

Tutorial: Laser Optics

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Abstract

This tutorial discusses fundamentals of experimental laser spectroscopy in the ultraviolet region associated with the study of electronic transitions of unstable molecules.

Origin and Nature of UV Spectra

UV absorption occurs because all atoms and molecules possess electrons that can undergo excitation and be raised to higher energy levels. Although, UV spectroscopy involves only a very narrow wavelength domain in the overall range of interactions of electromagnetic radiation with matter, it is of importance because it involves transitions associated with the energy differences corresponding to those of electronic states of atoms and molecules. Since the existence of specific electronic states in a molecule is governed by the number of electrons present, as well as the geometry and symmetry of the molecule in question, a successful analysis of the electronic spectra can help determine the precise structure of a molecule.

If molecular transitions involved only electron energy levels, the UV spectra of various substances would consist only of ultra-narrow absorption bands. However, molecular UV spectra are, more often than not, extended smooth curves (with built-in fine structure), rather than sharp peaks, because any electronic energy change is also accompanied by a concomitant change in the vibrational energy levels (see Fig. 1). Figure 2 illustrates these ideas further for a diatomic molecule. If we assume that the two nuclei of a diatomic molecule are fixed in position and are not free to vibrate or rotate, then there will be two levels as show in Fig. 2 (*i.e.*, G and H) which designate electronic energy levels for a pair of electronic states, where H may be the ground state and G the first excited state. Consider 3 of the lowest vibrational levels (assuming no rotation) associated with each of the

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two electronic states (H and G), and let there be 3 rotational levels associated with each vibrational state (assuming both vibrational and rotational motions). Then we can have a pure rotational transition (AB), a vibration-rotational transition (CD) and an electronic transition (EF). Since each electronic state is associated with a large number of vibrational and rotational states, a transition between electronic states will exhibit a large number of lines in the recorded UV spectrum, which may or may not be fully resolved.

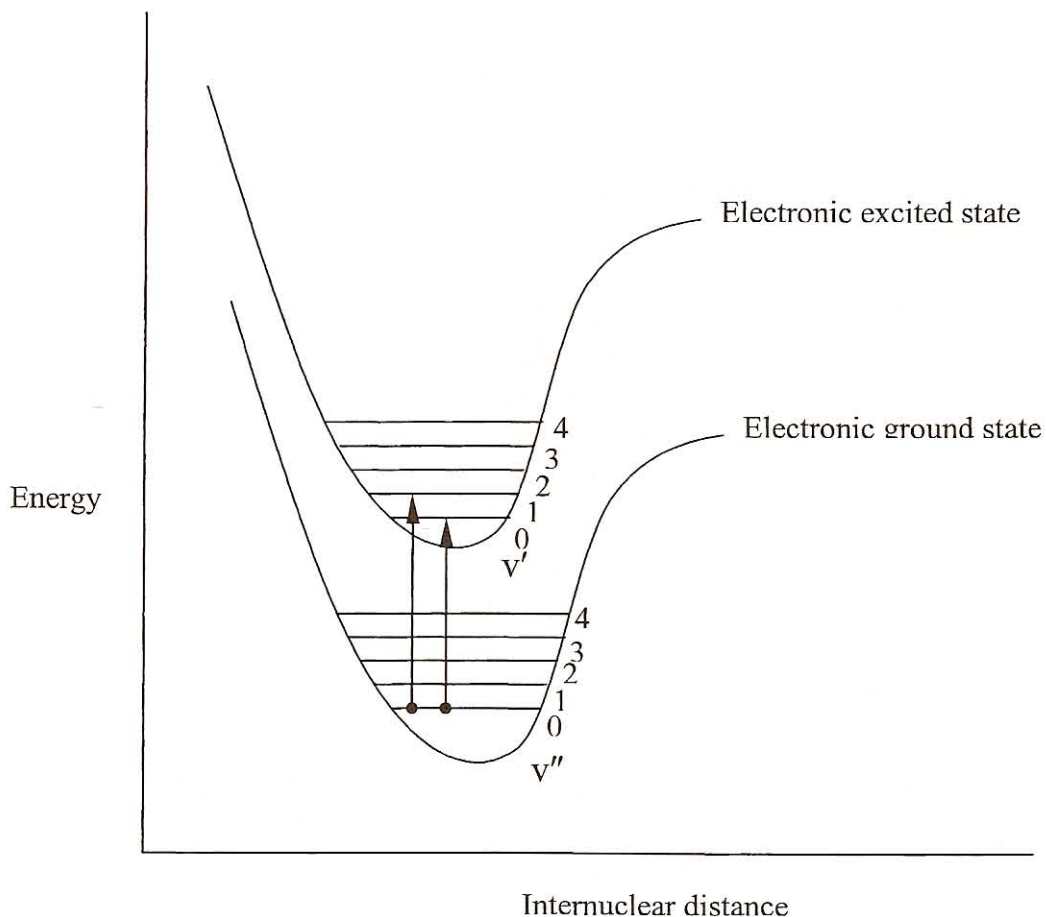


Fig. 1. Vibrational transitions between electronic states of a diatomic molecule.

In order to understand how electronic spectra truly arise, we need to address the question: What are the primary photophysical processes involving electronic states? In order to fix our ideas, let us initially ignore the vibrational states, and consider only a series of electronic energy levels that correspond to the different energies of electrons in both spin-wise

singlet and triplet states. Singlet states arise when the electrons involved are paired (with opposite spins as warranted by the Pauli exclusion principle) and the spin multiplicity ($2S+1$) is unity (i.e., $S=0$, $2S+1=1$), while triplet states occur when the overall spin multiplicity is 3 (i.e., $S=1$, $2S+1=3$). Let the vibrationally relaxed singlet levels in order of increasing energy be labeled $S_0, S_1, S_2, S_3, S_4, \dots$ and similarly the triplet levels in order of increasing energy be called $T_1, T_2, T_3, T_4, \dots$, respectively. The Triplet states are at significantly lower energies as compared to the corresponding singlet states. Conventional UV *absorption* spectroscopy deals with transitions such as $S_0 \rightarrow S_1, S_0 \rightarrow S_2, S_0 \rightarrow S_3, S_0 \rightarrow S_4, \dots$. The reverse singlet-singlet transition $S_1 \rightarrow S_0$, for example, gives rise to *fluorescence*; whereas, the triplet-singlet transition $T_1 \rightarrow S_0$ gives rise to *phosphorescence*. Besides such radiative transitions, atoms and molecules exhibit non-radiative transitions as well; such as *internal conversions* $S_3 \rightarrow S_1$ and $T_3 \rightarrow T_1$ and *intersystem crossings* $S_1 \rightarrow T_1$ and $S_2 \rightarrow T_3$, respectively.

Ultraviolet (UV) Spectroscopy

In order to perform ultraviolet spectroscopy effectively and successfully, one needs to be able to detect radiation with a high degree of sensitivity, measure wavelengths and line profiles precisely, and record UV spectra with good signal-to-noise ratio and under high resolution. Therefore, one requires the following spectroscopic components: (1) Sources of UV light: either lamps or/and lasers; (2) Monochromators and/or spectrographs; (3) Interferometers for

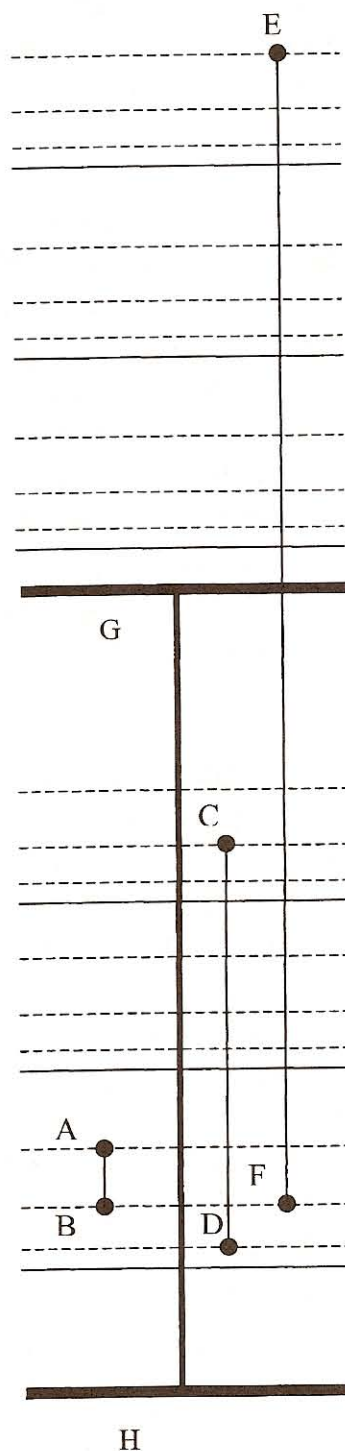


Fig. 2. A pure rotational transition (AB), a vibration-rotation transition (CD) and an electronic transition (EF) illustrated for a diatomic molecule.

laser spectroscopy; (4) Detection systems, which include photomultiplier tubes, Charge-Coupled Device (CCD) arrays and optical multichannel analyzers; and (5) A PC-controlled spectral data acquisition system.

Sources of Ultraviolet Light

Besides naturally occurring UV light from the sun, lamps and lasers are two of the primary sources of ultraviolet light. Solar UV light, though plentiful, cannot be efficiently stored and used for practical applications. A similar problem occurs with UV lamps, which are a good source of abundant radiation over a reasonable range of UV wavelengths, and yet collimation and subsequent delivery of the lamp light often results in such severe attenuation of intensity that the UV light cannot be used for demanding commercial applications. However, in many laboratory-based applications, UV lamps can prove very useful, such as in blood analyzers, wafer inspection systems, capillary electrophoresis, flow cytometers, chromatography and wavelength calibration.

UV Lasers

The problems of insufficient light intensities of UV lamps and their sometimes restricted spectral coverage can be overcome by using UV lasers as light sources. For efficient laser operation, there are three important criteria that must be met: (1) A suitable active medium must be present in order to generate photons via stimulated emission; (2) An appropriate energy source must be available to excite the active medium and create a population inversion; and (3) There must also be an adequate optical feedback mechanism to produce resonance oscillations and subsequent lasing in the active medium. These three overarching requirements govern the operation of all types of UV lasers. Some of the most widely-used UV lasers are: (1) Excimer lasers (2) Frequency-tripled and -quadrupled Nd:YAG lasers (3) Nitrogen lasers (4) Frequency-doubled Alexandrite lasers (5) Helium-Cadmium lasers and (6) Rare-earth (other than neodymium) doped lasers.

UV Spectrometers and Spectrographs

An optical spectrometer is an instrument that collects, spectrally disperses and reimages an optical signal. Individual discrete wavelengths present in the light imaged at the entrance slit show up as a series of monochromatic lines in the output signal. Two principal components of a spectrometer comprise of a monochromator (which enables the presentation of a *single* wavelength or bandpass at a given time) and a radiant power detector (e.g. a photomultiplier tube). The monochromator possesses a

dispersing element, usually a grating, that spreads the light intensity in space as a function of wavelength. After the incident radiation impinges on the entrance slit of the monochromator, a narrow spectral band is therefore selected and transmitted through the exit slit to an appropriate sample to be investigated and subsequently to a suitable detector surface. A spectrograph, on the other hand, allows a *range* of wavelengths to be simultaneously detected by a multichannel detector.

Laser-Induced Fluorescence (LIF) Spectroscopy in the UV

Laser-induced fluorescence (LIF) spectroscopy is a technique by which molecules are irradiated with laser radiation that is tuned to differences in energy levels of a specific molecule. Such resonantly tuned radiation has a high probability of inducing a molecular transition from a ground electronic state to a more energetic electronic state. Subsequently, the excited molecule can relax to the ground state by spontaneous emission of a photon of a specific frequency that corresponds to the energy separation between the two electronic states. The spontaneously emitted photons constitute the observed fluorescence and the twin processes of excitation and emission taken together symbolize the technique of *laser-induced fluorescence (LIF) spectroscopy*.¹⁻³ LIF spectroscopy is therefore a technique that involves the scanning of the wavelength of a probe laser and the simultaneous recording of the intensity and wavelength of the emitted radiation. Figure 3 is a typical arrangement used for recording the LIF spectra of molecules (that fluoresce in the UV) by exploiting dye laser-based multiple frequency conversion technology for generating tunable UV laser radiation necessary for the excitation process. A successful application of LIF spectroscopy depends on ensuring that the LIF process predominates over other competing processes (such as excitation of the molecules via collisions, collisional relaxation or quenching to the ground state and emission stimulated by the photons of the probe laser). Intensity of the fluorescence that corresponds to the population of the excited species and good spatial resolution by utilization of well-focused lasers are two important characteristics of LIF experiments. These characteristics have been exploited in a variety of applications, e.g. in mapping radical concentrations in combustion systems, plasma fusion devices, plasma etching reactors, and in measuring atmospheric species concentrations that result in serious air pollution. One of the chief advantages of using the LIF spectroscopic technique is that the method is relatively non-invasive and tends not to dramatically disrupt the physical processes under investigation.

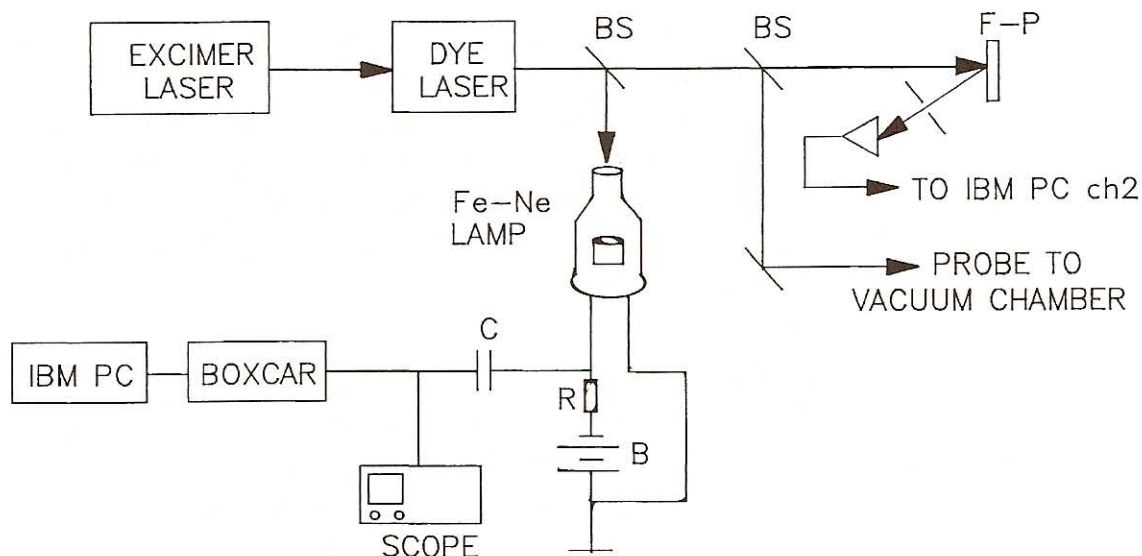


Fig. 3. A typical arrangement for recording the laser induced fluorescence spectra of molecules using a dye laser beam that probes the molecules in a chamber. The remainder of the beam is used to record calibration spectra using an Fe-Ne hollow cathode lamp. The Fabry-Perot etalon (F-P) simultaneously records interference fringes, which also aid precise calibration of the spectra.

High resolution LIF spectroscopy of moderately-sized and larger molecules can be done using supersonic jet expansions, whereby one can study rovibrationally cold samples. In a typical LIF experimental arrangement used to study jet-cooled free radicals for instance, an inert gas-precursor mixture is introduced into a vacuum chamber through a pulsed valve. The precursor molecules seeded in the supersonic jet expansion are photolyzed by excimer laser pulses (e.g. KrF at 248 nm) to generate the appropriate free radicals *in situ*. For example, alkyl nitrites (RONO; where R=CH₃, C₂H₅, i-C₃H₇) can be photodissociated to produce the corresponding alkoxy (RO) radicals. Similarly alkylthio (RS) radicals are produced by photodissociating R₂S₂ precursors. The free radicals are then excited by tunable dye laser radiation that has been frequency-doubled to produce UV wavelengths. The dye laser itself can be pumped either by the second harmonic of a ND:YAG laser (at 532 nm) or an excimer laser (e.g. XeCl at 308 nm). LIF from the excited radicals can be collected by a quartz lens at right angles to both laser beams and subsequently detected by a photomultiplier tube (PMT). Laser excitation spectra can be recorded by scanning the dye laser and using a boxcar averager in conjunction with a microcomputer-aided data acquisition system. Figure 4 is an example of a typical laser excitation spectrum of a jet-cooled free radical.

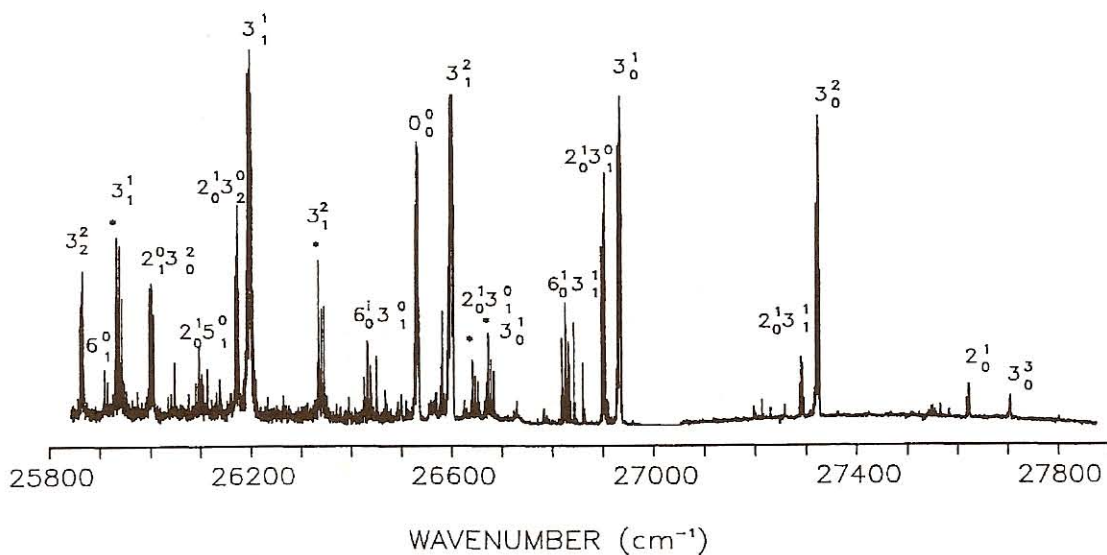


Fig. 4. A laser excitation spectrum of the jet-cooled methylthio radical in the 25800–27800 cm^{-1} region.

Wavelength calibration of the laser excitation spectra (that yield primarily vibrational intervals in the upper excited state) can be accomplished by simultaneously recording optogalvanic transitions excited within a hollow cathode discharge lamp (as detailed in one of the later chapters in this book). In order to obtain information concerning the vibrational intervals in the lower electronic state, the dye laser can be tuned to a specific wavelength where the radical emits the strongest fluorescence (within a select vibronic band). Single vibronic level dispersed fluorescence spectra can be recorded by focusing the total fluorescence onto the entrance slit of a scanning monochromator. The output signal at the exit slit of the monochromator is then collected by a PMT and relayed to the computer-aided data acquisition system. Alternatively, an optical multichannel analyzer (OMA) system can be employed to record the single vibronic level wavelength-resolved emission spectra. The OMA system typically includes a spectrograph, a lens-coupled intensifier, a cooled CCD array and a data processor. Wavelength calibration is usually accomplished for each dispersed spectrum in the UV (and visible) using emission lines from an iron-neon hollow cathode lamp. Figure 5 shows a typical wavelength-resolved spectrum of a jet-cooled free radical (e.g., ethoxy, $\text{C}_2\text{H}_5\text{O}$).

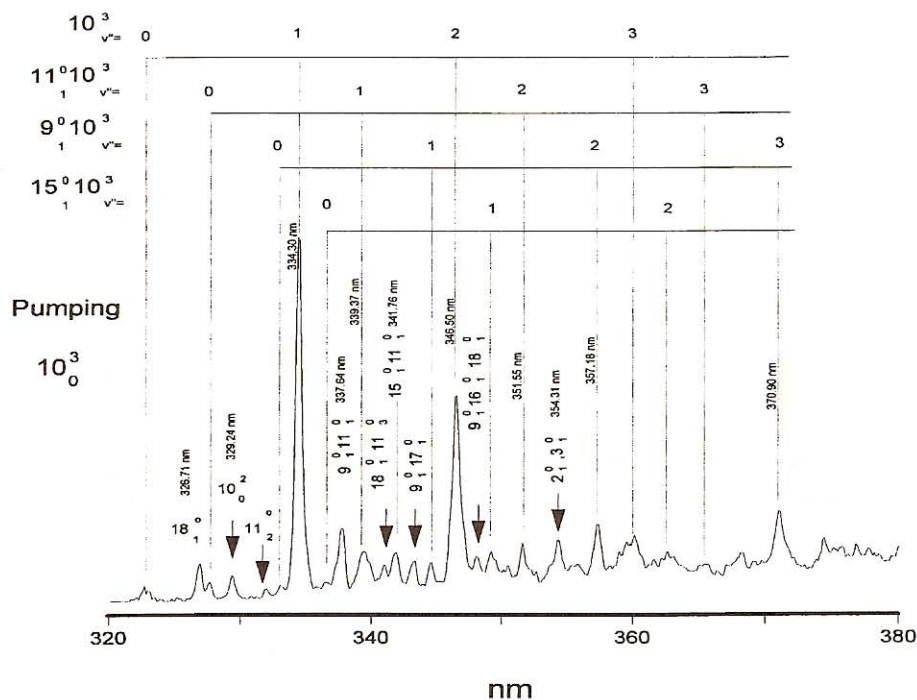


Fig. 5. The dispersed spectrum of the B-X 10^3_0 band of $\text{C}_2\text{H}_5\text{O}$. The frequency of the pump laser was 30972 cm^{-1} and the time delay between the excimer and dye laser was $5\mu\text{s}$.

Acknowledgments

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