

Ab Initio Determinations of Photoelectron Spectra Including Vibronic Features

An Upper-Level Undergraduate Physical Chemistry Laboratory

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Experimental molecular spectroscopy is a cornerstone of the physical chemistry laboratory. Undergraduate students are encouraged to probe electronic structure, molecular vibrations, rotational motion, and molecular geometry using light. Advances in spectroscopic equipment have brought sophisticated techniques into pedagogical use. While this has led to improved coverage of molecular structure and behavior, some fundamental concepts are still underrepresented.

Students have difficulty relating geometric deformations that accompany electronic transitions to the overall appearance of a spectrum. Various vibrational modes may be excited during a change in electronic state. Thus, these spectra have vibronic features. Students struggle to find the physical meaning lurking behind the intensity profile of these vibrational progressions because they are not observed in IR spectroscopy. In the laboratory, a thorough theoretical treatment of rotational–vibrational (rovibrational) methods is commonplace (1). Electronic transitions, on the other hand, typically receive either a cursory explanation or a thorough description limited to a single active vibrational mode (2–8).

Polyatomic systems offer unique challenges because of the probable excitation of multiple vibrational modes in a given electronic system ($X \leftarrow X$, for example). In addition, the observation of vibronic overtones, combination bands, hot bands, and sequence bands is routine. Thus the detailed assignment of observed vibronic structure in their spectra has been previously considered beyond the scope of the undergraduate laboratory.

The current work focuses on the use of a student-friendly Franck–Condon factor calculator to teach upper-level undergraduate students how to determine electronic spectra from first principles. Students are able to rapidly visualize the impact of geometric deformations upon the intensity profile of any predicted vibronic bands. Spectroscopists frequently compare theoretical and experimental results to resolve controversial or uncertain assignments. Our laboratory encourages students to probe electronic spectra in an analogous fashion.

Background

The relative intensity of any vibronic band in a given electronic system is directly proportional to the square of its vibrational overlap integral, referred to as its Franck–Condon factor (FCF)

$$\text{FCF} = \left| \int \psi_v'^* \psi_v \, d\tau \right|^2 \quad (1)$$

where $\psi_v'^*$ gives the complex conjugate of the normalized vibrational description of the initial electronic state and ψ_v gives the normalized vibrational description of the final electronic state (9). This *Journal* has published much work on the calculation of Franck–Condon factors and the subsequent prediction of electronic spectra in the physical chemistry laboratory (2–8). The complex matrix mechanics and integral evaluations required to complete these projects, however, obscure the physical meaning of the results and preclude coverage of systems with multiple active vibrational modes.

We have chosen to focus upon the ab initio determination of photoelectron spectra because it is a topic of modern research (10–12) interest and pedagogical value (7, 13–17). At its core, photoelectron spectroscopy is ionization under controlled circumstances. A molecular sample is irradiated with intense light of known frequency. If the photon energy ($h\nu$) exceeds the binding energy of any electron in the sample, photodetachment may occur.



Excess energy is carried away as electron kinetic energy (eKE).

$$h\nu - \begin{array}{l} \text{binding} \\ \text{energy} \end{array} = \text{eKE} \quad (3)$$

Measurement of eKE provides a direct probe of electron binding energy (ionization energy). In addition, photoelectron spectroscopy is not encumbered by optical selection rules. Any electronic state that is accessible via one-electron photodetachment may be observed.

The technique is both unique and intuitively satisfying for undergraduate students. Its pedagogical utility has been previously elaborated in this *Journal* (13–17). Few institutions possess photoelectron spectrophotometers, however. Fortunately, the spectra are relatively easy to predict because ionization between electronic ground states ($X \leftarrow X$) is common. Thus, it is possible to determine photoelectron spectra with rich vibronic band structure without the use of expensive, sophisticated techniques such as excited state calculations. Water and hypochlorous acid have been chosen as target species because of vibronic features found in their spectra (18, 19) and because of their computationally tractable size.

The motivation for this work comes largely from the development of the FCF calculator by Susan Green and her students.¹ We have found Green's calculator to be both powerful

and approachable. It incorporates an easy-to-use graphical user interface (GUI), handles mode mixing (20), uses an efficient algorithm for calculating overlap integrals (21), and requires no knowledge of matrix mathematics. A copy of this calculator is included in the online supplement.

Overview of the Experiment

To determine the photoelectron spectrum of a polyatomic molecule, optimized geometries for all species, as well as Cartesian displacements, frequencies, and reduced masses for their normal modes are required (20). Any theory capable of producing these parameters for ground state systems is sufficient. For the worked example, we have utilized the B3LYP flavor of density functional theory (22, 23) with the 6-31G* (24) basis. All geometry-optimized structures were verified to be absolute minima by ensuring the absence of imaginary harmonic frequencies for each of the normal modes. Gaussian03 (25) was used to acquire all necessary data. Sample Gaussian03 input decks and truncated output files are included in the online supplement. Students will generate the needed data through the use of modern computational software. The laboratory requires approximately three hours to complete.

Hazards, Supplies, and Instrumentation

This laboratory exercise has no significant hazards and requires no chemicals or chemical instrumentation. All that is needed is a personal computer with software capable of undertaking computational chemistry.

Results and Discussion

Table 1 summarizes the results of all required geometry optimizations. When water is ionized to its cation electronic ground state, the OH bond lengthens and HOH angle increases. These geometric changes are easily mapped to the vibrational modes of the cation. Because these deformations are symmetric with respect to both the principal rotation axis and the mirror planes, exclusive excitation of totally symmetric (A_1) vibrational

Table 1. Geometry Data in Internal Coordinates

Compounds	$r_{\text{OH}}/\text{\AA}$	$r_{\text{OCl}}/\text{\AA}$	$\angle_{\text{HOH}}^\circ$	$\angle_{\text{HOCl}}^\circ$
$\text{H}_2\text{O X}$	0.969	—	103.7	—
$\text{H}_2\text{O}^+ \text{X}$	1.013	—	109.6	—
HOCl X	0.976	1.728	—	102.4
$\text{HOCl}^+ \text{X}$	1.002	1.607	—	109.6

modes is expected. Figure 1 demonstrates typical results for the water $\text{X} \leftarrow \text{X}$ system. The vibrational envelope contains five peaks: the origin, the ν_1 fundamental (OH symmetric stretch), the ν_2 fundamental (HOH bend), the $\nu_1 + \nu_2$ combination band, and the ν_1 first overtone. At 298 K no significant hot bands are seen.

While the spectrum is simple, assignment of the combination band and overtone are not intuitive. Given their familiarity with IR spectroscopy, students frequently assume that each predicted transition represents excitation of an additional normal mode. To get students out of this rut, we ask them to modify their cation geometry to produce an artificial photoelectron spectrum where only ν_1 or ν_2 is active. This is an unusual request and students are somewhat apprehensive about tinkering with nature at such a fundamental level. They may have to make a number of proposals before they discover a viable geometry. In the water system, they need to fix either the OH bond length (ν_2 active) or the HOH angle (ν_1 active) to achieve success.

Photodetachment in the hypochlorous acid system produces a dramatic OCl bond contraction. Vibrational analysis of the cation shows that only ν_3 possesses a prominent OCl stretch. Thus, photodetachment is expected to produce profound excitation in this mode. At this point students should be able to conclude that ν_3 will be excited, but they should not be expected to predict the duration of the vibrational progression. Figure 2 shows typical results for the hypochlorous acid $\text{X} \leftarrow \text{X}$ system. The spectrum is dominated by an extensive vibrational progression in ν_3 . It also contains a ν_3 hot band. The hypochlorous acid example exposes students to a significantly nonvertical electronic

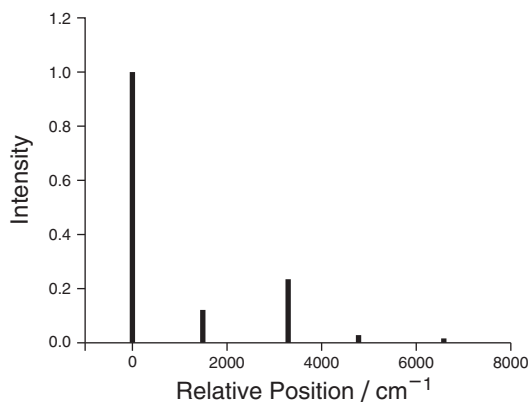


Figure 1. Water photoelectron spectrum.

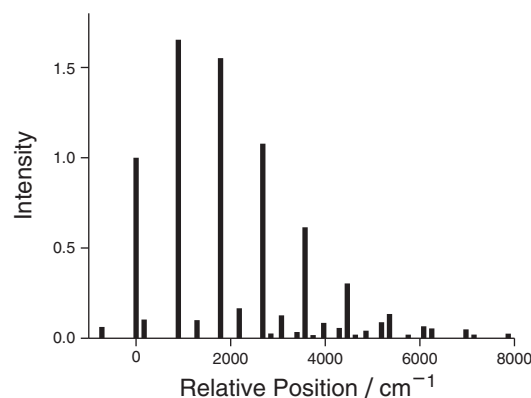


Figure 2. Hypochlorous acid photoelectron spectrum.

transition. If they have mastered the water exercises, however, they should be able to appreciate the difference in appearance and easily assign all predicted vibronic structures.

Conclusions

Students safely and quickly grasp the fundamentals of photoelectron spectroscopy through ab initio explorations. They are exposed to unique vibronic features not found in IR work (and typically unresolved in UV studies). They are also given an opportunity to actively modify cation parameters to produce spectra, unknown in the experimental domain, whose features are instructive. In essence, they are provided with a feedback loop. Once students get past the mechanics of the exercise and engage this loop, they are frequently captivated by their ability to manipulate the appearance of spectra. This activity would be time-prohibitive in an exercise where Franck–Condon factors are explicitly calculated, and equally untenable if the FCF calculation allowed no student intervention. Example species have been carefully chosen to give students broad exposure to vibronic features in a stepwise fashion. Activities are incorporated that allow students to conceptually process important spectroscopic features before moving forward.

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Note

1. The software for the Franck–Condon factor calculator has been released under GNU General Public License and is available in the online supplement.

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Supplement

Student handouts, including background information and instructions

Instructor notes with Gaussian03 input decks and truncated output files, as well as FCF input matrices

FCF calculator software