

Chapter 5

Photoelectron spectroscopy of the excited $^3\Pi_{0+u}$ B state of Br_2

5.1 Introduction

Photoelectron spectroscopy of molecular excited states has been a topic of interest in many research groups, largely since the introduction of pulsed lasers [56]. The pulsed laser allows for a technique termed Resonance Enhanced Multi-Photon Ionization, or REMPI. In REMPI, one or more photons are used to excite a molecule to an intermediate state, and several additional photons (either of the same wavelength or a new wavelength) are used to ionize the molecule, as is demonstrated in Fig. 5.1. In this example, the photoelectron spectrum observed is due to the Franck-Condon overlap (overlap of the vibrational wavefunctions) between the excited neutral state and the ground ionic state. Specifically, the REMPI technique has been used to study processes such as one-photon forbidden transitions (O_2), super-excited states (NO), small van der Waals complexes (NO-Ar), and structural isomers and IVR (internal vibrational relaxation) of several organic molecules [57].

While REMPI has been largely successful, some difficulty exists using a multi-photon ionization step, similar to the discussion in chapter 1. First of all, it is possible to inadvertently overlap a second resonance during the ionization step (such as a Rydberg state), in which case the photoelectron spectrum observed is due to the overlap of this second resonantly excited state and the ion state [58]. Secondly, the total energy of the probe is still limited by the number photons available, where the probability of adding an additional photon decreases as ρ^n , where ρ is the density of photons and n is the number of photons.

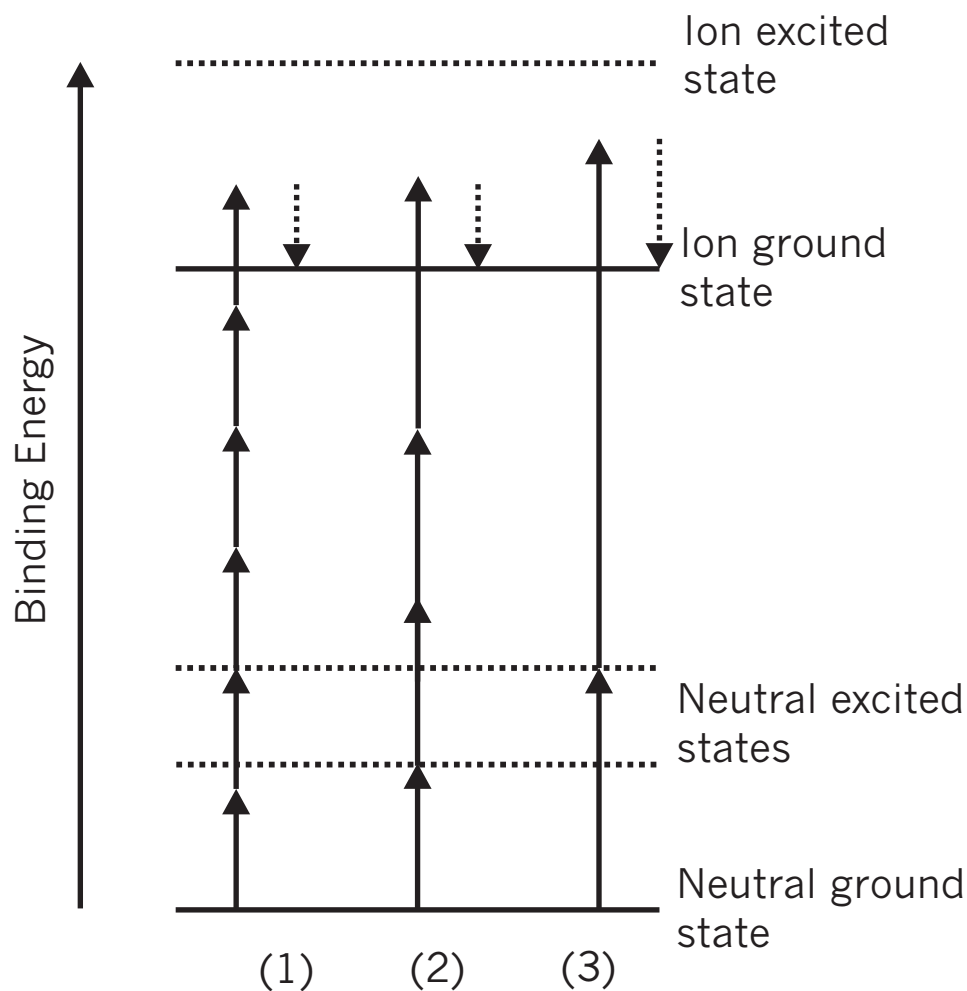


Figure 5.1: A schematic of resonantly-enhanced excited state photoelectron spectroscopy of a generic molecule. Process (1): A single frequency photon used to resonantly excite an intermediate state and ionize it with a multi-photon probe. Process (2): A two-color REMPI process where one photon resonantly excites the molecule and a photon of a different wavelength is used to multi-photon ionize the molecule. Process (3): A two-color excitation-ionization scheme where one visible photon is used to resonantly excite an intermediate state and a VUV photon is used for single photon ionization. The dotted arrows represent the photoelectrons ejected from the three different processes.

A two-color, two-photon excitation-ionization scheme has also been demonstrated in the literature as a supplement to the information already available using the REMPI technique [59] (also shown in Fig. 5.1). Here, a single photon ionization step eliminates unwanted resonances and simplifies the photoelectron spectrum. Four-wave mixing is used to create VUV light (around 8 eV photon energy) to extend the range of molecules studied. Using a tunable laser source for the excitation step also increases the amount of information available, as different vibrational states can be selected in the intermediate excited state. In particular, the excited state photoelectron spectra of NO and pyrazine are discussed in ref. [59].

The introduction of an XUV photon source to the field of excited state photoelectron spectroscopy has still further reaching applications. Again, multiple ion states are accessible with an XUV source, unlike multi-photon and VUV ionization steps, and both electronic and vibrational transitions can be probed between excited neutral states and ion states. Excited state photoelectron spectroscopy, specifically with an XUV light source, provides a link between the molecular orbital picture of a simple molecule and the electronic transitions observed in an experiment. The most important implication lies in the possibility of core-level photoelectron spectroscopy of molecules. While vibrational overlap and forbidden electronic transitions have been studied for some molecular systems, how a core-level electron distribution changes in an excited molecule is not well understood. Here we show the first attempts at experiments aiming to understand the valence level photoelectron spectrum of an excited bound state of Br_2 , with the hope that this excitation-ionization scheme can be extended to core level spectroscopy in the near future.

5.2 Excitation scheme

The two-photon scheme used to excite and probe the B state of Br_2 is shown along with the potential energy curves of $\text{Br}_2/\text{Br}_2^+$ in Fig. 5.2. A pulsed green laser (doubled Nd:YLF @ 527 nm, ≥ 100 ns, 600 mW) is used to promote a population of Br_2 molecules into the B excited state. Approximately 50 ns later, the high-harmonic beam (17th) is then used to ionize the

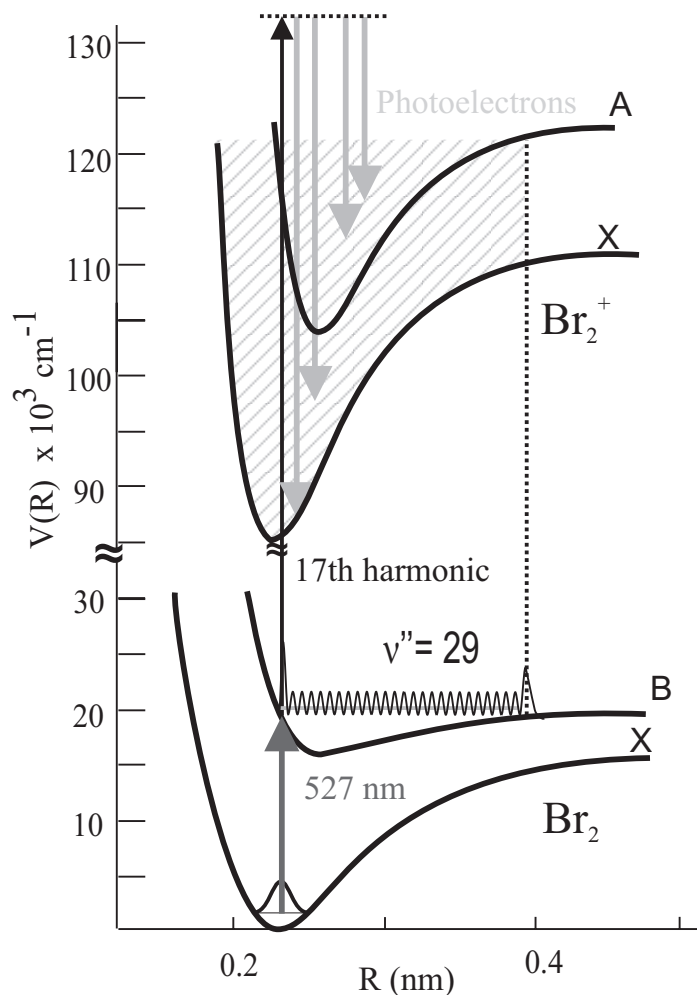


Figure 5.2: Potential energy curves for Br_2 and Br_2^+ . Only the X and B states of the neutral and the X and A states of the ion are shown for simplicity. The 527 nm excitation laser pumps the neutral into the ${}^3\Pi_{0+u}$ excited B state, and the 17th harmonic photoionizes the excited molecules. The $v'' = 26$ vibrational level reached by the 527 nm photon is shown, creating a large region of Franck-Condon overlap in the Br_2^+ ion electronic states. The shading represents the accessible region of the X^+ and A^+ ion states with the probe photon. The intensities and energies of the photoelectrons will then be determined by the Franck-Condon overlap.

sample, creating photoelectrons from both the excited Br₂ molecules and the molecules left in the X ground state. The lifetime of the Br₂ B state at 527 nm is $\sim 1 \mu\text{s}$ [60], therefore probing at a 50 ns delay with a ≥ 100 ns pulse should sample the excited state before complete predissociation. In this experiment, the intensities (and energies) of the photoelectrons generated from ionizing the excited state are determined by the maximum wavefunction overlap between the excited state and final ion state vibrational levels.

A calculation of the vibrational energy levels in the B state reveals that the narrowband Nd:YAG laser excites primarily the $v' = 26$ vibrational level of the B state (including the zero point energy of the ground X state). This calculation is given in equation 5.1.

$$E_{v''=0} + E_{h\nu} = T_e(X \Rightarrow B) - \left(\omega_e(v' + 1/2) + \omega_e x_e(v' + 1/2)^2 \right) \quad (5.1)$$

In this equation, $E_{v''=0}$ denotes the energy of the zero vibrational level of the ground X state, $E_{h\nu}$ is the photon energy of 527 nm, $T_e(X \Rightarrow B)$ is the transition energy from $v''=0$ of the X state to $v'=0$ of the B state, and ω_e and $\omega_e x_e$ are the vibrational constants of the B state given in ref. [61]. Thus far we have ignored the Boltzmann distribution [1] of the ground X state of Br₂ at room temperature. The weights of the v'' states in the X state of Br₂ calculated by the Boltzmann distribution (n_i/N , where n_i is the population of the i th energy level and N is the total population) are:

- $v'' = 0$, weight = 0.54
- $v'' = 1$, weight = 0.24
- $v'' = 2$, weight = 0.11
- $v'' = 3$, weight = 0.05
- $v'' = 4$, weight = 0.02
- $v'' = 5$, weight = 0.01.

Therefore, while the majority of the signal originates from $v'' = 0$, $v'' = 1$ and 2 cannot be discounted. The vibrational levels obtained in the B state originating from $v'' = 1$ and 2 would then be $v' = 33$ and 39 , respectively. Determining the vibrational level reached in the excited B state is important, since this will ultimately determine the extent of Franck-Condon overlap with the Br_2^+ ion states, and the energies of the ejected photoelectrons.

In a simple molecular orbital picture, the electron configurations (estimated) for the neutral and excited states of Br_2 and Br_2^+ are given in Fig. 5.3. From the ground neutral state, it is easy to reach the electron configuration of the ground and first two excited states of the ion, simply by removing an electron from the appropriate orbital. However, when starting from the electron configuration of the excited B state of the neutral, transitions into the ion configurations must involve the movement of 2 electrons, with the exception of the $\text{B} \Rightarrow \text{X}^+$ transition. This is the goal of excited state photoelectron spectroscopy, to link the understanding of a simple molecular orbital picture to the experimental observations of electronic transitions beyond ground state ionization spectroscopy.

5.3 Photoelectron spectra

The valence level photoelectron spectrum of Br_2 taken with the 17th harmonic of 800 nm is shown again in Figure 5.4. The three final electronic states of the molecular ion accessible with this photon energy are observed (labeled X, A and B). The solid lines in Fig. 5.4 indicate the known binding energies of the Br^+ atomic states [46]. In Fig. 5.5, the photoelectron spectrum of Br_2 with the introduction of the 527 nm excitation laser along with the 17th harmonic is expanded from the dotted box in Fig. 5.4. The expansion of the photoelectron spectra is due to a flight tube retarding voltage (~ -14 V) used to clearly observe small signals and obtain better energy resolution. The larger peaks labeled $\text{X} \Rightarrow \text{X}^+$ and $\text{X} \Rightarrow \text{A}^+$ are due to the ground state absorption of the 17th harmonic leaving the ion in the X and A states (10.5 and 13 eV binding energy, respectively). The new signal in the 527 nm + 17th harmonic spectrum at ~ 8.5 eV results from the ionization of the Br_2 neutral in the excited B state, leaving the ion in the X

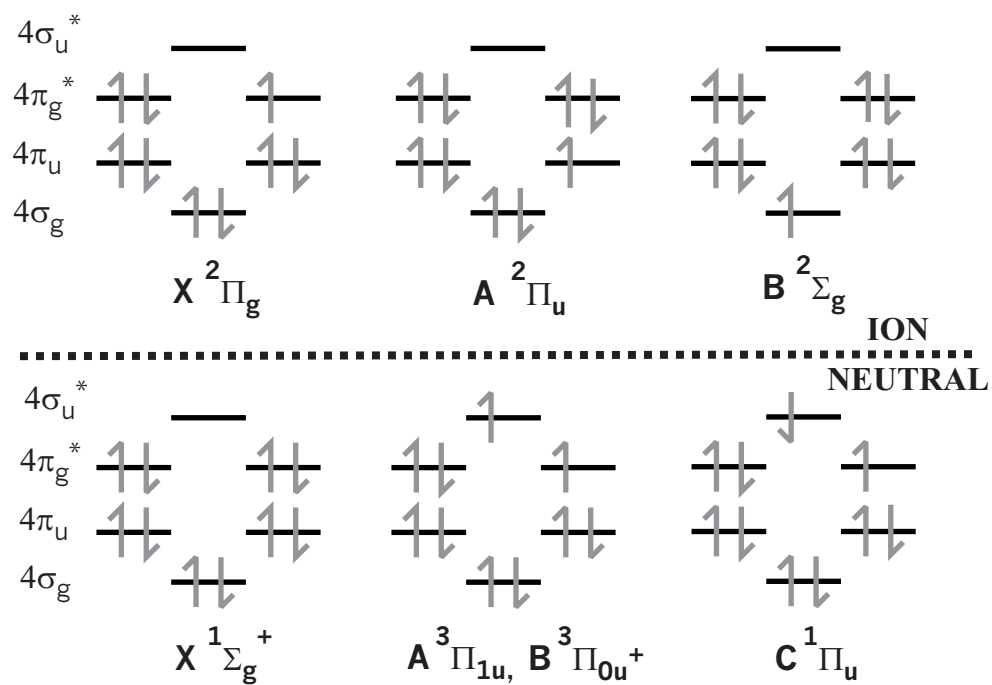


Figure 5.3: A molecular orbital diagram of the ground and excited states of Br_2 and Br_2^+ . The four molecular orbital levels shown result from combinations of Br atomic p orbitals (outer valence shell). The B and A states of the neutral have a similar configuration but differ in orbital angular momentum.

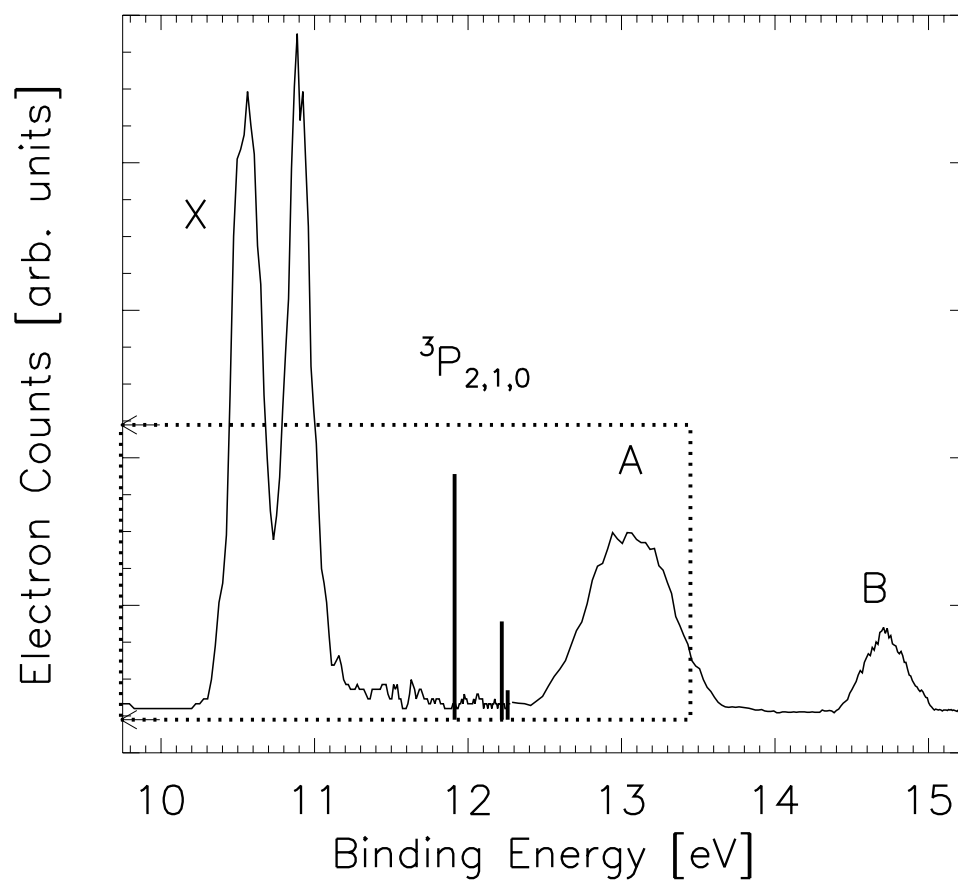


Figure 5.4: The photoelectron spectrum of gaseous Br_2 at 5×10^{-5} Torr taken with the 17th harmonic of 800 nm showing the final X, A and B states of the Br_2^+ ion. Solid black lines denoted $^3P_{2,1,0}$ are the known binding energies of the bare Br atom.

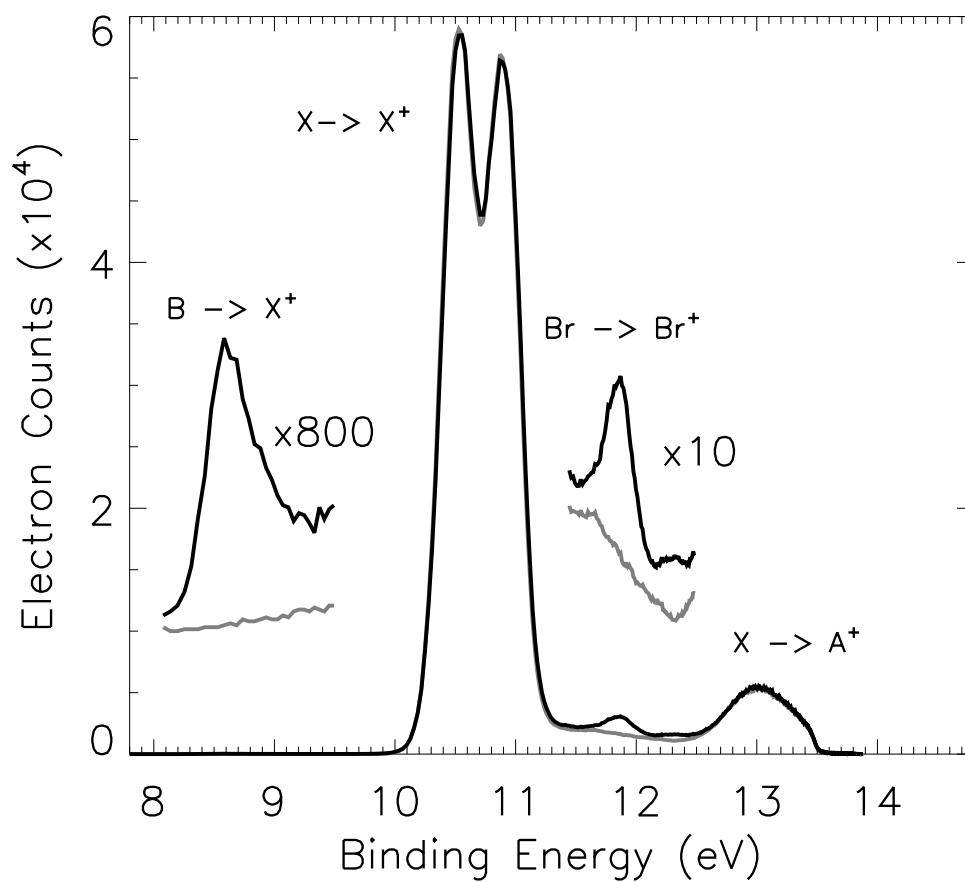


Figure 5.5: The photoelectron spectrum with the 17th harmonic only is shown in gray, while the photoelectron spectrum with the 527 nm + 17th harmonic is shown in black. Regions of small two-photon and atom signals are expanded for clarity.

ground state. The peaks at 11.8 and 12.2 eV are photoelectron signatures of the Br atoms. The B state of Br_2 is known to be predissociative [62], especially when excited to a high vibrational state, so the observation of Br atoms is not surprising. If the $\text{B} \Rightarrow \text{A}^+$ transition existed, the photoelectron peak would be expected to appear at 10.6 eV, and would be buried under the photoelectron peak from the $\text{X} \Rightarrow \text{X}^+$ transition. Similarly, the $\text{B} \Rightarrow \text{B}^+$ transition is expected to appear as a photoelectron peak at 12.3 eV, very close to the smaller Br atomic peak, but should be observable.

Figures 5.6 and 5.7 show the photoelectron spectrum of the $\text{B} \Rightarrow \text{X}^+$ transition expanded further by incrementally increasing the flight tube voltage. In both spectra, there are several interesting features. First, Fig. 5.6 demonstrates that the signal from the $\text{X} \Rightarrow \text{X}^+$ transition decreases as the $\text{B} \Rightarrow \text{X}^+$ signal increases. This is due to the depletion of ground state molecules as a population of the sample is pumped into the excited state. According to the absorption spectrum in appendix A, the cross section for absorption at 527 nm is $1.5 \times 10^{-19} \text{ cm}^2$. Using the photon flux of the 527 nm (1.6×10^{15} photons/pulse, or 0.6 mJ/pulse), the percentage of molecules excited to the B state is $\sim 0.02\%$. A second point is that there is no visible photoelectron peak corresponding to the $\text{B} \Rightarrow \text{B}^+$ transition. If it were of similar magnitude to the $\text{X} \Rightarrow \text{X}^+$ photoelectron signal, it should be visible above the background. However, according to molecular orbital diagrams, it would require a 2 electron transition to go from the B neutral state to the B ionic state. One expects such transitions to be very weak.

Lastly, Fig. 5.7 demonstrates that ionization from the B ($v' = 26$) in the neutral leaves the ion in excited vibrational states of the ground electronic state. If the ground X state of Br_2^+ was left in the $v'' = 0$ vibrational level after a two-photon resonant ionization, the photoelectron peak would be expected to appear at 8.15 eV binding energy (the energy of a 527 nm photon is 2.36 eV, and the 17th harmonic is 26.35 eV). However, in the experiment, the maximum of the $\text{B} \Rightarrow \text{X}^+$ photoelectron peak appears at 8.5 eV (corresponding to $\sim v = 8$). This indicates that the Br_2^+ (X) state is vibrationally excited, most likely due to the Franck-Condon overlap resulting from the change in geometry from the excited Br_2 to the Br_2^+ . Instead of a symmetric

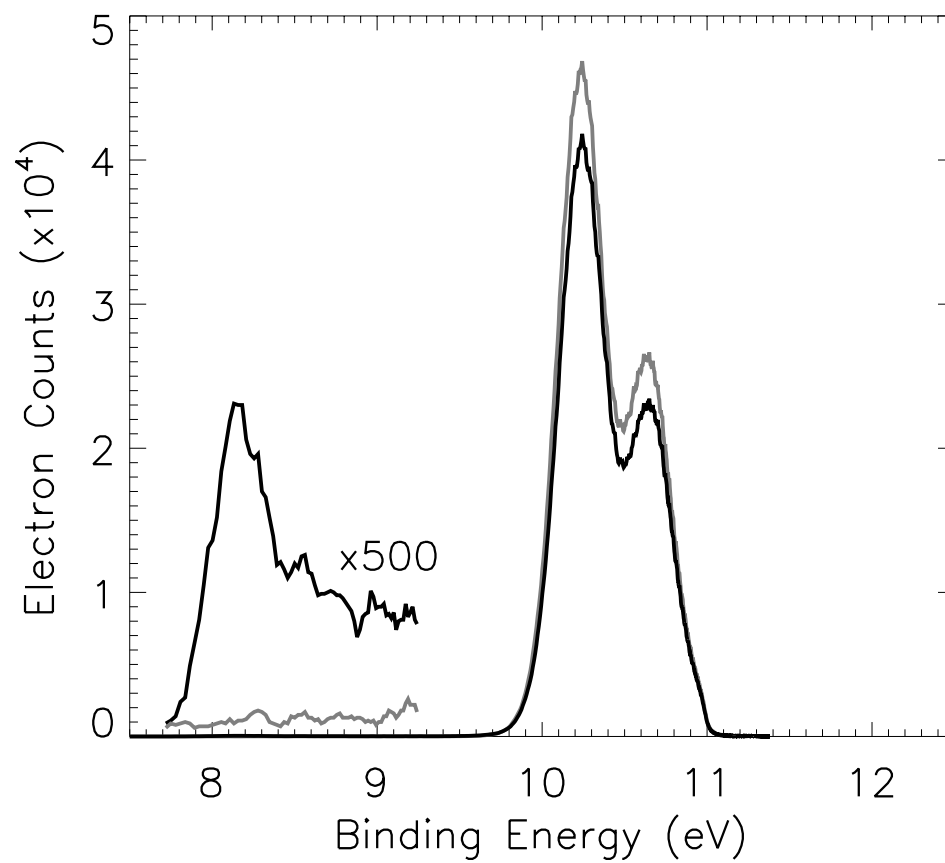


Figure 5.6: An expanded photoelectron spectrum of Br₂ with (black) and without (gray) the 527 nm excitation laser.

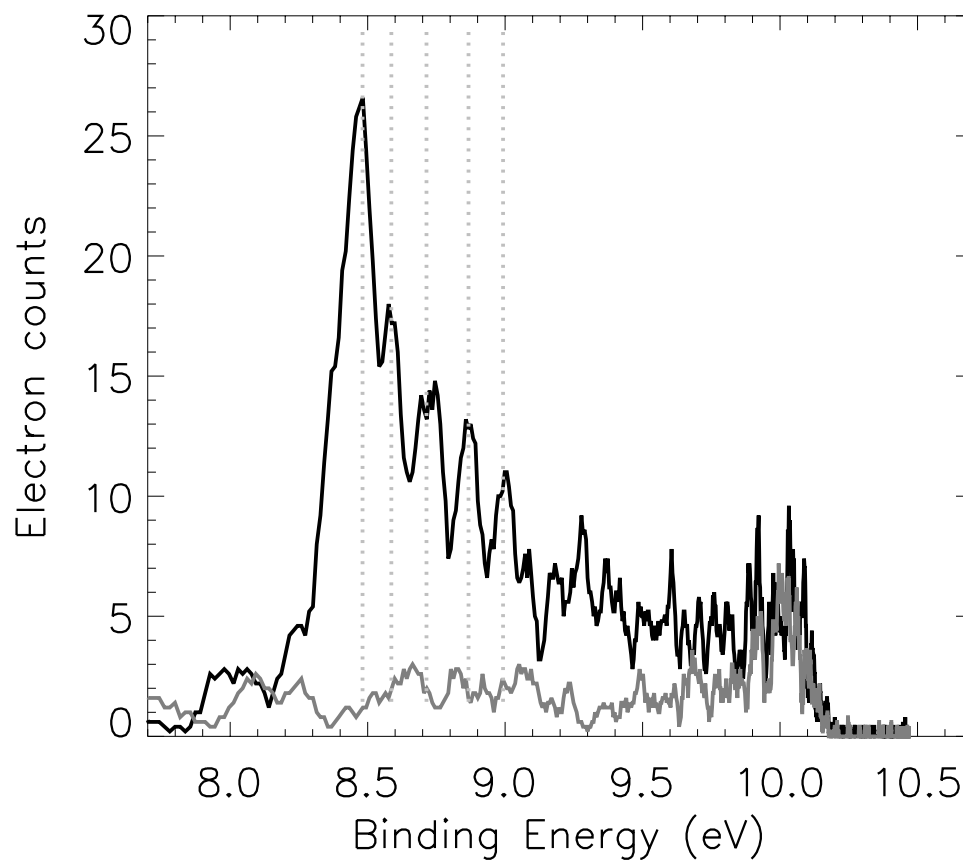


Figure 5.7: A further expanded photoelectron spectrum of the $B \Rightarrow X^+$ transition in Br_2 (gray line=17th harmonic only). The dotted gray lines mark the photoelectron energies of the peak heights.

peak, we also observe a long tail to higher binding energies, indicating even higher vibrational levels are excited (the multiple peak pattern is repeatable). The intensities of the vibrational peaks in Fig. 5.7 are likely due to Franck-Condon overlap between the neutral B state and the ionic X state vibrational levels. There is also the additional spin-orbit splitting of the Br_2^+ (X) state, which is ~ 0.4 eV. This energy splitting does not agree with the adjacent peak splittings in Fig. 5.7, but it is the difference between the peaks at 8.5 and 8.9 eV, for instance. There is probably some combination of spin-orbit splitting and vibrational Franck-Condon overlap responsible for the pattern of peaks observed.

These are the most recent results presented in this thesis, and the interpretations are still preliminary. A more comprehensive evaluation of the results, including a theoretical Franck-Condon overlap simulation, will be required to fully understand the data. However, this proves to be a successful extension of the well documented REMPI technique, and will allow for the study of gas phase molecules not accessible with lower energy probe lasers. Experiments in the near future will likely include core-level photoelectron spectroscopy of the B state of Br_2 , as well as low lying excited states of other simple molecules, such as IBr or I_2 .