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Predominant decay channel for superexcited organic molecules

Hitoshi Koizumi

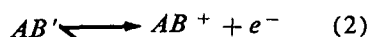
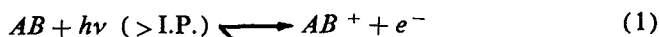
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Photoabsorption and photoionization cross sections of organic molecules are systematically compared for elucidating relation between superexcitation and ionization. The cross sections examined are of alkenes, alkanes, alcohols, and ethers in the energy range of about 2 eV above the first ionization potential. Although the photoabsorption cross sections are much different from one another, the photoionization cross sections are similar in each molecular group. This result indicates that ions are formed only through direct photoionization and most of superexcited molecules dissociate to neutral fragments. Ionization efficiency curves are calculated under the assumption of no autoionization, and they well reproduce the observed ionization curves, which mainly depend on energy difference between the first and second ionization potentials.

I. INTRODUCTION

A molecule excited by a photon with energy higher than its ionization potentials (I.P.) dissipates its energy in the following processes,



where AB' is a superexcited state.^{1,2} The superexcited state is a discrete state with energy higher than the first I.P., which is a doubly or inner-core excited state, or vibrationally and rotationally excited high Rydberg state converging to the first I.P.³⁻⁵ The superexcited molecule may either autoionize (2) or dissociate to neutral fragments (3).

In recent years there has been increased interest in the superexcited state. The branching ratios of the direct ionization (1) and the superexcitation, and of the autoionization (2) and the dissociation to neutral fragments (3), are important quantities to elucidate the mechanisms of excitation and decay for the superexcited state. For diatomic or triatomic molecules, several investigators have made experimental and theoretical studies in detail.⁶⁻⁹ For more complex molecules, such as hydrocarbons, alcohols, and ethers, however, the formation and decay channels of the superexcited states are ambiguous.

Ionization efficiency (η), or quantum yield of photoionization, is the sum of the yields of the processes (1) and (2). This quantity is one of the most fundamental in understanding the superexcited states, though, has been measured for limited kinds of molecules.⁹⁻¹⁵ The relation between η and the molecular structure has scarcely been known accordingly. Recently, we systematically measured η for hydrocarbons, alcohols, and ethers as a function of photon energy in the region between the first I.P. and 105 nm.¹⁰ The shape of the η curves depends mainly on the energy difference between the first and second I.P. (ΔE). The value of η

increases monotonically for the molecules with small ΔE , such as cyclopropane and cyclohexane. For the molecules with large ΔE , such as alkenes and ethers, however, η starts to increase at the first I.P., shows a peak or plateau, and then increases again at the second I.P.. For alcohols with medium ΔE , η shows only a shoulder. However, we have not elucidated the reason why the η curves show such a dependence on ΔE .

Since we have also determined absorption cross sections (σ),¹⁶⁻¹⁸ absolute total ionization cross sections (σ_i) can be obtained now by using the relation: $\sigma_i = \sigma \times \eta$. In this paper the author systematically examines the dependence of σ , and σ_i on molecular structure to elucidate the fate of a molecule after absorbing a photon with energy higher than the first I.P., and proposes a model to explain the observed η curves.

II. PHOTOABSORPTION AND IONIZATION CROSS SECTIONS FOR SEVERAL ORGANIC MOLECULES

A. Alkenes

Figure 1 shows photoabsorption¹⁶ and photoionization cross sections (σ , and σ_i) for butene isomers. The values of σ_i are calculated from σ ,¹⁶ and η .¹⁰ Although σ show different features depending on the molecular structure, σ_i are almost the same among the isomers. Johnson *et al.* also observed the broad σ_i bands for isobutene, *cis*-, and *trans*-2-butenes by using electron energy loss spectroscopy.¹⁹ They assigned the broadbands with the peaks at 9.9, 9.8, and 9.2 eV for isobutene, *cis*-, and *trans*-2-butenes, respectively, as $\sigma \rightarrow \pi^*$ or $\sigma \rightarrow \sigma^*$ transitions. On the other hand, Robin assigned them to $n = 3$ Rydberg excitations.

The comparison of the σ , and σ_i curves shows that σ are not related to σ_i . The similarity among the σ_i curves for butenes implies that σ_i are only due to direct ionization. In the same way, Person and Nicole have also explained the approximate equality of σ_i for C_2H_4 and C_2D_4 .²⁰ Since the direct ionization of butenes is of a π electron in the double

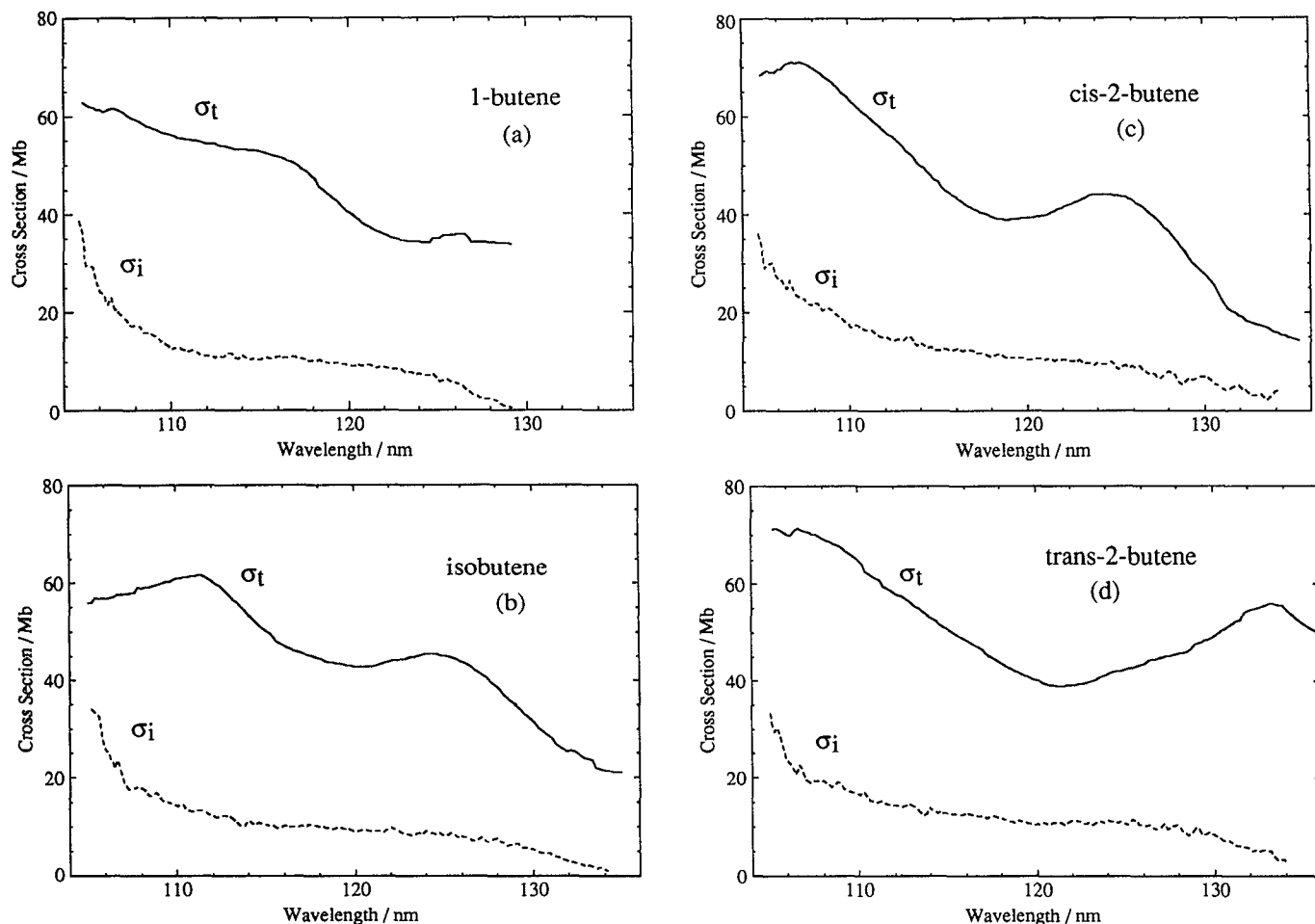


FIG. 1. Photoabsorption (σ_t) and photoionization (σ_i) cross sections for butenes (Refs. 10 and 16): (a) 1-butene; (b) isobutene; (c) *cis*-2-butene; (d) *trans*-2-butene.

bond, the cross sections are similar among the isomers accordingly.

Figure 2 shows the plots of σ_t and σ_i for several alkenes against energy difference between photon energy (E) and the first I.P. Although σ_t are much different from one another, the relative shapes of σ_i for all alkenes are similar. All σ_i start to increase at the first I.P., show a plateau and then increase again at the second I.P. Moreover, in the plateau region, the absolute values of σ_i are almost the same except for 1-hexene. The values are about 15 Mb for 1-hexene, and 10 Mb for the others.

These facts suggest that σ_i for all alkenes are due to direct ionization, which is direct photoelectron ejection from the similar π orbital. Nevertheless, the value of σ_i for 1-hexene is larger than for the others, the ionization of 1-hexene will also be due to the direct ionization. A photoelectron spectrum (PES) of alkenes consists of bands for π and σ electrons. Although the broadbands for various σ electrons overlap with one another, the band for the π electrons is sharp and generally isolated from those for the σ electrons,²¹ and hence only the photoionization of the π electrons contributes to σ_i from the first I.P. through the plateau region. In the PES of 1-hexene the band for the π electrons slightly

overlaps with the bands for the σ electrons,²² and consequently σ_i for 1-hexene is larger than for the other alkenes because of the contribution of direct photoejection of the σ electrons.

The value and shape of σ_t for alkenes are much different from one another because an excitation cross section to the superexcited states varies with the molecular structure. The superexcited states will mainly be Rydberg states converging to the higher ionic states produced by the ejection of one of the σ electrons, and hence the number and energy of these states much depend on the structure of alkenes.²¹ As shown in Fig. 2(a), σ_t increases with the number of carbon atoms in a molecule. This is because the number of the σ electrons, and then of Rydberg states, increases.

B. Alkanes

Figure 3 shows σ_t and σ_i for alkanes: cyclopropane,^{10,16} cyclohexane,^{10,18} methane,¹⁴ and *n*-butane.²⁰ The value of σ_t much depends on the structure of molecules, while the relative shape of σ_i is similar to one another: all σ_i linearly increase with increasing photon energy. No correlation between the σ_t and σ_i curves suggests that the ionization is

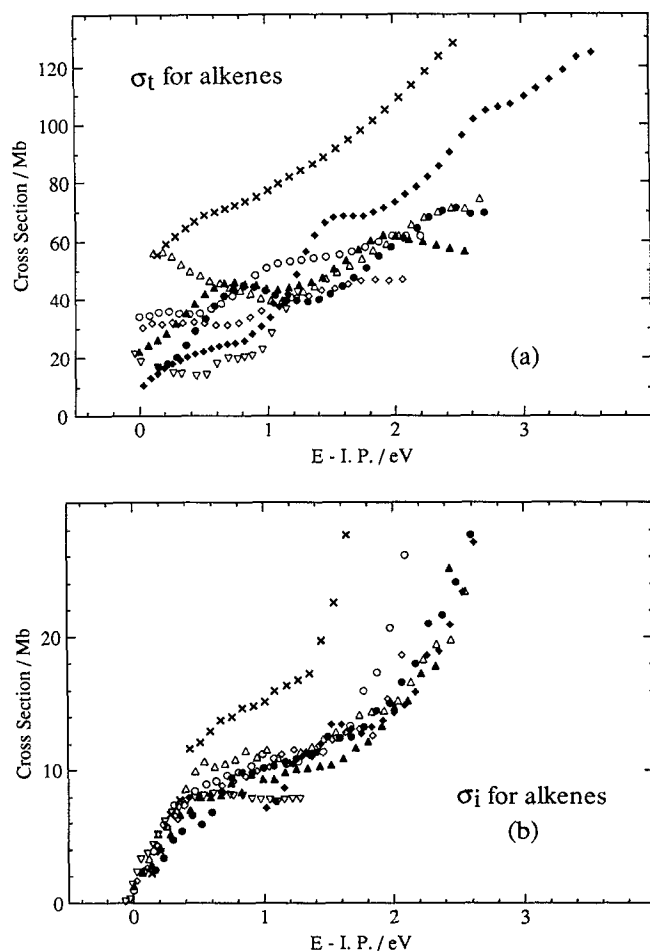


FIG. 2. (a) Photoabsorption and (b) photoionization cross sections for alkenes against energy difference between photon energy (E) and the first I.P.: ethylene (∇) (Ref. 20), propylene (Refs. 10 and 16) ($\diamond$), 1-butene (Refs. 10 and 16) ($\square$), isobutene (Refs. 10 and 16) ($\circ$), *cis*-2-butene (Refs. 10 and 16) ($\blacktriangle$), *trans*-2-butene (Refs. 10 and 16) ($\triangle$), 1-hexene (Refs. 10 and 18) ($\times$), and tetramethylethylene (Refs. 10 and 18) ($\blacklozenge$).

due to the direct photoejection of an electron, and the superexcited molecules result in neutral fragmentation.

The σ_i curves for cycloalkanes show a broadband at just above the first I.P. Several investigators have assigned the band to valence transition, which is $1a'_2 \leftarrow 3e'$ for cyclopropane²³⁻²⁶ or $1a_{1u} \leftarrow 4e_g$ for cyclohexane.²³ Valence excitation is rarely observed for alkanes because their antibonding orbitals are completely mixed with the conjugated ns and np Rydberg manifolds.²⁷ Robin has explained the existence of the valence transitions by the following way. Because of their symmetry, the antibonding orbitals, $1a'_2$ of cyclopropane and $1a_{1u}$ of cyclohexane, can mix only with nf Rydberg orbitals. The nf Rydberg electrons revolve far from valence core orbitals and have no penetration into the core differing from ns and np Rydberg electrons. Accordingly, the antibonding and Rydberg orbitals cannot mix, so that the valence excitations are observed.²³

In general, a direct photoionization cross section shows step increases at each I.P., and gently decreases with increas-

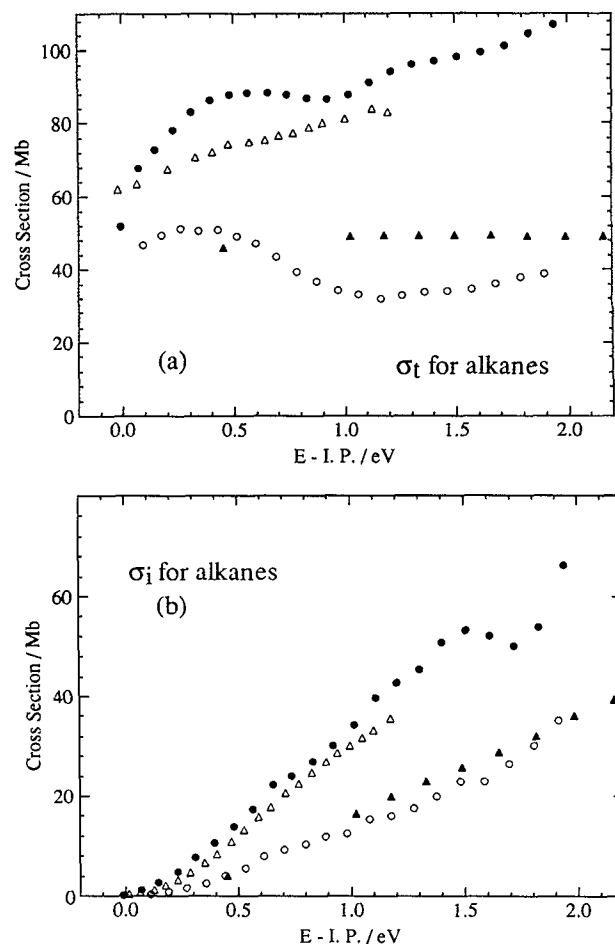


FIG. 3. (a) Photoabsorption and (b) photoionization cross sections for alkanes against energy difference between photon energy (E) and the first I.P.: cyclopropane (Refs. 10 and 16) ($\circ$), cyclohexane (Refs. 10 and 18) ($\square$), methane (Ref. 14) ($\blacktriangle$), and *n*-butane (Ref. 20) ($\triangle$).

ing photon energy. As illustrated in Fig. 4, it represents sawtooth shape.²⁸ The experimental curves in Fig. 3 are only due to the direct ionization, and correspond to the region with the step increases. Since the I.P. of alkanes exist in small energy intervals, the steps overlap with one another, and in

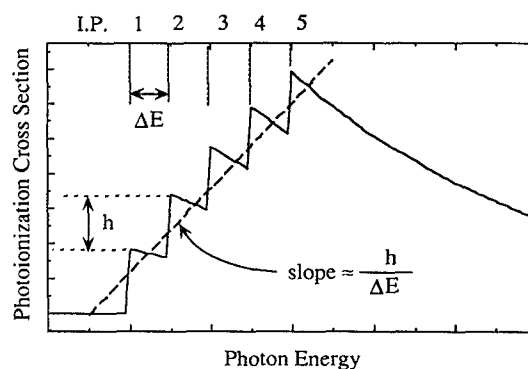


FIG. 4. Schematic diagram illustrating dependence of a photoionization cross section on the energy intervals of ionization potentials.

consequence, σ_i monotonically increases.

If this explanation is correct, as shown in Fig. 4, the slopes for the σ_i curves are expected to be proportional to the reciprocal of the energy intervals of I.P., and then we examine this relation. Table I shows a comparison of the slopes for the σ_i curves and the reciprocal of average I.P. intervals ($\overline{\Delta E}^{-1}$), which were calculated from the lowest group of the ionization bands in the photoelectron spectrum measured by Kimura *et al.*²¹ The slopes were obtained by fitting σ_i in Fig. 3 to straight lines. The ratios of the slope to $\overline{\Delta E}^{-1}$ are roughly the same as one another, and the slope is hence proportional to $\overline{\Delta E}^{-1}$. The values of the ratios are 12–14 Mb, and close to 10 Mb, which is the value of σ_i for alkenes at the plateau region. This result seems reasonable because the value of the ratio should be close to the height of the steps in Fig. 4, and as described later, the height should roughly be the same for all organic molecules. In conclusion, this comparison also supports that σ_i are mainly due to the direct ionization.

C. Alcohols, ethers, and water

Figure 5 shows σ_t and σ_i for ethanol,²⁹ *n*-, and isopropyl alcohols,^{10,17} dimethylether,^{10,17} ethylmethylether,^{10,17} and water,^{12,30} and the cross sections are plotted against E-I.P. Although σ_t are much different from one another, σ_i are almost the same in the region between the first and second I.P. The latter cross sections show similar energy dependence to alkenes: they start to increase at the first I.P., show a plateau, and then increase again at the second I.P., and their values in the plateau region are about 10 Mb. This result implies that σ_i are only due to direct ionization.

The uppermost filled MO of water, alcohols, and ethers is $2p$ atomic orbital on the oxygen. This orbital orients perpendicular to the molecular plane. In the PES for these molecules, the ionization band of these lone pair electrons is isolated from the other bands,²¹ and hence from the first I.P. through the plateau region the direct ionization is only due to the photoejection of one of these electrons. For water, ethers, and methanol the second lone pair on the oxygen atom corresponds to the second I.P. For the higher alcohols, however, MO corresponding to the second I.P. have C–C bond nature. For both the molecules, MO corresponding to higher I.P. have O–H, C–O, C–C, or C–H nature.²¹

In a similar manner as alkenes, we can explain the reason why σ_t increase although σ_i are nearly constant: the

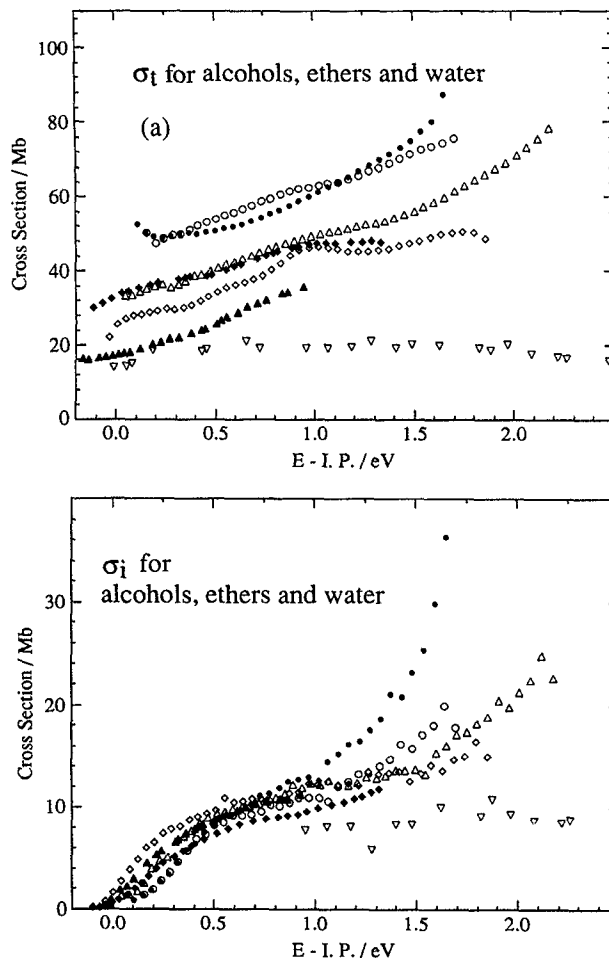


FIG. 5. (a) Photoabsorption and (b) photoionization cross sections for alcohols, ethers, and water against energy difference between photon energy (E) and the first I.P.: methanol (Ref. 29) ($\blacktriangle$), ethanol (Ref. 29) ($\blacklozenge$), *n*-propanol (Refs. 10 and 17) ($\bullet$), isopropanol (Refs. 10 and 17) ($\circ$), dimethyl ether (Refs. 10 and 17) ($\diamond$), ethylmethyl ether (Refs. 10 and 17) ($\triangle$), and water (Ref. 12) (∇).

value of σ_t increases because the number of superexcited states increases. The superexcited states are mostly Rydberg states, the number of which states increases with increasing the number of carbon atoms. On the other hand, the value of σ_i is almost the same because it is only due to the direct photoejection of a similar lone pair electron on the oxygen atom.

TABLE I. Comparison of average intervals of ionization potentials ($\overline{\Delta E}$) and slopes of ionization cross section curves for alkanes.

	I.P./eV (Ref. 21)	$\overline{\Delta E}$ /eV	$\overline{\Delta E}^{-1}$ /eV ⁻¹	Slope/ Mb eV ⁻¹	Slope $\times$ $\overline{\Delta E}$ / Mb
Cyclopropane	10.60, 11.30	0.7	1.4	17.4	12
Cyclohexane	10.32, 10.93, 11.38, 11.90, 11.90, 12.94, 12.94, 12.94	0.37	2.7	33.3	12
Methane	13.6, 14.4, 15.0	0.7	1.4	20.4	14
Butane	11.2, 11.7, 11.7, 12.2, 12.7, 13.2	0.4	2.5	32.5	13

D. Fate of superexcited molecules

As described previously, neutral fragmentation predominantly occurs in the decay of the superexcited states of alkanes, alkenes, ethers, and alcohols. However, superexcited states of other molecules do not always cause neutral fragmentation. It is interesting to examine what kind of superexcited states predominantly dissociate.

For alkenes, alkanes, alcohols, and ethers, most of superexcited states are formed by the excitation of a electron in a σ bond with C-H, C-C, C-O, or O-H bond character.²¹ The excitation of a σ bond electron stretches the bond, and lowers the dissociation energy.^{31,32} The molecule is hence excited to the repulsive part of a potential curve and dissociates along the curve.³³ The lack of autoionization suggests that this dissociation rate is much higher than the autoionization rate for these superexcited molecules.

Intense autoionization peaks are observed in σ_i for H_2 ,³⁴⁻³⁶ N_2 ,^{9,37,38} O_2 ,^{9,39} CO_2 ,^{9,40} CO ,⁹ N_2O ,^{9,41} and for NO ,^{9,42} molecules. Autoionization processes are not minor in the decay of these superexcited states. In these molecules, dissociative ionization threshold^{9,43-46} is much higher than their first I.P., and, to my knowledge, all of the assigned autoionization peaks are Rydberg states bound to dissociation accordingly.

On the other hand, neutral fragmentation seems to be dominant for the NH_3 molecule. Although σ_i for NH_3 shows many peaks between the first and second I.P., these peaks are not related to the structure of the σ_i curve.⁴⁷ The superexcited states of NH_3 molecule are produced by the excitation of a electron in the orbitals with N-H bond character,²¹ and these states will be dissociative as the states of hydrocarbons, alcohols, and ethers.

As far as we surveyed, autoionization is dominant only for superexcited states bound to dissociation, and neutral fragmentation is dominant in the decay of all dissociative superexcited states.⁴⁸ The author concludes that direct dissociation is generally much faster than autoionization, and the predominant decay channel for superexcited states is neutral fragmentation if the state may dissociate directly.

III. PHOTON ENERGY DEPENDENCE FOR IONIZATION EFFICIENCY CURVES

The above result has revealed that autoionization is negligible in the decay of superexcited organic molecules, and σ_i is almost identical with a direct ionization cross section. Since most of the superexcited states of organic molecules are Rydberg states,^{27,49} σ_i is approximately the sum of the direct ionization and Rydberg excitation cross sections, and thereby the qualitative estimation of σ_t , σ_i , and η is now possible.

In general, a direct photoionization cross section shows step increase at each I.P., and gently decreases with increasing photon energy.²⁸ The Rydberg series of organic molecules start from the energy 2–3 eV below each I.P.,³² and the lowest member, 3s Rydberg state has the largest excitation cross section. Rydberg excitation cross sections decrease with increasing a quantum number, n , and smoothly connect to an ionization continuum.^{28,50} This continuity arises from

the similar circumstances of an electron in the Rydberg orbital and ionization continuum. Both electrons in the Rydberg orbital and ionization continuum are far from the rest of the molecules and, consequently, move in a Coulombic field like one the highly excited electron of a hydrogen atom feels.^{28,51} As a first approximation we can hence reasonably use the excitation cross section of the hydrogen atom to the Rydberg and continuum states to estimate σ_t and σ_i . The distribution of Rydberg absorption intensity can be approximated by the extrapolation of the corresponding ionization continuum.

Here we simulate energy dependence for η under the following assumptions. Total absorption and ionization cross sections are composed of several spectral components characterized by specific ionization potentials, and these components overlap with one another. Each component has the same spectral shape, which is expressed as a function of energy difference between I.P. and incident photon energy, E , as

$$\sigma_{i,j} = 89.6 \exp\{-0.148[E - (I.P.)_j + 15.43]\},$$

$$E > (I.P.)_j - 2 \text{ eV}, \quad (4)$$

$$\sigma_{i,j} = 0, \quad E < (I.P.)_j - 2 \text{ eV}, \quad (5)$$

$$\sigma_{t,j} = 89.6 \exp\{-0.148[E - (I.P.)_j + 15.43]\},$$

$$E > (I.P.)_j, \quad (6)$$

$$\sigma_{t,j} = 0, \quad E < (I.P.)_j, \quad (7)$$

where $(I.P.)_j$ is the j th ionization potential. The equations (4) and (6) are the double of the function obtained by fitting σ_i of the hydrogen atom^{9,28} to an exponential one. For $(I.P.)_j - 2 \text{ eV} < E < (I.P.)_j$, the component of the total cross section (4) corresponds to transition to Rydberg states. For $E > (I.P.)_j$, it corresponds transition to a continuum state and is the same as of the ionization cross section (6). The total and ionization cross sections are given by

$$\sigma_t = \sum_j \sigma_{t,j}, \quad (6)$$

$$\sigma_i = \sum_j \sigma_{i,j}. \quad (7)$$

An ionization efficiency, η , is calculated by the equation $\eta = \sigma_i/\sigma_t$.

In Fig. 6, σ_t , σ_i , and η are plotted by changing energy difference between the first and second I.P. (ΔE). Energy differences between higher I.P. are kept constant and taken to be 1 eV. Figure 6(a) shows σ_t , σ_i and η curves for small ΔE , and they correspond to those for alkanes. The σ_t and σ_i curves show a peak at every Rydberg threshold and I.P., respectively, and monotonically decrease toward the next threshold. The η curve also shows step increases at every I.P. The abrupt increases of σ_t and σ_i at the thresholds, however, are smoothed out for alkanes because spectra for σ electrons in organic molecules are broad. The photoelectron bandwidth for σ electrons of organic molecules is roughly 1 eV.²¹ Figure 6(a) hence represents that η with small ΔE monotonically increases with photon energy, and Fig. 6(a) well reproduces the η curves¹⁰ of alkanes.

Figure 6(b) shows the σ_t , σ_i , and η curves for larger

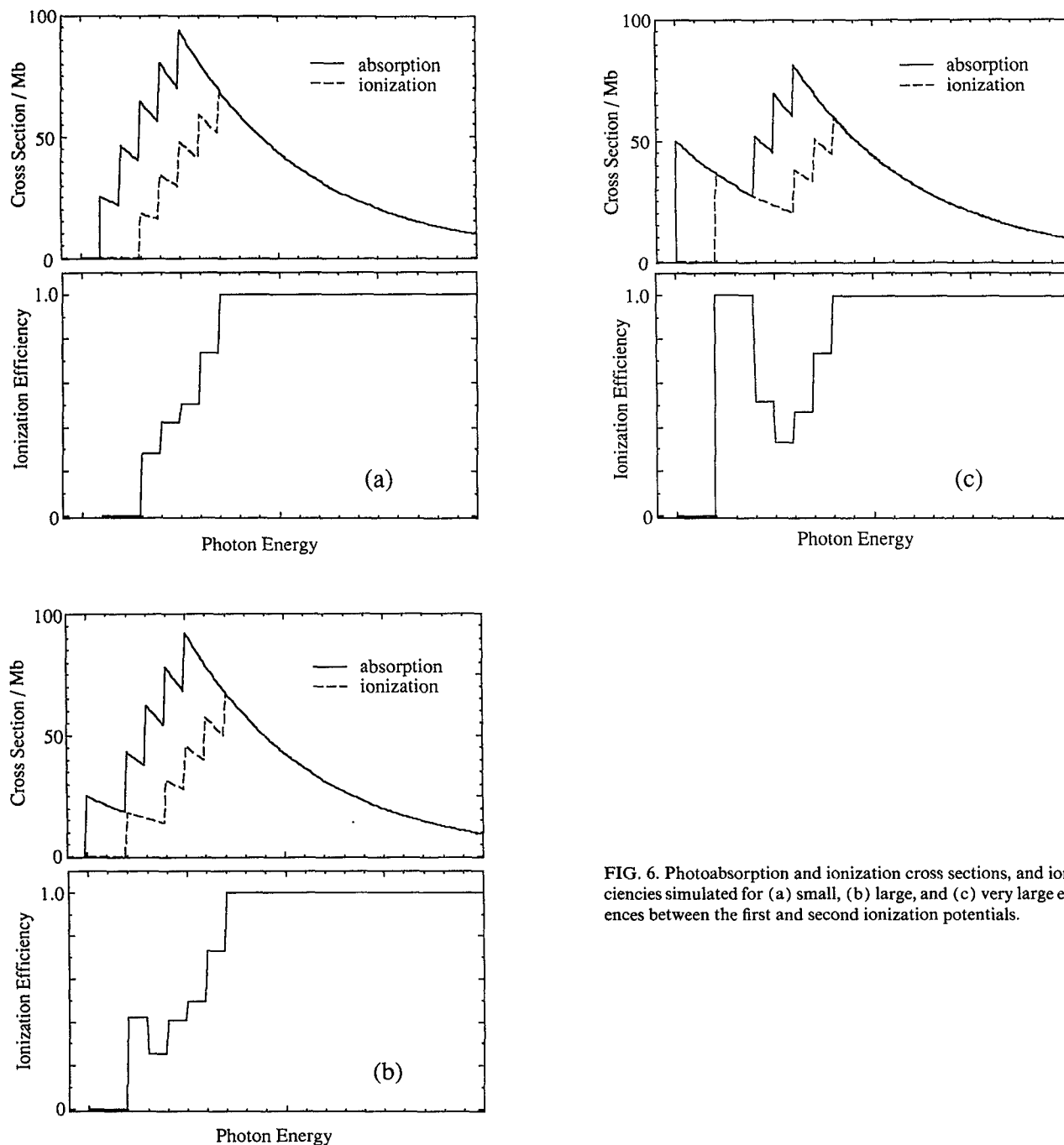


FIG. 6. Photoabsorption and ionization cross sections, and ionization efficiencies simulated for (a) small, (b) large, and (c) very large energy differences between the first and second ionization potentials.

ΔE , which is twice as large as the energy difference between higher I.P. They correspond to those for alkenes, alcohols, and ethers possessing π or lone pair electrons. The difference between Fig. 6(a) and 6(b) is only the position of the first I.P. The η curve shows a maximum at the first I.P., decreases, and increases again from the second I.P., and Fig. 6(b) well reproduces the η curves¹⁰ for alkenes, alcohols, and ethers.

Figure 6(c) shows the σ_i , σ_t , and η curves for very large ΔE , which is assumed to be 4 eV. They correspond to alkynes with degenerated π orbitals. Here ΔE for acetylene and propyne are 4.96 and 4.33 eV,²¹ respectively. The lowest ionic

states of alkynes are degenerate, and accordingly the value of the component is doubled in Fig. 6(c). When ΔE is much larger than 2 eV there are no Rydberg states between the first I.P. and 2 eV below the second I.P. The value of η , then, becomes unity in this region, and shows a dip near the second I.P. Near the first I.P. the observed η curves of acetylene and propyne show much higher values than other organic molecules.^{52,53} Moreover, the dip is observed at 2–3 eV below the second I.P.^{53,54} Fig. 6(c) hence well reproduces the η curves for alkynes.

In conclusion, the above model well explains the shape of the observed η curves. The author believes that most of

the superexcited organic molecules dissociate to neutral fragments.

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