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DFT Calculations of Photoabsorption Spectra for Alicyclic and Heterocyclic Compounds in the VUV Region

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Time-dependent density functional theory (TD-DFT) calculations using the B3LYP hybrid functional were performed to predict transparencies of alicyclic and heterocyclic compounds in the vacuum ultraviolet (VUV) region. Model compounds of conventional and novel polymer platforms for F_2 lithography (157 nm) are devoted for calculations, and the calculated spectra demonstrate very low absorbance of highly fluorinated alicyclic and heterocyclic compounds and also show the effectiveness of introduction of $-F$ and $-CF_3$ groups in reducing the optical absorption at the wavelength. In particular, devised fluorination, such as $-CF_3$ in close proximity of light-absorbing ester functionality, can significantly reduce the absorption of polymer platforms containing norbornane, γ-lactone, and δ-lactone strcutures.

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

1. Introduction

One of the most important factors in the design of photoresist materials for F_2 lithography is the transparency of polymer platforms at the wavelength of 157 nm. We have recently shown that the time-dependent density functional theory (TD-DFT) [1-3] calculations can reproduce well the observed spectra of model compounds for polymer platforms without incorporation of empirical corrections [4-7]. TD-DFT, which is a ground state theory, is now well known as a rigorous formalism within the DFT theory, and a molecular formulation was recently introduced [8,9]. The combination of efficiency, computational cost, as well as precision, *i.e.*, a few tenths of eV, even for high-excited or Rydberg states, make TD-DFT very attractive [10]. In addition, the method developed by the authors [4] to generate absorption spectrum from calculated transition energies and oscillator strengths is useful to infer transparency of polymers in the VUV region, and in particular helpful for design of photoresist materials for F_2 lithography [6,7]. In this study, we extend our investigations to the calculations of alicyclic and heterocyclic model compounds for conventional and newly proposed photoresist platforms. In particular, we examine the effect of fluorines and $-CF_3$ groups as '*absorption quenchers*' which cause significant reduction in absorbance at 157nm.

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 TD-DFT level of theory with the three-parameter Becke-style hybrid functional (B3LYP) [11] was adopted, and a 6-311G(d) basis set was used for geometry optimizations under no constraints. All the calculations were performed using the software of Gaussian-98 (Rev.A11)[12] on a Compaq Alpha server GS-320. For reproducing the shapes of experimental spectra, each calculated tran-

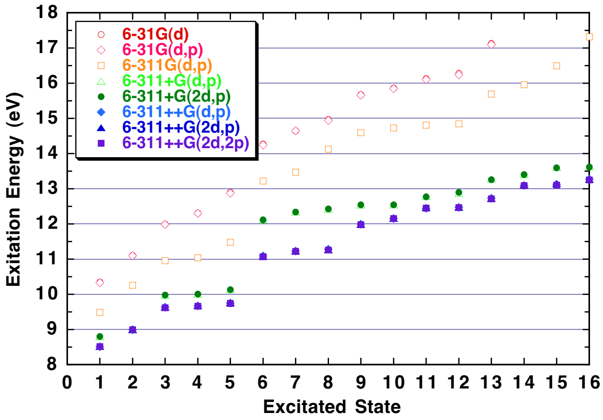

Fig. 1 Calculated excitation energies for fluoromethane by the DFT theory (B3LYP) with different basis-sets. The molecular geometry was optimized by B3LYP/6-311G(d,p).

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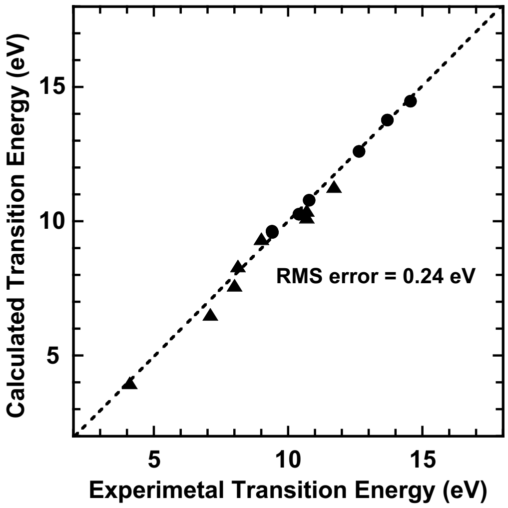

Fig. 2 Experimental versus calculated transition energies for formaldehyde (triangles) and fluoromethanes (circles).

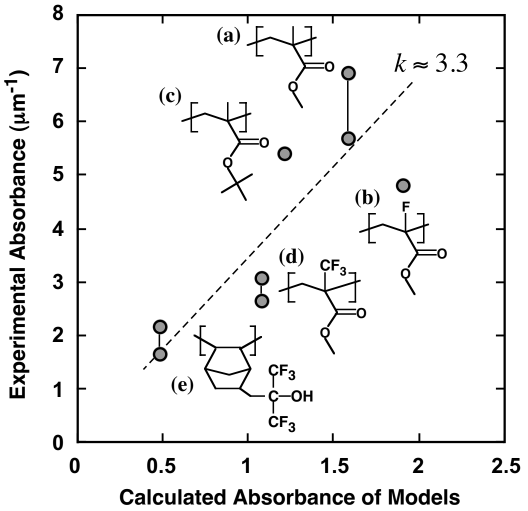

Fig. 3 Experimental absorbances of polymers versus calculated absorbances of model compounds. The experimental values of absorbance were taken from the ref.[19] for (a), [20] for (a), (d), (e), [21] for (b), [22] for (c), and [23] for (d), (e).

sition was replaced by a Gaussian broadening function with a full width at half height of 0.35 eV. The calculated absorbance was represented by a oscillator strength divided by a van der Waals volume (nm^3) of molecule. Van ver Waals volumes were calculated from optimized geometries using the Slonimski's method [13], in which the van der Waals radii of atoms reported by Bondi [14] were used.

3. Results & Discussion

3.1 *Basis-set Dependence on Excitation Energies*

As part of further validation of the calculation method, we estimated which basis-set gives the most reliable results for fluorinated compounds. Fig. 1 shows the calculated one-electron excitation energies for fluoromethane with different basis sets. The excitation energies obtained by two large basis sets, 6-311+G(d,p) and 6-311+G(2d,p) and those by three very large basis sets, 6-311++G(d,p), 6-311++G(2d,p), 6-311++G(2d,2p), give very similar results to each other. This fact indicates that, firstly, the addition of second *d*-function on heavy atoms and second *p*-function on hydrogens makes no differences, but secondly, the addition of a diffuse-function on hydrogens is important. The experimental transitions estimated from photoabsorption spectrum were 9.4, 11.4, and 13.7eV [15,16], and these values are well reproduced by the very large basis sets. The corresponding energies obtained from a 6-311++G(d,p) are 9.63eV (*f*=0.017), 11.23eV (*f*=0.028), and 13.41eV (*f*=0.184).

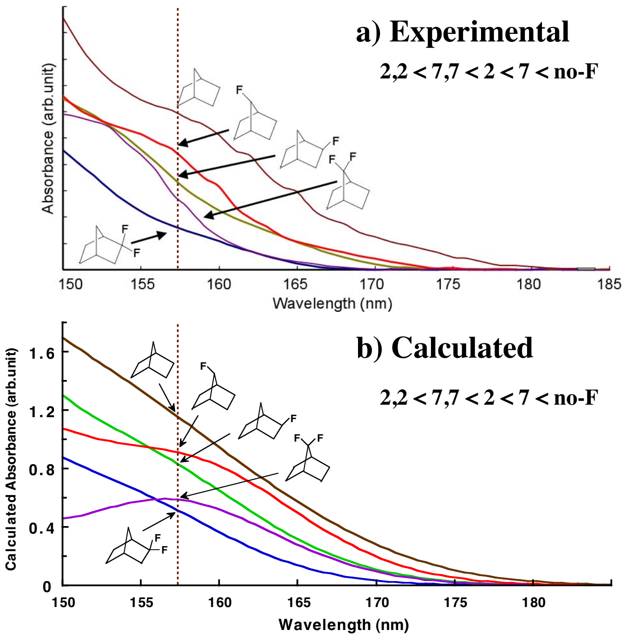

Fig. 4 Experimental [24] and calculated spectra of unsubstituted and fluorine-substituted norbornanes.

Fig. 2 shows relationships between the experimental and calculated transition energies for formaldehyde and fluoromethanes (CFH_3, C_2F_2, CF_3H and CF_4). The estimated rms error, 0.24 eV, is comparable to the value of 0.28eV obtained by a highly precise theoretical method, namely SAC-CI [17,18]. Fig. 3 shows the plots of the experimental absorbances of representative polymer platforms [19–23] versus the calculated absorbances of the corresponding models. Although the width of broadening function is arbitrary and it affects the lineshapes of skirts, the estimated absorbances are well estimated under the present condition. Hence, we decided to use hereafter 6-311++G(d,p) basis set. The slope of the linearly fitted line in Fig. 3 is ca.3.3.

Fig. 4 shows the experimental [24] and calculated spectra of norbornane and fluorinated norbornanes.

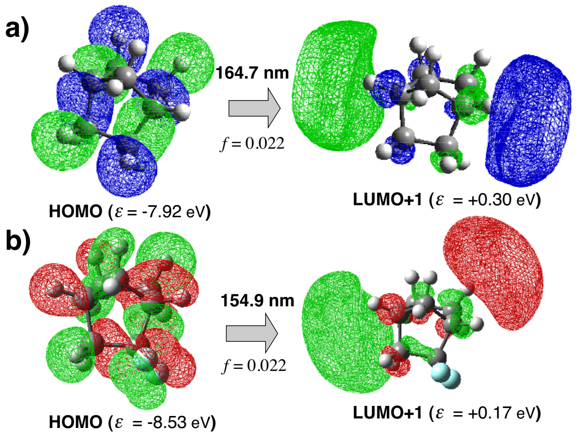

Fig. 5 Calculated wavelengths and oscillator strengths (*f*) of the most dominant transition on the absorbance at 157 nm for a) norbornane and b) 2,2-difluoronorbornane.

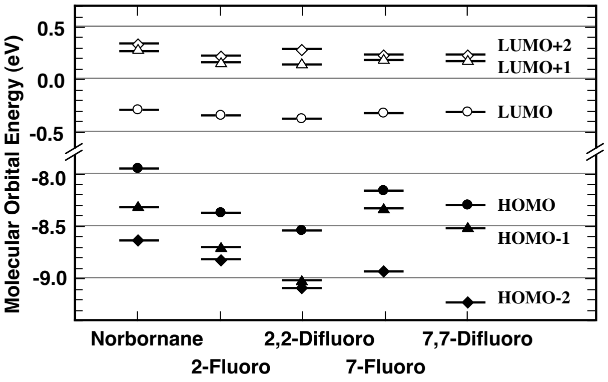

Fig. 6 Molecular orbital energies of norbornane and fluorinated norbornanes.

The spectral shapes and absorption edges are well reproduced by the calculated spectra except for 7,7-difluoronorbornane at shorter wavelengths. The substitution of fluorines into norbornane displaces the absorption edges to shorter wavelengths, and thus the absorbances at 157 nm are effectively reduced. It should be noted that the order of the absorbances (2,2-difluoro < 7,7- < 2-fluoro < 7- < unfluorinated) is perfectly reproduced. Fig. 5 shows the most dominant transitions on the absorbance at 157 nm for norbornane and 2,2'-difluoronorbornane. Both transitions are from their HOMO (σ-orbital) to LUMO+1 (Rydberg-orbital). The absorption is displaced to shorter wavelength by 9.8nm by 2,2'-difluorination, whereas the displacement is only 4.9 nm by 7,7'-difluorination. Fig. 6 shows the calculated molecular orbital energies (ε) for the norbornanes. The lowering of $\varepsilon_{\mathrm{HOMO}}$ and $\varepsilon_{\mathrm{HOMO\text{-}1}}$ by 2- and 2,2-fluorination are more significant than those by 7- and 7,7-fluorination. The descent of $\varepsilon_{\mathrm{HOMO}}$s should be originate from the high electronegativity and low polarizability of fluorine. In contrast, the variations in $\varepsilon_{\mathrm{LUMO}}$ and $\varepsilon_{\mathrm{LUMO+1}}$ are not remarkable.

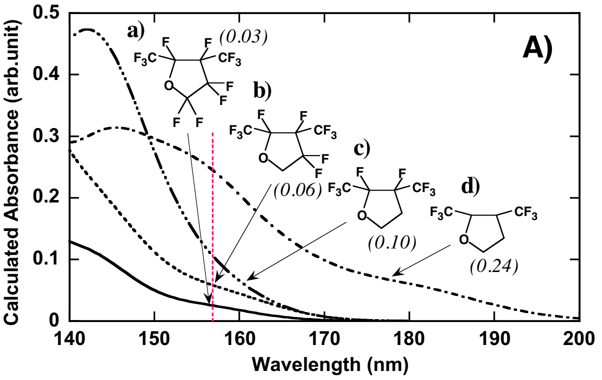

Fig. 7 Calculated spectra of fluorinated compounds having 5-membered heterocylic structures.

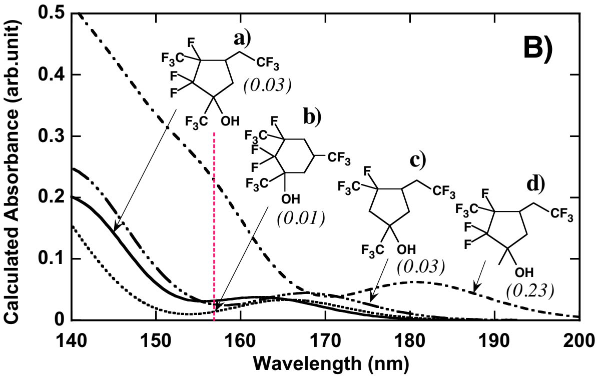

Fig. 8 Calculated spectra of fluorinated compounds having 5-membered heterocyclic and alicylic structures.

3.2 *Highly Fluorinated Systems*

The high transparency of fluorinated hydrocarbons was first pointed out by Kunz *et al*.[25,26], and we have shown that the calculated absorbances of models for perfluorinated polymers, Teflon-AF (DuPont) and Cytop (Asahi Glass), are more than one order of magnitude lower than those of esters, aromatics, and norbornanes [5]. Fig. 7 shows the effect of fluorines on the absorption spectra for a model for Cytop. The relatively high absorption of (d) with no fluorines in the 5-membered-ring is significantly reduced by the fluorination at 2- and 3-positions for (c). Additional fluorination further reduce the absorbance at 157 nm. Selete and Asahi Glass [27] have recently unveiled the molecular structures of a novel photoresist-platform, SAFARI, which exhibits a very low absorbance (<1.0μm^{-1}) at 157 nm. Fig. 8 shows the calculated spectra for models (a) and (b) for SAFARI. Although SAFARI is not a perfluorinated system, the calculated absorbances for both models are as low as that of Cytop ((a) in Fig. 7). It is interesting to note that the substitution of hydrogens for the fluorines on the alicyclic ring does not increase the absorbance (c), but the substitution of -CH_3 for -CF_3 at the F_3C-C-OH moiety causes significant increase in the absorbance (d). This results supports the low absorption of F_3C-C-OH structure.

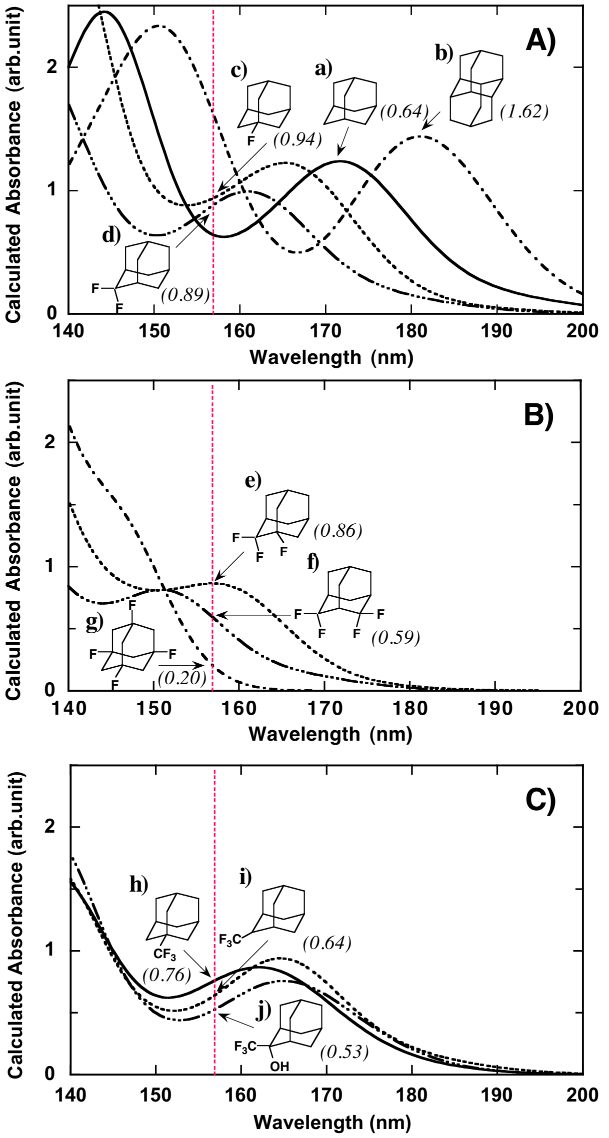

Fig. 9 Calculated spectra of adamantane and its fluorinated derivatives.

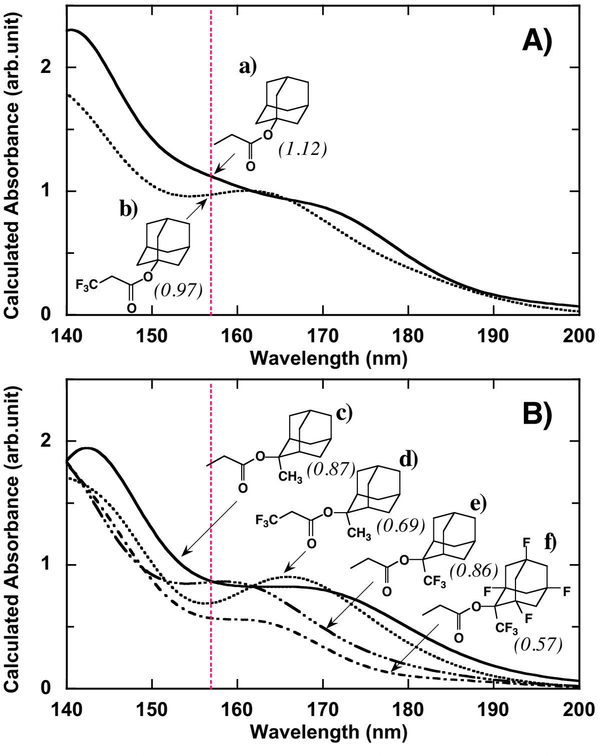

Fig. 10 Calculated spectra of unfluorinated and fluorinated adamantane-esters.

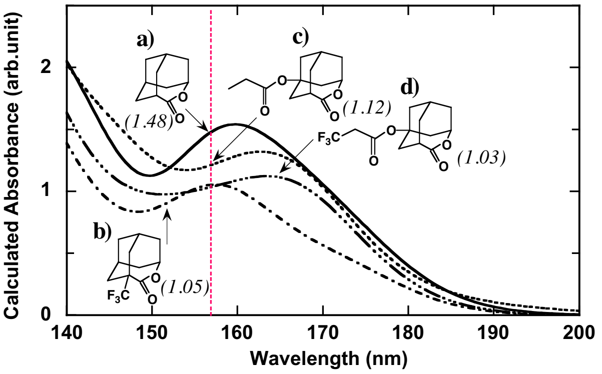

Fig. 11 Calculated spectra of unfluorinated and fluorinated quasi-adamantane-esters.

3.3 *Adamantane and Its Derivatives*

Polymers containing adamantane structure attract attention as novel platforms for its high structural stability and resistivity. Fig. 9 shows the calculated absorption spectra of adamantane, diadamantane, and their fluorinated derivatives. Adamantane itself exhibits a broad and distinct absorption peak around 172nm. This peak mainly originates from four transitions appearing at 172.7 ± 0.2nm, and the window thus generated around 158nm reduces the apparent absorbance at 157nm. Since six molecular orbitals except for LUMO (HOMO-2, HOMO-1, HOMO, LUMO+1, LUMO+2, and LUMO+3) contribute to these absorptions in complicated ways, it is difficult to clarify the assignments of each transition.

Diadamantane (b) shows a similar peak at a longer wavelength around 181nm, whereas mono- di-, and tri-fluorination of adamantane displaces the peak and the window to shorter wavelengths as seen for (c)–(e), but no significant decreases in absorbance are observed at 157nm. It should be noted that two tetrafluoroadamantanes, (f) and (g), show different spectra. The absence of peaks above 140nm in (g) leads to its high transparency. This fact also shows the importance of devised incorporation of fluorines.

Compounds (h)-(j) show the influence of -CF_3 group attached to adamantane. The spectral features and calculated absorbances are similar to each other, and the incorporation of -CF_3 is more effective than the directly bonded fluorines, (c)-(e). It should be noted that the hydroxy group (-OH) at 2-position in (j) does not increase the absorbance at 157nm, which supports the good nature of CF_3-C-OH moiety.

Fig.10 shows the calculated absorption spectra of

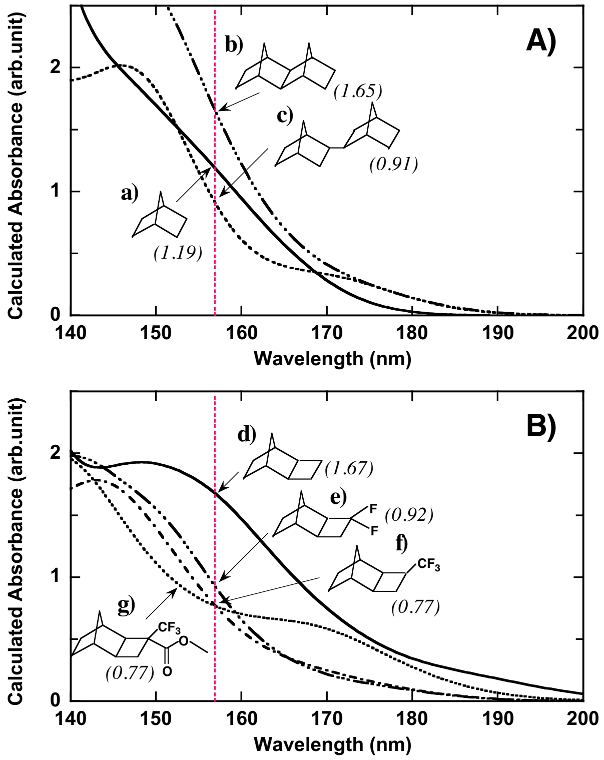

Fig. 12 Calculated spectra of unfluorinated and fluorinated adamantane-esters.

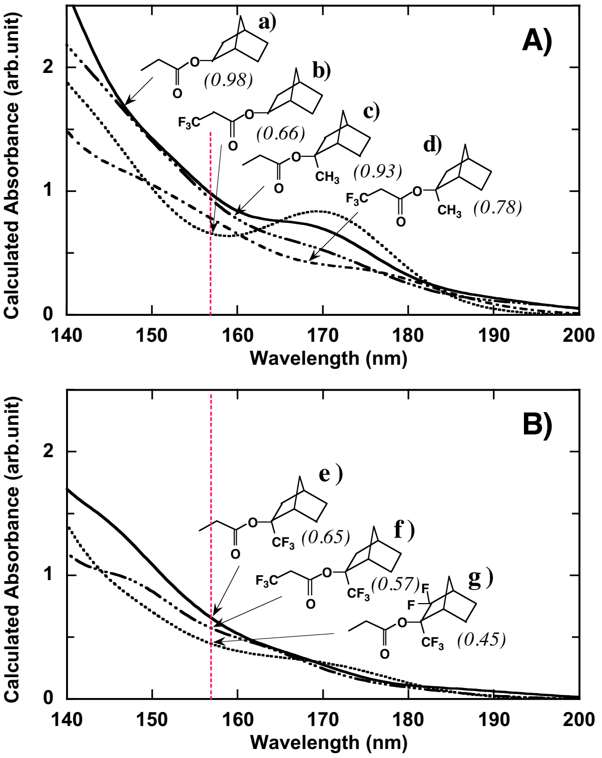

Fig. 13 Calculated spectra of unfluorinated and fluorinated norbornane-esters.

adamantanes substituted by propionic acid esters. The substitution of propionate at 1-position, (a) and (b), shows higher absorbances than that at 2-position with methyl group, (c) and (d). In addition, the trifluorination of C1-methyl of propionate (d) is more effective in reducing the absorbance than that at C2 of adamantane (e). Despite the low absorbance of (g) in Fig. 9, its propionate, (f) in Fig. 10, shows a broad peak around 163nm, which originate from the π-π* transition at the ester-carbonyl moiety.

Fig.11 shows the calculated absorption spectra of the compounds having a quasi-adamantane structure with a 7-membered ε-lactone ring. This structure was first applied to photoresist systems by Toshiba [28]. Since characteristic peaks with relatively narrow bandwidths are located around 160nm, these compounds exhibit relatively high absorbance at 157nm. The introductions of -CF$_3$ at the cyclic structure or at the propionate group exhibit limited effects in reducing the absorbance. As revealed in Fig.14 of ref.[5] and in Fig. 4 of this study, the direct fluorination and/or the substitution of -CF$_3$ to adamantane and its related compounds are not as effective as for the cases of norbornane and its related compounds. This can be attributed to the absorption band appearing at 172nm for adamantane.

3.4 *Norbornane-related Compounds*

Norbornane has been expected as main-chain or side-chain structure incorporated into photoresist platforms [29,30]. An advantage of norbornane structure is the absence of distinct absorption bands above 150nm. However, the synthesis of polymers having norbornanes in the main chain is generally difficult. Willson *et al.* have synthesized tricyclo-nonene (TCN) compounds, which show improved transparency over the norbornane hydrocarbon [31]. They recently reported that a fluorinated copolymer containing TCN shows an absorbance of 2 μm^{-1} at 157nm [32]. As shown in Fig.12, tricyclo[4.2.1,0^{2,5}]nonene (d) exhibits a higher absorbance than norbornane, but the introduction of fluorines is as effective as for norbornane, in which significant displacement of absorptions to shorter wavelengths occurs. In particular, the combination of -CF$_3$ and propionic acid ester (g) shows a good performance.

3.5 *Norbornane-substituted Esters*

Norbornane moiety is also used as a functional side-chain, and it is frequently connected to polymer main-chain by a carbonyl ester (-CO-O-) group. Carbonyl ester that gives good solubility and adhesion to polymers has been proved to show substantial absorption in the VUV region due to the π–π* transitions as summarized in [4,5]. Thus, a C=O moiety is not generally suitable for the design of 157nm photoresist platforms. However, Ito *et al.*[20,29] showed that the ester functionality in close proximity of -

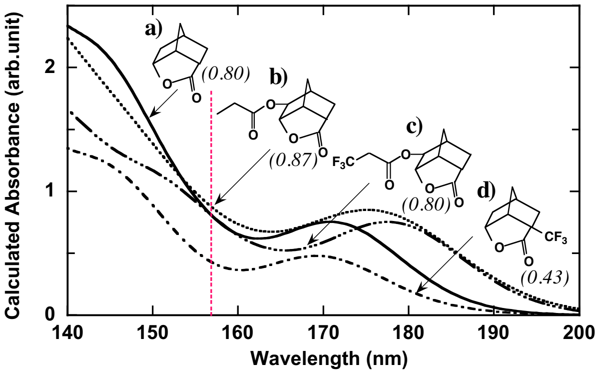

Fig. 14 Calculated spectra of molecules having a combined structure of norbornane and γ-lactone.

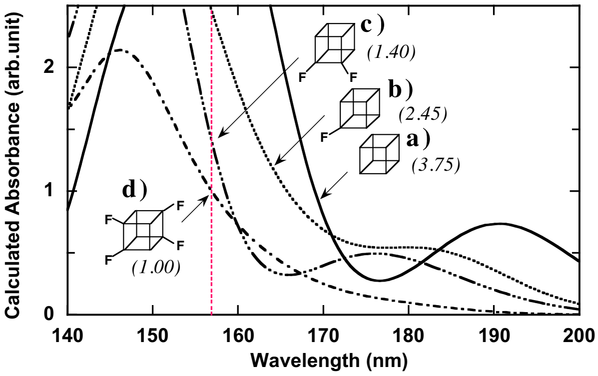

Fig. 15 Calculated spectra of cubane and fluorinated cubanes.

CF_3 is relatively transparent. Fig. 13 shows the calculated spectra of ester-substituted norbornanes. The comparison between (a) and (c) indicates that the addition of -CH_3 at 2-position does not change the spectral shapes and the absorbances at 157nm, whereas that of -CF_3 at 2-position (c→e, d→f) significantly lower the absorbance, and the additional difluorination at 3,3-positions (g) causes further decrease in absorbance.

3.6 *Alicyclic and Heterocyclic-Esters*

Fig.14 shows the calculated absorption spectra of compounds having a combined alicyclic structure of norbornane and γ-butyrolactone. The introduction of γ-lactone and/or ether structures is known to improve adhesion and solubility of photoresit materials. Acrylic polymers containing structure (a, b) was first applied to chemically amplified resists for ArF lithography by NEC [33]. The addition of ester groups (b, c) does not affect the absorbance at 157nm, but the addition of -CF_3 at 2-position (a→d) significantly decreases the absorbance. This clearly shows the hypsochromic and hypochromic effects of -CF_3 group located near carbonyl ester moiety.

3.7 *Cubanes*

Cubane is an interesting molecule because of its relative durability despite the high-strain structure. No report was found for applications of cubane-derivatives to photoresist systems. As shown in Fig. 15, all the cubanes exhibit intense absorption peaks between 145 and 160nm, and they are not suitable for transparent polymer platforms at 157nm. Although the effect of fluorination is significant as same as in other polymer systems, tetrafluoro-cubane still exhibits high absorbance. This is partly due to their small van der Waals volumes, in which carbon atoms are densely packed in the molecules.

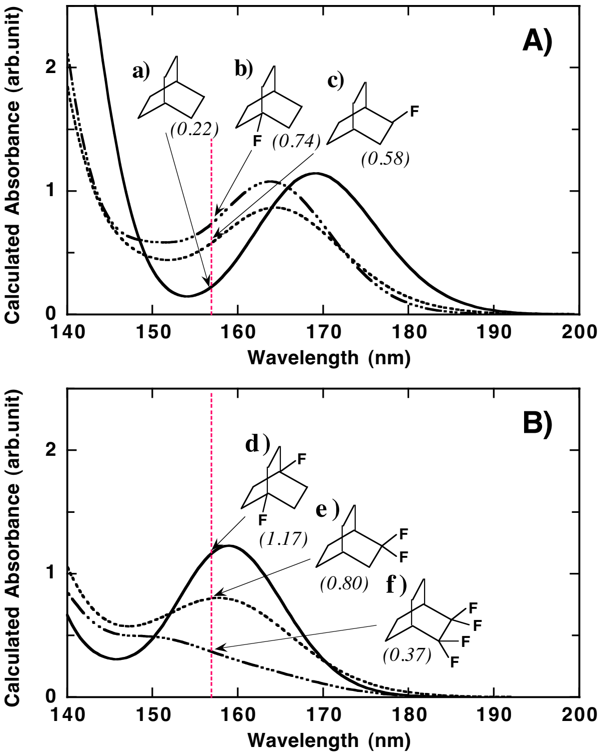

Fig. 16 Calculated spectra of bicyclo[2,2,2]octane and its fluorinated derivatives.

3.8 *Bicyclooctanes*

Bicyclo[2,2,2]octane (BCO) ((a) in Fig. 16) is another interesting polycyclic structure. As shown in Fig. 16, the spectral shapes and the effects of fluorination on the calculated spectra are similar to those of adamantane and its derivatives. Although BCO itself exhibits a distinct absorption peak around 169nm, the absorbance at 157nm is very low due to the window around 152nm. According to the calculated spectra, the addition of fluorines increases the absorbance at 157nm: the more fluorines, the higher absorbance. This is ascribed to the displacement of peaks to shorter wavelengths by fluorination in similar ways to other alicyclic/heterocyclic compounds. The fact that 2,2-difluoro-BCO (e) shows higher transparency than 1,4-difluoro BCO (d) coincides with the case of norbornane (see Fig.14a in [5]).

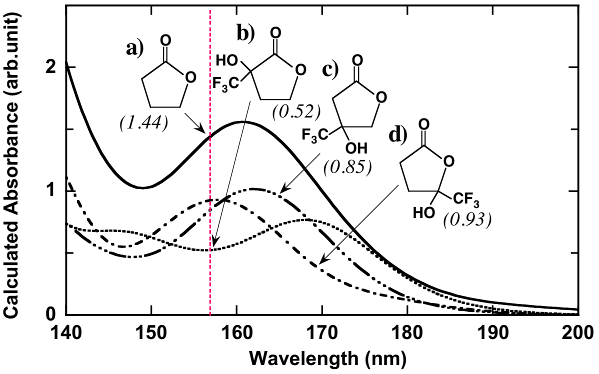

Fig. 17 Calculated spectra of compounds having a γ-lactone-ring structure.

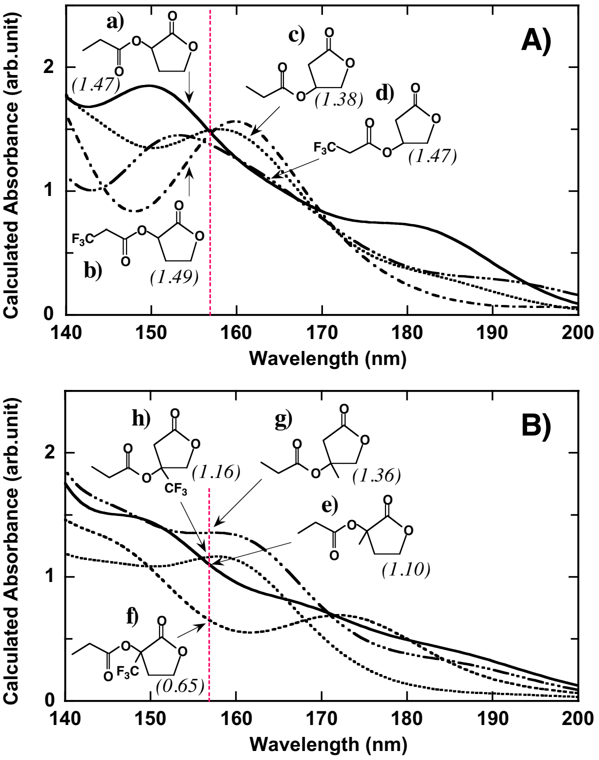

Fig. 18 Calculated spectra of propionic acid ester compounds having a γ-lactone structure.

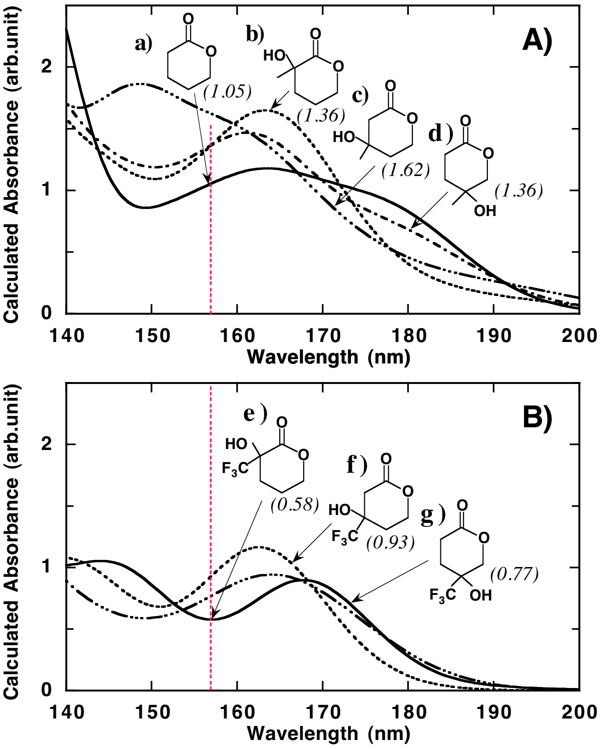

Fig. 19 Calculated spectra of compounds having a δ-lactone structure.

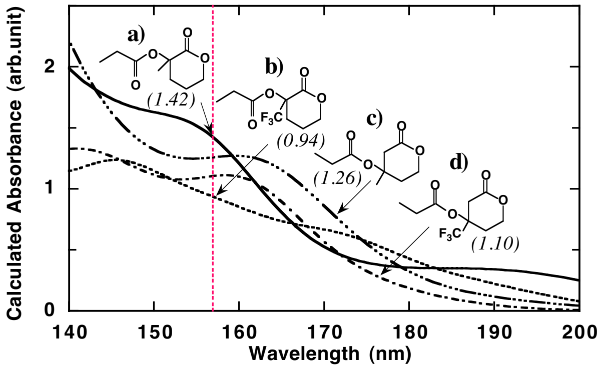

Fig. 20 Calculated spectra of propionic acid ester compounds having a δ-lactone structure.

3.9 *Lactone-ring Containing Compounds*

Polymers having γ-lactone and δ-lactone-ring structures as side-chains have been widely used as photoresist platforms for ArF (193nm) lithography. Although these materials usually show high absorption at 157nm, such conventional polymer platforms might be useful for F_2 lithography by devised substitution of fluorines or -CF_3. As shown in Fig.17, the simultaneous addition of -CF_3 and -OH at C3 of γ-lactone (b) is more effective than those at C4 (c) and C5 (d) for the compounds having a γ-lactone structure. This clearly indicates that the strong absorption of the ester moiety can be effectively quenched by the -CF_3 group. In a similar manner, Fig.18 shows that the substitution of -CF_3 at the C3 of γ-lactone with propionic acid ester (f) shows the lowest absorbance, while the -CF_3 at the C1 of propionic acid (b and d) gives limited effects. These facts indicate that -CF_3 should be located in close proximity of the light-absorbing ester functionality rather than the terminus. As shown in Fig.19, the addition of -CH_3 and -OH to a δ-lactone structure causes significant increase in the absorbance, but that of -CF_3 and -OH exhibits inverse effects in a similar manner to the γ-lactone case. In addition, the F_3C-C-OH group at C3 of δ-lactone exhibits the most effective reduction in absorbance at 157nm. Although the decrease in absorbance caused by F_3C-C-OH is significantly smaller than that for γ-lactone (see Fig.18B and Fig.20), the simultaneous substitution of -CF_3 and ester group at the C3 of δ-lactone-ring ((b) in Fig.20) provides the lowest absorbance in the figure.

4. Conclusions

The photoabsorption spectra of alicyclic and heterocyclic molecules, which are models for polymer platforms for F_2 lithography, in the VUV region were calculated using the TD-DFT theory. The calculated spectra demonstrate the effectiveness of devised introduction of –F or –CF_3 groups in proximity of light-absorbing moieties for reducing absorption at 157 nm. Significant reduction in absorbance is predicted for norbornane, γ-lactone, and δ-lactone structures.

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