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CRITICAL ASSESSMENT: USE OF SUPERSONIC JET SPECTROMETRY FOR COMPLEX MIXTURE ANALYSIS

(IUPAC Technical Report)

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Critical assessment: Use of supersonic jet spectrometry for complex mixture analysis

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Abstract: When cooled to a temperature of a few K using supersonic jet expansion into a vacuum, a molecule exists in the lowest vibrational level of the ground electronic state and is isolated at collision-free conditions. The absorption or excitation/fluorescence spectrum is then greatly simplified, when transitions occur from this single vibrational level to a limited number of vibrational levels in the excited electronic state. This method, called supersonic jet spectrometry, is a powerful analytical technique because of its high selectivity, since the chemical species can be accurately identified and selectively quantified using the sharp spectral features even for large molecules. Supersonic jet spectrometry has distinct advantages over other low-temperature spectrometries, in that it can be combined with gas-phase separation and detection techniques such as chromatography or mass spectrometry. Therefore, this spectrometric technique can be used as a versatile analytical means, not only for basic research on pure substances, but also for practical trace analysis of chemical species in multicomponent samples (e.g., in biological monitoring or in environmental monitoring).

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1. INTRODUCTION

Absorption and fluorescence spectrometries are widely used in chemical analysis. Due to a broad *spectral bandwidth* in room-temperature spectrometry (typically 20–50 nm), it is difficult to identify the analyte in a complex mixture from the spectral data, even when a narrow-line tunable laser is used as an excitation light source. The broadband feature can largely be attributed to homogeneous and inhomogeneous broadening processes [see ref. 1, Section 2]. When the sample is cooled to low temperature, both broadening processes are reduced, which can lead to simplification in the spectrum even for a large molecule. There are several approaches in low-temperature spectrometry, as defined in, i.e., Shpol'skii spectrometry [1, Section 3.1], line-narrowing spectrometry [1, Section 3.2], matrix isolation spectrometry [1, Section 3.3], hole-burning spectrometry [1, Section 3.4], and supersonic jet spectrometry [1, Section 3.5]. In supersonic jet spectrometry, the sample molecule is measured under isolated collision-free conditions, and, as a result, *collision-induced* broadening is negligible. Furthermore, there is no perturbation from a host matrix. It should also be noted that the analyte can be detected using multiphoton ionization/mass spectrometry, which provides information concerning molecular weight and chemical structure. Moreover, supersonic jet spectrometry can easily be combined with a separation technique, such as gas chromatography. This combination provides additional selectivity for complex mixture analysis.

2. DEFINITIONS

2.1 Cooling process

When an analyte gas is expanded with an inert gas, such as argon, into a vacuum from a thin pinhole, a *hydrodynamic flow* is produced (see Fig. 1A). By collisions with diluent gases, the *velocity distribution* of the analyte molecule becomes narrow. As the expansion proceeds, an isolated collision-free condition is attained, resulting in low translational temperatures. Through the collision process, the translational cooling is transferred to cooling of the rotations and vibrations. The efficiency of cooling is then in the order of translational > rotational > vibrational, which is determined by the efficiency of energy transfer among these motions and, therefore, by the densities of the energy levels. Therefore, the molecules are not necessarily populated in a Maxwell-Boltzmann distribution and high vibrational levels remain populated due to a high vibrational temperature. This phenomenon is in contrast to a *molecular flow* formed by injection of the analyte from a narrow channel into a vacuum (see Fig. 1B). In this latter case, the velocity distribution is rather broad, even when molecular collisions are negligible. Supersonic jet cooling and spectral line narrowing were first reported for di- and tri-atomic molecules [2,3]. Since then, this technique has been extended to large molecules containing more than 20 atoms.

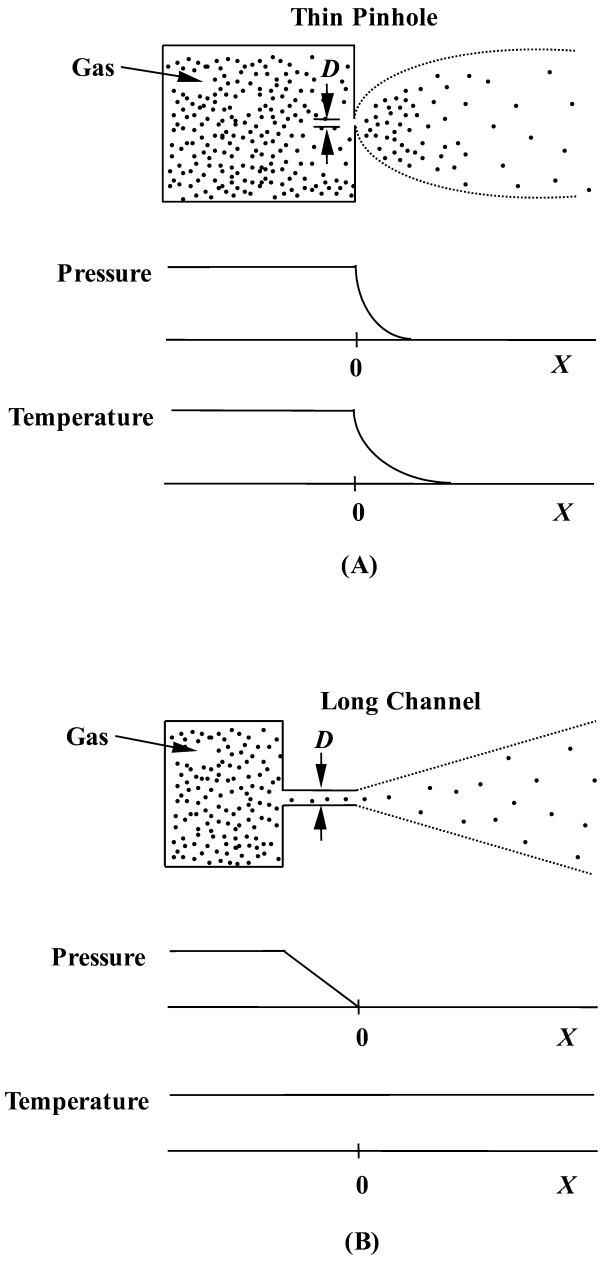

Fig. 1 Injection of gas into vacuum. (A) hydrodynamic flow; (B) molecular flow.

2.2 Excitation process

When an analyte molecule is cooled to near zero K, it exists in the lowest vibrational and *rotational level* of the ground electronic state. Using a narrow-band excitation source, absorption and excitation are introduced to a limited number of *vibrational level*s in the excited electronic state, and, as a result, only a small number of peaks with narrow line widths are observed in the absorption (excitation) spectrum. Similarly, emission transitions usually occur from a single level in the excited state to a limited number of vibrational levels in the ground electronic state, thus providing only a small number of peaks

with narrow line widths in the fluorescence spectrum. Thus, low-temperature spectrometry is capable of providing a simplified spectrum and, therefore, produces valuable information for identification of the analyte molecule.

3. OPERATING PRINCIPLES [4–8]

3.1 Parameters

At a low temperature, molecules move slowly, and the number of collisions is low. In the jet expansion processes, rapidly moving molecules collide with molecules moving more slowly, decelerating the former and accelerating the latter. As a result, the velocity distribution becomes narrow; its width decreasing with increasing *Mach number*. In other words, the molecules can be considered to be moving slowly when viewed in coordinates moving at the average velocity of the jet. More precisely, the relative velocity between molecules is low, a phenomenon that is independent of the coordinates. Thus, conditions for such a narrow velocity distribution are essentially maintained at a low temperature, until the molecules collide with a wall (e.g., a vacuum chamber). Also, the background pressure of the vacuum chamber is not necessarily zero, and the expanding molecules push away the gases, which remain in the vacuum chamber. At a certain distance from the nozzle, a wall consisting of congested molecules, called a *Mach disk*, is formed. At this distance, numerous collisions occur between atoms and molecules, and, as a result, they are no longer cooled. Therefore, the measurements should be performed in the space between the nozzle and the Mach disk.

3.2 Supersonic expansion processes

3.2.1 Mach number

The Mach number, M, which is defined as the ratio of the velocity of the molecules to the velocity of sound, is used for evaluating the characteristics of hydrodynamic flow:

$$M = A\left(\frac{X}{D}\right)^{\gamma-1} - \frac{\frac{1}{2}\left(\frac{\gamma+1}{\gamma-1}\right)}{A\left(\frac{X}{D}\right)^{\gamma-1}} \cong A\left(\frac{X}{D}\right)^{\gamma-1} \tag{1}$$

where A is a constant (A = 3.26 and γ = 5/3 for noble gases such as He and Ar; A = 3.65 and γ = 7/5 for diatomic molecules such as N_2 or H_2), X is the distance from the nozzle, D is the diameter of the nozzle, and γ is the ratio of the specific heats at constant volume and pressure (C_p/C_v). In order to increase the Mach number, it is necessary to measure the sample molecule far away from the nozzle, in comparison with the diameter of the nozzle (i.e., $X >> D$). However, eventually the Mach number approaches a constant value, M_t, the *terminal Mach number*, because the number of collisions decreases to zero by expansion of the gas. The terminal Mach number can be empirically calculated using the following equation:

$$M_t \cong 133\left(P_0 D\right)^{0.4} \text{: for Ar} \tag{2}$$

where P_0 is the gas pressure in the nozzle. Thus, in order to increase the Mach number, it is necessary to expand the sample gas using a high-pressure nozzle having a large diameter. However, then such a system requires a large-capacity pumping system, making the analytical system larger and more complicated.

3.2.2 Velocity distribution

The velocity distribution of the molecules depends on the Mach number, which is expressed by:

$$f(v_x) = \left(\frac{m}{kT_0}\right)^{\frac{3}{2}} \left(1 + \frac{\gamma - 1}{2} M^2\right)^{\frac{3}{2}} v_x^3 \exp\left(-\left\{ \left(\frac{m}{2kT_0}\right)^{\frac{1}{2}} \left(1 + \frac{\gamma - 1}{2} M^2\right)^{\frac{1}{2}} v_x - \left(\frac{\gamma}{2}\right)^{\frac{1}{2}} M \right\}^2 \right) \tag{3}$$

where T_0 is the temperature of the gas in the nozzle. Velocity distributions for various Mach numbers are shown in Fig. 2. The distribution becomes narrower with increasing Mach number. It should, however, be noted that the average velocity is changed only slightly, even when the Mach number is significantly increased.

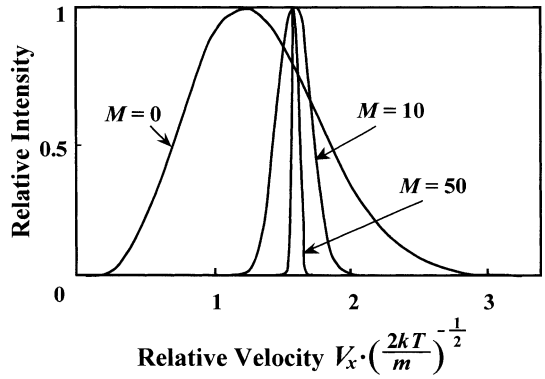

Fig. 2 Velocity distribution of mono-atomic gas in a supersonic jet. The Mach number used in calculation is indicated in the figure. Source: N. Mikami. *Oyo Buturi* **49**, 802 (1989).

3.2.3 Cooling effect

The degree of cooling, defined as T_0/T_s, is expressed as:

$$\frac{T_0}{T_s} = \left[1 + \frac{(\gamma - 1)M^2}{2}\right] \tag{4}$$

where T_0 and T_s are the (translational) temperatures in the nozzle and the jet, respectively. The degree of cooling calculated from eq. 4 for different Mach numbers is shown in Fig. 3. In order to cool the molecules from room temperature (e.g., 300 K) to 3 K, the Mach number should be ca. 20, which is easily achieved at X/D = 10 for an Ar carrier gas. However, as described above, the average velocity of the molecules in the jet is not greatly changed by supersonic jet expansion, indicating that the velocity of sound is significantly reduced by decreasing the temperature of the jet.

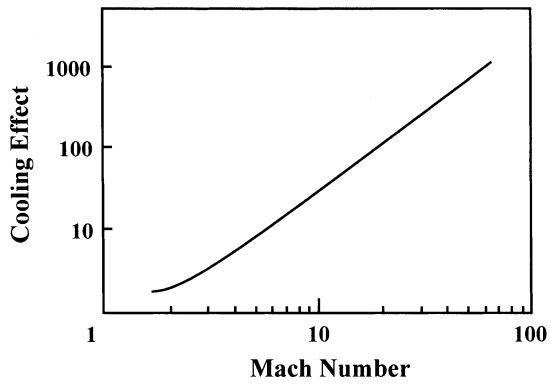

Fig. 3 Cooling effect. The ratio of the jet and room temperatures is plotted against the Mach number. The value of γ is assumed to be 5/3 (mono-atomic gas).

3.2.4 Mach disk

The distance from the nozzle to the Mach disk, X_M, is expressed by:

$$X_M = 0.67D\sqrt{\frac{P_0}{P_1}} \tag{5}$$

where P_0 and P_1 are the pressures of the gas in the nozzle and in the vacuum chamber, respectively. This equation shows that the capacity of the pumping system should be sufficiently large to achieve the desired value of X_M. In order to minimize the pumping capacity, a pulsed nozzle can be used to reduce the amount of gases introduced into the vacuum chamber. However, use of a pulsed nozzle necessitates the use of pulsed or gated excitation and fluorescence detection systems whose timings are synchronized with the nozzle pulses. A skimmer, a funnel-shaped component, which extracts a portion of the jet as a molecular beam, is sometime placed between the nozzle and the Mach disk. This skimmer is frequently used in multiphoton ionization/mass spectrometry to reduce the background pressure.

3.3 Spectral line shape

In supersonic jet spectrometry, a spectral line is split to two or three peaks in most cases. Owing to the *rotational selection rule* for electronic transitions (e.g., $\Delta J = \pm 1$ for parallel transitions and $\Delta J = 0, \pm 1$ for perpendicular transitions), only a few rotational lines are observed for each vibronic transition for simple di- and tri-atomic molecules such as NO and NO_2. However, many rotational lines appear to form a split vibrational band for a large molecule owing to a large moment of inertia. The intensity of the rotational lines for a polyatomic molecule is calculated by [9]:

$$I_{KJ} = C_v A_{KJ} g_{KJ} \exp\left[-\frac{F(K,J)}{kT_{\text{rot}}}\right] \tag{6}$$

where C_v is a constant independent of K and J, but dependent on the vibrational transition, K and J are the rotational quantum numbers (see ref. 5 for definitions), g_{KJ} and $F(K,J)$ are the statistical weight and the *term value* of the lower state, k is the Boltzmann's constant, T_{rot} is the *rotational temperature* (i.e., the temperature determined from the rotational structure in the spectrum), and A_{KJ} is the *line strength*, which is proportional to the square of the transition moment, is given by the *Hönl–London formulae* for a parallel band (see ref. 5 for a perpendicular band).

For the R branches ($\Delta J = +1$):

$$A_{KJ} = \frac{(J+1)^2 - K^2}{(J+1)(2J+1)} \tag{7}$$

for the Q branches ($\Delta J = 0$):

$$A_{KJ} = \frac{K^2}{J(J+1)} \tag{8}$$

for the P branches ($\Delta J = -1$):

$$A_{KJ} = \frac{J^2 - K^2}{J(2J+1)} \tag{9}$$

where K and J refer to the lower state. The g_{KJ} are $2J + 1$ for $K = 0$ and $2(2J + 1)$ for $K \neq 0$. The *term value* $F(K,J)$ is given for a prolate top molecule by (see ref. 9 for details):

$$F(K,J) = B\,J(J+1) + (A - B)\,K^2 \tag{10}$$

where A and B are the rotational constants, which are reciprocally proportional to the moments of inertia. On the other hand, the intensity of the vibronic bands is determined by the *Franck–Condon factor*, $R_{v'\,v''}$, which is the contribution of vibration to the transition moment, and is given by [9]:

$$R_{v'v''} = \int \psi_v'^{*} \psi_v'' d\tau_v \tag{11}$$

where ψ_v' and ψ_v'' are the vibrational wavefunctions. The Franck–Condon factor is, therefore, the overlap integral of the vibrational eigenfunctions of upper and lower states that determines the relative intensities of the vibronic bands in electronic transition. This factor depends on the change in geometry between the ground and excited states. High-resolution spectrometry (e.g., Doppler-free spectroscopy using a narrow continuous-wave laser excitation source) is required to resolve the rotational lines in a large molecule, such as benzene or anthracene, whose rotational moments of inertia are very large. In conventional spectrometry using a commercially available laser source with a line width of 0.01–0.001 nm, several, and sometimes many, rotational lines are unresolved, and what is observed is a spectral band split into two branches (P and R branches, corresponding to $\Delta J = \pm 1$) or three branches (P, Q, and R branches, corresponding to $\Delta J = 0, \pm 1$), depending on the nature of the transition. The observed bandwidth is determined by the number of rotational lines excited, which is affected by the temperature of the jet. Thus, it is possible to calculate the rotational temperature by comparing the data of the *rotational envelope* (band contour) obtained by a computer simulation with the experimental data. A typical value of bandwidth is 0.01 nm, although it strongly depends on the experimental conditions used. It is noted that flexible molecules (e.g., hydrocarbons with long chains such as prostaglandins, proteins, or DNA) have many rotational isomers, thus providing even a diffuse spectrum. Therefore, supersonic jet spectrometry has not been used successfully for such flexible molecules.

4. ANALYTICAL INSTRUMENTATION

In supersonic jet spectrometry, the analyte molecule is identified by excitation/fluorescence or multiphoton ionization/mass spectrometry in most cases. Figure 4 shows a typical analytical instrument for supersonic jet spectrometry, which allows detection by *fluorescence excitation*/emission and multiphoton ionization/mass spectrometries simultaneously [10]. The sample heated in a reservoir is diluted with argon and is injected from a pulsed nozzle into a vacuum chamber to produce a supersonic jet. The first laser beam is used for excitation of the analyte molecule with subsequent fluorescence detection by a

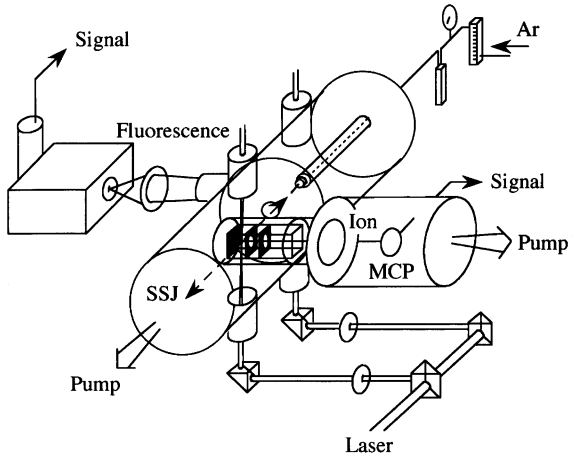

Fig. 4 Supersonic jet spectrometer based on excitation/fluorescence spectrometry and multiphoton ionization/mass spectrometry. Source: T. Imasaka, M. Hozumi, N. Ishibashi. *Anal. Chem.* **64**, 2206 (1992).

monochromator equipped with a photomultiplier. Other possible excitation sources are xenon arc and flash lamps, though sensitivity and spectral resolution are substantially decreased. Further detection systems are optical filters for efficient isolation of fluorescence, monochromators equipped with a photodiode array with an image intensifier for instantaneous spectral measurements, and Fourier transform interferometers having very high spectral resolution. The second laser beam is used for multiphoton ionization followed by mass analysis using a time-of-flight tube equipped with an assembly of microchannel plates. Other mass spectrometers that have been used successfully are quadrupole and ion-trap instruments coupled with microchannel plate and channeltron detectors. Fourier transform (ion cyclotron resonance: ICR) instrument equipped with a radio-frequency detector may also be used for high-resolution mass spectrometry. The electronic signal is processed by a boxcar integrator for optical spectrometry and by a digital oscilloscope for mass spectrometry. Other possible signal processors are a sampling oscilloscope combined with a personal computer and a time-to-amplitude converter (TAC) combined with a multichannel analyzer to measure and accumulate the time intervals between the laser pulse and the single ion pulse, allowing sensitive measurements of a high-resolution mass spectrum at the expense of the time for recording a spectrum. The background pressures are maintained below 10^{-4}, 10^{-6}, and 10^{-8} torr for the jet chamber, the ionization chamber, and the time-of-flight tube, respectively, by using a differential pumping system. A single-stage pumping system can also be used by reducing the pulse width of the jet (i.e., by reducing the flow rate of the sample gas).

The methods based on fluorescence excitation and multiphoton ionization/mass spectrometries are very sensitive and provide valuable information for identification of the analyte molecule. There are, however, several other possible spectrometric methods for sample detection. For example, phosphorescence spectrometry is attractive for the detection of molecules that are efficiently relaxed to a triplet state by intersystem crossing. Unfortunately, phosphorescence lifetimes (1 μs–1 s) are too long to detect the molecule in the observation region, since the velocity of the molecule in the jet is typically 1 mm/μs. In order to avoid this problem, the sample molecule is first excited in the jet and then deposited on a phosphor screen placed downstream, which is interfaced with a photomultiplier [11]. In a similar manner, it is possible to measure the heat generated by laser excitation using a bolometer, placed downstream [12–14]. *Coherent anti-Stokes Raman spectroscopy* [15], *diode laser infrared absorption spectroscopy* [16], and *cavity ringdown laser absorption spectroscopy* [17,18] are also used for sample detection. A *stimulated emission pumping technique* has been developed for high-resolution spectroscopy and lifetime measurement of the ground electronic state, in which the second laser is used for excitation, followed by a fluorescence measurement or for multiphoton ionization [19,20].

5. PERFORMANCE CRITERIA

5.1 Sensitivity

Laser-induced fluorescence and multiphoton ionization spectrometries are known to have very high sensitivity, and even a single molecule can be detected in the optimum case. It is, however, difficult to accomplish such high sensitivity in supersonic jet spectrometry, owing to a low sample density arising from gas expansion into a vacuum. The density of the gas jet along the propagation axis, n, is given by [21,22]:

$$n = n_0\left(\frac{D}{X}\right)^2\left(\frac{1}{C_n(\gamma)}\right) \tag{12}$$

where n_0 is the number density of gas molecules in the nozzle, and $C_n(\gamma)$ is the parameter depending on γ (values are given in the above references). Thus, the density decreases in proportion to the square of the distance from the nozzle. The number density at the distance l from the skimmer placed at the distance X from the nozzle is further reduced by a factor of $X^2/(X + l)^2$. As a result, the sensitivity in supersonic jet spectrometry is substantially degraded in comparison with the case in non-jet spectrometry. However, it is possible to increase the ionization and detection efficiencies, to 100 % in the extreme case, for analyte molecules within a detection volume in multiphoton ionization/mass spectrometry. The best detection limit reported so far is 3 pmol/mol for benzene, and the linear relationship between signal and concentration extends over almost six orders of magnitude [23]. Similar results are obtained for toluene and naphthalene. The absolute limit of detection is reported to be 300 fg for toluene, which is achieved in a combination with gas chromatography [24]. These results imply that the sensitivity in supersonic jet spectrometry is comparable to or better than that in conventional mass spectrometry combined with electron impact ionization.

5.2 Temperature dependence of line width

A typical supersonic jet fluorescence spectrum of perylene is shown in Fig. 5 and consists of several sharp lines [25]. Thus, supersonic jet spectrometry is useful for reliable analyte identification. The fluorescence spectrum, measured at an elevated temperature (290 °C) is also shown for comparison. The spectrum is broad and is similar to that measured in the condensed phase. As described above, the spectral bandwidth depends on the jet temperature, because numerous rotational levels in the ground electronic state are populated even within several degrees of absolute zero, due to the large moments of inertia of such large molecules. The spectral bandwidth (i.e., the rotational envelope) can be calculated by a computer simulation for large molecules at a specified temperature (cf. Section 3.3). The line width of the fluorescence spectrum observed in Fig. 5 (solid line) is, unfortunately, limited by the resolution of the monochromator, which can be reduced further at the expense of sensitivity by reducing the slit width of the monochromator. Thus, sensitivity and selectivity are not compatible in the measurement of a fluorescence spectrum. However, no such problem occurs in the measurement of a fluorescence excitation spectrum or a multiphoton ionization spectrum, since the spectral line width of the excitation/ionization source can be reduced (e.g., by using a dye laser, without the expense of the light intensity).

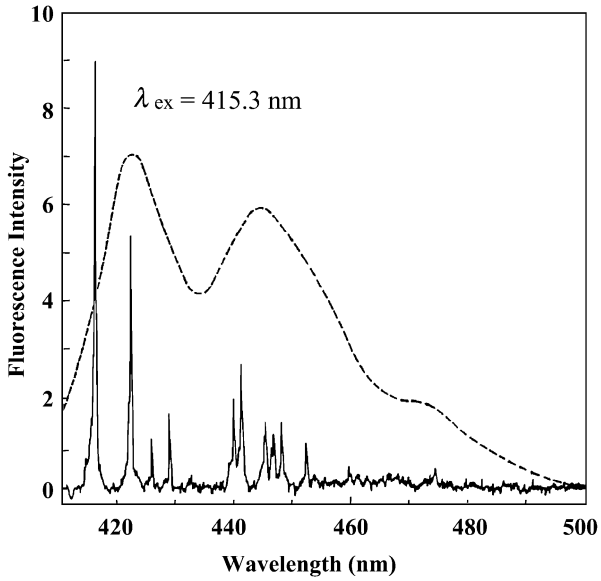

Fig. 5 Supersonic jet (solid line) and gas phase (broken line) fluorescence spectra for perylene. Source: T. Imasaka, H. Fukuoka, T. Hayashi, N. Ishibashi. *Anal. Chim. Acta* **156**, 111 (1984).

5.3 Selectivity

Analytical selectivity is determined by the product of the selectivities along independent coordinates, e.g., sample excitation wavelength, fluorescence detection wavelength, decay time, molecular weight, etc. In mass spectrometry, isotope molecules are readily distinguished via a difference in the molecular weights. It is, however, difficult to distinguish isomers, since their molecular weights are identical. For this reason, the isomers are distinguished by proper selection of the reagent gas in chemical ionization or by hyphenation with a separation technique such as gas chromatography. On the other hand, the isomer molecules are sometimes distinguished by conventional excitation/fluorescence spectrometry, though this is accomplished only when their spectral natures are sufficiently different. It is, however, difficult to distinguish the isotopes since the spectral natures related to electronic transition are essentially identical. In supersonic jet spectrometry, the achievable line width is typically 0.01 nm, and, as a result, it is possible to differentiate even the isomers with closely related structures. For example, the 0–0 *transition* for 1-chloroanthracene (367.31 nm) is nearly identical to that of 2-chloroanthracene (367.09 nm), but it is possible to completely resolve the components in the supersonic jet excitation spectrum [26]. The electronic transition energy is essentially identical for isotopes, as described. It is, however, possible to resolve these components by exciting them to upper vibrational levels in the excited electronic state, since there is an isotope effect in molecular vibration. The vibrational frequency is given by:

$$v = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}} \tag{13}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{14}$$

where f is the force constant, μ is the reduced mass, and m_1 and m_2 are the masses related to the vibration, respectively. When $m_1 << m_2$, μ becomes m_1. Thus, frequency is reciprocally proportional to the square root of the mass, m_1. In the case of an isotope pair for ^{37}Cl and ^{35}Cl, the vibrational frequency

differs by a factor of 0.973, which is sufficiently large for resolution of the vibrational peaks in supersonic jet spectrometry. In fact, the wavelengths of the 0–0 transition for (^{35}Cl, ^{35}Cl), (^{35}Cl, ^{37}Cl), (^{37}Cl, ^{37}Cl) isotopes of 9,10-dichloroanthracenes are 385.425 nm and are essentially identical. The vibrational excitation, however, exhibits three nearly equidistant peaks, as shown in Fig. 6, which are located at 380.740 nm, 380.787 nm, 380.831 nm, respectively [27]. Thus, these isotopes can readily be differentiated based on their excitation spectrum. The relative intensity ratios for these peaks (1:0.66:0.10) agrees well with the ratios calculated from the natural abundance of chlorine atoms (1:0.67:0.11).

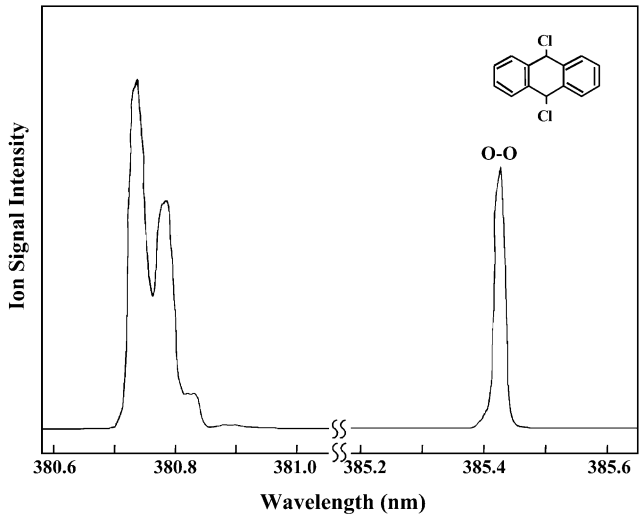

Fig. 6 Excitation spectrum for 9,10-dichloroanthracene. Source: A. Amirav, U. Even, J. Jortner. *Anal. Chem*. **54**, 1666 (1982).

5.4 Analyte introduction methods

In supersonic jet spectrometry, a gas sample should be expanded into a vacuum; otherwise, molecules are not cooled. For liquid and solid samples, they are heated to vaporize and mix with an inert gas. Some molecules are, however, nonvolatile or thermally labile and form carbonized substances when heated by a conventional method (e.g., by using a nichrome wire). This carbonization is minimized by lowering the heating temperature and also by rapid increase in the temperature and decrease in the time of heating. A supercritical fluid containing analytes can be expanded into a vacuum to form a supersonic jet [28–30]. Especially, carbon dioxide (CO_2) has a low critical temperature (31.0 °C), so that it can be used for the measurement of nonvolatile or thermally labile molecules. On the other hand, some of the biomolecules such as tryptamine can be directly heated in an oven and measured by supersonic jet spectrometry [31]. A laser desorption/ablation technique is applied, in order to minimize the heating time, not only to metal and inorganic substances to form clusters such as C_{60} [32], but also to biomolecules such as tryptophan peptides [33], tyrosine peptides [34], tyrosine analogs [35], indole, and catechol derivatives [36]. For uniform vaporization, the sample is sometimes mixed with glycerin [37]. An infrared laser such as a CO_2 laser emitting at 10.6 μm has been used for thermal vaporization [37] and an ultraviolet laser such as an excimer laser (KrF, 248 nm) for *photochemical ablation* [38]. The infrared laser is useful for moderate heating of the sample (e.g., thermally labile biological molecules), though infrared optics such as the lens and the windows made of ZnSe must be used. On the other hand, the ultraviolet laser is useful for decomposition of the sample (e.g., polymers) in which conventional quartz optics can simply be used. Other laser sources such as a tunable dye laser or a near-infrared Nd:YAG laser may also be used: the former is useful for efficient vaporization by matching the laser wavelength

with the analyte absorption band, and the latter is simple and allows moderate vaporization. Pulsed methods for *fast atom bombardment* can also be used for volatilization of thermally labile compounds [39].

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APPENDICES

A1. APPLICATIONS

A1.1 Complex mixture analysis

A1.1.1 Polycyclic aromatic hydrocarbons

Various aromatic hydrocarbons, some of which are highly carcinogenic, are emitted into the atmosphere by the combustion of fossil fuels. These compounds are numerous, and a simple spectrum is desirable, hopefully one giving a single peak for each component. *Synchronous scan luminescence spectrometry* combined with supersonic jet spectrometry detecting either only resonance fluorescence ($\Delta\lambda = 0$ nm) or nonresonance fluorescence ($\Delta\lambda \neq 0$ nm) can be used for the measurement of a mixture containing many polycyclic aromatic hydrocarbons [40,41]. The former gives a single peak for a single component in most cases, and the latter gives numerous peaks for each component. When the analyte molecule is excited to high vibrational levels (>2000 cm^{-1}) in the electronic state, the excitation spectrum becomes

broad and structureless owing to radiationless transition arising from an interaction with high vibrational levels in the ground state. This band broadening is a serious problem, especially in the application to a mixture sample, since it degrades analytical selectivity. Even in this case, synchronous scan luminescence spectrometry is capable of reducing the background and provides a limited number of sharp peaks in the spectrum [42]. This method has been applied to a sample of solvent-refined coal, and several components have been identified. Alternatively, polycyclic aromatic hydrocarbons can be detected from exhaust gas measured by supersonic jet/resonance-enhanced multiphoton ionization/time-of-flight mass spectrometry using an on-line flame sampling technique [43]. For polycyclic aromatic hydrocarbons having more than three aromatic rings, the ionization potential is sometimes larger than twice the excitation energy. Therefore, two-color laser ionization is necessary to enhance the sensitivity [44]. Recently, aromatic hydrocarbons containing chlorine atoms, such as polychlorodibenzodioxin and polychlorodibenzofuran, have attracted considerable attention as environmental pollutants because of their very potent toxicity. Many isomers exist, depending on the position of the substituent chlorine atoms. It should be noted that the toxicity depends on the isomer, so that isomeric selectivity is necessary in environmental analysis. Dioxin analogs such as 2,3-dichlorodibenzodioxin and 2,8-dichlorodibenzodioxin provide similar spectra, as shown in Fig. 7. However, one of these components is selectively ionized, due to slight difference in the wavelength for resonance ionization [45]. Unfortunately, the ionization efficiency is substantially decreased with increasing numbers of chlorine atoms in the molecule. This is due to the relatively high ionization potential and the short lifetime induced by intersystem crossing to a triplet state. The efficiency is improved by using a two-color ionization scheme [46] and by using a short laser pulse [47]. Some of the molecules that contain phosphorous and sulfur are known to be toxic compounds. Organophosphonate and organosulfide compounds, representing simulants to a class of toxic compounds, can be detected at levels as low as 300 pmol/mol (dimethyl sulfide) [48].

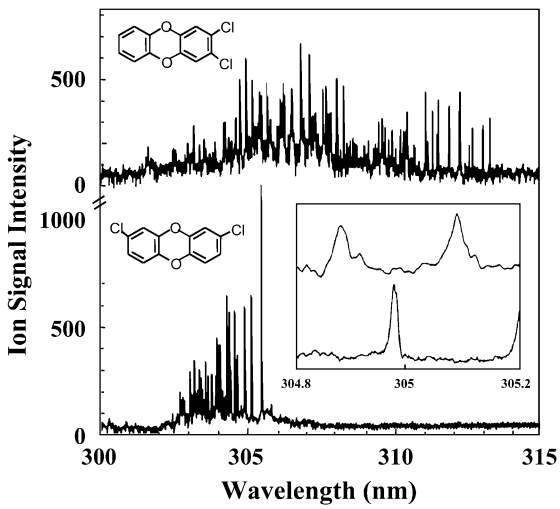

Fig. 7 Multiphoton ionization spectra for 2,3-dichlorodibenzodioxin (upper trace) and 2,8-dichlorodibenzodioxin (lower trace). Source: C. Weickhardt, R. Zimmermann, U. Boesl, E. W. Schlag. *Rapid Commun. Mass Spectrom.* **7**, 183 (1993).

A1.1.2 Polymers

Thermal decomposition products of polymers are suspected to be endocrine disrupters. In addition, thermal decomposition is sometimes utilized for characterization of polymeric materials in industry (e.g., pyrolysis/gas chromatography/mass spectrometry). Mass spectra for thermally decomposed prod-

ucts from polystyrene and polycarbonate are measured by supersonic jet spectrometry under on- and off-resonance conditions for major and minor components [9]. It is also possible to decompose polymers by laser ablation. Because this technique involves high temperature, thermally stable materials such as poly(*p*-methylstyrene), which is difficult to examine by thermal decomposition, even at 350 °C, can be examined [49]. The high selectivity provided by supersonic jet spectrometry allows the detection of minor species, e.g., styrene arising from poly(α-methylstyrene) by cleavage of the methyl group and by proton rearrangement. This spectrometric technique has been applied to the examination of several authentic samples, such as ABS resin (acrylonitrile-butadiene-styrene) and vacuum-seal O-ring (SBR, styrene-butadiene rubber), as well as polystyrene foam. This technique is also applicable to biopolymers. Mass and multiphoton ionization spectra have been measured for lignin pyrolyzates, and several chemical species have been identified [50].

A1.2 Hyphenated techniques

Supersonic jet spectrometry is a flowing analytical technique and can be combined with a separation technique, such as chromatography. This approach greatly improves the selectivity and permits more accurate identification. There are several chromatographic techniques that can be combined with supersonic jet spectrometry (i.e., gas, liquid, supercritical fluid, and thin-layer chromatographies). The flow rate of the capillary gas chromatograph is generally much smaller than the flow rate in supersonic jet spectrometry, and, as a result, a make-up gas is required in most cases. A pulsed nozzle with a small dead volume has been developed for injection of the sample into a vacuum [51,52]. In the other approach, the sample gas is first injected into an antechamber and then injected into a vacuum [53]. A sheath flow technique is used to enhance the sample density at the center of the jet [54]. In supersonic jet spectrometry, a gas-phase sample must be injected into a vacuum in order to cool the molecule. Most biological molecules are, however, nonvolatile and/or thermally labile, and high-performance liquid chromatography is used for their separation. A specially designed interface has been developed to entrain the sample into a supersonic jet. The carrier solution is maintained above the critical point, e.g., 239.4 °C and 79.9 atm for methanol, and is mixed with a make-up gas and then injected into a vacuum [26]. A similar technique has been applied to supercritical fluid chromatography [55]. Alternatively, the sample is first expanded as an aerosol into an antechamber and is then heated and mixed with an expansion (make-up) gas [56]. These combined techniques provide very high selectivity. However, they also have drawbacks. It is difficult to measure an excitation or multiphoton ionization spectrum for a sample eluting from a separation column, since the sample passes through the detector port in a few seconds and the wavelength of the pulsed laser (typical repetition rate, 10 Hz) cannot be tuned widely in such a short time period. As a result, the excitation wavelength is usually fixed at a resonance wavelength, which should be known prior to the experiment. To overcome this problem, the sample spotted in line on a thin-layer chromatographic plate can be developed and fitted beneath the nozzle throat, in which the plate can be moved two-dimensionally [57]. The chemical species in silica gel is ablated by laser pulses and is entrained into a supersonic jet. By a zigzag scan of the ablation point, the spectrum is measured by changing the laser wavelength. Thus, combining this technique with chromatography is useful for the analysis of multicomponent mixtures. Details of this technique are reviewed elsewhere [58–60].

A1.3 Assignment of chemical species

Mass spectrometry provides direct information concerning molecular weight and chemical structure. Though an excitation/fluorescence or multiphoton ionization spectrum provides information about molecular vibration, such as infrared or Raman spectrometry, it provides no direct information about chemical structure. Thus, the development of an analytical procedure for the assignment of the chemical species from the spectrum is needed. A possible approach is the use of quantum chemical calculation.

The energy of the 0–0 transition is estimated by calculation of the molecular orbital by the *Pariser–Parr–Pople (PPP) method* and by the complete neglect of differential overlap method for spectroscopy (*CNDO/S*) [61]. The error of the calculated energy is typically ±2 nm, which is, unfortunately, much larger than that of the experiment (±0.01 nm). An alternative approach is the use of a cross-correlation factor calculated between the sample and reference spectra to evaluate *spectral similarity* quantitatively [62]. The cross-correlation factors calculated between 2-ethylanthracene (sample) and anthracene derivatives (references) are listed in Table 1. Large values are obtained for alkyl-substituted and 2-substituted anthracenes, suggesting that the sample compound has a similar structure to 2-alkylanthracene, such as 2-ethylanthracene. Although this is not always the case, useful assignments can often be made. A more reliable method is the use of a database. It should be emphasized that the spectral line width is so narrow (0.01 nm) in supersonic jet spectrometry that definitive identification is possible only from a few spectral lines. The database of the 0–0 transition accumulated from the references is shown in Table 2. A database consisting of numerous spectra whose wavelengths are calibrated by a wave meter might be necessary for wide use of supersonic jet spectrometry in the future.

Table 1 Cross-correlation factors calculated for various aromatic hydrocarbons using 2-ethylanthracene as a standard sample.

Compound	Cross-correlation factor
2-Ethylanthracene	1
2-Methylanthracene	0.301
9-Methylanthracene	0.060
2-Chloroanthracene	0.008
9-Chloroanthracene	0.004
Anthracene	10^{-4}
1-Chloroanthracene	$<10^{-20}$

The line width is assumed to be 1 cm^{-1}.

Table 2 0–0 Transition for organic compounds.

Molecule	Wavelength	Reference
trans-2,5-Dimethylcyclohexanone	198.63	*AC* **64**, 2605 (1992)
cis-2ax/5eq-Dimethylcyclohexanone	198.70	*AC* **64**, 2605 (1992)
trans-2,3-Dimethylcyclohexanone	198.76	*AC* **64**, 2605 (1992)
cis-2,4-Dimethylcyclohexanone	199.41	*AC* **64**, 2605 (1992)
trans-2ax/4eq-Dimethylcyclohexanone	199.61	*AC* **64**, 2605 (1992)
trans-2eq/4ax-Dimethylcyclohexanone	200.42	*AC* **64**, 2605 (1992)
cis-2,6-Dimethylcyclohexanone	200.98	*AC* **64**, 2605 (1992)
cis-2eq/5ax-Dimethylcyclohexanone	201.01	*AC* **64**, 2605 (1992)
cis-2eq/3ax-Dimethylcyclohexanone	201.32	*AC* **64**, 2605 (1992)
cis-2ax/3eq-Dimethylcyclohexanone	201.32	*AC* **64**, 2605 (1992)
trans-2,6-Dimethylcyclohexanone	202.24	*AC* **64**, 2605 (1992)
2,2-Dimethylcyclohexanone	203.00	*AC* **64**, 2605 (1992)
Phenylacetylene	238.35	*JCP* **75**, 4758 (1981)
Pyrimidine(π–π^*)	248.08	*AC* **57**, 2911 (1985)
Azabicyclo[2,2,2]octane	255.79	*CP* **99**, 193 (1985)
Pyridine(π–π^*)	256.41	*AC* **57**, 2911 (1985)
Benzene	262.56	*AC* **66**, 543 (1994)
Fluorobenzene	264.44	*JPC* **87**, 4406 (1983)

(*continues on next page*)

Table 2 (*Continued*).

Molecule	Wavelength	Reference
tert-Butylbenzene	265.27	*JCP* **72**, 5039 (1980)
Isopropylbenzene	265.54	*JCP* **72**, 5039 (1980)
Ethylbenzene	266.04	*JCP* **72**, 5039 (1980)
n-Propylbenzene	266.08	*JCP* **72**, 5039 (1980)
n-Butylbenzene	266.12	*JCP* **72**, 5039 (1980)
n-Pentylbenzene	266.15	*JCP* **72**, 5039 (1980)
n-Hexylbenzene	266.15	*JCP* **72**, 5039 (1980)
o-Fluorotoluene	266.23	*JPC* **91**, 517 (1987)
1-*sec*-Butyl-2-methylbenzene	266.26	*JACS* **111**, 3140 (1989)
Neopentylbenzene	266.43	*JACS* **111**, 3140 (1989)
Isobutylbenzene	266.54	*JACS* **111**, 3140 (1989)
Toluene	266.83	*JCP* **72**, 5039 (1980)
m-Fluorotoluene	267.48	*JPC* **92**, 3774 (1988)
1-Ethyl-4-propylbenzene	267.60	*JACS* **111**, 3140 (1989)
Phenyltrimethylsilane	267.73	*CPL* **158**, 351 (1989)
1,3-di-*tert*-Butylbenzene	267.84	*JACS* **111**, 3140 (1989)
o-Xylene	268.00	*JCP* **87**, 1917 (1987)
1-Ethyl-3-isopropylbenzene	268.63	*JACS* **111**, 3140 (1989)
9,10-Dihydroanthracene	268.69	*CPL* **171**, 25 (1990)
2-Ethyltoluene	268.83	*JCP* **87**, 3269 (1987)
Phenylsilane	268.97	*CPL* **169**, 460 (1990)
anti-1,3-Diethylbenzene	269.07	*JCP* **87**, 3269 (1987)
syn-1,3-Diethylbenzene	269.13	*JCP* **87**, 3269 (1987)
1-Isopropyl-3-methylbenzene	269.14	*JACS* **111**, 3140 (1989)
1,2-Diethylbenzene	269.17	*JCP* **87**, 3269 (1987)
1-*tert*-Butyl-4-ethylbenzene	269.24	*JACS* **111**, 3140 (1989)
Chlorobenzene	269.81	*AC* **57**, 1186 (1985)
3-Ethyltoluene	269.88	*JCP* **87**, 3269 (1987)
1-Isobutyl-2-methylbenzene	270.00	*JACS* **111**, 3140 (1989)
o-Xylylene oxide (phthalan)	270.02	*CPL* **169**, 179 (1990)
a*nti*-1,4-Diethylbenzene	270.18	*JCP* **87**, 3269 (1987)
syn-1,4-Diethylbenzene	270.20	*JCP* **87**, 3269 (1987)
1-Isobutyl-3-methylbenzene	270.53	*JACS* **111**, 3140 (1989)
m-Xylene	270.59	*JCP* **87**, 1917 (1987)
Phenylpentamethyldisilane	271.00	*CPL* **158**, 5351 (1989)
4-Ethyltoluene	271.07	*JCP* **87**, 3269 (1987)
p-Difluorobenzene	271.46	*JCP* **86**, 4709 (1987)
trans-m-Fluorophenol	271.52	*JPC* **88**, 5180 (1984)
p-Xylene	272.24	*JCP* **87**, 1917 (1987)
1,2,4,5-Tetramethylbenzene-d_{14} (durene-d_{14})	272.89	*JPC* **94**, 2631 (1990)
cis-m-Fluorophenol	273.05	*JPC* **88**, 5180 (1984)
1,2,4,5-Tetrafluorobenzene	273.58	*JPC* **94**, 2631 (1990)
Benzonitrile	273.88	*JCP* **86**, 1111 (1987)
1,2,4,5-Tetramethylbenzene-h_{14} (durene-h_{14})	274.34	*JPC* **94**, 2631 (1990)
cis-o-Cresol	274.57	*AC* **66**, 543 (1994)
Benzonitrile dimer	274.60	*JCP* **86**, 1111 (1987)
Anisol	274.90	*AC* **66**, 543 (1994)

(*continues on next page*)

Table 2 (*Continued*).

Molecule	Wavelength	Reference
Methoxybenzene	274.87	*JACS* **111**, 1958 (1989)
Phenylethyne	274.95	*JCP* **74**, 5971 (1981)
Phenol	275.03	*AC* **66**, 543 (1994)
Phenetole	275.07	*CP* **115**, 119 (1987)
9,10-Dihydro-9,10-*o*-benzenoanthracene (triptycene)	275.09	*JCP* **79**, 2163 (1983)
o-Dichlorobenzene	275.92	*AC* **57**, 1186 (1985)
1-Phenylpropyne	275.96	*JCP* **74**, 5971 (1981)
o-Cresol	276.20	*AC* **56**, 1962 (1984)
trans-o-Cresol	276.21	*AC* **66**, 543 (1994)
m-Dichlorobenzene	276.35	*AC* **57**, 1186 (1985)
1-Phenyl-1-butyne	276.49	*JCP* **74**, 5971 (1981)
1-Phenyl-1-hexyne	276.54	*CP* **74**, 5971 (1981)
1-Phenyl-1-heptyne	276.62	*JCP* **74**, 5971 (1981)
o-Methylanisole	276.99	*AC* **66**, 543 (1994)
m-Dimethoxybenzene	276.99	*AC* **66**, 543 (1994)
1-Methoxy-2-methylbenzene	277.00	*JACS* **111**, 1958 (1989)
1,3-Dimethoxybenzene	277.00	*JACS* **111**, 1958 (1989)
trans-m-Cresol	277.02	*AC* **66**, 543 (1994)
m-Methylanisole	277.08	*AC* **66**, 543 (1994)
1-Methoxy-3-methylbenzene	277.41	*ACS* **111**, 1958 (1989)
cis-m-Cresol	277.98	*AC* **66**, 543 (1994)
Benzoic acid	278.08	*JPC* **94**, 4394 (1990)
Resorcinol	278.22	*AC* **66**, 543 (1994)
p-Dibromobenzene	278.22	*AC* **57**, 1186 (1985)
o-Methoxyphenol (guaiacol)	278.36	*AC* **66**, 543 (1994)
trans-m-Chlorophenol	278.60	*JPC* **88**, 5180 (1984)
Diazabicyclooctane	279.46	*CPL* **101**, 578 (1983)
Methylguaiacol	279.53	*AC* **66**, 543 (1994)
cis-m-Chlorophenol	279.54	*JPC* **88**, 5180 (1984)
1,2-(Dimethoxy-d_6)benzene	279.59	*JACS* **111**, 1958 (1989)
m-Chlorophenol	279.63	*AC* **57**, 1186 (1985)
p-Dichlorobenzene	279.81	*JPC* **93**, 101 (1989)
1,2-Dimethoxybenzene	279.81	*JACS* **111**, 1958 (1989)
o-Dimethoxybenzene (veratrole)	279.81	*AC* **66**, 543 (1994)
Benzoic acid dimer	279.93	*JPC* **94**, 4394 (1990)
Homovanillic acid	280.01	*AC* **66**, 543 (1994)
Catechol	280.52	*AC* **66**, 543 (1994)
1-Ethyl-4-methoxybenzene	281.11	*JACS* **111**, 1958 (1989)
Acetophenone	282.47	*JCP* **85**, 2365 (1986)
1-Methoxy-4-methylbenzene	282.48	*JACS* **111**, 1958 (1989)
p-Methylanisole	282.49	*AC* **66**, 543 (1994)
p-Cresol	282.98	*AC* **66**, 543 (1994)
Uracil(diketo tautomer)	283.38	*CPL* **126**, 583 (1986)
Biphenyl	283.62	*JCP* **88**, 7337 (1988)
Diphenylacetylene (tolane)	283.70	*JPC* **88**, 1711 (1984)
Indole	283.78	*JCP* **91**, 6013 (1989)
7-Methylindole	283.91	*JPC* **91**, 1375 (1987)
2-Methylindole	284.33	*JCP* **88**, 6146 (1988)

(*continues on next page*)

Table 2 (*Continued*).

Molecule	Wavelength	Reference
α-Methylstyrene	285.20	*JPC* **94**, 6692 (1990)
3-Indole acetic acid	285.40	*JCP* **84**, 6539 (1986)
3-Indole propionic acid	285.88	*JCP* **88**, 6146 (1988)
Tryptophol	285.93	*JCP* **88**, 6146 (1988)
3-Propionic acid	286.00	*JCP* **84**, 6539 (1986)
n-Acetyl-tryptophan amide	286.08	*JCP* **92**, 51 (1990)
n-Acetyl-tryptophan	286.30	*JCP* **92**, 51 (1990)
Tryptamine-d_3	286.34	*JCP* **91**, 5278 (1989)
Tryptamine	286.39	*JCP* **84**, 6539 (1986)
3-Methylindole	286.68	*JPC* **98**, 12834 (1994)
Tryptophan methyl ester	286.71	*JCP* **92**, 51 (1990)
Tryptophan	286.75	*JCP* **83**, 4819 (1985)
2,3-Dimethylindole	287.05	*JPC* **94**, 582 (1990)
p-Chlorophenol	287.17	*AC* **57**, 1186 (1985)
Tryptophan dimethyl amide	287.30	*JCP* **92**, 51 (1990)
1,2,3,4-Tetrahydrocarbazole	287.41	*JPC* **91**, 1375 (1987)
1,3-Benzodioxole	287.45	*CPL* **157**, 183 (1989)
Styrene	287.53	*JPC* **93**, 3470 (1989)
Pyridine(n–π^*)	287.55	*JPC* **92**, 5393 (1988)
Tryptophan amide	287.97	*JCP* **92**, 51 (1990)
trans-3-Fluorostyrene	288.34	*JMS* **136**, 31 (1989)
7-Azaindole-d_1	288.71	*JPC* **94**, 3531 (1990)
7-Azaindole	288.73	*JPC* **94**, 3531 (1990)
trans-β-Methylstyrene	289.13	*JPC* **99**, 4386 (1995)
1-Methylindole	289.47	*JPC* **91**, 1375 (1987)
cis-3-Fluorostyrene	290.64	*JMS* 1**36**, 31 (1989)
4-Ethylstyrene	290.80	*JPC* **93**, 3470 (1989)
5-Methylindole	291.10	*JPC* **91**, 1375 (1987)
trans-2-Fluorostyrene	291.19	*CPL* **154**, 14 (1989)
o-Toluidine	291.30	*AC* **57**, 59 (1985)
1,2,4,5-Tetrachlorobenzene	292.16	*JPC* **94**, 2631 (1990)
anti-3-Methylstyrene	292.27	*JPC* **93**, 3470 (1989)
p-Amino benzoic acid	292.63	*JCP* **92**, 7625 (1990)
syn-3-Methyl-d_3-styrene	293.11	*JPC* **93**, 3470 (1989)
syn-3-Methylstyrene	293.37	*JPC* **93**, 3470 (1989)
o-Methylstyrene	293.56	unpublished
Aniline	293.80	*CPL* **74**, 533 (1980)
Fluorene-d_{10}	294.97	*JPC* **94**, 2631 (1990)
cis-p-Dimethoxybenzene	295.41	*AC* **66**, 543 (1994)
m-Toluidine	295.70	*AC* **57**, 59 (1985)
m-Chlorostyrene	295.99	unpublished
Dibenzo-*p*-dioxine	296.09	*JMS/IP* **145**, 97 (1995)
Fluorene-h_{10}	296.09	*JPC* **94**, 2631 (1990)
2,5-Diphenyldiazole	296.64	*CPL* **133**, 214 (1987)
Fluorene-d_{10} dimer	296.98	*JPC* **94**, 2631 (1990)
Dibenzofuran	297.22	*CP* **103**, 163 (1986)
trans-p-Dimethoxybenzene	297.34	*CPL* **125**, 1 (1986)
Fluorene dimer	298.02	*JPC* **92**, 5693 (1988)
9-Ethylfluorene	298.06	*JPC* **92**, 5693 (1988)

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Table 2 (*Continued*).

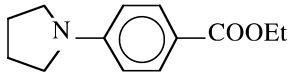
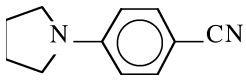
Molecule	Wavelength	Reference
c*is*-Hydroquinone	298.21	*AC* **66**, 543 (1994)
trans-Hydroquinone	298.52	*AC* **66**, 543 (1994)
4-Aminobenzonitrile	298.57	*CPL* **146**, 270 (1988)
Ethylfluorene	300.00	*CP* **103**, 163 (1986)
9-Ethylfluorene dimer	300.12	*JPC* **92**, 5693 (1988)
N-Methylanliline	300.30	*AC* **58**, 3242 (1986)
5-Methoxyindole	301.79	*JPC* **91**, 1375 (1987)
p-Toluidine	302.40	*AC* **57**, 61 (1985)
2,7-Dichlorodibenzo-*p*-dioxin	304.83	*JMS/IP* **145**, 97 (1995)
PYRBEE	304.88	*CPL* **145**, 273 (1988)
		
2,8-Dichlorodibenzo-*p*-dioxin	305.54	*JMS/IP* **145**, 97 (1995)
2-Monochlorodibenzo-*p*-dioxin	305.80	*JMS/IP* **145**, 97 (1995)
trans-Stilbene	310.10	*JPC* **88**, 4214 (1984)
Naphthalene-d_8	311.16	*JPC* **94**, 737 (1990)
Naphthalene trimer(D,D,D)	311.83	*JPC* **94**, 737 (1990)
PYRBN	312.21	*CPL* **145**, 273 (1988)
		
Naphthalene	312.30	*JCP* **73**, 2019 (1980)
Naphthalene dimer(D,D)	312.55	*JPC* **94**, 737 (1990)
Naphthalene trimer(D,H,D)	312.85	*JPC* **94**, 737 (1990)
Naphthalene trimer(H,D,H)	312.86	*JPC* **94**, 737 (1990)
Naphthalene trimer(H,H,H)	312.96	*JPC* **94**, 737 (1990)
Isoquinoline(π–π^*)	313.19	*CPL* **94**, 454 (1983)
2,3-Dichlorodibenzo-*p*-dioxin	313.36	*CS* **29**, 1877 (1994)
Naphthalene dimer(H,D)	313.52	*JPC* **94**, 737 (1990)
Naphthalene dimer(H,H)	313.64	*JPC* **94**, 737 (1990)
1-Fluoronaphthalene	313.81	*JCP* **90**, 1362 (1989)
Naphthalene pentamer	313.80	*JCP* **89**, 5962 (1988)
Naphthalene tetramer	313.87	*JCP* **89**, 5962 (1988)
2-Fluoronaphthalene	314.46	*JCP* **87**, 269 (1987)
1-Methylnaphthalene	314.73	*JCP* **80**, 1786 (1984)
4-Methyl-*trans*-stilbene	314.73	*CPL* **125**, 5 (1986)
trans-2-Ethylnaphthalene	314.97	*JSSJ* **34**, 86 (1985)
4-Ethyl-*trans*-stilbene	315.02	*CPL* **125**, 5 (1986)
1,1′-Binaphthyl	315.09	*JCP* **84**, 1573 (1984)
4-*n*-Propyl-*trans*-stilbene	315.32	*CPL* **125**, 5 (1986)
2-Methylnaphthalene	315.41	*JCP* **87**, 269 (1987)
4-Chloro-*trans*-stilbene	315.78	*JCP* **81**, 2330 (1984)
1-Chloronaphthalene	316.74	*CPL* **127**, 292 (1986)
Acenaphthene	317.59	*AC* **58**, 487 (1986)
1,2-Dimethylnaphthalene	317.73	*JCP* **102**, 4715 (1995)
1-Cyanonaphthalene	318.16	*CPL* **140**, 587 (1987)

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Table 2 (*Continued*).

Molecule	Wavelength	Reference
2-Chloronaphthalene	318.26	*CPL* **127**, 292 (1986)
2,5-Diphenyloxazole	318.71	*CPL* **133**, 214 (1987)
Phenyl-4-[(4′-cyano-1′-naphthyl)methyl] piperidine	320.28	*CPL* **140**, 587 (1987)
2,2′-Bithiophene	321.45	*JPC* **98**, 12893 (1994)
Pyrimidine(n–π*)	321.82	*CPL* **135**, 330 (1987)
Uracil(enol-keto tautomer)	323.45	*CPL* **126**, 583 (1986)
trans-2-Naphthol	323.57	*JPC* **88**, 5180 (1984)
Pyrazine($S_0 \rightarrow S_1$)	323.88	*JCP* **86**, 4471 (1987)
syn-Triazine	323.94	*JCP* **75**, 5271 (1981)
Pyrazine dimer	324.15	*JCP* **85**, 777 (1986)
Isoquinoline(n–π*)	324.45	*JCP* **86**, 6707 (1987)
Carbazole	325.80	*CP* **103**, 164 (1986)
2,5-Diphenylfuran	326.56	*CPL* **133**, 214 (1987)
cis-2-Naphthol	326.94	*JPC* **88**, 5180 (1984)
1-Azacarbazole	329.62	*JPC* **90**, 2309 (1986)
3-Cyclopenten-1-one	330.81	*JCP* **102**, 7789 (1995)
Methylsalicylate	332.75	*JCP* **75**, 5201 (1981)
Carbazole dimer	332.81	*CP* **138**, 413 (1989)
1-Aminonaphthalene	332.85	*JCP* **104**, 3935 (1996)
Acetaldehyde	335.92	*AC* **64**, 2604 (1992)
Ethylcarbazole	338.50	*CP* **103**, 163 (1986)
Phenanthrene-d_{10}	339.89	*CP* **102**, 323 (1986)
Phenanthrene	340.97	*CP* **102**, 323 (1986)
2-Naphthylamine	345.1	*AC* **57**, 59 (1985)
all-trans-Decatetraene	345.27	*JCP* **102**, 4726 (1995)
all-trans-Nonatetraene	345.41	*JCP* **102**, 4726 (1995)
trans,trans-Octatetraene	345.44	*JCP* **102**, 4726 (1995)
1-Azacarbazole dimer	350.19	*JPC* **90**, 2309 (1986)
3-Hydroxyflavone	356.02	*CP* **136**, 181 (1989)
Anthracene-d_{10}	360.16	*JPC* **88**, 4214 (1984)
Anthracene	361.08	*JCP* **81**, 2209 (1984)
1-Methylanthracene	363.95	*AC* **58**, 2825 (1987)
2-Methylanthracene	365.07	*JACS* **109**, 32 (1987)
2-Chloroanthracene	367.09	*AC* **59**, 419 (1987)
1-Chloroanthracene	367.31	*AC* **59**, 419 (1987)
Pyrene	367.44	*CPL* **133**, 222 (1987)
p-Fluorobenzaldehyde	367.55	*JPC* **94**, 5786 (1990)
Phenyl nitrene	368.42	*CPL* **150**, 249 (1988)
p-Methylbenzaldehyde	369.26	*JPC* **94**, 5786 (1990)
Tropolone-d	369.43	*JCP* **92**, 2790 (1990)
Tropolone	370.13	*JCP* **92**, 2790 (1990)
3-Isopropyltropolone-d	370.66	*JCP* **92**, 2790 (1990)
9-(3′-Fluorophenyl)anthracene	370.77	*ACS* **109**, 32 (1987)
2-Phenylanthracene	370.80	*ACS* **109**, 32 (1987)
9-(3′-Methylphenyl)anthracene	371.07	*JACS* **109**, 32 (1987)
9-(4′-Fluorophenyl)anthracene	371.10	*JACS* **109**, 32 (1987)
2-Methylpyrazine	371.13	*CPL* **129**, 339 (1986)
9-Phenylanthracene	371.14	*JACS* **109**, 32 (1987)

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Table 2 (*Continued*).

Molecule	Wavelength	Reference
9-Methylanthracene	371.15	*JPC* **88**, 4214 (1984)
9-Phenylanthracene-d_5	371.20	*JACS* **109**, 32 (1987)
4-Isopropyltropolone-d	371.24	*JCP* **92**, 2790 (1990)
3-Isopropyltropolone	371.47	*JCP* **92**, 2790 (1990)
Benzaldehyde	371.48	*JPC* **94**, 5786 (1990)
o-trans-m-Methylbenzaldehyde	371.50	*JPC* **94**, 5786 (1990)
9-(4′-Methylphenyl)anthracene	371.53	*JACS* **109**, 32 (1987)
o-cis-m-Methylbenzaldehyde	371.61	*JPC* **94**, 5786 (1990)
4-Isopropyltropolone	371.91	*JCP* **92**, 2790 (1990)
5-Isopropyltropolone	371.91	*JCP* **92**, 2790 (1990)
9-(2′-Naphthol)anthracene	372.62	*JACS* **109**, 32 (1987)
Pyrazine($S_0 \rightarrow T_1$)	372.8	*JPC* **92**, 5079 (1988)
9-Hexylanthracene	373.03	*JCP* **82**, 2896 (1985)
9-Chloroanthracene	373.25	*AC* **59**, 419 (1987)
9-Methoxyanthracene	373.40	*CPL* **153**, 112 (1988)
o-trans-m-Fluorobenzaldehyde	374.10	*JPC* **94**, 5786 (1990)
9-Bromoanthracene	374.20	*JPC* **88**, 4214 (1984)
o-cis-m-Fluorobenzaldehyde	374.32	*JPC* **94**, 5786 (1990)
Pyridazine	375.25	*JCP* **86**, 6707 (1987)
o-cis-o-Methylbenzaldehyde	375.36	*JPC* **94**, 5786 (1990)
9-Vinylanthracene	377.46	*JACS* **109**, 32 (1987)
p-Fluorobenzophenone	379.15	*JPC* **90**, 5615 (1986)
o-trans-o-Fluorobenzaldehyde	379.78	*JPC* **94**, 5786 (1990)
Benzophenone	381.04	*JPC* **90**, 5615 (1986)
9-Cyanoanthracene	382.10	*JPC* **88**, 4214 (1984)
Propynal (CH=CCHO)	382.22	*JCP* **84**, 3014 (1986)
9,10-Dimethylanthracene	382.52	*AC* **58**, 2152 (1986)
o-trans-o-Methylbenzaldehyde	382.78	*JPC* **94**, 5786 (1990)
2-Acetylanthracene	385.31	*CPL* **134**, 255 (1987)
9,10-Dichloroanthracene	385.35	*JPC* **88**, 4214 (1984)
9,10-Dibromoanthracene	386.45	*JPC* **88**, 4214 (1984)
Benzo[a]pyrene	395.80	*JPC* **91**, 570 (1987)
Fluoranthene	396.56	*JCP* **82**, 4771 (1985)
9,10-Dicyanoanthracene	397.84	*CPL* **140**, 447 (1987)
2-Methylcyclohexanone	398.7	*AC* **64**, 2605 (1992)
Furan	405.26	*JCP* **87**, 4435 (1987)
Oxalyl chloride	410.02	*JPC* **100**, 3354 (1996)
Perylene	415.45	*JPC* **88**, 4214 (1984)
Coronene-d_{12}	418.90	*PC* **91**, 4710 (1987)
Coronene	420.03	*JPC* **90**, 5029 (1986)
p-Difluorobenzene cation	420.98	*CPL* **168**, 173 (1990)
Tetracene	446.37	*JPC* **94**, 4025 (1990)
5-Phenyltetracene	456.03	*JPC* **94**, 4025 (1990)
5-Naphthyltetracene	456.58	*JPC* **94**, 4025 (1990)
1,3,5-Trifluorobenzene cation	457.27	*JCP* **90**, 6965 (1989)
5,12-Diphenyltetracene	464.63	*PC* **94**, 4025 (1990)
Ovalene	466.22	*CPL* **69**, 14 (1980)
1-Aminoanthraquinone-d_2	470.28	*JPC* **93**, 2337 (1989)
1-Aminoanthraquinone	472.07	*JPC* **93**, 2337 (1989)

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Table 2 (*Continued*).

Molecule	Wavelength	Reference
Quinizarin	502.03	*CPL* **109**, 1 (1984)
Pentacene	536.90	*CPL* **72**, 21 (1980)
Aminotetrazine	543.15	*JCP* **91**, 7302 (1989)
s-Tetrazine(n–π*)	551.72	*JPC* **91**, 2526 (1987)
Porphin	612.75	*CPL* **88**, 131 (1982)
Phthalocyanine	660.85	*JCP* **74**, 6612 (1981)
Azulene	700.08	*JPC* **91**, 3537 (1987)
Trifluoronitrosomethane	717.89	*CPL* **135**, 534 (1987)

JCP *Journal of Chemical Physics*
JPC *Journal of Physical Chemistry*
CPL *Chemical Physics Letters*
CP *Chemical Physics*
AC *Analytical Chemistry*
JACS *Journal of American Chemical Society*
JMS *Journal of Molecular Spectroscopy*
SCA *Spectrochimica Acta*
JMS/IP *International Journal of Mass Spectrometry and Ion Processes*
CS *Chemosphere*