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OPTICAL PROCEDURES FOR ANALYSIS*

Nomenclature, Symbols, Units, and their Usage in Spectrochemical Analysis—XVI

LASER-BASED MOLECULAR SPECTROSCOPY FOR CHEMICAL ANALYSIS—LUMINESCENCE

(IUPAC Recommendations 1997)

Prepared for publication by

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Nomenclature, symbols, units, and their usage in spectrochemical analysis—XVI. Laser-based molecular spectroscopy for chemical analysis—Luminescence (IUPAC Recommendations 1997)

This report is the 16th in a series on Spectrochemical Methods of Analysis issued by IUPAC Commission V-4. It is concerned with the use of lasers in molecular spectroscopy dealing with luminescence.

LASER-BASED MOLECULAR SPECTROMETRY FOR CHEMICAL ANALYSIS: LUMINESCENCE

1. INTRODUCTION

This report is the 16th in a series on Spectrochemical Methods of Analysis issued by IUPAC Commission V-4. A series of documents dealing with nomenclature, symbols and units used in spectrochemical analysis is issued by IUPAC.

Part I [*Pure Appl. Chem.*, **30**, 653–679 (1972)] is concerned mainly with general recommendations in the field of emission spectrochemical analysis.

Part II [*Pure Appl. Chem.*, **45**, 99–103 (1976)] gives some basic rules on data interpretation.

Part III [*Pure Appl. Chem.*, **45**, 105–123 (1976)] deals extensively with the nomenclature of analytical flame (atomic emission and absorption) spectroscopy and associated procedures.

Part IV [*Pure Appl. Chem.*, **52**, 2541–2552 (1980)] concerns X-ray emission (and fluorescence) spectroscopy.

Part V [*Pure Appl. Chem.*, **57**, 1453–1490 (1985)] deals with the classification and description of radiation sources.

Part VI [*Pure Appl. Chem.*, **56**, 231–345 (1984)] covers molecular luminescence spectroscopy. Part VII [*Pure Appl. Chem.*, **60**, 1449–1460 (1988)] is concerned with molecular absorption spectroscopy (UV/VIS).

Part VIII [*Pure Appl. Chem.*, **63**, 735–746 (1991)] deals with a new nomenclature system for X-ray spectroscopy.

Part IX [Pure Appl. Chem, in press] covers fundamental aspects of spectral dispersion and isolation of radiation.

Part X [*Pure Appl. Chem.*, **60**, 1461–1472 (1988)] deals with sample preparation for analytical atomic spectroscopy and other related techniques.

Part XI [*Pure Appl. Chem.*] deals with the detection of radiation.

Part XII [*Pure Appl. Chem.* **64**, 253–259 (1992)] deals with terms related to electrothermal atomization.

Part XIII [*Pure Appl. Chem.* **64**, 261–264, (1992)] deals with terms related to chemical vapor generation.

Part XIV [*Pure Appl. Chem.*, in preparation] deals with a new IUPAC Notation for laser-based atomic spectroscopy.

Part XV [*Pure Appl. Chem.*, in press] deals with the fundamental properties of lasers used in laser-based molecular spectroscopy for chemical analysis.

The various types of molecular luminescence processes have previously been defined in Part VI of the Series entitled, "Molecular Luminescence Spectroscopy" published in *Pure and Applied Chemistry*, Vol. 56, No. 2, pp. 231–245 (1984). The analytical advantages of laser-based techniques include the capability of high intensity, monochromaticity, spatial and phase coherence, and the ability to discriminate the homogeneous lines from the inhomogeneous bands. For this reason laser-based techniques have become powerful tools in low-temperature and solid-state luminescence spectroscopy.

The present document, Part XVI, deals with aspects related to laser-based molecular luminescence, especially high-resolution luminescence. Specific photophysical and photochemical processes, experimental techniques, and analytical applications that take advantage of laser properties are discussed in the present document.

2. NATURE OF EMISSION LINES (see also Ref. 1, IUPAC Green Book)

At room temperature, luminescence spectra of polyatomic molecules have very often highly diffuse structure. In the gas phase state, the molecules can rotate freely and the large moments of inertia give rise to a quasi-continuum of vibrational rotational states. There is further broadening due to the Doppler effect (see also Ref. 2 on Doppler Broadening, 10.1.2.4.2., IUPAC Orange Book) and to collisions that make the spectrum more diffuse. In solutions where the rotations are hindered, the spectra become discrete but the bands are still broad (halfwidths of about several hundred wavenumbers). The optimal conditions for high resolution spectra are obtained at low temperature either in cryogenic solvents or in *supersonic molecular beams*.

2.1 Homogeneously broadened line

Two types of processes contribute to the homogeneous *spectral width* of a particular band in the luminescence spectrum of a molecule. Firstly, due to the Heisenberg uncertainty principle, any spectral transition inherently exhibits a certain energy uncertainty which is related to its excited-state lifetime. This inherent contribution to the observed spectral *bandwidth* is referred to as *homogenous broadening*. The *homogeneous line** corresponds to the transition of a single molecule. The *homogeneous linewidth* determines the ultimate limit of spectral resolution.

Secondly, the width of a homogeneous line depends on *population relaxation* and *phase relaxation* processes and reflects both molecular relaxation processes and host dynamics. Generally, the linewidth is described by

$$G_{\text{hom}} = \frac{1}{2\pi T_1} + \frac{1}{\pi T_2} \tag{1}$$

where T_1 is the *population relaxation time* (longitudinal relaxation time) and T_2 the *phase relaxation time* (transverse relaxation time). The lifetime of the electronically excited state in molecules is only very weakly temperature dependent and defines the lower limit for the homogeneous linewidth. The phase relaxation time, however, is strongly temperature dependent, reflecting the fluctuations of the optical transition frequency induced by the host dynamics. When the temperature approaches 0 K, the emission

*The term "homogeneously broadened line" is more accurately descriptive but the shorter term "homogeneous line" is recommended.

linewidth of an isolated molecule approaches the *natural linewidth*, which is determined by T_1. Hence, information on population relaxation processes can be gained when very low-temperature measurements of G_{hom} are performed. The phase relaxation time and especially its temperature dependence provide information on the *host dynamics* and the *guest-host coupling*.

The homogeneous linewidth of the lowest electronic transition is mostly determined by dephasing processes and becomes smaller at lower temperatures. In contrast, the inhomogeneous distribution profile remains broad even at low temperatures, reflecting the matrix effect of different *micro-environments* on the analyte molecules (see also 2.2). The homogeneous linewidth may be smaller than the inhomogeneous bandwidth by several orders of magnitude, up to 10^5 (Figure 1). The homogeneous line profile, G, in a solid host is given by

$$G(w - w_0) = aL(w - w_0) + (1 - a)P(w - w_0 - d) \tag{2}$$

This profile is comprised of a narrow line, L, given by a normalized Lorentzian function:

$$L(w - w_0) = \frac{1}{\pi} \frac{G/2}{(w - w_0)^2 + (G/2)^2} \tag{3}$$

and a broad phonon band, P, which depends on the *photon density of states* of the host lattice, and on the guest-host coupling (see 2.2).

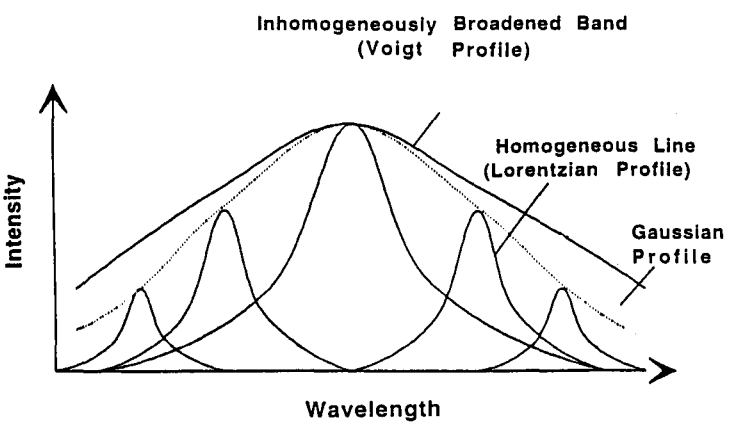

Fig. 1 Schematic Representation of Inhomogeneous and Homogeneous Line Broadening (The inhomogeneously broadened band is a superposition of homogeneous lines having a Lorentzian line profile. A Gaussian distribution of Lorentzian lines produces a Voigt profile).

2.2 Inhomogeneously broadened line

2.2.1 Electron–phonon coupling in solid matrices

Absorption/emission bands of *guest molecules* in solid *host matrices* are *inhomogeneously broadened* and cover typically a range from 100 to 300 cm^{-1}. The bands are formed from homogeneous lines densely distributed over a large spectral range. This distribution results from the interaction of the molecular energy states with the different individual molecular micro-environments leading to an inhomogeneous band. To a good approximation the inhomogeneous band profile can be described by a *Gaussian function* whereas the homogeneous line has a *Lorentzian profile*. A Gaussian distribution of Lorentzian lines produces a *Voigt profile*. (Figure 1).

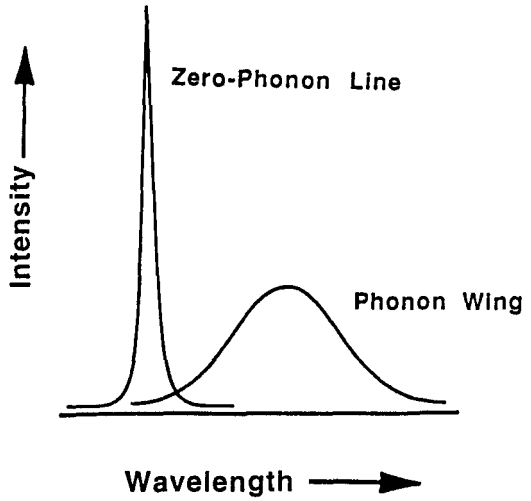

Fig. 2 Schematic Representation of a Zero-Phonon Line (ZPL) and a Phonon Wing (PW).

Quanta of lattice vibrational energy in the host matrix are referred to as *phonons*. The homogeneous line profile of an isolated molecular absorber/emitter in a solid host consists of a narrow *zero-phonon line* (ZPL), which corresponds to a purely electronic transition of the analyte, i.e., a transition in which the vibrational state of the host lattice does not change (Figure 2). On the low-energy (long-wavelength) side of the ZPL in emission (and high-energy, short-wavelength, side in absorption) a *phonon wing* (PW) occurs. Phonon wings correspond to electronic transitions in the guest molecule, which are coupled to changes in the vibrational state of the host lattice. This process is termed *electron-phonon coupling*. Weak electron-phonon coupling leads to intense ZPL and weak PW in the absorption/emission spectra.

2.2.2 Debye–Waller factor:

The ratio of the intensity of the ZPL (I_{ZPL}) to that of the total intensity ($I_{ZPL} + I_{PW}$) is commonly known as the *Debye-Waller factor*, *a*, which is a measure of the electron-phonon coupling.

$$a = \frac{I_{ZPL}}{I_{ZPL} + I_{PW}} \tag{4}$$

This a factor increases rapidly at low temperatures. At low temperatures, the PW decreases and the ZPL increases (Figure 3). Accordingly, measurements of the absorption or emission of a ZPL can only be performed at low temperatures (15 K or less).

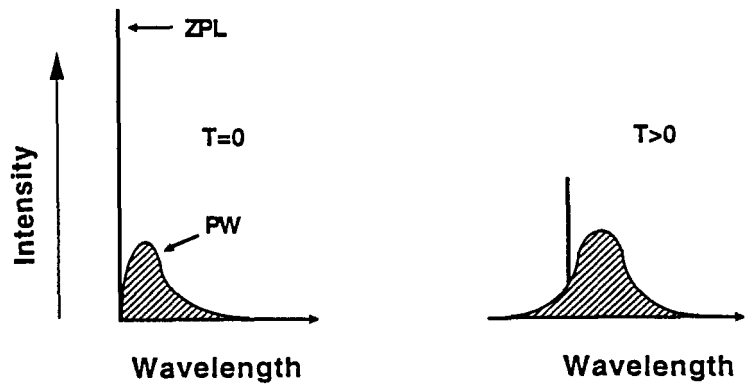

Fig. 3 Schematic Representation of the Temperature Effect on the Zero-Phonon Line (ZPL) and the Phonon Wing (PW). (As the temperature increases, the ZPL intensity decreases and the PW Intensity increases).

3. SPECTROCHEMICAL METHODS

3.1 Laser-induced Shpol'skii spectroscopy

In the *Shpol'skii technique* (*Pure Appl. Chem.*, Vol. 56, No. 2, paragraph 2.2.4, pp. 236, 1984) the bandwidths of absorption/emission lines of an analyte molecule (often containing a polyaromatic structure) are reduced by the choice of an appropriate matrix, i.e., an n-alkane as E. V. Shpol'skii suggested in 1951. After rapid cooling of the solution to approximately 77 K (liquid nitrogen temperature), a polycrystalline matrix is formed, in which the analyte molecules are trapped in a restricted number of *sites*, ideally one type. In this ideal situation all the molecules are surrounded in the same manner by the solvent molecules and the luminescence spectrum of the analyte consists, after excitation with a broad-band light source, of a sharp 0–0 band and a number of sharp vibrational bands often referred to as *quasi-lines*. The quasi-linear parts of a Shpol'skii spectrum correspond to zero-phonon transitions. The Shpol'skii technique reduces both the electron-phonon coupling and the inhomogeneous broadening in luminescence spectra, yielding narrow-band emission spectra at low temperature (Figures 4 and 5). It is noteworthy that such an effect also occurs in *doped crystal* systems, (referred to as isomorphic crystalline matrices) whereby the analyte is co-crystallized with host compounds that have similar shape and size (e.g., naphthalene in durene).

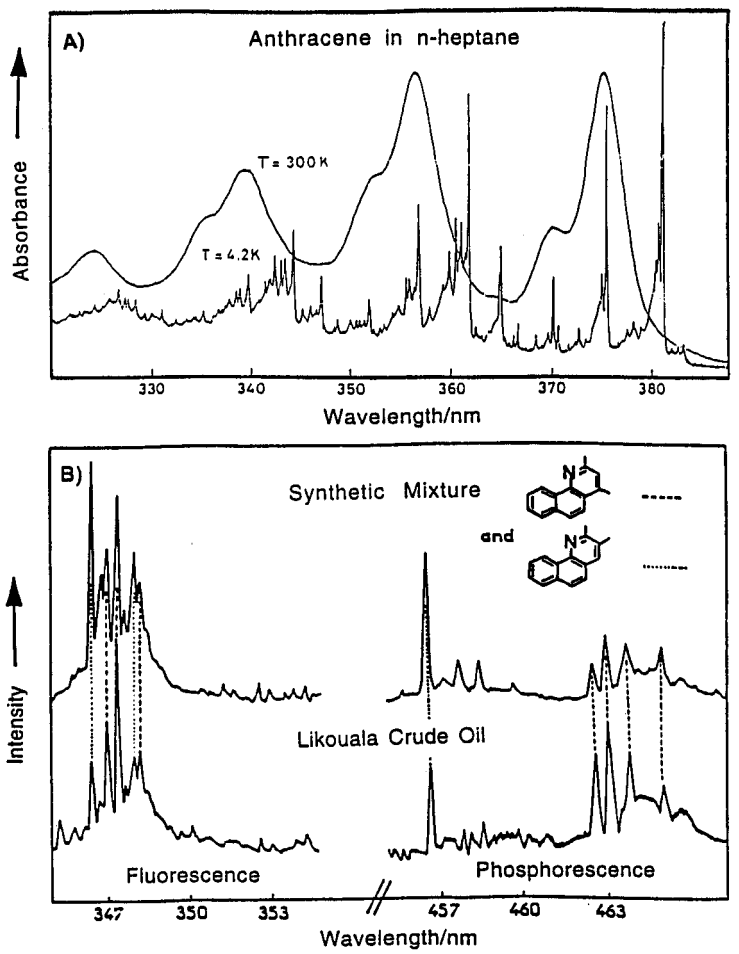

Fig. 4 The Shpol'skii Effect. The Shpol'skii Effect reduces both the electron-phonon coupling and the inhomogeneous broadening in absorption and luminescence spectra. (A) Line narrowing of absorption spectrum occurring upon cooling an anthracene solution in n-heptane from room temperature to 4.2 K. *Source:* I. Nakhimovsky, M. Lamotte, and J. Joussot-Dubien, Handbook of Low Temperature Electronic Spectra of Polycyclic Aromatic Hydrocarbons, Elsevier, Amsterdam, 1989. (B) Luminescence spectra of 2,3- and 2,4-dimethylbenzo[h]quinolines in a synthetic mixture and in a di- and triaromatic base concentrate from Likouala crude oil, frozen in n-hexane at 15 K. Excitation was at 330 nm. Each isomer is identified by several emission peaks, by fluorescence and phosphorescence. *Source:* P. Garrigues, R. De Valzelhes, M. Ewald, and J. Joussot-Dubien, *Analytical Chemistry*, **55**, 138 (1983).

If two or more types of sites are formed the luminescence spectrum displays two or more similar spectra, which are displaced relative to each other by a small *spectral shift* as depicted in the schematic representation in Figure 6. In this case the spectrum exhibits a *multiple site* structure* (see Figures 4 and 5). Absorption spectra of the analyte molecules in specific sites in a Shpol'skii matrix exhibit narrow bands. *Selective excitation* of such sites is possible when a monochromatic light source such as a laser is used. This technique is often referred to as *site-selection* (SS) or *energy-selection* (ES). The SS technique produces narrow-band luminescence spectra, viz., fluorescence (Figure 7) and phosphorescence (Figure 8) by exciting only a subset of analyte molecules that have their absorption energy matching the laser excitation radiation. For a complex mixture of analytes the technique of *laser-induced Shpol'skii spectroscopy* has the advantage that specific analytes, which usually exhibit narrow absorption bands, can be excited and detected selectively when a laser or several tunable lasers are used for selective excitation (Figure 9).

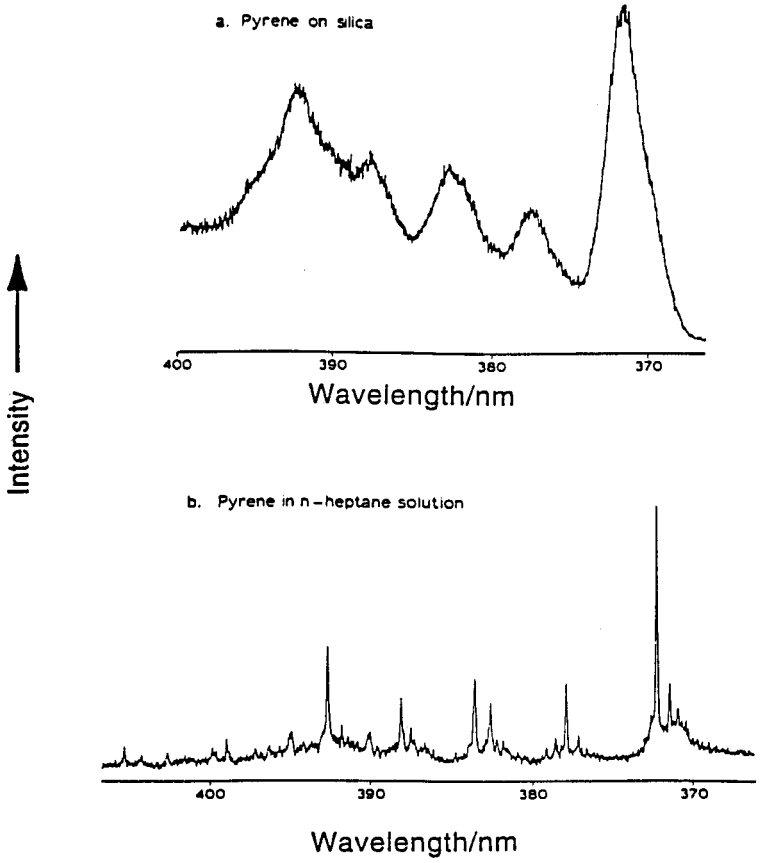

Fig. 5 (a) Fluorescence spectrum of pyrene on a silica thin layer chromatography plate. (b) Shpol'skii fluorescence spectrum of pyrene in n- heptane (concentration: 2×10^{-6} M).
Source: J. W. Hofstraat, C. Gooijer, and N. H. Velthorst, Applied Spectroscopy, 42, 614 (1988).

*Use of terms "doublet, triplet, multiplet" is discouraged since they have been defined in a different sense for atomic and molecular spectroscopy (Ref. E.U. Condon and Shortley, The Theory of Atomic Spectroscopy; McGlynn, and T. Aznni The Triplet State.).

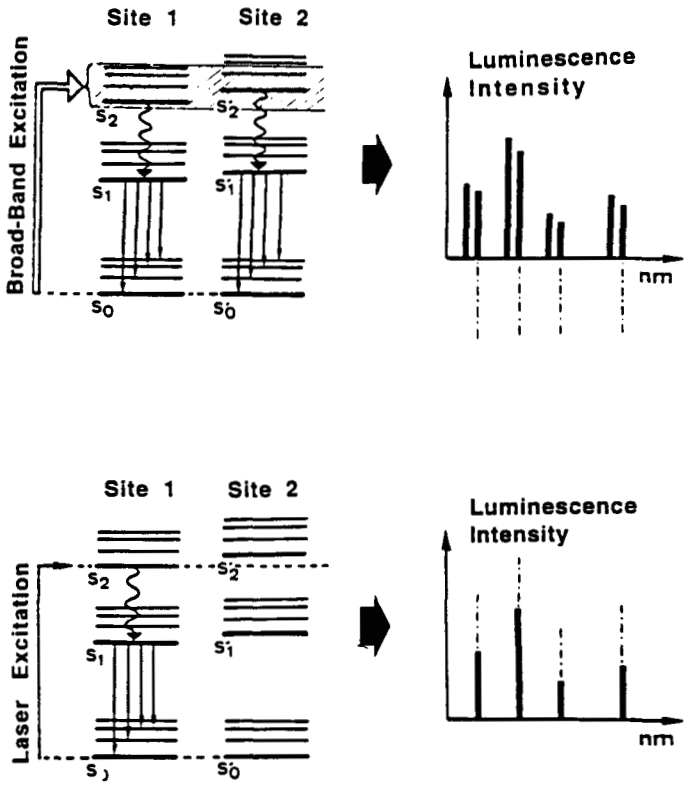

Fig. 6 Schematic Representation of the Site Selection Technique. (This example illustrates the case where the analyte molecules are trapped in two sites, which are energetically well-defined distribution of excited molecules, often referred to as isochromats. In the upper diagram, a broad-band excitation source is used to excite analyte molecules of two different sites, leading to fluorescence emission with a doublet structure. In the lower diagram, the monochromatic laser line excites only one type of site, thus producing a fluorescence spectrum from single-site analyte molecules).

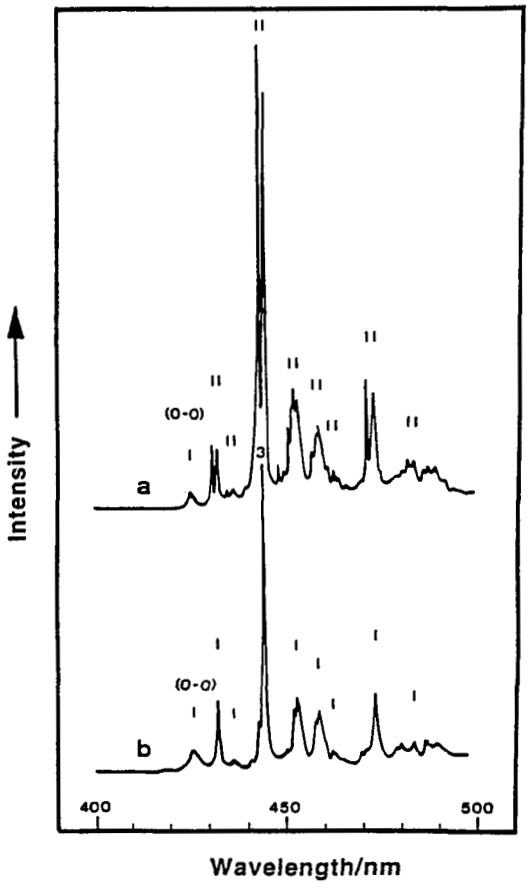

Fig. 7 Laser-Induced Site Selection Shpol'skii Technique in Fluorescence. (Curve a shows the doublet structure of the fluorescence emission spectrum of coronene in n-heptane at 77 K, using broad-band xenon lamp excitation at 350 nm, with a bandwidth of 10 nm. Curve b shows the fluorescence emission spectrum of the same sample at 77 K, using argon ion laser excitation at 351.1 nm. Laser excitation into a single site leads to fluorescence with a singlet structure. The concentration of the samples were 7×10^{-5} M when prepared at room temperature). *Source:* T. Vo-Dinh and U. P. Wild, J. *Luminescence*, **6**, 296 (1973).

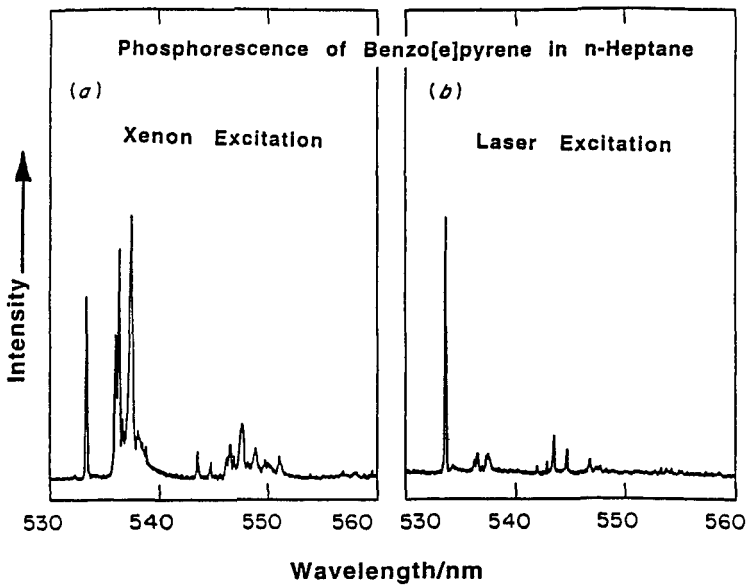

Fig. 8 Laser-Induced Site Selection Shpol'skii Technique in Phosphorescence. [Part of the phosphorescence emission spectra of benzo[e]pyrene in n-heptane 4 K: curve (a) broad-band excitation using xenon lamp at 301 nm with 3 nm bandwidth; curve (b) Site selection using a nitrogen-pumped dye laser at 364.8 nm with a 0.02-nm bandwidth]. *Source:* T. Vo-Dinh and M. Lamotte, *Applied Spectroscopy*, **42**, 65 (1988).

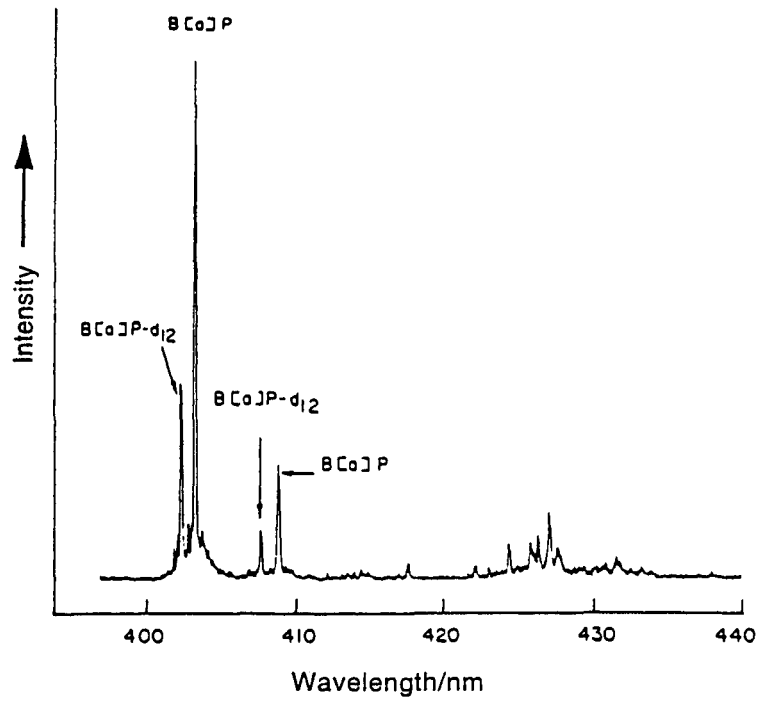

Fig. 9 Application of Laser-Excited Shpol'skii Spectrometry (Selectively excited fluorescence spectrum of benzo[a]pyrene (B[a]P) in shale oil sample with 10 ppb B[a]P-d_{12} added as internal standard). *Source:* Y. Yang, A.P. D'Silva and V.A. Fassel, *Analytical Chemistry*, **53**, 2107 (1981).

3.2 Line-narrowing spectroscopy

In luminescence *line-narrowing spectroscopy* (LNS), a high-power monochromatic light source such as a laser is used for excitation of molecules in low-temperature matrices. Only those molecules are excited whose energy difference between ground and excited states exactly matches the exciting photon energy. If the energetically well-defined distribution of excited molecules, denoted as an *isochromat*, does not change before luminescence takes place, a narrow-line luminescence spectrum is observed (Figure 10). In LNS only the inhomogeneous broadening of the spectral bands can be effectively reduced, but the homogeneous

broadening still plays an essential role. The LNS technique cannot be successfully applied if short-lived vibronic levels, which produce a large natural spectral broadening, are involved in the transition.

Line-narrowed spectra are strongly dependent on the laser *excitation frequency* and laser excitation close to the 0–0 band is recommended (Ref. 3). When excitation is accomplished in the inhomogeneously broadened 0–0 transition region ($S_{0,0} \leftrightarrow S_{1,0}$) , a simple one-site (i.e., isochromat) spectrum emerges. Since the emission wavelength is exactly equal to the excitation wavelength, the 0–0 transition is largely masked by scatter in the line-narrowed spectrum unless time-resolved detection is employed. Excitation into *higher vibronic bands* results in an increased complexity of the spectrum. In these *congested vibronic regions* the excitation probes several vibrational sub-bands, which overlap due to their inhomogeneous broadening. Since different groups of molecules are excited in different vibrationally excited states different isochromats are formed. As a result, the spectra will correspond to a *multiple-site structure*. The LNS technique is less sensitive than the Shpol'skii technique, but is more generally applicable due to a broader choice of solvents.

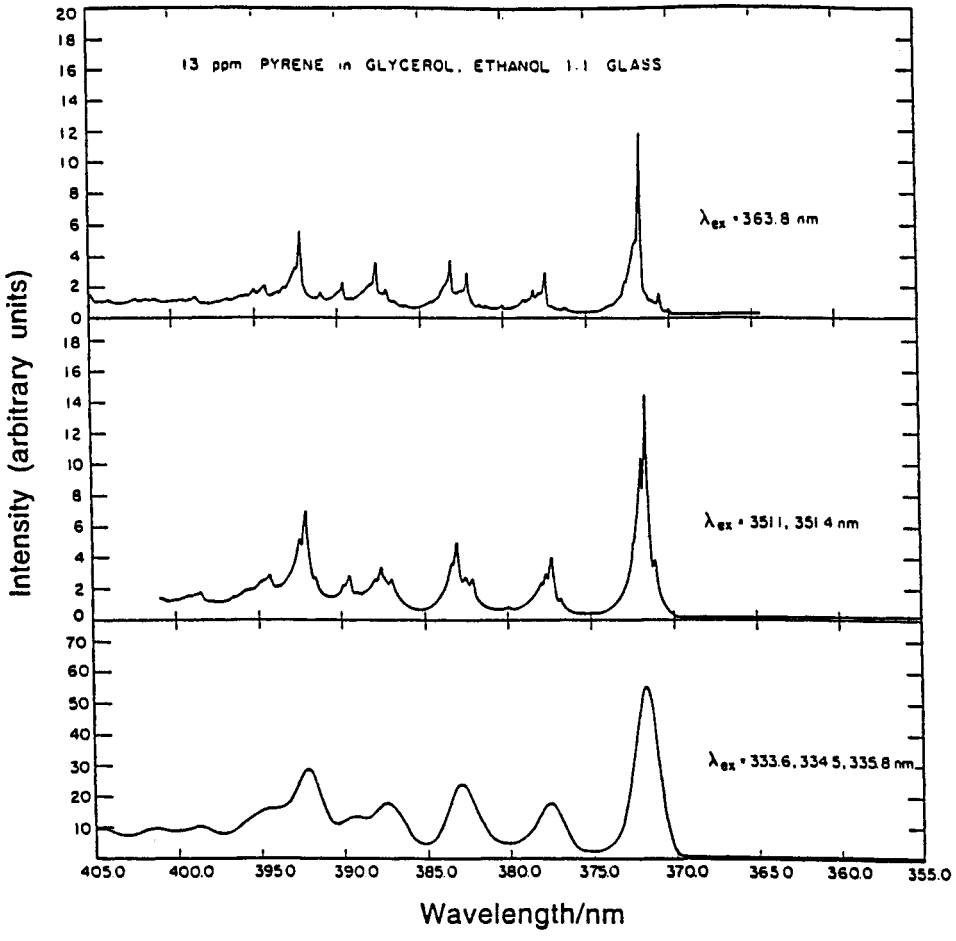

Fig. 10 Fluorescence Line Narrowing Spectra of Pyrene in Glycerol Glass at 4.2 K Using Various Excitation Wavelengths. *Source:* J. C. Brown, M. C. Edelson, and G. J. Small, *Analytical Chemistry*, **50**, 1394 (1978).

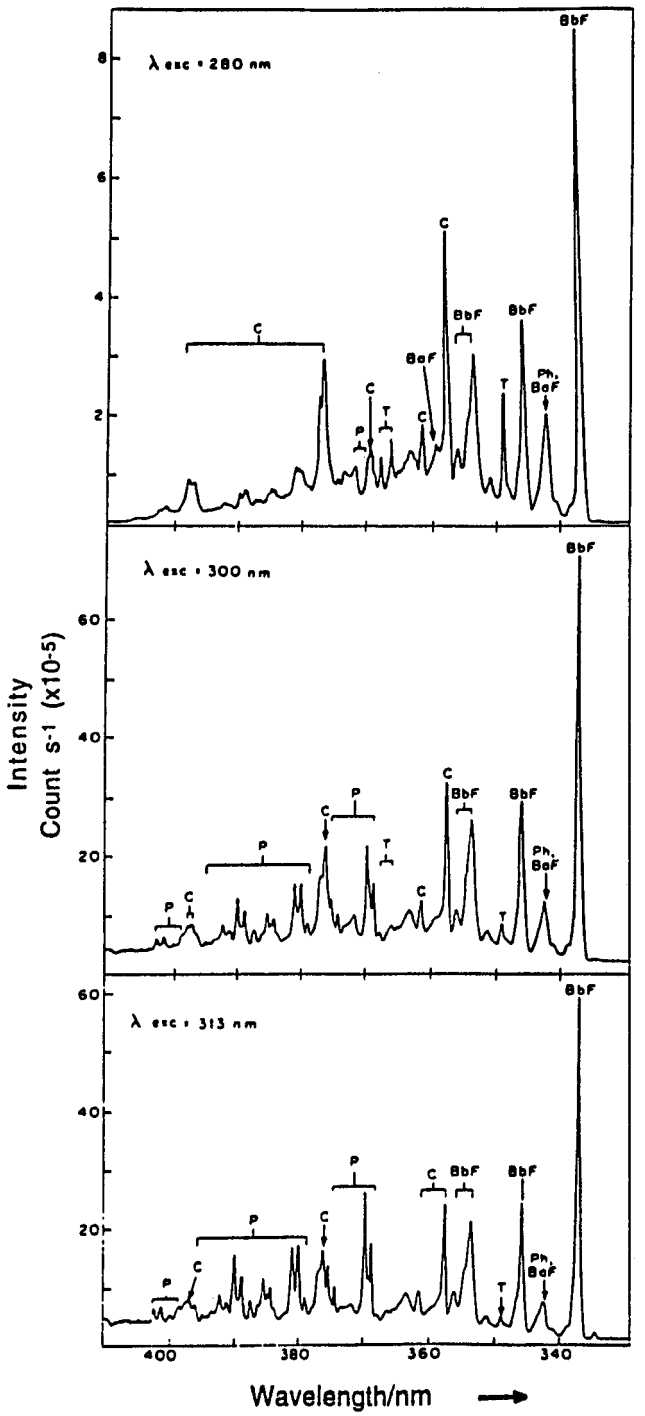

Fig. 11 Matrix Isolation Fluorescence Spectra. (The figure shows matrix isolation fluorescence spectra using three excitation wavelengths for the analysis of a six-component synthetic mixture of polyaromatic hydrocarbons: P = pyrene, 500 ng; C = chrysene, 400 ng; BaF = benzo(a)fluorene, 400 ng; BbF = benzo(b)fluorene, 250 ng; Ph = phenanthrene, 500 ng; T = triphenylene 1.37 μg). *Source:* R. C. Stroupe, P. Tokousbalides, R. B. Dickinson, Jr., E. L. Wehry, and G. Mamantov, *Analytical Chemistry*, **49**, 710 (1977).

3.3 Matrix isolation spectroscopy

In *matrix isolation spectroscopy* the sample is prepared by vaporizing, mixing with an inert gas, and then depositing on a cryogenic surface for spectral analysis. With this sample preparation, which partially reduces inhomogeneous broadening, the analyte molecules are isolated in a frozen, solid matrix. The resulting matrix isolation luminescence spectra exhibit quasi-line structure (Figure 11). Since inhomogeneous broadening is not negligible in *matrix isolation luminescence*, a laser can be used for excitation to further reduce the inhomogeneous broadening by utilizing the line-narrowing effect (see also 3.2). The matrix gases used in matrix isolation generally include nitrogen and argon. But this gas can be replaced by a Shpol'skii gas, i.e., n-alkanes, to produce a *combined Shpol'skii-matrix-isolation effect.*

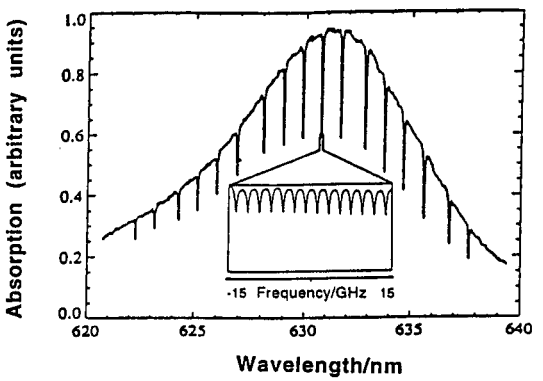

Fig. 12 Principle of Spectral Hole Burning. (Spectral holes "burnt" into the inhomogeneously broadened band are shown as recorded with "low" and "high" wavelength resolution techniques). *Source:* U.P. Wild, *Pure and Applied Chemistry*, **64**, 1335 (1992).

3.4 Hole-burning spectroscopy

In *hole-burning spectroscopy*, guest molecules embedded in a crystalline or glassy solid matrix at low temperatures are irradiated with a laser in the inhomogeneous absorption band. As a result, a narrowing of the luminescence spectral lines can be achieved (see also 3.1, 3.2 and 3.3). The hole-burning technique is distinguished from the LNS technique in that molecules absorbing the laser radiation can undergo a transformation so that the photoproduct absorbs at a different frequency. Not all of the excited molecules return to their initial state; a small fraction (of 0·01–1%) may undergo photochemistry and relax to different ground states, which absorb at different wavelengths, thus producing a narrow dip in the inhomogeneous absorption band (Figure 12). This process is known as *spectral hole-burning*. A spectral dip, which has a homogeneous linewidth, occurs at the frequency (wavelength) of irradiation and *vibrational satellites* can also be observed. With highly monochromatic light sources, such as tunable single-mode dye lasers, resolution on the order of less than 10^{-4} cm^{-1} can be achieved.

In general two categories of hole-burning are distinguished: 1) hole-burning leading to *static holes* (or *persistent holes*) as in *photochemical holes* and *photophysical holes*, and 2) hole-burning leading to *transient holes.*

A photochemical hole involves a photoinduced intramolecular reaction within the guest molecule or an intermolecular *guest-host reaction.* The photochemical holes exist for hours or even days, as long as the sample is kept at low temperatures (4 K).

Non-photochemical holes are characteristic of amorphous systems, in which excitation with a laser leads to a *structural rearrangement* of the local environment of the guest molecules.

In *transient hole-burning*, population is transferred from the ground state into a metastable excited state. The lifetime of the hole is determined by the lifetime of the metastable state.

Hole-burning allows the determination not only of the linewidth of the hole, but also *frequency shifts* with MHz (i.e., spectral shift of 10^{-4} cm^{-1}) accuracy which makes it most appropriate for studying the effects of external fields (magnetic, electric, and pressure effects) and related effects (see also Sections 10.1.2.4.7 and 1,2,4,4, in Reference 2). Also optical dephasing and relaxation processes of molecules and ions doped in solid hosts can be studied with this method.

3.5 Supersonic jet spectroscopy

Very-high-resolution molecular electronic spectra can be obtained by an alternative low-temperature approach, whereby *supersonic jet expansion* of a gas through an orifice into a vacuum is used to cool the gas to very low *translational, rotational* and *vibrational temperatures*. As the gas rapidly expands, collisions occur between the gas molecules; the result is a dramatic decrease in the range of *translational velocities* exhibited by the molecules of the gas. The distribution of molecular velocities can, by supersonic jet spectroscopy, be reduced to the extent that translational temperatures are lower than 1 K. In order to avoid formation of dimers or larger clusters in the expansion process, the analyte molecules are seeded into an inert gas such as helium. In *supersonic jet luminescence spectroscopy*, a laser beam is used to excite the analyte molecule in the supersonic beam, producing highly resolved luminescence spectra (Figure 13).

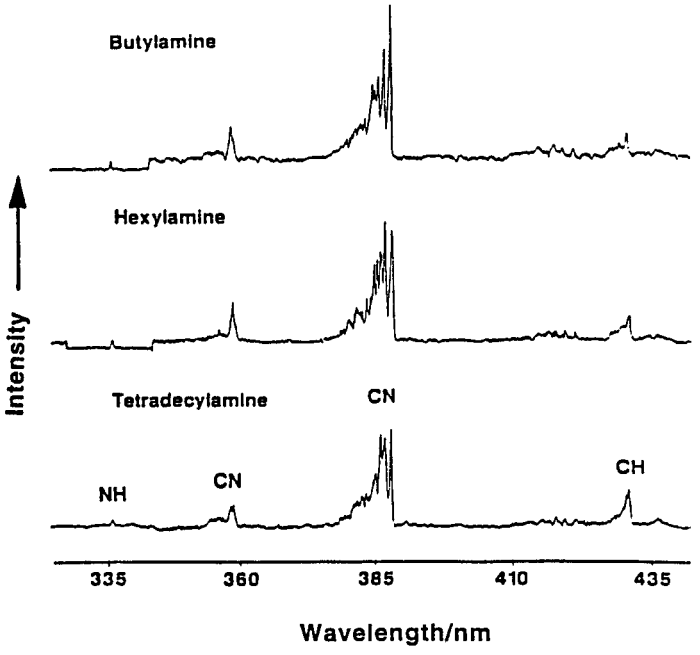

Fig. 13 Laser Photolytic Fluorescence Technique. (The figure shows fluorescence spectra produced by the 193-nm photolysis of three primary amines. Note the predominance of CN relative to CH and NH in the spectra. The pressure 1 × 10^{-4} Torr of the parent compound corresponds to 790 ng of *n*-butylamine, 1 μg of *n*-hexylamine, and 2.3 μg of *n*-tetradecylamine present prior to photolysis). *Source:* J.G. Jinkins and E.L. Wehry, *Applied Spectroscopy*, 43, 862 (1989).

3.6 Laser photolytic spectroscopy

In *photolytic luminescence spectroscopy* a non-luminescent analyte molecule in the gas phase is fragmented into smaller luminescent species, the spectra of which are measured. Many small molecular fragments such as CH, CN, NH, OH, CCl, HCO, exhibit intense luminescence in the visible or ultraviolet spectral regions. In addition, many atoms, atomic ions and molecular ions are luminescent. Most of the molecular fragments formed are neutral, which means that the photolytic luminescence technique produces information complementary to mass spectroscopy. In *laser photolytic spectroscopy*, lasers with their high power are used for fragmentation. Because absorption of a laser photon is the first step in this technique and because not all molecules absorb at the same wavelength, a *selective fragmentation* of specific analytes in a mixture may sometimes be achieved without prior separation (see Figure 14). Selective fragmentation can be most readily achieved if the sample is expanded in a supersonic free jet prior to laser photolysis.

In the photolysis process, electronically excited and ground state fragments can be formed. In the first case, the fluorescence of the fragments can be observed directly. In the second case, a second probe laser is used to excite the ground state of fragments produced by the first photolysis laser.

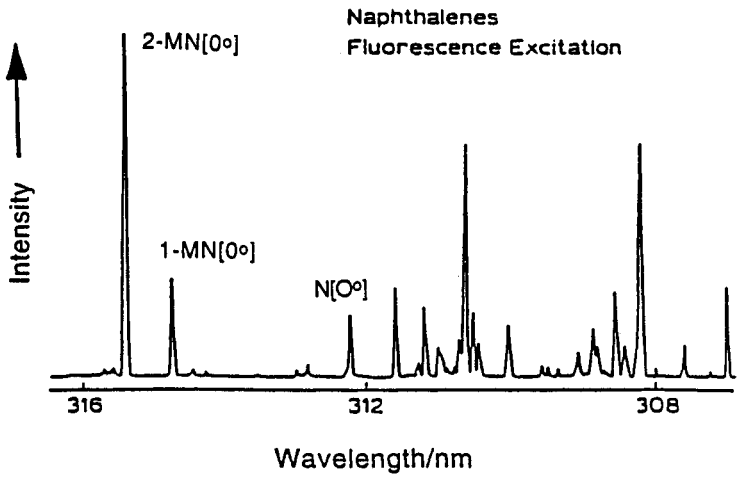

Fig. 14 Supersonic Jet Fluorescence Technique. (The figure shows the supersonic jet fluorescence excitation spectrum methyl naphthalenes, 1-methylnaphthalene (1-MN) and 2-methylnaphthalene (2-MN). N[0°], 1-MN[0°], and 2-MN[0°] denote their S_1 - S_0 0–0 transitions. The monitoring wavelength was 342.5 nm and 5-nm bandpass). *Source:* J.A. Warren, J.M. Hayes, and G.J. Small, *Analytical Chemistry*, **54**, 136 (1982).

ACKNOWLEDGEMENTS

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4. REFERENCES

1 I. Mills, T. Cvitas, K. Homann, N. Kallay, K. Kuchitsu, IUPAC *Quantities, Units, and Symbols in Physical Chemistry*, Blackwell Scientific Publications, Oxford, 2nd Edition, 1993 (IUPAC Green Book).

2 H. Freiser and G. H. Nancollas, IUPAC *Compendium of Analytical Nomenclature*, Blackwell Scientific Publications, Oxford, 2nd Edition, 1987 (IUPAC Orange Book).

3 Milliken, IUPAC, 5CP, 1959.

5. INDEX OF TERMS