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Frequencies and intensities of the C=C double bond stretching vibration in the Raman spectra of perfluoroolefins

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Abstract

The frequencies and integrated intensities of the $\nu_{C=C}$ vibration in the Raman spectra of 20 individual perfluoroolefins (PFOs) of various types were measured, allowing the authors to develop a quantitative method of group analysis of PFOs mixtures. Limitations of the method are discussed. A comparison of the $\nu_{C=C}$ Raman line parameters for fluorinated and non-fluorinated olefins is given.

Keywords: Raman spectra; Perfluoroolefins; Double-bond stretching vibration

1. Introduction

It is well known that the so-called 'stretching vibration of the C=C bond' ($\nu_{C=C}$) in the spectra of ordinary olefins is not localized. Along with the C=C bond stretching coordinate, the bending HCH and HCC coordinates are significantly involved in this normal vibration. However, this vibration is characterized by its frequency; and each olefin exhibits a Raman line in the spectral region 1600–1680 cm^{-1}, the exact value of this line frequency being determined by the structure of the olefin. The $\nu_{C=C}$ vibration has been shown to possess not only a characteristic frequency, but also a rather characteristic intensity in the Raman spectrum [1–3]. For instance, for olefins of the R–$CH{=}CH_2$ type, the Raman line corresponding to the $\nu_{C=C}$ stretching vibration has a frequency of 1642 cm^{-1} and an intensity of ca. 300 units (in the so-called 'cyclohexane scale'). It was this feature that made it possible to perform quantitative group analysis of olefin mixtures with use of Raman spectroscopy [3].

A step-by-step introduction of fluorine atoms to the C=C bond in α-position results in a gradual increase in the $\nu_{C=C}$ frequency, which reaches a value of 1872 cm^{-1} for tetrafluoroethylene (TFE), and also in a better localization of this normal vibration. In fact, normal coordinate analysis shows that for ethylene the contribution of the C=C bond stretching coordinate to the potential energy is only 53%, while for perfluoropropene this contribution reaches 80% [4–7].

Experimental data on the $\nu_{C=C}$ frequencies in the spectra of various perfluoroolefins (PFO) are given and surveyed in Ref. [8], based mainly on the IR spectra. However, it is well known that for centrosymmetric molecules, vibrations which are symmetrical with respect to the centre are not active in the IR spectra, in accordance with the selection rules. For this reason, the C=C vibrations of symmetrical *trans*-1,2-disubstituted ethylenes of the type R_f–CF=CF–R_f and of tetrasubstituted ethylenes of the type $R_f'R_f''C{=}R_f''R'_f$ are inactive in IR spectra. Additionally, our extensive experience shows that in the IR spectra of some PFOs, the band of the C=C vibration is either very weak or does not appear at all despite the fact that the structure of their molecules is not centrosymmetric. This is only due to the small value of the dipole moment derivative with respect to the normal coordinate $(d\mu/dQ)_0^2$ which determines the IR intensity. This is true of some *cis*-substituted perfluoroethylenes (PFE) and some other compounds, for example, $CF_3(OCH_3)C{=}CFC_2F_5$ (Fig. 1). For this reason, conclusions about the presence or absence of a double C=C bond in a fluorinated molecule based only on the IR spectra are often wrong. At the same time, the $\nu_{C=C}$ vibration is always active in the Raman spectra of PFOs and shows itself as an intense polarized line.

Better localization of this normal vibration for PFOs compared to their non-fluorinated analogues allows one to expect a higher specificity of frequency and intensity for this vibration in the Raman spectra of the former. If so, Raman spectroscopy can be applied for the group analysis of mixtures of higher PFOs. Such mixtures are formed, for example, in the process of anionic oligomerization of lower PFOs. Therefore, the development of a method of analysis of such mixtures is a topical challenge.

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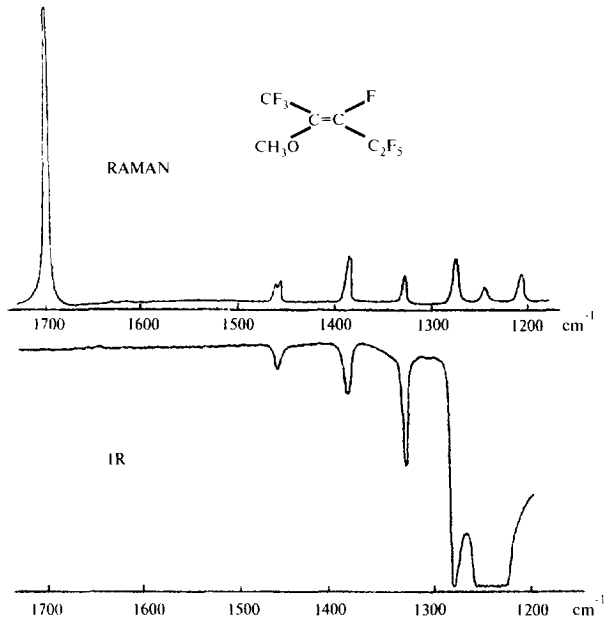

Fig. 1. Comparison of the Raman and IR spectra of 2-methoxyperfluoropentene (2).

We have studied in detail the Raman spectra of non-cyclic PFOs of various structure whose molecules contain from five to 10 carbon atoms. Comprehensive investigation of the Raman spectra of PFOs has not been performed previously; only a few separate publications are available [6,7,9–12].

2. Results and discussion

As was expected, a very strong polarized line is observed in the Raman spectra of non-cyclic PFOs corresponding to the $\nu_{C=C}$ vibration. This is situated in the 1630–1880 cm^{-1} region of the spectrum (see Fig. 2 and Table 1). No other vibrational frequencies appear in this region. As early as 1965, the authors of Ref. [8] noted that the frequency of this line depended on the number of fluorine atoms attached *directly* to the carbon atoms of the C=C bond. For TFE, $\nu_{C=C} = 1872\ cm^{-1}$ (cf. 1623 cm^{-1} for ethylene). When one of the fluorine atoms in TFE is replaced by a perfluoroalkyl radical (we shall call compounds of this type, i.e. R_f–CF=CF_2, 'monosubstituted' PFEs), the $\nu_{C=C}$ frequency is shifted to the 1770–1790 cm^{-1} region and exhibits only a slight dependence on the structure of R_f. If R_f is a linear chain containing three to seven carbon atoms, the $\nu_{C=C}$ frequency is of a constant value, i.e. 1785 cm^{-1}. A perfluorobutyl group decreases the $\nu_{C=C}$ frequency to a certain extent, i.e. to 1774 cm^{-1}. In the spectra of 'light' molecules, i.e. $CF_3CF=CF_2$ and $C_2F_5CF=CF_2$, the $\nu_{C=C}$ value is higher (1795 cm^{-1}) [8]. In general, it is obvious that the $\nu_{C=C}$ frequencies for monosubstituted PFEs lie in a narrow range. Thus, the presence of a line in the 1770–1790 cm^{-1} region of the Raman spectrum of a non-cyclic PFO points unambiguously to the presence in the molecule of a CF_2=CF–C moiety (see Fig. 3).

In the spectra of PFOs of the type R_f–CF=CF–R_f containing two fluorine atoms attached directly to the C=C bond ('1,2-disubstituted' PFEs), the $\nu_{C=C}$ frequency is shifted to the 1715–1735 cm^{-1} region. The $\nu_{C=C}$ frequencies of all *trans* isomers are observed in a narrow region ($\sim$1730 cm^{-1}) while those of the *cis* isomers occur at $\sim$1720 cm^{-1}. The only exception is the olefin $(CF_3)_3C$–CF=CF–CF_3 which is a *trans* isomer although its $\nu_{C=C}$ value is 1717 cm^{-1}. In this case it is a perfluoro-t-butyl group again which lowers the $\nu_{C=C}$ value so that its frequency falls in the region characteristic of *cis* isomers.

Only one *gem*-disubstituted PFE was available to us, i.e. $CF_3(C_3F_7)C=CF_2$; its $\nu_{C=C}$ value of 1730 cm^{-1} lies in the frequency region typical of the *trans*-1,2-substituted olefins. For $(CF_3)_2C=CF_2$, $\nu_{C=C} = 1750\ cm^{-1}$ has been reported in Ref. [8].

For PFOs containing only one fluorine atom at the double bond ('trisubstituted' PFEs), the frequency is again lowered and depends substantially on the length of the R_f substituents and their branching. Thus, the spectral region for the $\nu_{C=C}$ values for trisubstituted PFEs becomes wider and ranges from 1700 to 1600 cm^{-1}; a steric effect is also obvious. Again, olefins with branched substituents exhibit the lowest frequencies, as seen in Fig. 2 and Table 1.

As far as 'tetrasubstituted' PFEs were concerned, only two of them were available (see Table 1 and Fig. 2). Unfortunately, their $\nu_{C=C}$ frequencies lie within the low-frequency part of the range characteristic of trisubstituted PFEs.

Thus, the results obtained along with the literature data show that the $\nu_{C=C}$ vibrational frequencies for non-cyclic perfluoroolefins with various structures are quite characteristic. The $\nu_{C=C}$ values for mono- and 1,2-disubstituted PFEs lie within narrow regions of the Raman spectrum: 1795–1770 cm^{-1} and 1735–1715 cm^{-1}, respectively. The frequency region for the $\nu_{C=C}$ values of trisubstituted PFEs is more spread out – 1700–1660 cm^{-1} – and its low-frequency part overlaps with the high-frequency part of the $\nu_{C=C}$ region for tetrasubstituted PFEs.

Hence, it follows from these data that Raman spectroscopy makes it possible to identify in a mixture mono- and 1,2-disubstituted PFEs containing any R_f group, and trisubstituted PFEs with non-branched radicals (see Fig. 3). Trisubstituted PFEs with branched R_f groups and tetrasubstituted PFEs can only be identified as a whole, since this method is unable to distinguish between them.

We have also measured the relative integrated intensity ($I^{\infty}_{C=C}$) of the Raman lines corresponding to the $\nu_{C=C}$ vibration for various individual PFOs in the spectrum of a solution using an internal standard. In this case, 1,1,2-trichlorotrifluoropropylene, CF_3–CCl=CCl_2, whose $\nu_{C=C}$ frequency is 1590 cm^{-1}, was used as the internal standard [1]. The $\nu_{C=C}$ fre-

[1] The authors are indebted to Dr. V.A. Petrov for his suggestion to use, 1,1,2-trichlorotrifluoropropylene as an internal standard and for the synthesis of the compound.

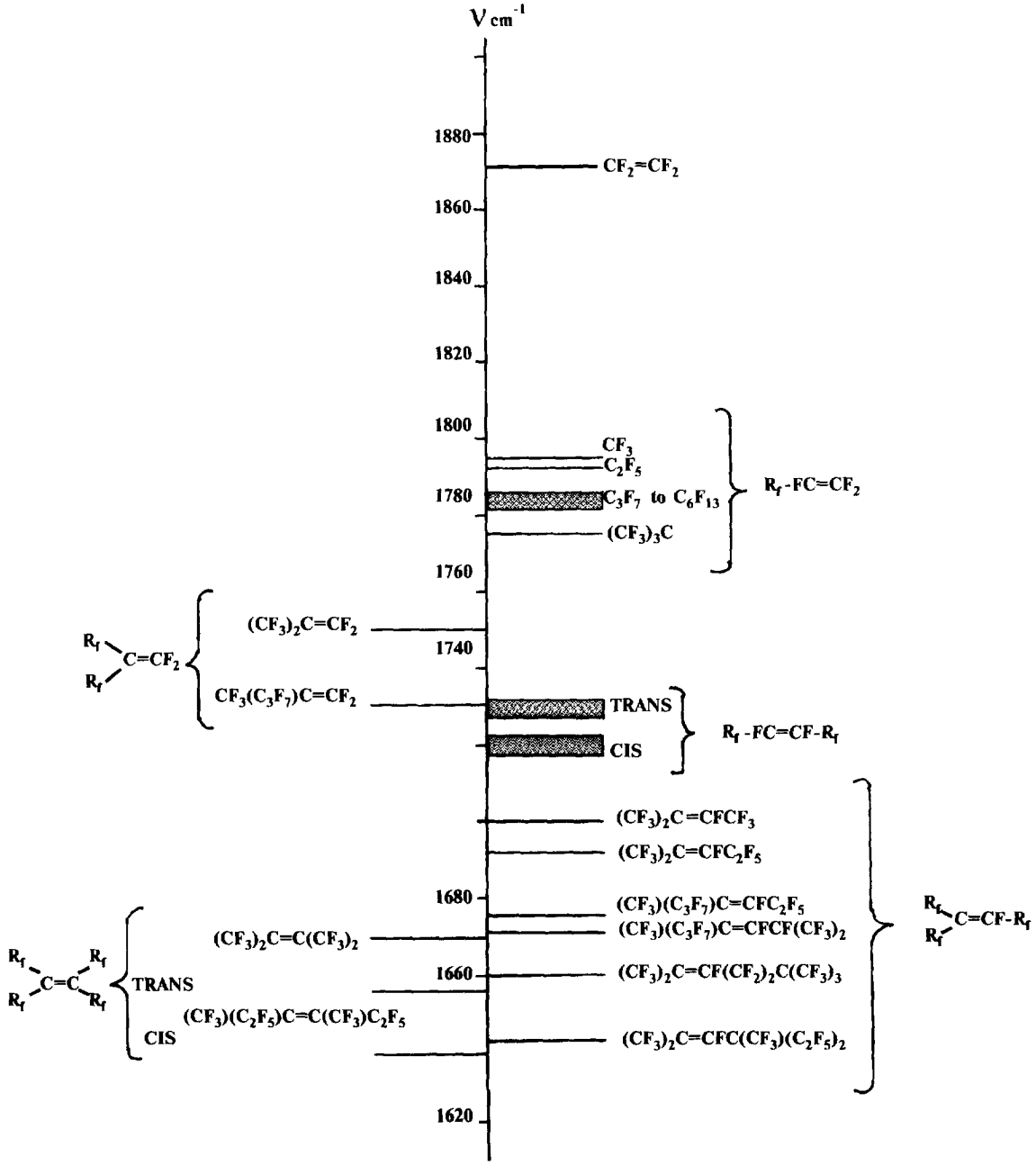

Fig. 2. Spectral region where the vibrational $\nu_{C=C}$ frequencies are situated for perfluoroolefins of various structure.

quency value for this standard is lower than the typical frequencies for the $\nu_{C=C}$ values of PFOs. This choice of standard proved to be correct because this substance is miscible with PFOs and does not interact with them. The integrated intensity of the line at 1590 cm^{-1} was taken as being 100 arbitrary units.

The internal standard was added to the substance studied in a definite molar ratio and then the integrated intensity of the Raman line corresponding to $\nu_{C=C}$ for the substance was measured with respect to that of the standard. The intensity values were recalculated for equal number of molecules in scattering volumes. The results of the measurements are summarized in Table 1.

It follows from the data in Table 1 that the $I^{\infty}_{C=C}$ value is constant (within the limits of experimental error) for all PFEs of a given type and does not depend either on the R_f chain length or, unlike the frequency, on the degree of R_f branching. Moreover, the intensity is only slightly dependent on the PFE type, remaining virtually constant for mono-, *trans*-1,2-di-, tri- and tetra-substituted PFEs. Only in the case of a *cis*-1,2-disubstituted PFE is intensity significantly higher.

Thus the results obtained, i.e. the dependence of the $\nu_{C=C}$ frequency on the PFO structure combined with the virtually constant value of the $\nu_{C=C}$ intensity for all types of PFEs, allow one to perform a quantitative group analysis of various PFO mixtures using Raman spectroscopy.

To check the applicability of this analytical method, we have prepared special-purpose mixtures of various PFOs and determined the total amount of each type, i.e. mono-, di- and tri-substituted PFEs, by measuring the $\nu_{C=C}$ frequencies and the integrated intensities in the Raman spectra, using the internal standard method.

We have also found that dilution of the PFO mixtures with saturated perfluorinated compounds does not preclude a quantitative determination of each type of PFO. Moreover, if necessary, the amount of perfluoroalkanes in a mixture can also be determined as the difference between the weighed specimen and the total amount of all PFOs present. An average molecular mass was calculated for each mixture. Table 2 depicts the results of such an analysis applied to three special-purpose mixtures to demonstrate the applicability of the technique.

Together with their analytical interest, the results obtained are of significant theoretical value because they provide the foundation for studies of such problems as conjugation in molecules of perfluorinated dienes and enones, as well as their conformational isomerism and the nature of any torsional barriers. With this in mind, it was of interest to compare the $I^{\infty}_{C=C}$ values obtained for PFOs with the corresponding values for non-fluorinated olefins. For this purpose we measured the integrated intensity of the Raman $\nu_{C=C}$ line for hexene-1 at 1642 cm^{-1}; it proved to be equal to 71.5 units, using the intensity scale taken above. Thus, the $I^{\infty}_{C=C}$ value for fluoroolefins appears to be only ca. one-half that for the non-fluorinated analogue. It also follows from these data, combined with those of Refs. [2] and [3], that the conversion

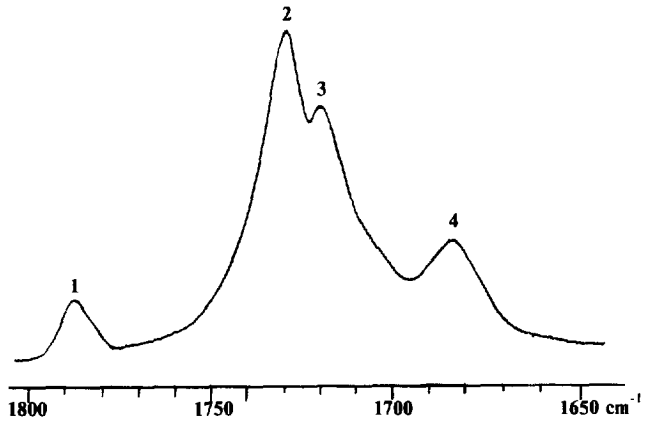

Fig. 3. A typical region of the Raman spectrum illustrating the $\nu_{C=C}$ bands of a PFO mixture. Raman lines correspond to (1) monosubstituted PFE; (2) and (3) *trans*- and *cis*-1,2-disubstituted PFE, respectively; and (4) trisubstituted PFE.

Table 1
Frequencies and relative integrated intensities of the $\nu_{C=C}$ lines in the Raman spectra of various perfluoroolefins

Olefin studied	$\nu_{C=C}$ (cm^{-1})	$I^{\infty}_{C=C}$				Reference to synthetic procedure
		I	II	Average value	Average value for given type of olefin	
1. CF_3–CCl=CCl_2 (standard)	1590			100		[20]
2. C_4H_9–CH=CH_2	1642	73.5	69.6	71.5		
Monosubstituted PFE						
3. C_3F_7–CF=CF_2	1785	37.4	35.2	36.3		[13]
4. C_4F_9–CF=CF_2	1785	37.8	36.8	37.3		[13]
5. C_5F_{11}–CF=CF_2	1785	37.5	40.9	39.2	38.4 ± 1.7	[13]
6. C_6F_{13}–CF=CF_2	1784	42.7	40.4	41.5		[13]
7. $(CF_3)_3$C–CF=CF_2	1774	32.2	42.9	37.6		[14]
trans-1,2-disubstituted PFE						
8. C_2F_5–CF=CF–CF_3	1732	38.6	38.6	38.6		[15]
9. C_2F_5–CF=CF–C_2F_5	1727	47.8	49.6	48.7		[12]
10. C_3F_7–CF=CF–CF_3	1730	42.6	41.8	42.2	42.7 ± 2.8	[15]
11. $(CF_3)_2$CF–CF=CF–CF_3	1732	44.5	44.0	44.3		[16]
12. $(CF_3)_3$C–CF=CF–CF_3	1717	38.8	38.2	38.5		[17]
13. C_5F_{11}–CF=CF–CF_3	1731	41.7	45.5	43.6		[15]
14. *cis*-C_2F_5–CF=CF–CF_3	1722	68.3	67.5	67.9		[18]
Trisubstituted PFE						
15. $(CF_3)_2$C=CF–CF_3	1700	30.5	–	30.5		[15]
16. $(CF_3)_2$C=CF–C_2F_5	1692	38.1	37.5	37.6	35.1 ± 2.6	[16]
17. $(CF_3)_2$C=CFCF_2C$(CF_3)_3$	1660	32.6	33.8	33.2		[14]
18. $(C_3F_7)(CF_3)$C=CF–C_2F_5	1676	37.7	37.7	37.7		[19]
Tetrasubstituted						
19. $(C_2F_5)(CF_3)$C=C$(CF_3)(C_2F_5)$	1656 1640	31.2	27.1	29.2		[21]
20. $(CF_3)_2$C=C$(CF_3)_2$	1670					[11]

Table 2
Results of an analysis of control purpose-made PFO mixtures (amount of substance in each case in mol × 10^4)

Olefin type	Mixture 1 [a]		Mixture 2 [a]		Mixture 3 [a]	
	Amt. taken	Amt determined by Raman method	Amt. taken	Amt. determined by Raman method	Amt. taken	Amt. determined by Raman method
Monosubstituted PFEs	4.47	4.48	3.67	3.74	3.21	3.76
Disubstituted PFEs	4.71	4.99	3.62	3.68	7.72	7.95
Trisubstituted PFEs	4.10	4.25	2.03	2.06	3.69	3.99
Fluoroalkanes	2.41	1.97	3.57	3.43	3.08	2.00

[a] Average molecular masses of mixtures were as follows: mixture 1, 401; mixture 2, 445; mixture 3, 417.

Table 3
Data relating to the experimental procedure for the measurement of the Raman line intensity. The example given is for the line at 1785 cm^{-1} in the Raman spectrum of $C_6F_{13}-CF=CF_2$ relative to the 1590 cm^{-1} line of the internal standard (see text) [a]

	Area under line profile (weight)		Area ratio	$I^{\infty}_{C=C}$	Average $I^{\infty}_{C=C}$
	Compound studied	Standard			
Weighed specimen 1					
Spectral record 1	0.1868	0.1980	0.9434	47.2	
Spectral record 2	0.1775	0.2280	0.7785	38.9	42.7
Spectral record 3	0.1763	0.2105	0.8375	41.9	
Weighed specimen 2					
Spectral record 1	0.1956	0.2322	0.8424	42.1	
Spectral record 2	0.1930	0.2130	0.9061	45.3	43.6
Spectral record 3	0.1898	0.2190	0.8667	43.3	
Weighed specimen 3					
Spectral record 1	0.1301	0.2034	0.6396	39.7	
Spectral record 2	0.1318	0.2034	0.6677	41.2	40.4
Spectral record 3	0.1270	0.1973	0.6437	40.0	

[a] The compound/standard ratio was 2.0 for weighed specimens 1 and 2, and 1.66 for weighed specimen 3, respectively.

coefficient relating our intensity scale to the commonly used cyclohexane scale (where the integrated intensity of the Raman line of cyclohexane at 802 cm^{-1} is taken as 500 units) is 4.5. Thus it is possible to compare the data obtained for PFOs with a wealth of corresponding data on ordinary olefins given in Refs. [2] and [3].

3. Experimental details

Raman spectra were recorded with a laser Raman spectrometer Ramanor-HG-2S using the excitation of a 5145 Å line of a CR-8 ion argon laser (power 0.2–0.5 W). The spectral slit width of the spectrometer was 3–4 cm^{-1}. Calibration of the frequency generated by the instrument was achieved using the spectra of benzene and CCl_4. The accuracy of such frequency determination was ± 2 cm^{-1}.

All samples were colourless liquids and were distilled just before recording the spectra, placed in thin-walled capillaries and sealed. In order to measure the relative integrated intensities of the Raman lines, the internal standard $CF_3-CCl=CCl_2$ was added to a sample in a definite molar ratio and the mixture well stirred.

Intensity measurement of the Raman lines corresponding to the $\nu_{C=C}$ vibrations was carried out using two or three weighed specimens for each compound, each spectrum being recorded at least three times. The integrated intensities of the Raman lines were measured by weighing the areas under the line profiles corresponding to a given compound and to the standard. The intensities were recalculated for an equal number of molecules in the scattering volume. The detailed experimental procedure for the intensity measurement of $\nu_{C=C}$ lines is illustrated for $C_6F_{13}CF=CF_2$ in Table 3. A typical spectral curve for analysis is presented in Fig. 3. Resolution of overlapping contours was made graphically. The calibration mixtures prepared from the individual PFOs are specified in Table 2.

All the PFOs used in this study were synthesized according to known procedures [12–21]. Their purity was checked by GLC and ^{19}F NMR methods. The latter was also used to determine the *cis/trans* ratio in the PFO isomer mixtures.

4. Conclusions

1. A comprehensive study of the Raman spectra of perfluoroolefins (PFOs) has been performed.

2. It has been shown that the frequency value of the C=C bond vibration is determined by the structure of the PFO molecule and the number of fluorine atoms attached directly to the C=C bond. For monosubstituted PFEs of the type R_f–CF=CF_2, the $\nu_{C=C}$ frequencies are located in a narrow spectral region, i.e. 1775–1790 cm^{-1} while those for 1,2-disubstituted PFEs of the type R_f–CF=CF–R_f are in the region 1715–1730 cm^{-1}. The spectral region for trisubstituted PFEs of the type $(R_f)_2C$=CF–R_f is wider, i.e. 1640–1700 cm^{-1} while the frequencies of tetrasubstituted PFEs appear in the low-frequency part of the latter region.

3. The relative integrated intensities of the lines corresponding to the $\nu_{C=C}$ vibrations have been measured in the Raman spectra of various PFOs. It has been shown that the intensity value depends only slightly on the PFO structure and is equal to ca. 35 units (with respect to the reference $\nu_{C=C}$ line at 1590 cm^{-1} of the internal standard CF_3–CCl=CCl_2, whose intensity was taken as 100 units) for all types of PFOs with the exception of *cis*-disubstituted PFEs.

4. The $I^{\infty}_{C=C}$ value for PFOs was found to be only one-half of that for non-fluorinated olefins.

5. On the basis of the experimental data obtained, a method of quantitative group analysis of PFOs mixtures has been developed. Raman spectra were shown to allow the identification in a mixture of mono- and di-substituted PFEs and combined tri- and tetra-substituted PFEs. The method was verified using control mixtures.

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