

Calculation of Polymer Blend Compositions from Vibrational Spectra: A Simple Method

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ABSTRACT: In this work, the application of a new approach for quantitative analysis, originally developed for Raman spectroscopy, is extended to IR spectroscopy. The attractive features of this methodology are its simplicity and ease of use in comparison with traditional approaches. Unlike other methods, rich spectral information containing several overlapped peaks can be used in the calculations. A robust and well-conditioned calculation scheme renders precise results, which are independent of the operator's decisions. The method was applied to study the chemical compositions of homogeneous polymer blends made of polystyrene and poly(vinyl methyl ether). Raman and IR blend spectra were acquired with confocal Raman microspectroscopy and attenuated total reflection/Fourier transform infrared, respectively. The blend compositions were calculated from the corresponding vibrational spectra with the proposed strategy, and excellent agreement between those values and the true ones was found for both techniques. © 2005 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 43: 1144–1151, 2005

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INTRODUCTION

Vibrational spectroscopies (i.e., Raman and IR) are among the most powerful tools for the examination of the phase structures and compositions of polymer blends. IR spectroscopy has been applied to studying aspects such as the polymer miscibility,^{1–4} segmental orientation,^{5–9} crystalline morphology,^{10,11} extent of interfacial reaction,^{12–14} polymer diffusion,^{15,16} and mapping of components.^{17–19} A vast body of literature is devoted to the study of interactions between components.^{20–24} Examples of Raman applications in some of these fields are listed in our previous publication.²⁵ These representative (but by no means comprehensive) examples illustrate the extensive use of these techniques for the

analysis of polymer blends, not only at the research level but also in routine applications.

This article concerns the methods of spectral processing employed when these techniques are applied to quantitative analysis, this being a very frequent situation. In these cases, we have to face the problem of determining the amounts of a given component in a blend from its composite spectrum. To translate the acquired raw spectral data into the quantitative variable of interest (i.e., chemical composition), mathematical manipulation of the data and the use of specific numerical techniques are usually required.

Extracting the significant information from the spectral data is in many circumstances a nontrivial task, even for intermediate-skilled operators. The primary information of interest for quantitative analysis is the band intensity, commonly associated with two parameters, the band height and the band area. The band height can be directly calculated from the spectrum as

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the peak maximum, but it is strictly related to the band intensity only for single isolated bands. If the spectrum is constituted of superimposed peaks, the overlapping of neighboring bands results in the fact that the actual band maximum is considerably less than the read (apparent) maximum, and this leads to lack of precision in calculations. In addition, inadequate baseline corrections can seriously affect this parameter.²⁶

Band areas are statistically more significant than band heights. They can be calculated from a complex spectrum composed of overlapped peaks with curve-fitting procedures.²⁷ This well-established method, sometimes called band deconvolution, consists of decomposing the spectral region into the constituent bands, with bell-shaped functions (Gaussian, Lorentzian, etc.) used to represent the contour of the vibrational peaks. A model spectrum is generated by the superpositioning of a pre-established number of such functions; to obtain the best fit, the differences between the model spectrum and the experimental data are minimized by the modification of the function parameters.

Other approaches have been proposed in the literature to resolve mixtures of components, those based on principal component analysis being the most remarkable.²⁸⁻³⁰ These powerful techniques (i.e., simplisma routines), based on self-modeling multivariate data analysis, are capable of extracting the spectra of pure components from a data set of mixtures without prior knowledge of the pure components.^{28,29} On the other hand, the application of these techniques requires skilled operators with extensive spectroscopic knowledge and user interaction; the calculations are complex, and the method requires specific software not accessible to standard users. In many ways, these techniques do not fall into the category of the simple methods explored here and are beyond the scope of this work.

Among the aforementioned techniques, the curve-fitting procedure is the preferred method for the quantitative analysis of vibrational spectra in standard applications. However, the approach has some drawbacks that make its use intricate. First, there are many steps in the procedure that depend on decisions made by the operator, such as (1) spectrum baseline corrections; (2) the type of function used to reproduce the band shapes; (3) the number of these functions used to generate the model spectrum; and (4) the input parameters, related to the positions and amplitudes of the pre-established functions,

used as seed values for the calculations. They are mostly determined by trial and error, and they are strongly dependent on the ability of the operator. Finally, because of the type of functions used to fit the vibrational peaks, the minimization problem for obtaining the optimum function parameters is nonlinear, and its solution is intricate and time-consuming.

A new approach for processing Raman spectra in quantitative analysis, the linear decomposition method (LDM), has recently been described,²⁵ and several applications for the analysis of polymer blends have been reported.³¹⁻³³ The method is based on generating a model spectrum in terms of a linear combination of discrete functions, represented by the spectra of the pure components. The coefficients of the linear expansion, obtained by least squares, are directly related to the contribution of each component in the mixture. The method is at least as precise as nonlinear curve fitting but remarkably simpler: the spectrum can be processed as acquired, without the need of baseline corrections; spectral information, including several vibrational bands, can be used for the calculations; and the calculation scheme leads to a linear problem that avoids complex calculations. No previous assumptions about the number of bands, band shapes, or peak parameters are required; in this sense, the methodology is completely independent of the operator's skills.

In previous work, the consistency and precision of the calculation scheme of LDM were thoroughly tested over a very wide range of acquisition conditions for the Raman spectroscopy.²⁵ In this work, the method is extended to IR spectroscopy to cover the spectrum of vibrational spectroscopies most commonly employed in scientific research and routine analysis. To show how it works, we studied homogeneous polymer blends made of polystyrene (PS) and poly(vinyl methyl ether) (PVME) with attenuated total reflection/Fourier transform infrared (ATR-FTIR) and Raman spectroscopy, and we analyzed their chemical composition with the proposed method.

PROPOSED METHODOLOGY

Fundamentals

A detailed explanation of LDM can be found elsewhere.²⁵ It is based on expanding linearly the

experimental spectrum of a blend with an unknown composition, in terms of the spectra of the pure components. The method, originally developed for Raman spectroscopy, can be readily extended to IR. To introduce the latter case, we start from a simple model that governs absorption spectroscopy (the Lambert–Beer law), which relates the logarithms of transmitted intensity (or absorbance for double-beam measurements) to the concentration of a given component. For pure components, we can write

$$A_i^p(\nu) = \log\left(\frac{I_{0,i}^p(\nu)}{I_i^p(\nu)}\right) = \left(\frac{\rho_i^p}{M}\right) \varepsilon_i(\nu) l_i^p \quad (1)$$

where $A_i^p(\nu)$ is the absorbance of the i component at frequency ν , $I_i(\nu)$ and $I_{0,i}(\nu)$ are the transmitted and incident intensities, ρ_i is the component concentration (g/L), M is the molar mass (g/mol), ε_i is the absorptivity coefficient, and l_i is the length of the optical path. The superscript p refers to properties of pure components. For a blend made of n components, the corresponding expression for the Lambert–Beer law can be written as follows:

$$A^b(\nu) = \log\left(\frac{I_0^b(\nu)}{I^b(\nu)}\right) = \sum_{i=1}^n \left(\frac{\rho_i^b}{M_i}\right) \varepsilon_i(\nu) l^b \quad (2)$$

where the meaning of the symbols is the same as before and the superscript b refers to properties in the blend. In writing eq. 2, we have assumed that the $\varepsilon_i(\nu)$ coefficients in the blend are the same as those in the pure state. This implies the absence of interactions between components that could affect $\varepsilon_i(\nu)$.

In single-beam measurements, the variable that we record is the transmitted intensity. In these cases, the blend and pure component spectra may be affected by different instrumental factors and/or background contributions, which have been explicitly included in our analysis. Here they are represented by individual I_0 factors (I_0^b for the blend and I_0^p for the pure components). Combining eqs. 1 and 2, we can express the transmitted intensity for the blend (I^b) as a function of the transmitted intensities for the pure components (I_i^p) and the instrumental/background contributions (I_0):

$$\log(I^b(\nu)) = \sum_{i=1}^n \left(\frac{\rho_i^b l^b}{\rho_i^p l_i^p}\right) \log(I_i^p(\nu)) - \sum_{i=1}^n \left(\frac{\rho_i^b l^b}{\rho_i^p l_i^p}\right) \log(I_{0,i}^p(\nu)) + \log(I_0^b(\nu)) \quad (3)$$

This can be written in a more compact form as follows:

$$\log(I^b(\nu)) = \sum_{i=1}^n \rho_i^b \sigma_i \log(I_i^p(\nu)) + P(\nu) \quad (4)$$

The σ_i factors only depend on instrumental/acquisition conditions but are independent of the blend composition. The P function includes all the instrumental/background contributions arising from the spectra of the blend and pure components. If the spectral range is not very large, the P function can be represented with a smooth function; a fifth-degree polynomial form has been shown to be adequate for reproducing the combination of background spectra in Raman spectroscopy. A detailed discussion about the role of $P(\nu)$ can be found in ref. 25.

For double-beam techniques, eqs. 1–2 can be reorganized in terms of absorbance; in this case, background contributions are cancelled with a background spectrum, and the analogue to eq. 4 can be written as follows:

$$A^b(\nu) = \sum_{i=1}^n \left(\frac{\rho_i^b l^b}{\rho_i^p l_i^p}\right) A_i^p(\nu) = \sum_{i=1}^n \rho_i^b \sigma_i A_i^p(\nu) \quad (5)$$

Equations 4 and 5 can be regarded as linear expansions of the blend spectrum in terms of the spectra of the pure components; the coefficients of the linear expansion are directly related to the concentration of the i component in the blend (ρ_i^b). A general expansion can be written for the blend spectrum that is valid for any vibrational spectroscopy (Raman or IR):

$$V^b(\nu) = \sum_{i=1}^n \varphi_i V_i^p(\nu) + P(\nu) \quad (6)$$

where V refers to the intensity (Raman), logarithm of the intensity (IR single beam), or absorbance (IR double beam) and φ_i ($i = 1..n$) is a weight coefficient that depends on the blend composition.

Application of the Method

Equation 6 is used here to calculate the chemical composition of the blend from its vibrational spectrum. In this context, $V^b(\nu)$ is our model blend spectrum, and $V_i^p(\nu)$ refers to the spectrum of the pure i component. They are considered discrete functions of frequency (or Raman shifts), defined for m nodal values. The $V_i^p(\nu)$

functions are experimentally determined from the corresponding vibrational spectra of each pure component. The cost function F to be minimized is written here for a blend with two components:

$$F = \sum_{j=1}^m [V_{\text{exp}}^{\text{b}}(v_j) - (\varphi_2 V_{1,\text{exp}}^{\text{p}}(v_j) + \varphi_2 V_{2,\text{exp}}^{\text{p}}(v_j) + P(v_j))]^2 \quad (7)$$

where m is the number of analyzed frequencies and $V_{\text{exp}}^{\text{b}}$ refers to the experimental blend spectrum. The subscript exp emphasizes that all these functions are experimentally determined. If $P(v)$ can be represented as a fifth-degree polynomial, there are eight parameters to be optimized. The first two (φ_1 and φ_2) are directly related to the blend composition, and the rest (φ_3 – φ_8) are used to fit $P(v)$. The minimization of eq. 7 with respect to the φ_k coefficients ($k = n + j + 1, j$ being the P degree) is analogous to the case of polynomial regression and always leads to the solution of a linear algebraic problem.³⁴ Finally, the blend chemical composition (i.e., weight fraction of a given component) can be calculated from the optimized φ_1 and φ_2 values via a simple calibration procedure with blends of known compositions, as described in ref. 25.

EXPERIMENTAL

PS [sample P1505-St; glass-transition temperature (T_g) = 103 °C, number-average molecular weight (M_n) = 217,000 g/mol, weight-average molecular weight/number-average molecular weight (M_w/M_n) = 1.05] and PVME (sample P2219-MVE; T_g = -32 °C, M_n = 3850 g/mol, M_w/M_n = 1.05) were purchased from Polymer Source (Dorval, Canada). Details of the molecular weight characterization were provided by the maker.

PS and PVME are both amorphous polymers, miscible over the complete range of compositions when the blends are cast from solutions with toluene or benzene as the solvent.³⁵ Homogeneous blends for Raman measurements were prepared by the dissolution of the polymers in the desired proportions in benzene. Then, the solutions, at about 10% (w/v), were freeze-dried. The obtained solid was further annealed slightly above T_g to remove traces of the solvent in a vacuum oven. Blend homogeneity was checked by optical inspection and by differential scan-

ning calorimetry (DSC). All the PS–PVME blends used here were optically clear; in addition, the DSC blend thermograms showed a single T_g intermediate between those of the pure components. Homogeneous blend films for ATR–FTIR measurements were cast from solutions in toluene. The solutions (ca. 2% w/v) were directly cast onto the ATR crystal via spin coating at 250 rpm. Films 10 μm thick were typically obtained. The films were annealed slightly above T_g to minimize molecular orientation due to the spinning process and to promote good contact between the sample and crystal. Blend homogeneity was checked, as explained previously.

Raman spectra of PS, PVME, and their blends were measured at room temperature on a Dilor LabRam confocal Raman microspectrometer with a 16-mW He–Ne laser beam (632.8 nm wavelength) with a wavelength of 632.8 nm. In the excitation and collection path, an Olympus 100 \times (numerical aperture (NA) = 0.9) dry metallurgical objective was used. A slit opening of 500 μm and a holographic grating of 1800 lines/mm were used, and this allowed the acquisition of data in a Raman shift range of 2700 and 3300 cm^{-1} with a spectral resolution of 4 cm^{-1} . Acquisition times varied from 60 to 300 s; the number of accumulated spectra varied between 5 and 20. Pinhole openings of 100–700 μm were used (the maximum aperture is 1000 μm).

IR spectra for pure components and blends were recorded in a Nicolet 800 FTIR spectrometer equipped with a liquid-nitrogen-cooled mercury–cadmium–tellurium (Hg–Cd–Te) detector. Nonpolarized light was used in these experiments. The ATR crystal was ZnSe ($n = 2.4$), with a face angle of 45°. The normal incidence to the entrance face of the internal reflection element was used. ATR spectra were collected (150–200 scans on average) with a spectral resolution of 4 cm^{-1} . As background emission, we used a spectrum of the free-standing internal reflection element without the sample.

The minimization of eq. 7 with respect to the φ_k weight coefficients was performed with a standard least-squares routine (Marquardt–Levenberg method, DUNLSF routine from the IMSL Math Library). The program was compiled and run with Microsoft Power Station 4.0 Fortran software. For comparison, some of the spectra were also processed with standard nonlinear curve-fitting procedures; a commercial Labcal Collect Arithmetic C2.24 software package from Galactic Industries Corp. was used for this purpose.

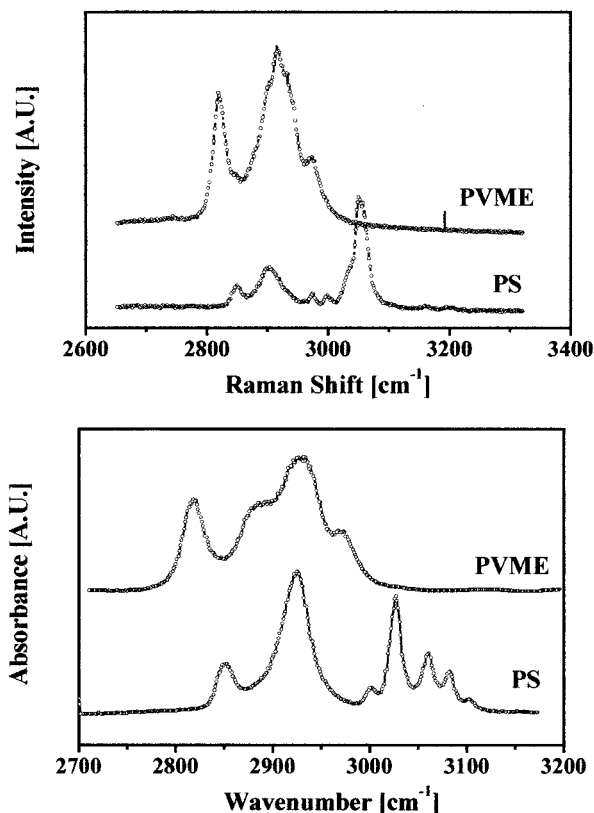


Figure 1. Experimental (A) Raman and (B) ATR-FTIR spectra of the pure components (PS and PVME). These spectra were used as the base functions for the linear expansion of the blend spectrum given by eq. 7.

RESULTS AND DISCUSSION

Figure 1(A) shows the Raman spectra of the pure components (PS and PVME), which were acquired in the range of Raman shifts of 2700–3300 cm^{-1} . Figure 1(B) shows ATR-FTIR spectra for pure PS and PVME in a similar wave-number region. These spectral ranges are suitable for composition analysis because the individual components (PS and PVME) show characteristic band profiles; in addition, the band shapes are not significantly affected by the interactions between the components.³⁶ The choice of spectral regions free of interactions is the only requirement of the method. This condition always yields better results in terms of the superposition principle on which the method is based, and this improves the precision of the calculations. Unlike other approaches that require either single isolated peaks or the decomposition of a spectral region to isolate a given peak, rich spectral information containing several overlapped peaks can be used in the calculations. As explained later, the spectra

shown in Figure 1 are used as the $V_i^{\text{P}(v)}$ base functions for blend composition calculations through eqs. 6 and 7.

To test the proposed method, we performed a quantitative analysis of the chemical compositions in a series of homogeneous PS/PVME blends. For each blend, the corresponding Raman or ATR-FTIR spectrum was measured. Raman measurements were performed with a spectrometer equipped with a confocal system. The spectra were taken at different sample spots, either at the surface or inside the sample. In addition, the spectra were acquired at different time lengths of previous sample exposures to the laser beam, which generated, particularly in fluorescent samples, different contributions of the background emission. As Raman is a single-beam technique, it usually produces large changes in the spectrum baseline. The acquisition conditions that affect the spectral resolution (and consequently the band shape), such as the type of grating or slit opening, were set to the same values used for the measurements of the base functions (pure components). Representative Raman spectra of PS/PVME blends (20, 50, and 80 wt % PVME) are shown in Figure 2(A). The spectra were shifted vertically for easier observation.

The same PS/PVME blends were also analyzed by ATR-FTIR. This technique was chosen for these experiments because measurements on thin films can be much more easily performed in comparison with FTIR. On the other hand, ATR-FTIR requires more precautions in quantitative analysis than standard FTIR measurements in the transmission mode. As the sampling mechanism arises from reflection phenomena, the profiles of absorption bands in the ATR spectra are influenced by factors other than the concentration and oscillator strengths, such as the wavelengths and optical constants of the sample and crystal. In particular, changes in the relative intensity caused by the ATR penetration depth (d_p) dependence on the radiation wavelength deserve special attention. In ATR-FTIR, d_p gives a measure of the thickness of the film sampled by the IR radiation. d_p is equivalent to l_i in eq. 1 and is defined as the distance from the sample surface at which the amplitude of the evanescent wave decays to $1/e$ of its value at the surface:³⁷

$$d_p = \frac{\lambda}{2\pi[\sin^2 \theta (n_p/n_c)^2]^{0.5}} \quad (8)$$

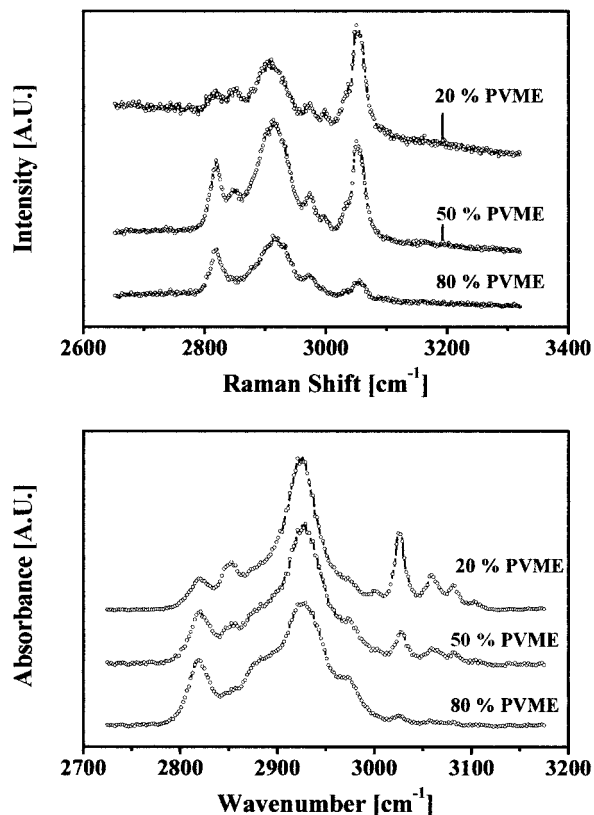


Figure 2. Experimental (A) Raman and (B) ATR-FTIR spectra for some of the PS-PVME blends studied. The blend compositions (wt %) are indicated.

where n_c and n_p are the refraction indices of the crystal and polymer, λ is the wavelength, and θ is the incident angle of the IR radiation. λ makes d_p vary with the frequency; in this way, the length of the optical path is not constant throughout the spectral range. However, it affects all the compositions in the same way, and the factor is cancelled in the calibration. Under the experimental conditions used in this work (refraction indices of 1.53 for the sample and 2.4 for the ZnS crystal and an incident angle of 45°), d_p calculated from eq. 8 at 3000 cm^{-1} is approximately $2.4\ \mu\text{m}$. Examples of ATR-FTIR spectra for blends containing 20, 50, and 80 wt % PVME are shown in Figure 2(B). As the use of a background spectrum to cancel background contributions is a common practice in IR spectroscopy, the results are presented in terms of absorbance.

The proposed method was applied to calculate the chemical compositions of the blends from their Raman and ATR-FTIR spectra. In processing the experimental data, we used the spectra as acquired; neither baseline correction nor nor-

malization is required for LDM. As reported elsewhere,²⁵ the method is quite tolerant of large changes in the spectrum baseline. To obtain the blend composition, the functional F (eq. 7) was minimized with respect to the φ_k coefficients, with the experimental spectra of the pure components shown in Figure 1(A,B) used as the base functions $V_{i,\text{exp}}^p$ and a polynomial of the fifth degree used to represent $P(\lambda)$. Once the optimum set of φ_k coefficients was obtained ($k = 8$ for a system of two components and six polynomial coefficients), the blend composition was calculated from φ_1 and φ_2 , via the calibration procedure detailed in ref. 25. The calibration is analogous to that performed in standard quantitative analysis, which usually consists of measuring the ratio of peak areas to heights for blends of known compositions. The results are plotted in Figure 3 for all the blends studied. The figure compares the calculated values of the blend composition (expressed as the PVME percentage) with those expected from the proportions of PS and PVME used to prepare the blends. Raman results are represented with open circles; ATR-FTIR results are shown as open squares. In both cases, the agreement between the calculated and expected blend compositions is excellent and demonstrates the precision and reliability of the method.

The superposition principle on which the method is based allows a precise representation of the experimental blend spectrum in terms of the pure component spectra, as shown in

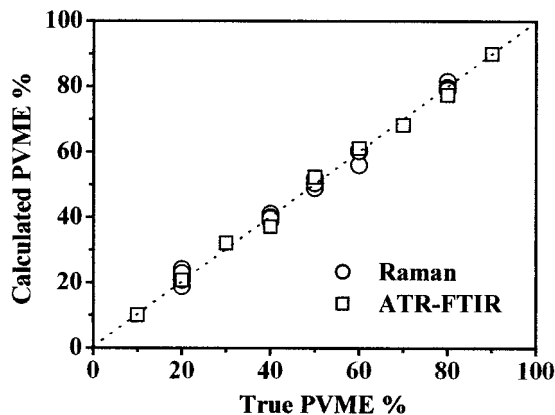


Figure 3. PVME blend compositions (wt %) calculated with LDM versus the expected (or true) values for all the blends studied. The true values of the PVME compositions were obtained from the proportions used to prepare the polymer blends.

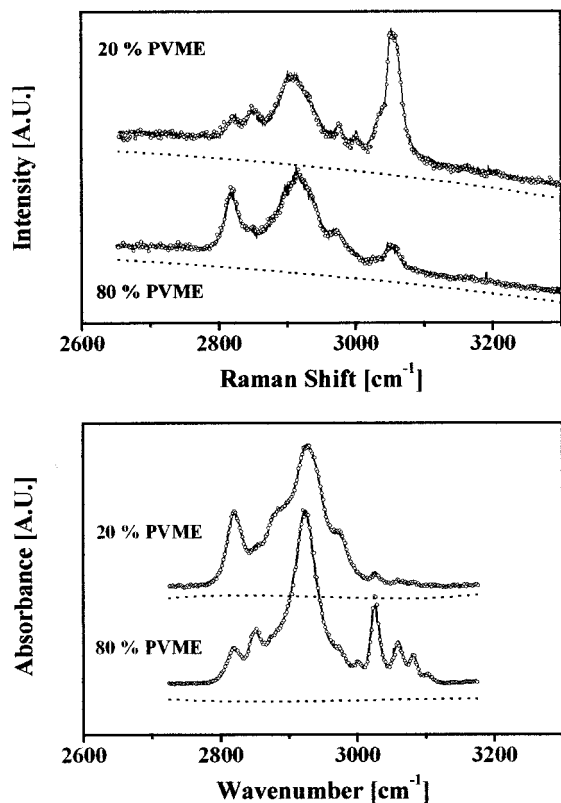


Figure 4. Comparison of the reconstructed spectra (solid lines) and those experimentally measured (symbols) for (A) Raman and (B) ATR-FTIR data. The dotted lines represent the corresponding $P(\lambda)$ functions. Reconstructed spectra were calculated with eq 6, as explained in the text.

Figure 4(A,B). Figure 4(A) shows Raman measurements, whereas Figure 4(B) presents ATR-FTIR data. The experimental spectra are represented by open symbols. The continuous line represents the best fit model spectrum, calculated from eq. 6 along with the base functions shown in Figure 1 and the optimum φ_k weight parameters obtained from eq. 7. The model spectrum is able to reproduce precisely the experimental data even when the instrumental acquisition conditions were different in each case (i.e., Raman measurements). The calculation scheme uses a combination of functions able to reproduce the sharp vibrational peaks (pure component spectra) and background contributions (P function) independently. $P(\lambda)$ (shown in the figures with dotted lines) represents a linear combination of background contributions from the pure components and the blend (eqs. 3–4). Individual background emissions have a bandwidth much larger than those of the vibrational peaks; the resulting lin-

ear combination is expected to have the same characteristics. We have shown that these contributions, which markedly affect the baseline spectra, can be precisely represented with smooth functions (i.e., polynomials of a low degree). This feature is thoroughly discussed in ref 25. The $P(\lambda)$ contribution is much more important in single-beam measurements [Fig. 4(A)] than in double-beam experiments [Fig. 4(B)]. In the latter case, $P(\lambda)$ is almost flat because most of the background contributions were cancelled with the background spectra.

The simplicity of the method is also reflected in the time required for numerical processing. The computing time needed to process any of the PS-PVME blend spectra shown in this work is approximately 1–2 s. Under similar conditions (including the same numerical recipe, the Marquardt–Levenberg method), the time required by standard nonlinear curve fitting is about 15 times longer; it depends on the seed values and does not include the time required to perform baseline corrections. The difference reflects the complexity of the calculations involved. In the case of LDM, only eight parameters need to be optimized, independently of the number of bands present in the frequency range analyzed. Good conditioning and a unique solution are guaranteed because the sharp peaks of the blend spectrum can only be fitted by the base functions associated with the pure component vibrational spectra. In the case of nonlinear curve fitting, at least four parameters for each decomposed band need to be optimized. The convergence to a proper solution is more intricate and may be very sensitive to the input values set by the operator as seeds. The global solution is not unique, and different combinations of individual functions can give equally good results; in this case, the selection of the most appropriate is made by the operator. Moreover, nonlinear curve fitting requires the use of intricate numerical routines and in most cases specifically designed software. Instead, LDM can be easily programmed; even when the calculations for this work were performed with a standard Marquardt–Levenberg optimization routine, the minimization of the functional F in eq. 7 can be solved as a standard polynomial regression case. The problem has a closed solution that can be obtained by the solution of a $k \times k$ system of linear algebraic equations with φ_k unknowns.³⁴

CONCLUSIONS

This work has introduced LDM as an appealing method for performing quantitative analysis on vibrational spectra. The methodology, originally developed for Raman spectroscopy, is naturally extended to IR spectroscopy, and its simplicity and precision are maintained. An integral approach, which includes a series of functions able to reproduce sharp vibrational peaks in combination with a smooth function that accounts precisely for instrumental/background contributions, allows the processing of the raw spectral data without previous manipulation (i.e., baseline corrections or normalization). Spectral information including several vibrational peaks can be used for the calculations, and this minimizes random errors. In this sense, LDM is expected to render results with the same order of precision (or better) as traditional approaches (i.e., curve-fitting procedures), but with a remarkably simpler calculation scheme and general strategy. As an additional advantage, the obtained results are entirely independent of decisions made by the operator, and this makes the method very convenient for intermediate-skilled users. The same general approach can be applied to the quantitative analysis of blends made out of any kind of substance that presents characteristic band profiles in the range of analyzed frequencies and can be generalized to multicomponent blends.

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