

Appendix 3: ZEKE Project Report by [REDACTED] of 1999

ZEKE Project

Report

Summer 1999



Introduction

In this project, we attempted to measure the photoelectron spectrum of the [redacted] radical. The technique used was zero kinetic energy photoelectron spectroscopy (ZEKE PES). In particular, the technique of pulsed field ionization (PFI) has been applied. ZEKE-PFI involves the photo-excitation of the molecule under investigation to long-lived hydrogen-like Rydberg states, just under the ionization potential. This is achieved resonantly (1+1'), as in [redacted], or non-resonantly (1+1), as in [redacted]. After a short time delay (of order 1 μ s), an electric field is applied, ionizing the molecule, and the resulting electron is detected. The time delay ensures that only electrons resulting from the Rydberg states are detected. The wavelength of the exciting photon(s) is varied, allowing a spectrum to be obtained. This technique allows the spectra to be determined with a resolution of approximately 1cm⁻¹.

The radical species are produced by the pyrolysis of a precursor ([redacted] has been produced from either [redacted] iodide or 1,5-hexadiene and [redacted] from [redacted] iodide). The vibrationally hot radicals are then cooled via supersonic expansion in a helium gas carrier, creating a molecular beam.

Due to technical difficulties with the equipment, this has not been successfully accomplished within duration of the project. However, the equipment has now been set up so that an alternative system, the [redacted] radical, can now be investigated, and this work is at present in progress.

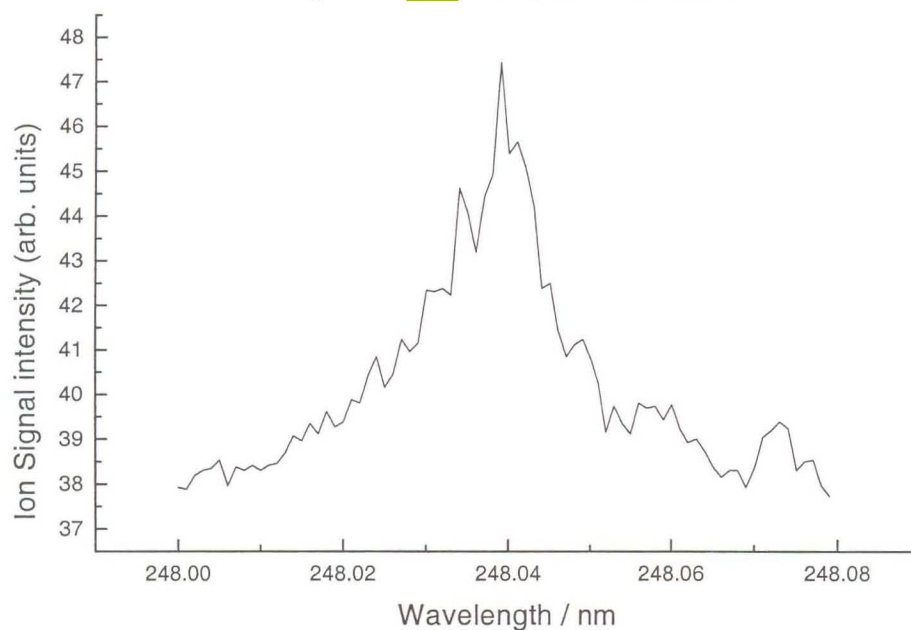
Schedule of Project

- | | |
|-----------------------|--|
| June 1999 | 1+1 resonant MPI spectrum of the [redacted] radical C 0 ₀ ⁰ state measured. |
| July 1999 | 1+1' resonant ZEKE spectrum of the [redacted] radical (from [redacted] iodide precursor) attempted.
Alternative precursor molecule (hexadiene) used.
MOPO realigned. |
| August 1999 | 1+1' resonant ZEKE spectrum of the [redacted] radical (from hexadiene precursor) attempted, unsuccessfully.
1+1 non-resonant ZEKE spectrum of CS ₂ attempted, but not completed due to MOPO instability.
MOPO realignment attempted unsuccessfully. |
| September 1999 | PDL3 dye laser set up for investigation of the [redacted] radical (1+1 non-resonant, produced from [redacted] iodide precursor).
1+1 non-resonant ZEKE spectrum of toluene attempted, to ascertain the suitability of the system. |

Results and Discussion

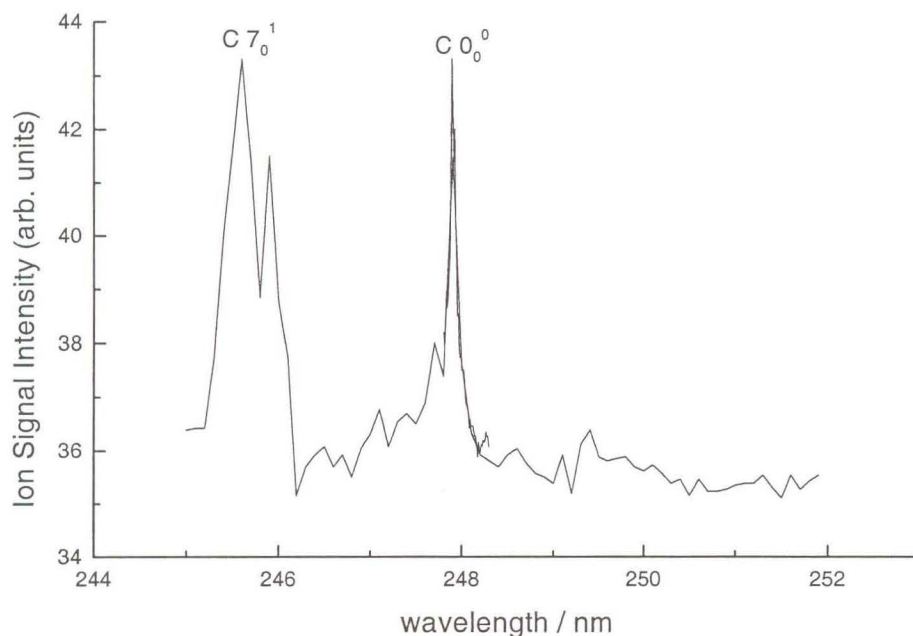
Initially, the 1+1' resonant ZEKE spectrum of C_7H_6 (prepared from $\text{C}_7\text{H}_6\text{I}^+$ iodide) was investigated. The resonant state used was the $C 0_0^0$ state. Figure 1 shows the 1+1 multiphoton ionization spectrum. The literature value for this state is 248.15 nm.

Figure 1. C_7H_6 Multiphoton Ionization



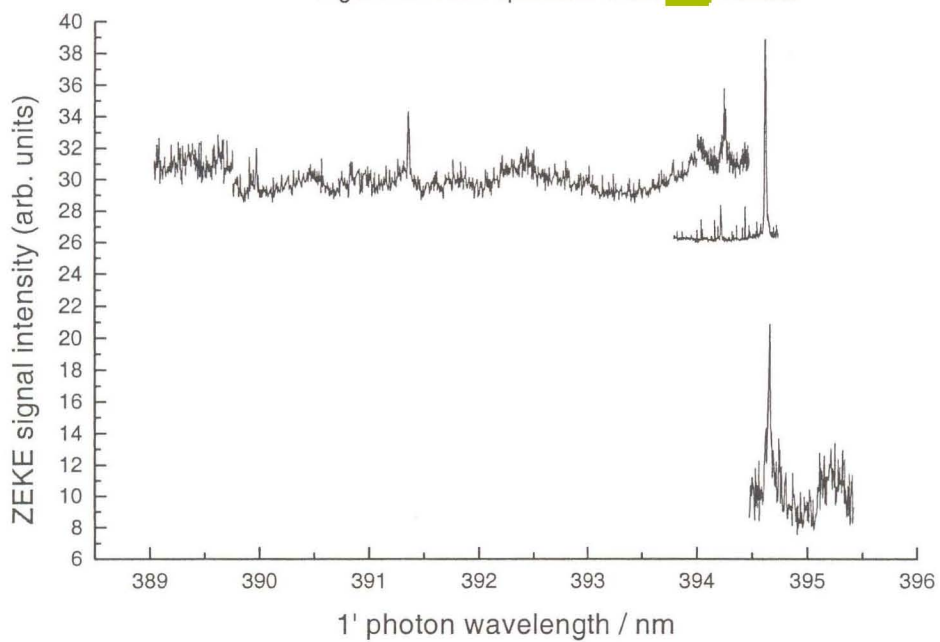
Later, a larger wavelength range was scanned (using hexadiene as a precursor). This MPI spectrum clearly resolves both the $C 0_0^0$ and $C 7_0^1$ states. See figure 2.

Figure 2. MPI



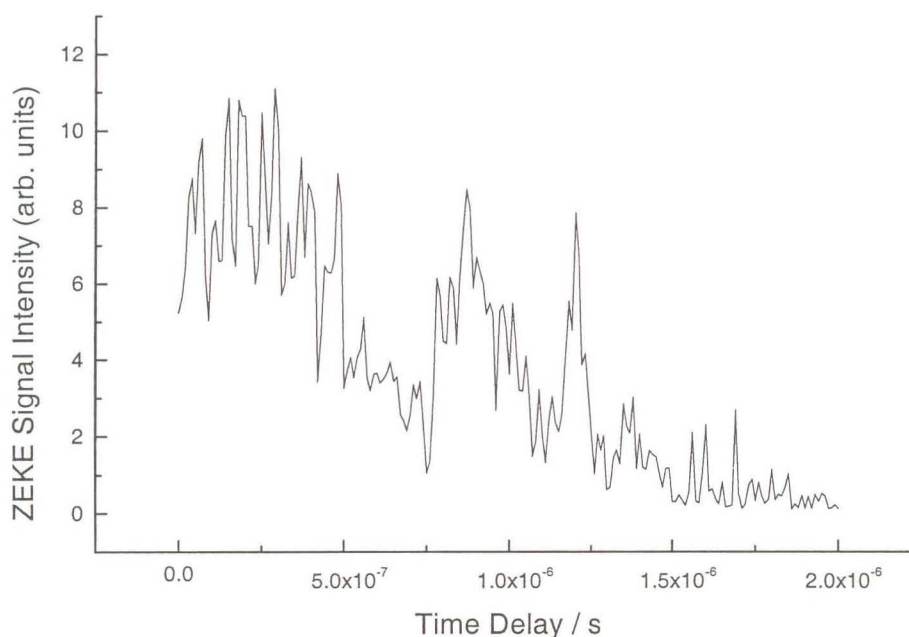
Once the resonant states had been identified, the pump laser (GCR-250 MOPO) was set to the wavelength where maximum intensity was found (248.039nm). The second laser (GCR-3A PDL-3) was then used to excite the resonant state to the Rydberg states. A ZEKE signal was obtained, and the second laser was scanned, producing the spectrum shown in figure 3.

Figure 3. ZEKE Spectrum of the Radical



Three peaks are clearly resolved at 394.6nm, 394.2nm and 391.4nm. However, the baseline is poor, and improvements in the signal to noise ratio were sought. The lifetime of the Rydberg states was also investigated, by varying the time delay between the photoexcitation and the application of the extraction field. The results are shown in figure 4.

Figure 4. Delay Time Dependence of Signal



A clear time dependency is observed, but the reproducibility of the signal was poor.

An alternative precursor molecule, hexadiene, was used. Again, pyrolysis was used to produce the radicals. However, when the MPI spectrum was measured, the C_0^0 resonance was uncharacteristically broad, and again, the signal suffered from poor reproducibility. The realignment of the MOPO was undertaken and successfully completed. Figure 2 shows the MPI spectrum after the MOPO realignment.

In order to verify that the electron detection system was functioning satisfactorily, the simpler molecule of CS_2 was used. Before a ZEKE spectrum could be taken, the MOPO light became unstable, eventually resulting in no UV output. The alignment was again undertaken. It was not possible to repair the system.

Without a second laser, a resonant ZEKE experiment was not possible. Also, as all available frequency doubling units utilized KD*P crystals, severe restrictions were placed on the wavelength range which could be investigated. A new system was constructed, in which the 1+1 non-resonant ZEKE spectrum of the [redacted] radical was to be investigated. Again, a test-substance (toluene) was used to verify that a ZEKE signal could be obtained from the system. At present, this work is underway.

Conclusions and recommendations

With the equipment in its present arrangement, it should be possible to obtain results from the [redacted] radical. When the MOPO is repaired, this should also be possible with the [redacted] radical. In view of the unreliability of the MOPO unit, and the presence of a second PDL-3 dye laser, it is recommended that the installation of a second suitable frequency doubling unit, using BBO crystals, is considered. This would provide a valuable back-up option for the system, or could be used to replace one of the KD*P units. It should be noted that one of the crystal modules for the WEX-1 system is, in its current state, unusable.

Acknowledgments

This project would not have been possible without the ERASMUS scheme. My thanks go to [redacted] for arranging things at [redacted] end, and to [redacted] and Peter Chen for the Swiss end.

Peter Chen has not only given me the opportunity to work in such a fantastic group, but also threw me right in the deep end of research. Within a few weeks of first encountering a laser, I was aligning the MOPO. For this baptism of fire, I thank him.

[redacted] [redacted] has been the most patient and helpful colleague that I could have hoped for. It was only through his guidance and experience that I could come to grips with the project. Thank you [redacted]

Ingo Fischer too has always been a valuable source of information and practical tips for the lab.

Finally, I should like to thank the rest of the Chen group. I could not have hoped for a better environment in which to work. The other group members were a constant source of conversation and the occasional humorous exchanges always served to brighten up the day. Special thanks must go to [redacted], specifically for beating me quite so soundly at chess on every occasion.