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Estimation of Total Infrared Intensities of Fluorinated Ethyl Methyl Ethers

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An excellent linear correlation was found between calculated and experimental total infrared intensities in the region of 500-2000 cm^{-1} for five partially fluorinated ethyl methyl ethers, HFC-134a, and CFC-11. The calculated results using ab initio molecular orbital method with D95V**(Huzinaga-Dunning's valence double zeta) show the best linear correlation among basis sets examined in this study. The correlation coefficient with D95V** is 0.9993 although the calculated values are on the average 32% higher than experimental ones.

Partially fluorinated ethers are now being considered as possible replacements for the fully halogenated chlorofluorocarbons (CFCs) because of concerns regarding the role of CFCs in ozone depletion and greenhouse warming. Since fluorinated ethers do not contribute to ozone depletion, global warming potential (GWP) is important in the selection of replacements for CFCs. Infrared absorption and atmospheric lifetime influence on GWP.1) There is information about lifetimes of fluorinated ethers from experimental rate constants for the reaction with hydroxyl(OH) radicals,2) and simple methods of lifetime estimation have been also reported.3) On the other hand, there is very little experimental and theoretical information on infrared intensities of partially fluorinated ethers.4) Previous theoretical works on small molecules, such as CH_3F, CH_2F_2, and CH_2O,5) have indicated that a large basis set with polarization and diffuse functions as well as electron correlation is necessary to obtain reasonably accurate intensity of each vibrational mode. But infrared absorption bands in the experimental spectra are not resolved in large molecules like fluorinated ethyl methyl ethers because of very severe overlapping of the bands due to the presence of C-F bonds. Therefore calculated results were compared to experimental ones not as individual band intensities but as total infrared intensities in the region of 500-2000 cm^{-1}. This region covers the atmospheric window (800-1250 cm^{-1}), which is the most important spectral zone for GWP.6) The principal objective of the present study is to find a reliable method to estimate total infrared intensities of fluorinated ethers in this region with theoretical calculations.

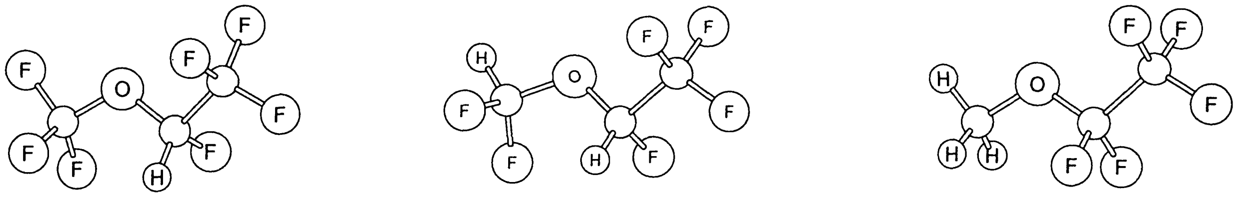
Infrared absorption of five partially fluorinated ethers, HFC-134a, and CFC-11 were measured in gas-phase under the vapor pressure of 1.5 Torr at 296 K. JAS. CO FT/IR-7300 was used to observe the spectra at an instrumental resolution of 1.0 cm^{-1}. Sample gas pressure was measured with an MKS baratron, which covered a pressure range of 10-0.001 Torr. The calculated and experimental total infrared intensities in the region of 500-2000 cm^{-1} are summarized later in Table 2.

Geometry optimizations for these seven fluorinated compounds were performed with Gaussian 92 program with 3-21G, 6-31G, D95V, 6-31G**, D95V**, and 6-31++G** at the Hartree-Fock level. Optimized geometries for five fluorinated ethers with HF/D95V** are shown in Fig. 1, and calculated energies are summarized in Table 1.

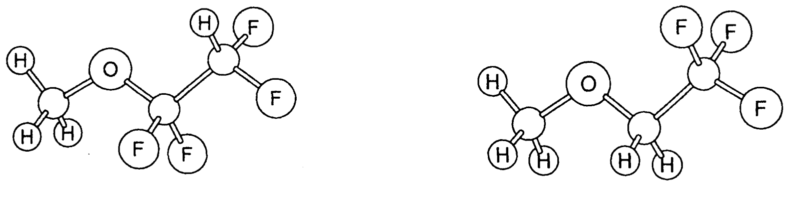
Table1. Calculated Energies (a.u.)

No	Fluorinated Ethers	Number of F Atoms	3-21G	6-31G	D95V	6-31G**	D95V**	6-31++G**
1	$CF_3CHF\text{-}O\text{-}CF_3$	7	-880.3534	- 884.8195	-885.0226	-885.1481	-885.3877	-885.1759
2	$CF_3CHF\text{-}O\text{-}CHF_2$	6	-782.0133	-785.9944	-786.1796	-786.2800	-786.4937	-786.3083
3	$CF_3CF_2\text{-}O\text{-}CH_3$	5	-683.6894	-687.1672	-687.3213	-687.4226	-687.6048	-687.4444
4	$CHF_2CF_2\text{-}O\text{-}CH_3$	4	-585.3530	-588.3403	-588.4767	-588.5550	-588.7113	-588.5767
5	$CF_3CH_2\text{-}O\text{-}CH_3$	3	-487.0250	-489.5083	-489.6182	-489.6974	-489.8236	-489.7142
6	CF_3CH_2F (HFC-134a)	4	-472.0899	-474.5026	-474.6182	-474.6618	-474.7943	-474.6817
7	CCl_3F (CFC-11)	1	-1508.3817	-1515.5831	-1515.5906$^{a)}$	-1515.7116	-1515.7259$^{b)}$	-1515.7196

$^{a)b)}$ D95 and D95* were used instead of D95V and D95V** since D95V and D95V** didn't support chlorine atom.



$CF_3CHF\text{-}O\text{-}CF_3$ $CF_3CHF\text{-}O\text{-}CHF_2$ $CF_3CF_2\text{-}O\text{-}CH_3$



$CHF_2CF_2\text{-}O\text{-}CH_3$ $CF_3CH_2\text{-}O\text{-}CH_3$

Fig. 1. Optimized Geometries for Fluorinated Ethers with HF/D95V**.

The harmonic vibrational frequencies and infrared intensities for these seven fluorinated compounds were calculated at the optimum geometries of each basis set. The calculated frequencies are scaled by a factor of 0.89. Rotational conformers were also calculated for $CF_3CHF\text{-}O\text{-}CHF_2$, $CHF_2CF_2\text{-}O\text{-}CH_3$, and CF_3CH_2-

O-CH_3. The stable conformer of CF_3CH_2-O-CH_3 in this study is consistent with experimetal one determined by an analysis of the microwave spectra.4) It was found that there were no significant differences of total intensities among rotational isomers(3-21G within 8%, 6-31G within 7%, 6-31G** within 6%, other basis sets within 5%). Calculations at MP2/6-31G** level were also performed for only three small fluorinated ethers, CF_3CH_2-O-CH_3, CHF_2CF_2-O-CH_3, and CF_3CF_2-O-CH_3. Calculated total infrared intensities at MP2 level for these three ethers are 991, 1183, and 1541(km/mole), which are in good agreement with the experimental ones.

Table2. Total Infrared Intensities in the Region of 500-2000 cm^{-1} a) (km/mole)

No	Fluorinated b) Ethers	Number of F Atoms	Calculated						Experimental c)
			3-21G	6-31G	D95V	6-31G**	D95V**	6-31++G**	
1	CF_3CHF-O-CF_3	7	2688	2697	2702	2796	2946	2849	2313
2	CF_3CHF-O-CHF_2	6	2022	2135	2164	2286	2410	2340	1855
3	CF_3CF_2-O-CH_3	5	1675	1773	1798	1909	2014	1943	1539
4	CHF_2CF_2-O-CH_3	4	1287	1406	1450	1501	1590	1541	1178
5	CF_3CH_2-O-CH_3	3	1062	1125	1133	1240	1313	1276	967
6	CF_3CH_2F (HFC-134a)	4	857	896	933	1027	1111	1077	861
7	CCl_3F (CFC-11)	1	731	713	734 d)	805	820 e)	773	602
Average Ratio (Calcd./Expt.) f)			1.11	1.15	1.17	1.25	1.32	1.27	

a) The calculated frequencies are scaled by a factor of 0.89.

b) These five fluorinated ethers were synthesized by ourselves with conventional methods. The purities of these fluorinated compounds are more than 99.5% by gas chromatography analysis.

c) All experimental results were within ±2.5% with respect to the average value of each compound.

d)e) D95 and D95* were used instead of D95V and D95V**. There is no significant change of total intensities between these basis sets.

f) Average ratio of calculated total infrared intensities relative to experimental ones of each basis set in the region of 500-2000 cm^{-1}

The relation between the experimental and calculated total infrared intensities with 6-31G and D95V** were shown in Fig. 2. The correlation coefficient of each basis set are summarized in Table 3. There is a linear correlation between the experimental and calculated results even with small basis sets, 3-21G and 6-31G. The calculated results with HF/D95V** show the best linear correlation among basis sets examined in this study. The correlation coefficients are 0.9993 with D95V**, and 0.9955 and 0.9980 even with small basis sets, 3-21G and 6-31G. It seems that the inclusion of diffuse functions has little effect on the correlation coefficient. Total intensities of these seven compounds were also calculated with 6-31G* and D95V*. The addition of polarization functions on hydrogen atoms makes a small improvement on the correlation coefficients. The correlation coefficients of 6-31G* and D95V* are 0.9984 and 0.9988, respectively.

Table 3. Correlation Coefficient

Basis Functions	R (Correlation Coefficient)
3-21G	0.9955
6-31G	0.9980
D95V	0.9981
6-31G**	0.9989
D95V**	0.9993
6-31++G**	0.9991

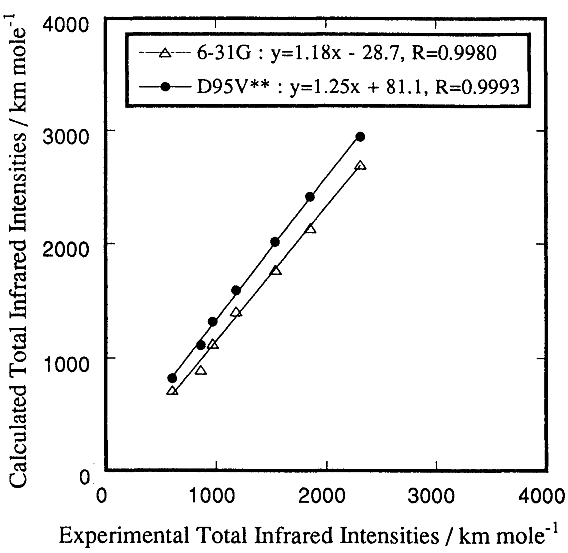


Fig. 2. Relation between Experimental and Calculated Total Infrared Intensities.

The average ratio of the calculated total infrared intensities relative to the experimental values of each basis set are also summarized in Table 2. After scaled by each appropriate factor, 0.90, 0.87, 0.85, 0.80, 0.76, and 0.78, respectively, for 3-21G, 6-31G, D95V, 6-31G**, D95V**, and 6-31++G**, the errors in the calculated intensities are within ± 4% at D95V** and 6-31++G**, within ± 8% at 6-31G** and D95V, and within ± 10% at even small basis sets, 3-21G and 6-31G. It becomes possible by using these factors to estimate total infrared intensities of fluorinated ethyl methyl ethers without using expensive MP2 calculations. Now simple estimation methods are established for both total infrared intensities and atmospheric lifetime of fluorinated ethyl methyl ethers,3) which influence on GWP. The 6-31G basis set is a good compromise between dependable results and computation time, and the D95V** basis set is best for accurate estimation among basis sets examined in this study. In subsequent reports, estimated total infrared intensities of fluorinated ethyl methyl ethers will be presented, and a linear correlation will be examined for fluorinated ethers with four carbon atoms and fluorinated compounds containing other hetro atoms. We acknowledge SHOWA DENKO K.K. and ASAHI GLASS CO.,LTD. for giving us HFC-134a and CFC-11, respectively. We would like to thank Dr. S. Misaki, T. Asawa, S. Kimura, and Y. Oba in Research Institute of Innovative Technology for the Earth, and also thank Kanae Miyashita for her fine infrared absorption measurements. This work was supported by New Energy and Industrial Technology Development Organization (NEDO).

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