Advances in Infrared and Raman Spectroscopy

VOLUME 1

Edited by
R.J.H. Clark and R.E. Hester

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R. J. H. CLARK
University College London

R. E. HESTER
University of York

LIST OF CONTRIBUTORS

R. J. H. CLARK, Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom (p. 143)

J. R. DOWNEY Jr., Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181, U.S.A. (p. 1)

B. G. FRUSHOUR, Monsanto Triangle Park Development Center, Inc., Research Triangle Park, North Carolina 27709, U.S.A. (p. 35)

G. J. JANZ, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181, U.S.A. (p. 1)

J. L. KOENIG, Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A. (p. 35)

T. M. LOEHR, Oregon Graduate Center, Beaverton, Oregon 97005, U.S.A. (p. 98)

N. MOHAN, Institute of Chemistry, University of Dortmund, 46 Dortmund, W. Germany (p. 173)

A. MÜLLER, Institute of Chemistry, University of Dortmund, 46 Dortmund, W. Germany (p. 173)

K. NAKAMOTO, Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233, U.S.A. (p. 173)

T. G. SPIRO, Department of Chemistry, Princeton University, Princeton, N.J. 08540, U.S.A. (p. 98)

D. STEELE, Department of Chemistry, Royal Holloway College, Egham, Surrey, TW20 0EX, United Kingdom (p. 232)

PREFACE

There are few areas of science which have not already benefited from the application of infrared spectroscopic methods, and progress in this field remains vigorous. Closely related information on chemical and biological materials and systems is obtainable from Raman spectroscopy, though there also are many important differences between the types of information yielded and the types of materials and systems best suited to study by each technique. The close relationship between these two sets of spectroscopic techniques is explicitly recognised in this Series. Advances in Infrared and Raman Spectroscopy contains critical review articles, both fundamental and applied, mainly within the title areas; however, we shall extend the coverage into closely related areas by giving some space to such topics as neutron inelastic scattering or vibronic fluorescence spectroscopy. Thus the Series will be firmly technique orientated. Inasmuch as these techniques have such wide ranging applicability throughout science and engineering, however, the coverage in terms of topics will be wide. Already in the first volume we have articles ranging from the fundamental theory of infrared band intensities through the development of computer-controlled spectrometer systems to applications in biology. This integration of theory and practice, and the bringing together of different areas of academic and industrial science and technology, constitute major objectives of the Series.

The reviews will be in those subjects in which most progress is deemed to have been made in recent years, or is expected to be made in the near future. The Series will appeal to research scientists and technologists as well as to graduate students and teachers of advanced courses. The Series is intended to be of wide general interest both within and beyond the fields of chemistry, physics and biology.

The problem of nomenclature in a truly international Series has to be acknowledged. We have adopted a compromise solution of permitting the use of either English or American spelling (depending on the origin of the review article) and have recommended the use of SI Units. A table on the international system of units is given on p. xi for reference purposes.

August 1975

R. J. H. CLARK
R. E. HESTER

THE INTERNATIONAL SYSTEM OF UNITS (SI)

Physical quantity	Name of unit	Symbol for unit
SI Base Units		
length	metre	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
thermodynamic temperature	kelvin	K
amount of substance	mole	mol
SI Supplementary Units		
plane angle	radian	rad
solid angle	steradian	sr
SI Derived Units having Special Names and Symbols		
energy	joule	$J = m^2\,kg\,s^{-2}$
force	newton	$N = m\,kg\,s^{-2} = J\,m^{-1}$
pressure	pascal	$Pa = m^{-1}\,kg\,s^{-2} = N\,m^{-2} = J\,m^{-3}$
power	watt	$W = m^2\,kg\,s^{-3} = J\,s^{-1}$
electric charge	coulomb	$C = s\,A$
electric potential difference	volt	$V = m^2\,kg\,s^{-3}\,A^{-1} = J\,A^{-1}\,s^{-1}$
electric resistance	ohm	$\Omega = m^2\,kg\,s^{-3}\,A^{-2} = V\,A^{-1}$
electric conductance	siemens	$S = m^{-2}\,kg^{-1}\,s^3\,A^2 = \Omega^{-1}$
electric capacitance	farad	$F = m^{-2}\,kg^{-1}\,s^4\,A^2 = C\,V^{-1}$
magnetic flux	weber	$Wb = m^2\,kg\,s^{-2}\,A^{-1} = V\,s$
inductance	henry	$H = m^2\,kg\,s^{-2}\,A^{-2} = V\,s\,A^{-1}$
magnetic flux density	tesla	$T = kg\,s^{-2}\,A^{-1} = V\,s\,m^{-2}$
frequency	hertz	$Hz = s^{-1}$

SOME NON-SI UNITS

Physical quantity	Name of unit	Symbol and definition

Decimal Multiples of SI Units, Some having Special Names and Symbols

length	ångström	$\text{Å} = 10^{-10}\,\text{m} = 0.1\,\text{nm}$ $= 100\,\text{pm}$
length	micron	$\mu\text{m} = 10^{-6}\,\text{m}$
area	are	$\text{a} = 100\,\text{m}^2$
area	barn	$\text{b} = 10^{-28}\,\text{m}^2$
volume	litre	$\text{l} = 10^{-3}\,\text{m}^3 = \text{dm}^3$ $= 1000\,\text{cm}^3$
energy	erg	$\text{erg} = 10^{-7}\,\text{J}$
force	dyne	$\text{dyn} = 10^{-5}\,\text{N}$
force constant	dyne per centimetre	$\text{dyn cm}^{-1} = 10^{-3}\,\text{N m}^{-1}$
force constant	millidyne per ångström	$\text{mdyn Å}^{-1} = 10^{2}\,\text{N m}^{-1}$
force constant	attojoule per ångström squared	$\text{aJ Å}^{-2} = 10^{2}\,\text{N m}^{-1}$
pressure	bar	$\text{bar} = 10^{5}\,\text{Pa}$
concentration	—	$\text{M} = 10^{3}\,\text{mol m}^{-3}$ $= \text{mol dm}^{-3}$

Units Defined Exactly in Terms of SI Units

length	inch	$\text{in} = 0.0254\,\text{m}$
mass	pound	$\text{lb} = 0.453\,592\,27\,\text{kg}$
force	kilogram-force	$\text{kgf} = 9.806\,65\,\text{N}$
pressure	standard atmosphere	$\text{atm} = 101\,325\,\text{Pa}$
pressure	torr	$\text{Torr} = 1\,\text{mmHg}$ $= (101\,325/760)\,\text{Pa}$
energy	kilowatt hour	$\text{kWh} = 3.6 \times 10^{6}\,\text{J}$
energy	thermochemical calorie	$\text{cal}_{\text{th}} = 4.184\,\text{J}$
thermodynamic temperature	degree Celsius[a]	$°\text{C} = \text{K}$

[a] Celsius or "Centigrade" temperature θ_C is defined in terms of the thermodynamic temperature T by the relation $\theta_C/°\text{C} = T/\text{K} - 273.15$.

OTHER RELATIONS

1. The physical quantity, the wavenumber (units cm^{-1}), is related to frequency as follows:

$$cm^{-1} \approx (2.998 \times 10^{10})^{-1} \, s^{-1}$$

2. The physical quantity, the molar decadic absorption coefficient (symbol ε) has the SI units $m^2 \, mol^{-1}$. The relation between the usual non-SI and SI units is as follows:

$$M^{-1} \, cm^{-1} = 1 \, mol^{-1} \, cm^{-1} = 10^{-1} \, m^2 \, mol^{-1}$$

The SI Prefixes

Fraction	Prefix	Symbol	Multiple	Prefix	Symbol
10^{-1}	deci	d	10^1	deca	da
10^{-2}	centi	c	10^2	hecto	h
10^{-3}	milli	m	10^3	kilo	k
10^{-6}	micro	μ	10^6	mega	M
10^{-9}	nano	n	10^9	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f	10^{15}	peta	P
10^{-18}	atto	a	10^{18}	exa	E

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Chapter 1

DIGITAL METHODS IN RAMAN SPECTROSCOPY

J. R. Downey Jr. and G. J. Janz

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181, U.S.A.

1 INTRODUCTION

The resurgence of Raman spectroscopy in the 1960s has generally been attributed to the development of reliable laser excitation sources. Coupled with the development of these powerful monochromatic sources has been the rapid development of photoelectric recording Raman instruments. During the same time period great strides have been made in the development of digital computers such that they are now readily available (or accessible) to most chemical laboratories. Thus, while as recently as 15 years ago neither was routinely available, many chemical laboratories today have both a photoelectric Raman instrument and a digital computer. The prospect of coupling these two machines has been evident for some time and comprises the subject matter for this chapter.

Our approach generally will be to point out the advantages and problems of coupling a computer to a Raman spectrometer and to discuss the hardware and software necessary to effect the interface. We do not intend this to be a critical review of the field although we will discuss specific Raman–computer interfaces with regard to their advantages and disadvantages.

The discussion will first center on what use may be made of computers in Raman spectroscopy and will then move onto the hardware and software considerations necessary to establish the linkage. Then a brief review will be given of existing Raman–computer interfaces followed by a detailed description of the system in use at Rensselaer Polytechnic Institute.

2 USES OF DIGITAL METHODS IN RAMAN SPECTROSCOPY

2.1 General

Why is it desirable to couple a computer to a Raman spectrometer? What can one do with the resulting system that cannot be done otherwise? Of what

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use is the computer to a Raman spectroscopist? These are the subjects that will be addressed in this section.

Three general uses of digital computers may be defined with regard to most experiments. They are:

(i) to acquire, average and store data;
(ii) to control the experiment;
(iii) to perform data evaluation or reduction including some means of display.

The first two functions are generally performed under active computer control, i.e. on-line, while the data evaluation step may be performed off-line at a later date. Indeed, the very potent potential of the computer to perform rapid data evaluation seems to be the primary purpose for coupling the computer to a Raman instrument.

2.2   Acquisition, Averaging and Storage of Data

It is this element that usually serves as a deterrent to most people interested in instituting an interface. One method of accomplishing this portion of the system is simply to read the chart recording visually and convert it to a point by point list of intensity versus frequency which may then be manually entered into the computer via teletype, paper punched tape or punched cards. This is, of course, a very trivial and time consuming method and makes no use of the computer for acquiring data. A more advanced method is desirable.

Since many Raman instruments scan at a fixed rate the frequency scale may be entered simply by entering the initial frequency, final frequency (or length of scan), and the increment at which points are taken (or total number of points). These three values may be conveniently entered into the computer via a teletype. The intensity values must generally be entered via some sort of automated process.

One simple way to do this is to feed the analog signal from the chart recorder (or detector output) to an analog to digital converter (ADC) which will digitize the signal at a fixed time interval. The output of the ADC can then be fed automatically to the computer and stored in core. Systems based on this principle are in wide use with a variety of instruments using either commercial ADCs or homemade devices built around digital voltmeters.[1-3]

The system described above is applicable to virtually any instrument whose analog output varies as a function of time. A slightly simpler system is possible with Raman spectrometers that use photon counting as a means of detection. In this case the signal is already digitized and one need merely count pulses for a specified period of time, transfer the number of pulses into core, reset the counter and count again for the next data point. Commercial scalars (ratemeters) are available to perform the counting step and this system has been widely used for Raman instruments.[4-10]

All known Raman–computer interfaces utilize one of the above methods of acquiring the intensity data. Since scan times are generally slow in Raman spectroscopy the rate of data point collection rarely exceeds a few points per second. Thus it is possible to dispense with the computer entirely during collection and simply allow a teletype to punch a paper tape with the corresponding information.[9] The data may then be input to the computer at a later time for evaluation. Some versatility is lost by this procedure but it is adequate in some cases.

Some means of permanent data storage must be provided since the computer core or disk can serve only as a limited temporary storage medium. Common means employed have been paper punched tape, magnetic tape or punched cards. Magnetic tape seems to be preferable but either of the others is satisfactory.

One big advantage of using a computer to acquire data is the possibility of improving the signal to noise ratio (SNR) during collection as shown in Fig. 1. There are several approaches to this problem. One of the most common is simply to collect the same spectrum a number of times and instruct the computer to average these spectra together point by point. This method, usually known as computer averaging of transients (CAT), has been in wide use in NMR spectroscopy for a number of years and is equally applicable to Raman spectroscopy. It is well known that the SNR increases as $\sqrt{N}$ where N is the number of scans that are averaged. Thus the largest improvement takes place in the first few averages.

Another method that can be used with photon counting instruments is to simply count for a longer period of time for each point. Since the SNR increases as $\sqrt{c}$ where c is the total number of counts a significant smoothing of the spectrum results at long count times (high number of counts). This is particularly easy to implement on Raman instruments which use a stepping motor for the monochromator drive rather than a continuous scan motor.

2.3 Experiment Control

In addition to collecting data a computer may also be used to control the course of the Raman experiment. Most systems in use provide, at a minimum, a means for the computer to start the scanning mechanism of the monochromator to ensure that the computer and spectrometer are synchronized during data collection. This can be effected by a simple relay switch activated through a pulse from the computer.

A somewhat more sophisticated control is to allow the computer to reset the instrument to the initial frequency at the end of a scan so that it can average scans without the operator resetting the spectrometer. Since this normally requires scanning past the initial frequency and approaching in a forward direction to remove backlash, it may require scanning through the exciting line. Accordingly it is desirable to have a shutter under the control of the computer as a safeguard for the detector.[7,11]

If the computer is allowed to reset the monochromator drive mechanism it is necessary to ensure that it is precisely reset to the original starting frequency. If not, the peaks in the resulting averaged spectrum will be broadened due to the variation in starting frequency. With monochromators driven by a stepping motor this represents no problem since the computer can easily count steps and reposition to precisely the step desired. With continuous drive monochromators problems arise because merely timing the forward and reverse scans may not be sufficient to ensure adequate reproducibility. In general it is necessary to provide some means of encoding the frequency scale (shaft encoders) so the computer can determine the exact frequency at all times. Frequency/wavelength encoding mechanisms for accomplishing this task have been described.[12,13]
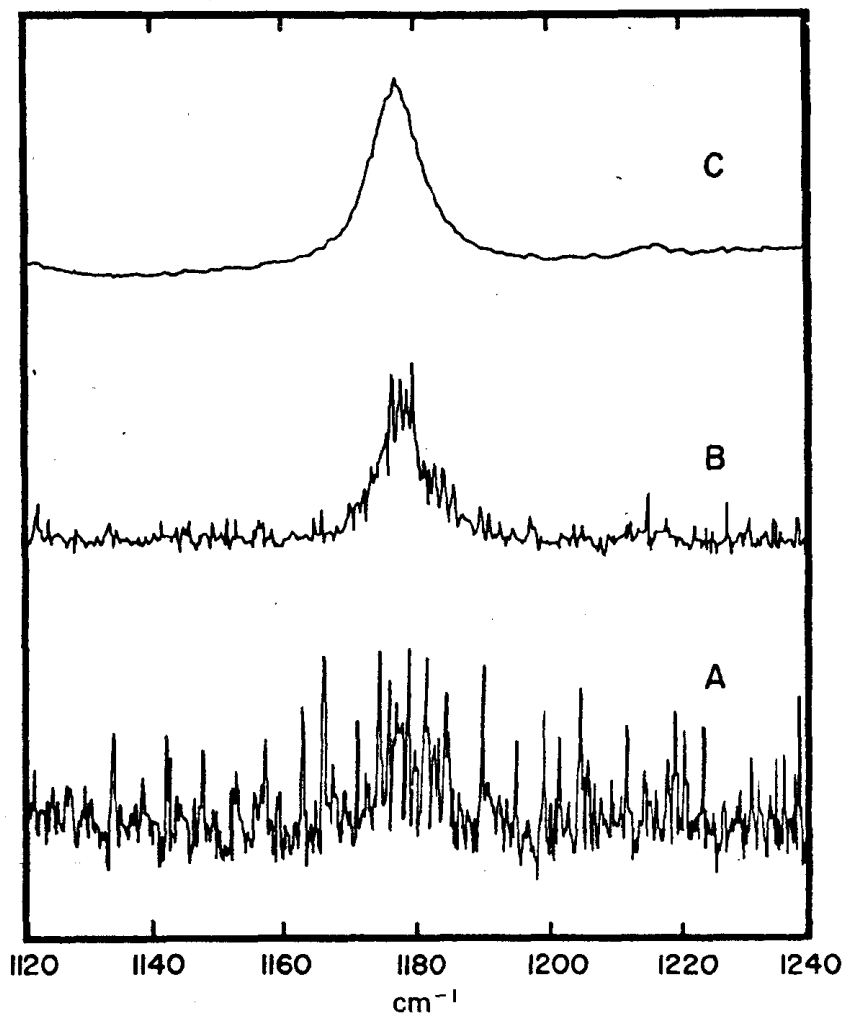

Fig. 1. Computer Averaging of Transients. The increase in signal to noise ratio via computer averaging of transients is illustrated for the 1178 cm^{-1} line of benzene in CCl$_4$ (3.5×10^{-3} M).[4]
A = single scan; B = average of 50 scans; C = average of 900 scans.

Other possible control functions include rotation of half wave plates or analyzers for depolarization ratio measurements as well as on–off functions for other filters, magnetic fields, electric fields, etc.[7] One may also program a sample changer for routine analyses.

2.4 Data Evaluation and Analysis

It is in the area of data evaluation that the computer is probably of most use to the Raman spectroscopist. There are many corrections which should be made to the raw data that have not been made in the past because of lack of a rapid, convenient means to do so. The computer now provides a powerful method of effecting these data manipulations. The topics considered below represent areas of wide interest where a computer may be helpful.

2.4.1 Data Display

How many times has an otherwise perfectly good spectrum been re-run merely to display it in a slightly different manner? With the advent of digital storage of spectra it is easy to re-display the spectra in virtually any configuration with a proper display system. In Fig. 2 the re-display of the spectrum of Na_2S_4, achieved
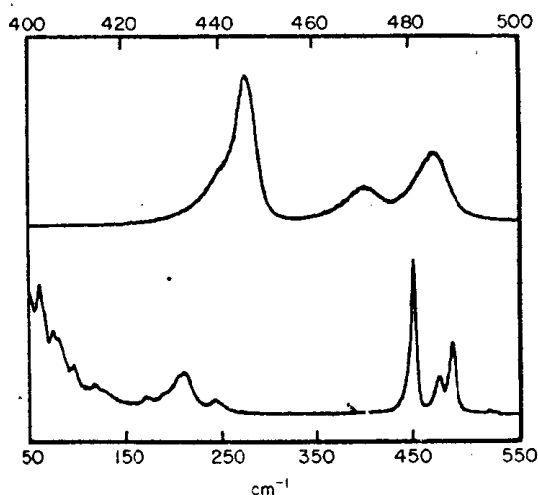

Fig. 2. Display. The spectrum of polycrystalline Na_2S_4 illustrating the versatility of a computer-controlled display system to accomplish various displays. The figure was produced in less than 10 seconds using the RPI CASH-DISPLAY system, see section 5 (laser = 5145 Å, 1.4 watt; slit = 3.5 cm^{-1}; spinning sample cell; digitizing increment = 0.2 cm^{-1}).

in this manner, is illustrated; thus the structural features of a small frequency region can be examined with a re-display of the spectrum, through computer-assisted techniques. The actual means of display, digital X—Y plotter, analog X—Y plotter or oscilloscope, is perhaps not as important as the ability to change scales via the controlling mechanism, the computer.

The display of at least two (preferably more) spectra simultaneously is highly desirable. In Fig. 3, the Raman spectrum for the 1050 cm^{-1} region of the nitrate ion has been displayed by computer control for a series of AgNO$_3$-acetonitrile
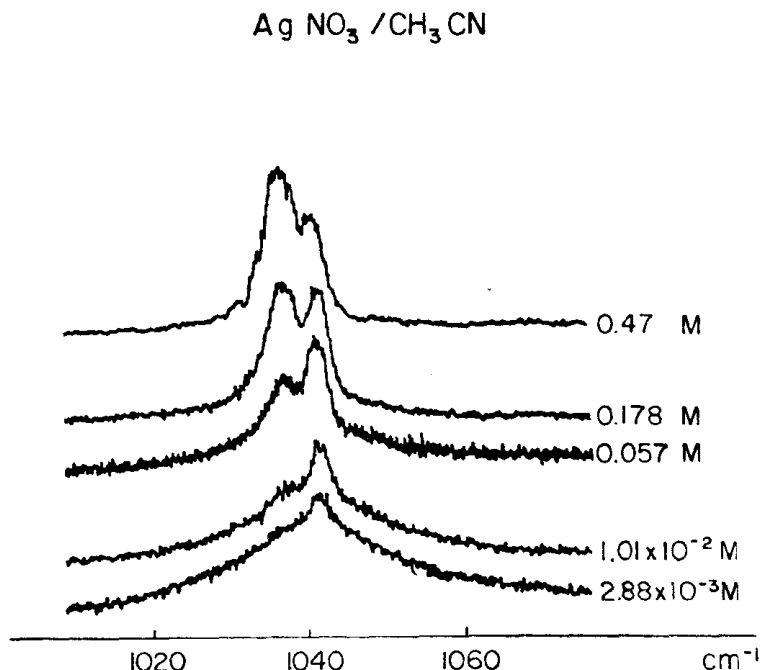

Fig. 3. Multiple display, concentration effects. The spectrum of the nitrate ion in AgNO$_3$/CH$_3$CN solutions illustrating the increase of the peak due to ion-paired nitrate (1037 cm^{-1}) relative to that for free nitrate (1042 cm^{-1}) as the concentration is increased (laser = 4880 Å, 1.3 watt; slit width = 3.5 cm^{-1}; room temperature, digitizing increment = 0.5 cm^{-1}). Figure produced by the RPI CASH-MULTI system, see section 5.

solutions of increasingly greater dilutions. Comparisons of the spectra for a series of structurally related compounds, or of temperature effects, as illustrated elsewhere in this work are readily achieved with such computer-assisted techniques.

2.4.2 Instrumental corrections

One area of interest in Raman spectroscopy is the comparison of absolute scattering intensities and the calculation of scattering coefficients.[14,15] In order to do this one must know the spectral sensitivity of the particular spectrometer used as a function of frequency and correct the raw data for this response. The instrumental response depends on such features as detection efficiency and grating efficiency. These generally vary as a function of frequency so the overall response of the instrument varies with frequency.

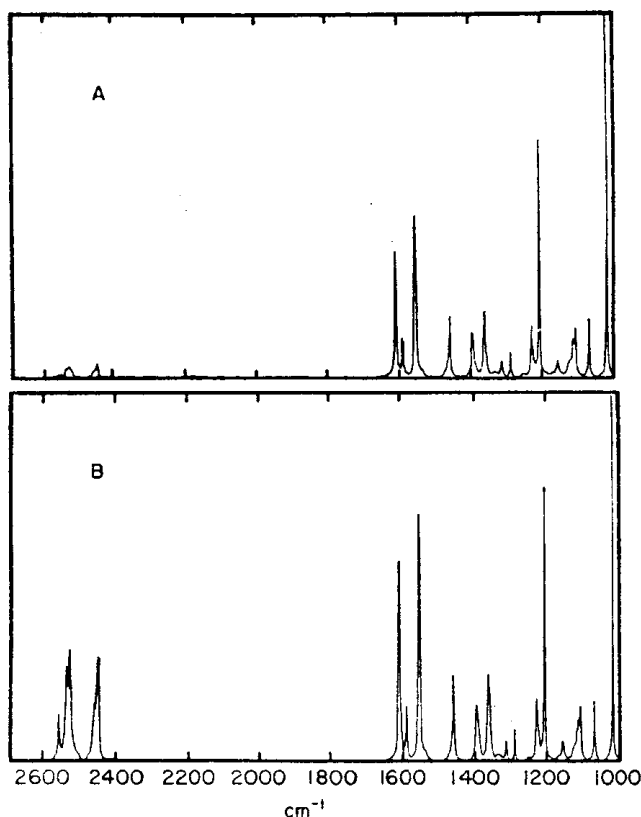It is a simple matter to measure the instrumental response using a standard

Fig. 4. Instrumental corrections. The Raman spectrum of indene illustrating the effect of instrumental corrections.[2] A = raw digitized spectrum; B = normalized intensity-corrected spectrum.

lamp.[2,4] The computer may then be programmed to correct the raw spectrum for the known instrumental response in order to obtain the true spectrum as shown in Fig. 4.

2.4.3 Isotropic–anisotropic spectra

One of the most powerful applications of Raman spectroscopy is in the area of structural determinations. It is possible to obtain some information about the symmetry of a molecule by studying the polarization characteristics of its Raman spectrum. In many cases a mere comparison of the so-called parallel and perpendicular polarized spectra is sufficient for this purpose. In other cases one would like to obtain the isotropic (which contains only totally symmetric vibrations) and anisotropic spectra. These are generally obtained as a linear combination of the experimentally obtainable parallel and perpendicular polarized spectra.[16] Using polarized exciting light and an analyzer to measure $I_{||}$ and $I_\perp$, isotropic ($\bar{\alpha}'^2$) and anisotropic (γ'^2) components are calculated as follows:

$$3\gamma'^2 = I_\perp$$
$$45\bar{\alpha}'^2 = I_{||} - 4/3 I_\perp$$