

A STATISTICAL MODEL FOR THE FRAGMENTATION OF BENZENE BY MULTIPHOTOIONIZATION

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A statistical products phase space model for the (multi) photon fragmentation/ionization of polyatomic molecules in strong laser fields is proposed and tested on benzene. The mechanism assumes multiple dissociations and branchings starting with energy rich benzene ions. Calculated and experimental fragment mass patterns versus laser fluence are shown to be in good agreement.

1. Introduction

Laser-induced multiphoton spectroscopy (including ionization spectroscopy) has by now become a rather popular area of study [1]. It is apparent that interests from quite different directions merge in this topic. One aspect, which is also essential for the following discussion concerns the mechanism and in particular the question of statistical versus non-statistical fragmentation pathways. There have been arguments by various authors that in view of potentially very high excitation rates with high-power laser sources a radiationless energy redistribution in the excited ions might be partly suppressed [2–4]. Experimental data in favour of such statements were claimed to be seen in the large abundance of small fragments (like C^+ and C_2^+) in the course of multiphoton ionization (MPI) of benzene) whose formation obviously requires very high amounts of deposited laser energy. Other puzzling features which seem to distinguish this type of photoionization from other ionization schemes are the variation in both the nature and the relative abundance of the observed sec-

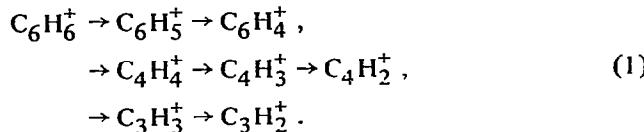
ondary ion fragments with laser fluence, seemingly providing some control over dissociation channels. Additionally, in some cases (e.g. benzene) total ion yields can be very high but show a strong dependence on the nature of the intermediate states and on their decay times [5–8]. In favourable cases this ionization scheme could be very interesting in mass spectrometry for very sensitive and very selective (if a spectral dependence of the ionization probability can be found) detection of molecules. These features have lead to the conceptual design of a two-dimensional mass spectrometer [5].

The validity of such a mass spectrometric concept and the conclusions to be drawn from this in general, however, all depend on a detailed mechanistic understanding which must be sufficiently general to account for molecules of different size and chemical nature. The following discussion presents itself as one step in this direction and in this way has to be considered along with other approaches aiming at the same goal, however starting from a different conceptual basis.

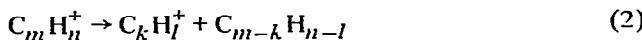
Benzene is among the most carefully studied molecules for this kind of ionization and was thus also chosen for the following discussion. The general success of treating ion fragmentations by statistical models and

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especially a recent study by Baer et al. [9] on the decomposition of $C_6H_6^+$ at excess energies of several electron volt encouraged us to investigate the MPI fragmentation of benzene by KrF or ArF high-power laser irradiation on similar grounds. Breakdown graphs of benzene [10] indicate that for parent ion excess energies of $\lesssim 15$ eV the fragmentation sequence follows the reaction scheme



The thresholds for the formation of the primary fragments $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$ and $C_3H_3^+$ lie around 4 eV. Subsequent H abstraction requires a similar amount of energy. H_2 elimination plays a minor role even though they are energetically favoured over a consecutive loss of two H atoms. Beyond the low-energy regime where $C_6H_5^+$ is the dominant ion, the fragmentation produces mainly C_4 and C_3 species in an approximate ratio of 3 : 1. In summary, it can be said that various experimental techniques used to investigate the decomposition of $C_6H_6^+$ at excess energies of several electron volts agree on fragmentation scheme (1) but do not provide an easy explanation for smaller C fragments observed in MPI. We therefore adopted (1) as describing also the first steps in MPI fragmentation up to moderate laser intensities. We generalize reaction scheme (1) by investigating a fragmentation tree with consecutive branchings including all decompositions of the type



Accordingly, we view the overall process as an ionization of benzene due to the absorption of two UV photons to reach the ionization limit, whereafter the ions continue to absorb. In this regime rapid non-radiative transitions quench the electronic excitation [11] and all the energy pumped into $C_6H_6^+$ appears as vibrational energy of the ion ground state where it leads to fragmentation. We also make the assumption that only $C_6H_6^+$ but none of its daughter fragments receives energy from the laser field. This *absorption-multiple-fragmentation* model can be tested quantitatively if the decomposition probabilities and energy contents of all fragments are evaluated statistically.

2 A statistical model calculation for MPI fragmentation

The quantity of principal interest is the probability function $P_{ij}(E_i, E_j)$ for obtaining ion j^+ with internal energy E_j in a single fragmentation step from i^+ with energy E_i . Derived quantities are the branching ratios

$$F_{ij}(E_i) = \int dE_j P_{ij}(E_i, E_j) \quad \sum_{j'} F_{ij'}(E_i) = 1. \quad (3)$$

and the energy distributions in the ionic fragments

$$f_{ij}(E_i, E_j) = P_{ij}(E_i, E_j)/F_{ij}(E_i) \quad (4)$$

Then given the initial energy distribution $P_1(E_1)$ of the parent ion, one obtains the energy distributions $P_j(E_j)$ prior to fragmentation by

$$P_j(E_j) = \sum_i \int dE_i P_i(E_i) P_{ij}(E_i, E_j) \quad (5)$$

The summation in (5) extends over all ions immediately preceding j^+ . The final probability to observe j^+ is

$$p_j = \int_0^{E_j^0} dE_i P_i(E_i) \quad (6)$$

where E_j^0 shall denote the smallest threshold for any further fragmentation $j^+ \rightarrow k^+$

In applications to mass spectrometry [12–14] $P_{ij}(E_i, E_j)$ is frequently synthesized via (3) and (4) from separate calculations of the branching ratios and the fragment energy distributions. In particular decomposition rates $k_{ij}(E_i)$ obtained by RRKM or QET theories are used to evaluate the branching ratios by

$$F_{ij}(E_i) = k_{ij}(E_i) \left[\sum_{j'} k_{ij'}(E_i) \right]^{-1}. \quad (7)$$

Since most ionic fragmentations seem to occur via loose (i.e. product like) transition complexes one can also base a direct evaluation of P_{ij} on the phase space of the products [15,16]

Within such a products phase space model

$$\begin{aligned} P_{ij}(E_i, E_j) &= \alpha_{ij} \rho_j(E_j) \\ &\times \int d\epsilon_t \rho_n(E_j - \epsilon_t) \rho_t(\epsilon_t) / \Omega_j(E_j) \end{aligned} \quad (8)$$

is given by the internal state (electronic and vibrational) densities ρ_j and ρ_n of the product ion j^+ and its com-

plementary neutral n . Ω_i is the total phase space density at energy E_i for all products formed from i^+

$$\Omega_i(E_i) = \sum_j \alpha_{ij} \int dE_j \rho_j(E_j)$$

$$\times \int d\epsilon_t \rho_n(\epsilon_n - \epsilon_t) \rho_t(\epsilon_t). \quad (9)$$

By energy conservation $E_i - E_{ij}^0$, E_{ij}^0 being the threshold, is the energy available for distribution among all products degrees of freedom. $E_n = E_i - E_{ij}^0 - E_j$ gives the energy content in the neutral and in the relative translational motion of a j^+, n pair. With the corresponding reduced mass μ_{jn} the translational state density is in the classical limit of the form

$$\rho_t(\epsilon_t) = C_t \mu_{jn}^{3/2} \epsilon_t^{1/2} \quad (10)$$

Finally in (8) α_{ij} denotes the reaction path degeneracy. For the practical evaluation of vibrotational state densities one usually assumes harmonic oscillators and classical rotators. Then P_{ij} is given as

$$P_{ij}(E_i, E_j) = [C_t \mu_{jn}^{3/2} / \Omega_i(E_i)] \alpha_{ij} g_i g_n Q_i Q_n$$

$$\times (E_j + a_i E_{0j})^{s_j + r_j/2 - 1} (E_n + a_n E_{0n})^{s_n + r_n/2 + 1/2} \quad (11)$$

$$\times \left[\Gamma(s_j + \frac{1}{2} r_j) \prod_{\alpha=1}^{s_j} h \nu_{\alpha j} \Gamma(s_n + \frac{1}{2} r_n + \frac{3}{2}) \prod_{\alpha=1}^{s_n} h \nu_{\alpha n} \right]^{-1}.$$

Here g are the electronic degeneracies, s and r the number of vibrational and rotational degrees of freedom, $Q(kT)^{r/2}$ is the classical rotational partition sum. The zero-point energies E_0 are given in terms of the vibrational frequencies ν_α , $\alpha = 1, \dots, s$. We evaluated (11) within the Marcus semiclassical approximation where $a = 1$, though also more accurate state counting is frequently used. It should be mentioned that most of the data needed are not known very reliably. In particular this applies to the vibrational frequencies of the ions which are only in a few cases measured by spectroscopy [17]. In all other cases either the frequencies of the corresponding neutrals were used or we estimated them from the characteristic group frequencies [17, 18]. Another source of error arises in determining the thresholds from the heats of formation [19, 20].

Finally, for a full specification of the model we need to make an assumption on the initial energy content of $C_6H_6^+$ which reflects the mechanisms of the ionization and absorption processes during the laser pulse. Our

calculation used the kinetic scheme

$$d[C_6H_6^*]/dt = \sigma_1 I [C_6H_6] - [(\sigma_2 + \sigma_3)I + 1/\tau] [C_6H_6^*],$$

$$d[C_6H_6^+(0)]/dt = \sigma_2 I [C_6H_6^*] - \sigma_4 I [C_6H_6^+(0)],$$

$$d[C_6H_6^+(n)]/dt = \sigma_4 I \{ [C_6H_6^+(n-1)] - [C_6H_6^+(n)] \}, \quad n \geq 1. \quad (12)$$

The first two equations were also used by Reilly and Kompa [7] to estimate the total ion yield in MPI experiments employing a KrF laser. Here we use the data quoted there on σ_1 , σ_2 , σ_3 and τ and on the laser pulse $I(t)$. Somewhat different equations would apply for MPI by visible lasers. The last equation in (12) was introduced to simulate the kinetics of the pumping of the ions and involves an absorption cross section σ_4 which was fitted to be $\sigma_4 = 2 \times 10^{-18} \text{ cm}^2$. $P_1(E_1)$ is therefore obtained by normalizing

$$P_1(E_1) = \sum_n \delta(E_1 - nE_\phi) [C_6H_6^+(n)], \quad (13)$$

where n is the number of photons absorbed by $C_6H_6^+$ and E_ϕ is the photon energy (5 eV for the KrF laser).

In fig. 1 we show calculated abundancies for the ion fragment groups C_n ($n = 1, 2, 3, 4, 6$) and their dependence on the laser fluence. Actually the C_1 group consists only of C^+ , in agreement with experiment where also no species like CH^+ or CH_2^+ were detected. The C^+ formation sets in at fluences around 2 J/cm^2 .

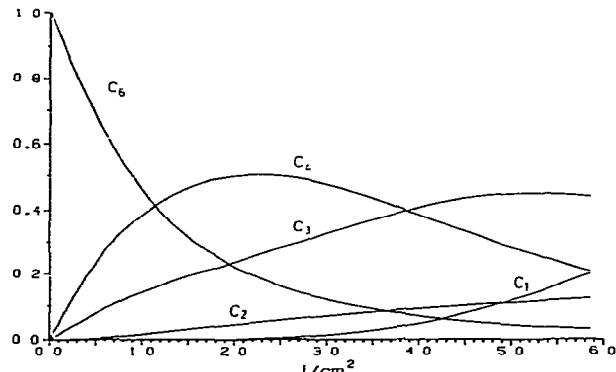


Fig. 1 Relative mass intensities calculated from the statistical model for the ion fragment groups $C_1 = C^+$, $C_2 = C_2^+$, C_2H^+ , $C_2H_2^+$, $C_2H_3^+$, $C_3 = C_3^+$, C_3H^+ , $C_3H_2^+$, $C_3H_3^+$, $C_4 = C_4^+$, C_4H^+ , $C_4H_2^+$, $C_4H_3^+$, $C_4H_4^+$ and $C_6 = C_6H_4^+$, $C_6H_5^+$, $C_6H_6^+$.

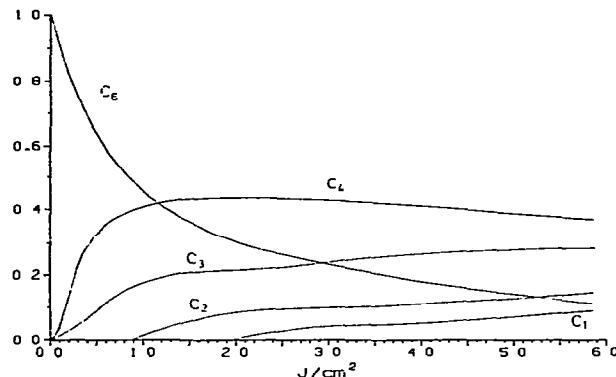
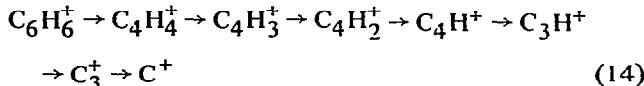


Fig. 2 Relative mass intensities for the ion fragment groups C_1 , C_2 , C_3 , C_4 and C_6 derived from the KrF laser MPI experiments by Reilly and Kompa [7]

(which corresponds to KrF laser intensities of 100 MW/cm²) and afterwards rises quite fast. A similar behaviour is found in experiments with visible lasers. Due to a rate limiting two-photon absorption $X^1A_{1g} \rightarrow ^1B_{1u}$ in benzene the overall ion production varies then with intensity as I^2 while the C^+ formation goes roughly as $I^{3.5}$ [2]. The occurrence of such non-integral power dependencies has recently been discussed by Fisanick et al. [21] on the basis of a direct multi-photodissociation mechanism. In the view of this calculation this does not indicate the presence of higher-order processes but rather is a consequence of the multiple fragmentation steps leading to C^+ . According to our findings the prominent route for C^+ formation involves the sequence



Similar trends as in fig. 1 are also seen in the experimental data shown in fig. 2 for MPI fragmentation by the KrF laser [7]. In particular the region of fluences or intensities agree quite well. Quite likely the statistical model should even be capable to reproduce also the relative fragment abundancies in a more quantitative manner if better input data were available.

3. Summary

By the statistical approach outlined in the preceding section it appears possible to reach good and even quan-

titative agreement with experiment. The agreement applies to the ion abundancies and to the range of laser fluences, which controls the overall extent of fragmentation. At the present time such an agreement must of course not be overstressed before the assumptions made in this treatment on the energy acquisition in $C_6H_6^+$ have been confirmed. Also the role of secondary ion absorption and photodissociation needs further investigation. A more detailed analysis is given in a subsequent paper [22].

What we believe to have learned from this preliminary study may be summarized as follows

(a) A model with multiple fragmentation steps is capable to describe the trends which are observed in the MPI fragmentation of benzene and likely also of other polyatomic molecules.

(b) In addition, support is obtained for the statistical content of the model. This latter point has also been investigated recently by Silberstein and Levine, who used a thermodynamic approach [23].

(c) By (a) and (b) fragmentations observed by MPI and other ionization methods (e.g. charge exchange, photoionization and electron impact) are linked, at least partially, to a common basis of interpretation. The difference of MPI fragmentation is mainly that much higher energies can be deposited.

(d) It is obvious from this discussion that the amount of energy is the main controlling factor and no laser frequency dependence of the fragmentation routes is to be expected as long as the fragmenting species exhibits absorption for the wavelengths in question.

(e) For further investigations of the mechanism it appears necessary to provide better controlled experimental starting conditions, for instance to study the fragmentation of C_4 compounds of the kind formulated as intermediates above. In addition, experiments starting with ions rather than with neutrals could give information on secondary photodissociation processes.

(f) As to the practical implications for the use of MPI in mass spectrometry it appears necessary to find experimental conditions where at the one hand the total ion yield is maximal and on the other hand the extent of fragmentation is minimal. This may be attainable by rapid quenching of the initially energized primary molecular ions ($C_6H_6^+$ in the case of benzene) by collisional relaxation or by coupling the test sample

to a heat bath (e.g. a solid substrate). Preliminary experimental results in this direction have recently been reported [24]. Statistical model considerations of the type used here might then aid in selecting the proper experimental parameters.

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