Multiphoton Ionization--Fragmentation Patterns of Alkyl Iodides

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Multiphoton ionization (MPI)--fragmentation patterns are reported for six alkyl iodides (methyl, ethyl, n-propyl, isopropyl, n-butyl, and tert-butyl) in the 400-360-nm region. Three- or four-photon ionization is resonantly enhanced via two-photon excitations to various spin--orbit components of the 5p→6s molecular Rydberg transition. For each of these molecules a minimum of seven photons (overall) must be absorbed to account for the observed ion fragments, (which include C3+ and H6+). For methyl iodide it appears that different intermediate Rydberg states can affect the rate of ionization and thus the subsequent ion fragmentation process, possibly due to retention by the ion of the differing Rydberg-state geometries. Such distinct fragmentation effects are not observed for different resonant states in the larger alkyl iodides. Although the resonant-state spectra are essentially continuous, significant structure-sensitive information can be obtained by means of the MPI mass spectral (MPIMS) technique. For the isomers n-propyl iodide and isopropyl iodide (whose electron impact mass spectra are essentially identical) the MPIMS patterns are significantly different; similarly for tert-butyl iodide and n-butyl iodide. This is attributed to differences in the spectroscopic and dynamics properties of the first-formed fragment ion in the MPI-fragmentation process. Specifically, the n-propyl and n-butyl cations do not isomerize appreciably within the 5-ns laser pulse duration but absorb the 368-nm radiation and photodissociate, whereas the isopropyl and tert-butyl cations are essentially transparent at this wavelength and thereby persist without fragmentation.

Introduction

Much progress has been made over the past several years in understanding resonance-enhanced multiphoton ionization--dissociation (REMPID) processes in polyatomic molecules. REMPI is, in itself, a mature branch of two- and three-photon spectroscopy in which the intensity of an excited electronic state, often a molecular Rydberg state,' is strongly enhanced by the existence of an intermediate Rydberg state. A (typically) three- or four-photon ionization process is reached via two- or three-photon absorption. Analysis of the usually extensive ion photofragmentation which takes place during the laser pulse duration has been the subject of much recent research. One motivation for such study is in the development of REMPI as a tool for analytical mass spectrometry.

Several techniques have been used to examine the successive steps in the REMPI process. Kinetic-energy analysis of the photoelectrons, cations, and anions has established for several molecules that fragmentation takes place up the "ionic ladder" (rather than via the neutral autoionization route). Two-laser studies have confirmed this for several cases and have also indicated the importance of the parent-ion absorption spectrum in determining the extent and the laser-power dependence of fragmentation. Much more detailed information on this aspect is provided by a combined electron impact--laser technique where (parent and daughter) ions are formed by electron impact and then selectively dissociated by a pulsed tunable dye laser.

A number of other studies, experimental and theoretical, have contributed to the understanding of the REMPID process. In many cases it appears that the total energy available to the parent ion after multiphoton ionization occurs is important, but the manner in which the ion was formed is not. This premise is tested for a number of simple alkyl iodides; evidence to the contrary will be presented for methyl iodide.

The usefulness of REMPID to analytical mass spectrometry will be governed by sensitivity and selectivity. Although the duty factor of present pulsed lasers is low (cf. CW electron impact sources), the ionization probability per pulse is typically greater for photons. Spectroscopic selectivity is the major advantage of MPI, however. Selective photoionization of isomeric and isotopic molecules has been demonstrated. For the isomers azulene and...
naphthalene the laser can be wavelength-tuned to a resonance of one molecule, ionizing it without exciting the other isomer.\(^{16}\) Similar results have been reported for substituted anilines.\(^{18}\) In both studies the fragmentation patterns, both EI and MPI, of the two isomers were readily distinguishable. The geometric isomers cis- and trans-dichloroethylene can be selectively ionized by appropriately tuning the laser.\(^{16}\) Here the fragmentation patterns, both EI and MPI, were found to be essentially identical. In the present study it will be shown that the isomers isopropyl iodide and n-propyl iodide, whose EI fragmentation patterns are almost indistinguishable, cannot be wavelength-selected because of overlapping absorption spectra; yet they can be easily distinguished by their very different REMPIID patterns. Similar results are also noted for the isomers tert-butyl iodide and n-butyl iodide.

As in the previously reported MPI-fragmentation study of the tertiary amines,\(^{11}\) considerable structure-sensitive information can be obtained from the REMPIID results despite the absence of resolvable spectroscopic features in the REMPI bands. Thus, many molecules formerly believed to be less interesting for study by MPI spectroscopy now become important subjects of investigation via laser mass spectrometry. These include the alkyl iodide family, six members of which have been chosen for the present study.

**Experimental Section**

The laser ionization time-of-flight mass spectrometer (TOFMS) has been described in detail previously.\(^{2\mathrm{a}}\) Laser wavelengths useful in this study were generated by mixing the fundamental of a Nd:YAG laser with the output of a tunable dye laser, pumped by the Nd:YAG second harmonic. A 250-mm f/ lens was used to focus the final laser beam into the ionization region of the TOFMS. Laser pulse energies (mJ) were measured by a calorimeter. Electron impact mass spectra at 70 eV were recorded for comparison with MPI-fragmentation patterns obtained in the same apparatus. Sample pressures were typically \(1 \times 10^{-5} - 2 \times 10^{-6}\) torr.

The samples used were commercial grade, degassed before use. The larger alkyl iodides were found to contain small fractions of isomeric impurities as well as some methyl iodide. No effort was made to correct for these, except that laser wavelengths were chosen to avoid methyl iodide absorptions. The integrated ion signal vs. wavelength (i.e., the MPI spectrum) for each molecule was found to be in good agreement with known MPI cell spectra\(^{17}\) (except for isopropyl iodide and tert-butyl iodide, whose spectra have not been published). In the next section TOFMS results for all six alkyl iodides will be summarized and discussed.

**Results and Discussion**

REMPIID patterns as a function of laser pulse energy will be presented for methyl, ethyl, n-propyl, isopropyl, n-butyl, and tert-butyl iodides and compared with EI spectra at 70 eV. Additional MPI mass spectra at different wavelengths will be displayed for methyl iodide. The excitation wavelengths were chosen to coincide with the vibrationless origins of the various spin–orbit components of the 5\(\pi\pi \rightarrow 6\) molecular Rydberg transition.\(^{18}\) Of particular interest are the A and E components (5\(\pi\pi\) and 1\(\pi\)) lying near 370 and 366 nm for each molecule.\(^{19}\) No significant differences in the total ion currents were observed between isopropyl iodide and n-propyl iodide or


between tert-butyl iodide and n-butyl iodide.

Methyl Iodide. Figure 1 shows the REMPID patterns for methyl iodide at several laser pulse energies, for a laser wavelength of 370 nm, resonant with the A1 origin by two-photon absorption. To be noted is the typically observed continuous shifting of fragmentation toward smaller masses with increasing laser pulse energy. The 70-eV EI spectrum of methyl iodide is shown in the bottom panel of Figure 1. The total ion current was found to increase as the square of the laser pulse energy, consistent with a two-photon resonant-state “bottleneck”.

Higher-resolution scans of the methyl iodide fragmentation pattern are shown in Figure 2 for low- and high-mass regions. These spectra were taken in separate scans in order to include H+, which has not been monitored in the other REMPID spectra in this paper. (The apparent relative intensity of H+ was found to vary from time to time much more than that for the larger ions.) Although the similarity of the CH+ and CHI+ patterns (n = 0, 1, 2, 3) is striking in this figure, such similarity was not always observed at other laser wavelengths and pulse energies. The low relative abundance of CH+ and CHI+ is general for REMPID of methyl iodide. However, this is not found in the EI spectrum.

The qualitative features of REMPID of methyl iodide can be interpreted with the aid of Figure 3. Shown are the appearance potentials of the possible ionic fragments of methyl iodide vs. the minimum number of near-UV photons. Level 1 is a virtual state in the two-photon resonance followed by successive two-photon resonant three-photon ionization process. The low relative abundance of CH+ and CHI+ is general for REMPID of methyl iodide. However, this is not found in the EI spectrum.

![Figure 3](image-url) Energy-level diagram for REMPID of methyl iodide showing two-photon resonant three-photon ionization followed by successive photofragmentation of CHI+ (level 3). Dashed lines are estimated; solid lines are known appearance potentials of (possible) ion fragments.

![Figure 4](image-url) Detailed energy-level diagram for REMPI of methyl iodide via several two-photon resonant states. Three-photon ionization is possible for photon energies above 27 250 cm⁻¹. The lower E [27] state correlates with the E [27] CHI+ potential; the upper E [27] A1 and E [27] E states correlate with E [27] CHI+ and E [27] CHI+. Also shown are the photoelectron spectrum and the UV absorption spectrum of CHIcluding the A1 (v = 0, 1) bands, marked by asterisks, which appear only in the two-photon spectrum.

The photoelectron spectrum of methyl iodide also included in Figure 4 shows the two spin–orbit components.


of ground-state CH$_3$I$^+$ and the first excited state lying near 12 eV. The photodissociation spectrum of CH$_3$I$^+$, which has also been reported$^{23}$ for the lower region of the first excited state, is similar (while resolving some vibrational fine structure).

The lowest observed state, E ($^3\Pi_g$) with vibrationless origin at 6.12 eV, correlates in the limit of strong spin-orbit coupling with the E$_{\sigma\pi}$ component of CH$_3$I$^+$ while the other two components, A$_1$ and E ($^3\Pi_u$ and $^1\Pi_u$), correlate with the E$_{\pi\sigma}$ component. For this upper level four laser photons (\(\lambda \geq 367\) nm) are required for ionization. The vibrationless origin of the second E state and the $\delta_0$ band of the A$_1$ state lie in the three-photon ionization region. MPI cell spectra$^{17}$ show only a slow rise in ionization signal when crossing this limit.

Figure 5 shows the REMPID patterns of methyl iodide at constant laser pulse power for the four resonances shown in Figure 4. The longest-wavelength excitation (402 nm) results in the most extensive fragmentation observed—as indicated by the almost complete loss of parent ion. The total ion yield is low because of the four-photon requirement, however, and is consistent with the relative intensities of the REMPI cell spectra.$^{17}$ Such fragmentation behavior can be easily understood from Figure 4, where the fourth photon is seen to lie in the region of the first excited states of CH$_3$I$^+$. The "doorway" to further absorption and resulting fragmentation is thus "open" compared to the shorter wavelengths where the fourth photon terminates in a region of weak ion absorption. This mechanism has recently been shown to control the extent of fragmentation in other molecules also, notably hexa diyne$^{10}$ and the tertiary amines.$^{11}$

Further information can be obtained from the three higher-energy resonances. The results shown in Figure 5 indicate a much larger degree of fragmentation for the (\(\nu = 0\) and 1) A$_1$ bands than for the interposed E($\nu = 0$) band. (To obtain the same degree of fragmentation, it is necessary to double the laser pulse energy when resonant with the E state.$^{21}$ The total ion current is again consistent with the REMPI cell spectra where the relative ion yield is roughly 2:1:0.5 for the A$_1$($\nu = 0$), E($\nu = 0$), and A$_1$($\nu = 1$) bands, respectively. Since the ion absorption spectrum is essentially continuous in this region,$^{23}$ it is difficult to rationalize this fragmentation trend through a chance doorway variation. A correlation with the type of intermediate resonant state selected (A$_1$ vs. E) seems indicated by the marked similarity of the two A$_1$ band fragmentation patterns.

A qualitative explanation for this possible dependence on the resonant intermediate state arises from consideration of the excited-state geometry. Rotational line-shape analysis$^{17}$ of the REMPI spectra suggested that the HCH bond angle is larger for the A$_1$ state than for the ground state, while the E-state and ground-state geometries are very similar. An approach toward planarity of the methyl group would elongate the C-I bond, making the molecule less stable. As noted, REMPID through the A$_1$ levels results in significantly more fragmentation (at a given laser pulse energy) that the E level. If the different geometries of the two Rydberg states are retained in the ion, different fragmentation could be expected. Successive photoabsorption must take place very quickly compared to collisional relaxation effects—with a long-time limit of the \(\sim 5\)-ns laser pulse length.

Similar effects were not detected in the REMPID patterns of the larger alkyl iodides. Because of the almost diffuse spectra of these systems, caused in part by sequence congestion, it is much more difficult to excite a single resonant state component.

**REMPID Patterns for Larger Alkyl Iodides.** Total ion currents were found to increase quadratically with laser pulse energies, as expected, for the four larger RI molecules. REMPID patterns for ethyl iodide at several laser pulse energies are compared with the 70-eV EI mass spectrum in Figure 6. The laser wavelength at 372 nm is two-photon resonant with the A$_1$ absorption region. Similar fragmentation patterns were observed with other wavelengths at similar laser powers. Almost no parent ion or parent minus hydrogen(s) is observed with MPI, even for the lowest laser pulse energies, indicating strong parent- ion absorption at these wavelengths. The appearance of C$^+$ and C$_2^+$ at higher pulse energy is also noted in Figure 6. The observed changes in the fragmentation patterns for a fourfold increase in laser power are rather small and will be discussed later. However, since the "expensive" C$^+$ ions are formed, a large number of photons must be absorbed at high laser powers.

Another interesting difference between the REMPID and EI mass spectra concerns mass 28 (C$_2$H$_4$I$^+$). As shown in more detail in Figure 7, almost no C$_2$H$_4$I$^+$ is observed with MPI, in contrast to EI. REMPID of molecules with similar alkyl groups (e.g., triethylamine) at similar laser wavelengths has been shown to produce an abundance of C$_2$H$_4$I$^+$. This ion is simply not formed in the REMPID of ethyl iodide.

The REMPID and EI patterns for the isomers n-propyl iodide and isopropyl iodide are compared in Figure 8. The
the laser photons of 368 nm. But consider the REMPID although atypical of most REMPID patterns, patterns for isopropyl iodide. No significant change in fragmentation is observed over a threefold range of laser pulse energy. The total ion yield is found to increase strongly with laser power, via REMPID.

Strong similarity of the E1 spectra, taken under identical conditions, precludes distinguishing these isomers by their EI spectra. However, their REMPID patterns are very different at the same wavelengths and pulse energy.

For both isomers the parent ions are "burned out" by the laser photons of 368 nm. But consider the REMPID patterns for isopropyl iodide. No significant change in fragmentation is observed over a threefold range of laser pulse energy. The total ion yield is found to increase strongly with laser power, as expected. Such behavior, although atypical of most REMPID patterns, has also been observed in the tertiary amines. A major difference, however, is that here a large number of fragments are observed and found independent of laser power in contrast to only two species (the parent and a large daughter ion) for the tertiary amines. It is to be expected that at least some of the fragments would further absorb photons from the laser pulse, leading to increasing fragmentation with increasing laser power.

Similar effects are observed for n-propyl iodide, though less pronounced. For a fourfold increase in pulse energy, only a small fraction of fragments (C⁺, C₂H₅⁺, and CH⁺ ions) are generated. This is again atypical REMPID behavior. Only the I⁺ yield shows a dependence on the laser power, for both propyl iodide and butyl iodide.

n-Butyl iodide and tert-butyl iodide are compared in Figure 9 for REMPID and 70-eV EI. The two molecules can be distinguished by EI, with the tert-butyl isomer fragmenting to a larger extent. The appearance of C₂H₄⁺ should also be noted in both EI spectra. The REMPID patterns are most surprising for tert-butyl iodide. Essentially only one ion is observed (a fragmentation) over a threefold energy range. In contrast, the REMPID patterns for n-butyl iodide show extensive fragmentation (no parent ion present) which, once more, has only a slight dependence on the laser power. tert-Butyl iodide fragments mainly to the (CH₃)₂C⁺ ion, with almost no parent ion formation. (As for ethyl iodide and the propyl iodides, again no C₂H₅⁺ is observed in the REMPID mass spectra.) For tert-butyl iodide, the lack of fragmentation with increasing laser pulse energy implies that the tert-butyl cation (or its precursor) does not dissociatively absorb at this laser wavelength. Either this cation is formed directly via the absorption of a fourth photon or a precursor such as a highly excited parent ion produces the tert-butyl ion in a short time (ca. 1 µs) after absorbing the fourth photon. The latter suggestion is attractive for interpretation of REMPID of the other alkyl iodides.

If the precursor of the observed fragments has a lifetime τ ≫ τ₀, the laser pulselength, most of these fragments will not be excited (and further dissociated) by the laser. The complicated fragmentation pattern will be unchanged with increasing pulse energies (although the overall ion yield increases). Less-stable precursors will yield fragments earlier (τ < τ₀) and thus show stronger fragmentation-pulse energy dependence.

Metastable ions, commonly found in EI studies, have been recently observed also in MPI mass spectra. Only when the precursor lifetime is of the order of the ion acceleration time (i.e., microseconds) can the metastable processes be detected (via peak broadening). Metastable lifetimes τ ≈ τ₀ (~5 ms) are consistent with this mechanism, which accounts for most of the general features of the REMPID spectra. For experiments at increasing laser power, multiphoton absorption by the precursor should eventually dominate, yielding more complex fragmentation behavior. Further experiments are obviously necessary to gain a better understanding of the REMPID process.

Concluding Remarks

For methyl iodide several resonant states have been compared and found to affect the subsequent ion fragmentation process. For all of the alkyl iodide molecules, the importance of the parent-ion absorption spectrum has been noted. The isomer pairs n-propyl iodide—isopropyl iodide and n-butyl iodide—tert-butyl iodide have been


(25) Unpublished results on tertiary amines from this laboratory.
examined by REMPID and EI. Even in the absence of wavelength selectivity, REMPID mass spectra contain significant structure-sensitive information on these molecules. A simple mechanism involving metastable precur-
sors has been proposed to account for the atypical behavior of the REMPID fragmentation patterns of the alkyl iodide molecules with increasing laser pulse energy. A key finding of the present study is that the n-propyl and n-butyl cations do not isomerize appreciably (to isopropyl or tert-butyl cations, respectively) within the 5-ns laser pulse duration but absorb the 365-nm radiation and photodisassociate, whereas the isopropyl and tert-butyl cations are essentially transparent at this wavelength and thereby persist without fragmentation.

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Kinetics of the Reactions of Methoxy and Ethoxy Radicals with Oxygen

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Rate constants have been obtained as a function of temperature for the gas-phase reactions of methoxy and ethoxy radicals with oxygen. The alkoxyl radicals were produced by the 266-nm photolysis of the corresponding nitrites, and their concentrations were monitored by using laser-induced fluorescence. The CH₃O + O₂ reaction was studied from 140 to 355 °C, and the rate constants obtained were used to derive an Arrhenius expression, 6.3 × 10^7 exp(-2.6 kcal/RT) M⁻¹ s⁻¹. The C₂H₅O + O₂ reaction was studied at two temperatures, and the rate constants obtained were 4.8 × 10^6 M⁻¹ s⁻¹ (23 °C) and 5.9 × 10^6 M⁻¹ s⁻¹ (80 °C). Upper limits for the rate of the isomerization reaction, CH₃O + M → CH₃OH + M, are calculated, and the possible use of the results of this study in atmospheric smog modeling is discussed.

Introduction

Alkoxyl radicals are important reaction intermediates formed during the gas-phase oxidation of most hydrocarbons. In the early, low-temperature stages of combustion these labile intermediates form largely through the decomposition of peroxycarbon species:

$$\text{ROOR}' \rightarrow \text{RO}^- + \text{R'O}^- \quad (1)$$

Subsequent reactions of these radicals ultimately produce such products as aldehydes, ketones, and alcohols. In photochemical smog cycles, alkoxyl radicals are produced from the oxidation of nitric oxide by alkylperoxyl radicals:

$$\text{RO}_2 + \text{NO} \rightarrow \text{RO}^- + \text{NO}_2^- \quad (2)$$

Under atmospheric conditions RO⁻ can react with oxygen

$$\text{RCH}_2\text{O} + \text{O}_2 \rightarrow \text{RCHO} + \text{HO}_2 \quad (3)$$

Isomerize or decompose.³

Although the reactions of alkoxyl radicals have been the subject of numerous studies, our present knowledge of the reactivity of these intermediates is still largely based on indirect kinetic measurements. The primary obstacle to performing direct studies has been the lack of a suitably sensitive method for dynamically monitoring these free radicals under well-defined reaction conditions. Recently Inoue, Akimoto, and Okuda have observed and analyzed the laser-induced fluorescence (LIF) spectra of three simple alkoxyl radicals.⁴ These studies have now provided the spectroscopic information needed to use LIF as a diagnostic method in future chemical kinetic studies of the reactions of the three radicals, CH₃O, C₂H₅O, and C₃H₇O.

The first direct study of an alkoxyl radical reaction was reported by Sanders, Butler, Pasternack, and McDonald.⁵ The investigation involved the production of CH₃O using pulsed UV laser photolysis of CH₃ONO and the subsequent monitoring of the decay of CH₃O by LIF in the presence of different reactant gases. A rate constant for the reaction with NO was obtained,⁶ as were upper limits on the rate constants of nine other reactions, all at room temperature. We wish to report that this same experimental procedure has now been used with a heated reaction vessel to study the reactions of CH₃O and C₂H₅O with oxygen at several temperatures.

Prior studies of RO + O₂ reactions have all been of the simplest of the series, namely

$$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2 \quad (4)$$

Three recent publications have focused on reaction 4, reporting rate constants at various temperatures.¹²-¹³ All

(1) On sabbatical from the Department of Chemistry, Illinois Institute of Technology, Chicago, IL 60616.

(9) Sanders, N.; Butler, J. E.; Pasternack, L. R.; McDonald Chem. Phys. 1980, 46, 203.
(10) Room-temperature value for the CH₃O + NO rate constant reported in ref 9 is valid only for the 15 ± 5 torr of SF₆ buffer gas pressure used in the experiments on this reaction. Subsequent work at other pressures confirms that this reaction is in the falloff region at 15 torr.