Ab initio calculations of the dissociative attachment resonance energies for an octafluorocyclopentene molecule with comparisons to electron attachment mass spectrometric measurements

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Dissociative electron attachment to an octafluorocyclopentene (c-C_5F_8) molecule has been investigated by means of *ab initio* molecular orbital calculations. Because of the antibonding character of the virtual valence orbitals, the temporary anions dissociate, producing neutral and negative radical fragments in reactive plasma. In order to identify the valence of virtual orbitals associated with the dissociative electron attachment in the calculation with the diffuse basis set, we examined the spatial distribution and antibonding characteristics of the virtual molecular orbitals. This theoretical approach reproduced experimental resonance energies of the dissociative electron attachment, which display rich resonance energy spectra as observed by electron attachment mass spectrometry. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1481212]

Perfluorocarbons such as octafluorocyclopentene (c-C_5F_8) are feed gases for plasma etching of silicon dioxide, which is a key process in manufacturing semiconductor microelectronics. In addition, fluorocarbon film prepared by plasma enhanced chemical vapor deposition (CVD) is regarded as promising for low-dielectric-constant interlayer dielectrics. The optimization of these microelectronics processes must be made on the basis of a deep understanding of decomposition and polymer deposition in fluorocarbon plasma. Recently, we have investigated the electronic excited states of various perfluorocarbons by using an *ab initio* molecular orbital calculation.[1] The chemical reactions via the excited states were predicted from the antibonding characteristics of the relevant molecular orbitals and the internal coordinate force of the excited state at the ground-state geometry. On the basis of quantum chemistry, types of perfluorocarbons, such as two-double-bonded, one-triple bonded, and aromatic perfluorocarbons, were predicted to show good performance for application to plasma processing.

Some properties of fluorocarbons of practical interest in plasma processing are related to the possible dissociative electron attachment yielding neutral and negative radical fragments. Electron attachment mass spectrometry (EAMS), which has been applied for the detection of polymerized neutral species,[2–4] gives the yield of negative ions as a function of the impact electron energy. In the high-frequency discharges recently used for surface processing, negative ions are trapped in reactive plasma, where they have sufficient time to participate in further chemical reactions. Thus, it is becoming more important to study the generation mechanism of negative species in processing plasma.

In fluorocarbon plasma processing, the c-C_5F_8 molecule has attracted increasing interest as one of the most promising feed gases due to its low possibility of contributing to global warming, its high etching selectivity of SiO_2 over Si, Si_3N_4,[5] and photoresist,[6] and its high deposition rate in plasma enhanced CVD of an amorphous fluorinated carbon film.[7] In this letter, we discuss the origin of the resonance structure seen in dissociative attachment of c-C_5F_8 by means of *ab initio* molecular orbital calculations.

All of the *ab initio* molecular orbital calculations have been carried out with the GAUSSIAN 98 program.[8] The equilibrium geometry was optimized by second-order Möller–Plesset perturbation (MP2) calculations with the 6-31G(d) basis set. The Hartree–Fock (HF) calculations with STO-6G, 6-31G(d), and 6-31+G(d) basis sets were performed at the MP2/6-31G(d) optimized geometry. In particular, the 6-31+G(d) basis set, including diffuse functions, was employed in order to take into account the valence/Rydberg mixing. Because electron attachment is rapid with respect to nuclear motion, temporary anions are formed at the equilibrium geometry of the parent neutral molecule. Thus, they are characteristic of a vertical process in which the geometry of the anion does not relax. The attachment energy for electron capture into the vacant orbital was evaluated as the eigenvalue of the corresponding virtual orbital where an extra electron is added. The experimental resonance energies were assumed to correspond to the energies required for attaching electrons to the C–F and/or C–C antibonding orbitals at the equilibrium geometries of the parent neutral molecules.

The yields of the fragment negative ions as a function of the incident electron energy were given by EAMS.[4,9] The experimental data on dissociative electron attachment to c-C_5F_8 are summarized in Table I. In gas-phase collisions, a c-C_5F_8 molecule can attach an electron of proper energy to its vacant molecular orbital, which usually has an antibonding character. As a preliminary calculation, qualitative information on expected resonance energies was obtained from the minimal-basis-set (STO-6G) HF energies shown in Table II. Some experimental attachment energy positions for which

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TABLE I. Dissociative attachment energies and detected fragment anions obtained from the EAMS spectra of c-C_5F_8.

Attachment energy (eV)	Detected fragment anion
2.1	F^-
3.4	$C_3F_3{}^-$
4.0	$CF_3{}^-$
5.5	$C_5F_7{}^-$
6.3	F^-, $C_3F_3{}^-$
6.6	$CF_3{}^-$
7.7	$C_5F_7{}^-$
8.8	$CF_3{}^-$, $C_3F_3{}^-$
10.1	F^-

FIG. 1. Correlation between the calculated virtual orbital energies and experimental resonance energies of c-C_5F_8.

the STO-6G calculation cannot give the corresponding empty energy levels are also found in Table II. In addition, we must shift the virtual orbital energies down by several electron volts to explain the experimental resonance energy positions due to the limits of the STO-6G basis set. Minimal basis sets are not affected by mixing with discretized continuum states.[10,11] The employment of the minimal basis set makes it possible to avoid the need for distinguishing solutions associated with anion valence states from those belonging to the discretized continuum. However, the virtual orbital energy should be stabilized to account for strong mixing with a nearby virtual orbital with considerable continuum character. Although a more extended basis set of 6-31G(d), which includes polarization functions, gives lower attachment energies, there remain problems with the experimental attachment energies that do not correspond to the calculated ones (see Table II).

The extension of the basis set, with inclusion of diffuse functions, improves the description of anion states but generates discretized continuum solutions not associated with empty valence molecular orbitals.[10] Thus, the inclusion of diffuse functions in the basis set leads to only an apparent breakdown of Koopmans' theorem.[12,13] As the basis set is expanded, virtual orbital energies tend to collapse toward zero, so a self-consistent-field calculation ultimately describes a neutral molecule and an unbound electron in the continuum. Using the basis sets with the diffuse functions, the so-called lowest unoccupied molecular orbital (LUMO) does not always have a valence character, and the corre-

TABLE II. Basis-set dependence of calculated virtual orbital energies of c-C_5F_8. The corresponding experimental attachment energies are also shown.

Calculated virtual orbital energy (eV)			Experimental attachment energy (eV)
HF/STO-6G	HF/6-31G(d)	HF/6-31+G(d)[a]	
5.92	2.67	2.15	2.1
...	...	3.84	3.4
...	...	4.49	4.0
11.5	5.76	5.57	5.5
...	...	5.94	6.3
12.1	5.19	6.01	6.6
12.7	7.63	7.68	7.7
12.9	7.85	8.02	8.8
15.3	10.5	10.1	10.1

[a]In the HF/6-31+G(d) calculation, the virtual orbital energies shown were obtained by distinguishing virtual orbitals with considerable valence character from all other virtual orbitals, including the discretized continuum solutions.
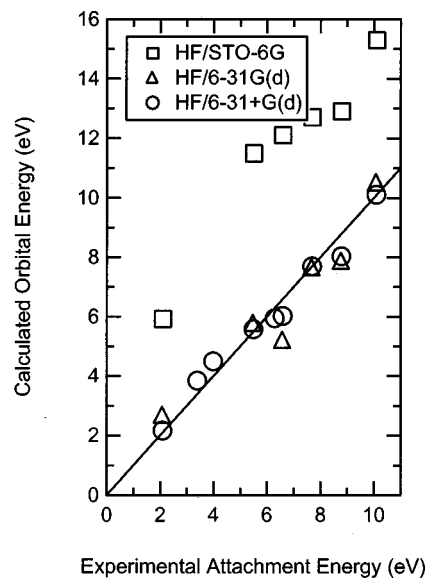
sponding virtual orbital with the same character as the minimal-basis-set LUMO appears as a slightly higher virtual orbital. In other words, as the basis set is enlarged with diffuse functions, the empty orbitals are liable to approximate continuum functions, and thus some further procedures are needed in order to identify the virtual orbitals associated with dissociative electron attachment. The resonance energies are associated with the eigenvalues of virtual orbitals localized mainly in the molecular region with a small amount of coupling between the valence states and the continuum, while the remaining solutions are given as a discretization of the continuum. With this diffuse basis set, the discretized continuum solutions appear in the same energy range as the valence empty orbitals of the resonance states.

In this study, we examined the spatial distribution and antibonding character of the HF/6-31+G(d) virtual molecular orbitals to identify the valence virtual orbitals associated with the dissociative electron attachment. The expected resonance energies obtained by this procedure with the HF/6-31+G(d) calculations are added in Table II. Figure 1 indicates the correlation between the calculated orbital energies and experimental resonance energies. The computed orbital energies obtained from the HF/6-31+G(d) calculations are in reasonable agreement with all of the observed resonance positions. Such a straightforward procedure can successfully assign the observed resonance energy positions by distinguishing virtual orbitals with considerable valence character from all other virtual orbitals, including the discretized continuum solutions.

In the molecular structure of unsaturated fluorocarbons such as c-C_5F_8, the maximum yield of fluorine anion fragments occurs close to the π^* resonance energy position. In the c-C_5F_8 structure, the out-of-plane character of C–F bonds adjacent to the ring permits large σ^*/π^* overlap.[14] Dissociation may follow the electron trapping into a ring π^* empty orbital at 2.1 eV and a subsequent intramolecular transfer to the fluorine atom in c-C_5F_8. Such an electron transfer due to orbital mixing may be one of the reasons why the antibonding character of the virtual valence orbital can-

not completely explain the fragmentation pattern of the corresponding dissociative attachment.

In summary, the correlations between the measured dissociative attachment energies and the calculated virtual orbital energies of C–F and/or C–C antibonding orbitals of c-C_5F_8 were explored by using *ab initio* molecular orbital calculations. The energies to attach an electron to the parent molecule were computed by HF/6-31+G(d) calculation. As discussed previously, some of the energies computed using this basis set actually correspond to discretized continuum solutions not anion valence states. The continuum solution energies should be discarded by looking for the computed orbitals that were not localized in the molecular region. Using this procedure, the EAMS resonance energy spectrum of c-C_5F_8 was predicted within 1 eV. The application of the present technique developed for predicting plasma chemistry to other perfluorocarbons with their low global warming potentials is now in progress.

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