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Single- and Multi-photon Ionization Studies of Organosulfur
Species

by

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CHAPTER 1. GENERAL INTRODUCTION

1. Introduction

Accurate ionization energies (IE's) for molecular species are used for prediction of chemical reactivity and are of fundamental importance to chemists.^{1,2} The IE of a gaseous molecule can be determined routinely in a photionization² or a photoelectron^{3,4} experiment. IE determinations made in conventional photoionization and photoelectron studies have uncertainties in the range of 3-100 meV (25-250 cm^{-1}).

In the past decade, the most exciting development in the field of photoionization and photoelectron spectroscopy has been the availability of high resolution, tunable ultraviolet (UV) and vacuum ultraviolet (VUV) laser sources.⁵⁻⁷ The laser pulsed field ionization photoelectron (PFI-PE) scheme is currently the state-of-the-art photoelectron spectroscopic technique and is capable of providing photoelectron energy resolution close to the optical resolution.⁸⁻¹⁰ For specific molecular species with IE values below 12 eV, the non-resonant two-photon (N2P) PFI-PE scheme involving the use of a UV laser is an attractive method for high resolution photoelectron measurements.^{11,12} Without doubt, the single-photon PFI-PE technique is the most versatile high-resolution photoelectron spectroscopic method. At the current technical level, VUV laser radiation with usable intensity can be generated at energies up to ≈ 17.7 eV by nonlinear optical mixing using commercial dye lasers.⁵

In my PhD study, I have focused my attention on the photoionization processes of some sulfur-containing species. The studies of the photoionization and photodissociation on sulfur-containing compounds [such as CS_2 ,^{13,14} CH_3SH ,¹⁵⁻¹⁷ CH_3SSCH_3 ,^{16,18,19}

$\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$,²⁰ $\text{HSCH}_2\text{CH}_2\text{SH}$ ²¹ and $\text{C}_4\text{H}_4\text{S}$ (thiophene)²² and sulfur-containing radicals, such as HS ,²³ CS ,¹⁴ CH_3S ,^{16,24,25} $\text{CH}_3\text{CH}_2\text{S}$ ²⁰ and CH_3SS ,¹⁹] have been the major subjects in our group because sulfur is an important species contributing to air pollution in the atmosphere. The modeling of the combustion and oxidation of sulfur compounds represents important steps for the control of both the production and the elimination of sulfur-containing pollutants.

Particularly, N2P-PFI-PE studies have been performed on some of the sulfur-containing species with the photoionization apparatus in our laboratory. As a continuation, I have employed similar techniques to study the photoionization of CH_3SH and $\text{CH}_3\text{CH}_2\text{SH}$ (see Chapter 2), CH_3SCH_3 (see Chapter 6) and to probe the $\text{CH}_3\text{CH}_2\text{S}$ radical generated in the photodissociation of $\text{CH}_3\text{CH}_2\text{SH}$ (see Chapter 3).

I have also modified the apparatus to generate VUV laser light. A single VUV photon has enough energy to ionize a molecule and hence single-photon ionization can be studied. The modified apparatus has been used to study the VUV single-photon ionization of CS_2 (see Chapter 4), CH_3SH and $\text{CH}_3\text{CH}_2\text{SH}$ (see Chapter 5) and CH_3SCH_3 (see Chapter 6). Photoionization mainly provides information on the IE of the neutral species and the energy levels (e.g. vibrational energy levels) of the neutral and cationic species. When appropriate, *ab initio* calculations have also been performed (mostly by myself, sometimes by collaborators). The theoretical results are usually very helpful in interpreting the experimental data.

To enhance the ability of the VUV laser technique, a much more sophisticated apparatus is under construction and I have been involved in its design and fabrication.

Although the construction is not finished, the critical parts of the new apparatus have been completed and are functioning very well. When operating, the new apparatus is expected to provide many new and interesting research opportunities. It will be introduced in Chapter 7 where the progress is reported.

2. Dissertation Organization

This dissertation consists of seven chapters, each of which has its own numbering system for equations, tables, figures and references.

Chapter 1 is a general introduction of the thesis. Chapters 2 to 6 contain five papers published in, or accepted for publication in, academic periodicals. Each paper is presented in accordance with the requirements of the periodical to which it was submitted. Because they were submitted to different periodicals, the formats between the papers may be different. Chapters 2 and 3 contain the N2P-PFI-PE spectroscopic studies of CH_3SH ,²⁶ $\text{CH}_3\text{CH}_2\text{SH}$ ²⁶ and $\text{CH}_3\text{CH}_2\text{S}$ radical formed in the photodissociation of $\text{CH}_3\text{CH}_2\text{SH}$.²⁷ Chapters 4 and 5 contain the VUV single-photon PFI-PE spectroscopic studies of CS_2 ,²⁸ CH_3SH ²⁹ and $\text{CH}_3\text{CH}_2\text{SH}$.²⁹ Chapter 6 contains the PFI-PE spectroscopic study of CH_3SCH_3 using N2P and VUV single-photon ionizations.³⁰

In Chapter 7, the progress of the construction in our laboratory of a new vacuum ultraviolet laser system equipped with a reflectron mass spectrometer is presented. A general conclusion of these studies are given in Chapter 8 followed by an appendix.

3. Literature Review

The use of lasers in photoionization is relatively old. The first multi-photon ionization (MPI) experiments on gaseous atoms were performed in 1966 by Voronov and Delone.³¹ The MPI technique is still a very important and popular tool in spectroscopic studies due to its simple experimental setup. On the other hand, single VUV photon ionization studies in the past have relied mainly on discharge lamps.³² As commercial lasers have become more and more powerful, the use of VUV laser systems becomes possible and affordable. In fact, some research groups in the world have constructed their own VUV laser systems for photoionization studies.^{5-7,33-36}

Parallel to the development of high power laser sources, technical progress has also been made in high-resolution photoelectron spectroscopy. With the introduction of the laser PFI-PE method,^{9,10,37,38} the energy resolution for photoelectron spectroscopy has been improved to sub-wavenumbers, approaching that achieved in optical spectroscopy.

In spite of these technical advances, few organosulfur compounds have been studied. Only conventional photoionization or photoelectron techniques have been used to study CH_3SH ,^{15,39,40} $\text{CH}_3\text{CH}_2\text{SH}$ ⁴ and CH_3SCH_3 .^{39,41}

On the other hand, the simpler and symmetric linear organosulfur molecule, CS_2 , has been studied in a number of high-resolution photoionization efficiency (PIE)^{13,42} and photoelectron spectroscopy experiments.^{12,43-45} The two approaches, however, have led to a discrepancy in the value of $\text{IE}[\text{CS}_2^+(\tilde{X}^2\Pi_{3/2,1/2})]$. This discrepancy is most likely caused by the Stark field ionization effect.⁴⁶ Furthermore, the $\text{IE}[\text{CS}_2^+(^2\Pi_{1/2})]$ value deduced by the previous

Rydberg series analysis⁴⁷ is not in agreement with those of the PIE^{13,37} and photoelectron spectroscopy^{12,43-45} studies.

Based on the vacuum ultraviolet (VUV) photoionization mass spectrometric sampling of photoproducts formed in the 193-nm photodissociation of $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$, Ma *et al.* conclude that the $\text{CH}_3\text{CH}_2\text{S}$ radical is predominantly produced in such a photochemical process.²⁰ In a recent laser induced fluorescence study⁴⁸, $\text{CH}_3\text{CH}_2\text{S}$ is also shown to be the predominant product in the 248-nm laser photodissociation of $\text{CH}_3\text{CH}_2\text{SH}$.

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CHAPTER 7. CONSTRUCTION OF A COMPREHENSIVE VACUUM ULTRAVIOLET LASER SYSTEM

1. Introduction

The study of vacuum ultraviolet (VUV) chemistry has been performed extensively. In the past, it mainly relied on laboratory discharge lamps¹ and synchrotron light sources. Due to advances in laser technology, generation of intense and coherent VUV light is possible.²⁻⁷ The VUV laser system provides much higher light intensity and energy resolution than conventional discharge lamps. The VUV laser system provides higher energy resolution than the synchrotron radiation source. Also important is the cost. The major components of a VUV laser system are commercially available lasers, which are affordable to many research laboratories. The pulsed nature of a coherent VUV laser source is an advantage in time-of-flight (TOF) mass spectrometry and pulsed-field-ionization photoelectron (PFI-PE) spectroscopy studies.⁸

As shown in Chapters 4 to 6 of this thesis, an existing apparatus has been modified to a VUV laser system for photoionization studies. The results are encouraging. To fully utilize the VUV laser technique, it is necessary to make significant modifications to the apparatus. Since the original apparatus was designed for multi-photon ionization (MPI) studies only, many desirable modifications are difficult or even impossible (e.g., due to limit space available).

In spite of the emerging impact of coherent VUV laser sources in experimental chemical research, currently only a few laboratories in the world have a comprehensive tunable VUV laser system⁹, even though many already have the ability to construct such

systems. For example, in North America, to our knowledge, only the John W. Hepburn group at the University of Waterloo in Canada and the Michael G. White group at the Brookhaven National Laboratory have actively participated in research using a comprehensive VUV laser system. Recognizing the potential importance of the coherent VUV light source in many related fields, it is worthy to build a dedicated multi-user VUV laser research facility.

The construction of such a facility has been started and I have participated in it. At the moment, the construction is not finished. However, I am glad that the critical parts of the new apparatus have been completed and are functioning very well. The final stage is expected to be finished soon. When operating, the new system is expected to provide many new and interesting research opportunities. In this chapter, the new system is introduced and the progress is reported.

2. Principle of coherent VUV light generation

The coherent frequency mixing technique is used in a VUV laser system to generate coherent VUV light. In the classical picture, the principle of coherent frequency mixing depends on the nonlinear response of a medium to applied electric fields.¹⁰ This is normally expressed as a series expansion in terms of the applied oscillating electric field $\mathbf{E}(\omega)$:

$$\mathbf{P}(\omega) = \chi^{(1)} \cdot \mathbf{E}(\omega) + \chi^{(2)} \cdot \mathbf{E}(\omega) \cdot \mathbf{E}(\omega) + \chi^{(3)} \cdot \mathbf{E}(\omega) \cdot \mathbf{E}(\omega) \cdot \mathbf{E}(\omega) + \dots, \quad (1)$$

where $\mathbf{P}(\omega)$ is the induced polarization and $\chi^{(n)}$ is the n^{th} order susceptibility of the medium.

The nonlinear terms, $\chi^{(2)} \cdot \mathbf{E}(\omega) \cdot \mathbf{E}(\omega)$, $\chi^{(3)} \cdot \mathbf{E}(\omega) \cdot \mathbf{E}(\omega) \cdot \mathbf{E}(\omega)$, etc., allow induced oscillating

polarization, which is the source of the generated light, to appear at frequencies other than ω , which is the frequency of the applied electric fields (and that of the input light).

For second harmonic generation, $\chi^{(2)}$ must be nonzero, requiring a nonlinear medium without a center of symmetry, such as crystalline materials. Up to date, the shortest wavelength of laser light generated by a nonlinear process with crystalline materials is 189 nm.¹¹ To generate laser light of wavelength shorter than 189 nm by nonlinear mixing, gaseous atoms must be used as the nonlinear medium.

In general, the more polarizable an atom is, the larger the value of $|\chi^{(3)}|^2$ will be. Commonly used nonlinear gaseous media are rare gases (such as Kr and Xe)^{5,12-14} and metal vapors (such as Hg and Mg).¹⁵⁻¹⁷ Since there is a center of symmetry in gaseous atoms, all the even order susceptibilities, including $\chi^{(2)}$, vanish. The $\chi^{(3)}$ term is then the first nonzero nonlinear term in Eq. (1).

In general, if there are three light beams, with frequencies ω_1 , ω_2 and ω_3 , are merged in a nonlinear medium, the resultant light frequency (ω_s) generated due to the $\chi^{(3)}$ term depends on the interaction of the three oscillating electric fields of frequencies ω_1 , ω_2 and ω_3 . Hence, we have

$$\omega_s = \omega_i \pm \omega_j \pm \omega_k \quad (i, j, k = 1, 2, 3) \quad (2)$$

Since ω_s results from four electric fields oscillating simultaneously in the nonlinear medium, this type of frequency generation is called four-wave mixing.

A special case of four-wave mixing is the third harmonic generation (THG), i.e., the frequency of the generated wave is three times that of the fundamental frequency: $\omega_s = 3\omega_1$.

Obviously, only laser light with single frequency (ω_1) is necessary in THG. The intensity of the generated third harmonic is described by:

$$I_{3\omega} = N^2 |\chi^{(3)}(3\omega)|^2 I_{\omega}^3 F(b\Delta k) \quad (3)$$

where I_{ω} is the intensity of the fundamental, N is the number density of the nonlinear medium and $\chi^{(3)}(3\omega)$ is the third order susceptibility for the third harmonic generation. The factor $F(b\Delta k)$ results from the macroscopic properties of the medium and the focussing of the fundamental, and it represents the phase matching between the input light and the generated VUV. For THG with focused laser beams at the medium, $F(b\Delta k)$ is non-zero only if the refractive index at 3ω is less than that at ω . Since $F(b\Delta k)$ is pressure dependent (pressure dependence of Δk), one cannot simply increase N to improve $I_{3\omega}$, but the $N^2 F(b\Delta k)$ term as a whole must be optimized. Although Eq. (3) is valid only for third harmonic generation, similar equations apply to the other forms of four-wave mixing. The very strong intensity dependence indicated by the $I_{3\omega}$ term essentially restricts four-wave mixing to pulsed lasers, although it is possible to generate cw coherent VUV.

The conversion efficiency of the nonlinear process can be greatly increased through resonant enhancement of $\chi^{(3)}$ when either ω , 2ω or 3ω absorption is resonant with a transition in the nonlinear medium. Since a resonance at ω or 3ω leads to absorption of the input fundamental or the generated third harmonic light, a two-photon resonance is best for enhancing $|\chi^{(3)}|^2$. With only one input frequency, fixing ω to make 2ω correspond to a resonance will not allow for tuning of the generated third harmonic light because 3ω is also fixed. As a result, two independently-tunable fundamental frequencies, ω_1 and ω_2 , must be

used to obtain both resonant enhancement and tunability of the generated light. In this case, we have $\omega_s = 2\omega_1 \pm \omega_2$. The two frequencies generated, $2\omega_1 + \omega_2$ and $2\omega_1 - \omega_2$, are called resonant sum frequency (RSFM) and resonant difference frequency (RDFM), respectively. The much higher conversion efficiency in RSFM and RDFM can be rationalized with a quantum mechanical picture. The absorption of the first two ω_1 photon is a resonance process in RSFM and RDFM but a non-resonance process in THG. As a result, the efficiency for the overall three-photon process is much higher in RSFM and RDFM than in THG (by a few orders of magnitude).

The range of VUV frequency generated by THG, RSFM and RDFM depends on 1) the value of ω_1 which depends on the nonlinear medium used, 2) the range of ω_2 which can be produced by an individual dye laser system, and 3) the phase matching condition in the mixing process chosen. The phase matching condition is the same for THG and RSFM but less stringent for RDFM. In practice, the most convenient methods for generating VUV light are: 65.5-100 nm by RSFM in pulsed jets of Kr and Xe; 109-190 nm by RDFM in gas cells of Kr and Xe; 100-109 nm (the gap between the RSFM and RDFM ranges of Kr and Xe) by THG in pulsed jets of Kr and Ar. The range of 105-190 nm can also be generated by RSFM and RDFM in gas cells of Hg and Mg vapors. These practical schemes allow the generation of coherent VUV laser light in the wavelength range of 65.5-190 nm without gap. Depending on the wavelength region, the VUV light intensity in the range 10^9 - 10^{14} photon/pulse can be achieved.^{2,7,17,18}

3. Components of the system

In Fig. 1, the schematic setup of the system is shown. Basically, commercial lasers are used to generate coherent light with frequencies ω_1 and ω_2 . The two laser beams are combined with a dichromatic mirror and brought into the jet chamber for VUV light generation. The outgoing beam consists of a mixture of light (with frequencies of ω_1 , ω_2 and $2\omega_1 \pm \omega_2$, for example) and are separated at the grating in the monochromator chamber. The light of desired frequency (either $2\omega_1 + \omega_2$ or $2\omega_1 - \omega_2$) goes to the main chamber. At the same time, the molecular beam comes from the source chamber in the direction perpendicular to the VUV laser beam direction. Ions and electrons formed from ionization are extracted upward to the mass spectrometer and downward to the electron detector, respectively (see Fig. 2). A light detector is located downstream from the photoionization/photoexcitation (PI/PEX) region to measure the VUV light intensity for spectrum normalization.

In the following part, different components of the system are described in detail. The differences between the new system and the modified apparatus (which was used to perform the VUV experiments in Chapters 4 to 6 in this thesis) will also be discussed.

3.1. Lasers

There are three lasers in the system: one pump laser and two dye lasers. The pump laser is a Nd-YAG laser (GCR-290, Spectra Physics) with output of about 1.6 J/pulse at 1064 nm. A harmonic generation unit is added to generate harmonic light for pumping the dye lasers. The second, third and fourth harmonics (532, 355 and 226 nm, respectively) can be

Fig. 1. Schematic setup of the new VUV laser system.

Fig. 2. Cross-section side view for the main chamber and reflectron mass spectrometer of the new VUV laser system. Also shown are the ion, electron and molecular beam paths.

generated (though the third and fourth harmonics cannot be generated at the same time).

The dye lasers can be pumped by either 532 or 355 nm, depending on the range of the outputs desired (which in turn depends on the range of the VUV desired). In terms of pumping light intensity, the worst case would be pumping both dye lasers at 355 nm. The maximum output at 355 nm is about 480 mJ/pulse, i.e., each dye laser is pumped by light energy of 240 mJ/pulse. For the purpose of comparison, the maximum pump beam power of the modified apparatus [by a ten-year old excimer laser (EMG 201 MSG, Lambda Physik) at 308 nm] is usually 250-300 mJ/pulse, i.e., each dye laser is pumped by light energy of ≥ 150 mJ/pulse. Also, the use of longer wavelength pump beam (355 versus 308 nm) on dye laser pumping results in higher conversion efficiency (by a low percentage). Therefore, the new system is expected to provide higher light intensity from the dye lasers.

Both dye lasers (LDL252, LAS) of the new system are equipped with harmonic generation units to produce continuously tunable laser light from the UV to the IR region. One of the harmonic generation units laser is simply a second harmonic generation unit whereas the other one consists of a second harmonic generation unit and a sum frequency unit. Such an assembly allows a dye laser to generate laser light of wavelength down to 189 nm by mixing the Nd-YAG laser fundamental output and the second harmonic of the dye laser fundamental output.¹¹

On the other hand, the dye lasers of the modified apparatus (FL3002, Lambda Physik) are pumped by 308-nm light and the shortest wavelength of photons is only 198 nm (by frequency-tripling of dye laser output at 594 nm).

Also important in high-resolution experiment is the bandwidth of the laser light. The LDL252 dye lasers used in the new system have ultra-narrow bandwidth of about 0.04 cm^{-1} , cf. 0.2 cm^{-1} of the one in the modified apparatus. As a result, the bandwidth of the VUV light generated in the new system is estimated to be $\sqrt{(2 \times 2 \times 0.04)^2 + 0.04^2} = 0.16 \text{ cm}^{-1}$.

3.2. Optics components

A couple of standard commercial optics components are used in the new system. Among them, two are specially designed for utilizing a light beam of two different frequencies, and they require extra description.

The first one is a dichromatic mirror. The content of the surface coating is designed in such a way that the mirror has high reflectivity for one frequency but high transmission for the other one. In our case, the mirror is highly reflective for a narrow range of an UV frequency (ω_1) but has a broad-band transmission for the visible region (covering ω_2). In this way, the two laser beams with different frequencies can be combined, and this kind of mirror is used in both the new system and the modified apparatus.

The second one is an achromatic focussing lens to focus the combined laser beam into the jet chamber. An achromatic focussing lens is an assembly of a convex lens and a concave lens of different curvatures and usually with coated lens surfaces. In the modified apparatus, a simple focussing lens is used. One of the problems of the simple focussing lens is that it has different focal lengths for the different components in the combined beam because the refractive index is different for different frequencies. Hence, the two components are

focussed at different spots. On the other hand, the achromatic focussing lens corrects this problem. When the two components are focused at the same spot, the VUV generation is expected to be more efficient.

3.3. Jet-mixing chamber

A pulsed valve inside the jet-mixing chamber introduces the nonlinear medium (Kr or Xe) as a free jet for VUV generation. The gas density of the non-linear medium near the tip is very high and it is the location at which the combined laser beams are focused. At the opposite port is a liquid-N₂ cooled trap (see Fig. 1) which allows recycling of the expensive Kr and Xe gases. A 210 L/s turbo pump maintains the vacuum. The pressure of the chamber is in the range of 10^{-4} Torr.

Gas cells of nonlinear media has been used in previous experiments performed with the modified apparatus (see Chapters 4-6). The best window material for light transmission is LiF, which has a cut-off of 105 nm. Therefore, the use of gas cells limits the wavelength of the VUV light generated to be >105 nm. On the other hand, the jet-mixing chamber can be connected to the downstream chambers without a window, and the wavelength of the VUV light generated can be extended to <105 nm.

3.4. Monochromator chamber

The VUV light generated in the jet mixing chamber (together with lights of other frequencies) goes into the monochromator chamber (Model 343, McPherson) to have the undesired wavelengths removed before entering the main chamber (see Fig. 1). The vacuum

of the chamber is maintained at about 10^{-7} Torr by a 520 L/s turbo pump. Inside the monochromator chamber is a platinum coated 142° toroidal grating which also re-focuses diffracted light 12.59 inches downstream. The groove density is 275 lines/mm. At first order, the maximum wavelength for diffraction is estimated to be about 500 nm (though the range of optimum efficiency is stated as 50-300 nm by the vendor).

The grating can be scanned either manually or by a remote computer. In remote control mode, the electrical stepping motor for the grating is connected to the grating controller (supplied with the grating), which is connected to a personal computer via RS232 interface. Remote control commands of the grating system are described in detail in the instruction manual provided by the vendor. In principle, the grating scans synchronously with the VUV wavelength. Preliminary testing suggests that it is unnecessary. In practice, the VUV range scanned each experiment is very narrow and the grating, if scanning synchronously with the VUV wavelength, virtually does not move. Therefore, it is only necessary to set the grating position at the beginning (via manual control or interactive computer control) and leave it unchanged during the experiment.

Note that a light-dispersing device such as a monochromator chamber of this kind does not exist in the modified apparatus. The monochromator chamber in the new system serves three purposes: 1) The grating separates the VUV light from the undesired UV and visible lights; 2) The VUV light coming out after jet mixing is always diverging (because focusing at the nonlinear gas jet is necessary), so it is an advantage to have a grating to re-focus the VUV light at the PI/PEX region; 3) The monochromator chamber pumped with a powerful turbo

pump plays an important role in differential pumping and maintains a vacuum gradient between the jet-mixing chamber (10^{-4} Torr) and the main chamber ($10^{-7} - 10^{-8}$ Torr).

Upon diffraction, the VUV light intensity is reduced due to light absorption on the grating surface and light diffraction at the undesired orders (e.g. zeroth order, second order and so on when first order diffraction is used). The specified first order diffraction efficiency is 8% at 250.0 nm, 11.5% at 161.0 nm and 19% at 121.6 nm. For wavelengths shorter than 100 nm, the diffraction efficiency is expected to be higher than 20%. Although a significant portion of VUV light intensity is lost, the re-focusing property of the grating used confines all remaining photons into a small region comparable to the size of the molecular beam. This makes the use of VUV light more efficient than a non-diffracted but diverging beam.

3.5. Source chamber, main chamber and extension chamber

The source chamber, main chamber and extension chamber are connected in series and perpendicular to the diffracted VUV light path from the monochromator chamber (see Fig. 1). Gaseous sample is introduced into the source chamber through a pulsed valve. The molecular beam is skimmed before entering the main chamber. The skimmed beam is intercepted perpendicularly at the center of the main chamber (the PI/PEX region) by the VUV light. The photoionization region is inside an electrostatic lens stack. Ions and electrons are extracted to the reflectron mass spectrometer and electron detector, respectively (also see the section below and Fig. 2). Molecules not ionized fly straight through the main chamber into the extension chamber and are pumped away.

The main chamber contains a window for laser alignment. There is also a window to perform pre-ionization processes on the molecular beam. For example, a separate laser may be used to dissociate the parent molecules into radicals which are photoionized by the VUV laser.

The pumping utilities of the new system are much more powerful than those of the modified apparatus. The source chamber of the new system is pumped by a 10-in. diffusion pump (5300 L/s, VHS-10, Varian) backed up by an ejector pump in series with a roots blower and a mechanical pump. On the other hand, the source chamber of the modified apparatus is pumped by a 6-in. diffusion (pumping speed = 2000 L/s) backed by a mechanical pump. The main chamber and the extension chamber of the new system are pumped together by a 520 L/s turbo pump, whereas the main chamber of the modified apparatus is pumped by a 330 L/s turbo pump. Therefore, a much better vacuum is expected for the new system.

The main chamber of the new system is much bigger than that of the modified apparatus. This allows a more complicated apparatus inside the chamber. For example, a longer lens stack is used in the new system for ion and electron extraction. The extension chamber, which does not exist in the modified apparatus, reserves room for future uses.

3.6. Reflectron mass spectrometer and electron detector

A lens stack is installed at the center of the main chamber at which VUV PI/PEX occurs. Lenses above and below the PI/PEX region extract ions and electrons, respectively. A double-stage micro-channel plate (MCP) for electron detection is located at the bottom of the lens stack.

For mass spectrometric studies, a reflectron tube assembly is installed on top of the main chamber (see Fig. 2). The vacuum is maintained at 10^{-8} Torr with a 230 L/s turbo pump. At the entrance, there is an X-Y deflector (consisting of two pairs of parallel electrostatic lens) for steering the ion beam into the drift tube. A lens stack is installed at the top of the assembly to reflect the ions to the end of the other leg of the assembly (refer to Fig. 2 for the schematic ion path) at which another double-stage MCP detector is located. The orientation of the lens stack can be adjusted via two mechanical feed-throughs on the top flange. In this way, the reflected beam direction can be adjusted for better resolution and/or signal intensity. When the high-resolution of the reflectron technique is not necessary, e.g., when searching the signal at the very beginning of the experiment, linear mass spectrometric detection is necessary due to higher signal intensity and easier operation. For this purpose, a third double-stage MCP detector is located above the reflector lens stack. When doing linear mass spectrometry, the reflector lens stack is turned off and the ions can go straight into the third detector.

The total length of the reflectron drift tube is 2 m, which is about double of that of the linear drift tube used in the modified apparatus. The longer total flight path increases the resolution of the TOF spectra and hence heavier molecules (such as biomolecules) can be studied.

3.7. Light detector

A detector for VUV light detection collects the VUV photons about 3.5" downstream from the PI/PEX region (see Fig. 1). VUV photons hitting the tungsten disc surface of the detector create photoelectrons which are collected by a positively biased copper anode.

The light detector previously used in the modified apparatus has a copper wedge to collect VUV photons. The use of tungsten for the cathode has two advantages over the copper. First of all, tungsten is more inert than copper towards air oxidation and thus has a more stable photoelectric yield. Secondly, the photoelectric yield of tungsten in the range 60 – 90 nm is 14 – 15%, which is slightly higher than that of copper (11 - 13%).¹⁹

3.8. Data acquisition system

The ion, electron and ion signals are fed into one of the dye laser controllers which also serve to acquire direct current signals. When necessary, the signals are amplified and/or gated before being fed into the controller. Data acquisition is controlled by the WAVESCAN program provided by the dye laser company (LAS) installed on a 486 PC via GPIB connection. The software also synchronizes the scanning of one of the dye lasers (for ω_2 laser light). The time sequence of laser firing, pulse valve opening, etc. are handled by two pulse generators (DG353, Stanford Research) which provide triggering pulses at user-specified time intervals.

4. Current status of the system

The three lasers (one Nd-YAG and two dye lasers) have been tested and the manufacturer specifications are met. All the vacuum chambers are assembled and the jet-mixing, monochromator and main chambers are carefully aligned. Components in various vacuum chambers (such as pulsed valves, lens stack and grating) have been installed. Vacuum-maintaining system including turbo pumps, diffusion pump and backup pumps have also been hooked up and are working normally.

We are now attempting to generate VUV light using Xe as a nonlinear medium in the range 102.4-104.1 nm. Oxygen molecules, whose ionization energy (97348 cm^{-1} , corresponding to 102.72 nm) is within this range,²⁰ will be used as a starting target for the photoionization and photoelectron studies. This species has been studied by Tonkyn et. al.²⁰ with a VUV laser system and the results can be compared.

5. Further prospective of the system

5.1. Photoionization and photodissociation studies of radical

The new system will be used mainly on radical systems in VUV photoionization mass spectrometric and PFI-PE spectroscopic studies. Up to date, many radicals, some of which are simple, have not been studied thoroughly and their properties are still not well-known.

The sulfur-containing radicals of interest are SO, CS, CH_3S , $\text{CH}_3\text{CH}_2\text{S}$, $\text{CH}_2\text{CH}_2\text{SH}$, CH_3SS and $\text{C}_6\text{H}_5\text{S}$, which can be prepared in abundance by 193- or 248-nm photodissociation (PD) of SO_2 , CS_2 , CH_3SH (or CH_3SCH_3), $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{SH}$, $\text{HSCH}_2\text{CH}_2\text{SH}$, CH_3SSCH_3 and $\text{C}_6\text{H}_5\text{SH}$ (or $\text{C}_6\text{H}_5\text{SCH}_3$), respectively. The conventional PI and PE

spectroscopic studies on are SO, CS, CH₃S, CH₃CH₂S and CH₃SS have been carried out in our group before and much understanding of the formation of these radicals have been gained.²¹⁻²⁵

We are also interested in some oxygen-containing radicals such as CH₃O, CH₂CH₃O, CH₃CH₂O, CH₃CO and C₆H₅CO. Most of them are important intermediates in combustion processes. These radicals have not been studied extensively. High-resolution laser-induced fluorescence (LIF) studies have been performed on CH₃O^{26,27} and CH₃CH₂O²⁸ by Miller and co-workers. The PI spectrum of CH₃O has also been obtained in a conventional VUV PI mass spectrometric experiment.²⁹ To our knowledge, however, the remaining radicals (CH₂CH₃O, CH₃CH₂O, CH₃CO and C₆H₅CO) have never been subjected to PI and PE studies. Previous studies show that the methoxy (CH₃O) and ethoxy (CH₃CH₂O) radicals can be prepared by photolysis of the corresponding nitrite²⁶⁻²⁸ whereas the vinoxy (C₂H₃O) radical can be formed by photolysis of ethyl vinyl ether.³⁰ Recently, in a 193- and 248-nm PD experiment, we found that the C₆H₅CO and CH₃CO radicals can be generated from C₆H₅COCH₃.³¹

Another interesting class of radicals is the halogen-containing radicals such as CCl₂, CBr₂, CClBr, CFBr, CHBr₂ and CF₃O. They are relevant to atmospheric degradation of halo-hydrocarbons. An important reason for choosing these radicals is that LIF jet studies on them have been made³²⁻³⁶ and thus the recipes are known for preparing these radicals. They can be prepared by photolysis or pyrolysis of the appropriate halogen-containing precursor molecules in supersonic jets. It is certain that many other halo-hydrocarbons can be prepared by similar methods.

The radicals listed above are by no means exhaustive but simply representative systems of our recent interest. The actual direction of our studies will be guided by our experience and the scientific pay-off.

Understanding the UV and VUV PD processes involved in the formation of these radicals represents an important step for future reactivity studies of these radicals. Furthermore, the detailed characterization of these radicals by high-resolution PI and PE spectroscopy will lead to new experimental schemes for state-selection (rotational, vibrational and electronic) of their cations for ion-molecule reaction studies. We have considerable interest in these topics and plan to pursue these studies in due course.

5.2 Collaborations with other research groups in Iowa State University

The VUV coherent light is an invaluable light source in studies of other fields under vacuum environment. This will certainly induce collaborations with the other research groups, especially those in the Iowa State University. For this purpose, we have designed the new system as a multi-user facility for the other groups to install specific devices necessary for their studies.

At the moment, several plans have been outlined. One of them is to combine VUV laser ionization and matrix-assisted laser desorption (MALA) for mass spectrometric analysis of biomolecules. Because of the soft ionization and prompt fragmentation induced by VUV excitation, the combination of VUV PI and MALA is potentially useful for mass and structural analysis of biomolecules. Another interesting class of experiments is the modification and ablation of surfaces by tunable VUV laser radiation. The high energy VUV

radiation is expected to lead to new surface morphologies as well as chemically active sites. We plan to investigate the changes in both physical and chemical properties of fluorinated polymers induced by irradiation with VUV photons. The change in surface topography and gaseous fragments can be examined by atomic force microscopy and mass spectrometry, respectively. The VUV modified Ag and Au surfaces will also be used as substrates for surface enhanced Raman scattering studies. Finally, we will incorporate VUV PI and excitations to inductively-coupled plasma (ICP) and ICP-MS for elemental analyses to investigate the energy transfer mechanisms concerning vaporization, atomization and ionization in ICP and to modification and ablation of surfaces by tunable VUV laser radiation.

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CHAPTER 8. GENERAL CONCLUSIONS

Single- and multi-photon ionization techniques have been employed for the photoionization and pulsed field ionization (PFI) studies of the following organosulfur species: CH_3SH , $\text{CH}_3\text{CH}_2\text{SH}$, $\text{CH}_3\text{CH}_2\text{S}$ and CS_2 . Accurate ionization energy (IE) have been determined for these neutral species using high-resolution lasers and PFI scheme. The uncertainty in ionization energy is a few wavenumbers. Information of the energy levels for the neutrals and/or the corresponding cations have been retrieved from the experimental results. In these studies, the resolution of PFI spectra by single vacuum ultraviolet photon ionization is higher than that by multi-photon ionization. The PFI spectra obtained are very similar in the two photoexcitation schemes, while the photoionization efficiency spectra could not be obtained in every case when using the multi-photon scheme. The VUV single-photon ionization/excitation technique is therefore considered cleaner, but MPI method is less demanding in terms of experimental setup. Hence the latter is a simple but more popular tool to be used in related fields.

APPENDIX

COMPUTER PROGRAM LISTING

In this appendix, the contents of two programs are listed. The first (shown in pp. 181-183) was used in the paper in Chapter 2 for calculating energy levels for a rotor potential energy surface. The second (shown in pp. 184-192) was used in the papers in Chapters 5 and 6 for simulation of rotational profile in single-photon pulsed-field ionization spectra.

The programs are written for the Mathcad Plus 6.0 (Professional Version). Note that it is an interactive environment and the programming statements and graphics are put together. Therefore, the content is reproduced here as it appears in the software.

Molecule: CH₃CH₂SH. C-S bond rotation. MP2/6-31G(d,p)

Sine functions, $\sin(n\phi)$ where $n = 1, 2, \dots, \text{Nbasis}$, are used for the odd eigenfunctions. A constant term and cosine functions, $\cos(n\phi)$ where $n = 1, 2, \dots, (\text{Nbasis}-1)$, are used for the even eigenfunctions. Note that the normalization constant for the constant term differs from those for the cosine functions.

A file with 2 columns is read in:

(angle)	(energy in hart.)
0	-476.8 ...
60	-476.8 ...
...	

The matrix will be sorted in ascending order of angle.

Define constants and conversion factors

$$h_bar_sq_over_two_nu = \frac{5}{4.184 \cdot 1000} \cdot \left(\frac{6.022 \cdot 6.626}{2 \cdot \pi} \right)^2 \quad red_I = 1.68 \quad T = \frac{h_bar_sq_over_two_nu}{red_I}$$

$$kcal_to_waveno = 349.755 \quad Nbasis = 50 \quad hart_to_kcal = 627.50955 \quad T = 0.029$$

Read in energy vs angle :

$$M := \text{READPRN}(\text{NEUTRAL}) \quad M := \text{csort}(M, 0) \quad \text{globalmin} := \min(M^{<1>})$$

$$M^{<1>} := (M^{<1>} - \text{globalmin}) \cdot \text{hart_to_kcal}$$

Extend PES from [0°, 180°] to [-180°, 540°] for fitting.

Assuming periodicity = 360°, symmetric about 180°.

$$i := 0..20 \quad \text{PES}_{i,0} := -(M_{20-i,0}) \quad \text{PES}_{i,1} := M_{20-i,1}$$

$$i := 21..40 \quad \text{PES}_{i,0} := M_{i-20,0} \quad \text{PES}_{i,1} := M_{i-20,1}$$

$$i := 41..80 \quad \text{PES}_{i,0} := \text{PES}_{i-40,0} + 360 \quad \text{PES}_{i,1} := \text{PES}_{i-40,1}$$

Convert angle from deg to rad : $\text{PES}^{<0>} := \frac{\pi}{180} \cdot \text{PES}^{<0>}$

Cubic spline fitting

$\text{ANGLE} := \text{PES}^{<0>}$ $\text{ENERGY} := \text{PES}^{<1>}$ $\text{vs} := \text{cspline}(\text{ANGLE}, \text{ENERGY})$

$V(\phi) := \text{interp}(\text{vs}, \text{ANGLE}, \text{ENERGY}, \phi)$

$\theta := 0, 0.25 \dots 360$

Create T, V and H matrix

$\text{ORIGIN} := 1$ $\text{TOL} := 0.0001$ $k := 1 \dots 2 \cdot \text{Nbasis} + 1$

$$\text{Vcos}_k := \int_0^\pi V(\phi) \cdot \cos((k-1) \cdot \phi) d\phi$$

$i := 1 \dots \text{Nbasis}$ $j := 1 \dots \text{Nbasis}$

$$\text{To}_{i,j} := i^2 \cdot \text{T} \cdot \delta(i,j) \quad \text{Vo}_{i,j} := 0 \quad \text{Vo}_{i,j} := \text{if } i > j, \text{Vo}_{j,i}, \frac{1}{\pi} \cdot (\text{Vcos}_{|i-j|+1} - \text{Vcos}_{i+j+1})$$

$$\text{Te}_{i,j} := (i-1)^2 \cdot \text{T} \cdot \delta(i,j) \quad \text{Ve}_{i,j} := 0 \quad \text{Ve}_{i,1} := \frac{1}{\pi} \cdot \text{Vcos}_1$$

$$i := 2 \dots \text{Nbasis} \quad \text{Ve}_{1,i} := \frac{\sqrt{2}}{\pi} \cdot \text{Vcos}_{i+1} \quad \text{Ve}_{i,1} := \text{Ve}_{1,i}$$

$$i := 2 \dots \text{Nbasis} \quad j := 2 \dots \text{Nbasis} \quad \text{Ve}_{i,j} := \text{if } i > j, \text{Ve}_{j,i}, \frac{1}{\pi} \cdot (\text{Vcos}_{|i-j|+1} + \text{Vcos}_{i+j-1})$$

$\text{Ho} := \text{To} + \text{Vo}$ $\Lambda_o := \text{eigenvals}(\text{Ho})$ $\lambda_o := \text{sort}(\Lambda_o)$

$\text{He} := \text{Te} + \text{Ve}$ $\Lambda_e := \text{eigenvals}(\text{He})$ $\lambda_e := \text{sort}(\Lambda_e)$

Now have a look at the eigenvalues: (in kcal/mol)

Nbasis = 50

$$\lambda_o^T = \begin{bmatrix} 0.311 & 0.899 & 1.272 & 1.413 & 1.8 & 2.049 & 2.41 & 2.831 & 3.308 & 3.847 & 4.444 & 5.1 & 5.814 & 6.586 & 7.416 \end{bmatrix}$$

$$\lambda_e^T = \begin{bmatrix} 0.367 & 0.689 & 1.089 & 1.207 & 1.603 & 1.922 & 2.045 & 2.428 & 2.832 & 3.308 & 3.847 & 4.444 & 5.1 & 5.814 \end{bmatrix}$$

Eigenvalues in cm⁻¹:

$$\text{kcal_to_waveno} \cdot \lambda_o^T = \begin{bmatrix} 108.78 & 314.45 & 444.89 & 494.3 & 629.52 & 716.59 & 842.92 & 990.06 & 1.16 \cdot 10^3 \end{bmatrix}$$

$$\text{kcal_to_waveno} \cdot \lambda_e^T = \begin{bmatrix} 128.28 & 241.12 & 380.9 & 422.31 & 560.81 & 672.23 & 715.36 & 849.07 & 990.59 \end{bmatrix}$$

Produce coeff-matrix such that $\underline{\psi} = \underline{C} \cdot \underline{\chi}$ where both $\underline{\psi}$ and $\underline{\chi}$ are column vectors.

$$k := 1..Nbasis \quad \text{coeffo}^{<k>} := \text{eigenvec}(H_o, \lambda_{o_k}) \quad Co := \text{coeffo}^T$$

$$\text{coeffe}^{<k>} := \text{eigenvec}(H_e, \lambda_{e_k}) \quad Ce := \text{coeffe}^T$$

Wavefunctions so obtained: (ψ in deg)

$$\psi_o(m, \phi) := \frac{1}{\sqrt{\pi}} \sum_{n=1}^{Nbasis} Co_{m,n} \cdot \sin\left(n \cdot \phi \cdot \frac{\pi}{180}\right)$$

$$\psi_e(m, \phi) := \frac{1}{\sqrt{\pi}} \left[\frac{1}{\sqrt{2}} \cdot Ce_{m,1} + \sum_{n=2}^{Nbasis} Ce_{m,n} \cdot \cos\left[(n-1) \cdot \phi \cdot \frac{\pi}{180}\right] \right]$$

Write coefficients onto files:

WRITEPRN(SINCOEFF) := Re(Co)

WRITEPRN(COSCOEFF) := Re(Ce)

Stimulation for CH₃SH.

Expt := READPRN(ExptData1)

TOL := 0.000001

EngConv := 0.69503877

A := 3.50

B := 0.43

C := 0.41

A_{cat} := 3.46

B_{cat} := 0.46

C_{cat} := 0.44

J_{trun} := 20

Pop_{thre} := 0.001

T := 20

kT := EngConv · T

kT = 13.901

Define Hamiltonian matrix elements:

$$H_{ij}(A, B, C, J, K_i, K_j) := \begin{cases} \left[\left(\frac{A+B}{2} \right) \cdot J \cdot (J+1) + \left(C - \frac{A+B}{2} \right) \cdot K_i^2 \right] & \text{if } K_i = K_j \\ \frac{A-B}{4} \cdot \sqrt{(J-K_j) \cdot (J+K_j+1) \cdot (J-K_j-1) \cdot (J+K_j+2)} & \text{if } K_i = K_j + 2 \\ \frac{A-B}{4} \cdot \sqrt{(J+K_j) \cdot (J-K_j+1) \cdot (J+K_j-1) \cdot (J-K_j+2)} & \text{if } K_i = K_j - 2 \\ 0 & \text{otherwise} \end{cases}$$

Define a procedure to work out the energy levels for the asymmetric tops using A, B, C:

```
EngLev(A, B, C) :=
  temp0 ← 0
  for J ∈ 1..Jtrun
    for i ∈ 0..2·J
      for j ∈ 0..2·J
        Hi,j ← Hij(A, B, C, J, i - J, j - J)
      temp ← stack(temp, sort(Re(eigenvals(H))))
  temp
```

```
NeuJ :=
  temp0 ← 0
  for J ∈ 1..Jtrun
    for i ∈ 0..2·J
      dummy0 ← J
      temp ← stack(temp, dummy)
  temp
```

NeuEng := EngLev(A, B, C)

$$\text{NeuPop} := \left[(2 \cdot \text{NeuJ} + 1) \cdot e^{-\frac{\text{NeuEng}}{kT}} \right]$$

Population of neutral r.w.t. J.

```

PopJ := | for i ∈ 0..J trun
        |   tempi ← 0
        |   for j ∈ i2..(i+1)2 - 1
        |     tempi ← tempi + NeuPopj
        | temp

```

```

Jmax := | temp ← (0 0)
        | for i ∈ 0..last(PopJ)
        |   temp ← | (i PopJi) if PopJi > temp0,1
        |             | temp otherwise
        | temp0,0

```

$J_{\max} = 4$

Population in energy.

SortNeuEng := csort(augment(NeuEng, NeuPop), 0)

```

(Emax Popmax) := | temp ← (0 0)
                  | for i ∈ 0..last(NeuPop)
                  |   temp ← | (SortNeuEngi,0 SortNeuEngi,1) if SortNeuEngi,1 > temp0,1
                  |             | temp otherwise
                  | temp

```

$E_{\max} = 8.399$

```

NeuEngCum := | temp0 ← SortNeuEng0,1
              | for i ∈ 1..rows(SortNeuEng) - 1
              |   tempi ← tempi-1 + SortNeuEngi,1
              | temp

```

NeuEngLst := last(NeuEng)

```

Etrun := | i ← 0
          | while  $\frac{\text{NeuEngCum}_i}{\text{NeuEngCum}_{\text{NeuEngLst}}} < (1 - \text{Pop thre})$ 
          |   i ← i + 1
          |   SortNeuEngi,0

```

$E_{\text{trun}} = 113.948$

```

Ka := | temp0 ← 0
      | for J ∈ 1..Jtrun
      |   dummy0 ← 0
      |   temp ← stack(temp, dummy)
      |   for i ∈ 1..J
      |     dummy0 ← i
      |     temp ← stack(temp, dummy)
      |     temp ← stack(temp, dummy)
      | temp

```

```

Kc := | temp0 ← 0
      | for J ∈ 1..Jtrun
      |   for i ∈ J, J-1..1
      |     dummy0 ← i
      |     temp ← stack(temp, dummy)
      |     temp ← stack(temp, dummy)
      |     dummy0 ← 0
      |     temp ← stack(temp, dummy)
      | temp

```

Create a matrix containing energy, J, K_a, K_c and population for each level, in ascending order of energy and energy smaller than or equal to E_{trun} .

```

Neutral := | i ← 0
           | for j ∈ 0..last(NeuEng)
           |   if NeuEngj ≤ Etrun
           |     tempi,0 ← NeuEngj
           |     tempi,1 ← NeuJj
           |     tempi,2 ← Kaj
           |     tempi,3 ← Kcj
           |     tempi,4 ← NeuPopj
           |     i ← i + 1
           | temp

```

Create a similar matrice for the cation (without truncation in energy):

$$\text{CatEng} := \text{EngLev}(A_{\text{cat}}, B_{\text{cat}}, C_{\text{cat}})$$

$$\text{Cation} := \text{csort}(\text{augment}(\text{augment}(\text{augment}(\text{CatEng}, \text{NeuJ}), \text{Ka}), \text{Kc}), 1)$$

Define a procedure to calculate the line spectrum with ΔJ as a parameter:

```

Branch( $\Delta J$ ) :=
  k ← 0
  CatLst ← rows(Cation) - 1
  for i ∈ 0..rows(Neutral) - 1
    J ← Neutrali,1
    Jcat ← J +  $\Delta J$ 
    if (CationCatLst,1 ≥ Jcat) · (Jcat ≥ Cation0,1)
      j ← 0
      while (j ≤ CatLst) · (Cationj,1 ≤ Jcat)
        if Cationj,1 = Jcat
          tempk,0 ← Cationj,0 - Neutrali,0
          tempk,1 ← Neutrali,4
          tempk,2 ← Cationj,2 - Neutrali,2
          tempk,3 ← Cationj,3 - Neutrali,3
          tempk,4 ← Neutrali,1
          tempk,5 ← Cationj,1 - Neutrali,1
          k ← k + 1
        j ← j + 1
      temp

```

Define a procedure to extract a sub-branch from a branch obtained with the "Branch(ΔJ)" procedure with specific ΔK . To get the lines for $\Delta K_a = 100$, set $\Delta K_{Col} = 2$ and $\Delta K = 100$. For $\Delta K_c = 54$, set $\Delta K_{Col} = 3$ and $\Delta K = 54$. By running this procedures two times, transition lines with both $\Delta K_a = 2$ and $\Delta K_c = 3$ can be obtained.

```

SubBranch(Branch,  $\Delta K_{Col}$ ,  $\Delta K$ ) :=
    i ← 0
    for j ∈ 0..rows(Branch) - 1
        if Branchj,  $\Delta K_{Col}$  =  $\Delta K$ 
            for k ∈ 0..5
                tempi, k ← Branchj, k
            i ← i + 1
    temp

```

Create O-, P-, Q-, R- and S-branch ($\Delta J = -2, -1, 0, +1$ and $+2$, respectively):

```

O := Branch(-2)      P := Branch(-1)      Q := Branch(0)
R := Branch(1)       S := Branch(2)

```

Pick up $\Delta K_a = -2, -1, 0, +1$ and $+2$ in O-branch:

```

Oo := SubBranch(O, 2, -2)   Op := SubBranch(O, 2, -1)   Oq := SubBranch(O, 2, 0)
Or := SubBranch(O, 2, 1)   Os := SubBranch(O, 2, 2)

```

Pick up $\Delta K_a = -2, -1, 0, +1$ and $+2$ in P-branch:

```

Po := SubBranch(P, 2, -2)   Pp := SubBranch(P, 2, -1)   Pq := SubBranch(P, 2, 0)
Pr := SubBranch(P, 2, 1)   Ps := SubBranch(P, 2, 2)

```

Pick up $\Delta K_a = -2, -1, 0, +1$ and $+2$ in Q-branch:

```

Qo := SubBranch(Q, 2, -2)   Qp := SubBranch(Q, 2, -1)   Qq := SubBranch(Q, 2, 0)
Qr := SubBranch(Q, 2, 1)   Qs := SubBranch(Q, 2, 2)

```

Pick up $\Delta K_a = -2, -1, 0, +1$ and $+2$ in R-branch:

$R_o := \text{SubBranch}(R, 2, -2)$ $R_p := \text{SubBranch}(R, 2, -1)$ $R_q := \text{SubBranch}(R, 2, 0)$
 $R_r := \text{SubBranch}(R, 2, 1)$ $R_s := \text{SubBranch}(R, 2, 2)$

Pick up $\Delta K_a = -2, -1, 0, +1$ and $+2$ in S-branch:

$S_o := \text{SubBranch}(S, 2, -2)$ $S_p := \text{SubBranch}(S, 2, -1)$ $S_q := \text{SubBranch}(S, 2, 0)$
 $S_r := \text{SubBranch}(S, 2, 1)$ $S_s := \text{SubBranch}(S, 2, 2)$

Define another batch of constants which are necessary for spectrum plotting and line spectrum convolution:

$\text{LinWid} = 2$ $\text{IP}_1 = 76252.5$

$\text{ExptLst} := \text{rows}(\text{Expt}) - 1$ $\text{ExptLst} = 600$ $\text{Expt}_{0,0} = 76209.95$ $\text{Expt}_{\text{ExptLst},0} = 76305.90$

$\text{SpectSrt} := \text{Expt}_{0,0} - \text{IP}_1$ $\text{SpectEnd} := \text{Expt}_{\text{ExptLst},0} - \text{IP}_1$ $\text{SpectStep} := \frac{\text{SpectEnd} - \text{SpectSrt}}{\text{ExptLst}}$

$\text{SpectSrt} := \text{SpectSrt}$ $\text{SpectEnd} := \text{SpectEnd}$ $\text{SpectStep} := \text{SpectStep}$

The followings are NOT parameters. Don't touch them.

$\text{SpectLst} := \text{ceil}\left(\frac{\text{SpectEnd} - \text{SpectSrt}}{\text{SpectStep}}\right)$ $\text{SpectStep} = 0.16$ $\text{SpectLst} = 600$

Create a grid table for lines to be convoluted.

```

GridTab :=
  temp0 ← 0.1 · SpectStep
  thres ← 0.001
  α ←  $\frac{4 \cdot \ln(2)}{\text{LinWid}^2}$ 
  x ← 0
  i ← 1
  temp1 ← 1
  while tempi ≥ thres
    x ← x + temp0
    i ← i + 1
    tempi ← e-αx2
  temp

```

Create a look-up table for the Gaussian function.

```

LkupGsn(x) :=
  idx ← floor( $\frac{|x|}{\text{GridTab}_0} + 0.5$ )
  temp ←
    | GridTabidx+1 if idx < last(GridTab)
    | 0 otherwise
  temp

```

Convolution procedure: put the branch or sub-branch as parameter:

```

Convolve(M) :=
  for i ∈ 0..SpectLst
    tempi ← 0
  for i ∈ 0..rows(M) - 1
    GsnHfWid ← length(GridTab) · GridTab0
    LftTail ← Mi,0 - GsnHfWid
    Low ← floor( $\frac{\text{LftTail} - \text{SpectSrt}}{\text{SpectStep}}$ )
    Low ← | Low if Low > 0
          | 0 otherwise
    temp1i,0 ← Low
    RgtTail ← Mi,0 + GsnHfWid
    High ← ceil( $\frac{\text{RgtTail} - \text{SpectSrt}}{\text{SpectStep}}$ )
    High ← | High if High < SpectLst
          | SpectLst otherwise
    temp1i,1 ← High
    temp1i,2 ← (High - Low) · SpectStep
    if (Low ≤ SpectLst) · (High ≥ 0)
      Eng ← SpectSrt + Low · SpectStep
      for j ∈ Low..High
        tempj ← tempj + Mi,1 · LkupGsn(Eng - Mi,0)
        Eng ← Eng + SpectStep
    temp

```

Convolute branches:

QoSpect := Convolve(Qo)	QpSpect := Convolve(Qp)	QqSpect := Convolve(Qq)
QrSpect := Convolve(Qr)	QsSpect := Convolve(Qs)	
PpSpect := Convolve(Pp)	PqSpect := Convolve(Pq)	PrSpect := Convolve(Pr)
PoSpect := Convolve(Po)	PsSpect := Convolve(Ps)	
RpSpect := Convolve(Rp)	RqSpect := Convolve(Rq)	RrSpect := Convolve(Rr)
RoSpect := Convolve(Ro)	RsSpect := Convolve(Rs)	

$OoSpect := Convolution(Oo)$ $OpSpect := Convolution(Op)$ $OqSpect := Convolution(Oq)$
 $OrSpect := Convolution(Or)$ $OsSpect := Convolution(Os)$
 $SoSpect := Convolution(So)$ $SpSpect := Convolution(Sp)$ $SqSpect := Convolution(Sq)$
 $SrSpect := Convolution(Sr)$ $SsSpect := Convolution(Ss)$

Create final spectra:

$ExptSpect := Expt^{<1>} + 2770$ $IP_1 = 76252.50$ $IP_2 := 0$ $IP := IP_1 - IP_2$
 $IP = 76252.50$

o:p:q:r:s = K2:K1:K0:K1:K2; O:P:Q:R:S = J2:J1:J0:J1:J2.

$K0 := 1$ $K1 := 1.2$ $K2 := 0.7$ $J0 := 1$ $J1 := 1.1$ $J2 := 0.6$
 $P01 := J1 \cdot (K1 \cdot PpSpect + K0 \cdot PqSpect + K1 \cdot PrSpect)$ $P2 := J1 \cdot (K2 \cdot PoSpect + K2 \cdot PsSpect)$
 $Q01 := J0 \cdot (K1 \cdot QpSpect + K0 \cdot QqSpect + K1 \cdot QrSpect)$ $Q2 := J0 \cdot (K2 \cdot QoSpect + K2 \cdot QsSpect)$
 $R01 := J1 \cdot (K1 \cdot RpSpect + K0 \cdot RqSpect + K1 \cdot RrSpect)$ $R2 := J1 \cdot (K2 \cdot RoSpect + K2 \cdot RsSpect)$
 $O012 := J2 \cdot (K2 \cdot OoSpect + K1 \cdot OpSpect + K0 \cdot OqSpect + K1 \cdot OrSpect + K2 \cdot OsSpect)$
 $S012 := J2 \cdot (K2 \cdot SoSpect + K1 \cdot SpSpect + K0 \cdot SqSpect + K1 \cdot SrSpect + K2 \cdot SsSpect)$

$Stimul := P01 + Q01 + R01 + P2 + Q2 + R2 + O012 + S012$

$max1 := \max(ExptSpect)$ $max2 := \max(Stimul)$ $Stimul := Stimul \cdot \frac{max1}{max2}$
 $i := 0 \dots \text{rows}(Stimul) - 1$ $j := 0 \dots \text{rows}(Expt) - 1$