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Intracluster photodimerization of thymine: Size-dependent modes of cluster ion fragmentation

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Clusters of thymine were found to undergo facile and extensive photodimerization upon strong UV irradiation. Multiphoton excitation/ionization yields cluster ions with excess energy, which undergo thermal fragmentation during flight in time-of-flight mass spectrometer. Reflectron mass spectrometry was employed to investigate the fragmentation dynamics. Remarkably size-specific modes of fragmentation were found: a cluster ion that consists of an even number of molecules tends to lose two molecules, while one that consists of an odd number of molecules loses one molecule. The strong alternation of intensity in the cluster mass spectrum was found to be due to such distinct fragmentation modes. The two-molecule loss was found to be a single fission process of a dimeric unit, which was in accord with a model of the cluster ion that consists of mostly dimeric units. The culprit was extensive intracluster photodimerization, which was shown to occur through absorption of anomalously large numbers of photons by the cluster system during excitation/ionization. © 2001 American Institute of Physics. [DOI: 10.1063/1.1406136]

I. INTRODUCTION

Photodimerization of the DNA base thymine by ultraviolet (UV) radiation is known to be a major cause of photoinduced mammalian mutagenesis and carcinogenesis.^{1–5} This reaction was discovered four decades ago,⁶ and has been extensively investigated under *in vitro* and *in vivo* conditions.^{7–11} Recently, we reported the first study of this reaction at a free isolated molecular level by using molecular clusters of thymine and its analogues produced in a supersonic jet.¹² A remarkable alternation of mass spectral intensities between even- and odd-numbered clusters was discovered in photoionization of thymine and uracil clusters. It was suggested that this resulted from intracluster photodimerization, based on the characteristic modulation period evident in the mass spectrum, and also by a control experiment involving different bases with different propensities known for photodimerization in the bulk. Using the occurrence of alternation as the microscopic criterion for photodimerization, it was suggested that intrinsic features of photodimerization could be examined at a molecular level. For example, the intrinsic UV “window” for photodimerization of thymine was found to cover a wavelength range of 210–280 nm, in stark contrast to the typically known range of 150–300 nm in the bulk. The discrepancy is mainly due to the bulk effect, i.e., rapid relaxation of electronic energy in this case.

Despite the phenomenological understanding and circumstantial evidence provided by our study, however, a question remains as to how intracluster photodimerization actually leads to the experimentally observed alternation of mass spectral intensity. In this paper, we report a mechanistic investigation of the processes following UV irradiation. A set of distinct and remarkably size-dependent modes of cluster

fragmentation were discovered, and identified as the main culprit for the striking mass distribution experimentally observed. Multiple absorption of photons was found to play a key role in such intracluster photodimerization.

II. EXPERIMENT

The experimental apparatus used in the present study has been described elsewhere.^{12–14} Briefly, it consists of a set of differentially pumped molecular beam chambers and a reflectron time-of-flight mass spectrometer (TOF-MS). The thymine powder sample was heated to 250 °C in a metal oven and expanded through a high-temperature pulsed nozzle with 2 atm argon carrier gas. The expanding gas was sampled by a skimmer and then ionized by the third or fourth harmonic of an Nd:YAG laser or the frequency-doubled output of a dye laser. The ionized molecules were accelerated to 2.6 keV in a double electrostatic field and directed toward a reflectron through a 1.1 m field-free drift region. At the end of the reflectron assembly, a microchannel plate detector is placed to detect ions when the TOF-MS is operated in the linear mode. In the reflectron mode, the reflected ions travel another 50 cm in the second field-free region and become detected by a second microchannel plate detector. The typical mass resolution $M/\Delta M$ of linear and reflectron TOF-MS was 150 and 900, respectively.

III. RESULTS AND DISCUSSION

A. The even–odd alternation

Figure 1 shows the photoionization mass spectrum for thymine clusters. As reported earlier,¹² all even number peaks have a predominant intensity over their odd number neighbors. This is somewhat different from the so-called “magic numbers,” which tend to represent certain stability

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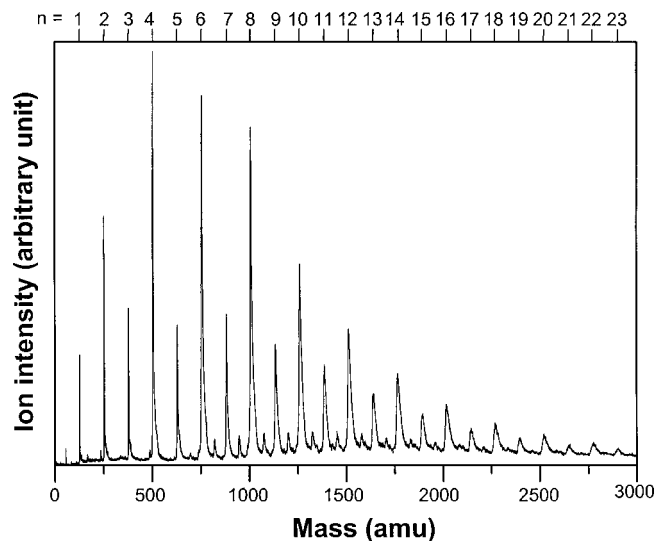


FIG. 1. 1-color R2PI mass spectrum of thymine clusters obtained by linear TOF-MS with a 6 ns laser pulse at 274 nm at a fluence of 1.6×10^6 W/cm². Strong enhancement of even-numbered peaks over odd-numbered ones is evident. Such alternation of mass spectral intensity, however, disappears when the laser fluence is low, or if the excitation is nonresonant with the lowest excited states.

of a cluster system at a particular cluster size. Examples are found in cases where a certain molecular geometry warrants exceptional thermodynamic stability, or when electronic structure became particularly favorable upon forming a closed shell. The present case of the alternating intensity, however, can hardly represent intrinsic stability of the *neutral* even-numbered clusters, since the occurrence of it depends so much on the method of ionization.¹² Therefore, it has been suggested that the intensity alternation is a consequence of secondary processes such as photoexcitation and/or photoionization followed by fragmentation, which in some way come to preferentially populate the even-numbered clusters.

B. Fragmentation dynamics

To unravel the nature of the process that results in the observed alternation pattern, we investigated the fragmentation features of photoexcited thymine cluster ions using reflectron TOF-MS. When a metastable cluster ion decomposes into a daughter ion and a neutral fragment in a field-free region, the daughter ion carries a kinetic energy of $E_d = (M_d/M_p)E_p$, where M_d and M_p are the masses of the daughter and parent ions respectively, and E_p is the parent ion energy.¹⁵ Because of the difference in the kinetic energy, the daughter and the parent ions penetrate into the reflectron over different distances to obtain different flight times, and thus, become separately detected.

Figure 2(a) is the mass spectrum obtained by reflectron TOF-MS under basically the same experimental conditions as used for Fig. 1. The small peaks between the main ion peaks represent daughter ions produced by fragmentation of metastable parent ions in the first field-free region. On close examination of the relative intensities of different daughter ions from a given parent ion, there appears a remarkable

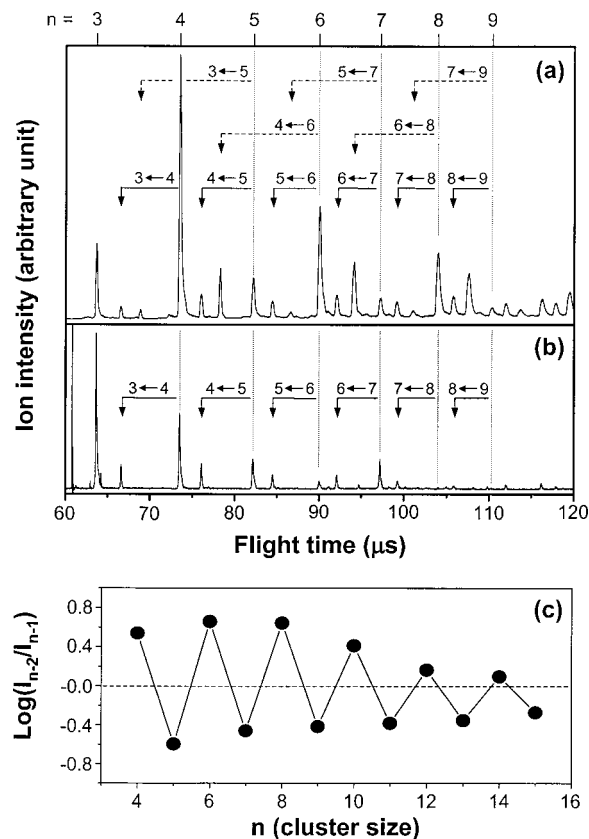


FIG. 2. (a) Reflectron TOF mass spectrum of thymine clusters obtained by 1-color R2PI with a 6 ns laser pulse at 266 nm. The daughter ion peaks with noninteger n values arise from fragmentation of parent cluster ions in the first field-free region. The origin of daughter ions is assigned, and indicated by solid and dashed arrows for the loss of one and two neutral molecules, respectively. The peaks at integer n values exhibit basically the same even-odd alternation pattern observed in linear TOF-MS (Fig. 1). The even-numbered clusters show a propensity to lose two molecules rather than one, while the odd-numbered clusters show the opposite trend. (b) The same kind of reflectron TOF mass spectrum as (a), obtained by 1-color (2+1) REMPI at 355 nm. The integer- n peaks now display a monotonically decreasing distribution, with a pronounced peak at $n=7$. (Ref. 12). Only the loss of monomers is detected exclusively, as represented by solid arrows. (c) The fragmentation branching ratio $\gamma = I_{n-2}/I_{n-1}$ plotted logarithmically as a function of the cluster size, n . I_{n-k} ($k=1,2$) is the flight-path normalized intensity of daughter ions of size $(n-k)$ from a parent cluster ion of size n .

trend: an odd-numbered parent ion tends to lose one neutral molecule than two, while the opposite is true for an even-numbered parent ion. For example, if we compare the raw intensity of the trimer and tetramer daughter ions generated from the pentamer parent ion, we see that the tetramer intensity is about three times higher than the trimer's (and four times after the flight path normalization¹⁵); But on the contrary, if we compare the tetramer and pentamer daughter ions from the hexamer parent ion, the pentamer intensity is only about one quarter of the tetramer intensity. Loss of more than two neutral molecules was not detected.

In order to better represent the two distinct modes of fragmentation, we came up with a quantity called the fragmentation branching ratio γ , which is defined as $\gamma = I_{n-2}/I_{n-1}$, where I_{n-k} ($k=1,2$) is the intensity of daughter ions from loss of k neutral molecules. This ratio γ is logarithmically plotted in Fig. 2(c) as a function of the parent cluster size n . It is quite evident that there exist starkly op-

posite trends between even-numbered and odd-numbered parent cluster ions. We also realize that these strongly opposite propensities for fragmentation during flight would certainly enhance the final ion intensity of even-numbered daughter ion clusters, as observed in Fig. 1.¹⁶

On the contrary, when the 355 nm photons were used in (2+1) REMPI, loss of only one neutral molecule was observed, irrespective of the size of the parent cluster ion [Fig. 2(b)]. In addition, the mass distribution does not show any sign of intensity alternation in this case.¹² Therefore, we conclude that the remarkable size-dependent of fragmentation modes of cluster ions are uniquely responsible for the observed intensity alternation in the 266 nm R2PI mass spectrum.

We propose that the ultimate cause of such strongly opposite trends in fragmentation should be the formation of dimeric molecular units in the cluster ion as a result of photoinduced reactions such as photodimerization. The existence of such intracuster dimeric units is supported by the following argument. The loss of two molecules in Fig. 2(a) may indicate a sequential loss of monomers or a single fission of a dimer. If the ionized cluster were a collection of loosely bound monomers, the loss of one molecule is always a more likely outcome than the loss of two molecules because fragmentation in this case must be sequential in the statistical limit. This would dictate that I_{n-1} be always larger than I_{n-2} , irrespective of n . The fact that this is certainly not the case, as clearly seen in Fig. 2(c), indicates that the fragmentation is far from a sequential loss process of monomeric units. It also strongly suggests that the two-molecule loss of Fig. 2(a) must occur as a single step fission of a dimeric unit. We propose that a given cluster ion be composed of a predominant number of dimers over monomers if it is to override the otherwise statistical monomeric loss and retain the alternation signature. For example, if the cluster ion of $n=12$ in Fig. 2(c) had contained only a dimeric unit or two, with all the rest of molecules in a monomeric form, it would have resulted in mostly monomeric losses. It appears that the photodimerization process is very facile and extensive in cold clusters, as in other constrained medium in the condensed phase at low temperatures.¹⁷

On the other hand, in the (2+1) REMPI using the 355 nm photons, no such dimeric units are to be formed in the first place since the two-photon excitation is nonresonant with the UV window for photodimerization.¹² Therefore in this case, the cluster ion remains to be composed of purely monomeric molecules, and statistical fragmentation gives an overwhelmingly dominant monomer loss pattern, as evident in Fig. 2(b). As a result, a series of monotonically decreasing main peaks are obtained, with no sign of alternation.¹²

C. Multiple absorption of photons

Since the formation of a single photodimer needs a one-photon absorption process, formation of multiple photodimer units in the cluster must require processes other than the simple two-photon ionization via intermediate level. We offer two possibilities. The first is to assume a very fast electronic energy transfer from the newly produced photodimer to a neighboring molecular pair in the ground state, which

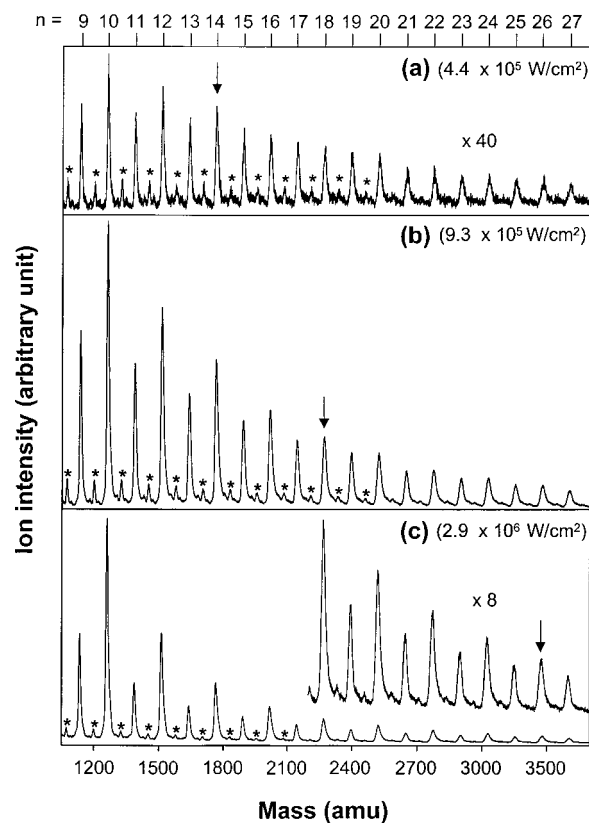


FIG. 3. Linear TOF mass spectra obtained by using a 6 ns, 266 nm laser pulse at fluences specified in each panel. Asterisks represent doubly charged ions. As the laser fluence is increased, larger clusters tend to undergo extensive fragmentation, and the mass distribution is steeply shifted toward lower masses. (a) At a low laser fluence of $4.4 \times 10^5 \text{ W/cm}^2$, the alternation is observed only up to $n=14$ (shown by arrow), followed by a monotonically decreasing distribution. (b) At a higher fluence, the alternation continues up to $n=18$. (c) At a still higher fluence, fragmentation is very severe, yet the alternation pattern is observed up to $n=26$.

then undergoes dimerization. This could ultimately lead to sequential photodimerization if the electronic energy transfer is faster than intramolecular relaxation. It has been pointed out that the energy transfer can be as fast as even intramolecular vibrational redistribution within a cluster system.¹⁸

The other, more likely, explanation is the multiple photon absorption phenomenon in clusters. Absorption of as many as eight photons was observed with a nanosecond laser pulse at a fluence an order of magnitude lower than used in our study, and multiply charged cluster ions were detected.¹⁹ If multiple photon absorption does indeed occur, and results in photodimerization that eventually leads to the observed alternation pattern, it is expected that a finite number of photons absorbed would allow formation of only a certain maximum number of photodimers. In other words, there should exist a maximum cluster size beyond which the alternation ceases. Furthermore, this maximum cluster size for alternation would be a function of laser fluence. These predictions correctly bear out in fluence-dependent mass spectra shown in Fig. 3. It is seen that there does exist a maximum cluster size (denoted by arrow) for intensity alternation and that it is indeed found to shift to a larger cluster size at higher fluences. In view of these results, the multiple photon absorption scheme appears to be a sound model. Furthermore, de-

tection of doubly charged ions (represented by asterisks in Fig. 3) also seems to support this model.²⁰ Multiple absorption of photons can lead to photodimerization as well as generation of multiply charged ions, which may compete against each other. We note from Fig. 3 that the relative intensities of doubly charged ions are reduced as higher fluences. This may indicate that photodimerization is a dynamically more favored process over multiple ionization for these clusters under the present experimental conditions.

ACKNOWLEDGMENT

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- ¹ Hollaender and C. W. Emmons, *Cold Spring Harbor Symp. Quant. Biol.* **11**, 78 (1946).
- ² H. F. Blum, *Carcinogenesis by Ultraviolet Light* (Princeton University Press, Princeton, NJ, 1959).
- ³ F. Urbach, *The Biological Effects of Ultraviolet Radiation* (Pergamon, New York, 1969).
- ⁴ J. H. Epstein, *Photophysiology* **5**, 235 (1970).
- ⁵ G. J. Kantor, *Photochem. Photobiol.* **41**, 741 (1985).
- ⁶ R. Beukers and W. Berends, *Biochim. Biophys. Acta* **41**, 550 (1960).
- ⁷ J. Eisinger and R. G. Shulman, *Proc. Natl. Acad. Sci. U.S.A.* **58**, 895 (1967).
- ⁸ P. J. Wagner and D. J. Bueckel, *J. Am. Chem. Soc.* **92**, 181 (1970).

- ⁹ R. Beukers and W. Berends, *Biochim. Biophys. Acta* **49**, 181 (1961).
- ¹⁰ W. Füchtbauer and P. Mazur, *Photochem. Photobiol.* **5**, 323 (1966).
- ¹¹ A. A. Lamola and J. Eisinger, *Proc. Natl. Acad. Sci. U.S.A.* **59**, 46 (1968).
- ¹² N. J. Kim, H. Kang, G. Jeong, Y. S. Kim, K. T. Lee, and S. K. Kim, *Proc. Natl. Acad. Sci. U.S.A.* **98**, 4841 (2001).
- ¹³ N. J. Kim, H. Kang, G. Jeong, Y. S. Kim, K. T. Lee, and S. K. Kim, *J. Phys. Chem. A* **104**, 6552 (2000).
- ¹⁴ N. J. Kim, G. Jeong, Y. S. Kim, J. Sung, S. K. Kim, and Y. D. Park, *J. Chem. Phys.* **113**, 10051 (2000).
- ¹⁵ S. Wei, W. B. Tzeng, and A. W. Castleman, Jr., *J. Chem. Phys.* **92**, 332 (1990).
- ¹⁶ If the fragmentation occurs within the acceleration region, what appear like parent ion peaks in mass spectrum can contain the daughter ion peaks from those ions that underwent fragmentation within the acceleration region. This is true of both the linear and reflectron mass spectra. The difference between them, however, is that in the latter, the daughter ions that fragment in the field-free region can be distinguished from those that have undergone fragmentation in the acceleration region. Since a large fraction of fragmentation occurs in the acceleration region, the gross features of the linear and reflectron mass spectra [Figs. 1 and 2(a), respectively] at integer n values are very similar. There is only the added feature of daughter ion peaks at noninteger values of n in the latter.
- ¹⁷ A. Wacker, *Prog. Nucleic Acid Res. Mol. Biol.* **1**, 369 (1963).
- ¹⁸ Y. Tomioka, H. Abe, N. Mikami, and M. Ito, *J. Phys. Chem.* **88**, 5186 (1984).
- ¹⁹ M. Y. Hahn, K. E. Schriver, and R. L. Whetten, *J. Chem. Phys.* **88**, 4242 (1988).
- ²⁰ A fluence dependence study of mass spectral intensities to confirm the multiple absorption of photons was severely hindered by extensive fragmentation.