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DFT Calculations of Photoabsorption Spectra in the VUV Region for Design of Photoresist Materials for 157 nm Lithography

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Time-dependent density functional theory (TD-DFT) calculations using the B3LYP hybrid functional were performed to investigate the transparencies of organic molecules and polymers in the vacuum ultraviolet (VUV) region. The calculated photoabsorption spectra obtained from the combination of geometry optimization using the 6-311G(d) basis set and subsequent calculations of transition energies and oscillator strengths using the 6-311++G(d,p) basis set agree well with the experimental spectra. This method is a useful to infer the transparency of polymers in the VUV region, and in particular helpful for design of photoresist materials for F_2 lithography (157 nm). The transparencies of the model compounds relating to the representative polymer platforms were estimated, and the calculated spectra demonstrate the effectiveness of judicious introduction of –F and $-CF_3$ groups in reducing optical absorption at the wavelength. In addition, the absorption spectra of model compounds having a sulfonyl fluoride ($-SO_2F$) and sulfonyl ester ($-SO_2OR$) groups, which were proposed by the present authors as novel resist platforms, were calculated and compared with the experimental spectra of corresponding homopolymers.

Keywords / Time-dependent density functional theory / Photoabsorption spectra / VUV lithography / Transition energy / Photoresist-materials

1. Introduction

The most important factor in the design of photoresist materials for F_2 lithography is the transparency of the polymer platforms at a wavelength of 157 nm. Bloomstein *et al*. have shown that organosiloxanes and fluorinated hydrocarbons are relatively transparent in the vacuum ultraviolet (VUV) region and are possible candidate platforms [1]. Crawford *et al*. have reported that a copolymer of tetrafluoroethylene and norbornene shows a low absorbance (1.3 μm^{-1}) at 157 nm for a 1:1 ratio [2]. Significant efforts have been devoted to developing resist materials, such as polymers based on fluorinated methylmethacrylate [3] and alicyclic [4] and styrenic [5] monomers substituted with hexafluoroisopropanol. The research group of Willson *et al*. recently reported the gas phase photoabsorption spectra of a series of model compounds to guide the modular development of photoresist systems for use at 157 nm [5-7]. Substituent interactions have been demonstrated to induce substantial shifts in the spectra of a wide range of materials including alcohols, esters, acrylates, aromatics, and alicyclics. However, it is generally difficult to predict how substituents affect the absorbance of molecules because the introduction of such substituents significantly affects energy levels and spatial distributions of occupied and unoccupied molecular orbitals. Dammel *et al*. have proposed an empirical increment scheme to estimate absorption of polymers at 157 nm ('STUPID' model) [8]. However, as they mentioned, such a simple approach cannot describe all aspects of absorptivity. There has been a strong demand for useful tools for calculating absorption spectra in the VUV region and/or predicting absorbances at 157 nm. Matsuzawa *et al*. demonstrated that time-dependent density functional theory (TD-DFT) calculation is useful to aid in the design of transparent materials [9-11]. In their calculations, the transition energies of the molecules had been adjusted using empirical equations because the employed methods exhibited systematic errors over a wide range of wavelengths (80–310 nm). Most recently, we have shown that the TD-DFT calculations using the 6-311++G(d,p) basis set can reproduce well observed spectra of model compounds without incorporation of empirical corrections [12]. In this study,

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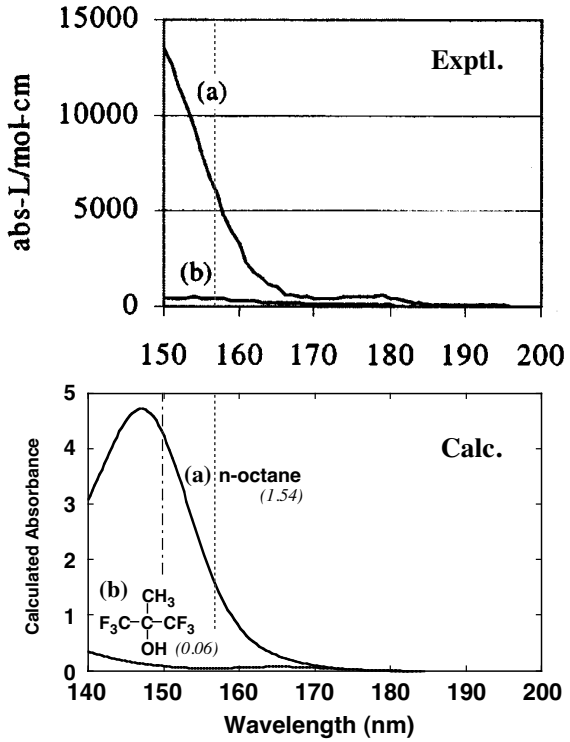

Fig. 1 Experimental [7] and calculated spectra of (a) *n*-octane and (b) 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (HMP). The calculated values of absorbance at 157 nm are indicated in parentheses.

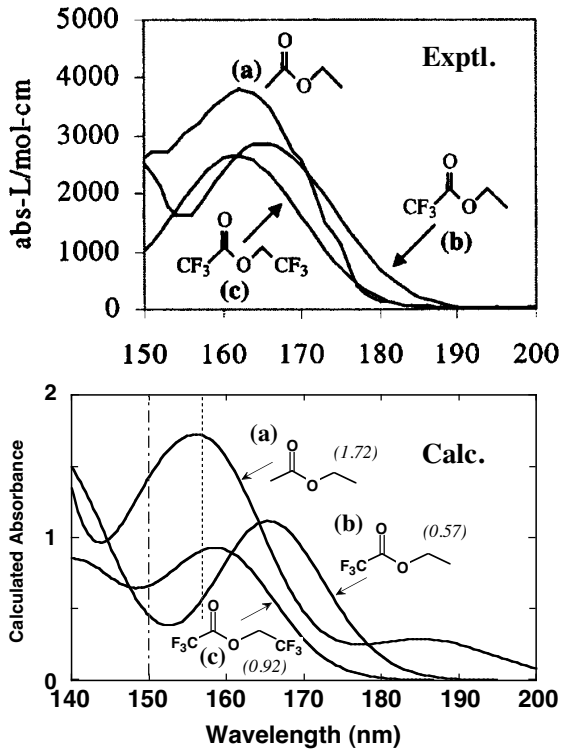

Fig. 2 Experimental [7] and calculated spectra of unsubstituted and fluorine substituted ethyl acetates.

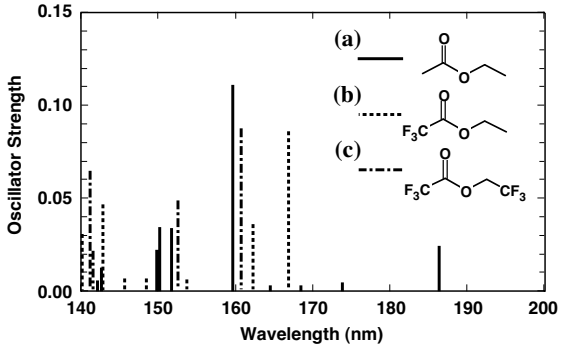

Fig. 3 Calculated oscillator strengths of unsubstituted and fluorine substituted ethyl acetates.

we extend our investigation to the calculations of model compounds of conventional and newly proposed resist platforms.

2. Method

We focus our interest on the degree of agreement between the experimental and calculated absorption spectra in a certain narrow range of VUV region (140–200 nm). The 6-311G(d) basis set was used for geometry optimizations under no constraints, and the 6-311++G(d,p) basis set was used for calculations of transition energies and oscillator strengths at the TD-DFT level [12] using the three-parameter Becke-style hybrid functional (B3LYP) [13]. No empirical corrections were incorporated into the estimation of transition energies. All the calculations were performed using the program of Gaussian-98 (Rev.A9 & A11)[14] on a Compaq Alpha server GS320. Each calculated transition was replaced by a Gaussian broadening function with a full width at half height (FWHH) of 0.35 eV so as to reproduce the shapes of experimental spectra. The calculated absorbance was represented by the oscillator strength divided by the van der Waals volume (nm^3) of molecules. The van ver Waals volumes were calculated from the optimized geometries using the Slonimski's method [15], in which the van der Waals radii of atoms reported by Bondi [16] were used.

3. Results & Discussion

3.1 *Verification of the Calculation Method*

Fig. 1 shows the experimental [7] and calculated spectra of *n*-octane and 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (HMP). The calculated values of absorbance at 157 nm are indicated in parentheses. These are the model compounds of hydrocarbon polymers and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) functionality, respectively. The strong absorption of *n*-octane and the very low absorption of HMP at 157 nm are well reproduced in the calculated spectra. The former fact agrees with the substantial absorptions of hydrocarbon polymers at the wavelength. Although the selection of the width of broadening function is arbitrary and it affects the lineshapes of skirts, the absorption edge of *n*-octane

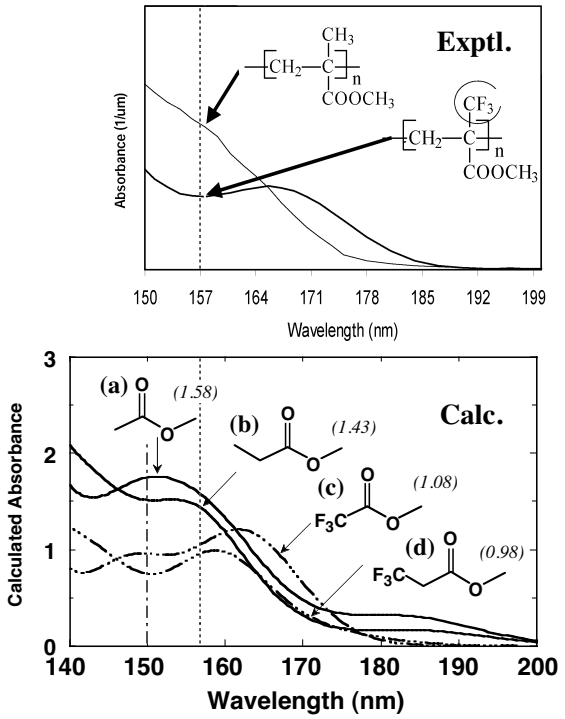

Fig. 4 Experimental spectra of PMMA and PMTFMA [17], and calculated spectra of the model compounds of PMMA and PMTFMA.

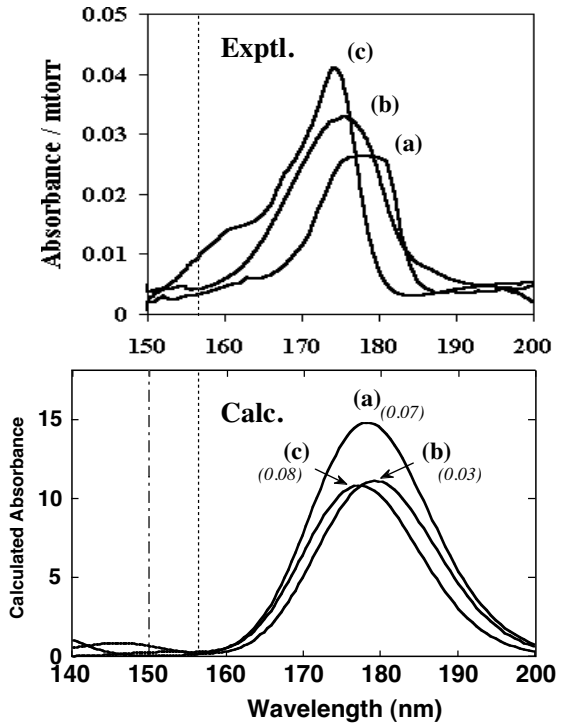

Fig. 5 Experimental [6,17] and calculated spectra of (a) benzene, (b) trifluorobenzene, and (c) hexafluorobenzene.

is well reproduced under the present condition.

Fig. 2 shows the experimental [7] and calculated spectra of unsubstituted and fluorine-substituted ethyl acetates. The peak positions and absorption edges of the compounds in the calculated spectra agree well with the observed spectra. When ethyl acetate (a) is taken as a standard, remarkable features of the experimental spectrum of ethyl trifluoroacetate (b) are an absorption window located around 155 nm and a bathochromic shift of the absorption edge by ca.5 nm. Another interesting feature is that the spectrum of 2,2,2-trifluoroethyl trifluoroacetate (c) is similar to that of ethyl acetate, not to that of ethyl trifluoroacetate. These situations are also well reproduced in the calculations. Fig. 3 shows the calculated oscillator strength of each transition for these compounds. The strongest transitions appearing at 159.6 nm for (a), 166.8 nm for (b), and 160.9 nm for (c) are assigned to the $\pi \rightarrow \pi^*$ transitions at the COO moieties. The peak displacement of (b) in Fig. 2 is well characterized by the bathochromic shift of this transition and by the absence of transition around 150 nm. The $\pi \rightarrow \pi^*$ transition in (a) is effectively displaced to a longer wavelength by the trifluorination of α-methyl group. On the other hand, the secondly strongest transitions at 186.3 nm for (a), 162.3 nm for (b), and 152.7 nm for (c) are mainly assigned to the $n \rightarrow 3s$ transitions, which are from a lone pair orbital at carbonyl oxygen to a spatially spreading Rydberg-type orbital. These transitions are significantly displaced to shorter wavelengths by fluorination.

Fig. 4 shows the experimental spectra [17] of polymethyl methacrylate (PMMA) and poly(methyl α-trifluromethylacrylate) (PMTFMA) together with the calculated spectra of (a) methyl acetate, (b) methyl propionate, (c) methyl trifluoro-acetate, and (d) methyl-3,3,3-trifluoropropionate as model compounds. The higher absorption at 157 nm for PMMA, and the shoulder peak (165 nm) and the shallow window (155 nm) for PMTFMA agree well with the calculated spectra of (b) and (d). Although the α-trifluorination of PMMA significantly decreases the absorption at 157 nm as reported by Brodsky *et al*.[7] and Ito *et al*.[18,19], the calculated absorptions of (c) and (d) are only 20-30 % smaller than those of (a) and (b). For estimating absorbance in the solid state, calculated oscillator strengths should be divided by molecular volume. It is well known that fluorinated substituents decrease molecular polarizability and weaken intermolecular interactions. The decreases in refractive indices and dielectric constants caused by fluorine substitutions can be assigned to local electronic polarization and fractional free volume effects. Hence, fluorinated compounds have larger molecular volumes than those expected from their van der Waals volumes, and this further reduces the absorbance.

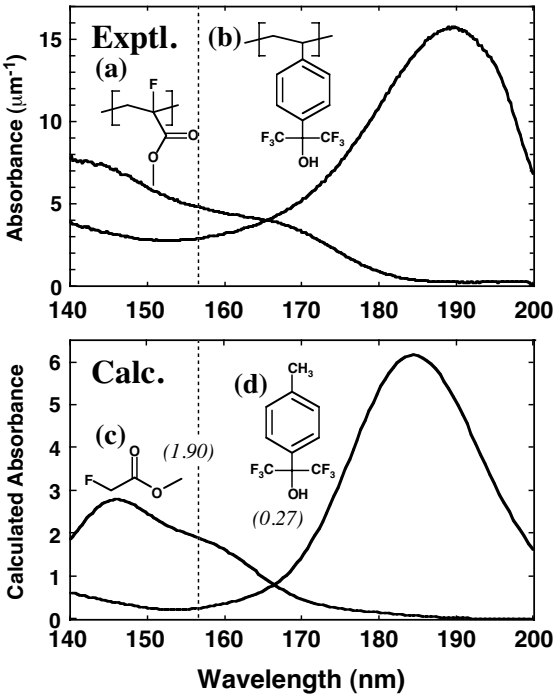

Fig. 6 a) Experimental spectra of poly(methyl α-fluoroacyrate and polystyrene substituted with hexafluoroisopropanol [21] and b) calculated spectra of their model compounds.

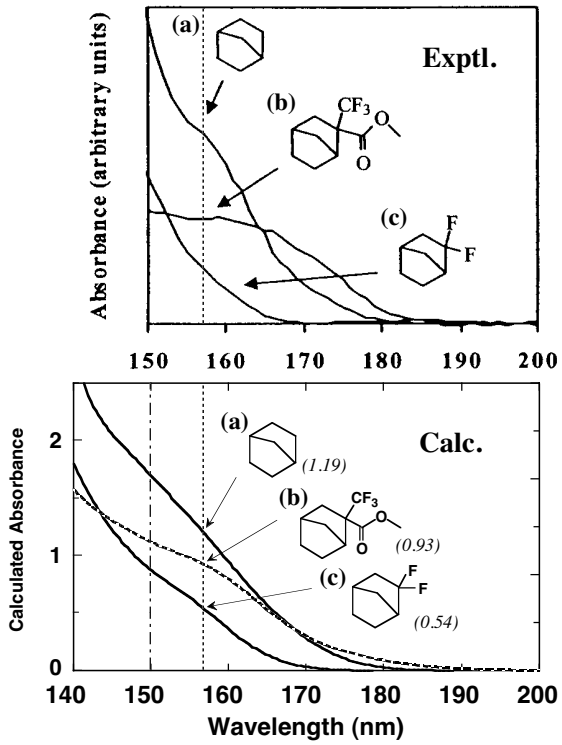

Fig. 7 Experimental [5] and calculated spectra of norbornane, TFNCM, and 2,2-difluoronorbornane.

Fig. 5 shows the experimental [6,17] and calculated spectra of benzene and fluorinated benzenes. The absorption peaks around 178 nm in the calculated spectra, which correspond to the π→π* transitions, are much broader than those in the experimental spectra. Although the average width of three major absorption peaks of benzene was reported as 0.2 eV [20], we applied Gaussian functions with a FWHH of 0.35 eV to predict spectral shapes of polymers. The hypsochromic shifts of C_6F_6 compared with benzene is well reproduced, whereas the similar shift of $C_6F_3H_3$ is not reproduced. The calculated spectra indicate that the absorptions of these aromatic compounds are not to be so high at 157 nm despite the very strong π→π* absorptions at the longer wavelengths. However, the experimental spectra of all the aromatic compounds in Fig. 5 show asymmetric xshapes due to the long skirt to shorter wavelengths. In particular, this causes significant absorption for C_6F_6 at 157 nm.

Fig. 6 shows the experimental spectra of (a) poly(methyl α-fluoroacrylate) and (b) polystyrene substituted with HFIP group [21] together with the calculated spectra of their model compounds. The spectrum (a) indicates that α-monofluorination is not effective in reducing the absorption of PMMA. This is well supported by calculated spectra as described below. On the other hand, the value of 0.35 eV for FWHH is reasonable for reproducing the spectral shape of (b). The spectrum (b) also shows a long skirt to shorter wavelengths, and this causes a significant absorption at 157 nm. The origin of the skirt, which results in the asymmetric shapes of the spectra for aromatic compounds, is unclear at present.

Fig. 7 shows the experimental [5] and calculated spectra of norbornane, 2-trifluoromethyl-norbornene-2-carboxylic acid methyl ester (TFNCM), and 2,2-difluoronorbornane. The spectral shapes and absorption edges are well reproduced in the calculated spectra. The incorporation of fluorines into norbornane displaces the absorption edges to shorter wavelengths, and thus the absorbances at 157 nm are effectively reduced. In contrast to the aromatic and ester compounds, the absence of absorption peaks above 157 nm is a big advantage of norbornane structure. The incorporation of $-CF_3$ and methyl ester in (b) generates a shoulder at 160–165 nm, which is similar to the calculated spectra of compounds (c) and (d) in Fig. 4.

Fig. 8 shows the experimental spectra of PMTFMA and polynorbornenes substituted with HFIP and its *tert*-Boc ester [5] together with the calculated spectra of their model compounds. Polymer (c) is one of the most attractive candidates for future resist platforms, and the calculated spectrum (e) agrees well with the experimental spectrum. On the other hand, although the spectral shapes of (a) and (d) are similar to each other, the absorption peak

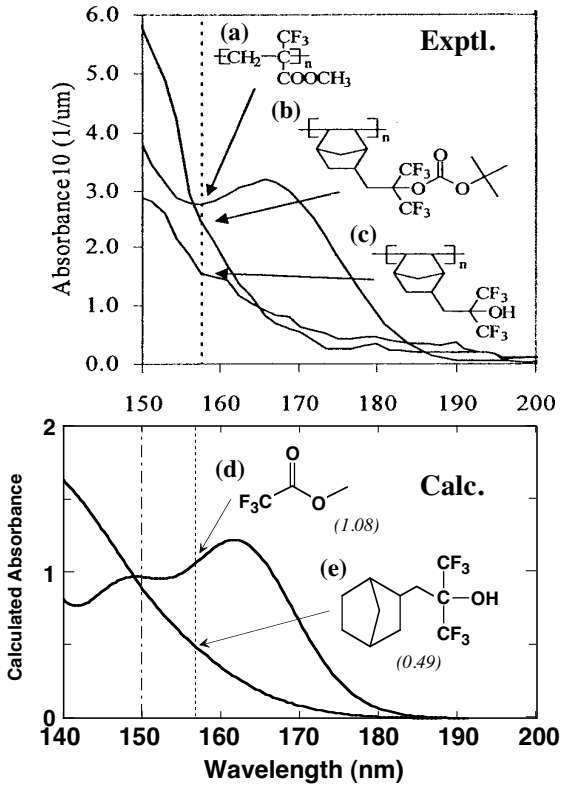

Fig. 8 a) Experimental [5] spectra of PMTFMA, polynorbornenes substituted with *t*-Boc hexafluoro isobutanol and hexafluoroisobutanol and b) calculated spectra of the corresponding model compounds.

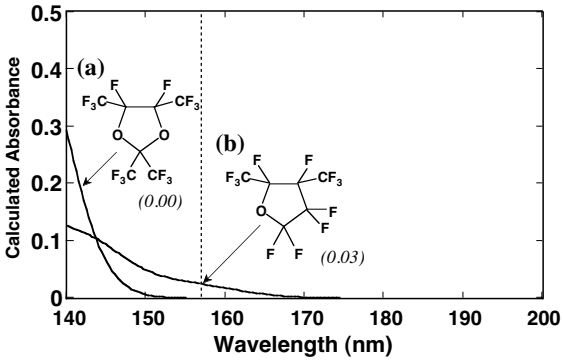

Fig. 9 Calculated spectra of model compounds of amorphous perfluoropolymers. (a) Teflon-AF and (b) Cytop.

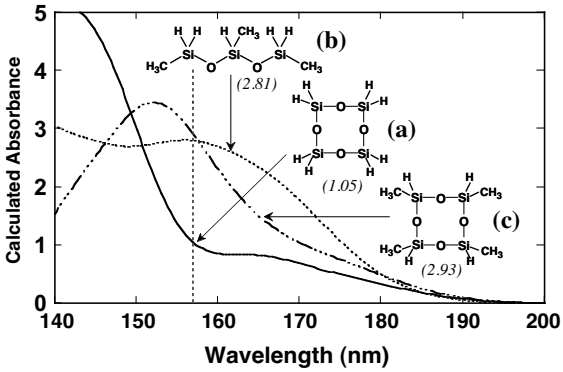

Fig. 10 Calculated spectra of model compounds of poly(methylsiloxane) and polysilsesquioane.

and edge of (d) are displaced to shorter wavelengths by ca.5 nm than those of (a).

As a consequence, the comparison between the experimental and calculated spectra in Figs. 1–8 indicates that the calculation method used in this study has good ability to reproduce absorption spectra of small molecules, and one can infer absorption spectra of polymers by choosing appropriate model compounds.

3.2 *Calculation of Photoabsorption Spectra of Model Compounds for Photoresist Platforms*

Fig. 9 shows the calculated spectra of model compounds of perfluorinated amorphous polymers, Teflon-AF and Cytop. The calculated absorbance of these compounds at 157 nm are more than one order of magnitude smaller than those of esters, aromatics, and norbornanes. The high transparency of Teflon-AF [1] is well understood from the spectra. On the other hand, Si–O linkages have been reported to be transparent at 157 nm [1]. Fig. 10 shows the calculated spectra of model compounds of poly(methylsiloxane) (PMS) and poly(silsesquioxane). The model of polyhydridosilsesquioxane (a) shows a low absorption at 157 nm, whereas those of PMS (b) and polydimethylsilsesquioxnxane (c) show much higher absorptions at the wavelength. This indicates that side groups should be carefully chosen to obtain transparent polymers having –Si–O– main chains.

Fig.11 shows the calculated spectra of unsubstituted and fluorine-substituted acetic acid and propionic acid and their methyl, ethyl, and *tert*-butyl esters. For all of the esters, the absorption peaks at 150–160 nm observed for unfluorinated compounds are shifted to longer wavelengths by fluorine substitutions, and thus absorption windows appear at 150–155 nm. This is supported by the fact that α-trifluorination straightforwardly reduces the observed absorbances at 157 nm as mentioned for Figs. 2 and 4. The general trend of the calculated absorbance in a decreasing order is $CFH_2COOR > CH_3COOR > C_2H_5COOR > CF_3CH_2COOR > CF_3COOR$. As seen in Fig. 6, monofluorination does not reduce absorbance of unfluorinated compounds. In contrast, the absorption peaks and edges of CF_3COOR are located at the longest wavelengths in all the esters. Figs. 2, 4, and 11 demonstrate the effectiveness of the judicious introduction of $–CF_3$ group and support the good transparency of poly(MTFMA) at 157 nm [18,19].

Fig.12 shows the calculated spectra of the esters of propionic acid (a-d) and 3,3,3-trifluoropropionic acid (e-h). The general trend of the calculated ab-

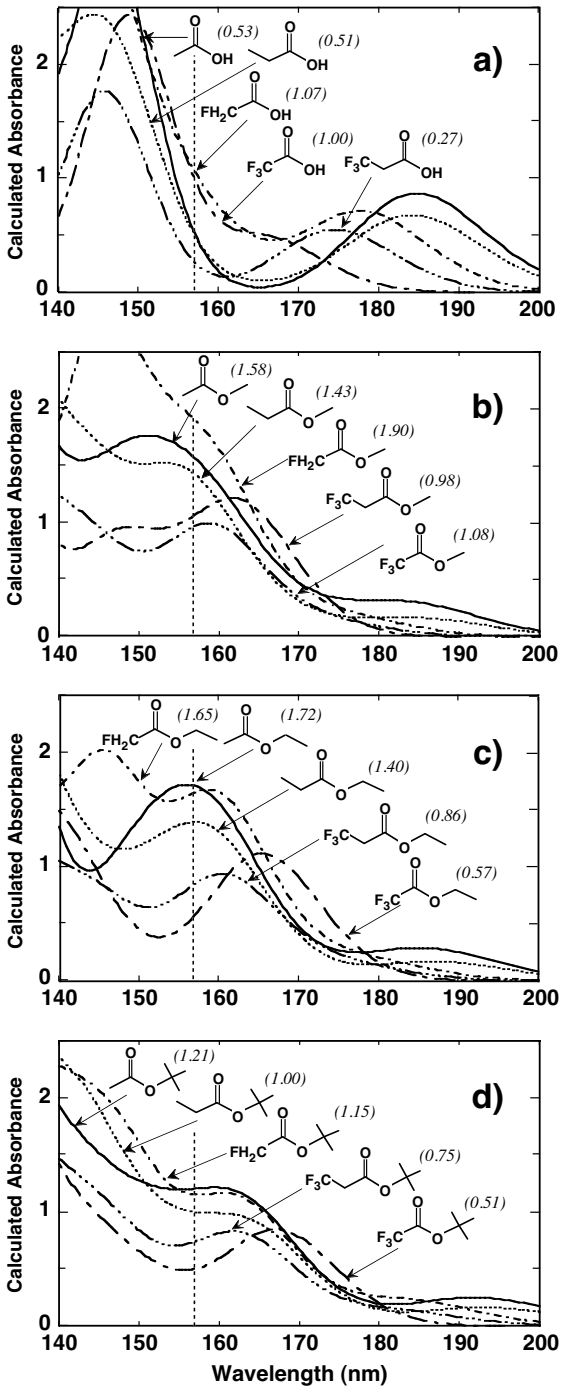

Fig. 11 Calculated spectra of a) unsubstituted and fluorine substituted carboxylic acids and their b) methyl esters, c) ethyl esters, and d) *tert*-butyl esters.

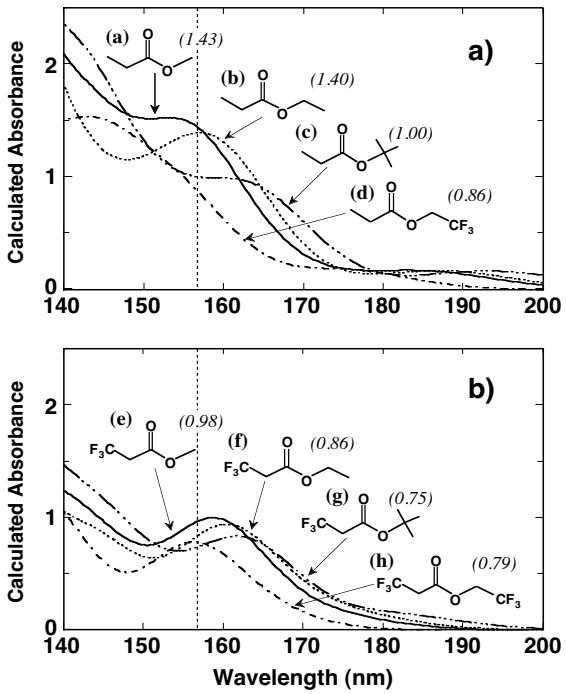

Fig. 12 Calculated spectra of methyl, ethyl, *t*-butyl, and 2,2,2-trifluoroethyl esters of a) propionic acid and b) 3,3,3-trifluoro-propionic acid.

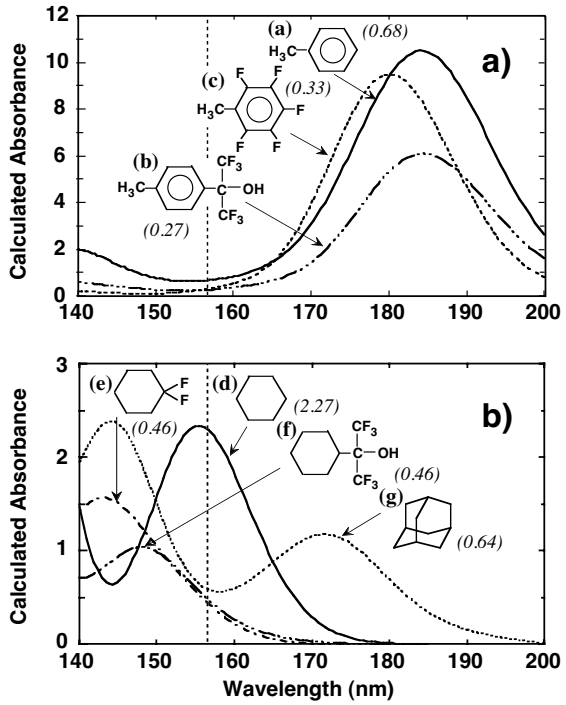

Fig. 13 Calculated spectra of a) aromatic compounds and b) alicyclic compounds.

sorbance in a decreasing order is $RCOOCH_3$ > $RCOOC_2H_5$ > $RCOOC(CH_3)_3$ > $RCOOCH_2CF_3$. The first incorporation of $-CF_3$ group into unfluorinated compounds (*e.g.* (a), (b)→(e), (d)) is very effective in reducing the absorbance at 157 nm, but the second incorporation, (d)→(h), is less effective.

Fig.13 shows the calculated spectra of aromatic and alicyclic compounds. The absorptions originating from the aromatic π→π* transitions (180–185 nm) are very strong. Although these absorptions have small effect at 157 nm in the calculated spectra, aromatic compounds and polymers usually exhibit high absorption at the wavelength due to the asymmetric broadening of the absorption peaks as described above. The incorporation of HFIP group in (b) effectively reduces the peak height. This can be ascribed to the significant increase in the van der

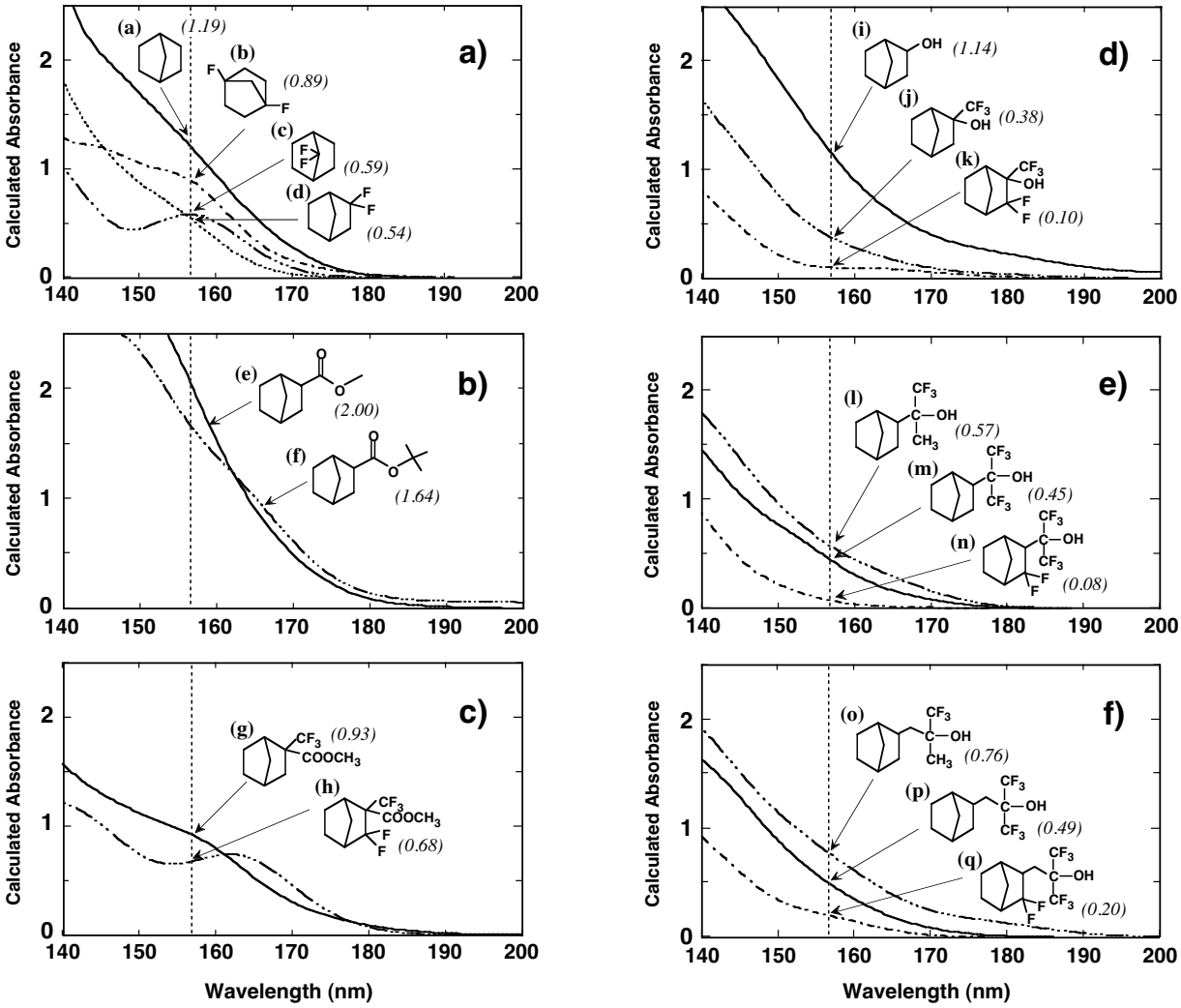

Fig. 14 Calculated spectra of unfluorinated and fluorinated norbornanes and their derivatives.

Waals volume (V_{vdw}), which is called 'dilution effect'. The V_{vdw} of (b) is 88 % larger than that of (a). In contrast, the perfluorination of aromatic ring in (c) is not as effective as the incorporation of HFIP, though the absorption peak is slightly displaced to a shorter wavelength. The similar spectral shapes of (a)–(c) indicates that the incorporation of fluorines does not cause significant change in the electronic states relating to the $\pi \rightarrow \pi^*$ transitions. On the other hand, fluorinated alicyclic compounds, (e) and (f), show very low absorptions at 157 nm. The large absorption peak of cyclohexane is significantly reduced and displaced to shorter wavelengths by the difluorination or incorporation of HFIP. In contrast to the aromatic compounds, the fluorine substitutions give substantial influence to the electronic structures of such alicyclic compounds. A similar effect was also observed for norbornanes (Fig. 7). In addition, another fundamental alicyclic compound, adamantane, shows a low absorption at 157 nm due to a window located around 158 nm.

Fig. 14 shows the calculated spectra of norbornane and its derivatives. The incorporation of geminal difluoride substitution on the two carbon bridge of norbornane was reported to decrease the absorption by 71% at 157 nm in the gas phase [7]. The calculations indicate that the incorporation of two fluorines into 2,2-position reduces the absorbance more effectively than into 7,7- and 1,4-positions, which agree well with the experimental results [22]. Although the incorporation of methyl ester and *tert*-butyl ester at 2-position significantly increases the absorption (Fig.14b), additional incorporation of $-CF_3$ and F_2 significantly lowers the absorbance (Fig.14c). In contrast, hydroxyl group does not change the absorption of norbornane (Fig.14d), and the incorporation of $-CF_3$ and F_2 significantly reduces the absorption. In a similar manner to the case of fluorine substitution of cyclohexane (Fig.13b), the incorporation of 1,1,1-trifluoro-2-isopropanol (TFIP) (l), HFIP (m), 1,1,1-trifluoro-2-methyl-butan-2-ol (o), and 1,1,1-trifluoro-2-trifluoromethyl-butan-2-ol (p) in Figs.14e and 14f significantly reduce the absorption of norbornane. The former two groups (l and m) are

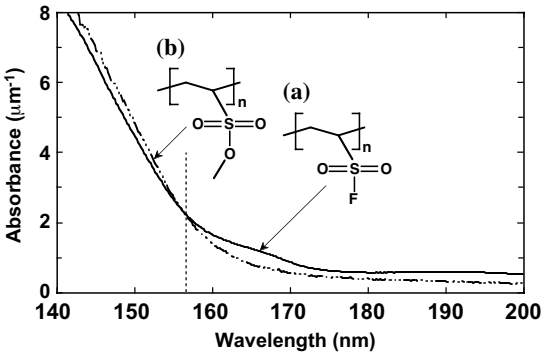

Fig. 15 Experimental spectra of (a) poly(vinylsulfonyl fluoride)[23] and (b) poly(vinylsulfonyl methylester)[24].

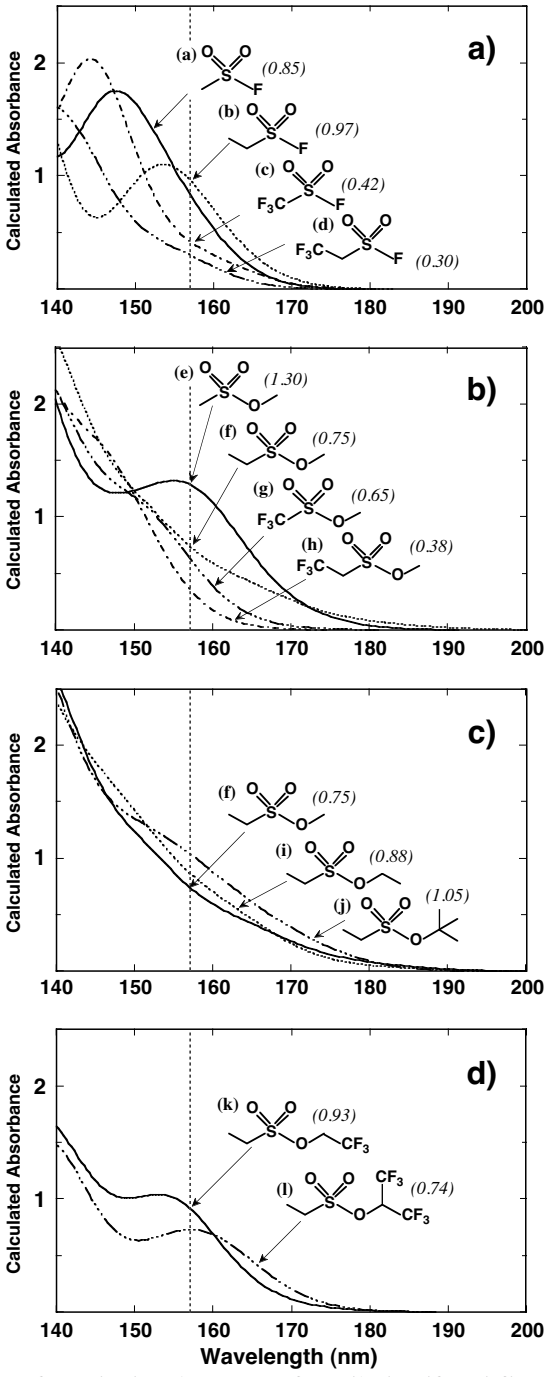

Fig. 16 Calculated spectra of a) alkyl sulfonyl fluorides and b)–d) alkyl sulfonyl esters.

more effective than the latters (o and p) due to the absence of methylene unit in the side chain. Note that additional incorporation of difluoride at 3-position in (n) and (q) further reduces the absorption.

The present authors have recently reported that poly(vinyl sulfonyl fluoride)(PVSF) [23] and poly(vinylsulfonyl methylester) (PVSM) [24] show low absorbance (2.1 and 2.2 μm^{-1}) at 157 nm. Since these polymers can be prepared by radical polymerization using AIBN as an initiator, they can be regarded as promising photoresist platforms. Fig. 15 shows the experimental spectra of these polymers, and Fig. 16 shows the calculated spectra of their model compounds. The absorbances of these polymers in the VUV region is lower than those of conventional polyacrylates and aromatic polymers. The experimental spectra of the two are very similar to each other, and no strong peaks are observed above 150 nm. This situation is similar to that of norbornane derivatives. The calculated spectra of the model compounds of PVSF ((a) and (b) in Fig.16a) exhibit peaks at 144 and 148 nm, which does not agree with the experimental spectrum, though the relatively low absorbance at 157 nm and the absorption edge (170 nm) are reproduced. The calculated spectra of (c) and (d) indicate the significant effects of fluorine substitution in reducing the absorbance at 157 nm. The comparison between Fig.11b and Fig.16b, and that between Fig.12a and Fig.16c indicate that the calculated absorbances of sufonyl esters (RSO_2OR') are significantly lower than those of the corresponding carbonyl esters (RCOOR'). This originates from the absence of $\pi \rightarrow \pi^*$ transitions in -SO_2O- moiety. In addition, it should be note that the compounds (d) and (h) in Fig. 16, which have -CH_2CF_3 moieties, show lower absorbances at 157 nm than (c) and (g) that have directly bonded -CF_3 moieties. This situation is different from the case of carbonyl esters. Since the calculated spectrum of (f) agrees with the experimental spectrum of PVSM, $C_2H_5SO_2O$- is taken as the skeletal structure of model compounds for estimating the influence of substituents. The calculated spectra of (g), (k), and (l) indicate that the effect of fluorine incorporation into sulfonyl esters is not as significant as the cases of carbonyl esters, norbornanes, cyclohexanes, and polyacrylonitrioles. Only compound (h) exhibits a very low absorbance at 157 nm. Furthermore, Fig.16c indicates that the structure of alkyl substituents in $C_2H_5SO_3R$ does not have significant effect on these calculated spectra, and these spectral shapes are similar to the experimental spectra of PVSM.

Shirai *et al*.[25] have reported that copolymers containing polyacrylonitrile (PAN) and

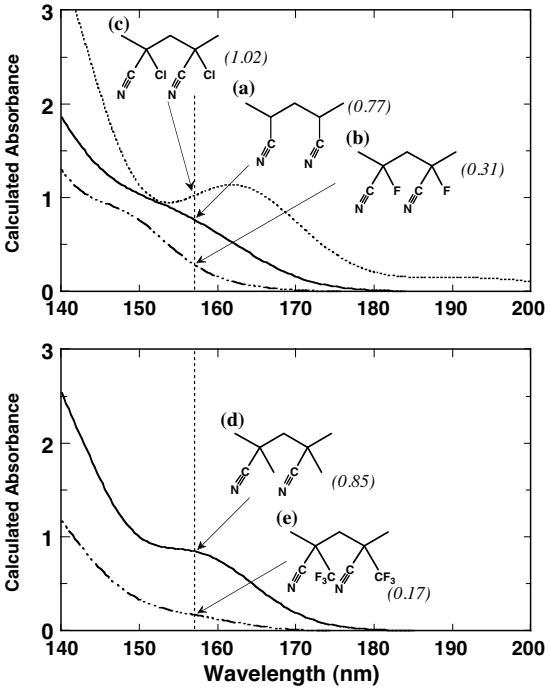

Fig. 17 Calculated spectra of model compounds of (a) polyacrylonitrile, (b) fluorine- and (c) chlorine-substituted polyacrylonitrile, (d) polymethacrylonitrile, and (e) CF_3-substituted polyacrylonitrile.

polymethacrylonitrile (PMN) exhibit relatively low absorbance at 157 nm. Fig. 17 shows the calculated spectra of model compounds of PAN, PMN and fluorine-, chlorine-, and -CF_3 substituted polyacrylonitrile. These compounds exhibit inherently low absorptions at 157 nm due to the high electron-withdrawing property of cyano group. In particular, the fluorine and -CF_3 substitutions are very effective in reducing the absorption.

Fig. 18 shows the calculated spectra of model compounds of protecting groups including HFIP moiety. The compound (b), which was recently proposed by Willson *et a1*. [17,26], is expected to show low absorbance at 157 nm. In addition, these groups can be used in dissolution inhibitors. The calculated spectra indicates that the absorbance at 157 nm will be significantly reduced by substituting (b) for (a). The low absorbance of (b) is due to the absence of carbonyl group.

4. Conclusions

The photoabsorption spectra of organic molecules in the VUV region were calculated using TD-DFT theory. The spectra obtained from the combination of geometry optimization using the 6-311G(d) basis set and subsequent calculations of transition energies and oscillator strengths using the 6-311++G(d,p) basis set agree well with the experimental spectra. The transparencies of the model compounds relating to the representative polymer platforms were estimated. The calculated spectra demonstrate the effectiveness of judicious introduction of –F and –CF_3 groups in reducing optical absorption at 157 nm. Significant effects of fluorine substitution are exhibited for carbonyl esters, cyclohexanes, norbornanes, and acrylonitriles. The experimental spectra of polymers and the calculated spectra of model compounds having a sulfonyl fluoride (-SO_2F) and sulfonyl ester (-SO_2OR) groups indicates that these functional groups are promising for novel photoresist platforms having low absorption at 157 nm. The calculation method used in this study is a powerful tool to infer the transparency of polymers in the VUV region, and in particular helpful for design of photoresist materials for F_2 lithography.

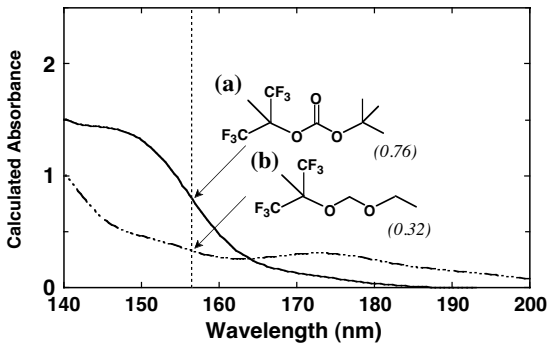

Fig. 18 Calculated spectra of model compounds of fluorine-containing protecting groups.

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