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Vibrations of the Ethynyl Group (C≡C-H), the Hydrogen Bond, and Intramolecular Interactions in Monosubstituted Acetylenes

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The problem of whether or not the vibrations of the ethynyl group are characteristic has been examined and data are presented for the vibration modes, the potential fields, and the electro-optical parameters. Much attention has been devoted to the spectroscopic model of the hydrogen bond. Various methods of investigating intramolecular interactions in acetylene derivatives (containing halogen, Si, Sn, and N atoms as well as groups with π-electrons) by vibrational (infrared) spectroscopy have been considered.
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I. INTRODUCTION

Acetylene and its derivatives are extensively used to synthesise a wide variety of compounds employed in industry. The physical and chemical properties of compounds of the acetylene series are largely determined (owing to the characteristics of the electronic structure of the C≡CH group) by intramolecular and intermolecular electronic interactions. The changes in the electronic structure of the molecules are clearly reflected in the vibration spectra. At the end of the 1950's and in the 1960's, there was an appreciable increase of interest by

spectroscopists in the study of acetylenic compounds. The simple linear structure of the ethynyl groups $-C\equiv C-H$ provided a convenient model for the investigation of the nature of the hydrogen bond and its manifestations, a problem which has been discussed for a long time. On the other hand, in order to create new polymers, new derivatives of acetylene containing various heteroatoms, particularly those of elements of Group VI and others, were synthesised. It was necessary to investigate the intramolecular interactions of these compounds of these compounds. However, the application of vibration spectroscopy to the study of electronic interactions in molecules is impossible without the knowledge of the spectroscopic characteristics of the vibrations considered. At present there is no complete review in the literature devoted to closely related problems such as the characteristics of the vibrations of the ethynyl group and the manifestation of intramolecular and intermolecular interactions in the vibration spectra of acetylene derivatives. Therefore we hope that the present review will be of interest to specialists working in the field of the chemistry and spectroscopy of acetylene and its derivatives.

II. VIBRATIONS OF THE ETHYNYL GROUP

The principle data on the vibration frequencies of the ethynyl group $C\equiv C-H$ have been presented, for example, in Bellamy's monograph [1], which contains information about the influence of various substituents in the molecule on the vibration frequencies of this group. Luneva's review [2] is devoted to acetylene derivatives containing Group IV elements, but it gives little space to spectroscopic studies on these compounds. We may note that the study of intramolecular interactions by infrared absorption (i.r) and Raman spectroscopy must be based on the knowledge whether or not the vibrations of a particular group of atoms are characteristic as regards frequency, mode, and intensity. When these vibrational characteristics are ignored, those conclusions concerning the mutual influence of individual groups of atoms in the molecule which are based only on experimental vibration frequencies and intensities of the corresponding bands and lines in infrared and Raman spectra become baseless.

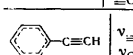
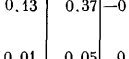
1. Vibration Mode and Frequency

The stretching vibration frequencies of the $C\equiv C$ and $\equiv CH$ groups in acetylenic compounds ($\nu C\equiv C$ and $\nu\equiv CH$) occur in a part of the spectrum which is free from the vibrations of most other polyatomic molecular groups (2250–1950 cm^{-1} and 3300 cm^{-1} respectively).

In the simplest example of compounds of this class, i.e. acetylene ($HC\equiv CH$), the sharp change in the vibration frequency of the $C\equiv C$ group following the substitution of the hydrogen atom by deuterium is associated with the mechanics of the vibrations [3]. The problem of whether or not the vibrations of the ethynyl group show characteristic frequencies and modes in acetylene derivatives of different structures has been considered by Gastilovich, Shigorin, and coworkers [4–8], Popov and coworkers [9–11], Duncan [12], and Zerbi and Gussoni [13].

Calculations on the vibrations in acetylene derivatives such as methylacetylene, t-butylacetylene, trimethylsilylacetylene, and halogenoacetylenes led to the conclusion that the $\nu C\equiv C$ vibration mode is not determined by the $C\equiv C$ group alone [4,12]. Having considered the $\nu C\equiv C$ and $\nu\equiv CH$ stretching vibrations in monoalkyl-, monosilyl-, monostannyl- and monovinyl-acetylenes, the present authors and their coworkers [4–8] concluded that the modes of these vibrations do not change and are characteristic for the $\nu C\equiv C$ vibrations of the entire $X-C\equiv C-H$ group and for the $\nu\equiv CH$ vibrations of the $C\equiv C-H$ group. Data concerning the mode of the stretching vibrations of the $X-C\equiv CH$ group in molecules with a very wide variety of structures—alkyl-, vinyl-, and phenyl-derivatives as well as derivatives containing Group IV atoms in the α-positions —are presented in Table 1†. The data in Table 1 show that the $\nu\equiv CH$ and $\nu C\equiv C$ vibrations are localised in the $X-C\equiv C-H$ group and their mode remains unchanged. An exception is the $\nu C\equiv C$ vibration in methylacetylene according to the data of Lubuzh and Popov, whose calculations showed that the C–H bonds of the methyl group are involved in this vibration [9]. Duncan's calculation for the same molecule, according to which the $\nu C\equiv C$ vibration is localised at the $C-C\equiv C-H$ group, is inconsistent with this conclusion [12].

Table 1. Modes of the stretching vibrations of the $X-C\equiv C-H$ group in certain monosubstituted acetylenes.

Compound	Vibration frequency ν, cm^{-1} (expt.)	Vibration modes: q	Q	Q_1	Q_2	β	explanation	References
$CH_3C\equiv CH$	$\nu_{\equiv CH}$ 3334	1.00	−0.13	0.03			Q_2(C–H) $\beta(\angle HCC\equiv)$	9
	$\nu_{C\equiv C}$ 2142	0.11	0.34	−0.17	−0.35	−0.12		
	$\nu_{\equiv C-Q}$ 931	0.03	0.06	0.29	0.01	−0.04		
$CH_3C\equiv CH$	$\nu_{\equiv CH}$ 3334	1.03	−0.13	0.03	0	0	Q_2(C–H) $\beta(\angle HCC\equiv)$	12
	$\nu_{C\equiv C}$ 2142	0.14	0.38	−0.25	−0.02	−0.02		
	$\nu_{\equiv C-C}$ 931	0.01	0.06	0.28	0.02	−0.10		
$R_3X-C\equiv CH$, X=C, Si $R_3=(CH_3)_3$; X=Sn $R_3=(C_2H_5)_3$	$\nu_{\equiv CH}$ C 3312	0.99	−0.13	0.03	—	—	Q_2(C–X) $\beta(\angle XCC\equiv)$	5,14
	Si 3292	0.99	−0.13	0.03	—	—		
	Sn 3287	0.99	−0.13	0.03	—	—		
	$\nu_{C\equiv C}$ C 2103	0.13	0.38	−0.25	—	—		
	Si 2035	0.12	0.38	−0.22	—	—		
	Sn 2005	0.12	0.39	−0.21	—	—		
	$\nu_{\equiv C-X}$ C 693		0.02	0.13	0.11	0.03		
	Si 556		0.02	0.19	0.09	−0.02		
	Sn 425		0.02	0.20	0.02	−0.01		
O ‖ C(H)–C≡CH	$\nu_{\equiv CH}$ 3326	1.00	−0.13	0.03			Q_2(C=O) $\beta(\angle OCH)$ $\beta(\angle OCC\equiv)$	11
	$\nu_{C\equiv C}$ 2106	0.12	0.38	−0.29	0.05	−0.10		
	$\nu_{\equiv C-C}$ 944	0.01	0.06	0.27	0.03	−0.23		
R'YCH= =CH–C≡ ≡C–H Y=N, S, O	$\nu_{\equiv CH}$ 3310–3315	0.99	−0.12	0.03	—	—	Q_2(C=C) $\beta(\angle HCC\equiv)$ $\beta(\angle HCC\equiv)$	15
	$\nu_{C\equiv C}$ 2075–2100	0.13	+0.38	−0.27	0.05	0.08		
	$\nu_{\equiv C-C}$ 930–960	0.01	0.05	0.24	0	−0.20		
	$\nu_{\equiv CH}$ 3315	0.99	−0.13	0.03	—	—	Q_2(C=C)arom 	16
	$\nu_{C\equiv C}$ 2119	0.13	0.37	−0.27	0.03	−0.07		
	$\nu_{C-C\equiv}$ 1192	0.01	0.05	0.22	−0.08	0.22		

The knowledge of the vibration mode is necessary to decide whether or not the vibrations have characteristic intensities. On the other hand, the knowledge of the modes of the $\nu\equiv CH$ and the $\nu C\equiv C$ vibrations makes it

†The vibration modes have been recalculated in terms of a single system of units (see text); the designations of the coordinates are indicated in the Figure.

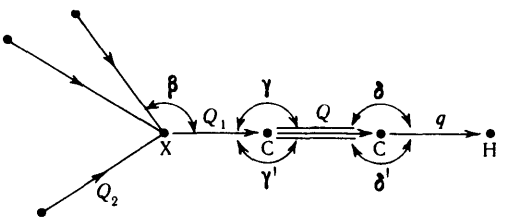
possible to calculate the dependence of these vibration frequencies on the changes of the dynamic (force) constants of the X—C≡C—H group. Thus the familiar expression for the derivative of the square root of the vibration frequencies with respect to the force constant K as a function of the vibration mode [17] yields the following relations:

$$\begin{array}{c|c|c} \Delta K_q = +1.0 & \Delta H_q^Q = +1.0 & \Delta H_{Q_1}^Q = +1.0 \\ \Delta\nu_{\equiv CH} = +136\ cm^{-1} & \Delta\nu_{\equiv CH} = -32\ cm^{-1} & \Delta\nu_{\equiv CH} = +2\ cm^{-1}; \end{array} \quad (1)$$

for the ≡C—H group ($\nu_{\equiv CH}$ = 3310 cm^{-1}) and

$$\begin{array}{c|c|c} \Delta K_Q = +1.0 & \Delta K_{Q_1} = +1.0 & \Delta H_{Q_1}^Q = +1.0 \\ \Delta\nu_{C\equiv C} = +34\ cm^{-1} & \Delta\nu_{C\equiv C} = +14\ cm^{-1} & \Delta\nu_{C\equiv C} = -43\ cm^{-1} \\ \Delta K_q = +1.0 & \Delta H_q^Q = +1.0 & \\ \Delta\nu_{C\equiv C} = +3\ cm^{-1} & \Delta\nu_{C\equiv C} = +22\ cm^{-1} & \end{array} \quad (2)$$

for the C≡C group ($\nu_{C\equiv C}$ = 2100 cm^{-1}). The generally accepted notation for force constants is employed here [17] (in units of 10^6 cm^{-2}). The designations of the normal coordinates are shown in the Figure. The relations show clearly the characteristic nature of the $\nu_{\equiv CH}$ and $\nu_{C\equiv C}$ vibrations as regards frequency. On the other hand, they make it possible to explain the differences between the force constants calculated by a different investigators from the experimental vibration frequencies of the same molecule.



Designation of the natural coordinates.

Certain dynamic constants of the X—C≡CH group in molecules of different structures, calculated by different investigators, are listed in Table 2. In the studies under consideration, the dynamic constants were expressed in different units. In Table 2 and throughout the text, all the constants are given in units of 10^6 cm^{-2}; 1 Å and one atomic mass unit (1/16 of the mass of the oxygen atom) being adopted as unit length and unit mass respectively.

The $\nu_{\equiv CH}$ vibration frequency is determined by only two constants: K_q and to some extent H_q^Q. Table 2 shows [5,9,12,14] that the large differences between the K_q in various studies can be accounted for by the fact that some investigators introduced the spectroscopic mass of the hydrogen atom (1.088 a.m.u.) when $K_q \simeq 10.88$–10.55 cm^{-2} while others assume that the mass of the hydrogen atom is 1.008 a.m.u. ($K_q \simeq 10.1$–9.83) (in this case the conversion factor for K_q is approximately 1.07. The coefficient H_q^Q plays a relatively small role and probably cannot be determined reliably from vibration frequencies in infrared spectra. Thus significantly different H_q^Q values are quoted by Duncan [12], by Popov and Gribov [19], and by Lubuzh and Popov [9] for almost the same set of molecules (Table 2 does not list all the data).

The $\nu_{C\equiv C}$ vibration is characteristic as regards mode and frequency for the X—C≡C—H group. Table 2 shows that the constants K_Q, K_{Q_1}, H_q^Q, and $H_{Q_1}^Q$ which determines the frequency of this vibration, are extremely different for the same or similar compounds (Table 2) [6,10,12,13,16]. Firstly, this difference is due to the fact that the $\nu_{C\equiv C}$ vibration frequencies were calculated by the authors with different accuracies ($\nu_{C\equiv C}^{exp} - \nu_{C\equiv C}^{calc}$). Secondly, since the vibration frequency depends to an almost equal extent on the four force constants, the uniqueness of this set of constants depends on the accuracy of the calculation for other vibrations too ($\nu_{\equiv C\text{-}X}$, ν_ρ). Otherwise the set of constants K_Q, K_{Q_1}, H_q^Q, and $H_{Q_1}^Q$ becomes arbitrary (Table 2) [6,10,16]. The variation of their values in each set obeys Eqns. (2). The sets quoted by Lubuzh and Popov for methylacetylene and by Zerbi and Gussoni [13] for the compounds $H_2XC-C\equiv CH$ constitute an exception. This is probably because the $\nu_{C\equiv C}$ vibration mode differs from that used in the remaining calculations. We noted above that this was the case in Lubuzh and Popov's study [9]. In contrast to the remaining investigations, Zerbi and Gussoni [13] employed a potential field of a mixed type: a valence force field for the C≡C—H group and a Urey–Bradley field for the H_2XC-group, which probably affected the vibration mode (data for the mode are not quoted).

The absorption bands for the deformation vibrations of the ≡C—H group lie in the range 610–680 cm^{-1}. [1] The stretching and deformation vibration in the ethynyl group are fully separated [19]. According to the data of Duncan [12], Lubuzh and Popov [9], Epshtein and Popov [11] and others, the amplitudes of the changes in the angles δ and γ (see Figure) in the $\delta_{\equiv CH}$ vibration differ by a power of ten. From the form of this vibration mode, it is possible to obtain relations between the changes in the dynamic constants for the —C≡C—H group and the changes in the $\delta_{\equiv CH}$ vibration analogous to Eqns. (1) and (2):

$$\begin{array}{c} \Delta K_\delta = \pm 0.1\ (\times 10^6\ cm^{-2})\ \ \Delta K_\gamma = \pm 0.1\ \ \Delta l_\gamma^\delta = \pm 0.1 \\ \Delta\delta_{\equiv CH} = \pm 90\ cm^{-1}\ \ \Delta\delta_{\equiv CH} = \pm 1\ \ \Delta\delta_{\equiv CH} = -18 \end{array} \quad (3)$$

The $\delta_{\equiv CH}$ vibration in acetylene is doubly degenerate. In monosubstituted acetylenes, this degeneracy is removed and two bands ($\delta_{\equiv CH}^{(1)}$ and $\delta_{\equiv CH}^{(2)}$) are observed in the spectrum. The different possible mechanisms of the intramolecular interactions, which leads to a splitting of the $\delta_{\equiv CH}$ band, have been considered by Nyquist and Potts [23]. The splitting can reach several units. Thus, in vinylacetylenes with a heteroatom Y = S, O, or N in the $-RYCH=CH-C\equiv CH$ conjugated chain, $\delta_{\equiv CH}^{\perp} - \delta_{\equiv CH}^{\parallel} = 48$, 50 and 107 cm^{-1} respectively [15], which corresponds to a change in $K_\delta^\perp - K_\delta^\parallel$ of about $(0.05$–$0.12) \times 10^6$ cm^{-1}. This is a considerable difference bearing in mind that the force constant K_δ is itself small ($K_\delta = 0.375 \times 10^6$ cm^{-2}, $\delta_{\equiv CH} = 633$ cm^{-1}) [9].

2. Electro-optical Characteristics from Infrared Spectra

The problem of whether or not the vibrations of the ethynyl group show characteristic intensities can be treated on the basis of the valence-optical theory of intensity [24]. As a result of its development by Gribov, a computational scheme was put forward where the electro-optical parameters (EP) μ_i, $\partial\mu_i/\partial q_i$. and $\partial\mu_i/\partial\alpha_j$ (μ_i is the dipole moment of the ith bond and q and α are the normal coordinates of the bond and angle) were introduced as the

Table 2. The force constants K (in units of 10^6 cm^{-2}) and the calculated and experimental frequencies ν (cm^{-1}) of the stretching vibrations of the X—C≡CH group in certain acetylene derivatives.

Compound	K_q	K_Q	K_{Q_1}	H_q^Q	$H_{Q_1}^Q$	calc $\nu_{\equiv CH}$	exp $\nu_{\equiv CH}$	calc $\nu_{C\equiv C}$	exp $\nu_{C\equiv C}$	calc $\nu_{\equiv C-X}$	exp $\nu_{\equiv C-X}$	Refs.
$H_3FC-C\equiv CH$	10.1	23.91	12.1	0	0	3335	3338	2149	2150	939	940	
$H_2ClC-C\equiv CH$	10.1	23.91	12.2	0	0	3335	3335	2137	2147	962	960	
$H_2BrC-C\equiv CH$	10.1	33.91	12.3	0	0	3335	3335	2137	2138	962	961	13
$H_2IC-C\equiv CH$	10.1	23.91	12.55	0	0	3335	3335	2142	3130	952	959	
$ClC\equiv CH$	10.15	26.8	9.15	0	0	3372	3340	2122	2110	759	756	
(D)						(2627)	(2612)	(1987)	(1980)	(742)	(742)	18
$CH_3-C\equiv CH$	10.1	26.9	9.00	0	0.31	3346	3334	2151	2141	929	931	
(D)						(2607)	(2617)	(2005)	(2008)	(916)	(—)	
$H_3C-C\equiv C-CH_3$	—	26.6	8.95	—	1.03	—	—	2240	2240	725	725	12
										1152	1152	
$H-C\equiv CH$	10.1	26.7	—	0.05	—	—	—	—	—	—	—	
$Cl-C\equiv CH$	10.15	26.3	9.05	0	0.51	3351	3340	2114	2110	756	755	
$HC\equiv CH$	10.70	26.8	—	0.22	—	3278	3287					
						(3317)	(3335)	(1856)	(1851)	(2573)	(2585)	
(D)												19
$DC\equiv DC$						2437	2428					
$H_3C-C\equiv CH$	10.88	26.6	8.7	0.22	0.11	3339	3334	2146	2142	914	931	
$F-C\equiv CH$	10.88	28.3	13.7	0.22	1.09	3358	3355	2230	2245	1059	1055	
$Cl-C\equiv CH$	10.88	26.1	9.35	0.22	0.54	3336	3340	2111	2110	742	756	
$Br-C\equiv CH$	10.80	25.5	7.8	0.22	0.32	3328	3325	2077	2085	616	618	9
$IC\equiv CH$	10.70	25.3	7.6	0.22	0.21	3324	3320	2073	2075	590	~600	
O ‖ C—C≡CH / H	10.77	24.6	10.9	0.22	0.22	3324	3326	2110	2106	938	944	11
$H_3C-O-C\equiv CH$	10.88	26.3	13.6	0.21	0.762	3338	3361 3352 3345	2182	2182 2171 2161	930[s] 1195[as]	943—895[s] 1221—1201[as]	20
$(CH_3)_3-C-C\equiv CH$	9.90	26.00	8.8	0.05	0.50	3303	3309	2122	2120	1060	930	
(D)						(2577)	(2593)	(1985)	(1971)			4,
$(CH_3)_3SiC\equiv CH$	9.83	25.2	5.90	0	0.25	3289	3292	2042	2035	554	556	5
(D)						(2552)	(2572)	(1913)	(1909)			
$(C_2H_5)_3Sn-C\equiv CH$	10.50	25.0	4.1	0	0.23	3286	3287	2009	2005	425	425	
(D)						(2566)	2560	1882	1879			14
$(C_2H_5)_2Sn(C\equiv CH)_2$	10.52	25.2	4.1	0	0.23	3290	3293	2017	2017	416[s]	420	
										439[as]	434	21
$C_2H_5-Sn(C\equiv CH)_3$	10.55	25.43	4.1	0	0.23	3295	3296	2026	2034	396[s]	—	
										444[as]	443	
$H_2C=HC-C\equiv CH$	10.88	24.2	12.0	0.22	0.54	3334	3335	2095	2099	920	929	
$H_2C=CH-C\equiv C-CH_3$	10.88	24.2	12.0	0.22	0.54	—	—	2227	2235	927	920	10
$H_2C=C(CH_3)C\equiv CH$								2098	2100	931	952	
$RHC=HC-C\equiv CH$	9.95	26.0	8.8	0.05	0.50	3310	3314	2113	2100	965	930—960	6
	10.6	26.0	8.3	0	0	3305	3315	2124	2119	1215	1192	
						(2628)	(2608)	(2002)	(1989)	(1210)	(1189)	16
$H-C\equiv C-C\equiv C-H$	10.70	24.1	12.8	0.22	0.54	3333	3329	2011	2020			
					−1.63*							22
$CH_3C\equiv C-C\equiv C-CH_3$						—	—	2166	2163	930	941	

* $H_Q^{Q'}$.

characteristics of the bonds and angles in the molecule[25]. Adopting further reasonable approximations (the zeroth approximation when only the diagonal elements are non-zero as well as higher degrees of approximation), it is possible to assess from the electro-optical parameters (and not from the intensities of the infrared absorption bands) for molecules of similar structures the mutual influence of the individual groups of atoms in the molecule. This treatment is analogous to the consideration of force constants instead of vibration frequencies in the study of the effect of intramolecular interactions on vibration frequencies.

The electro-optical parameters for acetylene[19,26], t-butylacetylene[5], vinylacetylene and diacetylene[27], trimethylsilylacetylene[5], and organotin derivatives of acetylene with several ethynyl groups[14,21] have now been

calculated from experimental intensities of infrared absorption bands and are listed in Table 3. Popov et al.[27] also determined the dipole moments of the C≡C bonds ($|\mu Q| = 1.0$ D) for diacetylene and vinylacetylene and the C=C bond ($|\mu Q_2| = 0.70$ D) for the latter.

Table 3. The electro-optical parameters $\partial\mu_i/\partial q_i$ [D/Å] and μ[D] of the CXC≡CH groups and the experimental absolute intensities B (in units of 10^4 cm^{-2} litre mole^{-1}) of the absorption bands associated with the C≡C—H groups in the infrared spectra.

Chemical formula	Electro-optical parameters					Intensity		References
	$\lvert\mu_q\rvert$	$\frac{\partial\mu_q}{\partial q}$	$\frac{\partial\mu_Q}{\partial Q}$	$\frac{\partial\mu_{Q_1}}{\partial Q_1}$	$\frac{\partial\mu_{Q_2}}{\partial Q_2}$	$B_{\nu C\equiv CH}$	$B_{\nu C\equiv C}$	
HC≡CH	0.94	0.826[a]					inactive	26
H—C≡CH	1.1	0.90					inactive	19
H_2C=CH—C≡CH	0.90	1.0	0.10	−0.35	1.0	0.41	0.004	27
HC≡C—C≡CH	0.80	0.90	−0.10[b]			0.61	0.013	27
$(CH_3)_3$C—C≡CH	1.24	1.22	−0.75[a]	0.90	—	0.73	0.063	5
$(CH_3)_3$Si—C≡CH	1.12	0.97	−1.02	−4.6	2.0	0.46	0.25	5
$(C_2H_5)_3$Sn—C≡CH	1.30	0.85	−1.85	−5.2	2.4	0.45	0.10	14
$(C_2H_5)_{4-n}$Sn$(C\equiv CH)_n$		0.85	−1.85	−5.2		0.89(n=2)	0.31(n=2)	21
				+1.2[c]	2.5	1.20(n=3)	0.63(n=3)	

Note. The values listed in the Table correspond to the following combinations of electro-optical parameters in the publications quoted: [a] $\partial\mu_q/\partial q - \partial\mu_q/\partial q'$; [b] $\partial\mu Q/\partial Q - \partial\mu Q/\partial Q'$; [c] for all the R_3X—C≡CH, $\partial\mu_q/\partial Q + \partial\mu Q/\partial Q + \partial\mu Q_1/\partial Q$; [d] $\partial\mu Q_1/\partial Q_1'$ (the prime indicates an equivalent but "foreign" coordinate).

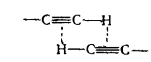
It has been shown[5,7,14] that the ν≡CH vibration in molecules of different structures is characteristic as regards intensity. In other words, the intensity of the corresponding absorption band in the infrared spectrum is determined mainly by the electro-optical parameters for this bond ($\partial\mu_q/\partial q$). On the other hand, the intensity of the νC≡C vibration band is characterised by the set of electro-optical parameters of the entire X—C≡C—H group and $\partial\mu Q/\partial Q$ does not play a decisive role. Thus, in compounds with a heteroatom (X = Si and Sn), both the direction of the dipole moment of the transition $\partial\vec{M}/\partial Q_{C\equiv C}$ ($\vec{M}$ is the dipole moment of the entire molecule and $Q_{C\equiv C}$ the normal coordinate of the νC≡C vibration) and the intensity of the νC≡C band are determined by the parameters of the X—C≡ bond and not the C≡C bond. A similar phenomenon has been observed for another class of compounds—ethylene derivatives, for which it has been shown that the intensity of the C=C absorption band ($\nu_{C=C}$) is not determined by the parameters of this bond[28]. The low contribution of the electro-optical parameters of carbon chains to the intensity of the absorption bands associated with the skeletal vibrations of the molecule was noted previously by Gribov and Popov[29]. Thus theoretical calculation of the absorption band intensities in the infrared spectrum of dimethylacetylene using only the electro-optical parameters of the C—H bonds in the ethane molecule[30] gave satisfactory agreement between the calculated and experimental values for all these vibrations. Hence it was found that the electro-optical parameters of the C—C≡C—C group in the dimethylacetylene molecule may be neglected. However, in the vinylacetylene and diacetylene molecules[27] as well as in other monosubstituted acetylenes (Table 3), the electro-optical parameters of the multiple bonds are fairly large.

In a study of the intensities of the νC≡C absorption bands in the spectra of compounds with a complex molecular structure, RYCH=CH—C≡CH and RYCH=CH—C≡C—Si$(CH_3)_3$ (R = alkyl; Y = S, O, or N atom), Gastilovich, Shigorin et al. concluded that the νC≡C intensity depends on the electro-optical parameters of the Y—C= group[7,15]. They also concluded that in molecules with conjugated bonds and with a heteroatom, the νC≡C vibration remains characteristic as regards frequency and mode for the C—C≡C—H group but cease to be characteristic as regards intensity for this group. The νC≡C intensity is determined by the electro-optical parameters of the entire YCH=CH—C≡CH group; this corresponds, within the framework of the valence-optical theory of intensity, to the employment of high degrees of approximation, which is probably impossible in practice.

The results of studies on intermolecular interaction (the hydrogen bond in acetylene derivatives), such as the electron-donating and electron-accepting properties of the —C≡C—H group and changes in the absorption band intensities in electron-donating solvents, can also be very useful for the solution of the problem of intramolecular interactions. Therefore, having considered the problem of whether or not the vibrations are characteristic, we proceed to the problem of the hydrogen bond in acetylene derivatives.

III. THE HYDROGEN BOND

As early as 1939, the anomalously high solubility of acetylene in electron-donating solvents (EDS) and the experimental heats of solution in such solvents led Copley and Holley to the conclusion that there is a specific intermolecular interaction in such solutions between the acetylene and solvent molecules[31]. In 1941 Standford and Gordy observed in the infrared spectra of phenylacetylene solutions in EDS a bathochromic shift of the absorption band due to the stretching vibration of the ≡C—H group. The shift was of the same order of magnitude as that observed for the OD group in deuteriated alcohols. The authors concluded that a hydrogen bond is formed in phenylacetylene solution in EDS.[32] In 1958, Shigorin and coworkers suggested, on the basis of a study of the spectra of vapours and liquids, the formation of a specific hydrogen bond between the molecules of acetylene derivatives involving the π-electrons of the C≡C group (electron-donating group) and the orbitals of the hydrogen atom (in the ≡C—H electron-accepting group), i.e. in the formation of π-complexes[33,34]:



The structure of the π-complex was subsequently refined by other investigators.

The existence of both π-complexes of acetylenic hydrocarbons and of a hydrogen bond between such hydrocarbons and the solvent has now been demonstrated. Hyong's studies[35] on hydrogen bonds in acetylenic compounds were published in 1963 in the form of a review. The review gives a detailed bibliography (153 references). A paragraph in Bellamy's familiar monograph (1968)[1] is devoted to the hydrogen bond in acetylenic hydrocarbons.

However, recently new data have appeared on the hydrogen bond in acetylenic compounds which are not quoted in the earlier publications. For example, the data of Iogansen and coworkers[36-39] concerning the nature and spectroscopic manifestations of the hydrogen bond,

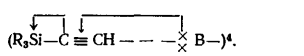
data for the hydrogen bond in acetylenic compounds containing Group IV atoms, and others. In his treatment of studies on the hydrogen bond, Bellamy [1] devoted insufficient attention to investigations published in Russian. We should like to fill this gap.

1. Effect of Molecular Structure on the Vibration Frequency Shift in the Formation of the Hydrogen Bond

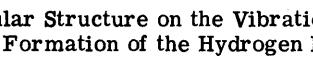
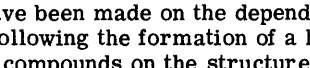
The first infrared spectroscopic evidence for the existence of a specific interaction in acetylenic hydrocarbons was obtained by Shuvalova [41], Murash et al. [42], Gastilovich et al. [43], Hyong and Lastondi [44], and Iogansen and Kurkchi [36,37]. They observed, using infrared spectra, a shift in the equilibrium between free and associated molecules of acetylenic hydrocarbons as a function of temperature and concentration of the solution.

Many studies have been made on the dependence of the band shift $\Delta\nu_{\equiv CH}$ following the formation of a hydrogen bond by acetylenic compounds on the structure of the R—C≡CH and solvent molecules [1,4,35,45-49].

Table 4 gives a compilation of certain data concerning the changes in the vibration frequency of the ≡CH group in acetylenes R—C≡CH of different structures dissolved in electron-donating solvents. Experimental studies have shown that an increase of conjugation in R—C≡CH molecules increases the $\Delta\nu_{\equiv CH}$ shift. Shigorin [52] explains this phenomenon by the fact that charge transfer on hydrogen bond formation is not localised at the A—H---⨯B- group but induces an additional change of electron density in all the rest of the electron-acceptor molecule. Electrons in the donor molecule ⨯B—R occupy the vacant p orbitals of the hydrogen atom and are therefore capable of participating in conjugation. Thus the increase of the $\Delta\nu_{\equiv CH}$ shift in both silyl- and arylacetylenes compared with the alkyl and stannyl derivatives can be accounted for by this type of conjugation:



Iogansen [39,53] has developed logically the concept of the additive influence of the acidity and basicity of the A—H and ⨯B—R components in the formation of a hydrogen bond. A somewhat different approach to the treatment of electron-donating properties of the solvent has been proposed by Plotnikov and Shigorin [54]. They suggested that the involvement in conjugation of the unshared electron pair of the donor in "its" molecule decreases the electron-donating capacity of the latter. For example, in nitrogen-containing electron-donating solvents, the $\Delta\nu_{\equiv CH}$ shift increases in the series R_2N- , , and $(C_2H_5)_3N$, while in oxygen-containing solvents it increases from acetone to dioxan [50].

The vibration frequency of the C≡C group changes little on formation of a hydrogen bond [35,55]. Molecules where the C≡C—H group is involved in conjugation constitute an exception. For example, in the spectrum of phenylacetylene and trimethylsilylacetylene dissolved in electron-donating solvents, two $\nu_{C\equiv C}$ bands are observed ($\Delta\nu_{C\equiv C} \simeq 7$–$12$ cm^{-1}), the intensity ratio of which changes with concentration [55]. These bands correspond to "free" and associated molecules in the R—C≡C—H—⨯B—R′ complex. The appearance in the spectrum of the solution of two $\nu_{C\equiv C}$ bands makes it possible to calculate the degree of association in the hydrogen-bonded complexes from the intensity of the $\nu_{C\equiv C}$ absorption band of the "free" molecule, as has been done on the basis of the $\nu_{\equiv CH}$ absorption band [48]. However, the splitting of the $\nu_{C\equiv C}$ bands is not observed for all types of conjugation but only when the conjugation promotes further charge transfer from the  group to the R group of the acetylene. Otherwise, the splitting of $\nu_{C\equiv C}$ is not observed. For example, spectroscopic data suggest a π-electronic interaction between the $R_2NCH{=}CH-$ and $-C{\equiv}C-H$ groups in the compound $R_2NCH{=}CH-C{\equiv}CH$ (Gastilovich et al. [15]); chemical data demonstrate a high reactivity of the C≡C group in this compound [56]. However, the $\Delta\nu_{\equiv CH}$ shift in the spectra of solutions of this compound in electron-donating solvents is the same as in alkylacetylenes (or smaller) and the $\nu_{C\equiv C}$ band is not split (a different type of conjugation is postulated here: ) [57].

2. π-Complexes

The hypothesis of the formation of π-complexes between acetylenic compounds has been confirmed experimentally by Murash et al. [42], Shuvalova [58], and others [1,35]. When π-complexes are formed, the $\nu_{\equiv CH}$ vibration frequency changes very little, by approximately 20 cm^{-1} (Table 4), while the change in the vibration frequency of the C≡C group [35,55] is even smaller (1–2 cm^{-1}). However, as for the hydrogen bond of the type R—C≡C—H---⨯B—R′, two $\nu_{\equiv CH}$ bands are observed in the spectrum of the solution, corresponding to free and associated molecules. It has been shown [59] that the π-complex is T-shaped and that not one but two $\nu_{\equiv CH}$ frequencies are due to the bound molecules.

The electron-donating properties of the C≡C groups in various acetylenic compounds were studied by West and Kreihancel [60] and Hyong [35] using changes in the vibration frequency of the O—H groups of phenol and p-chlorophenol respectively. Similarly the electron-donating properties of the C≡C groups in certain silyl- and stannyl-acetylenes [8] have been determined from the changes in the vibration frequency of the O—H group of ethanol in the complex

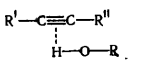


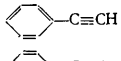
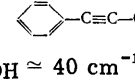
Table 5 presents some data for the electron-donating properties of the C≡C groups of various ethynyl compounds. Hyong [35] determined the energy of formation of the π-complex with p-dichlorophenol from the temperature variation of the degree of association. It varies in the range 2–3 kcal mole^{-1} for different acetylenes. Hyong showed that the π-electron-donating properties increase in the series alkenes < aromatic hydrocarbons < alkynes. According to the data of West and Kreihancel [60], the electron-donating properties of the C≡C group are more marked in disubstituted acetylenes compared with monosubstituted derivatives, and in the latter they decrease when the triple bond is conjugated with a ring. In disubstituted tin and silicon-containing acetylene derivatives (RXC≡CXR′), the electron-donating properties weaken in the series with X = Sn, C, and Si (Table 5).

Table 4. Vibration frequencies of the ≡C—H group ($\nu_{\equiv CH}$, cm^{-1}) in the infrared spectra of solutions of compounds of the type R—C≡CH.

Solvent or state of aggregation	Refs.35-38, 43, and 50				Refs.48 and 50	Ref.50	Ref.50	Ref.45	Ref.43	Ref.50	Ref.4	Ref.48	Refs.4 and 48
	R=H	CH_3	C_2H_5	C_4H_{10}	$(CH_3)_3C$			H—C≡C—	C_4H_9O—CH=CH—	$(C_2H_5)_2N$CH=CH—	$(CH_3)_3Si$	$(CH_3)_2$ Si=	$(C_2H_5)_3Sn$
	$\nu_{\equiv CH}$ and $\Delta\nu_{\equiv CH} = \nu_{\equiv CH}$ (in CCl_4) $-\nu_{\equiv CH}$ (in electron-donating solvent)												
CCl_4	3263	3314	3313	3313	3312	3312	3312	3311	3310	3315	3285	3293	3276
Acetone $(CH_3)_2C=O$	3218 45	3273 41	3270 43	3273 40	3273 39	3260 52	3250 62	3239 72	3263 47	3280 35	3235 50	—	3232 44
Pyridine 	—	3228 85	3225 88	3254 79	3233 79	3215 97	—	—	3195 115	3250 65	3185 100	3186 107	3202 74
Tiethylamine $(C_2H_5)_3N$	—	—	—	3206 107	3204 107	3175 137	—	—	—	3190 125	—	3156 137	3182 94
Liquid	Tв.[51] 3276 3258	3295 18	3295 18	3292 21	3290 22	3290 32	3293 19	—	3290 20	3300 15	3279 6	3282 9	3258 18

*The compound $(CH_3)_2Si(C\equiv CH)_2$.

Table 5. The electron-donating properties of the C≡C group. Variation of the vibration frequencies of the O—H groups ($\Delta\nu$, cm^{-1}) in compounds of the type R—OH forming a π-complex with acetylene derivatives in CCl_4 solution.

ROH	Compound	$\Delta\nu_{OH}$	ROH	Compound	$\Delta\nu_{OH}$
C_6H_5OH (Ref.60)	$C_4H_9C\equiv CH$	90	C_2H_5OH (Ref.8)	$(CH_3)_3C—C\equiv C—CH_3$	71
	$C_3H_7C\equiv CC_3H_7$	137		$(CH_3)_3SiC\equiv CH$	39
		41.80*		$(CH_3)_3Si—C\equiv C—Si(CH_3)_3$	64
		44.108*		$(C_2H_5)_3Sn—C\equiv C—Sn(C_2H_5)_3$	107

*$\Delta\nu_{OH} \simeq 40$ cm^{-1} corresponds to a π-complex with the benzene ring.

3. The Lateral Band

In all ethynyl compounds, a weak ν_X band, which does not disappear on dilution of the solution, is observed on the long-wavelength side of the absorption band of the ≡CH group. Its nature has been investigated in numerous studies[1,35]. The appearance of the ν_X band is explained in Bellamy's monograph by Fermi resonance. Kreihancel and West[61] and Hyong[35] interpret this band as due to a hot transition in alkylacetylenes: $\nu_X = \nu_{\equiv CH} + \delta_{\equiv CH} - \delta_{\equiv CH}$. The $\nu_X$band has a low intensity (the optical density ratio $D_X/D_{\equiv CH} \simeq 0.10$), is displaced relative to $\nu_{\equiv CH}$ towards longer wavelengths by about 20 cm^{-1}, and persists in the spectra of deuteriated compounds. At different temperatures, the intensity ratio of the $\nu_{\equiv CH}$ and ν_X bands varies in accordance with the calculated population of the "hot" $\delta_{\equiv CH}$ vibration level. In the spectrum of phenylacetylene, this additional band on the long-wavelength side (ν_C) is very intense ($D_C/D_{\equiv CH} \simeq 0.70$). Hyong[35] interprets its appearance by the Fermi resonance of the $\nu_{\equiv CH}$ and ν_C vibrations in a manner analogous to the interpretation of the ν_X band by Evans and Nyquist in the spectra of alkyl-substituted derivatives[62]. The latter postulate that $\nu_X = \nu_{C\equiv C} + 2\delta_{\equiv CH}$ or $\nu_{C\equiv C} + \delta_{\equiv CD}$ in deuteriated derivatives of acetylene. In a recent study, Bagdanskii et al.[51] studied the infrared spectra of acetylene in matrices at low temperatures. The band with a maximum at 3312 cm^{-1} (argon matrix) was interpreted as due to the $\nu_{C\equiv C} + \delta_{\equiv CH}$(i.r) + $\delta_{\equiv CH}$(Raman) = 1973.5 + 737 + 612 cm^{-1} transition intensified by Fermi resonance with the $\nu_{\equiv CH}$(i.r) = 3289 cm^{-1} vibration. The longer-wavelength band with a maximum at 3276 cm^{-1} was assigned to the $\nu_{\equiv CH}$ vibration (i.r) of the $^{12}C^{13}CH_2$ molecule. However, the authors noted that in this region there is a possibility of absorption by acetylene polymers.

The weak lateral bands ν_X are also observed in the spectra of dilute solutions of acetylenic compounds containing silicon and tin. In the latter [$(C_2H_5)_3Sn—C\equiv CH$], there are weak bands on the long-wavelength and short-wavelength sides of the main band (Table 6).

4. Spectroscopic Three-Atom Model of the Hydrogen Bond

The intensities of the absorption bands due to the ≡CH and C≡C groups in hydrogen-bonded complexes have been determined in a few studies. Brand et al.[63] observed a change (in different directions) of the stretching ($\nu_{\equiv CH}$) and deformation ($\delta_{\equiv CH}$) vibrations in hydrogen-bonded complexes as well as of the intensities of the corresponding absorption bands. Systematic studies of the $\nu_{\equiv CH}$ and $\delta_{\equiv CH}$ vibration frequencies and of the intensities of the absorption bands in different electron-donating solvents have been made by Iogansen and Kurkchi for acetylene and its alkyl-substituted derivatives[36-38,64]. Table 7 presents data for the changes in the intensity of the C≡C—H absorption band intensities on formation of a hydrogen-bonded complex with a solvent by certain acetylenic compounds of different structures.

On the basis of data showing that the $\nu_{\equiv CH}$ and $\delta_{\equiv CH}$ bands vary regularly in opposition and that $\Delta\nu_{\equiv CH}$ and $\Delta\delta_{\equiv CH}$ shift in opposite directions on formation of the hydrogen bonds, it was concluded [36-38,64] that the hydrogen bond is covalent. Using these concepts, Iogansen proposed a three-atom model for the formation of the hydrogen bond [39]. The model is based on the hypothesis that the charge transferred from the atom of the electron donor $\overset{\times}{}$B to the R—AH molecule is not delocalised over the latter. As a result, the change in the intensity of the absorption bands in the infrared spectra of the hydrogen-bonded complexes is caused by a change of the dipole moment of the H---B hydrogen bond itself during the vibration of the hydrogen atom and not due to a change in the dipole moment of the A–H bond.

Table 6. Positions of the absorption bands of the ≡CH group ($\nu_{\equiv CH}$) and the lateral ν_X bands (cm^{-1}) and their relative intensities (at the absorption maximum) $D_X/D_{\equiv CH}$ in the infrared spectra of compounds of the type R—C≡C–H (D) in carbon tetrachloride solutions [35].

	R										
	C_4H_9—	C_6H_{13}—	C_7H_{15}	C_7H_{15}— (D)*		 (D)*	$(CH_3)_3C$—	$(CH_3)_3Si$—	$(C_2H_5)_3Sn$**	$(C_2H_5)_3Sn$ (D)*	
$\nu_{\equiv CH}$	3315	3314	3313	2598	3313	2594	3312	3292	3290	2567	3288
ν_X	3296	3294	3294	2584	3302	2584	3293	3274	3270, 3310	2553	3270
$\nu_X - \nu_{\equiv CH}$	—19	—20	—19	—14	—11	—10	—19	—18	—20 +20	—14	—18
$\frac{D_X}{D_{\equiv CH}}$	0.12	0.10	0.11	0.18	0.81	—	0.15	0.10	0.09 0.09	0.19	0.12

*The compound R—C≡C–D.
**Solution in hexane.

In the $\nu_{\equiv CH}$ stretching vibration in the "free" R–C≡CH molecule, only the hydrogen atom is displaced from the equilibrium position (the displacements of the C atoms may be neglected). Then, in accordance with the valence-optical scheme [25], the absolute intensity of the $\nu_{\equiv CH}$ absorption band ($B^{(0)}_{\nu CH}$) is related to the amplitude of the vibration of the ≡CH–H bond (q) and the derivative of the dipole moment of the molecule M with respect to the normal coordinate q by the expression const. $(B^{(0)}_{\nu CH})^{1/2} \simeq -(\partial M/\partial q)q$. When the C≡C–H---$\overset{\times}{}$B–R complex is formed, one can assume that the ≡C and B atoms are stationary and that hydrogen vibrates between them. Then the vibration amplitude q_{H---B} is equal to q but with the sign reversed, i.e. $q_{H---B} = -q$. The dipole moment changes in the –H--$\overset{\times}{}$B– bond vibration:

$$(\partial\mu_{H---B}/\partial q_{H---B})q_{H---B}.$$

The intensity of the absorption band of the hydrogen-bonded complex ($B^{(C)}_{\nu CH}$) is in this case determined by the two components: const. $(B^{(C)}_{\nu CH})^{1/2} = (\partial M/\partial q)q + e(\partial\mu_{H---B}/\partial q_{H---B})(q_{H---B})$. It is readily seen that the difference $(B^{(C)}_{\nu CH})^{1/2} - (B^{(0)}_{\nu CH})^{1/2} = \Delta(B^{1/2}_{\nu CH})$ for such a model depends only on the change in the dipole moment of the H---B bond during the vibration: $\Delta(B^{1/2}_{\nu CH}) \simeq (\partial\mu_{H---B}/\partial q_{H---B})q_{H---B}$.

Similarly, for deformation vibrations, $(B^{(C)}_{\delta})^{1/2} - (B^{(0)}_{\delta})^{1/2} = \Delta(B^{1/2}_{\delta}) \simeq (\mu_{H---B}/\rho_{H---B})\Delta e_{\equiv CH}$ (according to the valence-optical theory [24,25]), where ρ_{H---B} is the length of the H---B bond and Δe is the change of direction of the unit vector of the ≡C–H bond in the $\delta_{\equiv CH}$ vibration. Data for the changes in the frequency and intensity of the absorption bands of the C≡CH group led to the conclusion [64] that the derivatives $\partial M/\partial q$ and $\partial\mu_{H---B}/\partial q_{H---B}$ are of the opposite sign, while the dipole moments μ_q and μ_{H---B} have the same direction.

Table 7. The frequencies (cm^{-1}) and intensities B (in units of 10^4 cm^{-2} litre $mole^{-1}$) of the absorption bands of the stretching and deformation vibrations of the C≡C–H group in the spectra of compounds of the type R—C≡C–H in solutions in an inert solvent (O) and an electron-donating solvent (C).

	R											
	C_4H_9— [38]		$(CH_3)_3C$— [46]		 [38,47]		$H_2C{=}CH$— [38]		$(CH_3)_3Si$— [47]		$(C_2H_5)_3Sn$— [48]	
	O	C	O	C	O	C	O	C	O	C	O	C
$\nu_{\equiv CH}$	3313 * 3319	3233 * 3308 3234	3312 3293	3228	3312 3321 [47]	3215 3211	3316	3220	3292 3274	3185	3310 3290 3270	3202
$B_{\nu CH}$	0.62 * 0.61	1.46 * 1.46	0.75	1.3	1.09 [47] 0.96 [38]	3.3 3.67	0.64	2.39	0.46	2.9	0.38	1.46
$\sigma_{\equiv CH}$	633	693	629	—	612, [38] 649	—	629	—	673	—	665	—
B_{δ}	0.93	1.1	1.2	—	1.01 [38]	—	0.94	—	1.0	—	1.2	—
$\nu_{C\equiv C}$	2121	2119 [35]	2105 2137	2103 2135	2112 [38]	2103	—	—	2033	2027	2008	1998
$B_{\nu C\equiv C}$	0.069	0.048 [35]	0.075	0.026	0.044	0.042	—	—	0.29	0.40	0.11	0.16

Note. Kurkchi and Iogansen [38] used iso-octane and carbon tetrachloride (distinguished by an asterisk) as the inert solvent (IS) and methylpyrrolidone or pyridine (asterisk) as the electron-donating solvent (EDS) and the corresponding values of B are quoted without taking into account the degree of association: Hyong [35] used carbon tetrachloride as IS and pyridine as EDS and the B are quoted without taking into account the degree of association; Gastilovich and coworkers [47,48] used carbon tetrachloride as IS and pyridine as EDS and the B are quoted with allowance for the degree of association.

The three-atom model of the covalent hydrogen bond discussed above have been confirmed by certain experiments. Thus the experimental intensities of the absorption bands corresponding to the vibrations of other bonds and the values calculated using the parameter $\partial\mu_{H---B}/\partial q_{H---B}$ agreed satisfactorily. For example, $(B^{(C)}_{\nu C\equiv C}) = 0.02 \times 10^4$ cm^{-1} litre $mole^{-1}$ was calculated for the $\nu_{C\equiv C}$ vibration frequencies of acetylene in the complex with acetone, the measured value being $B^{(C)}_{\nu C\equiv C} = 0.08 \times 10^4$ cm^{-1} litre $mole^{-1}$. [65]

5. Limitations of the Three-Atom Model

However, certain experimental data show that the three-atom model is apparently valid only to a first approximation and holds for A–H molecules in which the degree of conjugation of the donor electrons with the remainder of the A molecule is low. In molecules where there is such conjugation (R–C≡C–H---B), one cannot neglect the change in electron density in the remainder of the molecule on formation of the hydrogen bond. For example, an observation such as that of the appearance of two $\nu C{\equiv}C$ absorption bands in the spectra of the hydrogen-bonded complexes of certain acetylenic compounds contradicts the three-atom model discussed above. A numerical estimate shows that the vibration frequency of the C≡C group in the hydrogen-bonded complex may change only as a result of a change in the force constant K_Q. On the other hand, a change in the force constant of the ≡CH bond on formation of the hydrogen-bonded complex ($\Delta K_q \simeq -1.0 \times 10^6$ cm^{-2}) cannot change the $\nu C{\equiv}C$ vibration frequency[47] to such an extent (by about 10 cm^{-1}), despite the fact that the vibration mode of the latter is characteristic of the entire X–C≡C–H group.

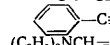
The inadequacy of the three-atom model has been pointed out by Gastilovich et al.[47], who measured the intensities of the absorption bands due to the ≡CH and C≡C groups in certain acetylene derivatives in various solvents. Taking into account the $\nu{\equiv}CH$ and $\nu C{\equiv}C$ vibration modes and using the parameter $\partial\mu H\text{---}B/\partial q H\text{---}B$, the intensities of the C≡C absorption bands were calculated[47,48] from the relations

$$\left(\frac{\partial M}{\partial Q_{\equiv CH}}\right)_c = \left(\frac{\partial M}{\partial Q_{\equiv CH}}\right)_0 - 0.90\frac{\partial \mu_{H\text{---}B}}{\partial q_{H\text{---}B}} e_{\equiv CH},$$
$$\left(\frac{\partial M}{\partial Q_{C\equiv C}}\right)_c = \left(\frac{\partial M}{\partial Q_{C\equiv C}}\right)_0 - 0.24\frac{\partial \mu_{H\text{---}B}}{\partial q_{H\text{---}B}} e_{\equiv CH}, \quad (4)$$

where $Q{\equiv}CH$ and $QC{\equiv}C$ are the normal coordinates of the $\nu{\equiv}CH$ and $\nu C{\equiv}C$ vibrations respectively; $(\partial M/\partial q{\equiv}CH)[D/Å] = 1.6 \times 10^{-2} (E\nu CH)^{1/2}$, and a similar expression holds for $B\nu C{\equiv}C$, E being measured in cm^{-2} litre mole^{-1}. A discrepancy has been found between the calculated and experimental intensities of the $\nu C{\equiv}C$ bands in the spectra of the hydrogen-bonded complexes of phenylacetylene and trimethylsilylacetylene. The discrepancy has been attributed to a change in the electro-optical parameter of the C≡C bond ($\partial\mu X\text{–}C{\equiv}C\text{–}H/\partial Q$) on formation of the hydrogen bond, which is inconsistent with the three-atom model. However, for alkylacetylenes and certain silyl- and stannyl-acetylenes, the calculated and experimental intensities agree within the limits of experimental error. This finding can be explained by the weak conjugation in molecules with this structure[48].

The intensity of the C≡C absorption band decreases on formation of the hydrogen bond in aryl- and alkyl-acetylenes[35,47,55] and increases in silyl- and stannyl-acetylenes[47,48] (Table 7). It has been shown[5,14] that the dipole moments for the transition of the $\nu{\equiv}CH$ and the $\nu C{\equiv}C$ vibrations have opposite directions in alkylacetylenes and the same directions in silyl and stannyl derivatives ($R_3X\text{–}C{\equiv}CH$). On this basis, the opposite sign for the change in the intensity of the $\nu C{\equiv}C$ band in the spectra of these compounds on hydrogen bond formation has been explained from the standpoint of Iogansen's three-atom model (zeroth approximation) and on the hypothesis of conjugation in the C≡C–H models involving the electrons of the donor B (next approximation)[49]. Thus the parameter $\partial\mu X\text{–}C{\equiv}C\text{–}H/\partial Q$ for phenylacetylene and trimethylsilylacetylene dissolved in an inert solvent has the same sign. The change of this parameter for substances dissolved in an electron-donating solvent is also of the same sign. For example, $\Delta(\partial\mu X\text{–}C{\equiv}C\text{–}H/\partial Q) \simeq -0.9$ for pyridine.

Table 8. The dipole moments μ_q of the ≡C–H bond and their derivatives $\partial\mu_q/\partial q$ based on the infrared spectroscopic data for solutions of compounds of the type R–C≡CH in carbon tetrachloride and the changes in vibration frequencies (wave-numbers) $\Delta\nu{\equiv}CH = \nu{\equiv}CH$ (solution in CCl_4) – $\nu{\equiv}CH$ (solution in pyridine).

R–C≡C–H	μ_q, D	$\partial\mu_q/\partial qD/Å$,	$\Delta\nu_{\equiv CH}$, cm^{-1}
HC≡CH[1]	1.10	0.90	—
$(CH_3)_3SiC{\equiv}CH$	1.12±0.06	0.97	—100
$(CH_3)_3C\text{–}C{\equiv}CH$	1. ±0.05	1.22	—80
$(C_2H_5)_2N(CH_2)_2OCH{=}CH\text{–}C{\equiv}CH$	1.28±0.07	1.26	—85
	1.27±0.07	1.56	—97
$(C_2H_5)_2NCH{=}CH\text{–}C{\equiv}CH$	1.42±0.1	1.50	—65
$(C_2H_5)_3Sn\text{–}C{\equiv}CH$	1.3±0.2	0.85	—74

The stretching and deformation vibrations of the ≡C–H group in acetylene derivatives are characteristic as regards mode. Therefore the intensity of the absorption bands associated with these vibrations in the spectra of solutions in an inert solvent is proportional to the derivative of the dipole moment of the ≡C–H group with respect to the coordinate q, i.e. $\partial\mu_q/\partial q$, and to the dipole moment μ_q of the ≡CH bond respectively. Thus information about the distribution of electron density in the ≡C–H group may be obtained from the infrared spectrum. Table 8 lists the values of $\partial\mu_q/\partial q$ and μ_q for various compounds R–C≡CH,[8] obtained from measurements of the intensity in the spectrum of the solution in an inert solvent. These parameters have been compared with the shift of the $\nu{\equiv}CH$ band in the spectrum of the solution in pyridine. The data in Table 8 demonstrate the absence of a monotonic relation between the dipole moment, its derivative, and the capacity of the compounds R≡C–CH to form a hydrogen bond ($\Delta\nu{\equiv}CH$), which apparently indicates a limitation of the three-atom model.

6. Energy of the Hydrogen Bond

The spectroscopic determination of the energy of the hydrogen bond from the change in the degree of association with temperature yielded a fairly low value (1.5–2 kcal mole^{-1}).[35] The energy ΔH of the hydrogen bond between acetylene and its simplest alkyl derivatives on the one hand and an electron-donating solvent on the other has been determined[64] from the heat of solution. For example, $\Delta H = 1.4$ kcal mole^{-1} for the hydrogen-bonded complex with acetone and $\Delta h = 2.4$ kcal mole^{-1} for the complex with hexamethylphosphoramide.

Iogansen proposed a method for the determination of the hydrogen bond energy on the basis of the three-atom model of the hydrogen bond[40]:

$$\Delta H \text{ (kcal mole}^{-1}) = g\,[(B^{(c)}_{\nu CH})^{1/2} - (B^{(0)}_{\nu CH})^{1/2}] \qquad (5)$$

where the coefficient $g = 2.9$ hardly differs for different classes of A—H compounds. This method is very simple, since it does not require measurements at different temperatures. Only the intensity of the A—H(≡C—H) absorption band in the spectrum of the hydrogen-bonded complex and in the spectrum of the solution in an inert solvent is measured. According to the valence-optical scheme, the above relation presupposes a direct dependence of the hydrogen bond energy on the derivative of the dipole moment of the hydrogen bond itself with respect to the coordinate $q_{H\cdots B}$: $\Delta H \propto \partial\mu_{H\cdots B}/\partial q_{H\cdots B}$.

The energies of the hydrogen bond between acetylene and its alkyl derivatives on the one hand and the solvent on the other, determined from the absorption intensity and from the heat of solution, agree satisfactorily: $\Delta h = 1.1$ and 2.4 kcal mole^{-1} from the intensities in the infrared spectra in acetone and hexamethylphosphoramide solutions respectively (the data based on the heat of solution were given above). The hydrogen bond energies in alkyl-, stannyl-, and certain silyl-acetylenes ($R_3X—C\equiv CH$, X = C, Si, or Sn) in hydrogen-bonded complexes with pyridine have been determined from Eqn. (5)[48]. The hydrogen bond energy increases in the sequence X = C < X = Sn < X = Si: 1.2, 2.0, and 3.6 kcal mole^{-1}. However, in the light of the hypothesis concerning the hydrogen bond[52], discrepancies should be observed in certain systems between the hydrogen bond energies measured directly and those determined from the equation [Eqn. (5)] proposed by Iogansen. Such discrepancies may be expected for R—C≡C—H derivatives where the π electrons of the C≡C bond interact with the π electrons of the R—C≡C—H group, for example in $R_3Si—C\equiv CH$ and phenylacetylene.

IV. VIBRATIONAL (INFRARED) SPECTROSCOPIC STUDY OF INTRAMOLECULAR ELECTRONIC INTERACTION

As already mentioned in the introduction, conclusions concerning the mutual influence of various groups in the molecule cannot be reached solely on the basis of the experimental vibration frequencies and band and line intensities in the vibration spectra. The problem of applying vibration spectra in the study of polyatomic molecular structures is considered in the review of Gribov and Popov[66]. However, in the majority of spectroscopic studies where the problems of structures were examined this finding was ignored. For example, in the section dealing with spectroscopic studies in Luneva's review[2], the conclusions of the investigators quoted on the spectroscopic manifestation of π–d conjugation in molecules are discussed uncritically in this sense. Since the $\nu C\equiv C$ vibration does not show characteristic intensities and its frequency may vary within fairly wide limits [see Eqn. (2)] when the atom X in the X—C≡C—H group is varied, we shall not discuss here purely experimental studies devoted to the investigation of intramolecular interaction.

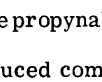
Certain conclusions about the mutual interaction of individual groups of atoms in the molecule can be reached by examining the force constants and electro-optical parameters of various molecules. However, we may note that these quantities may vary in different molecules both as a result of intramolecular interactions and as a result of a change of the hybridisation of the electrons forming the bonds under consideration. Moreover, since in the calculations on the vibrations the choice of the non-zero non-diagonal elements of the molecular force field is to some extent arbitrary, one cannot simply compare the force constant obtained by different investigators and arrive at conclusions concerning the change in the molecular force field on the basis of the differences between them. This is indicated by the data in Table 2. Finally the force constant itself and its changes in one direction or another for different molecules still cannot provide any information about the nature of the intramolecular interaction. A conclusion about the specific type of mutual interaction of groups in the molecule can be usually reached by considering data obtained in studies on the molecule by other methods. The problems of intramolecular interaction in acetylenic compounds have been discussed in a number of studies.[5,9–11,14,15,20–22,27,47,48,68]

1. Interaction with a Halogen and π–π Interaction

Lubuzh and Popov studied the effect of a halogen on the potential field of the ethynyl group[9]. Calculation on molecular vibrations showed that the replacement of hydrogen atoms in acetylene by the CH_3 group (methylacetylene) or Cl does not have an appreciable influence on the force (dynamic) constant of the C≡C—H group (Table 2).[9] In contrast to these groups, the remaining halogens (F, Br, and I) influence the ethynyl group. Thus in fluoroacetylene there is a sharp increase of the force constant of the C≡C bond ($K_Q = 27.2$) and of the dynamic interaction between the F—C≡ and C≡CH groups ($H^Q_{Q_1} = 1.09$). On the other hand, in bromo- and iodoacetylenes, $H^Q_{Q_1}$ decreases ($K_Q \simeq 25.5$) but the halogen does affect the ≡CH group: K_q decreases ($K_q = 10.4$). The results of this study are consistent with Duncan's data[12] for analogous compounds. Zerbi and Gussoni[13] showed that the halogen X separated from the C≡C—H group by a carbon atom ($H_2X—C—C\equiv CH$) does not alter the force constant of this group. However, the influence of the halogen distorts the cylindrical symmetry of the force field of the C≡C—H group and the spectra of these compounds show two bands corresponding to the δ≡CH deformation vibrations. Iodine has the greatest effect; the difference $K^{(1)}_\delta - K^{(2)}_\delta$ for this compound is high (about 0.09×10^6 cm^{-2}).

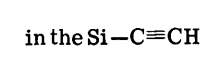
It has been shown[9,10,68] that the force constant of the C—C bond changes little (approximately by 10–15%) when the state of hybridisation of the electrons forming it alters: sp^3–sp^3, sp^3–sp^2, and sp^3–sp. The force constant is greatly influenced by the change in π-electron density: with increase of bond order K also increases. A considerable asymmetry of the force constants in the ≡C—O—C group was noted by Tenisheva et al.[20]: $K(\equiv C—O) = 13.6 \times 10^6$ cm^{-2} and $K(O—C) = 8.0 \times 10^6$ cm^{-2}. A similar phenomenon has been observed for silyl and stannyl derivatives of acetylene: $K(\equiv C—Si) = 5.7 \times 10^6$ cm^{-2} and $K(Si—C) = 5.1 \times 10^6$ cm^{-2} for the silyl derivative and $K(\equiv C—Sn) = 4.1 \times 10^6$ cm^{-2} and $K(Sn—C) = 3.60 \times 10^6$ cm^{-2} for the stannyl derivative[5,21]. However, in the latter the change in K can probably be accounted for mainly by a change in hybridisation.

Popov and coworkers carried out an interesting series of studies in which they established a definite correspondence between the type of force field and the nature of the intramolecular electronic interaction (conjugation). Popov and Lubuzh[22] determined the force field for diacetylene and dimethyldiacetylene. The force constant of the Q q_0 Q′ C≡C–C≡C groups (the designation of the normal coordinate is indicated above the bonds) for these molecules differ considerably from the corresponding values for the acetylene and methylacetylene molecules. Thus K_Q is appreciably reduced (24.1×10^6 cm^{-2}), K_{q_0} increases (12.8×10^6 cm^{-2}), and the dynamic constant for the interaction of triple bonds is also higher ($H^{Q}_{Q_1} = -1.64 \times 10^6$ cm^{-2}); $H^{Q}_{Q_0} = 0.54 \times 10^6$ cm^{-2}. The authors concluded that such a characteristic force field in the molecules investigated can be accounted for by electron delocalisation. They showed that the proposed set of force constants describes satisfactorily the vibration spectra of the polyacetylenes R–(C≡C)$_n$–R with n = 2–6 in contrast to the set obtained by other workers. The form of the force field of polyacetylenes led the authors[22] to the conclusion that the interaction between the triple bonds in the (C≡C)$_n$ chain decays rapidly and that the phenomenon of bond order equalisation does not occur. Having examined the force fields of molecules with different types of intramolecular electronic interaction, Popov and Kogan[67] proposed a classification of molecular force fields, involving a subdivision into four types depending on the diagonal and non-diagonal elements, so that each type of force field corresponds to a definite type of distribution of electron density in the molecule. Popov and coworkers carried out calculations on the vibrations of vinylacetylene and its methyl-substituted derivatives[10] on the basis of the force field classification and quantum-mechanical calculations which showed a delocalisation of electron density in the molecules under consideration. The authors concluded that the satisfactory agreement among more than 120 calculated and experimental vibration frequencies confirms the data showing a delocalisation of electron density in such a molecule and the initial postulates that the type of force field and the electronic structure of the molecule correspond.

Epshtein and Popov[11] obtained a distinctive type of force field for the propynal molecule (): K_Q and K(O=C) are reduced compared with acetylene and acetaldehyde, while K_{Q_1} is higher. The authors concluded that the type of force field of this molecule is consistent with quantum-mechanical calculations, which demonstrate a delocalisation of π electrons in this molecule.

Popov et al.[27] pointed out the similarity of the force constants and electro-optical parameters for the C=C–C≡C, C=C–C=C, and C≡C–C≡C carbon chains, which they explained by the same cause in each molecule—a partial delocalisation of electron density. Thus the calculated electro-optical parameters of the carbon chain in the vinylacetylene molecule are non-zero and large, in contrast to the data for dimethylacetylene[29]. The authors concluded that these results indicate a polarisation of the C=C and C≡C bonds in the molecule (C=C–C≡C). Calculation of the absorption band intensities in the spectrum of another substance (diacetylene) using the electro-optical parameters of vinylacetylene resulted in a satisfactory agreement between the calculated and experimental data.

2. Interaction Involving Groups Containing Si, Sn, N, O, and S Atoms

Gastilovich, Shigorin, and coworkers studied the mutual interaction of groups in acetylene derivatives containing silicon and tin as the X atom. The suggested electronic effects—the inductive effect and π–d conjugation–lead to the opposite changes in the distribution of electron density in the Si–C≡CH and Sn–C≡CH groups: .

Calculations on the vibrations of the C_3X–C≡CH groups in the $(CH_3)_3Si$–C≡CH (Gastilovich et al.[5]) and $(C_2H_5)_3Sn$–C≡CH (Gastilovich et al.[14]) groups showed that the dynamic constants K_Q and K_q for the compounds are smaller than for t-butylacetylene[5] $(CH_3)_3C$–C≡CH (Table 2). The changes in the electro-optical parameters of these compounds can be seen from Table 3. The changes in the electro-optical parameters of the X–C≡C–H groups and the almost constant value of the electro-optical parameter of the C_3–X group led the authors to the conclusion that the degrees of π-d conjugation in the silicon- and tin-containing compounds investigated are different[14]. The study of hydrogen bonding in these compounds showed that the electron-donating properties of the groups decrease in the sequence Sn–C≡C–Sn > C–C≡C–C > Si–C≡C–Si and the electron-accepting properties of R_3SiC≡CH are more pronounced than those of R_3C–C≡CH and R_3Sn–C≡CH (Tables 4 and 5). The authors concluded that the above findings indicate a shift of π-electron density in silylacetylenes from the C≡C group to ≡C–Si (π-d conjugation) and an appreciably smaller degree of such interaction in stannylacetylenes.

Another approach has been proposed[47] for the study of the problem of conjugation, which is based on the hypothesis that the three-atom model of the hydrogen bond is inadequate for molecules where the intramolecular interaction takes the form of conjugation (see Section III, 5). Calculation of the absorption band intensities associated with the νC≡C vibrations on formation of an intermolecular hydrogen bond with an electron-donating solvent showed that the calculation based on an additive scheme (three-atom model) yields satisfactory results for the stannylacetylene[48] $(C_2H_5)_3Sn$–C≡CH. However, the assumption of additivity for trimethylsilylacetylene[47] $(CH_3)_3SiC$≡CH and also for phenylacetylene leads to a discrepancy between the calculated and experimental quantities owing to the neglect of conjugation. A similar experiment and calculation led the authors to the conclusion that in silyl derivatives with several ethynyl groups π-d conjugation diminishes. Shakhovskii et al.[69] believe that the shift of the electron cloud towards the silicon atom (which they explained by π-d conjugation) is indicated by the magnitude and the direction of the dipole moments of substances of the type R_3SiC≡C–C≡CH.

On the basis of NMR data and measurements of the molecular dipole moments, Petrov et al. concluded that there is intramolecular charge transfer from the nitrogen atom to the ethynyl group in the compound R_2NCH=CH–C≡C–$Si(CH_3)_3$.[70] Considerable changes in the intensities of the absorption bands associated with the νC≡C and νC=C vibrations are observed in the spectra of compounds of the type RYCH=CH–C≡CH (Y = S, O, or N) as a function of the atom Y.[15,71,72] However, these changes arise mainly because the above vibrations do not have characteristic intensities[6,15]. It is suggested that there is an intramolecular interaction between

YCH=CH and −C≡C−H groups in such compounds on the basis of data showing that there is discrepancy between the experimental intensities and the values calculated assuming additivity [15]. Calculation of the intensities of the $\nu C{\equiv}C$ absorption bands in the spectra of the compounds $RYCH{=}CH{-}C{\equiv}C{-}Si(CH_3)_3$ from the $\nu C{\equiv}C$ band intensities in the spectra of the compounds $RYCH{=}CH{-}C{\equiv}CH$ and the electro-optical parameters of the $\equiv C{-}Si(CH_3)_3$ group showed a deviation from additivity only for compounds containing nitrogen. The authors concluded that other heteroatoms (S and O) have only a weak influence on the dynamic and electro-optical characteristics of the $=C{-}C{\equiv}C{-}H$ group.

Table 9. Vibration frequencies (wave-numbers) ν (cm^{-1}) and intensities B (in units of 10^4 cm^{-2} litre $mole^{-1}$) of the infrared absorption bands and I of the Raman lines [in relative units: $I_{313}(CCl_4) = 100$] in the spectra of compounds with several ethynyl groups.

Compound	Raman			Infrared			
	$\nu_{\equiv CH}$	$\nu_{C\equiv C}$	$I_{C\equiv C}$	$\nu_{\equiv CH}$	$B_{\equiv CH}$	$\nu_{C\equiv C}$	$B_{C\equiv C}$
$(CH_3)_3SiC{\equiv}CH$ (Ref.89)	3276	2040	141	3292 [90]	0.46	2035	0.25
$(CH_3)_2Si(C{\equiv}CH)_2$	3268	2046	292	3294	1.16	2043	1.0
$CH_3{-}Si(C{\equiv}CH)_3$	3270	2044	426	3288 *	1.80	2046	1.32
$Si(C{\equiv}CH)_4$	3268	2050	590	3296	2.56	2050	
				3290 *	—		1.52
$(C_2H_5)_3SnC{\equiv}CH$ [1]	3268	2008	161	3287 [14]	0.45	2005	0.10
$(C_2H_5)_2Sn(C{\equiv}CH)_2$				3293 [21]	0.89	2017	0.31
$C_2H_5Sn(C{\equiv}CH)_3$				3296	1.35	2019	0.60
$(C_6H_5)_3SnC{\equiv}C{-}C_6H_5$ (Ref.92)	—	2137	2000				
$(C_6H_5)_2Sn(C{\equiv}C{-}C_6H_5)_2$	—	2148	3260				
$Sn(C{\equiv}C{-}C_6H_5)_4$	—	2154	6560				

*Solution in CS_2.

A considerable mutual influence of the C≡C and ≡C−Sn groups (in contrast to CAlk−Sn) was also detected by calculating the electro-optical parameters of tin-containing compounds with several ethynyl groups [21]. However, we may note that a similar interaction has been observed also for H−C bonds in the methyl group [25].

Among purely experimental studies, mention should be made of those of Buchert, Zeil, and Haals [73-75], Sacher, and coworkers [76,77], and Miller and Lemmon [78], who quote the vibration frequencies of the molecules investigated and give their interpretation [for the compound $R_3SiC{\equiv}C{-}X$ with X = H, $Si(CH_3)_3$, or Hal, $H_3C{-}X(C{\equiv}C{-}H)_3$ and $X(C{\equiv}CH)_4$ with X = Si, Ge, or Sn, and $Y(C{\equiv}CH)_3$ with Y = P, As, or Sb]. The characteristic frequencies of compounds containing Group IV and V elements can be found in the reviews by Chumaevskii and coworkers [79,80]. In the majority of other experimental studies, certain vibration frequencies and absorption bands or line intensities were considered and the specific changes in these quantities for various molecules were explained by changes in the distribution of electron density in the XC≡CX′ group (see, for example, Refs. 71-72 and 81-88). However, examination of the vibrations of the ethynyl group (Section I of the present review) shows that the authors' conclusion concerning the electronegativities of various atomic groups, conjugation, vacant orbitals, and the activity of the lone electron pairs of various atoms are in the majority of cases groundless. However, these studies contain rich and remarkable experimental data. For example, there is an interesting variation of the absorption and line intensities in the infrared and Raman spectra corresponding to the $\nu C{\equiv}C$ vibration (Table 9) with the number of ethynyl groups. Thus in the Raman spectra the intensity increases in proportion to the number of these groups, which is not the case in the infrared spectra.

Table 10. Effect of molecular structure on the $\nu C{\equiv}C$ vibration frequency and the intensity B (in units of 10^4 cm^{-2} litre $mole^{-1}$) of the infrared absorption bands or I of the Raman lines (in relative units*).

Chemical formula	$\nu_{C\equiv C}$, cm^{-1}	$B_{C\equiv C}$ or $I_{C\equiv C}$	Method	References
$n\text{-}C_4H_9{-}C{\equiv}CH$	2120	0.067	i.r.	83
$(C_2H_5)_3Ge{-}C{\equiv}CH$	2027	0.10		
$(C_2H_5)_3Ge{-}CH_2{-}C{\equiv}CH$	2112	0.20		
$(C_4H_9)_3Ge{-}C{\equiv}C{-}C_4H_9$	2166	0.47		
$(C_2H_5)_3Ge{-}C{\equiv}C{-}C{\equiv}C{-}C_2H_5$	2242	0.25		
	2103	0.25		
$(CH_3)_3Si{-}C{\equiv}C{-}C(CH_3)_2{-}C{\equiv}CH$	2206	90	R**	93
	2174	162		
$(C_2H_5)_3Si{-}C{\equiv}C{-}C_6H_5$		1360	R	91
$(C_2H_5)_3Sn{-}C{\equiv}C{-}C_6H_5$	2136	2324		
$(C_4H_9)_3Sn{-}C{\equiv}C{-}C_4H_9$	2151	170	R	91
$(C_4H_9)_3Sn{-}C{\equiv}C{-}C_4H_9$	2160	240		
$(C_6H_5)_3Sn{-}C{\equiv}C{-}CH{=}CH_2$	2138	755		
$(C_2H_5)_3Pb{-}C{\equiv}C{-}C_6H_5$	2132	—	i.r.	88
$C_4H_9SCH{=}CH{-}C{\equiv}CH$	2094	0.08	i.r.	71,90
$CH_3OCH{=}CH{-}C{\equiv}CH$	2100	0.18		
$(C_2H_5)_2NCH{=}CH{-}C{\equiv}CH$	2075	0.74		
$C_4H_9SCH{=}CH{-}C{\equiv}C{-}Si(CH_3)_3$	2140	0.74	i.r.	90
$C_4H_9OCH{=}CH{-}C{\equiv}C{-}Si(CH_3)_3$	2148	0.90		
	2134			
$(C_2H_5)_2NCH{=}CH{-}C{\equiv}C{-}Si(CH_3)_3$	2116	2.90		
$C_2H_5{-}CH(OH){-}C{\equiv}CH$	2112	60	R	94
	2110	0.022	i.r.	
$C_2H_5{-}C(=O){-}C{\equiv}CH$	2092	109	R	
	2093	0.52	i.r.	

*$I_{C\equiv C}$ in monoalkylacetylene was taken to be 100 units.

We shall complete the present review by a Table (Table 10) providing a clear illustration (together with Table 9) of the changes, which are sometimes enormous, in the frequency and particularly the intensity of the absorption band associated with the $\nu C{\equiv}C$ vibrations as a function of molecular structure. Unfortunately, these changes in the infrared spectra and apparently to an even greater extent in the Raman spectra do not characterise the changes in the distribution of electron density directly in the C≡C group.

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