

Dissection of $^{13}\text{C}/^{12}\text{C}$ Isotope Effects on the Cyanoacetylene Partition Function

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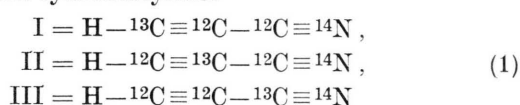
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Z. Naturforsch. **33a**, 1562–1574 (1978); received October 24, 1978

$^{13}\text{C}/^{12}\text{C}$ reduced isotopic partition function ratios for the three singly ^{13}C substituted cyanoacetylenes are calculated and are used to evaluate the thermodynamic equilibrium constants among these species. A perturbation theory method is employed to dissect both the partition function ratios and also the equilibrium constants in order to gain a better understanding of isotope effects.

Introduction

Churchwell et al. [1] have recently observed the relative abundances of the three singly ^{13}C substituted cyanoacetylenes



in a molecular cloud near the center of our galaxy. This finding stimulated us to study theoretically the distribution of ^{13}C among the three isotopic isomers I, II, III in thermodynamic equilibrium and to compare the results of this study with the observations of Churchwell et al. As will be shown in an other publication [2], this comparison leads to the conclusion that the ^{13}C distribution observed by Churchwell et al. does not correspond to thermodynamic equilibrium (at any temperature).

In order to study the thermodynamic equilibrium among I, II, and III, we calculated the (reduced) isotopic partition function ratios (with respect to the all ^{12}C molecule) of the three isotopic isomers I, II, and III. The thermodynamic equilibrium constants for the equilibrium among these three isomers are then calculated as ratios of isotopic partition function ratios. In the evaluation of the isotopic partition function ratios, it is adequate to consider only the ground electronic state at room temperature and below. The Born-Oppenheimer approximation was used so that only the rotational-vibrational and translational energy levels contribute to the partition function ratios [3]. The isotopic partition function ratios were furthermore

calculated in the so-called harmonic approximation — vibrations are assumed to be harmonic, rotational-vibrational interaction is ignored, the rotational degrees of freedom are assumed to correspond to those of a rigid rotor, and the rotational partition function is calculated classically without consideration of quantization [4]. These approximations introduce only negligible errors into the calculations [5]. Such calculations require as input atomic masses, the equilibrium internuclear geometry (isotope independent within the Born-Oppenheimer approximation) of this linear molecule and the harmonic force field (i.e. the force constants, which are isotope independent within the Born-Oppenheimer approximation). The force field used in such calculations is usually derived from observed spectroscopic data. The calculations were carried through with three different force fields, derived in somewhat different ways: A — derived by Mallinson [2, 6] on the basis of an analysis of spectroscopic data on HC_3N and DC_3N in which an anharmonic force field was used with terms up to quartic in the displacements from equilibrium, B — derived from observed vibrational fundamentals of HC_3N and DC_3N on the assumption that these could be equated to harmonic frequencies; the stretching force constants were calculated by Uyemura and Maeda [7] while the bending force constants were calculated by us, C — calculated like B by Cyvin and Kjaebo [8] just from the HC_3N fundamentals. While force field A is expected to be the most reliable of the three force fields, the calculations were carried through with all three force fields. The three force fields are shown in Table 1; while the force fields are similar, there are differences between them. The coordinates in terms of which the force fields are described are defined in Table 2.

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Table 1. The three different force fields, FF A, FF B, FF C for cyanoacetylene described in the text. The force constants F_{ij} are given in units $\text{mdyn}/\text{\AA}$ for stretches and $\text{mdyn}/\text{\AA}$ for bends. The coordinate definitions are given in Table II^a.

$i\ j$	FF A	FF B	FF C
1 1	6.366	5.904	5.92
2 2	16.02	16.92	15.2
3 3	8.13	6.866	7.7
4 4	15.66	16.05	15.8
5 5 = 6 6	0.254	0.213	0.189
7 7 = 8 8	0.231	0.230	0.337
9 9 = 10 10	0.445	0.420	0.330
1 2	-0.11	0.0	0.013
1 3	0.03	0.0	0.029
1 4	0.0	0.0	-0.114
2 3	0.42	1.55	0.166
2 4	-1.20	0.0	-0.825
3 4	-0.42	-0.208	0.253
5 7 = 6 8	0.079	0.033	0.00145
5 9 = 6 10	0.0	-0.0605	-0.0058
7 9 = 8 10	0.031	0.029	-0.015

^a The equilibrium geometry is linear with $R(\text{CH}) = 1.0538\ \text{\AA}$, $R(\text{C}\equiv\text{C}) = 1.202\ \text{\AA}$, $R(\text{C}-\text{C}) = 1.385\ \text{\AA}$, $R(\text{C}=\text{N}) = 1.154\ \text{\AA}$.

Table 2. Displacement coordinates employed to describe vibrational motion of cyanoacetylene $-\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$.

Coordinate Number	Description
1	H-C stretch
2	C≡C stretch
3	C-C stretch
4	C=N stretch
5, 6	H-C≡C bends, pair of perpendicular coordinates
7, 8	C≡C-C bends, pair of perpendicular coordinates
9, 10	C-C=N bends, pair of perpendicular coordinates

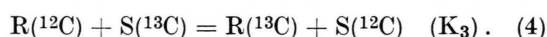
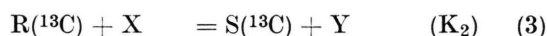
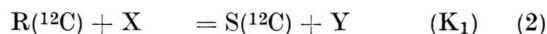
A method of analyzing isotopic partition function ratios by a perturbation theory approach has recently been introduced [9]. We will analyze here the partition function ratios calculated with the three different force fields and also the equilibrium constants calculated from these quantities. Attention will be given to the factors which contribute to the second order perturbation theory correction and also to how differences in force fields change the perturbation analysis.

In the next section, we briefly discuss the reduced partition function ratio. A discussion of the perturbation theory follows. Subsequently, the reduced isotopic partition function ratios are

dissected. Finally, the equilibrium constants are discussed.

Reduced Partition Function Ratios

Consider the equilibria



Here $\text{R}(^{13}\text{C})(\text{S}(^{13}\text{C}))$ refers to a compound in which ^{13}C has been substituted for ^{12}C in $\text{R}(^{12}\text{C})(\text{S}(^{12}\text{C}))$. The species X and Y have not been isotopically substituted. The isotope effects for the gas phase chemical equilibrium constant (K) can then be expressed in terms of ratios of isotopic molecular partition function ratios,

$$K_1/K_2 = K_3 = (Q_{\text{R}(^{13}\text{C})}/Q_{\text{R}(^{12}\text{C})})/(Q_{\text{S}(^{13}\text{C})}/Q_{\text{S}(^{12}\text{C})}), \quad (5)$$

where Q refers to molecular partition function. As pointed out before, it is adequate to consider only ground electronic states at room temperature and below when formulating these partition functions. One can then show that within the framework of the Born-Oppenheimer approximation there are no isotope effects if the molecules are subject to classical mechanics ($K_3[\text{classical}] = 1$) except for the relevant symmetry number factors which are of little interest and which will be ignored here [4, 10]. The interest is therefore in the reduced isotopic partition function ratio [4, 10], the ratio of the quantum mechanical partition functions of two isotopic molecules divided by the corresponding ratio of partition functions calculated classically. In the harmonic approximation one finds for the reduced isotopic partition function ratio

$$\begin{aligned} (s_2/s_1)f &= \frac{(Q_2/Q_1)}{(Q_2/Q_1)[\text{classical}]} \\ &= \prod_i^K \frac{u_{2i}}{u_{1i}} \frac{1 - e^{-u_{1i}}}{1 - e^{-u_{2i}}} \exp\{(u_{1i} - u_{2i})/2\}. \end{aligned} \quad (6)$$

Here $u = h\nu/kT$, T is the absolute temperature, h and k have their usual meanings, ν refers to harmonic normal mode vibrational frequency, and for the N atomic linear molecule the product is over the $K = 3N - 5$ ($3N - 6$ for non-linear molecule) normal mode vibrational frequencies. The subscripts 2 and 1 refer to the two isotopic molecules with 2 usually referring to the heavier molecule

(e.g. 1 = $\text{H}^{12}\text{C}_3\text{N}$, 2 = I of Equation (1)). Then

$$K_3 = \frac{(s_2/s_1) f(\text{R}(^{13}\text{C})/\text{R}(^{12}\text{C}))}{(s_2/s_1) f(\text{S}(^{13}\text{C})/\text{S}(^{12}\text{C}))}. \quad (7)$$

The equilibria among the ^{13}C substituted cyanoacetylenes of Eq. (1) can then be formulated in terms of reduced isotopic partition function ratios

$$K_4 = \frac{[\text{I}]}{[\text{II}]} = \frac{(s_2/s_1) f(\text{I}/\text{H}^{12}\text{C}_3\text{N})}{(s_2/s_1) f(\text{II}/\text{H}^{12}\text{C}_3\text{N})}, \quad (8)$$

$$K_5 = \frac{[\text{III}]}{[\text{II}]} = \frac{(s_2/s_1) f(\text{III}/\text{H}^{12}\text{C}_3\text{N})}{(s_2/s_1) f(\text{II}/\text{H}^{12}\text{C}_3\text{N})}. \quad (9)$$

Here [I] refers to concentration of species I at thermodynamic equilibrium. We note that the partition function of $\text{H}^{12}\text{C}_3\text{N}$ drops out in the evaluations of K_4 and K_5 ; we still prefer to formulate $(s_2/s_1)f$ as we do, and the $(s_2/s_1)f$ so evaluated can also be used in other equilibrium isotope effect calculations as exemplified in the above discussion, Eqs. (2)–(7). In subsequent discussion we shall refer to $(s_2/s_1)f(\text{I}/\text{H}^{12}\text{C}_3\text{N})$ as the isotopic partition function ratio of molecule I, etc.

With a given harmonic force field, it is straightforward to evaluate [11] by computer the normal mode vibrational frequencies of a pair of isotopic molecules and $(s_2/s_1)f$. Methods of calculating $(s_2/s_1)f$ without evaluating normal mode vibrational frequencies, such as the perturbation theory method here [9] and the methods of Bigeleisen and Ishida [12], are of interest because they can throw light on the nature of isotope effects calculated with these quantities.

Perturbation Theory

We develop the perturbation theory as applied to cyanoacetylene. The ten internal displacement coordinates q_i (4 stretches and 3 pairs of perpendicular bends) and corresponding conjugate momenta p_i in terms of which the vibrational motion is described are defined in Table 2. The vibrational Hamiltonian for cyanoacetylene can be partitioned into an unperturbed part H_0 and a perturbed part H_1 ,

$$H = H_0 + H_1, \quad (10)$$

$$H_0 = \frac{1}{2} \sum_i^{10} g_{ii} p_i^2 + \frac{1}{2} \sum_i^{10} f_{ii} q_i^2, \quad (11)$$

$$H_1 = \sum_{i < j} g_{ij} p_i p_j + \sum_{i < j} f_{ij} q_i q_j. \quad (12)$$

The f_{ij} 's are the harmonic force constants of cyanoacetylene (\mathbf{F} matrix) and the g_{ij} 's are the elements of Wilson's \mathbf{G} matrix [13]. The f_{ij} 's are isotope independent while the g_{ij} 's depend on atomic masses and on geometrical parameters. The unperturbed Hamiltonian corresponds to a system of ten uncoupled oscillators (4 stretching oscillators and 3 doubly degenerate bending oscillators), with frequencies given by $\nu_i' = (2\pi)^{-1}(f_{ii}g_{ii})^{1/2}$.

The evaluation of the reduced isotopic partition function ratio by a perturbation technique corresponding to Eq. (10) has been discussed previously [9]. The unperturbed reduced isotopic partition function ratio is given by

$$\text{TOTD} = \prod_j \frac{V_{2j}}{V_{1j}} \frac{1 - e^{-V_{1j}}}{1 - e^{-V_{2j}}} \cdot \exp \{ (V_{1j} - V_{2j})/2 \} = \prod_j c(j) \quad (13)$$

where $V_j = h\nu_j'/kT$. TOTD (total diagonal) is identical in form to Eq. (6), except that the normal mode frequencies ν_i have been replaced by the individual coordinate stretching and bending frequencies ν_j' . Some of the properties of the c factors of Eq. (13) are given in Appendix II which replaces a previous table of c factor properties [9].

The first order perturbation correction to TOTD vanishes and, to second order in the perturbation, the reduced isotopic partition function ratio is given by

$$\text{TOT} = \text{TOTD} \times \text{TOTOD}, \quad (14)$$

$$\begin{aligned} \text{TOTOD} &= \prod_{i < j} (\text{CORR})_{ij} \\ &= \prod_{i < j} \exp \{ F_{2ij} - F_{1ij} \}. \end{aligned} \quad (15)$$

Here the subscripts 1 and 2 refer again to the two isotopic molecules. Furthermore

$$\begin{aligned} F_{ij} &= \frac{1}{(kT)^2} \frac{1}{(1 - e^{-V_i})(1 - e^{-V_j})} \\ &\cdot \left[B_{ij}^2 \frac{1 - \exp \{ -(V_i + V_j) \}}{V_i + V_j} \right. \\ &\quad \left. + C_{ij}^2 \frac{e^{-V_i} - e^{-V_j}}{V_j - V_i} \right] - \frac{1}{2} \frac{g_{ij}^2}{g_{ii}g_{jj}} - \frac{1}{2} \frac{f_{ij}^2}{f_{ii}f_{jj}} \end{aligned} \quad (16)$$

with

$$\begin{aligned} B_{ij} &= \alpha_{ij} - \beta_{ij}, \\ C_{ij} &= \alpha_{ij} + \beta_{ij}, \\ \alpha_{ij}/kT &= \frac{1}{2} V_i V_j (f_{ij}/f_{ii}f_{jj})^{1/2}, \\ \beta_{ij}/kT &= \frac{1}{2} V_i V_j (g_{ij}/g_{ii}g_{jj})^{1/2}. \end{aligned}$$

$(\text{CORR})_{ij}$ can be dissected into a part $(\text{CORR-}G)_{ij}$, obtained by setting f_{ij} equal to zero, and a part $(\text{CORR-}F)_{ij}$ obtained by setting g_{ij} equal to zero. Then

$$(\text{CORR})_{ij} = (\text{CORR-}G)_{ij} \times (\text{CORR-}F)_{ij} \times (\text{CORR-}FG)_{ij}, \quad (17)$$

where $(\text{CORR-}FG)_{ij}$ results from those parts of F_{1ij} and F_{2ij} which contain $f_{ij}g_{ij}$ cross terms. Also

$$\begin{aligned} \text{CORR-}G &= \prod_{i < j} (\text{CORR-}G)_{ij}, \\ \text{CORR-}F &= \prod_{i < j} (\text{CORR-}F)_{ij}, \\ \text{CORR-}FG &= \prod_{i < j} (\text{CORR-}FG)_{ij}, \end{aligned} \quad (18)$$

and

$$\text{TOTOD} = \text{CORR-}G \times \text{CORR-}F \times \text{CORR-}FG.$$

Appendix I lists formulae for the diagonal and off-diagonal G matrix elements [13] needed for the perturbation theory calculations on cyanoacetylene. The conversion factors necessary to calculate V_i quantities from force constants given in Table 1 and with masses given in atomic mass units are also presented. Although this procedure may be somewhat tedious, it is quite straightforward to calculate the various perturbation theory terms for the isotopic partition function ratios with a hand calculator.

Cyanoacetylene Calculations

Tables 3 and 4 report reduced isotopic partition function ratio calculations for the three ^{13}C substituted compounds I, II, III at 150 K and 300 K respectively. We report the exact value of the

	FF A		FF B		FF C	
$(s_2/s_1) f$	1.310		1.320		1.307	
TOT	1.306		1.314		1.302	
$\ln(s_2/s_1) f$	0.270		0.277		0.268	
$\ln \text{TOT}$	0.267		0.273		0.264	
$\ln \text{TOTD}$	0.278	(1.043) ^d	0.277	(1.076)	0.268	(1.015)
$\ln 11^b$	0.046	(0.172)	0.044	(0.162)	0.044	(0.167)
$\ln 22$	0.179	(0.671)	0.185	(0.677)	0.174	(0.660)
$\ln 55 = \ln 66$	0.021	(0.078)	0.018	(0.068)	0.017	(0.064)
$\ln 77 = \ln 88$	0.006	(0.021)	0.006	(0.021)	0.008	(0.030)
$\ln \text{TOTOD}$	-0.011	(-0.043)	-0.004	(-0.016)	-0.004	(-0.015)
$\ln 12^c$	-0.012	(-0.044)	-0.013	(-0.046)	-0.012	(-0.046)
$\ln 23$	0.013	(0.047)	0.015	(0.054)	0.012	(0.044)
$\ln 57 = \ln 68$	-0.006	(-0.024)	-0.003	(-0.012)	-0.002	(-0.007)

^a Logarithmic dissection terms which only yield zero entries are omitted here and in all other tables, where relevant.

^b Diagonal notation ii stands for $c(i)$. Thus $\ln 11$ means $\ln c(1)$.

^c Off-diagonal notation ij stands for $(\text{CORR})_{ij}$. Thus $\ln 12$ means $\ln (\text{CORR})_{12}$.

^d Numbers in parenthesis refer to the ratio of the adjacent entry to $\ln \text{TOT}$ in the same column. Note that these numbers are given to greater accuracy than are the adjacent entries.

	FF A		FF B		FF C	
$(s_2/s_1) f$	1.353		1.328		1.379	
TOT	1.366		1.343		1.393	
$\ln(s_2/s_1) f$	0.302		0.284		0.322	
$\ln \text{TOT}$	0.312		0.295		0.331	
$\ln \text{TOTD}$	0.365	(1.170) ^d	0.357	(1.211)	0.366	(1.106)
$\ln 22^b$	0.179	(0.574)	0.185	(0.626)	0.174	(0.526)
$\ln 33$	0.122	(0.391)	0.111	(0.374)	0.118	(0.357)
$\ln 55 = \ln 66$	0.005	(0.015)	0.004	(0.014)	0.004	(0.011)
$\ln 77 = \ln 88$	0.020	(0.064)	0.020	(0.068)	0.028	(0.083)
$\ln 99 = \ln 1010$	0.007	(0.024)	0.007	(0.024)	0.006	(0.018)
$\ln \text{TOTOD}$	-0.053	(-0.170)	-0.062	(-0.211)	-0.035	(-0.106)
$\ln 12^c$	0.002	(0.008)	0.003	(0.009)	0.002	(0.008)
$\ln 23$	-0.046	(-0.148)	-0.058	(-0.195)	-0.042	(0.127)
$\ln 34$	0.010	(0.031)	0.009	(0.031)	0.011	(0.032)
$\ln 57 = \ln 68$	-0.006	(-0.018)	-0.003	(-0.010)	-0.001	(-0.004)
$\ln 59 = \ln 610$	0.000	(-0.001) ^d	-0.002	(-0.006)	0.000	(-0.001) ^d
$\ln 79 = \ln 810$	-0.004	(-0.012)	-0.003	(-0.012)	-0.001	(-0.004)

Table 3a. Calculation for $\text{H}^{13}\text{C}^{12}\text{C}^{12}\text{CN}/\text{H}^{12}\text{C}_3\text{N}$ of the exact reduced isotopic partition function ratio and the perturbation theory dissection of this ratio at 150 K corresponding to the three force fields of Table 1.^a

Table 3b. Calculation for $\text{H}^{12}\text{C}^{13}\text{C}^{12}\text{CN}/\text{H}^{12}\text{C}_3\text{N}$ of the exact reduced isotopic partition function ratio and the perturbation theory dissection of this ratio at 150 K corresponding to the three force fields of Table 1.^a Footnotes refer to Table 3a.

	FF A		FF B		FF C	
$(s_2/s_1)f$	1.408		1.391		1.381	
TOT	1.421		1.404		1.395	
$\ln(s_2/s_1)f$	0.342		0.330		0.323	
$\ln \text{TOT}$	0.351		0.340		0.333	
$\ln \text{TOTD}$	0.386	(1.098) ^d	0.373	(1.099)	0.371	(1.114)
$\ln 3\ 3^b$	0.122	(0.347)	0.111	(0.325)	0.118	(0.355)
$\ln 4\ 4$	0.183	(0.521)	0.186	(0.546)	0.184	(0.553)
$\ln 7\ 7 = \ln 8\ 8$	0.004	(0.012)	0.004	(0.013)	0.006	(0.018)
$\ln 9\ 9 = \ln 10\ 10$	0.036	(0.102)	0.034	(0.101)	0.028	(0.085)
$\ln \text{TOTOD}$	-0.034	(-0.098)	-0.034	(-0.099)	-0.038	(-0.114)
$\ln 2\ 3^c$	0.011	(0.030)	0.011	(0.032)	0.010	(0.030)
$\ln 3\ 4$	-0.038	(-0.108)	-0.038	(-0.112)	-0.045	(-0.135)
$\ln 7\ 9 = \ln 8\ 10$	-0.003	(-0.010)	-0.003	(-0.010)	-0.001	(-0.004)

Table 3c. Calculation for $\text{H}^{12}\text{C}^{12}\text{C}^{13}\text{CN}/\text{H}^{12}\text{C}_3\text{N}$ of the exact reduced isotopic partition function ratio and the perturbation theory dissection of this ratio at 150 K corresponding to the three force fields of Table 1.^a Footnotes refer to Table 3a.

	FF A		FF B		FF C	
$(s_2/s_1)f$	1.120		1.124		1.118	
TOT	1.120		1.123		1.118	
$\ln(s_2/s_1)f$	0.114		0.117		0.111	
$\ln \text{TOT}$	0.114		0.116		0.111	
$\ln \text{TOTD}$	0.119	(1.045) ^d	0.119	(1.019)	0.113	(1.019)
$\ln 1\ 1^b$	0.021	(0.189)	0.021	(0.177)	0.021	(0.185)
$\ln 2\ 2$	0.080	(0.702)	0.083	(0.710)	0.077	(0.694)
$\ln 5\ 5 = \ln 6\ 6$	0.007	(0.063)	0.006	(0.053)	0.006	(0.049)
$\ln 7\ 7 = \ln 8\ 8$	0.002	(0.014)	0.002	(0.014)	0.002	(0.021)
$\ln \text{TOTOD}$	-0.005	(-0.045)	-0.002	(-0.019)	-0.002	(-0.019)
$\ln 1\ 2^c$	-0.005	(-0.042)	-0.005	(-0.045)	-0.005	(-0.046)
$\ln 2\ 3$	0.004	(0.034)	0.005	(0.042)	0.003	(0.031)
$\ln 5\ 7 = \ln 6\ 8$	-0.002	(-0.018)	-0.001	(-0.008)	0.000	(0.022)

Table 4a. Calculation for $\text{H}^{13}\text{C}^{12}\text{C}^{12}\text{CN}/\text{H}^{12}\text{C}_3\text{N}$ of the exact reduced isotopic partition function ratio and the perturbation theory dissection of this ratio at 300 K corresponding to the three force fields of Table 1.^a Footnotes refer to Table 3a.

	FF A		FF B		FF C	
$(s_2/s_1)f$	1.136		1.125		1.142	
TOT	1.138		1.129		1.145	
$\ln(s_2/s_1)f$	0.127		0.118		0.133	
$\ln \text{TOT}$	0.129		0.121		0.135	
$\ln \text{TOTD}$	0.150	(1.157) ^d	0.146	(1.209)	0.148	(1.095)
$\ln 2\ 2^b$	0.080	(0.616)	0.083	(0.683)	0.077	(0.570)
$\ln 3\ 3$	0.051	(0.396)	0.046	(0.377)	0.049	(0.365)
$\ln 5\ 5 = \ln 6\ 6$	0.002	(0.012)	0.001	(0.011)	0.001	(0.009)
$\ln 7\ 7 = \ln 8\ 8$	0.006	(0.043)	0.006	(0.046)	0.008	(0.059)
$\ln 9\ 9 = \ln 10\ 10$	0.002	(0.017)	0.002	(0.018)	0.002	(0.012)
$\ln \text{TOTOD}$	-0.020	(-0.157)	-0.025	(-0.209)	-0.013	(-0.095)
$\ln 1\ 2^c$	0.001	(0.007)	0.001	(0.008)	0.001	(0.006)
$\ln 2\ 3$	-0.018	(-0.140)	-0.024	(-0.197)	-0.016	(-0.118)
$\ln 3\ 4$	0.002	(0.019)	0.002	(0.018)	0.003	(0.021)
$\ln 5\ 7 = \ln 6\ 8$	-0.002	(-0.014)	-0.001	(-0.007)	0.000	(-0.002)
$\ln 5\ 9 = \ln 6\ 10$	0.000	(-0.002)	-0.001	(-0.005)	0.000	(-0.001) ^d
$\ln 7\ 9 = \ln 8\ 10$	-0.001	(-0.006)	-0.001	(-0.006)	0.000	(0.000)

Table 4b. Calculation for $\text{H}^{12}\text{C}^{13}\text{C}^{12}\text{CN}/\text{H}^{12}\text{C}_3\text{N}$ of the exact reduced isotopic partition function ratio and the perturbation theory dissection of this ratio at 300 K corresponding to the three force fields of Table 1.^a Footnotes refer to Table 3a.

reduced isotopic partition function ratio [Eq. (6)] as $(s_2/s_1)f$. The perturbation theory approximation is reported as TOT. From Eq. (13)–(15),

$$\text{TOT} = \prod_j c(j) \prod_{i < j} (\text{CORR})_{ij} \quad (19)$$

so that

$$\ln \text{TOT} = \sum_j \ln c(j) + \sum_{i < j} \ln (\text{CORR})_{ij}. \quad (20)$$

The additive nature of Eq. (20) permits us to assess the fractional contribution of each term in the sum to $\ln \text{TOT}$. Consequently, the dissection of TOT into its components in the Tables is carried out in logarithmic form and the fractional contributions to $\ln \text{TOT}$ are reported. Thus, for the reduced isotopic partition function ratio of I (really $\text{I}/\text{H}^{12}\text{C}_3\text{N}$) with force field A at 150 K, Table 3a

	FF A		FF B		FF C	
$(s_2/s_1) f$	1.152		1.146		1.143	
TOT	1.154		1.148		1.146	
$\ln(s_2/s_1) f$	0.142		0.136		0.134	
\ln TOT	0.144		0.138		0.136	
\ln TOTD	0.156	(1.088) ^d	0.151	(1.089)	0.151	(1.107)
\ln 33 ^b	0.051	(0.357)	0.046	(0.329)	0.049	(0.363)
\ln 44	0.081	(0.563)	0.082	(0.594)	0.081	(0.598)
\ln 77 = \ln 88	0.001	(0.008)	0.001	(0.009)	0.002	(0.013)
\ln 99 = \ln 10 10	0.011	(0.075)	0.010	(0.074)	0.008	(0.060)
\ln TOTOD	-0.013	(-0.088)	-0.012	(-0.089)	-0.015	(-0.107)
\ln 23 ^c	0.003	(0.020)	0.003	(0.022)	0.003	(0.019)
\ln 39	-0.014	(-0.096)	-0.014	(-0.100)	-0.017	(-0.127)
\ln 79 = \ln 8 10	-0.001	(-0.006)	-0.001	(-0.006)	0.000	(0.000)

Table 4c. Calculation for $\text{H}^{12}\text{C}^{12}\text{C}^{13}\text{CN}/\text{H}^{12}\text{C}_3\text{N}$ of the exact reduced isotopic partition function ratio and the perturbation theory dissection of this ratio at 300 K corresponding to the three force fields of Table 1.^a Footnotes refer to Table 3a.

reports that $\ln c(1)$ is 0.172 of $\ln \text{TOT}$, that $\ln (\text{CORR})_{23}$ is 0.047 of $\ln \text{TOT}$, that $\ln (\text{CORR})_{57}$ is -0.024 of $\ln \text{TOT}$ and that $\ln (\text{CORR})_{68}$ makes the same contribution as $\ln (\text{CORR})_{57}$. The last equality as well as other equalities noted in Tables 3 and 4, which involve the perpendicular bending coordinates, follow from the equalities in Table 1 and in Appendix I, which in turn follow from symmetry considerations. These equalities lead to the result that each c factor for a bend and each CORR factor for bends makes two contributions; thus, bend effects are often larger than they seem to be at first sight.

It has been pointed out previously [9] that the second order perturbation development reproduces $(s_2/s_1)f$ better at higher temperatures than at lower temperatures. Thus, we see from Tables 4 that the maximum difference between $\ln(s_2/s_1)f$ and $\ln \text{TOT}$ at 300 K is 0.003 while Tables 3 show maximum difference at 150 K of 0.01. One would not want to employ the perturbation theory below 150 K.

Discussion of c Factors

We note that the c factors in Tables 3 are larger than those in Tables 4 (Rule 3, Appendix II). There are no c factor entries for coordinates 3, 4, 9, and 10 in Tables 3a and 4a since the logarithm of unity vanishes (Rule 2a, Appendix II). We also note that the largest c factors correspond to stretches. Thus for molecule I (Tables 3a and 4a) $c(1)$ and $c(2)$ are largest; for molecule II (Tables 3b and 4b) $c(2)$ and $c(3)$ are largest; for molecule III (Tables 3c and 4c) $c(3)$ and $c(4)$ are largest. Moreover, for molecule I, $c(1)$ is considerably smaller than $c(2)$. While the higher frequency of the C—H stretch compared to the C \equiv C stretch is expected to lead to a higher $c(1)$ value (Rule 4, Appendix II), the

larger carbon isotope effect [$g(\text{light})/g(\text{heavy})$] on the diagonal \mathbf{G} matrix element for the C \equiv C stretch ($m_{\text{C}1}^{-1} + m_{\text{C}2}^{-1}$) compared to that of a C—H stretch ($m_{\text{C}}^{-1} + m_{\text{H}}^{-1}$) is the deciding factor (Rule 5a, Appendix II). Similarly even $c(3)$ for molecule II is much larger than $c(1)$ for molecule I.

Before the numerical calculations were carried out, we recognized that the force constant for a C \equiv C stretch is approximately the same as that of a C \equiv N stretch and that moreover the carbon isotope effects on the diagonal \mathbf{G} matrix elements for these two coordinates are also very similar, so that $c(2)$ in molecule II approximately equals $c(4)$ in molecule III. We also knew that $c(1)$ for molecule I would be less than $c(3)$ for molecule II and that therefore the c factor for a C \equiv C stretch should be larger than for a C—C stretch (Rule 4a, Appendix II). Consequently we reasoned on the basis of c factors (zeroth order perturbation theory), with neglect of the bending effects which were expected to be (and are) smaller (lower force constants — Rule 4a, Appendix II), that the $(s_2/s_1)f$ magnitudes would rank themselves in the order $\text{I} < \text{II} \sim \text{III}$. The calculations bear out this prediction with respect to I, but it is found that $\text{II} < \text{III}$. The bending c factors and also the off-diagonal contributions are found to be of importance for quantitative considerations. Note that, in both the above qualitative predictions and also in the actual calculations, $c(2)$ is the same for both molecules I and II and likewise $c(3)$ is the same for both molecules II and III.

For the bends, the c factors are equal in pairs for the two perpendicular coordinates. For each case, the c factor is expected to be largest when the isotopic atom is the center atom of the bending coordinate (Rule 5a, Appendix II). Thus $c(5)$ is

largest for I; $c(7)$ is largest for II, and $c(9)$ is largest for III. $c(5)$ for molecule I is found to have the same magnitude as $c(7)$ for molecule II with force fields A and B; $c(7)$ for molecule II with force field C is larger because of the large f_{77} force constant in this force field. The equal magnitude of $c(5)$ and $c(7)$ noted above is the result of two opposing factors just as in the case of $c(1)$ and $c(2)$ for molecule I: on the one hand, the diagonal G matrix element for coordinate 5 is larger and leads to $v_5' > v_7'$ (the coordinate involves a hydrogen) while, on the other, g_{155}/g_{255} for I is smaller than g_{177}/g_{277} for II (Rules 4 and 5a, Appendix II). The outcome in the present case is somewhat different than in the $c(1)$, $c(2)$ case.

As for the different results obtained with the different force fields, the results in general can be anticipated from Rule 4a, Appendix II. For example, the $c(3)$ values in Tables 3b and 4b directly reflect the force constants; a similar statement holds for the $c(9)$ values in Table 3c and 4c. We refrain from giving further examples.

Discussion of $(\text{CORR})_{ij}$ Factors

Appendix II lists a set of rules for c factors. These rules are based on the mathematical structure of c and have general validity. Appendix III lists a set of rules for $(\text{CORR})_{ij}$ factors. Rules 5, 6, 7 here need not have general validity and merely represent the experience of the cyanoacetylene calculations presented here. The validity of these rules depends on the force constants and on the magnitudes of the G matrix elements, and on the isotope effects on these.

The magnitudes of the $\ln(\text{CORR})_{ij}$ factors in Tables 4 are smaller than the corresponding quantities in Tables 3 (Rule 1, Appendix III). This statement also applies to $\ln \text{TOTOD}$. All the interaction terms $(\text{CORR})_{ij}$ appear in Tables 3 and 4 where i and j have isotopically substituted atoms in common and the corresponding $\ln(\text{CORR})_{ij}$ values are negative (Rule 6a, Appendix III). $\ln(\text{CORR})_{59}$ in Table 3b and 4b is close to zero; $g_{59}^2/(g_{55}g_{99})$ and its difference isotope effect are quite small compared to other bend-bend cases, the interactions for which are listed in Tables 3 and 4. $\ln(\text{CORR})_{12}$ for molecule I is considerably smaller in magnitude than is $\ln(\text{CORR})_{23}$ for molecule II. This result is a direct consequence of the high value of g_{11} which leads to a decrease in the perturbation

strength $g_{12}/(g_{11}g_{22})^{1/2}$ and in the difference isotope effect on its square (Rule 6, Appendix III). The bend interaction terms tend to be smaller than the stretch interaction terms since the bending frequencies are smaller (Rule 1a, Appendix III). For the stretch interaction terms, we list not only the negative terms of Rule 6a but also the positive terms of Rule 6b, which tend to be smaller than the negative term (Rule 7). For the bending interactions, the latter terms are insignificant and consequently not listed. The perturbation strength of the seemingly large f_{24} force constant in force field A is actually not so large — $|f_{24}/(f_{22}f_{44})^{1/2}| \cong 0.076$. Rule 5a, Appendix III, is not violated for $(\text{CORR})_{24}$.

Tables 3 and 4 show that the sum of the $\ln(\text{CORR})_{ij}$ factors, $\ln \text{TOTOD}$, is negative in all cases. Tables 5a, b, c show the break-up of the $\ln(\text{CORR})_{ij}$ factors into component parts at 150 K for force field A. The lower temperature value was chosen for this complete analysis because the factors are larger at this lower temperature. These Tables confirm the statement in Rule 5, Appendix III, that $\ln(\text{CORR-}G)_{ij}$ tends to make the major contributions, with $\ln(\text{CORR-}FG)_{ij}$ making smaller contributions. The contributions of $\ln(\text{CORR-}F)_{ij}$ factors tend to be insignificant. While the sign of $\ln(\text{CORR-}G)_{ij}$ is independent of the sign of g_{ij} , $\ln(\text{CORR-}FG)_{ij}$ depends on the relative signs of f_{ij} and g_{ij} . From the simple formula for F_{ij} in Rule 4, Appendix III, we expect that $\ln(\text{CORR-}FG)_{ij}$ will have the same sign as $\ln(\text{CORR-}G)_{ij}$ if f_{ij} and g_{ij} have opposite signs, and the opposite sign if f_{ij} and g_{ij} have the same signs. This expectation is confirmed by the Tables. Significant $\ln(\text{CORR-}FG)_{ij}$ factors are found when $f_{ij}/(f_{ii}f_{jj})^{1/2}$ is large. The major contribution to $\ln(\text{CORR-}FG)$ (the sum of $\ln(\text{CORR-}FG)_{ij}$ factors) for molecules I and II does appear to come from the bending coordinates. Since the $(\text{CORR-}G)_{ij}$ values only depend on the diagonal force constants, the masses, and geometrical parameters, these quantities are approximately the same for all three force fields; consequently, the $(\text{CORR-}G)_{ij}$ values can be compared with all the $(\text{CORR})_{ij}$ values of Tables 3 to obtain estimates of $(\text{CORR-}FG)_{ij}$. Note that, as with force field A, $\ln(\text{CORR-}F)_{ij}$ values are generally not significant with force fields B and C.

We compare Table 3a and Table 5a. With force field A, the main difference between $(\text{CORR-}G)_{ij}$ and $(\text{CORR})_{ij}$ factors occurs for the interaction

$i\ j$	$\ln(\text{CORR-}G)_{ij}$	$\ln(\text{CORR-}F)_{ij}$	$\ln(\text{CORR-}FG)_{ij}$
1 2	-0.0126	0.0000	0.0009
2 3	0.0118	0.0000	0.0009
2 4	0.0000	-0.0001	0.0000
5 7 = 6 8	-0.0014	-0.0003	-0.0046
7 9 = 8 10	0.0001	0.0000	0.0001
$\ln \text{CORR-X}^b$	-0.0035	-0.0008	-0.0071

Table 5a. Dissection of $\ln(\text{CORR})_{ij}$ for $\text{H}^{13}\text{C}^{12}\text{C}^{12}\text{CN}/\text{H}^{12}\text{C}_3\text{N}$, Force Field A, 150 K.^a^a Logarithmic dissection terms which only yield zeros entries are omitted.^b $\ln \text{CORR-X}$ entries correspond to sums of entries in respective column. For the first sum, $\ln \text{CORR-X}$ means $\ln \text{CORR-}G$, etc.

$i\ j$	$\ln(\text{CORR-}G)_{ij}$	$\ln(\text{CORR-}F)_{ij}$	$\ln(\text{CORR-}FG)_{ij}$
1 2	0.0026	0.0000	-0.0001
2 3	-0.0415	-0.0001	-0.0045
2 4	0.0000	-0.0001	0.0000
3 4	0.0105	0.0000	-0.0007
5 7 = 6 8	-0.0012	-0.0007	-0.0038
5 9 = 6 10	-0.0002	0.0000	0.0000
7 9 = 8 10	-0.0021	0.0000	-0.0015
$\ln \text{CORR-X}^b$	-0.0354	-0.0016	-0.0162

Table 5b. Dissection of $\ln(\text{CORR})_{ij}$ for $\text{H}^{12}\text{C}^{13}\text{C}^{13}\text{CN}/\text{H}^{12}\text{C}_3\text{N}$, Force Field A, 150 K.^a Footnotes refer to Table 5a.

$i\ j$	$\ln(\text{CORR-}G)_{ij}$	$\ln(\text{CORR-}F)_{ij}$	$\ln(\text{CORR-}FG)_{ij}$
2 3	0.0100	0.0000	0.0006
2 4	0.0000	-0.0002	0.0000
3 4	-0.0426	-0.0001	0.0046
5 7 = 6 8	0.0000	-0.0001	0.0002
7 9 = 8 10	-0.0019	0.0000	-0.0015
$\ln \text{CORR-X}^b$	-0.0365	-0.0006	0.0028

Table 5c. Dissection of $\ln(\text{CORR})_{ij}$ for $\text{H}^{12}\text{C}^{12}\text{C}^{13}\text{CN}/\text{H}^{12}\text{C}_3\text{N}$, Force Field A, 150 K.^a Footnotes refer to Table 5a.

between 5 and 7. This finding reflects the relatively large magnitude of f_{57} (measured in terms of the perturbation strength $-f_{57}/(f_{55}f_{77})^{1/2}$). With force field B, the $(\text{CORR-}G)_{ij}$ factors and $(\text{CORR})_{ij}$ factors are very similar; the largest deviation occurs for the interaction between 2 and 3. This deviation is much smaller than the effect we had anticipated when we first noted the value of f_{23} in force field B (actually $f_{23}/(f_{22}f_{33})^{1/2}$ is only 0.14). In the force field C off-diagonal force constants are sufficiently small so that the $(\text{CORR})_{ij}$ factors and $(\text{CORR-}G)_{ij}$ factors show quite good agreement.

One could analyze the $(\text{CORR})_{ij}$ terms in Tables 3b and 3c in the detail used for 3a, but we shall not do so. We note from the comparison of $\ln(\text{CORR-}G)$ and $\ln \text{TOTOD}$ that the $\ln(\text{CORR-}G)$ evaluation correctly predicts that $\ln \text{TOTOD}$ is larger in magnitude for molecules II and III than for molecule I. With force field C, $\ln(\text{CORR-}G)$ approximates $\ln \text{TOTOD}$ in Tables 3a, 3b, 3c quite well. The same can be said in the case of force fields A and B in Table 3a and 3c. However, in Table 3b, one finds non-negligible effects from $(\text{CORR-}FG)_{ij}$ factors with force fields A and B,

$i\ j$	I	II	III
	$\text{H}^{12}\text{C}_3\text{N}$	$\text{H}^{12}\text{C}_3\text{N}$	$\text{H}^{12}\text{C}_3\text{N}$
1 2	-0.0052	0.0009	0.0000
2 3	0.0035	-0.0158	0.0026
3 4	0.0000	0.0028	-0.0162
5 7 = 6 8	-0.0002	-0.0002	0.0000
5 9 = 6 10	0.0000	0.0000	0.0000
7 9 = 8 10	0.0000	-0.0002	-0.0002
$\ln \text{CORR-G}$	-0.0021	-0.0130	-0.0140

Table 6. $\ln(\text{CORR-}G)_{ij}$ ^a, Force Field A, 300 K, for the three ^{13}C substituted cyanoacetylenes. Footnote refers to Table 5a.

which lead to differences between $\ln \text{TOTD}$ and $\ln (\text{CORR-}G)$ of 0.018 and 0.027 respectively. These contributions arise in part from the bending interaction force constants but the interaction force constant between coordinates 2 and 3 also makes a contribution, especially with force field B.

In Table 6, $\ln (\text{CORR-}G)$ and the $\ln (\text{CORR-}G)_{ij}$ factors are given at 300 K; these values can be compared with the $\ln (\text{CORR})_{ij}$ factors in Tables 4a, b, c. The comparison is similar to the comparison at 150 K. At 300 K, the contribution of the off-diagonal elements of the **F** matrix to the partition function ratio is usually much less than 1%.

Discussion of $\ln \text{TOT}$

If one has a qualitative understanding of the $c(i)$ factors and the $(\text{CORR})_{ij}$ factors discussed in the previous sections, then one also has an understanding of TOT , which is the product of these terms and also the perturbation theory approximation of the reduced isotopic partition function ratio. Tables 3 and 4 give the percentage contributions of each of the terms to the total reduced partition function ratio (in logarithmic form). Thus for molecule I, the largest single contributor is $c(2)$, which contributes about 67% at 150 K (with all three force fields) and about 70% at 300 K. For molecule II, the largest single contributor is again $c(2)$; at 150 K its percentage contribution varies between 53% and 63%, depending on which force field is employed. At 300 K, the percentage contribution varies between 57% and 68%. For molecule III, the largest contributor is $c(4)$ with a percentage contribution of about 54% at 150 K (depending on force field); this number increases to 58% at room temperature. We have found then that the triple bond coordinates adjacent to the isotopic position make the major contribution to the isotopic partition function ratios.

Many analyses of this type and also others could be given. We refrain from further analyses since the requisite data for doing so are included in the Tables.

Dissection of the Equilibrium Constants K_4 and K_5

As noted previously, reduced isotopic partition functions are evaluated because they can be combined to yield isotope effects on equilibrium constants or equilibrium constants of isotopic

exchange reactions. $(s_2/s_1)f$ itself is the isotope effect on the equilibrium constant for the reaction of the molecule dissociating into atoms. We shall only consider the equilibrium constants K_4 and K_5 here (see Eqs. (8) and (9)). The results are given in Table 7a (150 K) and in Table 7b (300 K).

The comparison of the results labeled $\ln (s_2/s_1)f$ and $\ln \text{TOT}$ in Tables 7a and 7b indicates that the perturbation theory shows good behavior except in the case K_4 at 150 K, where the perturbation theory makes an error of about 0.013. If one considers the magnitude of the equilibrium constants here, this error is high and consequently one should not use the perturbation theory below 150 K. In subsequent discussion here, we will talk about $c(j)$ when we really mean $\ln c(j)$, etc.

While a number of equilibria have been studied where TOTD by itself predicts the equilibrium constant [9], for K_4 and K_5 here TOTD is quite important. The sign of TOTD is in all the cases here the same as sign of TOT . Detailed consideration of Tables 7a and 7b permits one to assess the contributions of the various factors to the equilibrium constants and also to intercompare the various force fields. In order to conserve space, we will limit the discussion here to K_4 and K_5 calculated at 150 K with force field A. To some extent there may be overlap with the discussion of the previous section.

To discuss K_4 , one needs to consider Tables 3a, 3b, and 7a. The contribution of $c(2)$ cancels since it is common to both molecules I and II. $c(4)$ makes no contribution to either molecule I or molecule II. The stretching coordinate contribution to K_4 arises from the difference between the $c(1)$ contribution of molecule I (from $\text{H}-^{13}\text{C}$) and the $c(3)$ contribution of molecule II (from $^{13}\text{C}-\text{C}$). That the $c(3)$ contribution is larger follows from previous discussion; consequently the contribution of the stretches to the equilibrium constant is negative. The large bending c factor for molecule I corresponds to $c(5)$ while for molecule II it corresponds to $c(7)$. As discussed previously, these two have approximately the same value and hence tend to cancel in the equilibrium constant. Of course, there is a $c(7)$ contribution from molecule I and a $c(5)$ contribution from molecule II but those also cancel in the equilibrium constant. In fact, the main contribution to the equilibrium constant from bending coordinate c factors arises from the $c(9)$

$$K_4 = \frac{[\text{H}-^{13}\text{C} \equiv ^{12}\text{C}-^{12}\text{C} \equiv \text{N}]}{[\text{H}-^{12}\text{C} \equiv ^{13}\text{C}-^{12}\text{C} \equiv \text{N}]}$$

$$K_5 = \frac{[\text{H}-^{12}\text{C} \equiv ^{12}\text{C}-^{13}\text{C} \equiv \text{N}]}{[\text{H}-^{12}\text{C} \equiv ^{13}\text{C}-^{12}\text{C} \equiv \text{N}]}$$

	FF A	FF B	FF C	FF A	FF B	FF C
$\ln(s_2/s_1) f$	-0.032	-0.007	-0.054	0.040	0.046	0.001
$\ln \text{TOT}$	-0.045	-0.022	-0.067	0.039	0.045	0.002
$\ln \text{TOTD}$	-0.087	-0.080	-0.098	0.021	0.015	0.005
$\ln 11$	0.046	0.044	0.044	0.000	0.000	0.000
$\ln 22$	0.000	0.000	0.000	-0.179	-0.185	-0.174
$\ln 33$	-0.122	-0.111	-0.118	0.000	0.000	0.000
$\ln 44$	0.000	0.000	0.000	0.183	0.186	0.184
$\ln 55 = \ln 66$	0.016	0.014	0.013	-0.005	-0.004	-0.004
$\ln 77 = \ln 88$	-0.014	-0.014	-0.020	-0.016	-0.016	-0.022
$\ln 99 = \ln 1010$	-0.007	-0.007	-0.006	0.029	0.027	0.022
$\ln \text{TOTOD}$	0.042	0.058	0.031	0.019	0.028	-0.003
$\ln 12$	-0.014	-0.015	-0.014	-0.002	-0.003	-0.002
$\ln 23$	0.059	0.073	0.054	0.057	0.069	0.052
$\ln 34$	-0.010	-0.009	-0.011	-0.048	-0.047	-0.056
$\ln 57 = \ln 68$	0.000	0.000	-0.001	0.006	0.000	0.001
$\ln 59 = \ln 610$	0.000	0.002	0.000	0.000	0.002	0.000
$\ln 79 = \ln 810$	0.004	0.003	0.001	0.001	0.003	0.000

Table 7a. Equilibrium constants K_4 and K_5 at 150 K calculated from the information in Tables 3. The headings are the same as those of Tables 3. The left-hand designations refer to the contributions of the respective terms in Tables 3 to the respective equilibrium constants.

$$K_4 = \frac{[\text{H}-^{13}\text{C} \equiv \text{C}-\text{C} \equiv \text{N}]}{[\text{H}-\text{C} \equiv ^{13}\text{C}-\text{C} \equiv \text{N}]}$$

$$K_5 = \frac{[\text{H}-\text{C} \equiv \text{C}-^{13}\text{C} \equiv \text{N}]}{[\text{H}-\text{C} \equiv ^{13}\text{C}-\text{C} \equiv \text{N}]}$$

	FF A	FF B	FF C	FF A	FF B	FF C
$\ln(s_2/s_1) f$	-0.013	0.001	-0.022	0.015	0.018	0.001
$\ln \text{TOT}$	-0.015	-0.005	-0.024	0.015	0.017	0.001
$\ln \text{TOTD}$	-0.031	-0.027	-0.035	0.006	0.005	0.003
$\ln 11$	0.021	0.021	0.021	0.000	0.000	0.000
$\ln 22$	0.000	0.000	0.000	-0.080	-0.083	-0.077
$\ln 33$	-0.051	-0.046	-0.049	0.000	0.000	0.000
$\ln 44$	0.000	0.000	0.000	0.081	0.082	0.081
$\ln 55 = \ln 66$	0.005	0.005	0.005	-0.002	-0.001	-0.001
$\ln 77 = \ln 88$	-0.004	-0.004	-0.006	-0.005	-0.005	-0.006
$\ln 99 = \ln 1010$	-0.002	-0.002	-0.002	0.009	0.008	0.006
$\ln \text{TOTOD}$	0.015	0.023	0.011	0.007	0.013	-0.002
$\ln 12$	-0.006	-0.006	-0.006	-0.001	-0.001	-0.001
$\ln 23$	0.022	0.029	0.019	0.021	0.027	0.019
$\ln 34$	-0.002	-0.002	-0.003	-0.016	-0.016	-0.020
$\ln 57 = \ln 68$	0.000	0.000	0.000	0.002	0.001	0.000
$\ln 59 = \ln 610$	0.000	0.001	0.000	0.000	0.001	0.000
$\ln 79 = \ln 810$	0.001	0.001	0.000	0.000	0.000	0.000

Table 7b. Equilibrium constants K_4 and K_5 at 300 K calculated from the information in Tables 4. The headings are the same as those of Tables 4. The left-hand designations refer to the contributions of the respective terms in Tables 4 to the respective equilibrium constants.

factor in II which is not cancelled by a corresponding factor in molecule I. When one takes into account the fact that the bending coordinates are degenerate in pairs, the logarithmic contribution of the bending factors to K_4 is -0.011 while that of the stretches is -0.076 .

As for the interaction terms, the 1 2 interaction term in I is smaller in magnitude than the corresponding 2 3 stretching interaction term in II. Moreover, the sign of the 2 3 interaction term in I is the negative of the 2 3 term in II so that, in order to obtain the contribution of 2 3 in Table 7a, the two magnitudes are added. A similar statement

applies to the 1 2 interaction. The total 2 3 contribution to K_4 is quite large. There is also a negative contribution to K_4 which arises from the 3 4 interaction term in II. The bending interaction terms 5 7 in I and II cancel each other. The small 7 9 bending interaction in II has no analogue in I; when one considers the degeneracy of the bending coordinates in pairs, the 7 9 = 8 10 interaction makes a contribution of almost 0.01 to the (logarithm of the) equilibrium constant (contribution of about 1% to the equilibrium constant itself). The total interaction contribution to K_4 is opposite in sign to the c contribution and half of its magnitude.

K_5 involves molecules III and II so that Tables 3b, 3c, and 7a must be consulted. The contribution due to $c(3)$ cancels. The contribution of $c(2)$ in II ($\text{C}\equiv^{13}\text{C}$) almost cancels the contribution of $c(4)$ in III ($^{13}\text{C}\equiv\text{N}$). Thus the overall contribution of the c 's for stretches to K_5 is 0.004. The bending coordinate with the largest c value in III is coordinate 9. The c factor for the bending coordinate 9 in III is much larger than other bending c factors because the diagonal force constant for coordinate 9 is large. This large c factor leads to the result that the net contribution of the bending c factors to K_5 is positive (0.016) while the corresponding contribution to K_4 is negative.

The 3 4 interaction term in III is much larger in magnitude than the corresponding 1 2 term in I and has almost the same magnitude as the corresponding 2 3 term in II (these are all interaction terms involving the two stretches terminating at the respective isotopically substituted atom). Consequently, the 2 3 and 3 4 interaction contributions almost cancel each other in K_5 while 2 3 and 1 2 did not cancel each other very effectively in K_4 . The contribution of the bending interactions to K_5 is somewhat larger than the corresponding contribution to K_4 . This result is brought about largely by the fact that f_{57} is larger than f_{79} . The overall contribution of the interactions to K_5 is positive but is only half the magnitude of the corresponding contribution to K_4 . The interaction contribution has the same sign and the same magnitude as the c contribution to K_5 .

Summary

The reduced isotopic partition function ratios of the three singly ^{13}C substituted cyanoacetylenes with respect to the ^{12}C compound have been evaluated with three different vibrational force fields. The contributions of the individual stretching and bending coordinates (c factors) and of interactions among these coordinates (CORR_{ij} factors) have been obtained by a perturbation theory method. This dissection of the reduced isotopic partition function ratios permits a corresponding dissection of the thermodynamic equilibrium constants among the three ^{13}C cyanoacetylenes. Some explicit discussion of these dissections has been given in terms of the force fields employed with a knowledge of the behavior of the perturbation theory. The perturbation theory permits one

to assess the contributions of the various force constants to isotope effects. While we have emphasized that the perturbation theory calculations can be carried out with ease, we should also emphasize that the perturbation theory approach should largely be used as a qualitative tool and as a tool of analysis; the exact calculations which are being analyzed by the perturbation theory can be carried out straightforwardly with a digital computer.

Acknowledgements

Max Wolfsberg wishes to thank the Alexander-von-Humboldt-Stiftung for a Humboldt Award and also the Max-Planck-Institut für Chemie for its hospitality during his stay there. Research at the University of California, Irvine, was supported by U.S. Department of Energy, Office of Basic Energy Sciences, Contract No. EY-76-S-03-0034, PA 188. Financial support of P. Bopp by the Deutsche Forschungsgemeinschaft is also acknowledged.

Appendix I

G Matrix Elements and Numerical Factors

A) Diagonal G matrix elements [13]

- a) Stretch i between atoms A and B with masses m_A, m_B

$$g_{ii} = \frac{1}{m_A} + \frac{1}{m_B}$$

- b) Bends j and k of angle A–B–C from equilibrium angle of 180° : $R(\text{AB})$ is the equilibrium separation of A and B

$$g_{jj} = \frac{1}{m_A} \frac{1}{R(\text{AB})^2} + \frac{1}{m_C} \frac{1}{R(\text{BC})^2} + \frac{1}{m_B} \left(\frac{1}{R(\text{AB})} + \frac{1}{R(\text{BC})} \right)^2,$$

$$g_{kk} = g_{jj}.$$

Two linear bending displacement coordinates j and k corresponding to displacements in mutually perpendicular directions, are associated with each equilibrium configuration in which the angle between bond AB and bond BC is 180° .

B) Off-diagonal G matrix elements [13]

There can be no off-diagonal G matrix elements between two displacement coordinates which have no atoms in common. In a molecule the equilibrium

configuration of which is linear (e.g. cyanoacetylene), there are no off-diagonal elements (either in the **G** matrix or in the **F** matrix) between stretches and bends. In such a molecule, there are also no off-diagonal elements (either in the **G** matrix or in the **F** matrix) between bends which correspond to perpendicular directions. Thus, coordinates 5, 6 correspond to a set of linear bends in cyanoacetylene involving $\text{H}-\text{C}\equiv\text{C}$, while coordinates 7, 8 are a similar set involving $\text{C}\equiv\text{C}-\text{C}$. Then

$$g_{56} = g_{78} = g_{58} = g_{67} = 0,$$

$$g_{55} = g_{66},$$

$$g_{77} = g_{88},$$

$$g_{57} = g_{68}.$$

The non-zero equalities follow from symmetry considerations. The same equalities hold for the elements of the **F** matrix.

- a) i = stretch between atoms A and B,
 j = stretch between atoms B and C,

(In equilibrium configuration, angle between AB and BC is 180° .)

$$g_{ij} = -1/m_B.$$

- b) Bend-bend interactions in molecules with linear equilibrium configuration: i and j are linear bending coordinates involving motion in the same direction

- 1) i = bend A-B-C,
 j = bend B-C-D,

$$g_{ij} = -\frac{1}{R(\text{BC})} \left[\frac{1}{m_B} \left(\frac{1}{R(\text{AB})} + \frac{1}{R(\text{BC})} \right) + \frac{1}{m_C} \left(\frac{1}{R(\text{BC})} + \frac{1}{R(\text{CD})} \right) \right].$$

- 2) i = bend A-B-C,
 j = bend C-D-E,

$$g_{ij} = \frac{1}{m_C} \frac{1}{R(\text{BC}) R(\text{CD})}.$$

C) Numerical factors for calculations

- a) $v_i' = (f_{ii} g_{ii} / 5.89141 \times 10^{-7})^{1/2}$,
 units: v' (cm^{-1}), f_{ii} ($\text{mdyn}/\text{\AA}$), g_{ii} (inverse atomic mass units).
 b) $V = h v' / kT = 1.4387 v' / T$.

c) Atomic masses

$$\begin{aligned} \text{H} &= 1.007825 \text{ amu}, \quad ^{12}\text{C} = 12.000000 \text{ amu}, \\ ^{13}\text{C} &= 13.003350 \text{ amu}, \quad \text{N} = 14.003074 \text{ amu}. \end{aligned}$$

Appendix II

Some Properties of the c Factors

$$\begin{aligned} c(j) &= \frac{V_{2j}}{V_{1j}} \frac{1 - e^{-V_{1j}}}{1 - e^{-V_{2j}}} \exp \{ (V_{1j} - V_{2j})/2 \} \\ &= \frac{V_{2j}}{V_{1j}} \frac{\sinh(V_{1j}/2)}{\sinh(V_{2j}/2)} \end{aligned}$$

where

$$V_{1j} = h v_{1j}' / kT, \quad v_{1j}' = (2\pi)^{-1} (f_{jj} g_{jj})^{1/2}.$$

The subscript 1 here refers to the light molecule (e.g., $\text{H}^{12}\text{C}_3\text{N}$) while 2 refers to the heavy molecule (e.g., either I, II, or III).

Rule 1. $(g_{jj})_1 \geq (g_{jj})_2$ and $c(j) \geq \text{unity}$.

Rule 2. If $(g_{jj})_1 = (g_{jj})_2$, $c(j) = \text{unity}$.

a) If coordinate j does not involve movement of the isotopically substituted atom, $c(j) = \text{unity}$.

Rule 3. As T increases, $c(j)$ approaches unity.

Rule 4. At constant v_{1j}'/v_{2j}' , increase in v_{1j}' leads to an increase in $c(j)$.

a) Increase of f_{jj} at constant g_{1jj} , g_{2jj} leads to increase in $c(j)$.

Rule 5. At constant v_{1j}' (or v_{2j}'), increase of v_{1j}'/v_{2j}' leads to an increase in $c(j)$.

a) At constant v_{1j}' (or v_{2j}'), increase of g_{1jj}/g_{2jj} leads to an increase in $c(j)$.

Appendix III

Some Properties of $(\text{CORR})_{ij}$ Factors

Rule 1. $\ln(\text{CORR})_{ij}$ decreases in absolute magnitude with increasing temperature and approaches zero as $T \rightarrow \infty$.

a) At constant $f_{ij}/(f_{ii} f_{jj})^{1/2}$, $g_{ij}/(g_{ii} g_{jj})^{1/2}$, and given v_i'/v_j' , $\ln(\text{CORR})_{ij}$ decreases in absolute magnitude with decreasing values of V_i , V_j .

Rule 2. $\ln(\text{CORR})_{ij}$ is zero unless at least one of the coordinates i or j is isotopically substituted.

Rule 3. If both g_{ij} and f_{ij} equal zero, $\ln(\text{CORR})_{ij}$ equals zero.

a) There are no $(\text{CORR})_{ij}$ terms which couple stretching to bending coordinates in linear molecules.

b) For the cyanoacetylene molecule, the only bending interaction terms are $(\text{CORR})_{57} = (\text{CORR})_{68}$, $(\text{CORR})_{79} = (\text{CORR})_{810}$, $(\text{CORR})_{59} = (\text{CORR})_{610}$.

Rule 4. At low temperature or if $\exp(-V_i)$ and $\exp(-V_j)$ are sufficiently small, F_{ij} (Eq. (16)) can be written

$$F_{ij} = \frac{V_i V_j}{4(V_i + V_j)} \left[\frac{g_{ij}}{(g_{ii} g_{jj})^{1/2}} - \frac{f_{ij}}{(f_{ii} f_{jj})^{1/2}} \right]^2 - \frac{1}{2} \frac{g_{ij}^2}{g_{ii} g_{jj}} - \frac{1}{2} \frac{f_{ij}^2}{f_{ii} f_{jj}}.$$

This form of F_{ij} makes it easier to rationalize some of the following rules.

Rule 5*. When $\ln(\text{CORR})_{ij}$ differs significantly from zero, the main contribution is found usually to arise from $(\text{CORR-}G)_{ij}$ with lesser contribution from $(\text{CORR-F}G)_{ij}$, if f_{ij} is sufficiently large. $\ln(\text{CORR-F})_{ij}$ is never found to have significant magnitude. (See Eq. (17) for definition of above terms.)

a) If the coordinates i and j have no atoms in common, $\ln(\text{CORR})_{ij}$ vanishes. Under this circumstance g_{ij} vanishes and $\ln(\text{CORR})_{ij}$ equals $\ln(\text{CORR-F})_{ij}$.

Rule 6*. From Eq. (15),

$$(\text{CORR})_{ij} = \exp(F_{2ij} - F_{1ij}).$$

The relative magnitudes of F_{1ij} and F_{2ij} are found to depend on the relative magnitudes of $g_{ij}/(g_{ii} g_{jj})^{1/2}$ in the two isotopic molecules. When g_{ij} is isotope dependent, $g_{ij}/(g_{ii} g_{jj})^{1/2}$ is smaller in magnitude in the heavy molecule (molecule designated as 2). When g_{ij} is isotope independent and either g_{ii} or g_{jj} is isotope dependent, $g_{ij}/(g_{ii} g_{jj})^{1/2}$ is smaller in the light molecule.

a) If coordinates i and j are both isotopically substituted (g_{ij} isotope dependent), $\ln(\text{CORR})_{ij}$ is negative.

b) If only one of the coordinates i, j is isotopically substituted, $\ln(\text{CORR})_{ij}$ is positive.

Rule 7*. The isotope effect on F_{ij} tends to be large when g_{ij} is isotope dependent and somewhat smaller when only g_{ii} or g_{jj} are isotope dependent.

* These rules describe specifically the experience here with the $^{13}\text{C}/^{12}\text{C}$ cyanoacetylenes.

- [1] E. Churchwell, C. M. Walmsley, and G. Winnewisser, *Astron. Astrophys.* **54**, 925 (1977).
- [2] M. Wolfsberg, P. Bopp, K. Heinzinger, and P. D. Mallinson, *Astron. Astrophys.* in press.
- [3] For calculations in which deviations from the Born-Oppenheimer approximation were taken into account, see L. I. Kleinman and M. Wolfsberg, *J. Chem. Phys.* **59**, 2043 (1973); **60**, 4740 (1974); **60**, 4749 (1974).
- [4] J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.* **15**, 261 (1947).
- [5] J. Bron; C. F. Chang, and M. Wolfsberg, *Z. Naturforsch.* **28a**, 129 (1973).
- [6] P. D. Mallinson, to be published.
- [7] M. Uyemura and S. Maeda, *Bull. Chem. Soc. Japan* **47**, 2930 (1974).
- [8] S. J. Cyvin and P. Klaebo, *Acta Chem. Scand.* **19**, 697 (1965).
- [9] G. Singh and M. Wolfsberg, *J. Chem. Phys.* **62**, 4165 (1975); S. A. Skaron and M. Wolfsberg, *J. Amer. Chem. Soc.* **99**, 5253 (1977).
- [10] L. Waldman, *Naturwiss.* **31**, 205 (1943).
- [11] M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.* **8**, 225 (1964).
- [12] J. Bigeleisen and T. Ishida, *J. Chem. Phys.* **48**, 1311 (1968); J. Bigeleisen, T. Ishida, and W. Spindel, *ibid.* **55**, 5021 (1971); T. Ishida and J. Bigeleisen, *ibid.* **62**, 80 (1975) and references therein.
- [13] E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York 1955.