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**Abstract**

**Full Text**

**Physical Chemistry**

L. M. SVERDLOV

**CHARACTERISTIC FREQUENCIES OF OLEFINS**

*(Presented by Academician G. S. Landsberg, November 4, 1956)*

The question of the characteristic frequencies of olefins was considered most thoroughly in the work of Hubo <sup>(2)</sup>, in which, for each class of olefins, groups of characteristic frequencies are given, found by comparing observed spectra. It is obvious, however, that in order convincingly to confirm the selection of one or another group of frequencies as characteristic and to assign these frequencies to definite vibrations, a theoretical analysis is necessary (carried out according to the method of M. A. Elyashevich, B. I. Stepanov <sup>(6)</sup>, and L. S. Mayants <sup>(7)</sup>).

In order to clarify the regularities of the vibrational spectra of complex olefins of the six possible types: RHC=CH<sub>2</sub>, R<sub>1</sub>R<sub>2</sub>C=CH<sub>2</sub>, cis- and trans-

**Table 1**

Characteristic frequencies of monoalkyl-substituted ethylene RHC=CH<sub>2</sub>

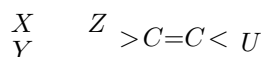
$$\begin{array}{c} \text{H}_2\text{C} \backslash \text{C}=\text{C} / \text{H} \\ \text{H} / \quad \backslash \text{H} \end{array}$$

Coordinate	Intensity,		Intensity, IR	Source (1)	Source (2)	Source (3)	Source (5)
	Our data	Ra-man					
$q_{\text{CH}_2}^- (\text{C}-\text{H})$	3087	med	med	3080	3079	3081	3082
$q_{\text{CH}_2}^+ (\text{C}-\text{H})$	2990	weak	med	3001	2998	2979	3001
$q_{=\text{CH}_2} (\text{C}-\text{H})$	3010	strong				3000	
$Q (\text{C}=\text{C})$	1642	strong	med	1642	1642	1642	1642
$\alpha_{=\text{CH}_2} (\text{HCH})$	1416	med	med	1416	1415	1416	1416
$\beta (\text{C}=\text{CH})$	1297	med	weak	1292*	1298*	1297	1292*
$\beta^- (\text{C}=\text{CH}_2)$	1170	weak	weak			1166	
$\chi_{\text{CH}_2}^{\text{CCH}}$	991	weak	strong	990*	992*	996	991*
$\rho_{\text{CH}_2}$	912	weak	strong	912*	911*	910	910*
$\rho_{\text{CCH}}$	632	weak	med		631*	630	
$\gamma (\text{C}=\text{C}-\text{C})$	432	weak	weak		435*		630

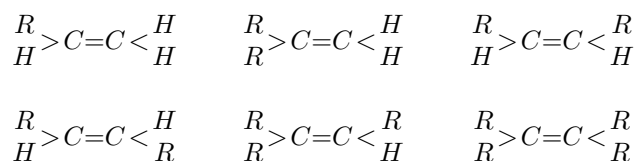
\* No exact assignment.

$R_1CH=CHR_2$ ,  $R_1R_2C=CHR_3$ ,  $R_1R_2C=CR_3R_4$ , we have carried out a complete theoretical calculation of the frequencies of normal vibrations of the simplest alkyl-substituted ethylenes: propylene, isobutylene<sup>(8)</sup>, cis- and trans-butene-2<sup>(9)</sup>, trimethylethylene, and tetramethylethylene<sup>(9)</sup>, since the spectrum of each of these molecules possesses its own characteristic features. As the calculation shows, each of the molecules considered has vibrations that are characteristic in form, in the broad sense<sup>(7)</sup>, for a group of coordinates, correspond-

...corresponding to the structural element



Since this structural group is included in compounds of the type



then, consequently, the molecules of each of the indicated homologous series will, respectively, possess essentially the same characteristic frequencies as the molecules of propylene, isobutylene, cis-trans-butene-2, trimethylethylene, and tetramethylethylene. Thus, the groups of characteristic frequencies established by us are frequencies of stable characteristic vibrations for a series of compounds containing a definite chemical group. This conclusion is well supported by a large amount of experimental material on the combination and infrared spectra of the indicated homologous series (we collected data for more than 90 olefins).

**Table 2**

Characteristic frequencies of asymmetrically dialkyl-substituted ethylene  $R_1R_2C=CH_2$

Coordinate	Our data	Intensity, comb.	Intensity, infr.	Source (2)	Source (3)
$q_{CH_2}^-(C-H)$	3081	sl	med	3078	3086
$q_{CH_2}^+(C-H)$	2985	s		2987	2985
$Q(C=C)$	1653	s	med	1653	1653
$\alpha_{=CH_2}(HCH)$	1412	med	med	1414	1412
$Q^-(C-C)$	1290	sl	med	888	
$\beta(C=CH_2)$	1000	sl		1383	1282
$\rho_{CH_4}$	888	sl	s	1002	887

Coordinate	Our data	Intensity, comb.	Intensity, infr.	Source <sup>(2)</sup>	Source <sup>(3)</sup>
$Q^+(C-C)$	804	s		804	
$\chi_{CH_2}^{CCC}$	703	sl	sl	703	700
$\gamma(C=CC)$	434	sl		434*	
$\gamma(CCC)+$	390	sl		394*	
$\rho_{CCC}$				261*	

\* Exact assignment is absent.

Tables 1-6 give the groups of characteristic frequencies established by us, with indication of the assignment (and with the approximate line intensity according to literature data <sup>(1-4)</sup>) for six homologous series, as well as data of other authors. In each table the structural element with which the entire group of characteristic frequencies is associated is indicated.

As follows from the tables, many frequencies have either been assigned incorrectly by other authors or have not been assigned at all to definite vibrations. In addition, in a number of cases Goubeau chose as characteristic such frequencies that apparently belong to the hydrocarbon radicals  $R$ , and therefore cannot be regarded as characteristic frequencies of olefins, since

they are also observed in the spectra of all saturated hydrocarbons with a long carbon chain.

Let us next consider the effect of branching in the chain on the spectrum. In the case where there is branching in the chain far from the double bond, the characteristic nature of the vibrations noted in the tables should not be disturbed, since the structural groups with which these vibrations are associated are fully preserved. If, however, the branching occurs at a carbon atom adjacent to the double

**Table 3**

**Characteristic frequencies of trans-alkenes  $RCH = CHR$**



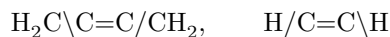
Coordinate	Our data	Intensity, comb.	Intensity, IR	Source <sup>(2)</sup>	Source <sup>(3)</sup>
$q(C-H)$	~ 3010	weak		3001	3007
$Q(C=C)$	1675	strong		1671	1676
$\beta(C=CH)$	1306	strong		1303	1308
$Q^+(C-C)$	870	medium		892	

Coordinate	Our data	Intensity, comb.	Intensity, IR	Source <sup>(2)</sup>	Source <sup>(3)</sup>
$\rho_{\text{CCH}}$	745	weak		742	742
$\gamma(\text{C}=\text{C}-\text{C})$	495	weak		488	
$q(\text{C}-\text{H})$	$\sim 3020$		medium		3021
$\beta(\text{C}=\text{CH})$	1306		weak	1376	1302
$Q^-(\text{C}-\text{C})\text{CCH}$	1070		weak	1023*	
$\chi_{\text{CCH}}$	966		strong	809*	964
$\gamma(\text{C}=\text{C}-\text{C})$	263			210	
$\rho_{\text{CCH}}$	233				

\* No exact assignment.

**Table 4**

**Characteristic frequencies of cis-alkenes  $\text{RCH} = \text{CHR}$**



Coordinate	Our data	Intensity, comb.	Intensity, IR	Source <sup>(2)</sup>	Source <sup>(3)</sup>
$q(\text{C}-\text{H})$	$\sim 3020$		medium	3013	3020
$q(\text{C}-\text{H})$	$\sim 3010$	medium		3013	2985
$Q(\text{C}=\text{C})$	1660	strong	medium	1656	1660
$\beta(\text{C}=\text{CH})$	1410		medium	1376	1406
$\beta(\text{C}=\text{CH})$	1267	strong		1263	1259
$Q^-(\text{C}-\text{C})$	972	medium		970	
$\rho_{\text{CCH}}$	895	medium		640	970(?)
$Q^+(\text{C}-\text{C})$	875			892	
$\rho_{\text{CCH}}$	700	weak	strong	702	700
$\gamma(\text{C}=\text{C}-\text{C})\text{CCH}$	590	weak		581	
$\chi_{\text{CCH}}$	402	weak		413	
$\gamma(\text{C}=\text{C}-\text{C})$	304	weak		297	

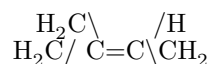
bond (for example,  $\text{R}-\text{CH}-\text{CH}=\text{CH}_2$ ), then this must already affect the characteristic nature of certain vibrations, since in this case there is no longer that smallest group of coordinates for which these vibrations are characteristic. Both of these propositions are fully confirmed. Thus, for example, in the spectrum of the molecule 4-methyl-4-ethylhexene-1<sup>(1)</sup> (with branching of the first type) all the characteristic frequencies noted in Table 1 are observed:

437, 627, 913, 995, 1180 (doublet), 1296, 1416, 1641, 3006, 3078  $\text{cm}^{-1}$ . On the other hand, in the case, for example, of the molecule 3,6-dimethylheptene-1

(with branching of the second type), the characteristic nature of the vibrations  $\gamma(\text{C}=\text{C}-\text{C})$  and  $\rho_{\text{CCH}}$  (which interact most strongly with the coordinates of the group  $-\text{CH}_2-\text{CH}=\text{}$ )

**Table 5**

Characteristic frequencies of trialkyl-substituted ethylenes  
 $\text{R}_1\text{R}_2\text{C}=\text{CHR}_3$



Coordinate	Our data	Intensity, Raman	Intensity, IR	Source (2)	Source (3)
$q$ (C-H)	3024	weak	medium	3023	3024
$Q$ (C=C)	1676	strong	medium	1673	1676
$\beta$ (C=CH)	1350	weak	weak	1350	1350
$Q^-$ (C-C)	1212	weak	medium	1003	
$Q$ (C-C)	950	weak	medium	806	
$\rho_{\text{CCH}}$	803	weak	strong	958	803
$Q^+$ (C-C)	760	medium	weak	745	
$\gamma$ (C=C-C)	520	weak		526*	
$\rho_{\text{CCC}}$	440	weak		470*	
$\gamma$ (CCC)	390	weak		385*	
$\gamma$ (C=C-C)	295	weak		301*	
$\chi_{\text{CCH}}$	254	weak		251*	
$\chi_{\text{CCC}}$	254	weak		251*	
				1382*	
				1304*	
				1112*	

\* No exact assignment is available.

**Table 6**

Characteristic frequencies of tetraalkyl-substituted ethylenes  
 $\text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4$

Coordinate	Our data	Intensity, Raman	Intensity, IR	Goub. (2)	Coordinate	Our data	Intensity, Raman	Intensity, IR	Goub. (2)
$Q$ (C=C)	1680	strong		1672	$Q^-$ (C-C)	1151	strong		821*
$Q^-$ (C-C)	1269	weak		1024	$Q^+$ (C-C)	893	strong		745*
$Q^+$ (C-C)	690	strong		690	$\gamma$ (CCC)	405			319*
$\gamma$ (C=C-C)	505	medium		503	$\rho_{\text{C}=\text{C}}$	273			

Coordinate	Intensity,			Coordinate	Intensity,		
	Our data	Raman IR	Goub. (2)		Our data	Raman IR	Goub. (2)
$\rho_{\text{CCC}}$	411	weak	547	$\gamma(\text{C}=\text{C}-\text{C})$	190		
$\gamma(\text{C}-\text{C}-\text{C})$	319	weak	409	$\chi_{\text{CCC}}^{\text{CCC}}$			

\* No exact assignment is available.

is already violated, whereas the characteristic nature of the remaining vibrations is still preserved: 914, 994, 1176, 1294, 1419, 1641, 2997, 3082  $\text{cm}^{-1}$ . Similar examples can also be given for olefins of the remaining five types.

Saratov Motor-Road Institute  
named after V. M. Molotov

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*Note: Figure translations are in progress. See original paper for figures.*

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