ=VHR-VHR2-G112*X*X1-X1-G122(11)*X*X1
343.      IF(YJ.GT.0.0) GO TO 301
344.      EX=DEXP(YJ)
345.      IF(Y-1.00-30/EX) 7.14.14
346. 14 TEST=G122(11)*X1
347.      IF(TEST-0.000) 4.4.4
348.      4 CALL ERFN(Y.F)
349.      GO TO 43
350.      44 E=0.5*PI
351.      45 TY=E*FX
352.      GO TO 10
353.      7 TY=0.000
354. 10 CONTINUE
355.      S=5*TY*TX
356.      XX=X+TX
357.      IF(1-N) 50.20.200
358. 301 WRITE(16,310) YJ
359.      310 FORMAT(1,' OFF-DIAG TERMS TOO LARGE ',E14.4)
360. 200 CALL EXIT
361.      20 IF(TY-YYSTOP) 150.150.50
362.      50 CONTINUE
363.      X=X+TX/2.000
364. 100 CONTINUE
365.      WRITE(16,350) TY,YYSTOP
366.      350 FORMAT(1,' TY AND YSTOP ARE ',2E16.7)
367.      S=5*1.0010
368. 150 01=S/PI
369.      A1=1.000/U
370.      C1=1.000+0.500/(K2+R2)
371.      RETURN
372.      END
373.      SUBROUTINE ERFN(Y,E)
374.      IMPLICIT REAL*8(A-H,O-Z)
375.  C FOR EVALUATING THE ERROR FUNCTION F=ERF(X) AS
376.  C E=ERF(X)*P(1,4141...+K1 + 1 , SEE ARAMOWITZ ,
377.      X=1.41421356*Y
378.      AX=DABS(X)
379.      T=1.000/11.000+0.2316*1900*AX
380.      IF(X-X-100112.11.11
381. 11 D=0.000
382.      P=1.000
383.      GO TO 13
384. 12 CONTINUE
385.      Q=0.5989922804*DEXP(-X*X/2.000)
386.      P=1.000-D*T+11(41.330279429+1-1.0212559781+T+1.7614779391+T*
387.      10.3565637021+T+0.51938153)
388. 13 CONTINUE
389.      IF(AX) 1.2.2
390.      1 P=1.000-P
391.      2 IF(P) 3.5.5
392.      3 WRITE(16,300)

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391. 3001 FORMAT(35H0 TROUBLE IN DISTRIBUTION FUNCTION.)
392. 4 VRTIF(6,3002) 3,P
393. 3002 FORMAT(4H X= E14.7,4H P= E14.7)
394. CALL EXIT
395. 5 F=7.000+P+1.000
396. IF(F) 6,7,7
397. 6 WRITE(6,3003)
398. 3003 FORMAT(25H0 TROUBLE IN ERROR FUNCTION.)
399. GO TO 4
400. 7 RETURN
401. END
402. SUBROUTINE LNFANH(I,TFNP,F112,F122,F112PI,F122PI,YNPU,X,YNPUP1,XPI
403. 2,EXACT,GP1,F,PERHAR,PERANH,AT,ET,DT)
404. IMPLICIT REAL*8(A-H,O-Z)
405. SUBROUTINE LNFANH
406. C LNIS/S*IF WILL BE CALCULATED IN TERMS OF LNIS/S*IFHARI
407. C * MORSE POTENTIAL CORRECTION TERMS (A'S) , CURIC OFF-
408. C DIAG TERMS (O'S) FOR OUR MODEL 2-D SYSTEM AT VARIOUS
409. C U AND X VALUES .
410. DIMENSION O(20),E(20),AT(20),U1(20),U2(20),GP1(20),EXACT(20),F(2
411. 0),EP1(20),DP1(20),U1P1(20),U2P1(20),ET(20),DT(20)
412. DIMENSION A(2,20),AP1(2,20),F(2,20),BP1(2,20),OA1(2,20),DA2(2,20),
413. 1OA3(2,20),F01(2,20),WC(2,20),WFP1(2,20),EUIPE1(2,20)
414. DIMENSION YNPUP1(2,20),YNPUP1(2,20),X(2,20),XPI(2,20),RH0(2,20),RHOP
415. 2((2,20),PR00(2,20),PR00P1(2,20),SUQ(2,20)
416. DIMENSION OAA1(2,20),OAA2(2,20),OAA3(2,20),OAA4(2,20),AA12(2,20),TEM
417. 6(2,20),TEM2(2,20),TEM1P1(2,20),TEM2P1(2,20)
418. DIMENSION GUN(20),GUNP1(20),PG(2,20),PGP1(2,20),F122(20),F122PI(20
419. 1),PERHAR(20),PERANH(20)
420. WRITE(6,161)
421. C WRITE(6,75)
422. 75 FORMAT(//////////)
423. C WRITE(6,417) 1,EXACT(1)
424. 417 FORMAT(/,' 1 = ',13,' EXACT = ',F12.4)
425. 101 FORMAT(72(' '))
426. C WRITE(6,75)
427. C WRITE(6,161)
428. HC=6.6255900+2.9979250-17
429. VALKT=1.360540+16*TEMP
430. DO 50 J=1,2
431. RH0(J,1)=0.500+OSORT(YNPUP1(J,1)/X(J,1))
432. RHNP1(J,1)=0.500+OSORT(YNPUP1(J,1)/XPI(J,1))
433. WC(J,1)=1*VALKT/HC(1+YNPUP1(J,1))
434. 50 WEP1(J,1)=1*VALKT/HC(1+YNPUP1(J,1))
435. VAL3=F112/WF(1,1)+OSORT(18.000)
436. VAR3=F122(1)/WF(2,1)+OSORT(18.000)
437. DO 15 J=1,2
438. B1(J,1)=YEP1(J,1)+X(J,1)
439. BPI(J,1)=YNPUP1(J,1)+XPI(J,1)
440. PR00(J,1)=1*YNPUP1(J,1)+DEXP(-YNPUP1(J,1)/2.000)/(1.000+DEXP(-YNPUP1(J,1)
441. 1))
442. PR00P1(J,1)=1*YNPUP1(J,1)+DEXP(-YNPUP1(J,1)/2.000)/(1.000+DEXP(-YN
443. 1PUP1(J,1))
444. OUD(J,1)=OLOG(PH0(J,1))-OLOG(PH0P1(J,1))
445. OA1(J,1)=(2.000+B1(J,1))/DEXP(YNPUP1(J,1))-1.000-(2.000+BPI(J,1))/
446. 1DEXP(YNPUP1(J,1))-1.000)
447. CHFC=YNPUP1(J,1)
448. IF(CHFC-70.000) 37,37,39
449. 37 CHFC2=YNPUP1(J,1)
450. IF(CHFC2-70.000) 47,47,39
451. 47 EUI(J,1)=DEXP(-YNPUP1(J,1)+2.000+B1(J,1))
452. EUP1(J,1)=DEXP(-YNPUP1(J,1)+2.000+BPI(J,1))
453. GO TO 30
454. 39 EUI(J,1)=0.000
455. EUP1(J,1)=0.000
456. 10 OAA1(J,1)=1+OAA2(J,1)+OAA3(J,1)+OAA4(J,1)+OAA5(J,1)+OAA6(J,1)+OAA7(J,1)+OAA8(J,1)+OAA9(J,1)+OAA10(J,1)+OAA11(J,1)+OAA12(J,1)+OAA13(J,1)+OAA14(J,1)+OAA15(J,1)+OAA16(J,1)+OAA17(J,1)+OAA18(J,1)+OAA19(J,1)+OAA20(J,1)
457.

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454. 2J,11+EUPI(J,1)*(1.000-EUPI(J,1))/(1.000-EUPI(J,1)+2)
460. 0A3(J,1)=0.500/IRHOPI(J,1)+21-0.500/IRHOPI(J,1)+21
461. C A(J,1)=1/4*(B+1)+... WILL BE BYPASSED TO ALLOW BETTER APPROX.
462. 0AA1(J,1)=11.000-DEXP(YNPU(J,1))/(1.000-EUPI(J,1))/(1.000-DEXP
463. 1-(YNPU(J,1))/(1.000-EUPI(J,1)))
464. 0AA2(J,1)=EXP(1/(J,1)+90/(J,1))/4.01
465. TEM1(J,1)=2.0/(DEXP(YNPU(J,1)-2.0+R(J,1))+2)
466. TEM2(J,1)=2.0/(DEXP(YNPU(J,1)-2.0+OP1(J,1))+2)
467. TEM2(J,1)=F0(J,1)/(1.000-CU(J,1)+2.0+CU(J,1))+2/(1.000-EU(J,1)
468. 21+21
469. TEM2P1(J,1)=EUPI(J,1)/(1.000-EUPI(J,1))+2.0+EUPI(J,1)+2/(1.000
470. 2+EUPI(J,1)+21
471. 0AA3(J,1)=11.000+R(J,1)+TEM1(J,1)+0.5+R(J,1)+2+TEM2(J,1)/(1.000+
472. 3BP(J,1)+TEMPI(J,1)+0.5+OP1(J,1)+2+TEM2P1(J,1))
473. PG(J,1)=DEXP(YNPU(J,1)+0.5+R(J,1)+0.25)/(1.000+R(J,1)+TEM1(J,1)+0
474. 2.5+BP(J,1)+2+TEM2(J,1))/(1.0+FU(J,1))
475. PBP(J,1)=DEXP(YNPU(J,1)+0.5+BP(J,1)+0.25)/(1.000+BP(J,1)+TEM
476. 2P1(J,1)+0.5+OP1(J,1)+2+TEM2P1(J,1))/(1.0-EUPI(J,1))
477. 0AA4(J,1)=11.000+0.5/IRHOPI(J,1)+21/(1.000+0.5/IRHOPI(J,1)+21)
478. C WRTF(6.519) J,0AA1(J,1),0AA2(J,1),0AA3(J,1),0AA4(J,1)
479. 919 FORMAT(1/,' DAA FOLLOW+ J=,13,9F10.4)
480. AA(J,1)=DLOG(DAA1(J,1))+DLOG(DAA2(J,1))+DLOG(DAA3(J,1))+DLOG(DAA4
481. 1(J,1))
482. C A(J,1)=0.2500*(R(J,1)+BP(J,1)+PA1(J,1)+0AA2(J,1)+0AA3(J,1)
483. 15 CONTINUE
484. GPT(1)=QUO(1,1)+QUO(2,1)
485. GUN(1)=PG(1,1)+PG(2,1)
486. GUNP(1)=PGP(1,1)+PGP(2,1)
487. VN1=DEXP(YNPU(1,1))/(DEXP(YNPU(1,1))-1.000)
488. VN11=VN1/(DEXP(YNPU(1,1))-1.000)
489. VN12=VN1*(DEXP(YNPU(1,1))+1.000)/(DEXP(YNPU(1,1))-1.000)
490. VN2=DEXP(YNPU(2,1))/(DEXP(YNPU(2,1))-1.000)
491. VN21=VN2/(DEXP(YNPU(2,1))-1.000)
492. VN22=VN2*(DEXP(YNPU(2,1))+1.000)/(DEXP(YNPU(2,1))-1.000)
493. VN1P=DEXP(YNPU(1,1))/(DEXP(YNPU(1,1))-1.000)
494. VN11P=VN1P/(DEXP(YNPU(1,1))-1.000)
495. VN12P=VN1P*(DEXP(YNPU(1,1))+1.000)/(DEXP(YNPU(1,1))-1.000)
496. 11
497. VN2P=DEXP(YNPU(2,1))/(DEXP(YNPU(2,1))-1.000)
498. VN21P=VN2P/(DEXP(YNPU(2,1))-1.000)
499. VN22P=VN2P*(DEXP(YNPU(2,1))+1.000)/(DEXP(YNPU(2,1))-1.000)
500. 11
501. U112=(DEXP(2.0+YNPU(1,1)+YNPU(2,1))-1.000)/(2.0+YNPU(1,1)+YNPU(2
502. 1))+(VN12+VN11+VN21
503. U118=(DEXP(2.0+YNPU(1,1)+YNPU(2,1))-1.000)/(2.0+YNPU(1,1)+YNPU(2
504. 1))+(VN12+VN11)+(VN21+VN2)
505. U992=(DEXP(-2.0+YNPU(1,1)+YNPU(2,1))-1.000)/(2.0+YNPU(1,1)+YNPU(
506. 2,1))+(VN12+3.0+VN11+2.0+VN1)*VN21
507. U998=(11.000-DEXP(-2.0+YNPU(1,1)+YNPU(2,1)))/(2.0+YNPU(1,1)+YNPU(2
508. 3,1))+(VN12+2.0+VN11+VN21+VN21+VN2)
509. U271=(DEXP(2.0+YNPU(2,1)+YNPU(1,1))-1.000)/(2.0+YNPU(2,1)+YNPU(1,
510. 1))+(VN22+VN21)*VN11
511. U229=(DEXP(2.0+YNPU(2,1)+YNPU(1,1))-1.000)/(2.0+YNPU(2,1)+YNPU(1,
512. 1))+(VN22+VN21)+(VN11+VN1)
513. U861=(DEXP(-2.0+YNPU(2,1)+YNPU(1,1))-1.000)/(2.0+YNPU(2,1)+YNPU(
514. 1,1))+(VN22+3.0+VN21+2.0+VN2)*VN11
515. U869=(11.000-DEXP(-2.0+YNPU(2,1)+YNPU(1,1)))/(2.0+YNPU(2,1)+YNPU(1
516. 1,1))+(VN22+3.0+VN21+VN21)+(VN11+VN1)
517. U112=(DEXP(2.0+YNPU(1,1)+YNPU(2,1))-1.000)/(2.0+YNPU(1,1)+Y
518. 2P1(J,1))+(VN12P+VN11P+VN21P)
519. U118=(DEXP(2.0+YNPU(1,1)+YNPU(2,1))-1.000)/(2.0+YNPU(1,1)+Y
520. 2P1(J,1))+(VN12P+VN11P+VN21P)+(VN21P+VN2P)
521. U992=(DEXP(-2.0+YNPU(1,1)+YNPU(2,1))-1.000)/(2.0+YNPU(1,1)+Y
522. 2P1(J,1))+(VN12P+3.0+VN11P+2.0+VN1P)+(VN21P+VN2P)
523. U998=(11.000-DEXP(-2.0+YNPU(1,1)+YNPU(2,1)))/(2.0+YNPU(1,1)+Y
524. 2P1(J,1))+(VN12P+2.0+VN1P+VN1P)+(VN21P+VN2P)

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591.      IF (P.EC.500) GO TO 12
592.      GO TO 1
593.      25 RMAX=21M1
594.      IF (RMAX.LF.0.0) GO TO 12
595.      GO TO 43
596.      12 CONTINUE
597.      C WRITE(6,15) M,21M1
598.      15 FORMAT(/,' ERROR IN CONVERGENCE P ',I4,E14.4)
599.      43 RETURN
600.      END
601.      //60.SYSIN DD *
602.      +01 9      0.0      0.0      100.0
603.      500.0      0.002      475.0      0.002
604.      3200.0      0.002      3140.0      0.002
605.      500.0      0.002      475.0      0.002
606.      3200.0      0.005      3140.0      0.005
607.      500.0      0.002      475.0      0.002
608.      3200.0      0.010      3140.0      0.010
609.      500.0      0.005      475.0      0.005
610.      3200.0      0.002      3140.0      0.002
611.      500.0      0.005      475.0      0.005
612.      3200.0      0.005      3140.0      0.005
613.      500.0      0.005      475.0      0.005
614.      3200.0      0.010      3140.0      0.010
615.      500.0      0.010      475.0      0.010
616.      3200.0      0.002      3140.0      0.002
617.      500.0      0.010      475.0      0.010
618.      3200.0      0.005      3140.0      0.005
619.      500.0      0.010      475.0      0.010
620.      3200.0      0.010      3140.0      0.010
621.      +01 9      0.0      0.0      300.0
622.      500.0      0.002      475.0      0.002
623.      3200.0      0.002      3140.0      0.002
624.      500.0      0.002      475.0      0.002
625.      3200.0      0.005      3140.0      0.005
626.      500.0      0.002      475.0      0.002
627.      3200.0      0.010      3140.0      0.010
628.      500.0      0.005      475.0      0.005
629.      3200.0      0.002      3140.0      0.002
630.      500.0      0.005      475.0      0.005
631.      3200.0      0.005      3140.0      0.005
632.      500.0      0.005      475.0      0.005
633.      3200.0      0.010      3140.0      0.010
634.      500.0      0.010      475.0      0.010
635.      3200.0      0.002      3140.0      0.002
636.      500.0      0.010      475.0      0.010
637.      3200.0      0.005      3140.0      0.005
638.      500.0      0.010      475.0      0.010
639.      3200.0      0.010      3140.0      0.010
640.      99
641.      //
642.      //

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1. // JOB 'ACTIVE', REGION=140K, TIME=7
2. // *MAIN *IMFS=3
3. // PNOG EXIT FORTGCS
4. // FORT.SYSIN ON *
5. C PROGRAM FFXACT FOR 3-D SYSTEM
6. C Q-QM AND Q-CL WILL BE CALCULATED EXACTLY AND LM45/S*IF
7. C EQUALS (Q-QM/Q-CL)/(Q-QM/Q-CL) *
8.
9. IMPLICIT REAL*8(A-H,O-Z)
10. DIMENSION G122(20),G122P(20),N(20),QRM(20),QRMPI(20),C1(20),C2(20)
11. 11,Y13(20),YPI13(20),ALPHA1(20),ALPHA2(20),FSU2(20),FSU2P(20)
12. DIMENSION YMPI(3,20),X(3,20),WE13(20),YMPI(3,20),XPI13(20),WEPI1
13. 13,20),QUO1201,QUOPI(20),EXACT(20)
14. DIMENSION FSU1(20),F111(20),FH(20),FSUBP(20),F111P(20),EHP1(20),
15. 15,X12(20),X12P(20),V12(20),V12P(20),EHO(20),EHOPI(20),T(3,20),TPI(
16. 23,20),ALF1P(20),ALF2P(20),F122(20),F122P(20),PEN(20),PENPI(20)
17. DIMENSION FH(20),F(20),PERIM(20),PENANN(20),AT(20),ET(20),OT(20)
18. DIMENSION V13(20),V23(20),V13P(20),V23P(20),ALPHA3(20),ALF3P(20)
19. 11,F31201,C3P(20)
20. DIMENSION X13(20),X13P(20),X23(20),X23P(20)
21. 1311 READ(5,300) INDEX,MP,F133,F133P,TEMP
22. 300 FORMAT(2F13,3F8,3)
23. MC=6.6255900+2.9479250-17
24. VALKT=1.300540+16*TEMP
25. IF(INDEX+1) 200,311,200
26. 311 WRITE(6,313) INDEX,MP,F133,F133P,TEMP
27. 313 FORMAT(11H1,' INDEX= ',I3,' NUMBER OF POINTS = ',I3,' F133= ',F8,3,
28. 2' F133P= ',F8,3,' TEMP= ',F8,3)
29. READ(5,1309) F122(1),F122P(1)
30. 1309 FORMAT(2F12,5)
31. WRITE(6,671)
32. 671 FORMAT(//,' * WEP) , XPI , WE , X ..125 ARE *')
33. DO 305 I=1,MP
34. DO 305 J=1,3
35. READ(5,307) WEP1(J,I),XPI(J,I),WE(J,I),X(J,I)
36. WRITE(6,307) WEP1(J,I),XPI(J,I),WE(J,I),X(J,I)
37. 307 FORMAT(4F12,5)
38. 305 CONTINUE
39. WRITE(6,672)
40. 672 FORMAT(//,' X12,X13,X23,X12P,X13P,X23P ARE *')
41. READ(5,6701) X12(1),X13(1),X23(1),X12P(1),X13P(1),X23P(1)
42. WRITE(6,5001) X12(1),X13(1),X23(1),X12P(1),X13P(1),X23P(1)
43. 6001 FORMAT(6F12,5)
44. DO 601 I=1,MP
45. DO 601 J=1,3
46. YMPI(J,I)=WE(J,I)/(VALKT/MC)
47. YMPI(J,I)=WEPI(J,I)/(VALKT/MC)
48. X1(J,I)=X(J,I)/WE(J,I)
49. XPI(J,I)=XPI(J,I)/WEPI(J,I)
50. Y1(J,I)=X1(J,I)*WE(J,I)+(MC/VALKT)
51. YPI(J,I)=XPI(J,I)*WEPI(J,I)+(MC/VALKT)
52. 601 CONTINUE
53. WRITE(6,7471)
54. 7471 FORMAT(//,' * HERE FOLLOW PAIRS OF U UPRIME 125*')
55. WRITE(6,7571) YMPI(J,I),YMPIPI(J,I),J=1,3)
56. 7571 FORMAT(//,6F12,4)
57. DO 517 J=1,MP
58. ALPHA1(J)=DSORT(4.0+3.14159*X(1,J))
59. ALPHA2(J)=DSORT(4.0+3.14159*X(2,J))
60. ALPHA3(J)=DSORT(4.0+3.14159*X(3,J))
61. ALF3P(J)=DSORT(4.0+3.14159*XPI(1,J))
62. ALF2P(J)=DSORT(4.0+3.14159*XPI(2,J))

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64. ALF3P1(I)=NSORT(4,0,3,14159*XP1(I),I)
65. C WRITE(6,702) ALP(A1(I),ALPHA2(I),F11(I),F11P1(I),F122(I),F122P1
66. C 1(I))
702 FORMAT(///,' ALPHA1,2, F11,P1, F122,P1 ARE *.6E14,3)
67. SUP=0.0
68. C2(I)=(1.000-X(2,I)/(2.000*X(2,I))
69. NC2P1=(1.000-XP1(2,I))/(2.0*XP1(2,I))
70. NC2=C2(I)
71. V1P(I)=X12(I)+INC/VALKT)
72. V2(I)=X23(I)+INC/VALKT)
73. V13(I)=X13(I)+INC/VALKT)
74. V1P(I)=X1P1(I)+INC/VALKT)
75. V23P1(I)=X23P1(I)+INC/VALKT)
76. V13P1(I)=X13P1(I)+INC/VALKT)
77. DO 401 N2=1,NC2
78. V2P=N2*1.000+0.500-1.000
79. C1(I)=WC(I,I)-X(C1,I)+WE(I,I)+X12(I)+V22)/(2.0*X(I,I)+WE(I,I))
80. NC1=C1(I)
81. DO 401 N1=1,NC1
82. V1=N1+1.000+0.500-1.000
83. C3(I)=WP(I,3,I)-X(3,I)+WE(3,I)+X13(I)+V11+X23(I)+V22)/(2.0*X(3,I)+W
84. 2E(3,I))
85. NC3=C3(I)
86. DO 401 N3=1,NC3
87. V33=N3+1.000+0.500-1.000
88. DO 401 N4=1,NC3
89. V44=N4+1.000+0.500-1.000
90. EH(I)=YNPU(I,I)+V11+YNPU(2,I)+V22+Y(1,I)+V11+2+Y(2,I)+V22+2+Y(2,
91. 1)+V11+V22+YNPU(3,I)+V33+Y(3,I)+V33+2+V23(I)+V22+V33+V13(I)+V11+V
92. 33+YNPU(3,I)+V44+Y(3,I)+V44+2+V23(I)+V22+V44+V13(I)+V11+V44
93. CHECK=EH(I)
94. IF(CHECK-60) 405,409,401
95. 405 SUM=SUM+DEXP1-EH(I)
96. 401 CONTINUE
97. RHO1=0.500+NSORT(YNPU(1,I)/X(1,I))
98. RHO2=0.500+NSORT(YNPU(2,I)/X(2,I))
99. RHO3=0.500+NSORT(YNPU(3,I)/X(3,I))
100. WRITE(6,703) VALKT,RHO1,RHO2,RHO3
101. 703 FORMAT(///,' KTF= *.E14,5,' RHO1, RHO2, RHO3 ARE *.3E15,4)
102. G133=NC+G133/41ALPHA1(I)+2*ALPHA1(I)+VALKT+RHO3+2+RHO1+NSORT(8
103. 1.0E0)
104. G122(I)=HC*(G122(I)/(41ALPHA2(I)+2*ALPHA1(I)+VALKT)+RHO2+2+RHO1)+0
105. ISORT(8,000)
106. C708 WRITE(6,701) G133,G122(I)
107. 701 FORMAT(///,' G112= *.E15,5,' G122=*.E15,5)
108. WRITE(6,778) RHO1,RHO2,RHO3,G133,G122(I)
109. 778 FORMAT(//,' 1,R1,R2,R3,G133,G122 *.1E12,4)
110. 707 CALL QUAD(RHO1,RHO2,RHO3,G133,G122,W)
111. EMO(I)=0.500*(YNPU(1,I)+YNPU(2,I))+0.2500*(YNPU(3,I)+Y(1,I)/WE(I,I
112. 1+YNPU(2,I)+Y(2,I)/WC(2,I)+YNPU(1,I)+V12(I)/WE(I,I))
113. QDM(I)=SUM
114. QDM(I)=(YNPU(1,I)+YNPU(3,I)+2*YNPU(2,I)+QDM(I))/W(I)
115. SUP1=0.0
116. DO 507 N2=1,NC2P1
117. V2P=N2*1.000+0.500-1.000
118. NC1P1=(WEPI(1,I)-KPI(1,I)+WEPI(1,I)+X12P1(I)+V22)/(2.0*XP1(1,I)+WE
119. 1P1(I,I))
120. DO 507 N1=1,NC1P1
121. V11=N1+1.000+0.500-1.000
122. C3P1(I)=WP(I,3,I)-XP1(3,I)+WEPI(3,I)+X13P1(I)+V11+X23P1(I)+V22)/
123. 22.0*X(I,3,I)+WEPI(3,I))
124. NC3P1=C3P1(I)
125. DO 507 N3=1,NC3P1
126. V33=N3+1.000+0.500-1.000
127. DO 507 N4=1,NC3P1
128. V44=N4+1.000+0.500-1.000

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129.      EHP1(1)=YHPUP1(1,1)+V11+YHPUP1(2,1)+V22+YPI(1,1)+V11+2+YPI(2,1)+V
130.      S22+2+V12P1(1,1)+V11+V22+YHPUP1(3,1)+V33+YPI(3,1)+V33+2+V23P1(1,1)+V2
131.      62+V33+V13P1(1,1)+V11+V33+YHPUP1(3,1)+V44+YPI(3,1)+V44+2+V23P1(1,1)+V2
132.      72+V44+V13P1(1,1)+V11+V44
133.      CHECK=EHPI(1)
134.      IF(CHECK-601) 505,505,507
135.      505 SUM1=SUM1+REFXP1+EHPI(1)
136.      507 CONTINUE
137.      RH01P1=0.500*DSORT(YHPUP1(1,1)/XPI(1,1))
138.      RH02P1=0.500*DSORT(YHPUP1(2,1)/XPI(2,1))
139.      RH03P1=0.500*DSORT(YHPUP1(3,1)/XPI(3,1))
140.      G133P1=HC+F133P1/((ALF3P1(1)+2*ALF1P1(1)+VALKT+RH03P1+2+RH01P1)
141.      1+DSORT(8.000))
142.      G122P1(1)=HC+F122P1(1)/((ALF2P1(1)+2*ALF1P1(1)+VALKT+RH02P1+2+R
143.      1H01P1+DSORT(8.000))
144.      WRITE(6,779) I,RH01P1,RH02P1,RH03P1,G133P1,G122P1(1)
145.      779 FORMAT(1,' I,R1,R2,R3,G133,G122 ALL PRIME ',I3,5E12.4)
146.      CALL QUAD(I,RH01P1,RH02P1,RH03P1,G133P1,G122P1,W)
147.      EHP1(1)=0.500*(YHPUP1(1,1)+YHPUP1(2,1))+0.2500*(YHPUP1(1,1)+YPI(1
148.      1,1)/VEP1(1,1)+YHPUP1(2,1)+YPI(2,1)/VEP1(2,1)+YHPUP1(1,1)+V12P1(1,1)/
149.      2VEP1(1,1))
150.      QUOP1(1)=SUM1
151.      QUOP(1)=4*YHPUP1(1,1)+YHPUP1(3,1)+2*YHPUP1(2,1)+QUOP1(1)/W(1)
152.      WRITE(6,511) I,QUO(1),QUOP1(1)
153.      511 FORMAT(1,' I = ',I3,' QUO = ',E12.4,' QUOP = ',E12.4)
154.      WRITE(6,521) I,QUO(1),QUOP1(1)
155.      521 FORMAT(1,' I = ',I3,' QUO = ',F12.4,' QUOP = ',E12.4)
156.      EXACT(1)=DLOG(QUO(1))-DLOG(QUOP1(1))
157.      WRITE(6,531) EXACT(1)
158.      531 FORMAT(1,' LNI-EXACT = ',F12.4)
159.      512 CONTINUE
160.      GO TO 1311
161.      280 CALL EXIT
162.      END
163.      SUBROUTINE QUAD(I,R,R2,R3,G133,G122,W)
164.      C SUBROUTINE TO INTEGRATE QUAD INTEGRAL
165.      IMPLICIT REAL*8(A-H,O-Z)
166.      C QCL : FOR COMPUTING THE ANHARMONICITY CORRECTION FACTOR FOR
167.      C Q(CL,EXACT), A FUNCTION OF RHD AND GAMMA, A 2-D SITUATION
168.      DIMENSION G122(20),W(20),NUP(12),NDOWN(12)
169.      U=1.000
170.      PI=1.772453851
171.      N=4
172.      NUP(1)=40
173.      NUP(2)=40
174.      NUP(3)=40
175.      NDOWN(1)=400
176.      NDOWN(2)=100
177.      NDOWN(3)=50
178.      NUP(4)=400
179.      60 CONTINUE
180.      IF(R-2.3) 2,2,5
181.      2 NDOWN(4)=500/(40.0+3.0+H*R)
182.      GO TO 10
183.      5 NDOWN(4)=7.0+R
184.      WRITE(6,311) N,U,R,G133,G122(1),R2,R3
185.      311 FORMAT(1,' N,U,R,G133,G122,R2,R3 ARE ',I3,6E12.3)
186.      10 CALL SUBCL2(I,N,U,R,R2,R3,G133,G122,NUP,NDOWN,0,C1,C2)
187.      W(1)=C1
188.      WRITE(6,3002) I,W(1)
189.      3002 FORMAT(1,' I = ',I3,' C1 = ',F16.7)
190.      RETURN
191.      END
192.      SUBROUTINE SUBCL2(I,N,U,R,R2,R3,G133,G122,N1,M2,A,B,C)
193.      IMPLICIT REAL*8(A-H,O-Z)
194.      C INPUT: U=1 (R=0.5) SORT(U,X); 6=NO. OF SUBRANGES

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195. C IN EACH OF WHICH THE RANGE IS EQUALLY DIVIDED: N1(1)=NO.OF
196. C EQUAL INTERVALS IN I-TH RANGE: N2(1)=NO. INTO WHICH R=LN2
197. C IS DIVIDED TO OBTAIN EQUAL INTERVALS IN I-TH SUBRANGE.
198. C SUBCLS WILL BE CALLED TO EVALUATE THE INNER INTEGRALS.
199. C DIMENSION G(12(20),N1(12),N2(12))
200. STOP=1.00-7
201. N=4
202. P1=1.772453851
203. CALL ERFN(P,YYMAX)
204. YYSTOP=YYMAX*STOP
205. S=0.000
206. RR=R*LOG(2.000)
207. X=0.000
208. C FOR EVERY SUBRANGE:
209. DO 100 I=1,N
210. DX=RR/N2(1)
211. X=X+DX/2.000
212. NN=N1(1)
213. C FOR EVERY SUBDIVISION:
214. DO 50 J=1,NN
215. IF(X/R-10012.1.1
216. 1 V=1.000
217. Y=0.000
218. GO TO 7
219. 2 V=(1.000-DEXP(-X/R))**2
220. Y=R*DSQRT(1.000-V)
221. VRR=V+R
222. IF(VRR-1001 3.3.7
223. 3 EX=DEXP(-VRR)
224. IF(Y-1.00-30/EX) 7.4.4
225. 4 CALL ERFN(Y,E)
226. CALL SUBCLS(11,N,R,R2,R3,X,G133,G122,VRR,A1,B1)
227. YY=ERF(Y)*DEXP(-VRR)
228. GO TO 10
229. 7 YY=0.000
230. 10 CONTINUE
231. S=S+YY*DX
232. X=X+DX
233. IF(I-N) 50,20,200
234. 200 CALL EXIT
235. 20 IF(YY-YYSTOP) 150,150.50
236. 50 CONTINUE
237. X=X-DX/2.000
238. 100 CONTINUE
239. S=S+1.0010
240. 150 G=S/PT
241. WRITE(6,205) 0,S
242. 205 FORMAT(1,' 0 AND S = ',2E14.4)
243. A=1.000/U
244. C=1.000+0.500/(R*N)
245. RETURN
246. END
247. SUBROUTINE SUBCLS(11,N,R,R2,R3,X,G133,G122,VRR,A1,B1)
248. C SUBCLS TAKES CARE OF THE INNER INTEGRAL
249. C IMPLICIT REAL*8(A-H,O-Z)
250. C INPUT: UX1 : R=0.5*DSQRT(U/X); N=NO. OF SUBRANGES
251. C IN EACH OF WHICH THE RANGE IS EQUALLY DIVIDED: N1(1)=NO.OF
252. C EQUAL INTERVALS IN I-TH RANGE: N2(1)=NO. INTO WHICH R=LN2
253. C IS DIVIDED TO OBTAIN EQUAL INTERVALS IN I-TH SUBRANGE
254. C SUBCLS WILL BE CALLED TO EVALUATE THE INNER INTEGRALS.
255. C DIMENSION G(12(20),N1(12),N2(12))
256. STOP=1.00-7
257. N=4
258. P1=1.772453851
259. N2(1)=400
260. N1(1)=100

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261.      N2(3)=0
262.      N1(1)=40
263.      N1(2)=40
264.      N1(3)=40
265.      N1(4)=0
266.      IF(R2-2.85 21.21.25
267.      21 N2(4)=500/148.0-5.0*R2*R2)
268.      GO TO 110
269.      25 N2(4)=7.0+P2
270.      110 CALL ERFA(R2,YYMAX)
271.      CALL MCWTON(11,R,X1,G122,R2,0MAX)
272.      YYSTOP=YYMAX*STOP
273.      S=0.000
274.      RK=R2*0.00012.000)
275.      X=-RK
276.      C FOR EVERY SUBRANGE
277.      GO 100 I=1,N
278.      IF(I-4) 30,35,35
279.      35 YES=G122(11)*X1
280.      IF(TFS-0.000) 37,30,30
281.      37 CONTINUE
282.      IF(RMAX-GE.200) GO TO 30
283.      DY=RMAX/N1(1)
284.      GO TO 32
285.      30 DY=R2/N2(1)
286.      32 X=X*OX/2.000
287.      NM=P1(1)
288.      C FOR EVERY SUBDIVISION
289.      GO 50 J=1,NM
290.      IF(X/R2-1.000) 2,1,1
291.      1 V=1.000
292.      Y=0.000
293.      GO TO 7
294.      2 V=(1.000-DEXP(-X/R2))**2
295.      V1=(1.000-DEXP(-X1/R1))**2
296.      Y=DSORT((R2+R2+11.000-V1)
297.      YH=R2+R2*(1.000-V)-G122(11)*X*X1*X
298.      YH=R2+R2*(1.000-V)
299.      IF(YH-GE.YP) GO TO 300
300.      IF(YH-LF.1.00-30) GO TO 300
301.      YL=R2+R2*(1.000-(1.000-DEXP(-RMAX/R2))**2)-0.00*X1*X1=RMAX-G122(11)
302.      21=RMAX-RMAX*X1
303.      IF(YL-LE.0.0) GO TO 300
304.      T=DSORT(YL)
305.      300 CONTINUE
306.      VRR2=V+R2+R2
307.      IF(VRR2-100) 3,3,7
308.      3 CX=DEXP(-VRR2)
309.      IF(Y-1.00-30/CX) 7,4,4
310.      4 CALL ERFA(Y,F)
311.      CALL SURCL(11,N,H,R2,R3,X1,Y,G133,G122,VRR,VRR2,A2,R2)
312.      GO TO 45
313.      45 E=0.5*P1
314.      5 CHEK=VRR2+G122(11)*X1*X*X
315.      IF(CHEK-100) 9,9,7
316.      9 YY=E*(R2+R2)*DEXP(-CHEK)
317.      GO TO 10
318.      7 Y=0.000
319.      10 CONTINUE
320.      S=S+YY*DX
321.      X=X+DX
322.      IF(I-N1 50.20.200
323.      200 CALL EXIT
324.      20 IF(Y-Y-(YSTOP) 150,150,40
325.      50 CONTINUE

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327.      X=X-PX/2.000
328.      100 CONTINUE
329.      WRITE(16,3501) YI,YYSTOP
330.      350 FORMAT(7,' YI AND YYSTOP ARE ',2C16.7)
331.      S=S+1.0010
332.      150 G1=S/P1
333.      A1=1.000
334.      C1=1.000+0.500/(H2+R2)
335.      RETURN
336.      END
337.      SUBROUTINE SUBCLL(11,N,R,R2,R3,X1,X2,G133,G122,VRR,VRR2,A2,02)
338.      C SUBCLL TAKES CARE OF THE INNERMOST INTEGRAL
339.      IMPLICIT REAL*8(A-H,N-Z)
340.      C INPUT: U=U, N=0.5*SORT(U/X), N=NO. OF SUBRANGES
341.      C IN EACH OF WHICH THE RANGE IS EQUALLY DIVIDED; N1(1)=NO. OF
342.      C EQUAL INTERVALS IN I-TH RANGE; A2(1)=NO. INTO WHICH R+1/2
343.      C IS DIVIDED TO OBTAIN EQUAL INTERVALS IN I-TH SUBRANGE
344.      C SUBCLL WILL BE CALLED TO EVALUATE THE INNER INTEGRALS.
345.      DIMENSION C122(20),N1(12),N2(12)
346.      STOP=1.00-7
347.      N=4
348.      PI=3.1415926535
349.      N2(1)=800
350.      N2(2)=200
351.      N2(3)=160
352.      N1(1)=80
353.      N1(2)=80
354.      N1(3)=80
355.      N1(4)=1600
356.      IF(R,R0,R3) 50 TO 110
357.      IF(R3-2.3) 21,21,25
358.      21 N2(4)=500/(98.0-5.0+R3+R3)
359.      GO TO 110
360.      25 N2(4)=7.0+R3
361.      110 CALL TRFN(R3,YTHAX)
362.      CALL NEWTN2(11,R,K1,G133,R3,RMAX)
363.      YYSTOP =YYPAX+STOP
364.      S=0.000
365.      RR=R3+ULOG(12.000)
366.      X=-PR
367.      C FOR EVERY SUBRANGE I
368.      DO 100 I=1,N
369.      IF(I-4) 30,35,35
370.      35 TES=G133*X1
371.      IF(TES-0.000) 37,30,30
372.      37 CONTINUE
373.      IF(RMAX,66.200) GO TO 30
374.      DX=RMAX/N1(I)
375.      GO TO 32
376.      30 DX=RR/N2(I)
377.      32 X=X+DX/2.000
378.      NM=N1(I)
379.      C FOR EVERY SUBDIVISION J
380.      DO 50 J=1,NM
381.      IF(X/R3-1.00) 2,1,1
382.      1 V=1.000
383.      Y=0.000
384.      GO TO 7
385.      2 V=1.000-DEXP(-X/R3)**2
386.      V1=(1.000-DEXP(-X1/R3))**2
387.      V2=DSORT(R3+K3*(1.000-V))
388.      V3=K3+K3+1.000-V1-G133*X+K1*X
389.      YR=R3+K3+1.000-V2
390.      IF(YH,66.YP) GO TO 300
391.      IF(YH,1.00-30) GO TO 300
392.      VL=R3+K3+1.000-1.000-DEXP(-0.000/R3)**2-G133*X1+RMAX+RMAX

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391.      IF(YI.LT.0.01) GO TO 380
394.      Y=CSORT(YI)
395.      300 CONTINUE
396.      VAR3=Y+R3+R3
397.      CHECK=VAR3+G133*X*X*X1
398.      IF(CHECK-100) 3,3,7
399.      3 YJ=-CHECK
400.      IF(YJ.GT.0.0) GO TO 301
401.      EX=DEXP(YJ)
402.      IF(Y-1.00-30/EX) 7,14,14
403.      14 TEST=G133*X1
404.      IF(TEST-0.000) 4,4,4
405.      4 CALL FRFN(Y,E)
406.      GO TO 45
407.      44 E=0.5*PI
408.      45 YY=E*EX
409.      GO TO 18
410.      7 YY=0.000
411.      18 CONTINUE
412.      S=S+YY*OX
413.      X=X+OX
414.      IF(T-DE 50.20,200
415.      301 WRITE(6,310) YJ
416.      310 FORMAT(/,' OFF-DIAG TERMS TOO LARGE ',E14.4)
417.      200 CALL EXIT
418.      20 IF(YY-YYSTOP) 150,150,50
419.      50 CONTINUE
420.      X=X-OX/2.000
421.      100 CONTINUE
422.      WRITE(6,350) YY,YYSTOP
423.      350 FORMAT(/,' YY AND YSTOP ARE ',2E16.7)
424.      S=S+1.0010
425.      150 U2=S/PI
426.      A2=1.000
427.      C2=1.0000+0.500/(R3+R3)
428.      RETURN
429.      END
430.      SUBROUTINE ERFN(Y,E)
431.      IMPLICIT REAL*8(A-H,O-Z)
432.      C FOR EVALUATING THE ERROR FUNCTION E=ERFN(X) AS
433.      C ERFN(X)=2*PI*(1.4141...)*X + 1 . SEE ABRAMOWITZ .
434.      X=1.41421356*Y
435.      AX=0.4851X
436.      T=1.000/(1.000+0.231641900*AX)
437.      IF(X*X-100)12,11,11
438.      11 D=0.000
439.      P=1.000
440.      GO TO 13
441.      12 CONTINUE
442.      D=0.3989422804+DEXP(-X*X/2.000)
443.      P=1.000-D*T*(1.135274429*T-1.821255976)*T+1.781477939)*T-
444.      10.354563782)*T+0.31938153)
445.      13 CONTINUE
446.      IF(X) 1,2,2
447.      1 P=1.000-P
448.      2 IF(P) 3,5,5
449.      3 WRITE(6,3001)
450.      3001 FORMAT(35H0 TROUBLE IN DISTRIBUTION FUNCTION.)
451.      4 WRITE(6,3002) X,P
452.      3002 FORMAT(4H X= E14.7,4H P= E14.7)
453.      CALL EXIT
454.      5 E=2.000*P-1.000
455.      IF(P) 6,7,7
456.      6 WRITE(6,3003)
457.      3003 FORMAT(26H0 TROUBLE IN ERROR FUNCTION.)

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459.      7 RETURN
460.      END
461.      SUBROUTINE NEWTON1(R,X1,G122,R2,RMAX)
462.      IMPLICIT REAL*8(A-H,O-Z)
463.      C THIS SUBROUTINE SERVES TO FIND THE UPPER LIMIT OF Q2 FOR CASE 1
464.      C WHEN G122*X IS LESS THAN 0 USING NEWTON'S METHOD
465.      C NEWTON IS NOW CALCULATED POINT BY POINT
466.      DIMENSION G122(201),Z(500),UMAX(500)
467.      USTAN=R2+R2-1.0D-4
468.      M=1
469.      Z(1)=1.0
470.      UMAX(1)=R2+R2+(1.0D0-DEXP(-Z(1)/R2))*2-0.0D0Z(1)*X1-G122(1)*X1
471.      1*(Z(1)+2)
472.      1 IF(UMAX(M).GE.USTAN) GO TO 23
473.      M=M+1
474.      Z(M)=Z(M-1)+1.0
475.      UMAX(M)=R2+R2+(1.0D0-DEXP(-Z(M)/R2))*2-0.0D0Z(M)*X1-G122(M)*X1
476.      1*(Z(M)+2)
477.      IF(UMAX(M).LT.UMAX(M-1)) GO TO 23
478.      IF(M.EQ.500) GO TO 12
479.      GO TO 1
480.      23 RMAX=Z(M)
481.      IF(RMAX.LE.0.0) GO TO 12
482.      GO TO 43
483.      12 CONTINUE
484.      C WRITE(6,15) M,Z(M)
485.      15 FORMAT(/,' ERROR IN CONVERGENCE M ',14,'C14.4)
486.      43 RETURN
487.      END
488.      SUBROUTINE NEWTON2(R,X1,G133,R3,RMAX)
489.      IMPLICIT REAL*8(A-H,O-Z)
490.      C THIS SUBROUTINE SERVES TO FIND THE UPPER LIMIT OF Q2 FOR CASE 1
491.      C WHEN G132*X IS LESS THAN 0 USING NEWTON'S METHOD
492.      C NEWTON IS NOW CALCULATED POINT BY POINT
493.      DIMENSION Z(500),UMAX(500)
494.      USTAN=R3+R3-1.0D-4
495.      M=1
496.      Z(1)=1.0
497.      UMAX(1)=R3+R3+(1.0D0-DEXP(-Z(1)/R3))*2-G133*Z(1)**2*X1
498.      1 IF(UMAX(M).GE.USTAN) GO TO 23
499.      M=M+1
500.      Z(M)=Z(M-1)+1.0
501.      UMAX(M)=R3+R3+(1.0D0-DEXP(-Z(M)/R3))*2-G133*Z(M)**2*X1
502.      1*(Z(M)+2)
503.      IF(UMAX(M).LT.UMAX(M-1)) GO TO 23
504.      IF(M.EQ.500) GO TO 12
505.      GO TO 1
506.      23 RMAX=Z(M)
507.      IF(RMAX.LE.0.0) GO TO 12
508.      GO TO 43
509.      12 CONTINUE
510.      C WRITE(6,15) M,Z(M)
511.      15 FORMAT(/,' ERROR IN CONVERGENCE M ',14,'C14.4)
512.      43 RETURN
513.      END
514.      //GO,SYSIN DD *
515.      -01 1 0067.86 0069.84 300.0
516.      -238.54 -245.53
517.      1349.97 -2.32 1349.97 -2.56
518.      2395.69 -12.40 2327.41 -11.64
519.      674.65 -2.30 655.65 -2.20
520.      -18.05 0.9980 -11.82 -18.500 01.018 -12.61
521.      09
522.      //
523.      //

```

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ANNUAL PROGRESS REPORT
TO
U.S. DEPARTMENT OF ENERGY
OFFICE OF BASIC ENERGY SCIENCES

STABLE ISOTOPE STUDIES

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Contract No. EY-76-S-02-3127

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STABLE ISOTOPE STUDIES

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Annual Progress Report to
U.S. Department of Energy, Office of Basic Energy Sciences
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STABLE ISOTOPE STUDIES

Abstract

The BBIR-Type precision cryostat has been debugged, and interfacing of the cryostat with an LSI-11-based microcomputer has been completed. A program for the cryostat control and data acquisition has been written. A spiral quartz gauge for the absolute pressure measurements up to 1500 torr has been calibrated against a dead-weight gauge. The vapor pressures of $^{12}\text{CHF}_3$, $^{13}\text{CHF}_3$, and $^{12}\text{CDF}_3$ have been measured in the cryostat at temperatures between -139.85°C and -80.81°C . The carbon isotope effects observed are inverse effect, i.e., $P(^{13}\text{C}) > P(^{12}\text{C})$, while the hydrogen isotope effect observed are normal effect, $P(\text{H}) > P(\text{D})$. The observed carbon vapor pressure isotope effects point to a second cross-over temperature at 218.66°K , at which $P(^{13}\text{C}) = P(^{12}\text{C})$. A plot of $T \ln(P'/P)$ against $1/T$ for the observed D/H vapor pressure isotope effects indicates a positive intercept with the ordinate. These anomalies are explainable on the basis of the blue-shift in the C-H stretching frequency in fluoroform. Besides the isotopic species of fluoroform, methylfluoride was also purified to reduce all chemical impurities to a level below 10 ppm.

The construction of nitrogen-15 fractionation system using gaseous nitric oxide under pressure and liquid dinitrogen trioxide, which had been started during last year, has been continued. A pneumatically operated bellows compressor for nitric oxide has been designed. A packed exchange column, liquid-composition equilibrator column, and an all stainless steel fume hood have been fabricated.

A new scheme for the determination of unit stage separation factor for isotope exchange reactions has been devised. It is an attempt to combine the advantages of the cascade method and the single-stage method for the determination of α . A product reflux is provided to each separation stage. Determination of α is achieved by isotopic analyses of the feed to Stage No. 1 and the heads from Stage No. n and by chemical analyses of the cuts in each stage.

An analytical expression has been developed for the effect of a differential change in a vibrational force constant upon isotopic reduced partition function ratio. The method is based on the WIMPER approximation of $\ln(s/s')$ and the analytical formula for the derivative of the trace of various powers of the $\underline{H} = \underline{FG}$ matrix with respect to a force constant, the latter having been reported by this project a few years ago.

This year has been marked by the acceptance of a position of Professor of Chemistry at the State University of New York at Stony Brook as of September 1, 1979 by the principal investigator of this project. All laboratory and computational equipment purchased by this project over the years have been moved from Brooklyn College to Stony Brook, and the moving has been financed by the State University.

II. SUMMARY

II-A. SCOPE OF ACTIVITIES

This has been a special year in that the principal investigator of this project has accepted an offer of the position of Professor of Chemistry with tenure at the State University of New York at Stony Brook, effective as of September 1, 1979. A significant part of late summer months and the months of September and October has been spent for moving the laboratory and computational equipment. Brooklyn College and the Research Foundation of City University of New York allowed us to transfer all the equipment purchased by this project, which started as an AEC Contract, AT (30-1)-4266 in 1971 and has since been continued under AEC Contract No. (11-1)-3127, ERDA Contract No. E(11-1)-3127 and the present DOE Contract No. EY-76-S-02-3127. The moving has been facilitated by the State University of New York.

During the past year, one principal investigator, one postdoctoral fellow, and four graduate students have worked in this research project. In addition, Dr. William Spindel of National Academy of Sciences collaborated in the studies of nitrogen-15 fractionation systems.

Our studies encompassed various experimental and theoretical investigations of isotope effects and fractionation of the isotopes of light elements. However, a major effort has been focused upon the completion of the cryostat control systems and the cryostatic determination of vapor pressure isotope effects in fluoroform. One Ph.D. thesis has been completed, and another will be issued before the current project year is over. Abstract of the completed Ph.D. thesis will be found in Section II-B. Other scientific progress made during this year will be summarized in six parts in Section II-C, and the detailed accounts will be presented in Section III, "SCIENTIFIC PROGRESS."

We have not received any support, external or internal, other than this Department of Energy funding during this period.

II-B. PUBLICATIONS

Abstract for the following paper published will be found on the following page.

Thesis Completed

"Approximation Methods for The Partition Functions of Anharmonic Systems", Peter Lew, Ph.D. Dissertation, The City University of New York, July, 1979; [DOE Report C00-3127-30]

[C00-3127-30]

Approximation Methods
for
The Partition Functions of Anharmonic Systems

by
Peter Lew

ABSTRACT

The analytical approximations for the classical , quantum mechanical and reduced partition functions of the diatomic molecule oscillating internally under the influence of the Morse potential have been derived and their convergences have been tested numerically . This successful analytical method is used in the treatment of anharmonic systems . Using Schwinger perturbation method in the framework of second quantization formalism , the reduced partition function of polyatomic systems can be put into an expression which consists separately of contributions from the harmonic terms , Morse potential correction terms and interaction terms due to the off-diagonal potential coefficients . The calculated results of the reduced partition function from the approximation method on the 2-D and 3-D model systems agree well with the numerical exact calculations .

II-C. SUMMARY OF SCIENTIFIC INVESTIGATIONS

The following is a six-part summary of various achievements for the past year that are still in progress.

(1) Cryostat Fabrication and Computer Interfacing :

The BBIR-type precision cryostat has been debugged. Interfacing of the cryostat with an LSI-11 microcomputer, the MICROFLOP-11, with a dual double-density floppy disc drives, has been completed. The description of the interfacing hardware and related flow-chart are given in Section III-A-1-a. A program in RT-11 Fortran has been written to facilitate fully automatic, fully manual, or semi-manual control of temperatures (and the rate of increase of temperatures) of the various important parts of the cryostat and to provide a computer-assisted acquisition of data on the isotopic vapor pressures and temperatures. The program is described in Section III-A-1-c. The quartz spiral gauge for measurement of the absolute pressure of reference isotopic species has been calibrated against an NBS-certified Ruska dead-weight gauge (cf: Section III-A-1-b).

(2) Purification of Fluoromethanes :

Following the synthesis of $^{13}\text{CH}_3\text{F}$ and purification of $^{13}\text{CH}_3\text{F}$ and $^{12}\text{CD}_3\text{F}$ carried out and reported last year, we have purified $^{12}\text{CH}_3\text{F}$, $^{12}\text{CHF}_3$, $^{13}\text{CHF}_3$, and $^{12}\text{CDF}_3$, purchased from various commercial sources, to reduce all impurities to a level below 10 ppm. The procedure and the results of these purifications are reported in Section III-A-2.

(3) Measurements of Vapor Pressure Isotope Effects in Fluoroform :

The $^{13}\text{C}/^{12}\text{C}$ and D/H vapor pressure isotope effects (VPIE) in fluoroform, CHF_3 , were determined using the precision cryostat in a computer-assisted manual operation. The vapor pressure data were obtained at temperatures between -139.85°C and -80.81°C , corresponding to the pressures from 4.51 torr to 814.05 torr. Preliminary numerical results are presented in Section III-A-3. The $^{13}\text{C}/^{12}\text{C}$ -VPIE actually observed are all inverse

effect, i.e., $P(^{13}\text{C}) > P(^{12}\text{C})$, and is representable by

$$T \ln \frac{P'}{P} = \frac{(1217.5 \pm 79.3)}{T} - (21.12 \pm 1.00) + (0.0711 \pm 0.0031) T.$$

The D/H-VPIE in this range of temperature is normal, i.e., $P(\text{H}) > P(\text{D})$, and can be best expressed as

$$T \ln \frac{P'}{P} = \frac{(506.99 \pm 3.86)}{T} + (0.778 \pm 0.024).$$

The least squares fitted line for the carbon isotope effect indicates the existence of a second cross-over (at which $P' = P$) at 218.66°K, in addition to the ordinary cross-over at 78.30°K. The unusual features of the VPIE in CHF_3 , i.e., the second cross-over in the $^{13}\text{C}/^{12}\text{C}$ -effect and the apparently positive intercept in the plot of $T \ln(P'/P)$ vs $1/T$ in the D/H-effect, are explained in Section III-A-3 in terms of the blue-shift in the C-H stretching frequency upon condensation of the gas molecules.

(4) Studies of Nitrogen Isotope Exchange Systems :

The construction of nitrogen-15 fractionation columns using the countercurrent flows of gaseous nitric oxide and liquid N_2O_3 that was started and reported on last year has been continued. The exchange column and the liquid composition equilibrators, both packed with Helipak column packing material and thermostatted, have been fabricated from Type 316 stainless steel. The compressor which utilizes the cryogenic condensation-vaporization cycles and on which we reported last year has been abandoned due to the potential explosion hazard of the condensed nitric oxide, and a pneumatically activated bellows pump has been designed. When two such units are used at 180° out of phase of each other, they produce a compression ratio of 20:1 at a flow rate of 2.5 liters NTP/min, which is appropriate for our purpose. An all-stainless steel, California-type fume hood has also been constructed. Details of these progress will be found in Section III-B.

(5) Precision Measurement of Isotope Exchange Separation Factors :

We have devised a new scheme for determination of unit stage separation factors for isotope exchange reactions, which is to combine the advantages

of the cascade method and the single-stage method for the determination of α . In each stage of the multistage scheme, a part of the liquid feed is converted to the gas phase with which the liquid exchanges isotopes until the equilibrium is reached, and then the liquid is withdrawn and fed to the next stage. The separation factor α is determined from isotopic analyses of the feed to Stage No. 1 and the head from Stage No. n and from determinations of the cuts (the ratio of the number of moles of the heads to that of the feed) in each stage. An error analysis shows that, at cut = 0.5 for example, a 0.3% precision in the determination of the cuts will be consistent with the ordinary uncertainties in the isotopic analysis. A piece of apparatus is being designed to demonstrate this method with the carbon isotope fractionation between carbon dioxide and the carbamate of di-n-butyl amine in triethylamine. This aspect of work is discussed in more detail in Section III-C.

(6) Effect of Differential F-Matrix Changes on Isotope Effects :

Analytical expression has been developed for the effect of differential change in a force constant on the isotopic reduced partition function ratio. The expression has been obtained by combining the partial derivative,

$$\frac{\partial \text{Tr}(\underline{H}^j)}{\partial f_{pq}} = j \left[\underline{GH}^{j-1} \right]_{pq} ,$$

With the WIMPER approximation of $\ln(s/s')f$, and Bigeleisen-Mayer's $S(u)$ function. The precision of the method is adjustable to any desired level by including an appropriate number of terms in the WIMPER formula. A computer program is being written to find the bounds of errors of this method for the hydrogen, carbon, and oxygen isotope effects.

II-D. PERSONNEL

The scientific personnel who participated in this project during the current year are: one principal investigator, one postdoctoral fellow, four Ph. D. students, and one consultant. No non-scientific personnel has been directly involved.

The Principal investigator, Professor Takanobu Ishida, spent an average of 45 hours per week of his time for the project during the academic year and two full-time months during the summer.

Dr. Takao Oi arrived from Tokyo in May, 1979 and has since worked full time. He has been fully supported by the project. Mr. Pater Lew finished his Ph. D. dissertation, on which he worked since 1973, and received the degree in June, 1979. Mr. Anthony Popowicz, fully supported by the project, worked full time until the end of the summer and has completed his thesis research on the vapor pressure isotope effects in fluoroform. He is in the process of writing up the dissertation. At the same time he has started working as a postdoctoral fellow in the project of Prof. Jacob Bigeleisen.

Mr. Jan Shulman has been fully supported by the project and has worked full time throughout the year. He elected to remain a Ph.D. student at the City University of New York after we moved. We expect him to complete his thesis study by the end of the summer, 1980, and until then he will commute to Stony Brook from Brooklyn. Mr. Michael Prencipe was supported by the Department of Chemistry at Brooklyn College until June, 1979, and by this project since then. He worked full time throughout the year. He elected to transfer to the State University of New York as of September, 1979.

Dr. William Spindel of National Academy of Sciences participated in our study of nitrogen-15 fractionation systems and spent an average of 2 to 3 days a month, for which he was compensated by the project.

III. SCIENTIFIC PROGRESS

Four areas in which we have made significant progress during the current year will be reported in the following. In Section A, we report the overview of the computerized control of the precision cryostat that has been completed, the chemical purification of isotopic fluoromethanes for use in the cryostat, and the results of cryostatic measurements of the $^{13}\text{C}/^{12}\text{C}$ and D/H vapor pressure isotope effect in fluoroform. In Section B, we present a progress in the fabrication of the all stainless steel nitrogen isotope exchange column system utilizing the $\text{NO}/\text{N}_2\text{O}_3$ combination, which we started and reported on last year. In Section C, we report on our new attempt for precision measurement of the separation factor in isotope exchange reactions. Section D deals with a theoretical development of a new method for analytically evaluating the effects of differential changes in an $\underline{F}$ -matrix upon the magnitudes of isotopic reduced partition function ratios.

(A) VAPOR PRESSURE ISOTOPE EFFECTS BY CRYOSTATIC MEASUREMENTS

(A-1) CRYOSTAT FABRICATION AND COMPUTER INTERFACING

by Anthony Popowicz

During the current year the electronic control and measurement systems for the cryostat have been installed and made operational. This includes the computer as well as the analog aspects. Control and data acquisition software has been developed under a RT-11-based Fortran language compiler. The Mensor Spiral Quartz Gauge was calibrated over its functional range of 0 - 1500 torr using a Ruska Dead Weight Gauge. The cryostat was used under computer-assisted manual operation to measure the vapor pressure isotope effect for fluoroform at temperatures ranging from -140°C to -81°C , which correspond to the pressures ranging from 4.5 torr to 814 torr. The hydrogen/deuterium effect and the carbon-12/carbon-13 effect were determined.

(a) Cryostat Electronics :

Figure 1 is a flow-diagram of the electronic control and data acquisition interface. This scheme provides for fully manual or fully automatic control of the cryostat temperatures and acquisition of vapor pressure isotope effect (VPIE) data, as well as for mixed mode operations due to its modular design. The analog-to-digital converter, the digital-to-analog converter, and the heater interface were discussed previously⁽¹⁾. However, a major modification has been made on the design of the platinum resistance thermometer (PRT) interface. The PRT interface has been simplified from an originally conceived one by using the direct logic level output from two of the digital-to-analog interface boards (manufactured by Data Translation) to power a set of drivers (GE-28 NPN silicon power transistor) to operate the mercury-wetted reed relays which switch the cryostat PRTs to the Keithley (Model # 5900) digital volt-ohm meter (DVOM). This direct operation requires no additional interfacing via a multiplexer, because each of the D/A channels provides for 3 bits of

Figure 1: Flow Diagram of Electronic Control and Data Acquisition Interface for Cryostat

information or 3 independent logic levels: Two D/A channels, therefore, provide control of six relays and their respective PRTs.

(b) Absolute Pressure Gauge Calibration :

Calibration of the cryostat thermal sensors were reported last year.⁽¹⁾ Before the cryostat could be used, it was necessary to calibrate the spiral quartz gauge, manufactured by Mensor, which measures the absolute pressure of the reference gas. The calibration was performed in place using a Huska Dead Weight Gauge Model #2460, a courtesy of Professor Jacob Bigeleisen. The standard weights were calibrated by the National Bureau of Standards, Job #14662; 7/20/76. One hundred and fifty one calibration points were taken over a pressure range of 0 - 1500 torr using atmospheric pressure as reference for both the spiral quartz gauge and the dead weight gauge. This data was then fit to several functional form. The best form is a cubic polynomial. The calibration, however, is practically linear throughout a major part of the operating range of the gauge, each calibration point being within 0.01% of the best-fit line. Deviations occur at both extremes of the operating range, the deviations from the linear relationship increasing to 0.1%. This is accounted for by the non-linear terms in the best-fit equation:

$$P = a Q^3 + b Q^2 + c Q ,$$

where

$$\begin{aligned} a &= -1.9256 \times 10^{-14} \\ b &= 1.6857 \times 10^{-9} \\ c &= 1.5235 \times 10^{-2} , \end{aligned}$$

in which P is the absolute pressure in torr and Q is the spiral quartz gauge counter reading (nominally, 100,000 counts per 1500 torr). In any area in the calibration we did not observe any periodic oscillatory behavior in the plot of P vs. Q.

(c) Control Software :

Software for temperature control and data acquisition was developed using RT-11 Fortran. RT-11 Fortran is a fully structured Fortran language in that it allows true usage of subroutines and overlays during compilation

and linkage. The major distinction is that it is interactive: It allows for access to individual memory locations, such an access being required for control and data acquisition operations.

The control program for the cryostat was written so as to provide as flexible a control system as possible, that is, the control and data acquisition can be performed manually, fully automatically or to varying degrees of automatic control. The type of control desired is determined by the cryostat operator.

The CRYostat Pressure/Temperature Interactive Control program, or CRYPTIC, is structured in the following manner: Various routines or subprograms which perform a specific task (temperature readings using thermocouple or platinum resistance thermometer, heater feedback, pressure measurements, etc.,) are accessed via interaction of the console operator with the program main. The operator calls the desired subroutine and, once its operation is complete, control is transferred back to the main program and the console operator. Some routines can cycle continuously, and control can be transferred back to the main using interrupts from the console terminal. This scheme allows for maximum flexibility and allows routines to be added or deleted as required. Presently the program CRYPTIC consists of the main program and eleven subroutines. Their functions are outlined in the following.

KBQ (KeyBoard Query) is the main program and it allows for the operator access to the various subroutines.

TCAR (ThermoCouple Automatic Read) is subroutine #1, and it measures the temperatures of the cryostat components twice over a specified period of time. The routine calculates the rate of change of temperatures. This data is printed out on the console terminal as well as made available to other routines.

RTAR (Resistance Thermometer Automatic Read) is subroutine #2, and is identical in function as TCAR, but the temperature measurements are performed with PRTs.

HAMAN (Heater Adjust MANual) is subroutine #3, and it allows the operator to access the D/A converter channels from the console terminal to adjust the cryostat heaters.

HAUTO (Heater Adjust AUTomatic) is subroutine #4, and it automatically adjusts the cryostat heaters. The feedback data is determined by HAUTO which calls TCAR or RTAR. The feedback logic is essentially a proportional control type with a built-in damping/amplification and power factors. The input parameters used are the temperature-differences between various cryostat components, e.g., sample holder,

lower radiation shield, etc., and set points (cf: NUTEM) and also the differences among the cryostat components. Rates of approach to the temperature set point are also used. This routine cycles constantly and the return to KBQ can occur by console interrupt only.

PTIN (Pressure/Temperature INput) is subroutine #5, and accepts as input from the console terminal the precision pressure and temperature data read from the spiral quartz gauge, capacitance gauges and sample holder PRT. This data is printed out and stored for later access.

NUTEM (New TEMperature) is subroutine #6. This routine allows the operator to set the next desired set point temperature, which would be an approximate value of the temperature at which the next VPTE data will be taken.

INPUT (INPUT of control program data) is subroutine #7. This subroutine accepts from the console terminal the necessary operating parameters and constants. For example: the run's starting temperature, temperature increment, wait time between sensor readings for T/Cs and PRTs, query wait time for automatic operation, and the various power gain and damping factors for heater control operations. This information is made available to all other subroutines.

DDUMP (Data DUMP) is subroutine #8, and its function is to dump all the pressure and temperature data obtained from PTIN onto a disk. A full printout on the console terminal is also provided.

PRESS (PRESSure measurement) is subroutine #9. This routine performs a 12-bit measurement of the absolute pressure of the reference gas on one of the capacitance gauge channels; the particular channel is manually set by the operator.

INSTR (INSTRuctions) is subroutine #10, and is simply a printout of CRYPTIC's operating instructions for the operator.

CON (CONVersion) is subroutine #11, and it provides conversions of sensor signals (voltage, resistance, etc.) to physical parameters (temperature, pressure, etc.).

A listing of the entire CRYPTIC program can be found in Section (d) below.

Presently various routines are being modified based on the information obtained during the manual and computer-assisted manual operation of the cryostat for the VPTE measurements of fluoroforms. Such manual operations are necessary so as to determine such factors as the time lags between the initiation of a new heater power level and the corresponding response at one of the temperature sensors, the power damping factors, and the cycle times, etc., which are peculiar to each cryostat component and its immediate environment.

(d) Listing of Program CRYPTIC

```

C      CRYOSTAT PRESSURE/TEMPERATURE INTERACTIVE CONTROL PROGRAM:KBD/MAIN
C
C      THIS ROUTINE ALLOWS THE USER TO ENTER WHATEVER SUBROUTINE REQUIRED
C      TO PERFORM THE DESIRED TASK, THAT IS; T,P HEAS OR HEATER ADJ,ETC
C
C                      CRYPTIC/MAIN
C                      KBD VERSION 01 8/21/79
C                      ANTHONY B. POPWICZ
C
C
C      DOUBLE PRECISION TSH(100),ABSP(100),BP31(100),DP21(100),BP11(100),
C      .TLMP1(100),TLMP2(100),TLMP3(100)
C      DIMENSION TEMP(2,7),DAMPF(7),POURF(7),WINDS(7),P(7),RATE(7),
C      .DELTA(7)
C      COMMON /BLK1/TEMP,IERR
C      COMMON /BLK2/P
C      COMMON /BLK3/TCUT,ICYLE
C      COMMON /BLK4/RTUT,IPRT
C      COMMON /BLK5/TSH,ABSP,DP31,BP21,BP11,TLMP1,TLMP2,TLMP3,IPPOINT
C      COMMON /BLK6/OUT,FRRS,RLIN,DAMPF,POURF,WINDG
C      COMMON /BLK7/TSET,TINC
C      COMMON /BLK8/RATE,DELTA
C      DO 3 I=1,7
C 3 P(I)=0.0
C      IPPOINT=0
C      CALL INSTR
C 5 IERR=0
C      DO 33 I=1,3
C 10 IF(ITTOUT("007").NE.0) GO TO 10
C 33 CONTINUE
C      TYPE 101
C 101 FORMAT(// 'KBD= (12)? '0)
C      ACCEPT 102,IROOT
C 102 FORMAT(12)
C      GO TO (14,24,34,44,54,64,74,84,94,104,114,124),IROOT
C      GO TO 5
C 14 TYPE 111
C 111 FORMAT(// 'ROUTE=TCAR (11)? '0)
C      ACCEPT 112,I0K
C      IF (I0K.EQ.0) GO TO 5
C      CALL TCAR
C      GO TO 5
C 24 TYPE 121
C 121 FORMAT(// 'ROUTE=RTAR (11)? '0)
C      ACCEPT 112,I0K
C      IF (I0K.EQ.0) GO TO 5
C      CALL RTAR

```

```

GO TO 5
34 TYPE 131
131 FORMAT(/// ROUTE=HAMAN (I1)? '0)
ACCEPT 112,IOK
IF (IOK.EQ.0) GO TO 5
CALL HAMAN
GO TO 5
44 TYPE 141
141 FORMAT(/// ROUTE=HAUTO (I1)? '0)
ACCEPT 112,IOK
IF (IOK.EQ.0) GO TO 5
CALL HAUTO
GO TO 5
54 TYPE 151
151 FORMAT(/// ROUTE=PTIN (I1)? '0)
ACCEPT 112,IOK
IF (IOK.EQ.0) GO TO 5
CALL PTIN
GO TO 5
44 TYPE 161
161 FORMAT(/// ROUTE=NUTEN (I1)? '0)
ACCEPT 112,IOK
IF (IOK.EQ.0) GO TO 5
CALL NUTEN
GO TO 5
74 TYPE 171
171 FORMAT(/// ROUTE=INPUT (I1)? '0)
ACCEPT 112,IOK
IF (IOK.EQ.0) GO TO 5
CALL INPUT
GO TO 5
84 TYPE 181
181 FORMAT(/// ROUTE=BDUMP (I1)? '0)
ACCEPT 112,IOK
IF (IOK.EQ.0) GO TO 5
CALL BDUMP
GO TO 5
94 TYPE 191
191 FORMAT(/// ROUTE=PRES0 (I1)? '0)
ACCEPT 112,IOK
IF (IOK.EQ.0) GO TO 5
CALL PRES0
GO TO 5
104 TYPE 1101
1101 FORMAT(/// ROUTE=INSTR (I1)? '0)
ACCEPT 112,IOK
IF (IOK.EQ.0) GO TO 5
CALL INSTR
GO TO 5
114 TYPE 1111
1111 FORMAT(/// ROUTE=CONV (I1)? '0)

```

```
ACCEPT 112,ION
IF (ION.EQ.0) GO TO 5
CALL COMU
GO TO 5
124 TYPE 1121
1121 FORMAT(// ' ROUTE=EXIT (11)? '9)
ACCEPT 112,ION
IF (ION.EQ.0) GO TO 5
TYPE 1131
1131 FORMAT(//T10, ' CRYPTIC EXIT---RUN TERMINATED
CALL EXIT
END
```



```

25 TYPE 11,I
11 FORMAT(//T10,' READ PROBLEM ON CHANNEL # ',I)
   GO TO 9999
35 IBATA(ITRY,I)=IPEEK(IABBUF)
   IBATA(ITRY,I)=IBATA(ITRY,I)-170000
3 CONTINUE
   ITRY=ITRY+1
   TIME1=SECND$(0.)
45 TIME2=SECND$(TIME1)
   IF (TIME2.LT.TCMT) GO TO 45
   IF (ITRY.GT.2) GO TO 55
   GO TO 5
55 DO 13 I=1,2
   DO 13 J=1,7
   DATA(I,J)=AJFLT(IBATA(I,J))
13 CONTINUE
   DO 23 I=1,2
   DO 23 J=1,7
   DATA(I,J)=DATA(I,J)*20.000/4096.0
23 CONTINUE
   DO 33 I=1,2
   TEMP(I,1)=287.16-40.510*DATA(I,1)+4.2251*(DATA(I,1)**2)-0.67463*(D
   ATA(I,1)**3)-273.15
   TEMP(I,2)=286.25-39.781*DATA(I,2)+4.0049*(DATA(I,2)**2)-0.65301*(D
   ATA(I,2)**3)-273.15
   TEMP(I,3)=289.50-44.148*DATA(I,3)+4.9115*(DATA(I,3)**2)-0.68631*(D
   ATA(I,3)**3)-273.15
   TEMP(I,4)=288.93-42.701*DATA(I,4)+4.8974*(DATA(I,4)**2)-0.73749*(D
   ATA(I,4)**3)-273.15
   TEMP(I,5)=287.76-42.583*DATA(I,5)+4.4939*(DATA(I,5)**2)-0.69291*(D
   ATA(I,5)**3)-273.15
   TEMP(I,6)=295.37-47.817*DATA(I,6)+5.9273*(DATA(I,6)**2)-0.78990*(D
   ATA(I,6)**3)-273.15
   TEMP(I,7)=294.36-47.424*DATA(I,7)+5.8376*(DATA(I,7)**2)-0.77014*(D
   ATA(I,7)**3)-273.15
33 CONTINUE
   DO 43 I=1,7
   DELTA(I)=TEMP(2,I)-TEMP(1,I)
43 RATE(I)=DELTA(I)/TCMT
   ICYCLE=ICYCLE+1
   TYPE 21,ICYCLE
21 FORMAT(//T45,' READ # ',I6//T35,' SM ',T45,' LS ',T55,' RS ',T45,'
   ' US ',T75,' AS ',T85,' LC ',T95,' UC '//T20,'
   -----
   ----- ')
   DO 53 I=1,2
   TYPE 31,TEMP(I,1),TEMP(I,2),TEMP(I,3),TEMP(I,4),TEMP(I,5),TEMP(I,6
   ),TEMP(I,7)
31 FORMAT(///'      TEMP (DEG C): ',7(F10.3))
53 CONTINUE
   TYPE 41,DELTA(1),DELTA(2),DELTA(3),DELTA(4),DELTA(5),DELTA(6),DELT

```

```
      .X(7)  
41  FORMAT(////'      DELTA (DEB C): ',7(F10.3))  
    TYPE 51,RATE(1),RATE(2),RATE(3),RATE(4),RATE(5),RATE(6),RATE(7)  
51  FORMAT(////'      RATE (DEB/SEC): ',7(F10.3))  
    ITRY=1  
    GO TO 8888  
1199 IERR=1  
8888 CONTINUE  
    RETURN  
    END
```



```

ICHAN(1)="2415
ICHAN(2)="3015
IDONE(1)="2414
IDONE(2)="3214
IADDR(1)="4401
IADDR(2)="4405
IDONE(1)="4600
IDONE(2)="4604
IPREC(1)=12
IPREC(2)=13
SCALE(1)=10.00
SCALE(2)=1.000
IADDR="177000
IADDR="177002
5  CALL IPKKE("170446,"4000)
    CALL IPKKE("170456,"4000)
    CALL IPKKE(IADDR,"5001)
15  ITEST=IPEEK(IADDR)
    IF (ITEST.EQ."5200) GO TO 35
    IF (ITEST.GT."5200) GO TO 25
    GO TO 15
25  TYPE 11
11  FORMAT(/T10,' READ PROBLEM ON CHAN #11(UREF) ')
    GO TO 9999
35  IREF=IPEEK(IADDR)
    IREF=IREF-"170000
45  UREF=AJFLT(IREF)
    UREF=UREF*10.000/4096.0
    IF (UREF.GE.0.50) GO TO 55
    J=1
    GO TO 60
55  J=2
60  CALL IPKKE("170446,"4000)
    CALL IPKKE("170456,"4000)
    CALL IPKKE(IADDR(6),IADDR(6))
    TIME1=SECHDS(0.0)
65  TIME2=SECHDS(TIME1)
    IF (TIME2.GE.5.0) GO TO 75
    GO TO 65
75  CALL IPKKE(IADDR,"4401)
85  ITEST=IPEEK(IADDR)
    IF (ITEST.EQ."4400) GO TO 105
    IF (ITEST.GT."4600) GO TO 95
    GO TO 85
95  TYPE 21
21  FORMAT(/T10,' READ PROBLEM ON CHAN #10(VSIG-REF/PRT) ')
    GO TO 9999
105 IREFR=IPEEK(IADDR)
    IREFR=IREFR-"170000
    REFR=AJFLT(IREFR)
    REFR=REFR*10.000/4096.0

```

```

115 DO 3 I=1,3
    CALL IPOKE("170444,"4000)
    CALL IPOKE("170454,"4000)
    CALL IPOKE(IADDR(1),IADF(1))
    TIME1=SECHRS(0.0)
125 TIME2=SECHRS(TIME1)
    IF (TIME2-SE.5.0) GO TO 135
    GO TO 125
135 CALL IPOKE(IADDR,JADR(J))
145 ITEST=IPEEK(IADDR)
    IF (ITEST.EB.JDONE(J)) GO TO 145
    IF (ITEST.ST.JDONE(J)) GO TO 135
    GO TO 145
155 TYPE 31,I
    31 FORMAT(/T10,' READ PROBLEM ON CHAN #10(USIG) PRT # ',I)
    GO TO 9999
165 IDATA(ITRY,I)=IPEEK(IADF)
    IDATA(ITRY,I)=IDATA(ITRY,I)-"170000
    DATA(ITRY,I)=AJFLT(IDATA(ITRY,I))
    DATA(ITRY,I)=(DATA(ITRY,I)/4096.0)*SCALE(J)+VREF-REFR
    1 CONTINUE
    DO 13 I=1,2
        N=I+5
        CALL IPOKE(IADDR,ICHAN(I))
175 ITEST=IPEEK(IADDR)
    IF (ITEST.EB.IDONE(I)) GO TO 195
    IF (ITEST.ST.IDONE(I)) GO TO 185
    GO TO 175
185 TYPE 41,N
    41 FORMAT(/T10,' READ PROBLEM ON CHAN # ',I)
    GO TO 9999
195 IDATA(ITRY,N)=IPEEK(IADF)
    IDATA(ITRY,N)=IDATA(ITRY,N)-"170000
    DATA(ITRY,N)=AJFLT(IDATA(ITRY,N))
    DATA(ITRY,N)=DATA(ITRY,N)+20.000/4096.0
    13 CONTINUE
    ITRY=ITRY+1
    IF (ITRY.LE.2) GO TO 115
    DO 23 I=1,2
        TEMP(I,1)=3.3558/DATA(I,1)+34.870+2.2008*DATA(I,1)+2.2642E-03*DATA
        .(I,1)**2-5.0296E-04*DATA(I,1)**3-273.15
        TEMP(I,2)=2.8528/DATA(I,2)+30.963+2.2742*DATA(I,2)+1.6939E-03*DATA
        .(I,2)**2-2.2344E-04*DATA(I,2)**3-273.15
        TEMP(I,3)=3.9408/DATA(I,3)+30.803+2.2471*DATA(I,3)+2.1929E-03*DATA
        .(I,3)**2-4.1826E-04*DATA(I,3)**3-273.15
        TEMP(I,4)=3.4789/DATA(I,4)+31.354+2.2489*DATA(I,4)+2.0573E-03*DATA
        .(I,4)**2-3.7857E-04*DATA(I,4)**3-273.15
        TEMP(I,5)=3.8118/DATA(I,5)+31.434+2.2452*DATA(I,5)+2.1355E-03*DATA
        .(I,5)**2-4.1016E-04*DATA(I,5)**3-273.15
        TEMP(I,6)=295.37-47.817*DATA(I,6)+5.9273*DATA(I,6)**2-0.78990*DATA
        .(I,6)**3-273.15

```

```

      TEMP(1,7)=294.34-47.424*DATA(1,7)+5.8376*DATA(1,7)**2-0.77014*DATA
      (1,7)**3-273.15.
23  CONTINUE
      DO 33 I=1,7
      DELTA(I)=TEMP(2,I)-TEMP(1,I)
33  RATE(I)=DELTA(I)/(RTUT+40)
      IPRT=IPRT+1
      TYPE 51,IPRT
51  FORMAT(//T45,' READ 8 ',I4//T35,' ON ',T45,' LS ',T55,' RS ',T45,
      ' US ',T75,' AS ',T85,' LC ',T95,' UC '//T20,' -----
      ----- ')
      DO 43 I=1,2
      TYPE 61,TEMP(I,1),TEMP(I,2),TEMP(I,3),TEMP(I,4),TEMP(I,5),TEMP(I,6
      ),TEMP(I,7)
61  FORMAT(///'      TEMP (DEG-C): ',7(F10.3))
43  CONTINUE
      TYPE 71,DELTA(1),DELTA(2),DELTA(3),DELTA(4),DELTA(5),DELTA(6),DELTA
      (7)
71  FORMAT(///'      DELTA(DEG-C): ',7(F10.3))
      TYPE 81,RATE(1),RATE(2),RATE(3),RATE(4),RATE(5),RATE(6),RATE(7)
81  FORMAT(///'      RATE(DEG/SEC):',7(F10.3))
      ITRY=1
      CALL IPKCE('170446','4000)
      CALL IPKCE('170456','4000)
      GO TO 8888
9999  IERR=1
8888  CONTINUE
      RETURN
      END

```



```

      J,B(8),B(7)
      TYPE 1
21 FORMAT(///T24,' SH=1 ',T34,' L8=2 ',T44,' RS=3 ',T54,' US=4 ',T64,
      ' AB=5 ',T74,' CL=6 ',T84,' IS=7 ',T20,' -----
      '///T10,' ZP(OLD)',7
      .(4X,F6.2)//T10,' U(OLD)'//T10,7(4X,E9.3)//T10,' -----
      ')
15 TYPE 31
31 FORMAT(///T10,' HEATERS(8) TO ADJUST(LIST DIR FORMAT)? '4)
      ACCEPT *,IN(1),IN(2),IN(3),IN(4),IN(5),IN(6),IN(7)
      DO 33 I=1,7
      GO TO (115,125,135,145,155,165,175),IN(I)
      GO TO 33
115 TYPE 111
111 FORMAT(//T10,' ZPSH(LIST DIR) = '4)
      ACCEPT *,P(1)
      GO TO 33
125 TYPE 121
121 FORMAT(//T10,' ZPLS(LIST DIR) = '4)
      ACCEPT *,P(2)
      GO TO 33
135 TYPE 131
131 FORMAT(//T10,' ZPRS(LIST DIR) = '4)
      ACCEPT *,P(3)
      GO TO 33
145 TYPE 141
141 FORMAT(//T10,' ZPUS(LIST DIR) = '4)
      ACCEPT *,P(4)
      GO TO 33
155 TYPE 151
151 FORMAT(//T10,' ZPAS(LIST DIR) = '4)
      ACCEPT *,P(5)
      GO TO 33
165 TYPE 161
161 FORMAT(//T10,' ZPCL(LIST DIR) = '4)
      ACCEPT *,P(6)
      GO TO 33
175 TYPE 171
171 FORMAT(//T10,' ZPIS(LIST DIR) = '4)
      ACCEPT *,P(7)
33 CONTINUE
      U(1)=P(1)*.1707
      U(2)=P(2)*.2839
      U(3)=P(3)*.02547
      U(4)=P(4)*.4462
      U(5)=P(5)*.4370
      U(6)=P(6)*.1393
      U(7)=P(7)*.04827
      V(1)=0.2641*SQRT(U(1))+0.568
      V(2)=0.1595*SQRT(U(2))+0.542
      V(3)=2.083*SQRT(U(3))+0.549

```



```

V(4)=0.09487*SQRT(U(4))+0.555
V(5)=0.09400*SQRT(U(5))+0.699
V(6)=0.3121*SQRT(U(6))+0.559
V(7)=0.9252*SQRT(U(7))+0.514
DO 43 I=1,7
DADF(I)=(-V(I)+2048.0/10.00)+2048.0
IDADF(I)=INT(DADF(I))
IDADF(I)=ABS(IDADF(I))
TYPE 41,I,P(I),U(I),DADF(I),IDADF(I)
41 FORMAT(///T10,' 4',I1,'      IP= ',F10.3,2X,'U= ',E9.3,2X,' VB= ',
.F10.4,2X,' DADF= ',F10.1,2X,' IDADF= ',06)
43 CONTINUE
TYPE 51
51 FORMAT(//T10,' OK TO LOAD(I1)T '4)
ACCEPT 12,IOK
12 FORMAT(I1)
IF (IOK.EQ.0) GO TO 15
DO 53 I=1,7
CALL IPOKE(IDADF(I),IDADF(I))
53 CONTINUE
TYPE 61
61 FORMAT(//T10,' D/AS LOADED-NANAN EXIT ')
RETURN
END

```



```

2  FORAT(I)
   CALL TCAR
   IF (IERR.NE.0) GO TO 9999
   DO 3 I=1,7
     N(I)=0
3  BT(I)=TSET-TEMP(2,I)+TS(I)
5  IF (ISEN.EQ.1) GO TO 15
   CALL TCAR
   GO TO 20
15 CALL RTAR
20 IF (IERR.NE.0) GO TO 9999
   IF (N.EQ.0) GO TO 25
   TMIN=AMIN1(TEMP(2,2),TEMP(2,4),TEMP(2,5),TEMP(2,6),TEMP(2,7))
   IF (TMIN.GT.TEMP(2,1)) GO TO 25
   P(I)=0.0
   GO TO 35
25 DO 33 I=1,6
   IF (I.EQ.3) GO TO 33
   T=TEMP(2,I)
   Q=TSET-T+TS(I)
   IF (Q.GT.WINDO(I)) GO TO 115
   R=RATE(I)-RLIN
   IF (R.LE.0.0000) GO TO 145
   IF (RATE(I).GE.0.0) GO TO 125
   N(I)=N(I)+1
   GO TO 145
115 IF (RATE(I).GT.2.0E-03) GO TO 145
   N(I)=N(I)+1
145 P(I)=(2*N(I))*(((TSET-T+TS(I))/BT(I))*POURF(I)*DANPF(I))
   GO TO 33
125 P(I)=P(I)
33 CONTINUE
   T=TEMP(2,3)
   Q=TSET-T+TS(3)
   IF (Q.LE.WINDO(3)) GO TO 155
   F=(TSET-T+TS(3))/BT(3)
   IF (F.LE.FRRS) GO TO 155
   P(3)=POURF(3)*DANPF(3)
   GO TO 145
155 IF (RATE(3).GE.0.0) GO TO 145
   N(3)=N(3)+1
145 P(3)=(2*N(3))*(((TSET-T+TS(3))/BT(3))*POURF(3)*DANPF(3))
35 DO 43 I=1,6
   PT=POURF(I)*DANPF(I)
   IF (P(I).GT.PT) GO TO 175
   IF (P(I).LT.0.0) GO TO 185
   GO TO 30
175 P(I)=POURF*DANPF(I)
   GO TO 30
185 P(I)=0.0
30 TYPE 11,1,P(I)

```

```

11 FORMAT(//T10,' 2P(8',I1,')= ',F10.2)
43 CONTINUE
  U(1)=P(1)*.1707
  U(2)=P(2)*.2839
  U(3)=P(3)*0.02547
  U(4)=P(4)*.4462
  U(5)=P(5)*.4362
  U(6)=P(6)*.1393
  V(1)=0.2661+SQRT(U(1))+0.548
  V(2)=0.1595+SQRT(U(2))+0.542
  V(3)=2.083+SQRT(U(3))+0.549
  V(4)=0.09487+SQRT(U(4))+0.553
  V(5)=0.09400+SQRT(U(5))+0.499
  V(6)=0.3121+SQRT(U(6))+0.559
  IDAB(1)='170444
  IDAB(2)='170442
  IDAB(3)='170440
  IDAB(4)='170450
  IDAB(5)='170454
  IDAB(6)='170452
  DO 53 I=1,6
    BABF(I)=(-U(I)+2048.0/10.00)+2048.0
    IDABF(I)=INT(BABF(I))
    IDABF(I)=ABS(IDABF(I))
    CALL IPONE(IDAB(I),IDABF(I))
53 CONTINUE
  DO 43 I=1,3
10 IF (ITTOUR('007').NE.0) GO TO 10
43 CONTINUE
  TYPE 21
21 FORMAT(//T10,'  QUERY TIME')
  TIME1=SECHNS(0.0)
45 TIME2=SECHNS(TIME1)
  IF (TIME2.GE.0.01) GO TO 55
  GO TO 45
55 ICHAR=ITTIME
  IF (ICAR.GE.0) GO TO 9999
  N=N+1
  GO TO 5
9999 CONTINUE
  RETURN
  END

```

CRYPTIC/PTIN: SUBROUTINE 45

THIS ROUTINE ACCEPTS INPUT FROM THE CONSOLE TERMINAL. THIS INPUT CONSISTS OF THE PRECISION SAMPLE HOLDER PRT READING, THE SPIRAL QUARTZ GAUGE COUNTER READING AND THE CAPACITANCE GAUGE SIGNALS. THE ROUTINE AVERAGES MULTIPLE INPUTS OF THE SAME POINT IF SO DESIRED; THEN PERFORMS THE NECESSARY CONVERSIONS ON THE RAW SIGNAL. IT ALSO CALCULATES THE APPROPRIATE $TLMP/P$ DATA AND STORES THE RESULTS FOR A DATA RUNUP AT THE APPROPRIATE TIME.

PTIN:VERSION 61 9/4/79
ANTHONY M. POPOWICZ

```

SUBROUTINE PTIM:
COMMON /BLKS/ TSH, ABSP, BP31, BP21, DP11, TLNP1, TLNP2, TLNP3, IPOINT
DOUBLE PRECISION TEMP, BK, P3, P2, P1, P0
TEMP=0.0B0
IPOINT=IPOINT+1
K=0
J=IPOINT
TSH(J)=0.0B0
ABSP(J)=0.0B0
BP31(J)=0.0B0
BP21(J)=0.0B0
DP11(J)=0.0B0
K=K+1
TEMP=TSH(J)
TYPE 1,J
FORMAT(/T10,' INPUT TSH(OHNS) FORMAT:F10.4 TSH(',I4,')='9)
ACCEPT 2,TSH(J)
FORMAT(F10.4)
TSH(J)=TEMP+TSH(J)
TEMP=ABSP(J)
TYPE 11,J
FORMAT(/T10,' INPUT ABSP(CR.0) FORMAT:F10.1 ABSP(',I4,')='9)
ACCEPT 12,ABSP(J)
FORMAT(F10.1)
ABSP(J)=TEMP+ABSP(J)
TEMP=BP31(J)
TYPE 21,J

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```

21 FORMAT(/T10,' INPUT DP31(VOLTS)XSCALE:FORMAT E14.5 DP31(',I4,')
   * '8)
   ACCEPT 22,DP31(J)
22 FORMAT(E14.5)
   DP31(J)=TEMP+DP31(J)
   TEMP=DP21(J)
   TYPE 31,J
31 FORMAT(/T10,' INPUT DP21(VOLTS)XSCALE:FORMAT E14.5 DP21(',I4,')=
   * '8)
   ACCEPT 32,DP21(J)
32 FORMAT(E14.5)
   DP21(J)=TEMP+DP21(J)
   TEMP=DP11(J)
   TYPE 41,J
41 FORMAT(/T10,' INPUT DP11(VOLTS)XSCALE:FORMAT E14.5 DP11(',I4,')=
   * '8)
   ACCEPT 42,DP11(J)
42 FORMAT(E14.5)
   DP11(J)=TEMP+DP11(J)
   TYPE 51
51 FORMAT(/T10,' DO YOU WANT TO AVERAGE IN ANOTHER SET OF DATA?'8)
   ACCEPT 52,IOK
52 FORMAT(I1)
   IF (IOK.EQ.1) GO TO 5
   AK=FLOAT(K)
   BK=BBLE(AK)
   TSH(J)=TSH(J)/BK
   ABSP(J)=ABSP(J)/BK
   DP31(J)=DP31(J)/BK
   DP21(J)=DP21(J)/BK
   DP11(J)=DP11(J)/BK
   TSH(J)=(3.355880)/TSH(J)+(3.4070801)+(2.200880)*TSH(J)+(2.2642D-03
   )*(TSH(J)**2)-(5.0296D-06)*(TSH(J)**3)-2.7315D02
   ABSP(J)=(-0.19254D-13)*ABSP(J)**3+(0.14857D-08)*ABSP(J)**2+(0.1523
   .5D-01)*ABSP(J)
   DP31(J)=DP31(J)+1.0D01
   DP21(J)=DP21(J)+1.0D01
   DP11(J)=DP11(J)+1.0D01
   TYPE 41,TSH(J),ABSP(J),DP31(J),DP21(J),DP11(J),J
41 FORMAT(/T10,' TSH(DEG-C)= ',E13.4//T10,' ABSP(TORR)= ',E13.4/
   ./T10,' DP31(TORR)= ',E13.4//T10,' DP21(TORR)= ',E13.4//T10,' DP
   .11(TORR)= ',E13.4//T10,' POINT N= ',I4//T10,' OK TO SAVE(I1)?'8)
   ACCEPT 42,IOK
42 FORMAT(I1)
   IF (IOK.EQ.1) GO TO 25
   GO TO 15
25 P3=ABSP(J)+DP31(J)
   P2=ABSP(J)+DP21(J)
   P1=ABSP(J)+DP11(J)
   P0=ABSP(J)
   TLNP3(J)=(TSH(J)+2.7315D02)*BL08(P3/P0)

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      TLMP2(J)=(TSH(J)+2.7315D02)*BLQ6(P2/P0)
      TLMP1(J)=(TSH(J)+2.7315D02)*BLQ6(P1/P0)
      TYPE 71, J, TSH(J), ABS(P(J), DP31(J), DP21(J), DP11(J), TLMP3(J), TLMP2(J)
      ., TLMP1(J)
71  FORMAT(///T20,' *****'//T24,' @ ',I4//
      .T20,'      TSH(C)= ',B13.6//T20,'      ABS(P)= ',B13.6//T20,'      DP31
      .(T)= ',B13.6//T20,'      DP21(T)= ',B13.6//T20,'      DP11(T)= ',B13.6
      .//T20,'      TLMP3(C)= ',B13.6//T20,'      TLMP2(C)= ',B13.6//T20,'
      . TLMP1(C)= ',B13.6//T20,' *****')
      RETURN
      END

```

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CRYPTIC/MUTEN: SUBROUTINE M4

THIS ROUTINE IS USED TO SET THE NEW DESIRED TEMPERATURE FOR THE NEXT POINT IN THE RUN. THE OPERATOR MUST PERFORM THIS FUNCTION. IT IS NOT DONE AUTOMATICALLY AND THIS DATA IS REQUIRED BY THE VARIOUS ROUTINES.

MUTEN: VERSION #1 8/30/79
ANTHONY N. POPOWICZ

```

SUBROUTINE MUTEN
COMMON /BLK7/TSET,TINC
CALL IPKOE('177000','15')
5 ITEST=IPEEK('177000')
IF (ITEST.EQ.'214') GO TO 25
IF (ITEST.EQ.'214') GO TO 15
GO TO 5
15 TYPE 1
1 FORMAT(//T10,' READ PROBLEM ON CHAR #1 TSN/TC ')
GO TO 9999
25 ITSN=IPEEK('177002')
ITSN=ITSN-'170000'
SHT=A.FLT(ITSN)
SHT=SHT*20.000/4096.0
SHT=287.14-40.510*SHT+4.2251*SHT**2-0.47485*SHT**3-273.15
TSET=SHT+TINC
35 TYPE 11,SHT,TINC,TSET
11 FORMAT(//T10,' MUTEN ACTIVE: TSN(DEG-C)= ',F10.3,5X,' INCREMENT=
',F10.4,5X,' NEW TSET(DEG-C)= ',F10.3)
TYPE 31
31 FORMAT (//T10,' IS THIS TSET OK? ')
ACCEPT 2,10K
2 FORMAT(I1)
IF (10K.EQ.1) GO TO 9999
TYPE 41
41 FORMAT(//T10,' INPUT THE DESIRED NEW TSET(LIST DIR)? ')
ACCEPT *,I
GO TO 35
9999 CONTINUE
RETURN
END

```


CCCCCCCCCCCCCCCC

CRYPTIC/INPUT: SUBROUTINE #2

THIS ROUTINE ACCEPTS AS INPUT FROM THE CONSOLE TERMINAL THE PROGRAM CONSTANTS AND OPERATING PARAMETERS. THESE VALUES MUST BE DEFINED PRIOR TO EXECUTION OF ALL ROUTINE EXCEPT: KBO, INSTR, HANAN, PTIN, INPUT, DDUMP, PRESS, CONV. INPUT CAN BE ENTERED AT ANY TIME, HOWEVER CARE SHOULD BE TAKEN SO AS NOT TO FORCE THE CRYOSTAT TO BACK TRACK IN TEMPERATURE, THAT IS SET TIME AND TSET APPROPRIATELY.

INPUT:VERSION 01 8/10/79
ANTHONY N. POPONICZ

```

SUBROUTINE INPUT
COMMON /BLK3/TCUT,ICycle
COMMON /BLK4/RTUT,IPT
COMMON /BLK6/GUT,FRS,RLIN,DAMPF,POWRF,WINDO
COMMON /BLK7/TSET,TINC
DIMENSION ICODE(10)
5  DO 3 I=1,10
3  ICODE(I)=0
    TYPE 1
1  FORMAT(/T10,' INPUT OF DATA INSTRUCTIONS: LIST DIR ACCEPT FORMA
.1'//T15,' TSET(=1)'//T15,' TINC(=2)'//T15,' TCUT(=3)'//T15,' R
.TUT(=4)'//T15,' GUT(=5)'//T15,' POWRF(1...7)=(6)'//T15,' DAMPF(
.1...7)=(7)'//T15,' WINDO(1...7)=(8)'//T15,' RLIN(=9)'//T15,' FR
.RS(=10)'//T10,' LIST CODE VALUES FOR DATA INPUT(LIST DIR): '0)
ACCEPT *,ICODE(1),ICODE(2),ICODE(3),ICODE(4),ICODE(5),ICODE(6),ICO
DE(7),ICODE(8),ICODE(9),ICODE(10)
    DO 33 I=1,10
    GO TO (15,25,35,45,65,75,85,95,105),ICODE(I)
    GO 18 33
15 TYPE 11
11 FORMAT(/T10,' TSET= '0)
ACCEPT *,TSET
GO TO 33
25 TYPE 21
21 FORMAT(/T10,' TINC= '0)
ACCEPT *,TINC
GO TO 33
35 TYPE 31

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```

31 FORMAT(//T10,' TCUT= '*)
   ACCEPT *,TCUT
   GO TO 33
45 TYPE 41
41 FORMAT(//T10,' RTUT= '*)
   ACCEPT *,RTUT
   GO TO 33
55 TYPE 51
51 FORMAT(//T10,' OUT= '*)
   ACCEPT *,OUT
   GO TO 33
65 TYPE 61
61 FORMAT(//T10,' POURF(1 TO 7)= '*)
   ACCEPT *,POURF(1),POURF(2),POURF(3),POURF(4),POURF(5),POURF(6),POU
   RF(7)
   GO TO 33
75 TYPE 71
71 FORMAT(//T10,' DANPF(1 TO 7)= '*)
   ACCEPT *,DANPF(1),DANPF(2),DANPF(3),DANPF(4),DANPF(5),DANPF(6),DAN
   PF(7)
   GO TO 33
85 TYPE 81
81 FORMAT(//T10,' WINDO(1 TO 7)= '*)
   ACCEPT *,WINDO(1),WINDO(2),WINDO(3),WINDO(4),WINDO(5),WINDO(6),WIN
   DO(7)
   GO TO 33
95 TYPE 91
91 FORMAT(//T10,' RLIN= '*)
   ACCEPT *,RLIN
   GO TO 33
105 TYPE 101
101 FORMAT(//T10,' FRRS= '*)
   ACCEPT *,FRRS
13 CONTINUE
   TYPE 211,TSET,TINC,TCUT,RTUT,OUT,RLIN,FRRS
211 FORMAT(///T10,' TSET= ',F10.3//T10,' TINC= ',F10.3//T10,' TCUT=
   ',F10.3//T10,' RTUT= ',F10.3//T10,' OUT= ',F10.3//T10,' RLIN =
   ',F10.3//T10,' FRRS= ',F10.3)
   DO 43 I=1,7
   TYPE 221,I,POURF(I),I,DANPF(I),I,WINDO(I)
221 FORMAT(//T10,' POURF(',I,',)= ',F10.3,5X,' DANPF(',I,',)= ',F10.
   3,5X,' WINDO(',I,',)= ',F10.3)
43 CONTINUE
   TYPE 231
231 FORMAT(///T10,' INPUT OK(I1)? '*)
   ACCEPT 12,IOK
12 FORMAT(I1)
   IF (IOK.EQ.0) GO TO 5
   RETURN
END

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CRYPTIC/PRESS: SUBROUTINE #9

THIS ROUTINE MEASURES THE TEMPERATURE OF THE SAMPLE HOLDER USING ITS THERMOCOUPLE AS THE SENSOR, THE ABSOLUTE PRESSURE AND DIFFERENTIAL PRESSURES USING THE SPIRAL QUARTZ GAUGE AND CAPACITANCE GAUGES RESPECTIVELY. CONVERSIONS AND CALCULATIONS ARE PERFORMED AND A PRINTOUT IS PROVIDED.

PRESS: VERSION #1 9/4/79
ANTHONY N. POPOVICZ

```
SUBROUTINE PRESS
DIMENSION ILOAD(4),IDUN(4),IDATA(4),DATA(4)
ILOAD(1)='15
ILOAD(2)='3411
ILOAD(3)='4001
ILOAD(4)='5401
IDUN(1)='214
IDUN(2)='3416
IDUN(3)='4200
IDUN(4)='5400
5 DO 3 I=1,4
  CALL IPOKE('177000,ILOAD(I))
15 ITEST=IPEEK('177004)
  IF (ITEST.EQ.IDUN(I)) GO TO 35
  IF (ITEST.GT.IDUN(I)) GO TO 25
  GO TO 15
25 TYPE 11,I,ILOAD(I)
11 FORMAT(//T10,' READ PROBLEM ON CYCLE= ',I1,2X,'A/S LOAD= ',04)
  GO TO 9999
35 J=IPEEK('177002)
  IDATA(I)=J
  IDATA(I)=IDATA(I)-'170000
  DATA(I)=FLOAT(IDATA(I))
3 CONTINUE
  DATA(1)=DATA(1)*20.000/4096.0
  DATA(1)=287.14-40.510*DATA(1)+4.2251*(DATA(1)**2)-0.67485*(DATA(1)
  **3)-273.15
  DATA(2)=DATA(2)*100.0/4096.0
  DATA(2)=DATA(2)*1000.0
  DATA(2)=(-0.19256E-13)*DATA(2)**3+(0.16857E-08)*DATA(2)**2+(0.1523
```

```

      .SE-01)*DATA(2)
      DATA(3)=DATA(3)*100.0/4096.0
      DATA(4)=DATA(4)*100.0/4096.0
      TYPE 21,DATA(1),DATA(2),DATA(3),DATA(4)
21  FORMAT(//T10,' TSH= ',F10.3,2X,'DEG-C',5X,'PSOS= ',F13.3,2X,' TOR
      .R',5X,'+PCS= ',F10.3,2X,'XSCALE TORR',5X,'-PCS= ',F10.3,2X,'XSCALE
      . TORR'///T10,' DO YOU WANT ANOTHER READ ? '0)
      ACCEPT 12,INORE
12  FORMAT(I1)
      IF (INORE.EQ.1) GO TO 5
9999 CONTINUE
      RETURN
      END

```

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CRYPTIC/INSTR; SUBROUTINE 410

THIS ROUTINE PRINTS OUT THE OPERATING INSTRUCTIONS FOR CRYPTIC AS WELL AS ACCEPTS RUN IDENTIFICATION INFORMATION FROM THE OPERATOR AT THE KEYBOARD. IT ALSO PERFORMS SOME NECESSARY INITIALIZATIONS. IT THEREFORE IS CALLED ONCE AUTOMATICALLY AS SOON AS CRYPTIC IS LOADED AND RUN. INSTR CAN BE CALLED BY KDD AT ANY TIME THE OPERATOR DESIRES.

INSTR: VERSION 01 8/23/79
ANTHONY M. POPONICZ

SUBROUTINE INTR

TYPE 101

```
101 FORMAT(/T10'  MB: 1=YES; 0=NO'//T10'  PRINT INSTR(I1)'0')
ACCEPT 102-IHANT
```

102 FORMAT(11)

```
IF (INANT.EQ.0) GO TO 3
```

TYPE 111

```

111 FORMAT('1110,'SYSTEM OPERATING INSTRUCTIONS: '//T15,' THE MAIN
.(K90) ALLOWS DETERMINATION BY THE OPERATOR THE EXECUTION OF THE
.DESIRED SUBROUTINE '//T16,' SUBR1=TCAR(CODE=1) MEASURES COMPONENT
.TEMPERATURES USING TC-5 '//T16,' SUBR2=RTAR(CODE=2) MEASURES COMP
.ONENT TEMPERATURES USING RT-9 '//T16,' SUBR3=HAMAN(CODE=3) ALLOWS
.THE OPERATOR TO ADJUST THE HEATERS FROM THE KEYBOARD '//T16,'
.SUBR4=HAUTO(CODE=4) HEATER ADJUST IS DONE UNDER PROGRAM CONTROL
.(HAUTO USES TCAR OR RTAR) '//T16,' SUBR5=PTIN(CODE=5) ACCEPTS
.CONSOLE INPUT OF THE PRECISION TEMP/PRESS DATA. THIS DATA IS REDUC
.ED AND STORED '//T16,' SUBR6=NUTEN(CODE=6) MEANS BY WHICH THE
.OPERATOR CAN SET THE NEW DESIRED TEMPERATURE '//T16,' SUBR7=INPUT
.(CODE=7) ACCEPTS INPUT DATA, THAT IS, THE OPERATING PARAMETERS AND
.CONSTANTS '//T16,' SUBR8=DSUMP(CODE=8) PRINTS OUT AND WRITES TO
.DISK THE PRECISION DATA '//T16,' SUBR9=PRESS(CODE=9) READS SQB AND
.CO PRESSURES '//T16,' SUBR10=INSTR(CODE=10) PRINTS OUT OPERATING
.INSTRUCTIONS, ACCEPTS RUN ID INFORMATION AND PERFORMS SOME INITIALI
.ZATIONS (POWER TO HEATERS SET TO ZERO POWER) '//T16,' SUBR11=CONV(C
.ODE=11) CONVERTS KEYBOARD INPUT OF SENSOR SIGNAL VALUES TO TEMP AN
.D PRESSURE DATA '//T16,' SUBR12=EXIT(CODE=12) ALLOWS USER TO TERMIN
.ATE THE RUN.')

```

TYPE 121

121 FORMAT('1'/////////T50.' * * * * *'//T54.' ROUTE=CODE'

```

      //T55, 'ICAR= ' //T55, 'RTAR= ' //T54, 'NANAR= ' //T54
      //NAUTO= ' //T55, 'PTIN= ' //T54, 'NUTEN= ' //T54, 'INPUT
      // ' //T54, 'DBUNP= ' //T54, 'PRESB= ' //T54, 'INSTR=10' //
      T55, 'CONU= ' //T55, 'EXIT= ' //T50' *****
      //T55, 'NOTE: 0=NO AND 1=YES')
5 TYPE 121
131 FORMAT('1' //T10, ' WANT TO INPUT RUN ID INFORMATION(1)? ')
   ACCEPT 112, INANT
112 FORMAT(I1)
   IF (INANT.EQ.0) GO TO 25
   TYPE 141
141 FORMAT('1' //T20, ' RUN ID = ')
   ACCEPT 122
122 FORMAT(20H RUN ID# GOES HERE )
   TYPE 151
151 FORMAT('//T20, ' DATE = ')
   ACCEPT 132
132 FORMAT(20H DATE GOES HERE )
   TYPE 161
161 FORMAT('//T20, ' OPERATOR = ')
   ACCEPT 142
142 FORMAT(25H OPERATOR NAME GOES HERE )
   TYPE 171
171 FORMAT('//T20, ' SAMPLE ID = ')
   ACCEPT 152
152 FORMAT(35H SAMPLE ID GOES HERE )
   TYPE 181
181 FORMAT('//T20, ' SAMPLE PORT#1 = ')
   ACCEPT 162
162 FORMAT(35H SAMPLE PORT ID GOES HERE )
   TYPE 191
191 FORMAT('//T20, ' SAMPLE PORT#2 = ')
   ACCEPT 162
   TYPE 201
201 FORMAT('//T20, ' SAMPLE PORT#3 = ')
   ACCEPT 162
   TYPE 211
211 FORMAT('//T20, ' SAMPLE PORT#4 = ')
   ACCEPT 162
   TYPE 221
221 FORMAT('//TS, ' COMMENT(100CHAR): ')
   ACCEPT 202
202 FORMAT(100H
   HERE
25 CALL IPOKE("177000,"0)
   CALL IPOKE("170440,"4000)
   CALL IPOKE("170442,"4000)
   CALL IPOKE("170444,"4000)
   CALL IPOKE("170446,"4000)
   CALL IPOKE("170450,"4000)
   CALL IPOKE("170452,"4000)

```

COMMENT GOES

```
CALL IPKCE("170454,"4000)
CALL IPKCE("170456,"4000)
* TYPE 231
231 FORMAT(//T10,' HAS INPUT DATA BEEN SPECIFIED AS OF YET(11) ? ')
ACCEPT 212, IYES.
212 FORMAT(11)
IF (IYES.EQ.1) GO TO 15
CALL INPUT
15 CONTINUE
RETURN
END
```



```

T=288.93-42.701*U+4.8974*U**2-0.73749*U**3-273.15
TYPE 81,T
81 FORMAT(/T10,' TUS= ',F10.3)
TYPE 91
91 FORMAT(/T10,' VAS= ')
ACCEPT *,U
T=287.74-42.583*U+4.6939*U**2-0.69291*U**3-273.15
TYPE 101,T
101 FORMAT(/T10,' TAS= ',F10.3)
TYPE 111
111 FORMAT(/T10,' VLC= ')
ACCEPT *,U
T=295.37-47.817*U+5.9273*U**2-0.78990*U**3-273.15
TYPE 121,T
121 FORMAT(/T10,' TLC= ',F10.3)
TYPE 131
131 FORMAT(/T10,' VUC= ')
ACCEPT *,U
T=294.34-47.624*U+5.8376*U**2-0.77014*U**3-273.15
TYPE 141,T
141 FORMAT(/T10,' TUC= ',F10.3)
GO TO 5
25 TYPE 151
151 FORMAT(/T10,' RSH= ')
ACCEPT *,R
T=3.3558/R+34.870+2.2008*R+2.2642E-03*R**2-5.0296E-06*R**3-273.15
TYPE 161,T
161 FORMAT(/T10,' TSH= ',F11.4)
TYPE 171
171 FORMAT(/T10,' RLS= ')
ACCEPT *,R
T=2.8528/R+30.943+2.2742*R+1.6939E-03*R**2-5.0296E-06*R**3-273.15
TYPE 181,T
181 FORMAT(/T10,' TLS= ',F11.4)
TYPE 191
191 FORMAT(/T10,' RRS= ')
ACCEPT *,R
T=3.9408/R+30.803+2.2471*R+2.2929E-03*R**2-4.1826E-06*R**3-273.15
TYPE 201,T
201 FORMAT(/T10,' TRS= ',F11.4)
TYPE 211
211 FORMAT(/T10,' RUS= ')
ACCEPT *,R
T=3.67891/R+31.354+2.2489*R+2.0573E-03*R**2-3.7857E-06*R**3-273.15
TYPE 221,T
221 FORMAT(/T10,' TUS= ',F11.4)
TYPE 231
231 FORMAT(/T10,' RAS= ')
ACCEPT *,R
T=3.8118/R+31.434+2.2452*R+2.1355E-03*R**2-4.1016E-06*R**3-273.15
TYPE 241,T

```

```

241 PUNCH(1//T10,' T00= ',F11.4)
GO TO 5
35 TYPE 251
251 FORMAT(//T10,' S00(CR)= '9)
ACCEPT *,8
P=-0.19254E-13*0**3+0.14837E-08*0**2+0.15235E-01*0
TYPE 261,P
261 FORMAT(//T10,' P000= ',F11.4)
TYPE 271
271 FORMAT(//T10,' DP31,SCALE= '9)
ACCEPT *,8,8
P=0*8*10.000
TYPE 281,P
281 FORMAT(//T10,' DP31= ',F11.5)
TYPE 291
291 FORMAT(//T10,' DP21,SCALE= '9)
ACCEPT *,8,8
P=0*8*10.000
TYPE 301
301 FORMAT(//T10,' DP21= ',F11.5)
TYPE 311
311 FORMAT(//T10,' DP11,SCALE= '9)
ACCEPT *,8,8
P=0*8*10.000
TYPE 321,P
321 FORMAT(//T10,' DP11= ',F11.5)
GO TO 5
9999 CONTINUE
RETURN
END

```

(A-2) PURIFICATION OF FLUOROMETHANES

by Jan Shulman

Last year, we reported on the synthesis of $^{13}\text{CH}_3\text{F}$, the chemical purification of $^{13}\text{CH}_3\text{F}$ and $^{12}\text{CD}_3\text{F}$, and preliminary runs for obtaining the best procedures for purification of fluoroform. This year, we have purified $^{12}\text{CH}_3\text{F}$, $^{12}\text{CHF}_3$, $^{13}\text{CHF}_3$, and $^{12}\text{CDF}_3$ to reduce all impurities to a level of 10 ppm or less.

Methyl fluoride, $^{12}\text{CH}_3\text{F}$, purchased from Linde contained 1% CO_2 and 0.2% H_2O as the only impurities. The chemical purification was carried out by passing it three times through a tube of Ascarite (15mmOD x 60 cm), conditioned by heating at 150°C for 48 hours under vacuum. This reduced the CO_2 -level to below the 10 ppm level. A well-conditioned Ascarite also aided in the removal of water, but a bulb-to-bulb distillation removed all remaining water.

Fluoroform, $^{12}\text{CHF}_3$, was also purchased from Linde, which contained 50ppm carbon dioxide and an unknown impurity, which we have become to call D-peak. The Unknown D, which is much higher-boiling than fluoroform, seems to be present in other fluoroforms, $^{12}\text{CDF}_3$ and $^{13}\text{CHF}_3$, its identity being based on the retention time relative to that of fluoroform. The amount of the impurity in the Linde's $^{12}\text{CHF}_3$ was about 300ppm, according to the relative peak areas. As was the case with the other two isotopic fluoroforms, the first step of purification was a bulb-to-bulb distillation to remove very high-boiling and very low-boiling impurities, in case they had not been detected in the gas-chromatographic analysis. The fluoroform was then passed through an Ascarite tube (15 mmOD x 60cm) several times. To remove the Unknown D, the gas was then slowly passed through an U-tube (15mmOD x 60 packed length) packed with Chromosorb 102, submerged in a slurry of iso-propanol (-50°C). The passage through Chromosorb-102 was repeated six to eight times. The gas was finally dried by passing it through an Ascarite tube. This procedure reduced the impurities to less than 3 ppm CO_2 and 10 ppm for the Unknown D.

Fluoroform, $^{12}\text{CDF}_3$, was purchased from Stohler Isotope Chemicals and contained 60 ppm CO_2 and 5 ppm (by peak area) of the Unknown D. The same

procedure as the one used for the purification of $^{12}\text{CHF}_3$ was used, which reduced the impurities to 8 ppm for CO_2 and less than the detection limit (0.1 ppm) for the Unknown D.

Fluoroform, $^{13}\text{CHF}_3$, was also purchased from Stohler Isotope Chemicals. It was custom-synthesized, and it took them one year to deliver one liter (NTP) of the gas. It contained at least nine detectable peaks. (However, we stopped the gas chromatographic analysis after one hour of operation at the carrier (helium) flow rate of 18.5 cc/min, at temperatures programmed between 117°C and 227°C , through a 6 ft column of Spherocarb 80/100.) The nine impurities detected were, in the order of elution: 0.2% CO , 85 ppm CO_2 , 2.2% Unknown 1, 60 ppm Unknown 2 (=Unknown D), 160 ppm Unknown 3, 35 ppm Unknown 4, 1.95% Unknown 5, 780 ppm Unknown 6, and 350 ppm Unknown 7. The magnitudes of the unknown impurities were calculated as the ratios of the chromatographic peak areas. Prior to the GC-analysis, a bulb-to-bulb distillation had eliminated at least one very high-boiling substance of yellowish orange color which appeared to sublime when heated with a blower but easily condensed on the vessel walls at room temperature. After a slow (2 hr) process of bulb-to-bulb distillation, the gas was passed slowly (twice) through the Chromosorb-102 tube at -50°C and then through an Ascarite tube. The purified gas contained 7 ppm CO_2 , 7 ppm Unknown D, and less than the detection limit for all other impurities.

(A-3) MEASUREMENTS OF VAPOR PRESSURE ISOTOPE EFFECTS IN FLUOROFORM

by Anthony Popowicz
 Jan Shulman
 Takao Oi

The $^{13}\text{C}/^{12}\text{C}$ and D/H vapor pressure isotope effects for trifluoromethane were investigated using the precision cryostat in the computer-assisted manual operation, as described in Section A-1. A temperature range covered was from -139.85°C to -80.81°C . Thermal stability of the sample holder temperature during the vapor pressure determinations was ± 1 millidegree or less for all data points. The temperature stability was determined by the change in absolute pressure of the reference gas, $^{12}\text{CHF}_3$, as measured by the error signal output of the spiral quartz gauge. The data obtained is summarized in Table 1. The same data for the $^{13}\text{C}/^{12}\text{C}$ and D/H effects (except for several points depleted as a result of a preliminary test) have been plotted in Figures 2 and 3, respectively. The depleted points are: Nos. 1, 8, 55, 56, 62, and 63 of Table 1 for the $^{13}\text{C}/^{12}\text{C}$, and Nos. 7, 8, 14, and 63 of Table 1 for the D/H effect.

Figure 2 shows two remarkable features which have never been observed so clearly in previous VPIE measurements. First, the plot of $T \ln(P'/P)$ vs $1/T$, where P' and P are the vapor pressures of the lighter and the heavier isotopic species, has a negative slope. Secondly, the plot clearly points to a cross-over with the zero-line at which $T \ln(P'/P) = 0$, or $P' = P$. These observations are consistent with the prediction made recently by Borodinsky, Wieck, Mayfield, and Ishida,⁽²⁾ who observed the qualitatively similar results in their cryogenic distillation study of the VPIE in $^{13}\text{CHF}_3/^{12}\text{CHF}_3$.

We would have liked to make the measurements at even higher temperatures to actually observe the cross-over with the zero-line but the impending moving of the whole laboratory forced us to suspend the further data-taking until after the moving. Having moved, we are in the process of rebuilding and, the first experiments on our agenda is to resume the measurement of VPIE for fluoroform. The discussion below, therefore, is only a tentative one. However, the qualitative nature of the VPIE that emerges out of the discussion will hold even after more data are accumulated.

Table 1: Carbon and Hydrogen Vapor Pressure Isotope Effects in Fluoroform

No.	T (°K)	$10^3/T$ (°K ⁻¹)	P (Torr)	T ln(P*/P)		Date
				¹² C/ ¹³ C	H/D	
1	133.30	7.502	4.5097	-2.625	+4.592	10/16
2	134.27	7.448	5.1344	-2.508	+4.545	10/16
3	135.17	7.398	5.7895	-2.505	+4.500	10/16
4	135.95	7.356	6.4295	-2.481	+4.475	10/16
5	136.85	7.317	7.2965	-2.450	+4.466	10/16
6	137.82	7.256	8.1512	-2.472	+4.431	10/16
7	138.63	7.213	8.8064	-2.498	+4.468	10/02
8	138.89	7.205	9.1568	-2.617	+4.370	10/03
9	139.08	7.190	9.5378	-2.470	+4.414	10/17
10	140.53	7.116	11.016	-2.490	+4.376	10/02
11	141.93	7.046	13.317	-2.516	+4.344	10/03
12	143.91	6.949	16.570	-2.448	+4.290	10/03
13	145.12	6.891	18.909	-2.429	+4.276	10/03
14	146.88	6.809	23.420	-2.363	+4.316	10/03
15	146.24	6.838	21.927	-2.364	+4.283	10/04
16	147.98	6.758	26.362	-2.346	+4.213	10/04
17	149.03	6.710	29.394	-2.338	+4.178	10/04
18	150.06	6.664	32.610	-2.324	+4.177	10/04
19	152.02	6.578	39.714	-2.294	+4.121	10/04
20	152.02	6.578	39.424	-2.288	+4.155	10/07
21	152.95	6.538	43.479	-2.274	+4.096	10/04
22	153.98	6.494	47.595	-2.244	+4.050	10/10
23	154.05	6.491	48.266	-2.264	+4.075	10/04
24	154.67	6.465	50.918	-2.229	+4.084	10/07
25	155.15	6.445	53.632	-2.243	+4.047	10/04
26	155.41	6.435	54.486	-2.229	+4.016	10/10

[continued]

[Table 1; continued]

No.	T (°K)	$10^3/T$ (°K ⁻¹)	P (Torr)	T ln(P'/P)		Date
				¹² C/ ¹³ C	H/D	
27	156.11	6.406	58.694	-2.223	+4.025	10/04
28	157.07	6.367	64.031	-2.209	+4.015	10/04
29	157.26	6.359	64.839	-2.184	+3.976	10/10
30	158.03	6.328	69.063	-2.146	+3.997	10/07
31	159.20	6.281	77.023	-2.138	+3.943	10/10
32	159.35	6.275	78.426	-2.143	+3.975	10/17
33	161.19	6.204	92.168	-2.038	+3.926	10/17
34	162.61	6.150	104.02	-2.032	+3.898	10/17
35	164.06	6.095	117.26	-2.031	+3.876	10/17
36	165.33	6.049	129.65	-1.994	+3.864	10/11
37	165.96	6.026	136.31	-1.998	+3.840	10/11
38	167.14	5.983	149.89	-1.977	+3.821	10/11
39	168.05	5.951	160.96	-1.954	+3.802	10/11
40	169.45	5.901	179.08	-1.923	+3.787	10/11
41	170.89	5.852	193.82	-1.892	+3.777	10/11
42	171.38	5.835	207.49	-1.856	+3.757	10/11
43	171.79	5.821	213.80	-1.769	+3.744	10/08
44	172.78	5.788	230.52	-1.774	+3.724	10/08
45	173.60	5.766	244.19	-1.770	+3.724	10/11
46	173.87	5.751	248.79	-1.733	+3.700	10/08
47	174.98	5.714	269.30	-1.730	+3.682	10/08
48	175.59	5.695	280.94	-1.715	+3.696	10/11
49	175.95	5.683	288.02	-1.663	+3.657	10/08
50	176.92	5.652	308.22	-1.634	+3.644	10/08
51	177.89	5.621	329.70	-1.631	+3.633	10/08
52	179.85	5.560	375.99	-1.482	+3.591	10/08

[continued]

[Table 1; continued]

No.	T (°K)	$10^3/T$ (°K ⁻¹)	P (Torr)	T ln(P'/P)		Date
				¹² C/ ¹³ C	H/D	
53	180.24	5.548	387.14	-1.590	+3.577	10/18
54	181.18	5.519	412.35	-1.578	+3.563	10/18
55	181.71	5.503	425.54	-1.347	+3.551	10/68
56	182.15	5.490	438.79	-1.558	+3.555	10/18
57	183.12	5.461	466.79	-1.498	+3.527	10/18
58	184.09	5.432	496.64	-1.453	+3.507	10/18
59	185.07	5.403	527.89	-1.395	+3.489	10/18
60	186.57	5.360	579.36	-1.273	+3.471	10/18
61	188.01	5.319	631.18	-1.180	+3.457	10/18
62	189.42	5.279	687.16	-1.062	+3.418	10/18
63	192.34	5.199	814.05	-0.8440	+3.448	10/18

Figure 2: $^{12}\text{C}/^{13}\text{C}$ Vapor Pressure Isotope Effect in Fluoroform

Figure 3: H/D Vapor Pressure Isotope Effect in Fluoroform

The solid lines through the experimental points of Figures 2 and 3 have been obtained by a least-squares fit in the form of

$$T \ln \frac{P'}{P} = \frac{A}{T} + B + C T \quad (1)$$

For the $P'(^{12}\text{CHF}_3)/P(^{13}\text{CHF}_3)$ effect, we found

$$\begin{aligned} A &= 1217.5 \pm 79.3 \quad (^{\circ}\text{K}) \\ B &= -21.12 \pm 1.00 \\ C &= 0.0711 \pm 0.0013 \quad (^{\circ}\text{K}^{-1}) \end{aligned} \quad (2)$$

According to Eqs. (1) and (2), there would be two cross-overs: One at 78.30° , which is the ordinary one, and the other at 218.66°K . For the $P'(^{12}\text{CHF}_3)/P(^{12}\text{CDF}_3)$ effect, we found

$$\begin{aligned} A &= 336.7 \pm 34.1 \quad (^{\circ}\text{K}) \\ B &= +2.93 \pm 0.43 \\ C &= -0.0067 \pm 0.0013 \quad (^{\circ}\text{K}^{-1}) \end{aligned} \quad (3)$$

According to Eqs. (1) and (3), there would be one cross-over at 529.12°K . For the H/D effect, we also fitted to the form of

$$T \ln \frac{P'}{P} = \frac{A}{T} + B' \quad (4)$$

which yielded

$$\begin{aligned} A &= 506.99 \pm 3.86 \quad (^{\circ}\text{K}) \\ B &= +0.778 \pm 0.024 \end{aligned} \quad (5)$$

According to Eqs. (4) and (5), there would be no cross-over temperature, because B' of Eq.(5) is positive. Usually, this quantity is negative, giving rise to one cross-over. The use of the more sophisticated functional form of Eq. (1) did not help the situation, as the B -value of Eq.(3) is also positive. The errors given in Eqs. (2), (3), and (5) are the root-mean-square deviation of the experimental points relative to the least-squares fit lines. A comparison of the errors in the constants given by Eq. (3) and (5) indicate that Eq. (4) is a better functional form than Eq. (1) for the deuterium effect.

The least-squares fit line for the carbon effect given by Eq. (1) has one minimum, becomes linear with a positive slope at large values of $1/T$ (low T), and becomes hyperbolic with negative slopes at small values of $1/T$ (high T). Obviously, the temperature range of our experimental points lie to the left of the minimum in the plot against $1/T$.

The observed behaviors of the carbon VPIE and D/H-VPIC in CHF_3 can be explained in the following way. The quantity $\ln(P'/P)$ is approximately equal to $\ln(f_c'/f_g')$, where $(s/s')f_c$ and $(s/s')f_g$ are the isotopic reduced partition function ratios of the condensed and gas phases, respectively:

$$\ln \frac{P'}{P} \approx \ln \frac{s}{s'} f_c - \ln \frac{s}{s'} f_g, \quad (6)$$

and

$$\ln \frac{s}{s'} f_g = \frac{3N-6}{\sum_{i=1}} [\ln b(u_i') - \ln b(u_i)], \quad (7)$$

where

$$\ln b(u) = - \ln \frac{u e^{-u/2}}{1 - e^{-u}}, \quad (8)$$

in which $u = hv/kT$. When T is not so large or when v is large, we have $u_i \gg 1$, so that

$$\ln b(u) \approx \frac{u}{2}, \quad (9)$$

which is the ZPE approximation. When T is very large, or when v is small, we have $u_i \ll 1$, so that

$$\ln b(u) \approx W_1 A_1 u^2 = \frac{u^2}{24}, \quad (10)$$

which is the first term of the orthogonal approximation. In general, $\ln b(u)$ behaves as shown in Figure 4a, and $T \ln b(u)$ behaves as shown in Figure 4b. The asymptotic value of $T \ln b(u)$ at $1/T \rightarrow \infty$ ($T \rightarrow 0$) is $hv/2k$, so that its absolute value is larger, the larger the vibrational frequency. One also notes that the isotopic difference in $\ln b(u)$, or $\delta \ln b(u)$, levels off much faster than $\ln b(u)$ does, because the term of $\ln u$ on the right-hand side of Eq. (8) becomes independent of temperature when its isotopic difference is taken.

Figure 4a

Figure 4b

According to the simple cell model of liquid,

$$\ln \frac{s}{s_c} f_c = \sum_{i=1}^6 [\ln b(u_i') - \ln b(u_i)] + \sum_{i=1}^{3N-6} [\ln b(u_i') - \ln b(u_i)], \quad (11)$$

In which the first summation is taken over the six external motions which are regarded to be weak (small frequency) oscillatory motions, and the second summation is taken over all internal vibrational modes which are usually of the much higher frequencies than those for the external motions. Thus, usually, the terms in the first summation are approximated by Eq. (10), and the terms in the second summation are approximated by Eq. (9). Therefore,

$$\ln \frac{s}{s_c} f_c \approx \frac{1}{24} \sum_i^{\text{ext}} \delta u_{ic}^2 + \frac{1}{2} \sum_i^{\text{int}} \delta u_{ic}^2, \quad (12)$$

where δ denotes the isotopic difference, the lighter minus the heavier: $\delta u_{ic} = (u_i' - u_i)$ condensed, and $\delta u_{ic}^2 = (u_i'^2 - u_i^2)$ condensed. And, correspondingly,

$$\ln \frac{s}{s_c} f_g \approx \frac{1}{2} \sum_i^{\text{int}} \delta u_{ig}^2. \quad (13)$$

Combining Eqs. (12) and (13),

$$T \ln \frac{P'}{P} \approx \frac{1}{T} \left[\frac{1}{24} \frac{h}{k} \sum_i^{\text{ext}} \delta v_{ic}^2 \right] - \left[\frac{h}{2k} \sum_i^{\text{int}} (\delta v_{ig} - \delta v_{ic}) \right] \quad (14a)$$

$$= \frac{A}{T} - B, \quad (14b)$$

in which A is always positive, and B is usually positive. This is the theoretical basis for the functional form of Eq. (4), in which B' (= -B) is usually expected to be negative. The sign on our least-squares fit value of B for the D/H effect is "wrong" according to the usual expectation. However, both the "wrong" sign on the B value for the D/H effect and the second cross-over phenomenon in the carbon isotope effect can be explained in terms of a blue-shift of the C-H stretching frequency upon condensation of CHF_3 molecules. Table 2 is a summary of observed vibrational frequencies of $^{12}\text{CHF}_3$.

Table 2: Observed Frequencies of $^{12}\text{CHF}_3$

Mode	Gas (cm^{-1})			Liquid (cm^{-1})	
	Long ⁽¹⁴⁾	Galasso ⁽¹⁵⁾	D'Cunha ⁽¹⁶⁾	Glockler ⁽¹⁷⁾	Rank ⁽¹⁸⁾
$\nu_1(A_1)$	3035	3031	3031	3062	3062
$\nu_2(A_1)$	1137	1140	1140	1117	1117
$\nu_3(A_1)$	700	700	700	697	697
$\nu_4(E)$	1376	1372	1372	1376	1376
$\nu_5(E)$	1152	1152	1152	---	1160
$\nu_6(E)$	508	507	507	508	508

It is clear that the frequency ν_1 for the C-H stretching mode blue-shifts upon condensation by about 30 cm^{-1} from about 3030 cm^{-1} to about 3060 cm^{-1} . Usually, all vibrational frequencies red-shift upon condensation. Then, the corresponding frequencies of all the isotopic species also red-shift, and the phase difference of the isotopic difference, i.e.,

$$\begin{aligned} \delta\nu_{ig} - \delta\nu_{ic} &= (\nu'_{ig} - \nu'_{ic}) - (\nu_{ig} - \nu_{ic}) \\ &= \Delta\nu'_i - \Delta\nu_i, \end{aligned} \quad (15)$$

is usually positive, because the condensation shift $\Delta\nu'_i$ of the lighter isotope is usually greater than the condensation shift $\Delta\nu_i$ of the heavier isotope. This is in turn due to the fact that the phase shift in a given frequency is usually greater, the greater the magnitude of the individual frequency. Thus, ordinarily, the zero-point energy shift term for every vibrational mode in Eq. (14a), $(h/2k)(\delta\nu_{ig} - \delta\nu_{ic})$, is positive. Figure 5a schematically shows the composite effects of the two terms of Eq. (14b).

In reality, however, Eqn. (14b) is applicable only at temperatures which is not too high, so that the ZPE approximation of Eq. (9) may be applicable, but at the same time not too low, so that the first quantum correction term of Eq. (10) may be sufficient. Outside of this temperature range, Eq. (14b) breaks down. Thus, when the temperature is raised sufficiently, the internal vibrational modes start to get excited, and the higher vibrational states contribute positively and significantly

to $\ln(s/s')f$, $\ln(P'/P)$, and $T \ln(P'/P)$. At infinitely high temperature, all vibrational modes are fully excited, when the quantum mechanical partition function approaches the classical partition function, and the logarithm of the reduced partition function $\ln(s/s')f$ approaches zero. This high temperature behavior is depicted by the solid lines in Figure 5b. In the same figure, the plot of $-B$ is a composite effect of the plots of phase differences of isotopic differences of the individual vibrational modes, each of which behaves according to Figure 4b. The deviation from the linearity in the plot of $T \ln(P'/P)$ at high temperature is due to excitation of internal vibrational modes.

If a frequency (say $i=1$) shows a significant blue-shift upon condensation, the corresponding ZPE-shift term, $\delta v_{1g} - \delta v_{1c}$, for the frequency would be negative, and Eq. (14a) may be re-written as

$$T \ln \frac{P'}{P} = \frac{A}{T} + B_b - \bar{B}, \quad (16)$$

where

$$B_b = \frac{h}{2k} (\delta v_{1c} - \delta v_{1g}) > 0 \quad (17)$$

and

$$\bar{B} = \frac{h}{2k} \sum_i^{3N-6-1} (\delta v_{ig} - \delta v_{ic}) > 0. \quad (18)$$

If, furthermore, one considers the excitation of the internal modes at the higher temperature, B_b and $\bar{B}$ behave as shown in Figure 5c. This leads to the second cross-over (at the higher temperature than the first), as observed in the carbon VPTE in CHF_3 .

For the D-for-H substitution, the isotope shifts, δv_{1c} and δv_{1g} , are expected to be greater than those for the ^{13}C -for- ^{12}C substitution, as the zero-th order approximation, $\delta v \approx \delta(1/\sqrt{\mu_{\text{CH}}})$, gives the ratio of δv for D/H to that for $^{13}\text{C}/^{12}\text{C}$ to be 0.277 to 0.003. So, one expects

$$(\delta v_{1c} - \delta v_{1g})_{^{13}\text{C}/^{12}\text{C}} > (\delta v_{1c} - \delta v_{1g})_{\text{D/H}}, \quad (19)$$

which may lead to the normal VPTE for the D/H effect at the temperatures of our interest, as shown in Figure 5d.

Figure 5a

Figure 5b

Figure 5c

Figure 5d

These analyses are quite qualitative in nature. First, the vapor pressure ratio will have to be corrected for the isotopic and chemical impurities, the non-ideality of the gas phase, and the molal volume effects. Then, there is a strong indication⁽³⁾ that fluoroform is at least partially dimerized at temperatures below about 500°K. For instance, at 200°K and under 1 atm, our calculation based on the dissociation energy of dimer computed by a molecular orbital method⁽¹⁾ showed that 23% of CHF_3 is dimerized. Then, one would have to take into account the presence of the dimer in our cell-model discussion. Perhaps, we will have to even consider the use of the medium cluster model^(4,5) as a basis of representation of the liquid. With regard to the argument which is based on the blue-shifting C-H stretch frequency, we plan to spectrophotometrically show the blue-shifts in this frequency for $^{13}\text{CHF}_3$ and CDF_3 , which have not been experimentally demonstrated.

(B) STUDIES OF NITROGEN ISOTOPE EXCHANGE SYSTEMS

by Michael Prencipe

The construction of an all-stainless steel nitrogen-15 fractionation system based on the isotope exchange between gaseous nitric oxide and the liquid dinitrogen trioxide has been continued. As reported previously,^(1,6) an increase in the gaseous pressure by an addition of nitric oxide should increase the effective stage separation factor, due to the fact that it would increase the mole fraction of +2 nitrogen in the gas phase, while it would not affect the liquid phase composition so markedly. Accordingly, we designed a system of exchange columns and the refluxers, to be constructed of Type 316 stainless steel, which was reported on last year.⁽¹⁾ The diagram of the whole design is reproduced in Figure 6 for the purpose of orientation.

Last year, we reported on the constructions of the product refluxer, the compressor, the liquid flowmeter, and the scrub tower. Because the product refluxer was the most delicate apparatus that requires the most careful attention in the design and its operation, and because the Pyrex reflux column system designed by Monse, Spindel, Kauder and Taylor,⁽⁷⁾ had shown its satisfactory performance, and further because the purpose of this study is to demonstrate the predicted possibility of the enhanced separation under pressure rather than to demonstrate the performances of any other components of the system, we chose to use the Pyrex reflux column of the Monse-Spindel-Kauder-Taylor design, which is to be operated under the atmospheric pressure. This created a need for a compressor for nitric oxide to be placed on the return line between the refluxer and the exchange column as shown in Figure 6. Accordingly, last year we designed and fabricated a compressor and its control, which was based on an alternate condensation-and-vaporization steps. However, we have since decided to abandon this design due to the potential hazard that the condensed nitric oxide poses.

During the current year we have designed another compressor. This utilizes two bellows pumps, operating at 180° out of phase of each other. The reason for the need for the pair of pumps is a slow cycle time of these pumps as explained in the following.

Figure 6: Flow Diagram of NO/N₂O₃ System

Figure Legends for Figure 6

C	Cryo-compressor chamber
CG	Capacitance gauge for cryo-compressor
CV	Magnetically operated valve, normally open
C1	NO ₂ condenser
C2	Wast-end condenser
C3	Product reflux condenser
E	Exchange column
FL	Flange or vacuum/pressure coupling
F1	Gas NO ₂ rotameter
F2	Liquid drop flowmeter
LS1	Liquid level sensor
LS2	" " "
LS3	" " "
P	Product refluxer, Packed Pyrex column
PC1	Photocell for SO ₂ control
PC2	" " "
RH	Reservoir, high pressure
RL	Reservoir, low pressure
RSV1	Regulating solenoid throttle valve for waste gases
RSV2	Regulating solenoid throttle valve for product
RSV3	Regulating solenoid throttle valve for refluxed NO
S	Packed equilibrator for liquid phase
SSV1	Gas-sampling 3-way valve
SSV2	Gas-sampling 3-way valve
SV1	Solenoid/air-operated valve for cryo-compressor
SV2	" " " " " "

The bellows has to be considerably flexible in order to produce an acceptably large compression ratio. Such bellows usually withstands only about 3 atmospheres of pressure difference between the inside and outside of the bellows. In order to create a compression ratio of 20:1 per pump, the pressure surrounding the bellows has to be controlled. By alternating the pressure of air surrounding the bellows one can move the bellows between its compressed length and the expanded length. However, care must be taken not to exceed the differential pressure limit of 3 atmospheres at any time during the cycle. A preliminary study showed that the cycle time cannot be reduced much below 5 seconds per cycle. This would mean that a large reservoir must be provided on both sides of such a single pump to damp out the oscillations of pressures and flow rates. This would require a large product holdup. To avoid this, we needed two pumps working at 180° out of phase with respect to each other.

A prototype design of the bellows pump is presented below. Referring to Figure 7, the bellows are available from Servometer Corp., Cedar Grove, New Jersey. It is made of nickel. After the closed top-end of the bellows is silver-soldered to the top plate, and the open bottom-end of the bellows is electron-beam welded to the bottom flange, inside of the bellows is custom-coated by Union Carbide's Parylene, which has a satisfactory mechanical property for this purpose and an excellent chemical resistance against nitric acid and nitric oxide.

A bellows with an O.D. of 3.480" and I.D. of 2.980", making the effective area of 7.993 in^2 , can be compressed by a stroke length of 0.802". The insert (cf. Figure 7) of 2.750" O.D. and an intrusion length of 1.88" from the open end of the bellows would reduce the dead volume at compression, so that a compression ratio of 20:1 is achieved. The volume delivered per full compression stroke is $0.802 \times 7.993 = 6.41 \text{ in}^3$ of gas at 1 atm. If the cycle time is 5 second, a single bellows pump will produce a flow rate of $6.41 \text{ in}^3 \times 12 \text{ cycles/min} = 77 \text{ in}^3/\text{min}$, or 1.26 liters (NTP)/min of nitric oxide. This flow rate is appropriate for our purpose, because the required NO flow rate of 2 liter NTP/min can be handled by the pair of such pumps.

A twin bellows pump of this design will cost about \$3,000, each bellows being priced at \$1,300. The bellows is expensive, partly because it is guaranteed for one million cycles of the compression/expansion operation: Other bellows such as the stainless steel bellows manufactured by Metal

Figure 7: Bellows Compressor for Nitric Oxide

Bellows Co. are guaranteed typically for only 10,000 cycles. We are, therefore, seriously considering an alternative to this design. For instance, a diaphragm pump, Model 154 "Bullfrog" compressor, manufactured by Kamlon Products & Development Corp. is made of stainless steel Type 316 and a reinforced Teflon diaphragm. For the compression ratio of 10:1, the flow rates up to 11 liter NTP/min is obtained using up to 175 cycles/min. This enables us to use only one such pump, rather than the twin pump configuration, making the total cost for the diaphragm pump about \$5,000.

Beside the experimentation and design for the compressor, we have fabricated the exchange column (E in Figure 6), the packed equilibrator (S), and are in the process of designing the magnetically operated valve at the bottom of the exchange column (CV). The valve is necessary for obtaining the column holdup. We have also constructed a fume-hood to house the entire $\text{NO}/\text{N}_2\text{O}_3$ system, which is accessible from both sides. Inside of the hood has been lined with stainless steel sheets, and the vacuum rack inside has been fabricated of stainless steel tubing. The sliding doors of the fume-hood have been made from Plexiglas sheets, sliding on Teflon rails. We have resumed the construction of the $\text{NO}/\text{N}_2\text{O}_3$ system, after it had been interrupted by the moving.

(C) PRECISION MEASUREMENT OF SEPARATION FACTORS FOR ISOTOPE EXCHANGE REACTIONS

by Takao Oi

Separation factor, α , for a given isotope exchange reaction between two chemical species is usually measured either by observing a behavior of a cascade of stages or by directly measuring it in a single-stage equilibration apparatus.

In the cascade method, α could be obtained either by determining the overall separation as a function of product-withdrawal rate or by observing the rate with which the isotopic concentration profile along the length of the column approaches a steady state under a total reflux. In both methods of cascade operation, the precision of isotopic analysis increases, because the quantity measured is the overall separation, S , which is approximately given by α^n , where n is the number of stages. However, the determination of n presents a problem, which usually renders the resulting α a high degree of uncertainty.

In the single-stage equilibration method, two chemical species are mixed, isotopic exchange equilibrium is established, and samples of both substances are taken and analyzed. By this method, the separation parameter, $\epsilon = \alpha - 1$, of the magnitude of 10^{-3} would be determined, at best, to an uncertainty of $\pm 5\%$ of the magnitude.

In the past, attempts have been made to combine the best features of the cascade method and the single-stage method to increase the precision of the measurements of α . For instance, T. I. Taylor and M. Ghatge attempted to obtain α for the $^{13}\text{C}/^{12}\text{C}$ exchange between carbon dioxide and carbamate solutions by cascading five equilibration vessels and counter-currently flowing CO_2 and carbamate through these vessels. In this particular case the attempt failed primarily because it was too time-consuming. The only way by which one could ascertain a 100% stage efficiency in each of five stages was by carrying out the countercurrent operations repeatedly,

until a large volume of statistics about the overall separation has been accumulated. Since any non-ideality, such as the back-mixing between stages and excessive flow rates relative to the exchange and diffusion rates, would reduce the overall separation, it follows that the larger the observed value of overall separation, the closer would it be to the true value. Thus, all attempts in the past for a multistage determination have suffered from the uncertainties in the assessment of the effective number of stages in the cascade.

In order to develop a new method for a multistage determination of α , we have worked out a new scheme. The method goes as follows. Let an exchange reaction be

where X' and X are the lighter and the heavier isotopes, respectively. Let AX be a gas and EX be a liquid. As the reaction goes from left to right the heavier isotope enriches in the liquid. We set up n distinct equilibration stages. The i -th stage is fed with a part of the liquid-phase output, $EX + EX'$, of the $(i-1)$ th stage. A part of the output from the preceding stage is converted to $(AX + AX')$ by a chemical, electrolytic, or thermal means. The i -th stage is then equilibrated, and a part of the equilibrated liquid, $EX + EX'$, is withdrawn and fed to the $(i+1)$ th stage.

Referring to Figure 8, the number of moles and the atom fraction of X in the liquid fed to the i -th state are L'_{i-1} and f_{i-1} , respectively. The i -th stage produces L_i moles of liquid at the atom fraction of f_i and the corresponding gas phase. The heads-to-feed separation factor β_i and the heads-to-tails separation factor α are related by the usual formula,

$$\beta_i = \frac{\alpha}{1 + \epsilon \theta_i}, \quad (21)$$

where $\epsilon = \alpha - 1$ and θ_i is the cut in the i -th stage defined as

$$\theta_i = \frac{L_i}{L'_{i-1}}. \quad (22)$$

Since it is hard to make a quantitative transfer of liquid from one vessel to another without disturbing the chemical, phase, and isotopic equilibria, we take only a portion of the equilibrated liquid from the i -th stage to feed to the $(i+1)$ th stage. Thus, $L'_i < L_i$.

Figure 8: Multistage Scheme for Determination of Separation Factor

A cascade of n such stages will produce a liquid output from the n -th stage at an atom fraction f_n given by

$$f_n = f_0 \prod_{i=1}^n \beta_i, \quad (23)$$

and the overall separation S given by

$$S = \frac{f_n}{f_0} = \frac{\alpha^n}{\prod_{i=1}^n (1 + \epsilon \theta_i)}, \quad (24)$$

where f_0 is the enrichment of the liquid initially fed to the first stage.

From Eq. (24),

$$S \prod_{i=1}^n (1 + \epsilon \theta_i) = (1 + \epsilon)^n, \quad (25)$$

which may be regarded as defining the functional relationship between S , ϵ and θ_i 's. Eq. (25) may be solved for ϵ . The uncertainty on ϵ , σ_ϵ may be obtained as

$$\sigma_\epsilon^2 = \left(\frac{\partial \epsilon}{\partial S} \right)_{\theta_i \text{ (all } i)}^2 \sigma_S^2 + \sum_{i=1}^n \left(\frac{\partial \epsilon}{\partial \theta_i} \right)_{S, \theta_j (j \neq i)}^2 \sigma_{\theta_i}^2. \quad (26)$$

It can be shown that

$$\left(\frac{\partial \epsilon}{\partial S} \right)_{\text{all } \theta_i} = \frac{1}{S} \frac{1}{\frac{n}{1+\epsilon} - \sum_{i=1}^n \frac{\theta_i}{1+\epsilon \theta_i}}, \quad (27)$$

and

$$\left(\frac{\partial \epsilon}{\partial \theta_i} \right)_{S, \theta_j (j \neq i)} = \frac{\epsilon}{\frac{n(1+\epsilon \theta_i)}{1+\epsilon} - \sum_{j=1}^n \theta_j \left(\frac{1+\epsilon \theta_i}{1+\epsilon \theta_j} \right)}. \quad (28)$$

If

$$\theta_i = \theta, \text{ and } \sigma_{\theta_i} = \sigma_\theta \quad [\text{all } i], \quad (29a, b)$$

then, it follows that

$$\left(\frac{\sigma_{\epsilon}}{\epsilon}\right)^2 = \left[\frac{\alpha(1+\epsilon\theta)}{n\epsilon(1-\theta)}\right]^2 \left(\frac{\sigma_S}{S}\right)^2 + \frac{1}{n} \left[\frac{\alpha\theta}{1-\theta}\right]^2 \left(\frac{\sigma_{\theta}}{\theta}\right)^2. \quad (30)$$

If $\epsilon \ll 1$, as it usually is the case,

$$\left(\frac{\sigma_{\epsilon}}{\epsilon}\right)^2 = \left[\frac{1}{n\epsilon(1-\theta)}\right]^2 \left(\frac{\sigma_S}{S}\right)^2 + \frac{1}{n} \left[\frac{\theta}{1-\theta}\right]^2 \left(\frac{\sigma_{\theta}}{\theta}\right)^2. \quad (31)$$

It is obvious that the precision of the ϵ -determination increases with decreasing θ , but it is at a price of the necessity of using a large initial amount of liquid feed at Stage No.1. The optimum conditions can be obtained by requiring that two errors, corresponding to two terms on the right-hand side of Eq. (31), be equal. Thus, typically, $\sigma_S/S \approx 5 \times 10^{-5}$. Then, for a case of $n = 10$ and $\epsilon = 10^{-3}$, Table 3 summarizes the magnitudes of two sources of error for various values of the cut, and the corresponding precision in the determination of the cut that would be required to make two errors comparable. Considering the fact that the case considered for Table 3 would have given $\sigma_{\epsilon}/\epsilon = 0.05$ in the ordinary single-stage method of determination of ϵ , use of θ equal or greater than

Table 3. Comparison of Sources of Error :

$$n = 10, \quad \epsilon = 10^{-3}, \quad \sigma_S/S = 5 \times 10^{-5}$$

θ	$\frac{1}{n\epsilon(1-\theta)}$	$\frac{\sigma_S}{S}$	$\frac{1}{\sqrt{n}}$	$\frac{\theta}{1-\theta}$	$\frac{\sigma_{\theta}}{\theta}$	σ_{θ}/θ required for equal error
0.1	0.0056		0.3514		σ_{θ}/θ	0.016
0.2	0.0063		0.7906		σ_{θ}/θ	0.0079
0.5	0.0100		3.162		σ_{θ}/θ	0.0032
0.8	0.025		12.65		σ_{θ}/θ	0.0020
0.9	0.05		28.46		σ_{θ}/θ	0.0018

0.9 certainly does not make sense. If $\theta = 0.5$ is used, the precision of isotopic analysis would increase by the factor of 5 compared to the precision of the single-stage determination. If $\theta = 0.1$ is used, the precision would increase by the factor of almost ten. The last column of Table 3 shows that

the requirement for the precision of the cut determination is relaxed as θ decreases. Certainly, the required precision of 0.3% for $\theta = 0.5$ seems not so hard to accomplish. As stated previously, however, the better precision achievable in the isotopic analysis and the easier analytical chemistry for the cut determination are gained at the price of the smaller θ and the larger amount of liquid one has to handle. It seems that $\theta = \frac{1}{2}$ is a good compromise to start with.

In order to demonstrate the principle outlined above, we are in the process of developing an apparatus in which to carry out a precision measurement of α for the carbon isotope exchange between carbon dioxide and carbamate of di-n-butylamine dissolved in triethylamine. The generation of CO_2 from the carbamate in each stage is achieved thermally. A Pyrex vessel for each stage will be equipped with (a) a thermostating jacket, which is used for the thermal decomposition of carbamate and for thermostating the equilibrating mixture, (b) temperature and pressure sensors, (c) a high compression-ratio, stainless steel bellows to adjust the internal pressure, (d) liquid volume measuring buret, and (e) gas and liquid withdrawal ports.

(D) EFFECT OF DIFFERENTIAL F-MATRIX CHANGES ON ISOTOPE EFFECTS

by Takanobu Ishida

According to the WIMPER approximation,⁽⁸⁾ the isotopic reduced partition function ratio, $\ln(s/s')f$, can be expressed as

$$\ln \frac{s}{s'} f = \ln \frac{s}{s'} f_0 + \sum_{j=1}^n W_j A_j \left(\frac{h}{kT} \right)^{2j} \delta [\text{Tr}(\underline{H}^j) - \text{Tr}(\underline{H}_0^j)] , \quad (32)$$

where

$$\ln \frac{s}{s'} f_0 = \sum_{i=1}^{3N-6} [\ln b(u_{i0}') - \ln b(u_{i0})] , \quad (33)$$

in which

$$\ln b(u) = - \ln \frac{u e^{-u/2}}{1 - e^{-u}} , \quad (34)$$

and

$$u_{i0} = \frac{h}{kT} \sqrt{f_{ii} g_{ii}} . \quad (35)$$

Also, $\underline{H}^j$ and $\underline{H}_0^j$ are the j -th power matrices of $\underline{H} = \underline{F}\underline{G}$ and $\underline{H}_0 = \underline{F}_0 \underline{G}_0$, respectively, where $\underline{F}_0$ and $\underline{G}_0$ are the diagonal portions of $\underline{F}$ and $\underline{G}$, respectively, so that the i -th element of the diagonal matrix $\underline{H}_0$ is

$$(h_0)_{ii} = f_{ii} g_{ii} . \quad (36)$$

The other symbols appearing in Eq. (32) have their usual meaning: A_j is the j -th Bernoulli coefficient, e.g., $A_1 = 1/24$, $A_2 = -1/2880$, $A_3 = 1/181440$, etc., W_j is the modulating coefficient for the j -th term, which is always less than unity no matter whether one uses the orthogonal approximation^(9,10) or the WINIMAX approximation,⁽¹¹⁾ and δ means the isotopic difference of the quantity that follows it, the lighter isotopic molecule minus the heavier one.

The terms under the summation in Eq. (32) may be regarded as a correction to the diagonal element approximation,

$$\ln \frac{s}{s'} f \approx \ln \frac{s}{s'} f_0 , \quad (36)$$

and the level of correction can be improved to any desired precision by increasing the number of terms, n , in the correction. It has been shown⁽⁸⁾ that only one correction term ($n=1$) is sufficient to give the WIMPER approximation, Eq. (32), of any D/H isotope effect within 1% of the exact value of $\ln(s/s')f$, while two correction terms ($n=2$) in Eq. (32) give the WIMPER approximation for carbon and oxygen isotope effect within 3% of the exact values of $\ln(s/s')f$.

Some time ago, on the other hand, we developed⁽¹²⁾ an analytic formula for the effect of differential changes in the vibrational force constants upon the j -th trace of the $\underline{H}$ -matrix:

$$\ln \frac{s}{s'} f = \sum_{j=1}^n (T'_j - T_j) , \quad (37)$$

where

$$T_j = W_j A_j \left(\frac{h}{kT} \right)^{2j} \text{Tr}(\underline{H}^j) , \quad (38)$$

and

$$\frac{\partial \text{Tr}(\underline{H}^j)}{\partial f_{pq}} = j [\underline{GH}^{j-1}]_{pq} . \quad (39)$$

In the last equation, $[\underline{GH}^{j-1}]_{pq}$ means the (p,q) -element of the matrix formed by pre-multiplying the $(j-1)$ -th power of the $\underline{H}$ -matrix by $\underline{G}$. It is noted that

$$\frac{\partial \text{Tr}(\underline{H}^j)}{\partial f_{pq}} = \frac{\partial \text{Tr}(\underline{H}^j)}{\partial f_{qp}} , \quad (40)$$

since the matrix, $\underline{GH}^{j-1}$, is a symmetric matrix.

During the course of our past isotope effect studies we have encountered many times with the situations in which we had to evaluate possible effects of a change in force constants being contemplated upon the value of $\ln(s/s')f$. The exact method for this would involve solutions of secular equations for two isotopic compounds using a newly suggested $\underline{F}$ -matrix and the consequent calculation of $\ln(s/s')f$ using the exact values of frequencies obtained. This tedious process has been greatly abbreviated by the development of the orthogonal expansion and the use of Eq.(39). However, one would still have to perform the time-consuming matrix-multiplications indicated by $\underline{GH}^{j-1}$. So, we have reasoned that, if we can successfully use the WIMPER approximation in conjunction with Eq. (39), we would have achieved a further significant short-cut.

Differentiating Eq. (32) with respect to an $\underline{f}$ -matrix element, f_{pq} , we obtain

$$\frac{\partial}{\partial f_{pq}} [\ln \frac{s}{s'}, f] = D_{pq}^0 + \sum_{j=1}^n W_j A_j \left(\frac{h}{kT} \right)^{2j} P_{pq}^j, \quad (41a)$$

where

$$D_{pq}^0 = \frac{\partial}{\partial f_{pq}} [\ln \frac{s}{s'}, f_0], \quad (41b)$$

and

$$P_{pq}^j = \delta \left[\frac{\partial}{\partial f_{pq}} [\text{Tr}(\underline{H}^j)] - \frac{\partial}{\partial f_{pq}} [\text{Tr}(\underline{H}_0^j)] \right]. \quad (41c)$$

Of the various terms in Eq. (41), the derivative of $\ln(s/s')f_0$ is easy to calculate, if one realizes the fact that Bigeleisen-Mayler's $G(u)$ approximation⁽¹³⁾ is a very good one:

$$\ln \frac{s}{s'}, f_0 \approx \sum_i G(u_{i0}), \quad (42)$$

where

$$G(u) = \frac{1}{2} - \frac{1}{u} + \frac{1}{e^u - 1}. \quad (43)$$

Since

$$\frac{dG(u)}{du} = \frac{S(u)}{u}, \quad (44)$$

where

$$S(u) = \frac{1}{u} - \frac{ue^u}{(e^u - 1)^2}, \quad (45)$$

it follows that

$$D_{pq}^0 = \frac{\partial \ln(s/s')f_0}{\partial f_{pq}} = \frac{S(u_{po})}{2f_{pp}} \delta_{pq}, \quad (46)$$

where δ_{pq} is the Kronecker delta, and

$$u_{po} = \frac{h}{kT} \sqrt{f_{pp} \epsilon_{pp}}, \quad (47)$$

in accordance with Eq. (35). Since the function $S(u)$ has been well-documented,⁽¹³⁾ Eqs. (46) and (47) provide a means for computing the differential change in the zero-th order term of Eq. (41).

The effect on the term of $\text{Tr}(\underline{H}_o^j)$ in Eq. (41) is obtained from Eq. (39):

$$\frac{\partial}{\partial f_{pq}} [\text{Tr}(\underline{H}_o^j)] = j f_{pp}^{j-1} \epsilon_{pp}^j \delta_{pq} \quad (48)$$

Now, the only remaining differential effect still to be evaluated is that of $\partial [\text{Tr}(\underline{H}_p^j)] / \partial f_{pq}$. For $j = 1$,

$$\frac{\partial \text{Tr}(\underline{H}_p)}{\partial f_{pq}} = \epsilon_{pq} \quad (49a)$$

and

$$\frac{\partial \text{Tr}(\underline{H}_p)}{\partial f_{pq}} = \epsilon_{pp} \delta_{pq} \quad (49b)$$

so that the $j=1$ correction term is equal to

$$W_1 A_1 \left(\frac{h}{kT} \right)^2 P_{pq}^1 = -W_1 A_1 \left(\frac{h}{kT} \right)^2 (\delta \epsilon_{pq}) (1 - \delta_{pq}) \quad (50)$$

in which $\delta \epsilon_{pq} = \epsilon'_{pq} - \epsilon_{pq}$ which does not vanish only if the coordinates p and q both involve motions of the isotopic atom. When they do, then $\delta \epsilon_{pq} \approx \delta \mu$, the difference between the reciprocal masses of the isotopic atoms.

For $j = 2$, the similar analyses led to the following conclusion:

(1) Effect of Diagonal f_{pp} : P_{pp}^2

Set

$$P_{pp}^2 = 2 (\delta R_{2pp1} + \delta R_{2ppo}) \quad (51)$$

where

$$\begin{aligned} R_{2pp1} &= \text{Terms containing one diagonal elements} \\ &= \sum_{i \neq p} f_{ii} (\epsilon_{pi})^2 + 2 \sum_{i \neq p} f_{pi} \epsilon_{pp} \epsilon_{pi} \end{aligned} \quad (52)$$

and

$$\begin{aligned} R_{2ppo} &= \text{Terms containing no diagonal elements} \\ &= \sum_{i \neq p, j \neq p, j \neq i} f_{ij} \epsilon_{pi} \epsilon_{jp} \end{aligned} \quad (53)$$

(1a) If the coordinate p does not involve the isotopic atom (hereafter abbreviated as IA), then

$$P_{pp}^2 = 0. \quad (54)$$

(1b) If p does involve the IA, then the only non-vanishing terms in P_{pp}^2 are;

$$\begin{aligned} (i) \quad & 2 \sum_{i \neq p} f_{ii} \delta(g_{pi})^2 \quad [i \text{ shares the IA with } p.] \\ (ii) \quad & 4 \sum_{i \neq p} f_{pi} \delta(g_{pi} g_{pp}) \quad [i \text{ shares at least one atom, not necessarily the IA, with } p.] \\ (iii) \quad & 2 \sum_{i \neq p, j \neq p} \sum_{i \neq j} f_{ij} \delta(g_{pi} g_{jp}) \quad [\text{Either } i \text{ or } j, \text{ or both, share the IA with } p.] \end{aligned}$$

(2) Effect of Off-Diagonal $f_{pq} : P_{pq}^2 [p \neq q]$

Set

$$P_{pq}^2 = 2 (\delta R_{2pq2} + \delta R_{2pq1} + \delta R_{2pq0}) \quad , \quad (56)$$

where

$$\begin{aligned} R_{2pq2} &= \text{Terms containing two diagonal elements} \\ &= (f_{pp} g_{pp} + f_{qq} g_{qq}) g_{pq} + (g_{pp} g_{qq}) f_{pq} \quad , \quad (57) \end{aligned}$$

$$\begin{aligned} R_{2pq1} &= \text{Terms containing one diagonal elements} \\ &= \sum_{\substack{i \neq p \\ i \neq q}} f_{ii} g_{pi} g_{qi} + \sum_{\substack{i \neq p \\ i \neq q}} f_{qi} g_{qq} g_{pi} + \sum_{\substack{i \neq p \\ j \neq q}} f_{pi} g_{pp} g_{qi} \quad , \quad (58) \end{aligned}$$

and

$$\begin{aligned} R_{2pq0} &= \text{Terms containing no diagonal elements} \\ &= \sum_{i \neq p, j \neq q} \sum_{i \neq j} f_{ij} g_{pi} g_{qj} \quad . \quad (59) \end{aligned}$$

For R_{2pq2} , R_{2pq1} , or R_{2pq0} to be non-vanishing, either p or q , or both, coordinates have to involve motions of the IA.

We are in a process of writing a computer program (1) to test the precision of one ($n=1$) term formula [Eqs. (41), (46), (47), and (50)],

and (2) to test the effects of inclusion of the various terms of P_{pp}^2 and P_{pq}^2 . By applying this program to the typical molecules such as H_2O , CO_2 , CH_2O , CH_4 , C_2H_4 , C_2H_6 , and C_6H_6 for the hydrogen, carbon, and oxygen isotope effects, we hope to be able to make a statement about the error limit associated with the $n=1$ method and, hopefully, this error limit is acceptably small.

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