

## A comparative estimate of the electron-withdrawing effect of polyfluorinated substituents on the polarization of the O-NO<sub>2</sub> bond in nitro esters of perfluorocarboxylic acids

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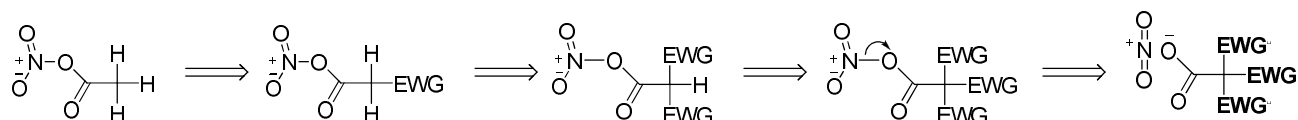
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**Abstract:** Spectral (Raman and <sup>14</sup>N NMR spectroscopy) and quantum-chemical methods were used for comparative estimation of the electron-withdrawing effect of a fluorine-containing substituent on the polarization of the nitro ester bond in nitro esters of perfluorocarboxylic acids. It has been shown that the electron-withdrawing effect of the trifluoromethyl group is somewhat stronger than that of the fluorine atom.

**Keywords:** nitrate ester of perfluorocarboxylic acid, electron-seeking group, bond polarization

It is known that the nitronium cation, NO<sub>2</sub><sup>+</sup>, is the most efficient nitrating species.<sup>1</sup> Covalent nitro esters of carboxylic acids also react as nitrating agents.<sup>2,3</sup> Obviously, polarization of the O<sub>2</sub>N-O bond in a nitro ester by electron-withdrawing groups (EWG) located at the β carbon atom results in a redistribution of charges on the oxygen and nitrogen atoms (Scheme 1) and should favor the electrophilic replacement of a proton by a nitro group. An increase in the number of EWGs in a nitro ester molecule elongates the O<sub>2</sub>N-O bond. Charge separation to give a nitronium cation, *i.e.*, ionization, may be considered as the limiting case of such polarization. Within the scope of ongoing studies on the structure-property relationship in the series of *O*-nitro compounds, we have previously obtained trifluoroacetyl nitrate (TFAN) and studied its behavior in solutions of acids.<sup>3,4,5,6</sup> In this work, the structure and properties of 2,2,3,3,3-pentafluoropropionyl nitrate (PFPN) by spectral and quantum-chemical methods was investigated.



### Scheme 1

One of the principal goals of the study was to find out how the replacement of a fluorine atom in a trifluoroacetyl nitrate molecule by a trifluoromethyl moiety (TFAN → PFPN) alters the properties of the perfluorocarbonyl acid nitro ester. It is convenient to perform this comparison by

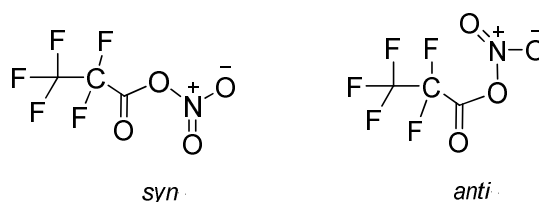
quantum-chemical calculations and by physicochemical methods, e.g., by estimating the changes in the frequencies of the nitro group symmetric vibrations,  $\nu^s_{\text{NO}_2}$ , in the Raman spectra and the change in  $\delta$  for the nitrogen signal in the  $^{14}\text{N}$  NMR spectra (see Ref.<sup>3</sup>).

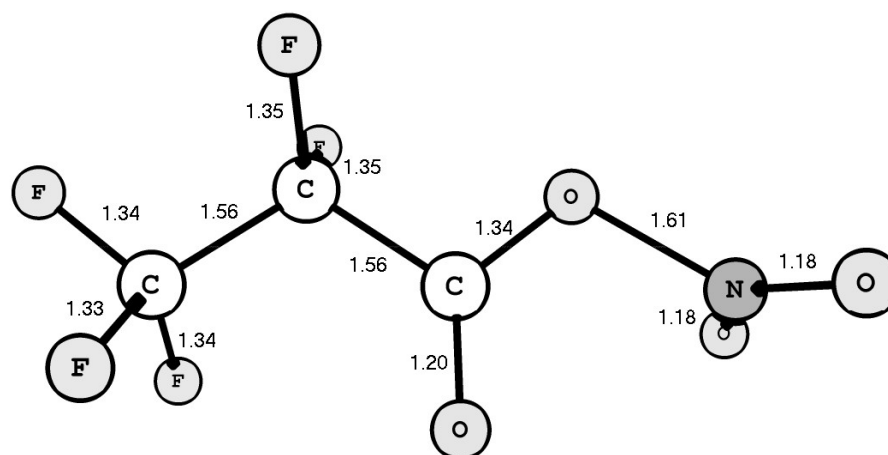
It should be noted that studies of the electron-withdrawing effect of  $\text{CF}_3$  and  $\text{C}_2\text{F}_5$  groups in the series of compounds  $(\text{CH}_3)_3\text{SnC}_F$  by the Mössbauer effect studying<sup>7</sup> as well as by the methods of vibrational spectroscopy of the corresponding perfluoro acids<sup>8</sup> were previously carried out, but led to diametrically opposite conclusions.

The  $\text{NO}_2^+$  cation, including a monodently bound to an oxygen of the anion, is a nearly linear structure and the  $\nu^s_{\text{NO}_2}$  frequency in the Raman spectra of nitronium salts is a characteristic frequency.<sup>9</sup> However, the symmetric vibration of the nitro moiety in covalent nitro esters is not characteristic since it involves the entire molecule and is more strongly affected by conjugation with the carbonyl group. We have shown previously that the experimental Raman spectrum of TFAN is in good agreement with the calculated spectrum of the *syn*-conformer of the nitro ester whose nitro group is turned by  $90^\circ$  with respect to the C-C(O)-O plane.<sup>3</sup> In the current study we assumed that, if the *syn*-conformation of the molecule is preserved, replacement of a fluorine atom in the trifluoromethyl group of TFAN by the heavier  $\text{CF}_3$  substituent through three bonds would affect the symmetric  $\text{NO}_2$  vibration less strongly in comparison with the additive electron-withdrawing effect of the  $\text{C}_2\text{F}_5$ - substituent. Thus, the frequency of the symmetric vibration of the nitro group ( $\nu^s_{\text{NO}_2}$ ) in the Raman spectra of compounds could serve as a one of the parameters for estimating the electron-withdrawing effect of a substituent.

The electron-withdrawing effect of substituents on the shift of the  $\text{ONO}_2$  moiety signal ( $\Delta\delta_{\text{N}}$ ) in the  $^{14}\text{N}$  NMR spectra of nitro esters (if the solvent is the same) was discovered by us previously<sup>3</sup> and was used in this study as a second parameter for comparison.

According to the calculation data obtained, the *syn*-conformation of PFPN (Fig. 1) is 6.17 kcal/mol more beneficial than the *anti*-conformation. It is important to note that the O- $\text{NO}_2$  bond of the PFPN *syn*-conformer (1.61 Å) is much longer than the similar bond of the TFAN *syn*-conformer (1.56 Å<sup>3</sup>).





**Fig. 1.** Structure of the *syn*-conformer of 2,2,3,3,3-pentafluoropropionyl nitrate. The bond lengths are specified in Å.

To perform an experimental synthesis of pentafluoropropionyl nitrate, we had to bear in mind the specific features of the synthesis of nitro esters containing electron-withdrawing substituents. In fact, the reaction of  $\text{N}_2\text{O}_5$  with trifluoroacetic anhydride takes a long time (up to 7 days), unlike its reaction with acetic anhydride (0.5 h).<sup>3</sup> The synthesis of TFAN is an equilibrium reaction shifted to the right. An equimolar mixture of trifluoroacetic anhydride and nitrogen pentoxide gave TFAN containing less than 10 mol. % of the starting trifluoroacetic anhydride. In the gas phase, TFAN is liable to homolytic decomposition into the anhydrides, their content may reach 15 molar %<sup>3</sup> (Scheme 2). Apparently this is the reason why concentrated TFAN readily explodes upon mechanical impact, even if cooled with ice. However, the synthesis times of the nitro esters are nearly the same in reactions of  $\text{HNO}_3$  with both acetic and trifluoroacetic anhydride (~10 min at 10 °C).<sup>3</sup>



### Scheme 2

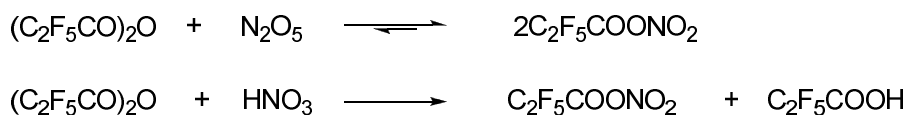
**Table 1.** Spectral characteristics of nitro esters

R-C(O)ONO <sub>2</sub>	<sup>14</sup> N NMR, δ <sub>N</sub> (Δv <sub>1/2</sub> , Hz), ppm, [CDCl <sub>3</sub> ]	Raman, ν <sup>s</sup> <sub>NO<sub>2</sub></sub> , cm <sup>-1</sup>	
		Calc.	Exp. [solvent]
	-70 (30) <sup>3</sup>	—	1308 <sup>3</sup> [CCl <sub>4</sub> ]
	-79 (35) <sup>3</sup>	1371 <sup>3</sup>	1339–1340 <sup>3</sup> [CCl <sub>4</sub> ], [CF <sub>3</sub> COOH]
	-80 (50) <sup>a</sup>	1374	1338 [CCl <sub>4</sub> ] <sup>a</sup> , 1339 [C <sub>2</sub> F <sub>5</sub> COOH] <sup>b</sup>

<sup>a</sup> PFPN was obtained from an equimolar mixture of pentafluoropropionic anhydride and  $\text{N}_2\text{O}_5$  (5 °C, 5 days).

<sup>b</sup> PFPN was obtained from an equimolar mixture of pentafluoropropionic anhydride and  $\text{HNO}_3$  (0–5 °C, 2 h).

PFPN was obtained by two alternative methods, namely, by reactions of 2,2,3,3,3-pentafluoropropionic anhydride with  $\text{N}_2\text{O}_5$  or with  $\text{HNO}_3$  (Scheme 3). The spectral characteristics of the resulting solutions are presented in Table 1 and in Figs. 2,3. The Raman spectra of 2,2,3,3,3-pentafluoropropionic acid and its anhydride are shown in Figs. 4 and 5.

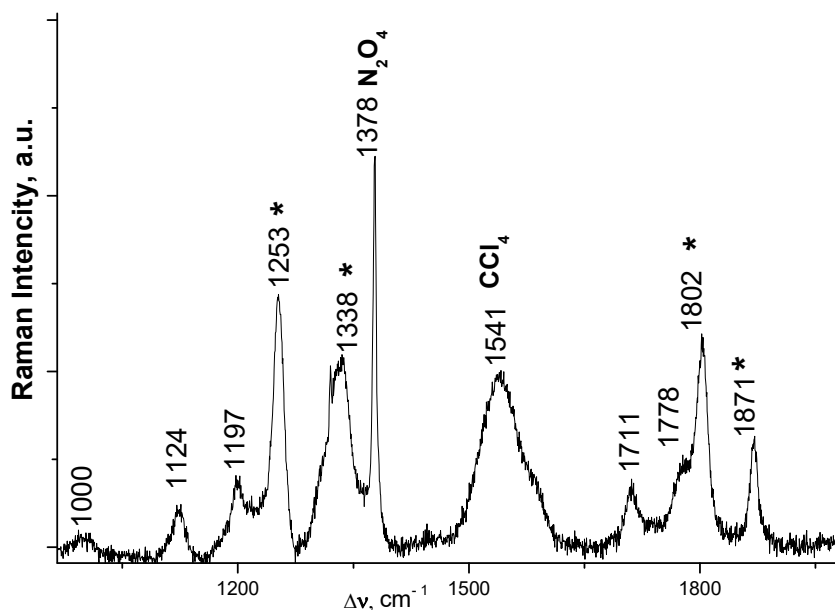


### Scheme 3

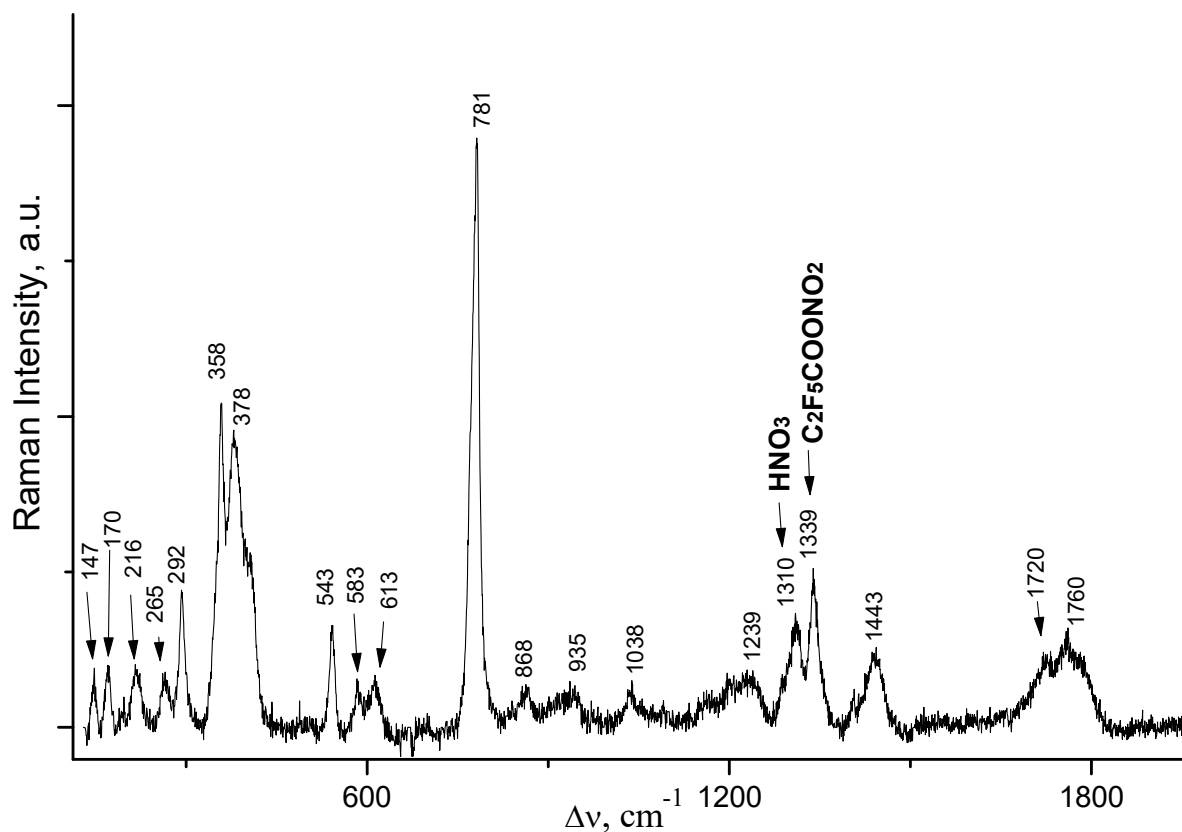
The experimental values of  $\nu^s_{\text{NO}_2}$  Raman spectral frequencies of TFAN and PFPN are similar, their difference is within the accuracy of the device. However, quantum-chemical calculations of the PFPN Raman spectrum in the gas phase give somewhat higher  $\nu^s_{\text{NO}_2}$  frequencies (by  $\sim 3 \text{ cm}^{-1}$ ) in comparison with the calculated spectrum of TFAN, while in the  $^{14}\text{N}$  NMR spectra of the compounds in question the signal of PFPN nitrogen is shifted upfield by  $\sim 1$  ppm in comparison with TFAN (Table 1). These facts, along with the increased length of the nitro ester bond in PFPN (1.61 Å), allow us to believe that the electron-withdrawing effect of the trifluoromethyl substituent is somewhat stronger than that of the fluorine atom. It should be noted that the electron-withdrawing effect of the  $\text{CF}_3$  substituent on the nitro ester bond is weakened since it is effected through three bonds.

The electron-withdrawing effects of F and  $\text{CF}_3$  substituents can also be compared by comparing the characteristic  $\nu^s_{\text{NO}_2}$  frequencies of the corresponding nitronium sulfates and the shifts of the  $^{14}\text{N}$  signal of the nitronium cations in these salts. In nitronium salts  $\text{NO}_2^+[\text{FSO}_3]^-$  and  $\text{NO}_2^+[\text{CF}_3\text{SO}_3]^-$  these substituents affect the nitronium cation through two bonds, therefore the electron-withdrawing effect of the  $\text{CF}_3$  substituent in comparison with that of the fluorine atom is more distinct than in nitro esters of perfluorocarboxylic acids. The  $\nu^s_{\text{NO}_2}$  line of  $\text{NO}_2^+[\text{CF}_3\text{SO}_3]^-$  at  $1410 \text{ cm}^{-1}$  is appreciably shifted to short wavelength field with respect to the similar frequency of  $\text{NO}_2^+[\text{FSO}_3]^-$  ( $1404 \text{ cm}^{-1}$ ).<sup>9</sup> In the  $^{14}\text{N}$  NMR spectra of these salts, the difference in the shifts,  $\Delta\delta_{\text{N}}$ , reaches 2 ppm (in sulfolane,  $\delta_{\text{N}}$  for  $\text{NO}_2^+[\text{FSO}_3]^-$  –131, for  $\text{NO}_2^+[\text{CF}_3\text{SO}_3]^-$  –133).<sup>9</sup>

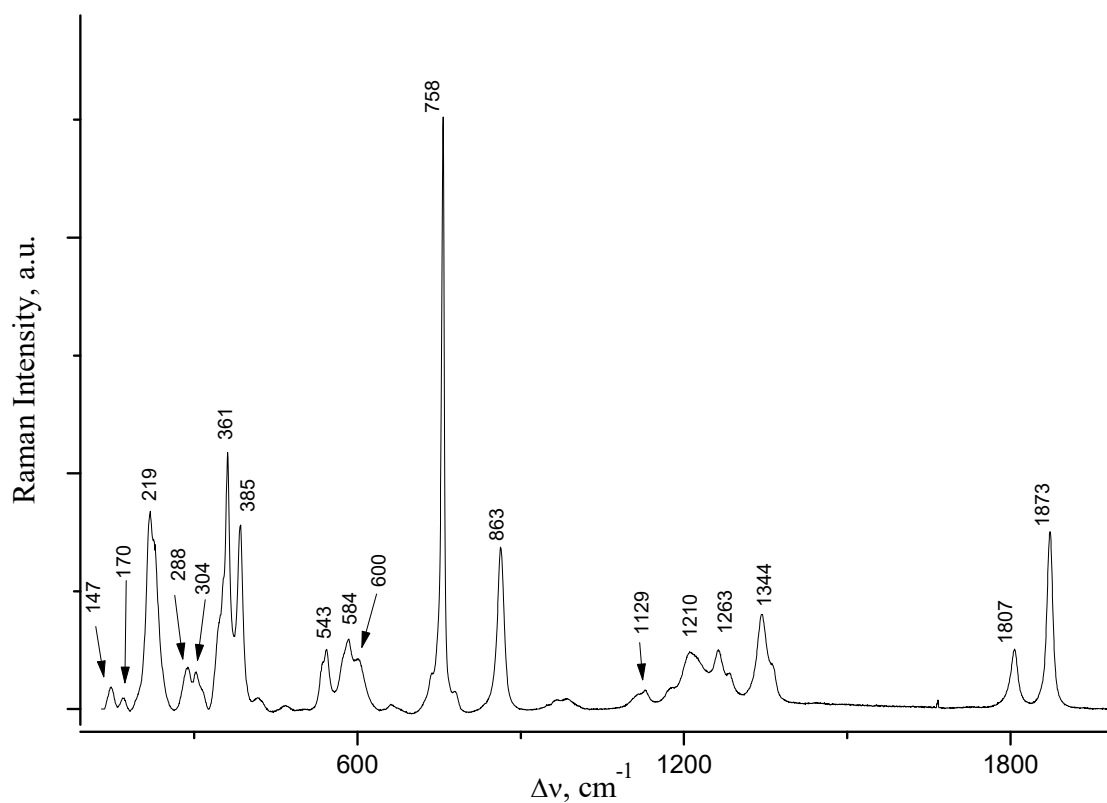
Thus, we performed a comparative estimate of the effect of polyfluorinated substituents on the degree of polarization of nitro ester bonds in nitro esters of perfluorocarboxylic acids. It has been shown that 2,2,3,3,3-pentafluoropropionyl nitrate exists in the *syn*-conformation. Furthermore, the electron-withdrawing effect of the trifluoromethyl substituent on the nitro ester moiety through three bonds is similar to, and slightly higher than, the electron-withdrawing effect of the fluorine atom.



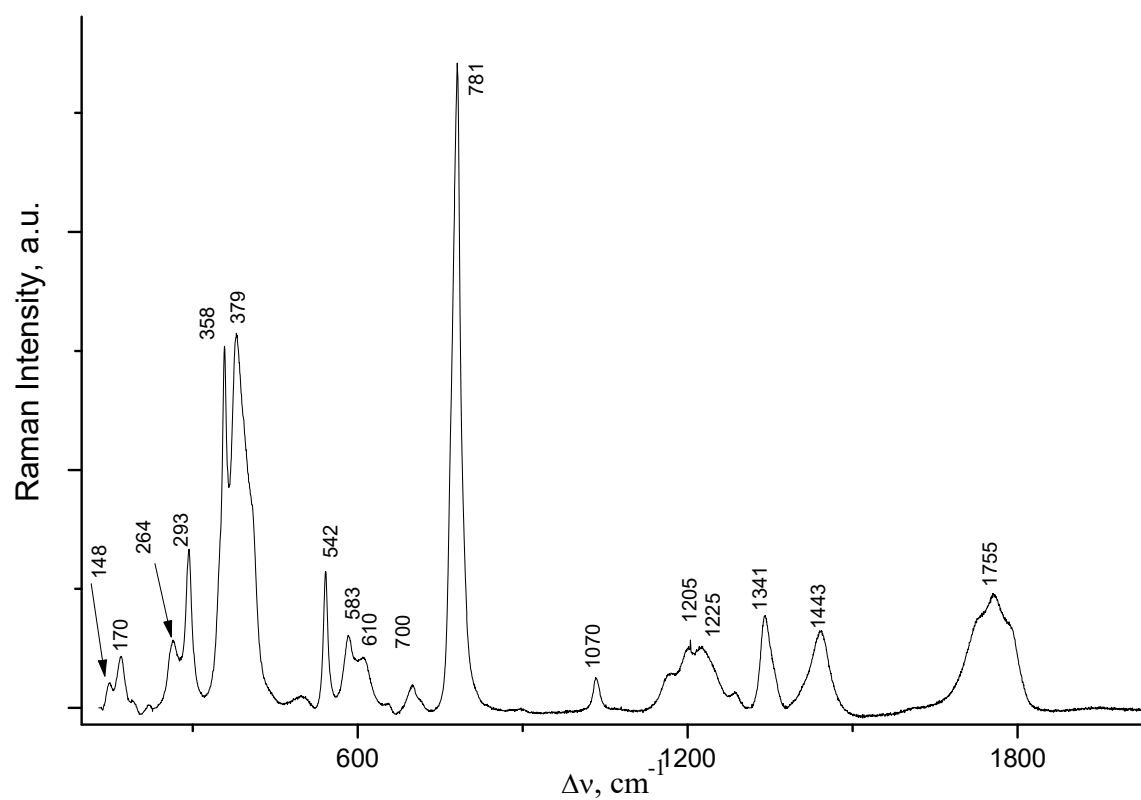
**Fig. 2.** Raman spectrum of a  $\text{CCl}_4$  solution of  $\text{C}_2\text{F}_5\text{COONO}_2$  obtained from an equimolar mixture of  $(\text{C}_2\text{F}_5\text{CO})_2\text{O}$  and  $\text{N}_2\text{O}_5$ ,  $5^\circ\text{C}$ , 5 days (in the  $900\text{--}1900\text{ cm}^{-1}$  region). The frequencies corresponding to  $\text{C}_2\text{F}_5\text{COONO}_2$  spectrum are marked with asterisks.  $\text{N}_2\text{O}_4$  was formed due to spontaneous decomposition of  $\text{N}_2\text{O}_5$ .



**Fig. 3.** Raman spectrum of a mixture of  $C_2F_5COONO_2$  and  $C_2F_5COOH$  ( $\approx 1 : 1$ ) obtained from an equimolar mixture of  $(C_2F_5CO)_2O$  and  $HNO_3$  ( $0-5\text{ }^\circ C$ , 2 h).



**Fig. 4.** Raman spectrum of  $(C_2F_5CO)_2O$ .



**Fig. 5.** Raman spectrum of C<sub>2</sub>F<sub>5</sub>COOH.

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### Experimental

Nitric acid ( $d^{20} = 1.5 \text{ g}\cdot\text{cm}^{-3}$ ) was preliminarily purified by distillation *in vacuo*, the colourless fraction was used. Dinitrogen pentoxide was prepared by the known procedure from HNO<sub>3</sub> and P<sub>2</sub>O<sub>5</sub>.<sup>3</sup> Raman spectra were recorded with an Acton Research spectrometer with 500 mm focus distance, on a 1200 lines/mm grid. A CCD from Princeton Instruments cooled with liquid nitrogen was used as the light-sensitive detector for the optical signal. The spectra were measured on the 641.7 nm line of a krypton laser with up to 100 mW power, in the 180° Raman line scattering configuration (back scattering). The spectral resolution was 1.5 cm<sup>-1</sup>. The optical path of the instrument was designed by the confocal microscope scheme with a spatial resolution of 2 μm. To record the spectra, individual compounds were placed into glass ampoules and tightly sealed; reaction mixtures were prepared by mixing the components directly in ampoules. Ampoules with solutions containing C<sub>2</sub>F<sub>5</sub>COONO<sub>2</sub> were kept in ice until the Raman spectra were recorded; the irradiation power used to record these spectra did not exceed 10 mW. The <sup>14</sup>N NMR spectrum (21.69 MHz) was recorded on a Bruker AM300 instrument using CH<sub>3</sub>NO<sub>2</sub> (10 mg) as the inner standard; the upfield shifts are negative. The quantum-chemical calculations were performed using the Gaussian 09 Revision D.01 DFT B3LYP/6-311++g(d,p) software complex.<sup>10</sup>

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