

An Investigation of Benzene Using Ultrafast  
Laser Spectroscopy

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## **Introduction**

Molecular spectroscopy has been used throughout the past century to obtain information about the structure of molecules. The research that I participated in this summer here at Ohio State should be classified into this field. More specifically, I studied the behavior of the molecule benzene under intense, ultrafast laser fields by using time of flight (TOF) spectroscopic methods which I will explain below.

Ultrafast laser spectroscopy (using lasers which emit pulses of light of femtosecond duration) is a relatively new method which has matured in only the past decade. The vast majority of studies using this method have been done on atoms (Ar, Xe) and small molecules ( $\text{H}_2^+$ ). It was not until the recent pioneering studies of Levis and Dewitt [1], [2], [3] that ultrafast laser spectroscopy was extended to molecules the size of benzene and larger. It was the lack of studies in the field of ultrafast spectroscopy on large molecules which motivated our exploratory project.

## **Methods Used and Data**

To obtain our data we used TOF spectroscopy. For this, the laser beam is focused down using a spherical lens into the gas of molecules

which is benzene in our case. Then what typically happens is that some the molecules are ionized. To obtain the mass spectra, we use a static electric field to accelerate the ions down the time of flight tube into the detector. The TOF to mass conversion formula can be derived in a straight-forward way by using Newtonian mechanics and is given by

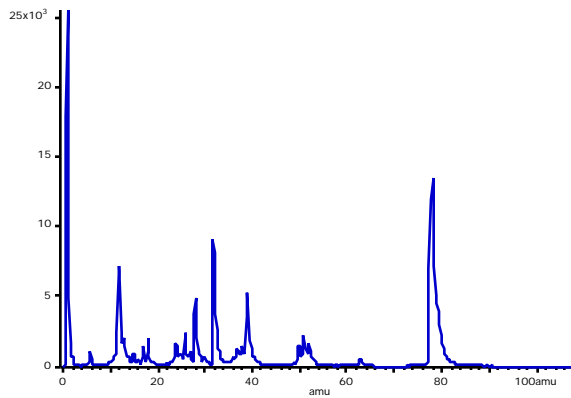
$$m = 1/2 Eq/L (TOF)^2$$

where E is the magnitude of the DC electric field, q is the net charge of the ion, and L is the length of the TOF tube. To obtain photoelectron spectra, we do not use a static electric field. For this case, we measure the TOF of the small fraction of the electrons which make it to the detector. The kinetic energy of these electrons is given by

$$KE=1/2 m_e v^2 = 1/2 m_e (L/TOF)^2$$

where  $m_e$  is the mass of an electron.

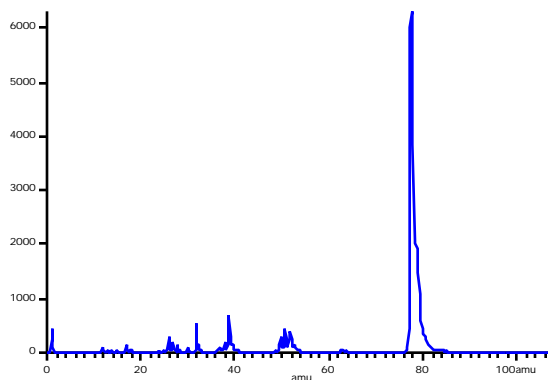
Below is one of our mass spectra of benzene for a laser power of 800mW.



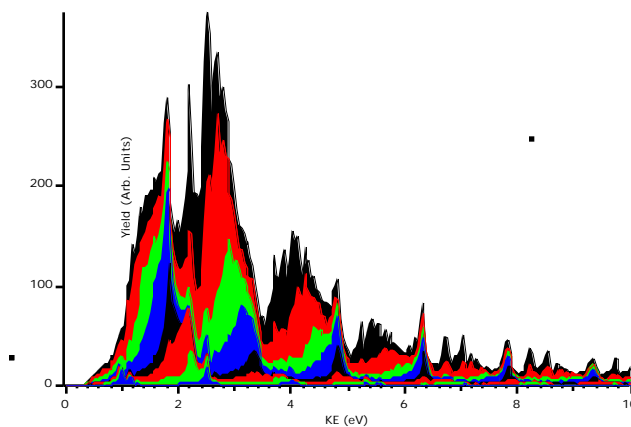
The peak at 78 amu is benzene. The other peaks are from dissociation.

We have identified these peaks as  $C_5H_x$ ,  $C_4H_x$ ,  $C_3H_x$ ,  $C_2H_x$ , C, and H.

Another spectrum is shown below for a lower laser power of 400mW. Notice that much less dissociation (<20%) occurs for this power. It is because of this that we only consider laser powers less than or equal to 400mW for our photoelectron spectra. This will insure us that nearly all of the electrons that we consider are from benzene and not its fragments.

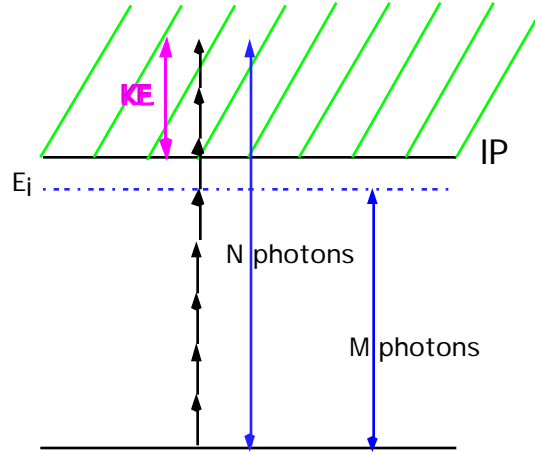


Below is a photoelectron spectrum for laser powers of 400 through 200 mW (different colors represent different powers).



The analysis of the features of this will be given below.

### Discussion of data



Above is a diagram representing the process of ionization of an atom or molecule.  $N$  photons are absorbed by an electron in the ground state. Once enough energy is gained to reach the ionization potential (IP), the electron is no longer bound. The kinetic energy of the electron can then be seen to be

$$KE = N\hbar\omega - IP \quad (1)$$

where  $\omega$  is the angular frequency of the photons.

Now one must consider the fact that the IP and intermediate energy levels will shift under the presence of an electromagnetic field. This phenomenon is known as Stark Shifting.

The energy of a free electron oscillating in an electromagnetic field is given by

$$U_p(I) = \frac{e^2 I}{2m_e \omega^2}$$

where  $I$  is intensity. This is known as the pondermotive energy. For an electron to reach the continuum under the presence of an electromagnetic field, it must have enough energy to reach the original ionization potential in addition to enough energy to obtain this "wiggle" motion of an electron in an oscillating field. Thus we have found the Stark shift in the ionization potential:

$$IP(I) = IP(O) + U_p(I).$$

The shift of the energy of the intermediate states is calculated by using perturbation theory and is given by

$$E_i = U_p(I) \left\{ 1 - \frac{f_{fi}^2}{\omega_{fi}^2 - \omega^2} \right\}$$

where  $f_{fi}$  is the probability of a transition between state  $f$  and  $i$ ,  $\omega_{fi}$  is the difference in energy between states  $f$  and  $i$  divided by  $\hbar$ , and  $\omega$  is the angular frequency of the laser. It turns out that for high lying Rydberg states (which are of primary interest to us), that the term in the parenthesis is approximately equal to one. Thus

$$E_i(I) = E_i(0) + U_p(I).$$

The resonance peaks in our photoelectron will occur when there is an integer number of photons between the ground state and one of the Rydberg states. That is,

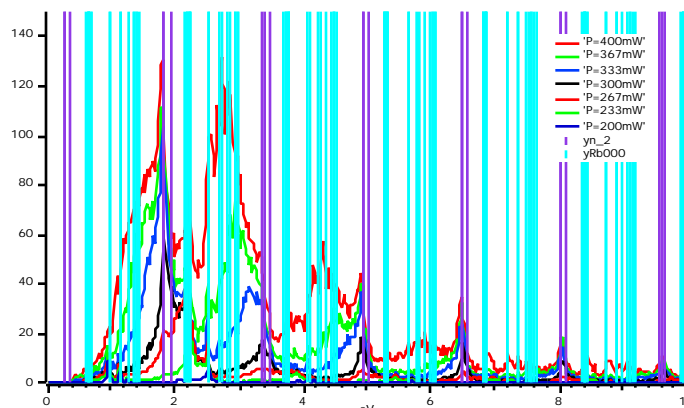
$$M\hbar = E_i(I) \quad (2)$$

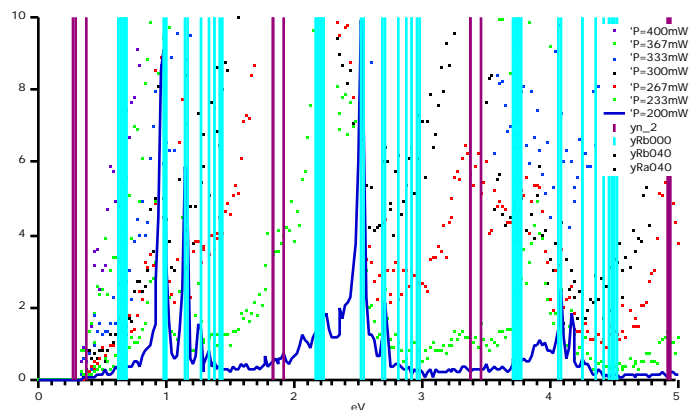
where M is an integer. Now combining (1) and (2) and eliminating the pondermotive energy from our newly obtained expressions of IP(I) and  $E_i(I)$ , we obtain

$$KE = (s + 1)\hbar - E_b \quad (3)$$

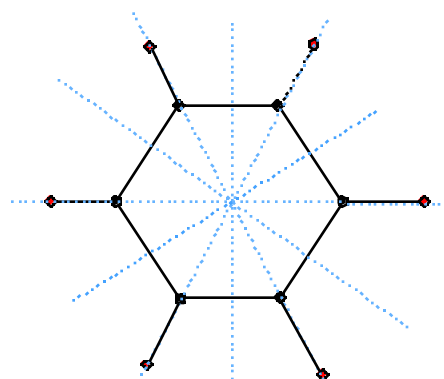
where  $s = N - M$  and  $E_b = IP(0) - E_i(0)$ . This equation will predict where the resonance peaks in our photoelectron spectra will occur.

Much of the spectrum of benzene has been determined experimentally by using absorption spectroscopy by Wilkinson in 1956 [4]. Using this data and (3) to put it into a useable format, we compared our data. Below are graphs of this data superimposed over ours for laser powers of 400 to 200 mW and 200mW.





In order for one to better understand these photoelectron spectra, one must consider vibrational as well as electronic transitions. To determine vibrational transition selection rules, group theory is typically used. Below is a diagram of benzene.



There are several symmetries to this geometry: a 6-fold rotational axis of symmetry coming out of the paper; six planes of symmetry perpendicular to the page represented by the blue lines; and a horizontal plane of symmetry. The point group to which these symmetries belong is designated as  $D_{6h}$  and has 24 elements [5].

The coupled differential equations for the populations  $c_a$  and  $c_b$  for a quantum mechanical two level system under and electromagnetic field are

$$\frac{dc_a}{dt} = \frac{i}{\hbar} \langle \psi_a | \vec{\mu} \cdot \vec{E} | \psi_b \rangle e^{-i\omega t} c_b(t)$$

$$\frac{dc_b}{dt} = \frac{i}{\hbar} \langle \psi_b | \vec{\mu} \cdot \vec{E} | \psi_a \rangle e^{i\omega t} c_a(t)$$

where  $\vec{\mu}$  is the dipole operator of the molecule and  $\psi_a$  and  $\psi_b$  are the two vibrational levels [6]. Using group theoretical arguments, one can tell when

$$\langle \psi_a | \vec{\mu} \cdot \vec{E} | \psi_b \rangle$$

is zero. When this happens, one sees by considering the two-level equations that no transition will be allowed. Thus by using group theory, one can determine the selection rules for transitions between vibrational energy levels.

By using this technique, we found that the majority of vibrational transitions are forbidden. Furthermore, some of the few vibrational transitions that are not forbidden account fairly well for some of the peaks in our spectra.

### **Conclusion / Future**

In conclusion, this summer I have taken mass and photoelectron spectra of benzene. I have compared this data with known spectral lines of

benzene obtained by using absorption spectroscopy and found the data to agree fairly well. Also, I have investigated the selection rules for vibrational transitions by using group theoretical arguments and saw that some of the allowed transitions support our data. Finally, while taking this benzene data and analyzing it, I was reading papers and texts to learn the quantum mechanics and group theory necessary for informed research in this field.

In the future, (I plan on continuing working in this lab throughout the school-year) I hope to take more benzene data with different experimental parameters. I plan to use circularly polarized light. By using angular momentum arguments, one can see that the resonance peaks should not be present for this experiment. This will help us determine which parts of our data are from resonant activity. In addition, I hope to use frequency double light. This experiment will therefore be done with photons of twice the energy and should enable us to observe the lower Rydberg energy levels.

[1] M. J. Dewitt, R. Levis, Phys. Rev. Lett. 81, 5101 (1998)

[2] M. J. Dewitt, R. Levis, J. Chem. Phys. 108, 7739 (1998)

[3] M. J. Dewitt, R. Levis, J. Chem. Phys. 110, 11368 (1999)

- [4] P. G. Wilkinson, *J. Chem. Phys.*, 596 (1956)
- [5] G. Herzberg, *Infrared and Raman Spectra* (1945)
- [6] D. J. Griffiths, *Introduction to Quantum Mechanics* (1995)