

# Multiple Photon High Vibrational CH Overtone Resonant and One-Photon Dissociation of Toluene Radical Cation

A. P. SIMONOV, G. A. ABAKUMOV, V. T. YAROSLAVTZEV,  
V. A. LUNCHEV and E. A. FEDOROV

*Karpov Physical Chemistry Institute, 10 Ul. Obukha, 107120 Moscow, USSR*

*(Received April 5, 1985; in final form May 6, 1985)*

Photodissociation of molecular radical cations of toluenes  $C_7H_8^+$  (I),  $C_6H_5CD_3^+$  (II),  $C_7D_8^+$  (III), cycloheptatriene  $C_7H_8^+$  (IV), and benzene has been studied by the method of two-pulse two-colour laser photolysis of molecules in a mass spectrometer using wavelengths 1064, 532, and 355 nm. The I ions formed due to sequential two-photon ionization of toluene molecules by the 266 nm radiation isomerize supposingly into 5-methylene-cyclohexadiene (VI). Two- and three-photon stepwise dissociation of the I and II isomers (VI and VI-d<sub>3</sub>, respectively) induced by the 1064 nm radiation has a resonance at the third overtone level of CH aliphatic bond stretching vibrations. Internal energy randomization in the two-photon dissociation is much less for VI-d<sub>3</sub> as compared to VI. The mechanisms of isoenergetic dissociation (two- and one-photon processes induced by the 1064 and 532 nm radiations, respectively) are different: the one-photon decay via an electronically excited state proceeds considerably faster than the two-photon decomposition does in the ground state. The photodissociation cross sections have been determined. It has been shown that the intensity of CH stretching vibration overtones can be essentially higher for radical cations than for the neutral molecules.

## INTRODUCTION

Studies of the dissociation of polyatomic molecules induced by direct excitation of stretching vibration high overtones of the hydride bonds<sup>1-5</sup> plays a significant part in the search for non-statistical photochemical reactions which are selective in vibrational modes. On the other hand, the properties of the overtones themselves have become

the subject of much investigation.<sup>6-12</sup> New data that are of interest both for the selective laser photochemistry and for further development of the local mode theory which describes overtones can be obtained in studies of molecular radical cation dissoication caused by direct excitation of CH stretching vibration high overtones. This idea is based on the expectation that the intensities of such overtones can be much higher than for neutral molecules because of significant changes in electronic structure and decrease of the CH bond dissociation energy for many radical cations.

Indeed, the overtone intensity of an anharmonic oscillator depends on its dipole moment coordinate function, the anharmonicity constant, and the mechanical frequency. For example, the transition intensity from the zeroth to a high vibrational level  $v$  for a Morse oscillator with the dipole moment  $\mu(r)$  linearly depending on the coordinate

$$\mu(r) = \mu_0 + \mu_1(r - r_e)$$

( $r_e$  is the coordinate of the equilibrium configuration) is proportional to  $\mu_1^2 x_e^{v-1} / \omega_e^{13}$ , where  $x_e$  and  $\omega_e$  are the anharmonicity constant and mechanical frequency. Two of these quantities characterize the oscillator dissociation energy

$$D_0 = \omega_e(1 - x_e)^2 / 4x_e.$$

Therefore the lowering of the dissociation energy should increase the intensity of such transition. The intensity may also grow due to a possible rise of the oscillator dipole moment gradient  $\mu_1$  caused by a change in the radical cation electronic structure induced by a positively charged hole.

An essential increase of the CH stretching vibration overtone intensity can be expected for the toluene radical cation because the CH bond dissociation energy is significantly lowered (by  $\sim 1.6$  eV) as compared to the neutral (all thermochemical estimates use<sup>14-16</sup>). It can be assumed taking into account a change in electronic structure on the ionization of molecular toluene that the mechanical frequency of the aliphatic oscillator (the CH bonds in the methyl group) falls off in the radical cation by 150–200  $\text{cm}^{-1}$  and is 2900  $\text{cm}^{-1}$  ( $\omega_e \approx 3060 \text{ cm}^{-1}$  for toluene<sup>17</sup>). Then we can estimate using the known value of the aliphatic CH bond dissociation energy for the radical cation,  $D_0^+ = 2.2$  eV, the  $x_e$  value and the energy of the overtone levels accord-

ing to Birge-Sponer equation

$$E_{0,v} = v(A + vB)$$

with  $A \approx 2790 \text{ cm}^{-1}$  and  $B \approx -110 \text{ cm}^{-1}$  and see that the third overtone of these oscillators may be in resonance with the YAG:Nd<sup>3+</sup> laser fundamental frequency

$$E_{0,4} \approx \omega_1 \approx 9400 \text{ cm}^{-1}.$$

The main goal of this work was to find out whether the toluene radical cation absorbs this radiation markedly and, if it does, to investigate its stepwise photodissociation as compared with that at other wavelengths and of some other species.

It is noteworthy that the studies of the toluene radical cation photodissociation may be of independent interest. In spite of the fact that this compound is a classical object in mass spectroscopy<sup>18-21</sup> many features of intramolecular rearrangements, the role of electronic states in the decomposition, the mechanisms of fragmentation via different channels have not been comprehensively understood so far. Besides, results of such studies could be useful in the determination of general laws for the molecule fragmentation in the process of laser multiphoton ionization.<sup>22-24</sup>

## EXPERIMENTAL

The method of the present study involving laser mass spectrometry was developed in our earlier works<sup>25,26</sup> to investigate the molecular cation photodissociation. In fact, it is a two-pulse two-colour laser photolysis of molecules.

The molecules are ionized in a stepwise two-photon process by an UV pulse of the YAG:Nd<sup>3+</sup> laser fourth harmonic ( $\omega_4$ ) in the chamber of a modified monopole mass spectrometer APDM-1 (Figure 1) and the radical cations formed are irradiated, with a delay of 10 ns after the end of the first pulse, by the second (photolysing) pulse of the first ( $\omega_1$ ), the second ( $\omega_2$ ) or the third ( $\omega_3$ ) laser harmonic. The duration of all pulses was  $\sim 10$  ns. The ionizing and photolysing radiations were focussed and entered the chamber coaxially from the opposite sides. They had a common focus in the interaction zone but different diameters of the focal spot: 0.15 mm for  $\omega_4$  and 0.45, 0.85, and 0.80 mm

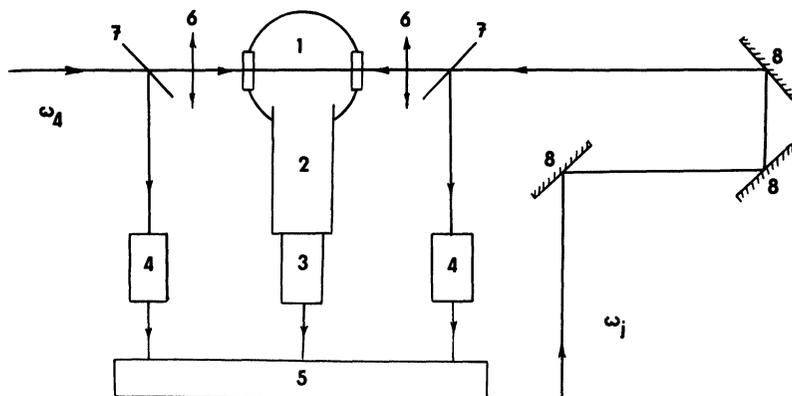


FIGURE 1 Experimental scheme. 1, ionization chamber; 2, mass-spectrometer; 3, detector (electron multiplier); 4, photomultiplier; 5, peripheries and microcomputer; 6, lens; 7, beamsplitter; 8, photolysing pulse optical delay line ( $\omega_j = \omega_1, \omega_2, \omega_3$ ).

for  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$ , respectively. Thus, it can be assumed that all radical cations were irradiated and the photolysing radiation was uniform over the cross section of the beam. The vapour pressure in the mass spectrometer chamber was  $\sim 10^{-5}$  Torr.

The decomposition of the molecular radical cation was detected using the dependence of the ion current for the corresponding mass on the intensity of the photolysing radiation. The pulse repetition rate was 3–5 Hz and the ion current signals were accumulated and averaged on a microcomputer. An important characteristic of the mass spectrometer is the time of the ion flight from the formation site to the mass-filter exit which is typically of  $\sim 30 \mu\text{s}$  for  $m/e = 90$ – $100$  ions. This value is the upper limit for the time of observable radical cation dissociation.

The substances used were chromatographically purified. The content of deuterated molecules in the isotopically substituted toluenes was 98% for  $\text{C}_6\text{H}_5\text{CD}_3$  and 99% for  $\text{C}_7\text{D}_8$ .

## RESULTS AND DISCUSSION

Figure 2 shows the results of the photolysis of radical cations of toluene (I), toluene with fully deuterated methyl group (II), fully

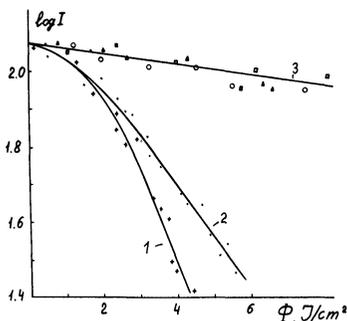


FIGURE 2 Dependence of the radical cations current on the energy fluence of the photolysing  $\omega_1$  radiation. 1,  $C_7H_8^+$  (toluene); 2,  $C_6H_5CD_3^+$ ; 3,  $C_7D_8^+$  ( $\Delta$ ),  $C_7H_8^+$  ( $\square$ ) (cycloheptatriene),  $C_6H_6^+$  ( $\circ$ ).

deuterated toluene (III), toluene isomer-cycloheptatriene (IV), and benzene (V) for the case of fundamental laser radiation ( $\omega_1$ ). It is seen that I decomposes effectively, i.e., the toluene radical cations markedly absorb near IR radiation, as expected. It was necessary, however, to prove that this absorption was not due to electronic excitation of I or IV.

The PES data on IV<sup>27,28</sup> indicates that its lowest electronically excited state lies near  $\omega_1$ . Thus, in the case of fast isomerization I $\rightarrow$ IV (cf. Figure 6), the radiation can be absorbed by the IV electronic transition. IV is not formed by toluene ionization because the internal energy of the radical cation  $E \leq 0.5$  eV ( $E = 2\omega_1 - IP - E_k$ , where IP is the toluene ionization potential, 8.82 eV,  $E_k$  is the kinetic energy of the ejected electron) is insufficient for such rearrangement which requires 0.87 eV. The absorption of a single photon  $\omega_1$  makes it energetically possible. However, the results of direct experiments with the cycloheptatriene (Figure 2, IV) show that the decomposition of IV is negligible though produced in a sequential two-photon ionization of the molecule it has approximately the same internal energy as I after absorption of one  $\omega_1$  photon. This leads us to the conclusion that the fast isomerization I $\rightleftharpoons$ IV does not take place under the conditions of the experiment.

Figure 3b gives the scheme of electronic terms for I whose energies were obtained in analogy with Ref. 29 using the *ab initio* calculated energies of toluene molecular orbitals<sup>30</sup> and the experimental PES data on toluene<sup>31</sup>. The origins of the first ( $\sim 8.8$  eV), the second ( $\sim 11.1$  eV), and the fifth ( $\sim 16.3$  eV) PES bands were taken as reference

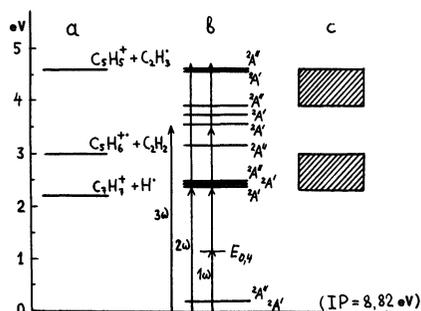


FIGURE 3 Thermochemical decomposition thresholds (a, calculation), electronic terms (b, calculation, see text), and experimental photodissociation spectrum of toluene radical cation,  $C_7H_8^{+\bullet}$  (c; regions from the origins to the band maxima are dashed; from Refs. 21, 28, 29, 40). The lowest known value  $\Delta H_f = 254$  kcal/mol of the heat of  $C_5H_5^+$  formation<sup>41</sup> is used. Energy of the first, the second and the third YAG: Nd<sup>3+</sup> laser harmonic photons are designated by arrows.  $E_{0,4}$  is the third overtone of the aliphatic CH bond stretching vibrations.

points in the calculation. As is seen, there are no electronically excited states of I near  $\omega_1$ .

The experimental proof of the fact that the photodissociation of I induced by the  $\omega_1$  radiation is due to vibrational rather than electronic excitation consists in observation of very weak decomposition of fully deuterated toluene radical cation (Figure 2, 3). Another evidence for this could be weak decomposition of II because the resonance with  $\omega_1$  must be suppressed by the change of aliphatic CH oscillators for CD. However, II dissociates with the efficiency comparable to I (Figure 2, 2). This important result will be discussed below.

Weak decomposition of V (Figure 2, 3) complies with the assumption that the aliphatic rather than aromatic CH oscillators are responsible for the absorption.

The dissociation of I via the lowest energy channel involving the H atom detachment requires an absorption of at least two  $\omega_1$  photons. The dissociation threshold is reached either by two- (or multi-) photon sequential absorption in the vibrational quasicontinuum of the ground electronic state or by the resonant two-photon absorption associated with a transition to the first electronically excited state (Figure 3b). In the latter case, the decomposition of electronically excited I should proceed by analogy to the one  $\omega_2$  photon dissociation. This similarity, however, is not observed as will be shown below.

Thus, the monomolecular dissociation of I observed is caused in the general case by sequential multiphoton absorption of near IR radiation in the vibrational quasicontinuum. The decrease of I molecular ion current as depending on the photolysing radiation intensity can be described by the solution of the simple system of equations:

$$\begin{aligned}
 dN_0/dt &= -\sigma_0 FN_0 \\
 dN_1/dt &= \sigma_0 FN_0 - \sigma_1 FN_1 \\
 &\dots \\
 dN_n/dt &= \sigma_{n-1} FN_{n-1} - \sigma_n FN_n
 \end{aligned}
 \tag{1}$$

where  $N_i$  is the population of an  $i$ th vibrational level of the radical cation,  $\sigma_i$  is the photon absorption cross section for an  $i$ th level,  $F$  is the photon flux density. Because of high density of states, their mixing in the radiation field and large difference in the state density for each consecutive step of the absorption process (the step value is  $\omega_1 \approx 9400 \text{ cm}^{-1}$ )<sup>32</sup> these equations do not take into account the stimulated reverse transitions. It is assumed that the radical cation after absorption of the first  $\omega_1$  photon and the fast (on a scale of a picosecond) relaxation of CH overtone and intramolecular energy redistribution over vibrational modes<sup>8,10,11</sup> retains its ability to absorb at least one or two more  $\omega_1$  photons. It is also assumed that all radical cations which absorb  $n+1$  photons required to be dissociated decompose within the flight time interval ( $\sim 30 \mu\text{s}$  in our case).

The ion current detected is proportional to the total number  $N_k$  of radical cations which have absorbed no photons and from 1 to  $n$  photons during the laser pulse. The solution of (1) gives the general expression for the dependence of  $N_k$  on the laser fluence  $\Phi$  in the form

$$N_k(\Phi) = N \sum_{i=0}^n \exp(-\sigma_i \Phi) \prod_{\substack{j=0 \\ j \neq i}}^n \sigma_j / (\sigma_j - \sigma_i)
 \tag{2}$$

where  $k = n+1$ ,  $N$  is the radical cation concentration, and the product equal to 1 at  $n=0$ .

As follows from (2), if one of the cross sections is much greater than the others  $\sigma_m \gg \sigma_0, \sigma_1, \dots, \sigma_n$ , the dependence  $N_k(\Phi)$  reduces to  $N_{k-1}(\Phi)$ , i.e., the apparent nonlinearity of the process is decreased

by 1 as compared to the real one. If, on the contrary,  $\sigma_m \ll \sigma_0, \sigma_1, \dots, \sigma_n$  ("bottleneck") is the case the dependence  $N_k(\Phi)$  is described by the formula with  $k = 1$  and characterizes an apparent one-photon dissociation with the cross section  $\sigma_m$ . In the particular case of  $k$ -photon dissociation with the absorption cross sections equal at all steps of the process,  $\sigma_0 = \sigma_1 = \sigma_2, \dots, = \sigma$ , (2) reduces to the form

$$N_k(\Phi) = N \exp(-\sigma\Phi) \sum_{m=1}^k (\sigma\Phi)^{m-1} / (m-1)! \quad (3)$$

Comparison of experimental dependences of the ion current on radiation intensity with the calculated by (2) or (3) determines the minimum nonlinearity of the photodissociation:  $k = k_{\min}$ , i.e., the minimum number of photons required for the absorbing radical cation to be dissociated during the time of flight from the formation site to the mass-filter exit.

The experimental dependence for I shown in Figure 2 is compared in Figure 4 with the calculations using (3). It is seen that a three-photon dissociation takes place and its effective cross section can be estimated as  $\sigma(\omega_1) = (2 \pm 0.5) \times 10^{-19} \text{ cm}^2$  at each step. In this case, one cannot describe the results by two-photon dissociation curves using variation of absorption cross sections for both steps.

Thus, at least three-photon dissociation of I is observed under experimental conditions. The two-photon decomposition which is energetically possible (Figure 3a) proceeds too slowly to be detected.

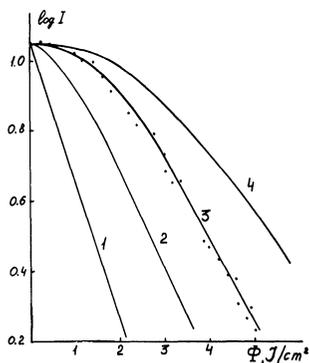


FIGURE 4 Dependence of the toluene radical cation current on the energy fluence of the photolyzing  $\omega_1$  radiation: experiment ( $\cdot$ ) and calculation (—). The numbers by the curves are degrees of nonlinearity of photodissociation process.

This implies that I is probably dissociated according to the fluctuation mechanism described by the statistical theory of unimolecular decomposition. The estimate of the dissociation rate constant was made using Kassel formula

$$K(E) = \nu(E - E_0)^{s-1} / E^{s-1} \quad (4)$$

with the frequency factor  $\nu = 2.7 \times 10^{12} \text{ s}^{-1}$  and the number of vibrational degrees of freedom  $(s-1)/2 = 19$  instead of  $s-1$  which were chosen to fit best the experimental and calculated data on fragment ion intensities in the toluene mass spectrum.<sup>33</sup> This yields  $K(2.83) \approx 1 \text{ s}^{-1}$  at I internal energy  $E = 2\omega_4 - \text{IP} + 2\omega_1 = 2.83 \text{ eV}$  and dissociation threshold  $E_0 = 2.2 \text{ eV}$ . Formula (4) is not adequate near the threshold, however, the analysis of the slowest decompositions of the cation<sup>34</sup> also estimates the dissociation rates of I near the threshold as not exceeding tens of  $\text{s}^{-1}$ , i.e., unobservable in our experiment. The three-photon dissociation, when  $E = 4 \text{ eV}$ , has  $K(4) \approx 10^6 \text{ s}^{-1}$  and is detectable.

Let us consider now photolysis of II. Two factors are of importance here. The first one is the existence of radiation absorption for this radical cation. It is not due to aromatic CH bonds and aliphatic CH bonds are substituted by CD. So one must admit that some other CH oscillators in II are responsible for the absorption in the case of deuteration of toluene methyl group. The second one, as seen in Figure 5 which compares the experimental (Figure 2, 2) and calculated

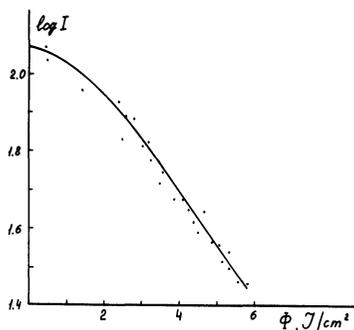


FIGURE 5 Dependence of the ion current on the energy fluence of the photolysing  $\omega_1$  radiation for the radical cation of toluene with the deuterated methyl group. Experiment ( $\cdot$ ) and calculation according to formula (3) for two-photon ( $k=2$ ) stepwise process (—).

dependences of ion current of II on the energy fluence, is that the photodissociation of II is a quadratic process and, thus, the decomposition proceeds at a much higher rate as compared to possible two-photon dissociation of I. The cross section is  $(1 \pm 0.5) \times 10^{-19} \text{ cm}^2$  for absorption at both steps.

These and discussed above facts become clear if we suppose that I isomerizes at the moment of formation or 10–20 ns later (Figure 6) to the structure of 5-methylene-cyclohexadiene (VI) whose possible role in the dissociation of I was noted, for example in Refs. 20 and 28. In this case, two aliphatic CH oscillators absorb radiation in the nondeuterated VI and one in the partially deuterated VI- $d_3$ , i.e., absorption is retained on deuteration of the methyl group. In accordance with the local mode model its intensity should decrease two times with respect to VI which is consistent with the experiment. Further, such isotopic substitution should reduce interaction of the excited CH oscillator with other vibrational modes: there is a single nondegenerate oscillator left and vibrational frequencies of neighboring bonds can change so that possible resonance interactions of this local mode with other modes<sup>11</sup> are disturbed. Thus, considerably smaller number of vibrational modes of VI- $d_3$  could be involved in dissociation as compared to VI and one could expect a sharp rise in the dissociation rate that was actually observed in the experiment. If we equate the rate constants for the VI three-photon dissociation and VI- $d_3$  two-photon dissociation it appears that only 10 of 39 vibrational modes, i.e., about half as compared with VI (19 modes), are involved in quasistatistical decomposition of VI- $d_3$  described by (4).

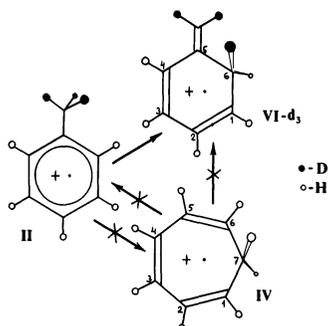


FIGURE 6 Rearrangement of the radical cation of toluene with the deuterated methyl group. II, toluene; IV, cycloheptatriene; VI, 5-methylene-cyclohexadiene.

It is noteworthy that in spite of the apparent similarity of CH oscillators in VI and IV (Figure 6, positions 6 and 7, respectively) they differ in fact: the dissociation energy of CH bond is much lower for IV (~1.3 eV) than for I (or VI) so that the mechanical frequency and anharmonicity of CH oscillator are also different in IV and VI. Further, the rearrangement  $IV \rightleftharpoons VI$  is hindered<sup>28</sup> and fails to proceed on the time scale of our experiment (10–20 ns). So, this accounts for difference in the behavior of the radical cations I (VI) and IV.

Visible and UV light irradiation results in one-photon dissociation of I (Figure 3c). In this case, it involves electronically excited states located near the dissociation threshold or above it (Figure 3b). It could be expected that low electronic terms of VI negligibly differ from those of I<sup>35,36</sup> so that the one-photon dissociation of VI (it is shown by the straight lines in Figure 7, their slopes with respect to the abscissa giving the cross sections for photodissociation<sup>26</sup>) induced by  $\omega_2$  or  $\omega_3$  radiation also proceeds via excited electronic states. This implies that the same internal energy  $E = \omega_2 = 2\omega_1$  provides the much faster decomposition of radical cations via electronically excited states as compared to highly excited vibrational levels of the ground electronic state. This leads to the conclusion that, if the mechanism of fast radiationless relaxation of an electronically excited state by electronic to vibrational energy conversion and subsequent radical cation dissociation takes place, the conversion proceeds with energy localization on the most anharmonic high-frequency oscillators,<sup>37</sup> i.e., on the discussed above aliphatic CH oscillators. In this case, the localization degree is about the same as in the two-photon decomposition of VI- $d_3$ , which means that the dissociation is not completely statistical.

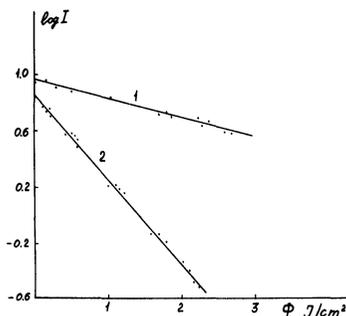


FIGURE 7 Dependence of the toluene radical cation current on the energy fluence of the photolysing  $\omega_2$  (1) and  $\omega_3$  (2) radiations.

The alternative mechanism is a direct fragmentation in the electronically excited state. The nonadiabatic hydrogen atom detachment, for example, can proceed in our case with a rate of  $10^7$ – $10^9$  s<sup>-1</sup> 37 which is observable.

The photodissociation cross sections of radical cations at  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$  are presented in Table I. It should be noted that the cross sections for I photodissociation which we actually assign to VI differ from those given for VI in Ref. 38. The authors of Ref. 38, however, point out that the assignment of the radical cation, for which the photodissociation spectrum was measured, as VI is rather suggestive. We also cannot prove that I rearranges precisely to the VI structure rather than to some other one having similar properties.

## CONCLUSIONS

The present results support the idea that the lower CH bond dissociation energy of radical cations as compared to the neutral molecules, as in our case, leads to higher overtone intensities for CH stretching vibrations of the cations with respect to the neutrals. The rise in overtone intensity is first of all, in our opinion, due to strong change in electro-optical characteristics of CH bonds caused by a rearrangement of electronic structure in the ionized molecule and also by the

TABLE I  
The radical cation photodissociation cross sections (cm<sup>2</sup>)

Radical cation	$\omega_1(\lambda = 1064 \text{ nm})$	$\omega_2(\lambda = 532 \text{ nm})^*$	$\omega_3(\lambda = 355 \text{ nm})^*$
$C_7H_8^+$ (toluene, 5-methylenecyclohexadiene)	$(2 \pm 0.5) \cdot 10^{-19}$ <sup>a</sup>	$(1.2 \pm 0.2) \cdot 10^{-19}$	$(9 \pm 2) \cdot 10^{-19}$
$C_7H_8^+$ (cycloheptatriene)	$\sim 10^{-21}$ <sup>b</sup>	$\sim 10^{-21}$	$(8 \pm 2) \cdot 10^{-19}$
$C_6H_5CD_3^+$	$(1.2 \pm 0.3) \cdot 10^{-19}$ <sup>c</sup>	$(2.2 \pm 0.3) \cdot 10^{-19}$	—
$C_7D_8^+$	$\sim 10^{-21}$ <sup>b</sup>	$(7 \pm 1) \cdot 10^{-19}$	—

\* One-photon dissociation.

<sup>a</sup> Three-photon dissociation.

<sup>b</sup> Estimate.

<sup>c</sup> Two-photon dissociation.

considerable growth of anharmonicity and some decrease of the vibration frequencies. It is not excluded that all this is true in some cases also for stretching vibration overtones of other hydride bonds.

The observation of overtones under collisionless conditions at low gas pressures offers new possibilities for studies of local mode vibrations, intramolecular energy redistribution, selective excitation and unimolecular decomposition as well as electronic structure of polyatomic radical cations. Especially promising is the use of continuously tuned lasers, picosecond laser technique, and time-of-flight mass reflectrons.

In particular, the toluene radical cations produced by two-photon stepwise ionization of toluene molecules at 266 nm are shown to rearrange rapidly (rate constant is higher than  $10^8 \text{ s}^{-1}$ ) supposedly into 5-methylene-cyclohexadiene radical cation (the heat of formation  $\Delta H_f \approx 226 \text{ kcal/mol}$  in this case). No rearrangement of this isomer into cycloheptatriene and vice versa takes place under the experimental conditions.

The isomer of toluene radical cation effectively, with a cross section  $\sigma \sim 10^{-19} \text{ cm}^2$ , absorbs the fundamental radiation of the YAG:Nd<sup>3+</sup> laser on the direct transition to the third overtone level of the aliphatic CH bond stretching vibration and undergoes two- and/or three-photon dissociation.

The degree of internal energy randomization in the process of the IR two-photon stepwise radical cation isomer dissociation for the toluene with deuterated methyl group is much lower than for the non-deuterated one so that the dissociation of the former is not a fully statistical process.

The mechanisms of isoenergetic dissociation of the toluene radical cation isomers are different for irradiation by visible and near IR lights: the one-photon dissociation via an electronically excited state induced by the visible radiation implies a considerably lesser randomization of internal energy as compared to the decomposition in the case of IR sequential two-photon absorption involving highly excited vibrational levels of the ground electronic state.

At present, for lack of some important data the interpretation given above may not be unique. For example, little to nothing is known of the properties of VI (electronic spectra, thermochemistry, rates of formation by rearrangements of I, II, III, or IV). Experiments with tunable around 1.06  $\mu\text{m}$  photolyzing radiation and various time delays

between ionizing and photolyzing pulses would be useful for the unambiguous elucidation of the nature of toluene radical cation dissociation described.

### Acknowledgements

The authors are gratefully indebted to O. P. Syutkina, Z. N. Parnes, and G. D. Kolomnikova for presenting samples of deuterated toluenes and cycloheptatriene.

### References

1. K. V. Reddy and M. J. Berry, *Chem. Phys. Lett.* **72**, 29 (1980).
2. B. D. Cannon and F. F. Crim, *J. Chem. Phys.* **75**, 1752 (1981).
3. T. R. Rizzo and F. F. Crim, *J. Chem. Phys.* **76**, 2754 (1982).
4. D. W. Chandler, W. E. Farnethe and R. N. Zare, *J. Chem. Phys.* **77**, 4447 (1982).
5. A. Schwebel, M. Brestel and A. Yogev, *Chem. Phys. Lett.* **107**, 579 (1984).
6. B. R. Henry, *Acc. Chem. Res.* **10**, 207 (1977).
7. A. C. Albrecht, in: *Advances in Laser Chemistry* ed. A. H. Zewail (Springer-Verlag, 1978) p. 235.
8. A. A. Ovchinnikov and N. S. Erichman, *Usp. fiz. nauk.* **138**, 289 (1982).
9. H. L. Fang and R. L. Swofford, in: *Advances in Laser Spectroscopy* Vol. 1, eds. B. A. Garetz and J. R. Lombardy (Heyden, 1982) p. 1.
10. J. W. Perry and A. H. Zewail, *J. Chem. Phys.* **80**, 5333 (1984).
11. E. L. Sibert, III, W. P. Reinhardt and J. T. Hynes, *J. Chem. Phys.* **81**, 1115 (1984).
12. H. L. Fang, D. M. Meister and R. L. Swofford, *J. Phys. Chem.* **88**, 405, 410 (1984).
13. H. S. Heaps and G. Herzberg, *Z. Phys.* **133**, 48 (1952).
14. *Energii razryva khimicheskikh svyazei*, ed. V. N. Kondratjev (Nauka, 1974).
15. H. M. Rosenstock, K. Draxl, B. W. Steiner and J. T. Herron, *J. Phys. Chem. Ref. Data*, **6**, Supp. 1 (1977).
16. D. F. McMillen and D. M. Golden, *Ann. Rev. Phys. Chem.* **33**, 493 (1982).
17. K. M. Gough and B. R. Henry, *J. Phys. Chem.* **88**, 1298 (1984).
18. M. L. Vestal, in: *Fundamental Processes in Radiation Chemistry* ed. P. Ausloos (Intersci. Publ., 1968) p. 59.
19. P. J. Derrick, in: *Mass Spectrometry Intern. Rev. of Science. Phys. Chem.*, Series 2, Vol. 5, ed. A. Maccoll (Butterworths, 1975) p. 1.
20. R. C. Dunbar, in: *Gas Phase Ion Chemistry* Vol. 2, ed. M. T. Bowers (Academic Press, 1979), p. 181.
21. L. Andrews, in: *Molecular Ions. Geometric and Electronic Structures* eds. J. Berkowitz and K. O. Groeneveld (Plenum Press, 1983) p. 183.
22. V. S. Antonov and V. S. Letokhov, *Appl. Phys.* **24**, 89 (1981).
23. R. B. Bernstein, *J. Phys. Chem.* **86**, 1178 (1982).
24. A. Gedanken, M. B. Robin and N. A. Kuebler, *J. Phys. Chem.* **86**, 4096 (1982).
25. V. T. Yaroslavtzev, G. A. Abakumov and A. P. Simonov, *Digest of the 4th Conference on Luminescence*. Hungary, Szeged, 1982, p. 293.
26. V. T. Yaroslavtzev, G. A. Abakumov and A. P. Simonov, *Kvantovaya Elektronika*, **11**, 752 (1984).
27. N. Bodor, M. J. S. Dewar and S. D. Worley, *J. Am. Chem. Soc.* **92**, 19 (1970).

28. B. J. Kelsall and L. Andrews, *J. Am. Chem. Soc.* **105**, 1413 (1983).
29. R. W. Bigelow, *J. Chem. Phys.* **70**, 2315 (1979).
30. W. C. Ermler and R. S. Mulliken, *J. Am. Chem. Soc.* **100**, 1647 (1978).
31. W. L. Stebbings and J. W. Taylor, *Int. J. Mass Spectr.* **9**, 471 (1972).
32. V. S. Letokhov, *Nonlinear Laser Chemistry Multiple Photon Excitation*. Vol. 22. Springer Ser. in Chem. Phys. (Springer, Berlin, 1983) p. 218.
33. I. Howe and D. H. Williams, *J. Am. Chem. Soc.* **91**, 7137 (1969).
34. R. C. Dunbar, *Int. J. Mass Spectr.* **54**, 109 (1983).
35. T. Shida, T. Kato and Y. Nosaka, *J. Phys. Chem.* **81**, 1095 (1977).
36. M. Allan, J. Dannacher and J. P. Maier, *J. Chem. Phys.* **73**, 3114 (1980).
37. V. G. Plotnikov and A. A. Ovchinnikov, *Usp. khimii.* **47**, 444 (1978).
38. R. C. Dunbar and R. Klein, *J. Am. Chem. Soc.* **99**, 3744 (1977).
39. P. P. Dymerski, E. Fu and R. C. Dunbar, *J. Am. Chem. Soc.* **96**, 4109 (1974).
40. J. R. Eyler, *J. Am. Chem. Soc.* **98**, 6831 (1976).
41. D. A. McCrery and B. S. Freiser, *J. Am. Chem. Soc.* **100**, 2902 (1978).