Vibrational Spectrum of Cyclic $C_{34}H_{68}$ and Chain Folding in Polyethylene Single Crystals

S. Krimm* and J. Jakeš

Harrison M. Randall Laboratory of Physics and Macromolecular Research Center,
University of Michigan, Ann Arbor, Michigan 48104.
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ABSTRACT: A complete normal vibration analysis has been done for cyclic $C_{34}H_{68}$. These results support the assignment of a band at 1342 cm^{-1} to the fold region of the molecule. Our analysis, however, does not support the conclusion previously suggested, *viz.*, that the spectrum of this molecule shows that tight folding does not occur in polyethylene single crystals. A calculation of the longitudinal acoustic modes of some linear paraffins shows that the relationship obtained for finite chains probably cannot be carried over directly to planar segments which are connected by folds.

The nature of the fold structure in polymer single crystals has been the subject of extensive studies using a number of techniques.[1] Until recently none of these provided direct information about the details of the molecular organization involved in chain folding. On the basis of normal vibration calculations, however, it was possible to show that an infrared study of mixed crystals of polyethylene and perdeuteriopolyethylene could reveal the organization of chain stems in polyethylene single crystals.[2] Subsequent experimental studies of such systems indicated that in crystals grown from dilute solution the chain reentry could not be random, and that in fact (110) folding with predominantly adjacent reentry was favored.[3] While these results could not reveal the nature of the fold itself, lattice frequency studies[4] suggested that the fold was closer to being "tight" than to being "loose."

It has been suggested[5] that the fold configuration of the cyclic paraffin $(CH_2)_{34}$ could serve as a possible model for the fold regions of polyethylene single crystals. In particular, the crystal structure of this paraffin[6] indicates that the configuration is representative of a tight fold. An infrared study of the spectrum of this cyclic paraffin, as well as of the spectra of some linear paraffins, was therefore used to determine the kind of folding present in polyethylene single crystals.[7] It was concluded[7] that such crystals ". . . do not have appreciable adjacent reentry (tight fold)," and that ". . . the surface structure of the monolayer single crystal is somewhat between the amorphous state and that of a tightly folded structure (adjacent reentry)."

Since the spectroscopic analysis depends upon the assignment of bands to folds, and because this molecule can provide a model for studying the longitudinal acoustic (LA) vibrations of extended planar zigzag segments in polyethylene single crystals,[8,9] we have undertaken a complete normal vibration analysis of cyclic $(CH_2)_{34}$. The results confirm the fold band assignment previously used,[7] but our analysis does not support the conclusions drawn with respect to fold structure in polyethylene single crystals. Our results also show that the relationship obtained for the LA vibrations of finite chains probably does not carry over to cases in which coupling between adjacent polymethylene segments is possible.

Calculations and Results

The structure of $(CH_2)_{34}$ was taken to be the conformation given by X-ray diffraction,[5,6] with tetrahedral geometry. Bond lengths of C–H = 1.093 Å and C–C = 1.54 Å were used, all valence angles were tetrahedral, and dihedral angles were taken as 180° for trans and ±60° for gauche. This structure has C_{2h} symmetry, and the 300 normal modes are divided up as follows: A_g, 77 (of which 18 are CH_2 stretching vibrations; B_g, 73 (of which 16 are CH_2 stretch); A_u, 74 (of which 16 are CH_2 stretch); and B_u, 76 (of which 18 are CH_2 stretch). The force field used was that refined for planar and nonplanar normal paraffins[10] and applied in a recent study of the normal vibrations of polyamides.[11]

The calculated frequencies below 1500 cm^{-1} are listed in Tables I and II together with their approximate assignments based on calculated eigenvectors. Assignments are not given in the region below 600 cm^{-1} because of the strong mixing of modes of the planar chain and of the fold regions, as well as strong mutual mixing of CCC bend and CC torsion modes below 200 cm^{-1}. The first three harmonics of the A_g LA modes (ω_1, ω_3, and ω_5) are, however, designated, since they are reasonably well identified from the eigenvectors. The symbols B, W, T, R, and S represent CH_2 bending, wagging, twisting, and rocking and C–C stretching modes, respectively. The subscript indices represent the modes for the allowed sequential phase relationships of the $(CH_2)_{13}$ all-trans chain segments. As a result of the interaction between the two such segments, the $A_g + A_u$ modes form one sequence obeying eq 10 of ref 12 with a particular $\vartheta(\varphi)$ function, while the $B_g + B_u$ modes form another sequence obeying eq 10 but with another particular $\vartheta(\varphi)$ function. The carbon atoms in the fold are labeled C_7, C_8, and C_9 and correspond to C_1, C_{16}, and C_{17} of ref 5. The superscript plus signifies a mode symmetric with respect to the C_2 axis passing through the center of the C_8–C_9 bond, while the superscript minus signifies a mode which is antisymmetric with respect to this axis. The designation C_7 or C_8 in parentheses following B, W, T, or R refers to the mode of the CH_2 group centered on that carbon atom. A comparison is given

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(1) A. Keller, *Rep. Progr. Phys.*, **31**, 623 (1968).
(2) M. Tasumi and S. Krimm, *J. Polym. Sci., Part A-2*, **6**, 995 (1968).
(3) M. I. Bank and S. Krimm, *ibid., Part A-2*, **7**, 1785 (1969).
(4) M. I. Bank and S. Krimm, *J. Appl. Phys.*, **39**, 4951 (1968).
(5) B. A. Newman and H. F. Kay, *ibid.*, **38**, 4105 (1967).
(6) H. F. Kay and B. A. Newman, *Acta Crystallogr., Sect. B*, **24**, 615 (1968).
(7) H. Schonhorn and J. P. Luongo, *Macromolecules*, **2**, 366 (1969).
(8) R. F. Schaufele and T. Shimanouchi, *J. Chem. Phys.*, **47**, 3605 (1967).
(9) R. F. Schaufele, *Macromol. Rev.*, **4**, 67 (1970).
(10) R. G. Snyder, *J. Chem. Phys.*, **47**, 1316 (1967).
(11) J. Jakeš and S. Krimm, *Spectrochim. Acta, Part A*, **27**, 19 (1971).
(12) J. Jakeš, *Collect. Czech. Chem. Commun.*, **30**, 1523 (1965).

TABLE I

INFRARED-ACTIVE FREQUENCIES OF CYCLIC $C_{34}H_{68}$

	Calcd		
Exptl[a]	A_u	B_u	Assignment
	1476		B_{10}
		1476	B_9
		1475	B_{11}
	1474		$B_8 + B_{12}$
	1473		$B_8 + B_{12}$
1469 vs		1473	B_{13}
1462 ms		1472	$B^-(C_8)$
		1470	B_7
	1466		B_6
1442 s	1464		$B^+(C_7)$
		1462	$B^-(C_7)$
		1460	B_5
1435 mw	1455		$B^+(C_8)$
	1454		B_4
		1448	B_3
	1444		B_2
		1440	B_1
	1385		W_{13}
		1384	W_{12}
	1381		W_{11}
		1375	W_{10}
1368 mw	1374		$W^+(C_8)$
1361 vw	1363		W_9
1342 s		1355	$W^-(C_7)$
	1352		$W^+(C_7)$
1350 vw		1348	W_8
1327 vw	1328		W_7
1314 w		1312	W_6
	1310		T_5
		1310	T_4
	1307		T_3
		1306	T_6
1304 mw		1304	$W^-(C_8)$
		1303	T_2
	1302		T_1
	1298		T_7
		1291	T_8
1293 w	1289		W_5
		1278	$T^-(C_8)$
	1277		T_9
1274 m		1269	W_4
1257 vw	1256		$T^+(C_7)$
		1248	T_{10}
1240 mw	1247		W_3
1228 vw		1229	W_2
	1213		T_{11}
1209 vw		1207	$T^-(C_7)$
1197 w	1201		W_1
1180 w		1180	T_{12}
1162 vw	1160		$T^+(C_8)$
	1142		T_{13}
1127 w		1136	S_1
1104 vw	1103		$S^+(C_7C_8)$
		1095	R_{13}
1083 w		1083	$S^-(C_7C_8)$
	1069		S_{10}
		1068	S_{11}
1068 m	1067		S_2
		1067	S_9
		1063	S_7
	1062		S_{12}
1051 w	1053		S_8
	1044		R_{12}
		1025	S_5
	1019		S_6
1007 w		1005	$S^-(C_6C_7)$
	1004		$S\ (C_8C_9)$
		989	S_3
	981		S_4
965 w		964	$R^-(C_8)$
	935		R_{10}
919 w		931	R_{11}
	900		$S^+(C_6C_7)$
867 w		877	R_9
	857		R_8
818 w		829	$R^-(C_7)$
803 w	823		$R^+(C_7)$
785 w		786	R_7
768 mw	782		R_6
742 w		745	R_5
	742		R_4
732 w		724	R_3
	723		R_2
714 vs		717	R_1
700 ms	714		$R^+(C_8)$
		543	
	541		
	520		
		464	
	461		
		435	
	363		
		346	
	311		
		292	
	232		
		208	
	189		
		149	
	147		
		146	
		141	
	130		
	124		
		118	
		106	
		103	
	87		
	76		
		66	
	62		
		37	
	30		
		24	
		17	
	12		

[a] See ref 13.

TABLE II
RAMAN-ACTIVE FREQUENCIES OF CYCLIC $C_{34}H_{68}$

Exptl[a]	Calcd A_g	Calcd B_g	Assignment
	1476		B_9
		1476	B_{10}
	1475		B_{11}
		1474	$B_8 + B_{12}$
	1473		B_{13}
		1473	$B_{12} + B_8$
		1472	$B^-(C_8)$
	1470		B_7
		1465	B_6
	1464		$B^+(C_7)$
		1462	$B^-(C_7)$
	1460		B_5
1461 w	1455		$B^+(C_8)$
		1454	B_4
	1448		B_3
		1444	B_2
1449 ms	1440		B_1
~1400 m (b)		1385	W_{13}
	1384		W_{12}
		1381	W_{11}
	1376		W_{10}
1375 m	1372		$W^+(C_8)$
		1364	W_9
		1355	$W^-(C_7)$
	1353		$W^+(C_7)$
	1347		W_8
1330 w		1330	W_7
	1310		T_4
		1310	T_5
	1309		W_6
		1307	T_3
		1306	$W^-(C_8)$
	1305		T_6
	1303		T_2
1301 ms		1302	T_1
		1298	T_7
		1290	W_5
	1289		T_8
		1282	$T^-(C_8)$
	1273		$T^+(C_7)$
		1265	T_9
	1263		W_4
		1251	W_3
	1237		T_{10}
		1228	$T^-(C_7)$
	1226		W_2
		1205	T_{11}
	1188		T_{12}
		1187	W_1
1174 w	1161		$T^+(C_8)$
1140 m	1152		R_{13}
		1120	T_{13}
1110 w	1104		$S^+(C_7C_8)$
1096 m	1096		S_1
		1091	$S^-(C_7C_8)$, $S^-(C_7C_8)$
		1079	S_2
		1069	S_{10}
	1068		S_9
	1063		S_{11}
1065 ms		1062	S_{12}
		1050	S_8
	1047		S_3
		1041	R_{12}
	1032		S_7
		1029	S_4
	1009		R_{11}
		992	S_6
	987		S_5
985 vw	972		$S(C_8C_9)$
		970	$R^-(C_8)$
		956	R_{10}
		904	$S^-(C_6C_7)$ $S^-(C_7C_8)$
891 m	899		$S^+(C_6C_7)$
	895		R_9
		851	R_8
	832		$R^+(C_7)$
		809	$R^-(C_7)$
	808		R_7
		764	R_6
	759		R_5
		732	R_4
	730		R_3
		719	R_2
	718		R_1
	714		$R^+(C_8)$
540 w	553		
		521	
		512	
496 w	507		ω_5
431 w	440		ω_3
400 w	404		
		403	
		345	
303 w	296		
		282	
		239	
257 w	232		
		164	
147 vs	154		ω_1
	147		
		147	
	138		
		132	
		127	
123 w	122		
100 w	105		
	95		
		94	
77 w		72	
66 w		60	
	56		
40 w	42		
		41	
21 w	24		
		15	
13 w	11		

[a] See ref 14.

in Tables I and II with the observed infrared[13] and Raman[14] frequencies.

In order to better evaluate the calculations of the LA modes of $(CH_2)_{34}$, normal vibration calculations were done of the LA modes of some planar normal paraffins (C_nH_{2n+2}) for which data are available.[8] The results for n = 18, 20, 24, 28, 32, 36, 44, and 94 are given in Table III, using the same force field as above.

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(13) We are indebted to Mr. Jack Ching for obtaining the infrared spectra.

(14) M. Tasumi, T. Shimanouchi, and R. F. Schaufele, manuscript in preparation.

TABLE III
LONGITUDINAL ACOUSTIC VIBRATIONS OF C_nH_{2n+2} PARAFFINS

n	ν_{obsd}	ν_{calcd}	n	ν_{obsd}	ν_{calcd}
18	132.5	124.9	36	67.4	63.2
	355	353.7		189	185.4
	493	500.0[a]		303	302.8
20	113.6	112.2		403	408.8
	324	321.1		475	487.4
	475	491.9[a]	44	56.5	51.8
24	97.8	94.6		155	154.1
	279	277.0		259	252.6
	422	426.1	94	26	24.3
28	84.7	81.2		71	72.8
	241	238.2		121	120.9
	377	367.8[a]		168	168.3
32	75.8	71.1		216	214.8
	211	209.4		265	260.3
	337	337.9		305	302.6[a]
				346	345.4
				386	382.1[a]
				417	421.5
				444	453.2

[a] Mixed with other branches of the dispersion curve.

Discussion

Assignments. Band assignments in Tables I and II have been made largely on the basis of frequency correlation and of the expected intensities of various modes as indicated by the eigenvectors. Thus, in the R_i series the odd members are expected to be more intense than the even in the infrared, and both are expected to be weak in the Raman spectrum. In the infrared, $R^+(C_8)$ is expected to be more intense than $R^-(C_8)$. Twisting modes are generally very weak in the infrared but of moderate intensity in the Raman. The lower members of the wagging series in the infrared should be stronger than the higher (this may not appear to be strictly true from Table I, but it must be recalled that the assignments do not represent pure modes but only the largest component of the eigenvector). This is what justifies assigning the medium-strong band at 1342 cm^{-1} to a mode in the fold region rather than to one of the W_i modes. The B_u mode is favored over the A_u mode, since the intensity of the former is expected to be greater than that of the latter (a similar argument holds for the assignment of $B(C_7)$ and $B(C_8)$ modes).

The overall agreement between observed and calculated frequencies is good, the average difference being 0.5% for the infrared bands and 0.9% for the Raman. The relatively large discrepancy for the 1342-cm^{-1} band may be a result of the fact that no molecule with the GG conformation was used in the refinement of the force field.[10] However, it may also be associated with the large distortions in the actual structure which occur in the fold region as a result of steric hindrance.[5,6]

Fold Structure in Polyethylene Single Crystals, The present analysis substantiates the assignment[7] of the 1342-cm^{-1} band to a vibrational mode in the fold region of (CH$_2$)$_{34}$. It also helps shed light on the difficulties involved in using this result alone to infer information on fold structure in polyethylene single crystals. With respect to the arguments presented in the above paper,[7] the following points should be noted.

(1) The calculated frequencies of the $W(C_7)$ and $W(C_8)$ modes agree very well with those for the GG and GTG structures, respectively, calculated for normal paraffins.[10] This is not too surprising, since precisely these topological conformations occur in the fold region of (CH$_2$)$_{34}$, and coupling to the external chains should not be very different from that in the paraffins. Whereas the observed frequencies for the $W(C_8)$ modes are in good agreement with those calculated, this is less so for the $W(C_7)$ mode. As was noted above, this may in part be due to the distortion which exists in the fold region of the molecule in its crystalline conformation. In support of this, it should be noted that upon melting the 1342-cm^{-1} band essentially disappears and is replaced by a strong band at 1350 cm^{-1}, while the 1365-cm^{-1} band increases in intensity.[7] Both the 1350- and 1365-cm^{-1} bands are found in liquid *n*-paraffins[7,10] and are assignable predominantly to GG and GTG structures, respectively[10] (although the 1350-cm^{-1} band may also contain contributions from G structures). The enhanced intensity ratio of 1350 to 1365 in melted (CH$_2$)$_{34}$, as compared to this ratio in the liquid *n*-paraffins, may be indicative of the larger fraction of GG conformations which can persist in the cyclic paraffin even in the liquid state as a result of its topology. If these assignments are valid, they indicate that a significant part of the 1342-to-1350-cm^{-1} shift which occurs on melting (CH$_2$)$_{34}$ is due to the release of strain on the TGGT regions of the molecule, rather than to the replacement of these by G conformations as previously suggested.[7]

(2) The presence of a band at 1342 cm^{-1} does not necessarily indicate the presence of a specific structure (although the reverse is in general true, *viz.*, a specific structure results in a specific absorption band). Thus, the 1342-cm^{-1} band of crystalline (CH$_2$)$_{34}$ probably arises, as we have seen, from a distorted GG conformation. In contrast to the previous assignment,[7] similar bands of the liquid C_6, C_8, C_{10}, and C_{12} paraffins are clearly due[10] to terminal GTT structures (which would also be expected to be of relatively constant intensity in the series[7]), and the ~1340-cm^{-1} absorption of melted (CH$_2$)$_{34}$ and of polyethylene most likely originates from TG and GTTG structures.[10] In the former case these could be associated with bent (CH$_2$)$_{13}$ chain segments and in the latter case with fold regions or, more likely, cilia.[15] In other words, the presence of slight absorption at ~1340 cm^{-1} in polyethylene single crystals can in no way be related uniquely to the tight fold structure of crystalline (CH$_2$)$_{34}$, and in fact it most probably has another origin. Similarly, the 1350-cm^{-1} band of crystalline (CH$_2$)$_{34}$ most likely originates (*cf.* Table I) from the W_8 mode of the (CH$_2$)$_{13}$ segments rather than from any additional gauche conformations in the molecule.

(3) The absence of a band at 1342 cm^{-1} in the spectrum of polyethylene single crystals can be taken as an indication of the probable absence of the (strained) GGTGG fold geometry of crystalline (CH$_2$)$_{34}$, but it says nothing about whether the fold is tight or not. In the first place, the fold in polyethylene simply cannot be the same as that in (CH$_2$)$_{34}$, since the chain stems (for (110) folding) have a completely different relationship to one another than is the case for the cyclic paraffin.[1] On this basis alone a band at 1342 cm^{-1} would not be expected in polyethylene. Secondly, if the 1350- and 1365-cm^{-1} bands in polyethylene are taken to indicate the presence of GG and GTG conformations, respectively,[10] this in no way excludes the possibility of a regular tight fold. Some of the intensity of these absorption bands may be due to cilia,[15] but the remainder may arise from a fold structure which utilizes these conformations. If, for example, the fold contains an unstrained GG conformation, then its absorption would probably be expected near 1350 rather than 1342 cm^{-1}. The ratio of 1340- to 1350-cm^{-1} absorptions in polyethylene single

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(15) M. I. Bank and S. Krimm, *J. Appl. Phys.*, **40**, 4248 (1969).

crystals (which in any case should *not* be similar to that of $(CH_2)_{34}$ since the band origins are different) therefore implies nothing about the presence or absence of regular folding, contrary to previous assertions.[7]

We conclude that an analysis of the vibrational spectrum of $(CH_2)_{34}$ does not permit a determination of whether folding in polyethylene single crystals is tight or not, beyond the statement that it cannot involve the specific tight fold of $(CH_2)_{34}$. Our analysis does suggest that if GG conformations are present in the fold they are (relative to $(CH_2)_{34}$) unstrained.

Longitudinal Acoustic Modes. It has been suggested[8,9] that the LA modes of polyethylene single crystals would be characteristic of their fold length. It was, however, noted that the relationship obtained for the finite paraffins would be valid for polyethylene only if it could be assumed that oscillations in a planar zigzag segment were completely decoupled from oscillations in segments joined to it by folds. In order to determine whether or not such an assumption is valid, we have calculated the LA modes of some linear paraffins (see Table III) for purposes of comparison with the calculation for $(CH_2)_{34}$.

A comparison first of the observed LA modes of $(CH_2)_{34}$ with the relationship found for linear paraffins (*cf.* Figure 4 of ref 8) shows that these frequencies do not fit in with those of the finite molecules. If we assume $n = 15$ for each planar segment of the $(CH_2)_{34}$ molecule, then the observed frequencies of 147, 431, and 496 cm^{-1} are far from their expected values of about 153, 410, and 560 cm^{-1}. This suggests that coupling effects are not negligible. A similar conclusion is reached by comparing the ω_1 modes of the linear paraffins (Table III) and of $(CH_2)_{34}$ (Table II). In all cases the observed frequency for the former is higher than the calculated frequency, while for the latter (using the same force field) the observed frequency is lower than the calculated frequency. This suggests that for cyclic structures such as $(CH_2)_{34}$ the ω_1 LA mode of the planar segments will be consistently lower than the value for a linear chain. If this effect extends to n values appropriate to polyethylene crystals, *viz.*, about 100, then use of the relationship for finite paraffins will tend to overestimate the planar zigzag chain length. This effect is of the order of 6% for $(CH_2)_{34}$, but may be different for longer segments and for different fold geometries (for example, folds in polyethylene single crystals may not consist of GGTGG conformations, but in addition they do not give rise to cyclic structures).

We conclude that caution must be used in applying the relationship for LA frequencies in finite paraffin chains to the determination of the lengths of planar zigzag segments in folded chain polyethylene.[16]

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(16) W. L. Peticolas, G. W. Hibler, J. L. Lippert, A. Peterlin, and H. Olf, *Appl. Phys. Lett.*, 18, 87 (1971).

Inelastic Light-Scattering Study of Macromolecular Reaction Kinetics. I. The Reactions $A \rightleftharpoons B$ and $2A \rightleftharpoons A_2$

Victor A. Bloomfield*[1] and Jülyet Aksiyote Benbasat

Department of Biochemistry, College of Biological Sciences, University of Minnesota, St. Paul, Minnesota 55101. *Received May 10, 1971*

ABSTRACT: This paper considers the effect of chemical reactions on the spectrum of light scattered from macromolecular solutions. A general formalism is developed, taking into account only diffusion and chemical reaction, using the matrix eigenvalue technique of Salsburg and coworkers. This formalism is applied to the reactions $A \rightleftharpoons B$ and $2A \rightleftharpoons A_2$, which are shown to yield identical results after appropriate definition of relaxation times and effective equilibrium constants. Particular attention is focused on the case where the diffusion coefficients of reactants and products are different, while their polarizabilities are identical. Numerical calculations, using plausible values of diffusion coefficients and chemical relaxation times for macromolecular solutions, indicate that macromolecular reaction processes should measurably perturb inelastic light-scattering spectra in the audiofrequency region.

Inelastic light scattering, which measures the spectrum of Rayleigh light scattered from solutions illuminated with monochromatic laser light, has emerged as a significant new technique for studying macromolecules in solution. A useful review of this technique, with extensive bibliography, has been written by Chu.[2] Most of the applications to polymers have been concerned with measurement of diffusional motion. However, one of the potentially most significant applications is measurement of the kinetics of fast reactions. This has been the subject of many theoretical[3-11] and a few experimental[12,13a] investigations.

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(1) Alfred P. Sloan Foundation Fellow.

(2) B. Chu, *Annu. Rev. Phys. Chem.*, 21, 145 (1970).

(3) (a) B. J. Berne and H. L. Frisch, *J. Chem. Phys.*, 47, 3675 (1967); (b) B. J. Berne, J. M. Deutsch, J. T. Hynes, and H. L. Frisch, *ibid.*, 49, 2864 (1968).

(4) B. J. Berne and R. Pecora, *ibid.*, 50, 783 (1969).

(5) L. Blum and Z. W. Salsburg, *ibid.*, 48, 2292 (1968).

(6) L. Blum and Z. W. Salsburg, *ibid.*, 50, 1654 (1969).

(7) L. Blum, *ibid.*, 51, 4025 (1969).

(8) D. L. Knirk and Z. W. Salsburg, *ibid.*, 54, 1251 (1971).

(9) J. M. Schurr, *J. Phys. Chem.*, 73, 2820 (1969).

(10) Y. Yeh and R. N. Keeler, *Quart. Rev. Biophys.*, 2, 315 (1969).

(11) M. Weinberg and R. Kapral, *J. Chem. Phys.*, 53, 4409 (1970).

(12) Y. Yeh and R. N. Keeler, *ibid.*, 51, 1120 (1969).

(13) (a) Y. Yeh, *ibid.*, 52, 6218 (1970); (b) G. A. Korn and T. M. Korn, "Mathematical Handbook for Scientists and Engineers," 2nd ed, McGraw-Hill, New York, N. Y., 1968, p 416.