Fig. 4-1. Raw patterns (left) acquired by 4 minute exposure and the pattern generated by averaging 100 raw patterns (right). Patterns are obtained for (a) detector background (no gas), (b) carbon dioxide, (c) xenon, (d) ground state sample, and (e) time-resolved diffraction at each time point, t. The filter function is present in each pattern and observable as the darker region within the intense white ring.

(a) $F^N(x,y)$ — $F^B(x,y)$

(b) $F^{Xe}(x,y)$ — $F^B(x,y)$

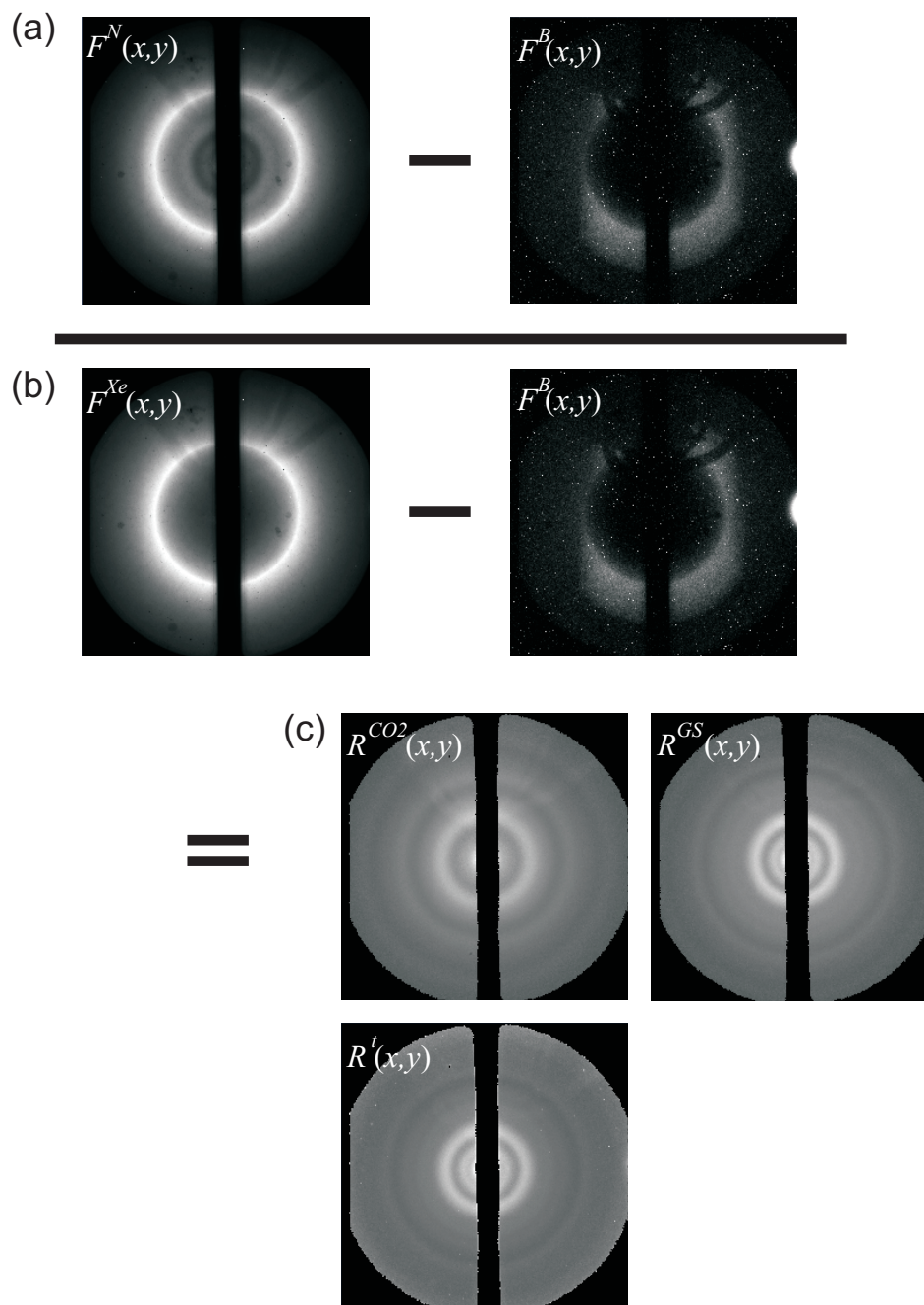(c) $=$ $R^{CO2}(x,y)$ $R^{GS}(x,y)$

$R^t(x,y)$

Fig. 4-2. The removal of the filter function and the formation of ratio patterns. Detector background is first subtracted from the image (a) and from xenon (b). Division by the background-subtracted xenon yields the ratio patterns (c) leveled by the xenon atomic scattering and relieved of the filter function. The patterns used in this, $F^N(x,y)$, can be that of carbon dioxide or ground-state sample (for time-resolved diffraction images detector background is not subtracted here since it will be eliminated by the frame- reference step).
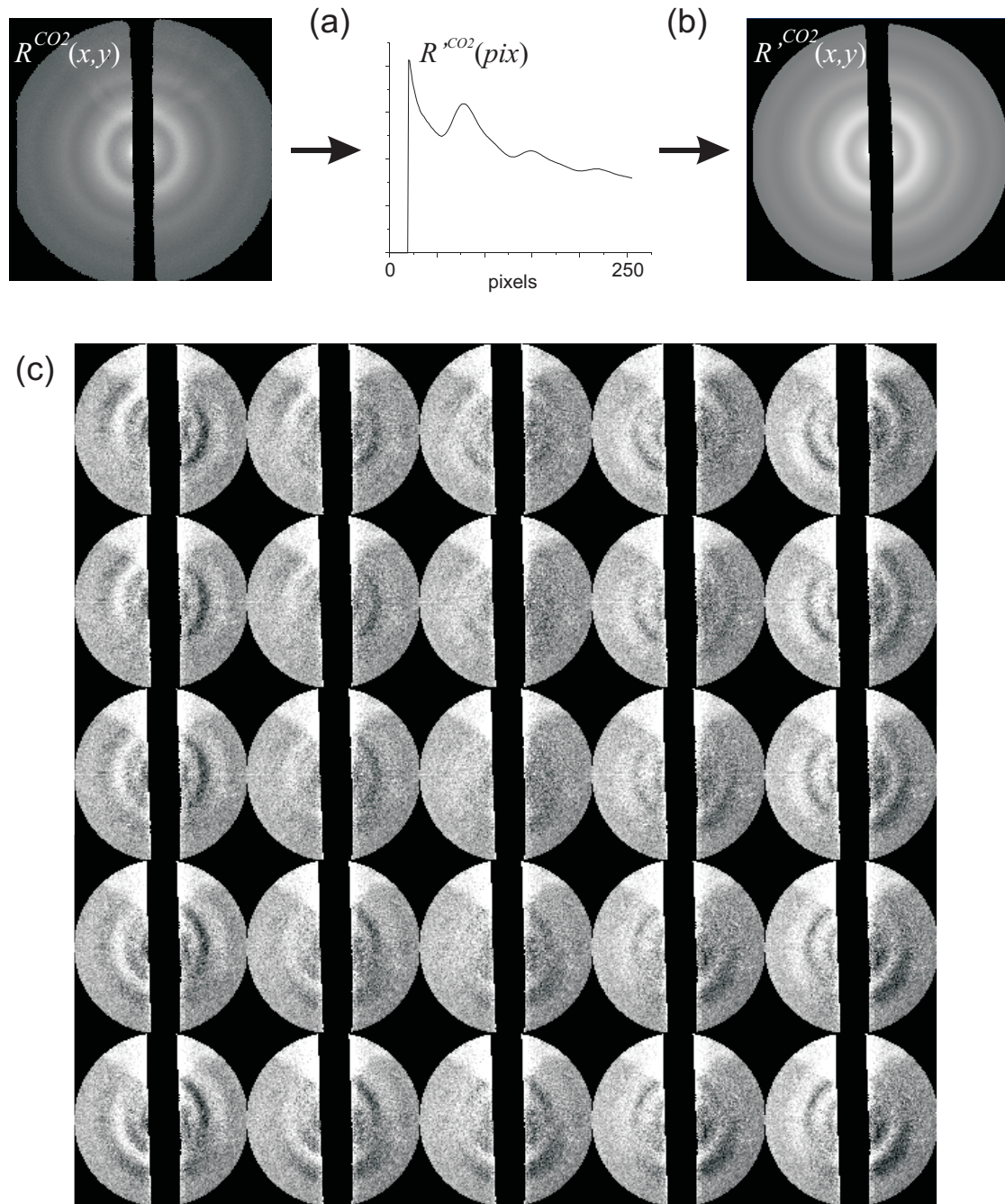
Fig. 4-3. Determination of the center of the diffraction pattern. This step must be performed with all ratio patterns, but $R^{CO_2}(x,y)$ is used in the example here. An arbitrary center is chosen and a radial average (a) of the image is calculated. Using the radial average, $I^{,CO_2}(pix)$, a fake diffraction pattern, $R^{,CO_2}(x,y)$, is constructed (b). The ratio pattern is divided by the fake ratio pattern. The arbitrary center position is varied until the ratio and the fake ratio match such that their division results in a flat image (c).
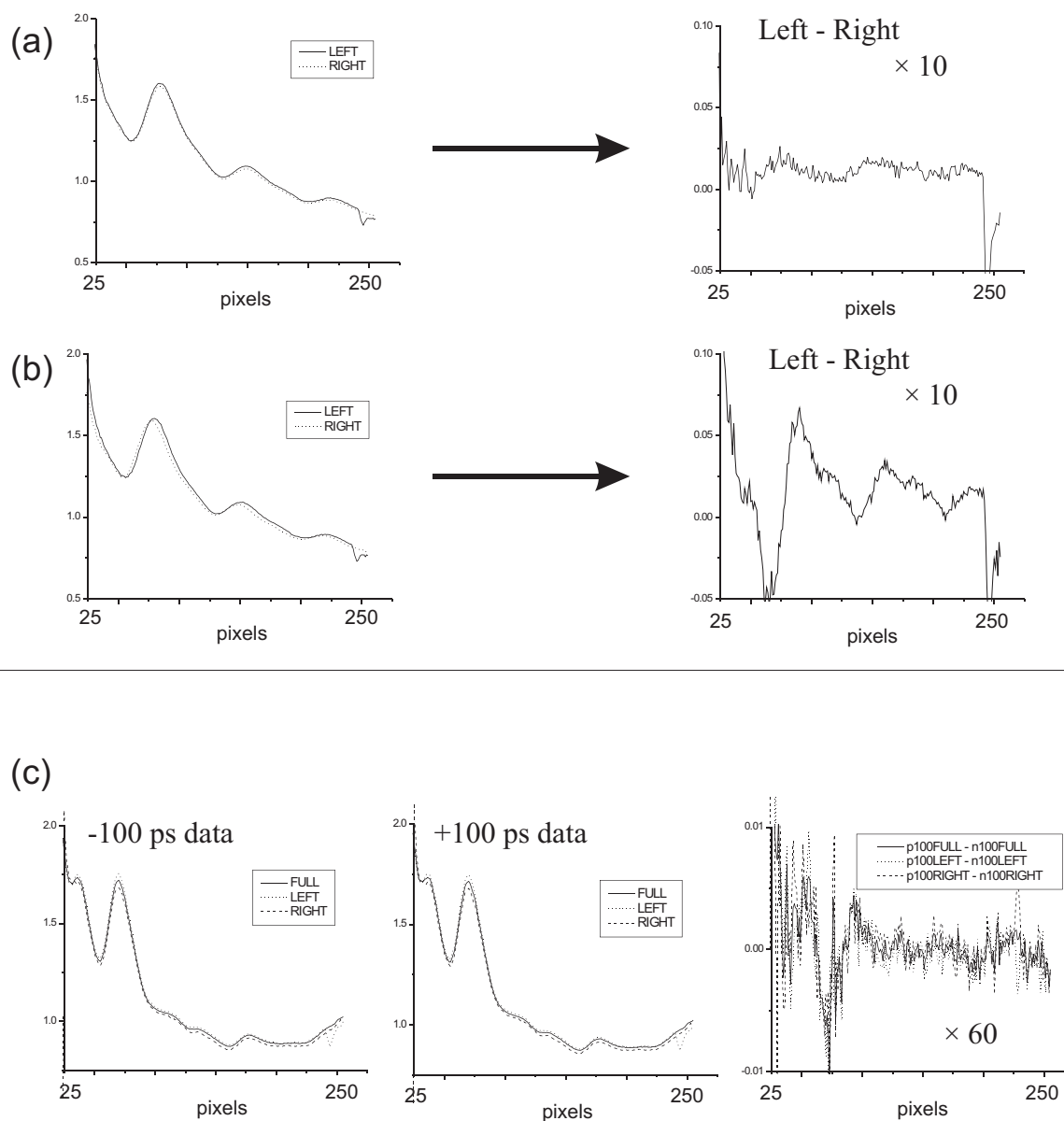
Fig. 4-4. The center positions are confirmed by separating the left and right sides of the detector, taking radial averages of the ratio pattern from each half, then subtracting one curve from the other. Although the intensities are not always the same a mostly flat curve should result (a). If the center is off by even 1 pixel the difference between left and right sides will show strong oscillations (b). Since the time-resolved data signal will be dramatically reduced by the frame-referencing procedure, the center position is even more critical. The center position is checked (c) by confirming the match between frame-referenced data from the full detector with that from the left and right sides. These peaks will not line up if the center position is off by as little as 0.2 pixels.
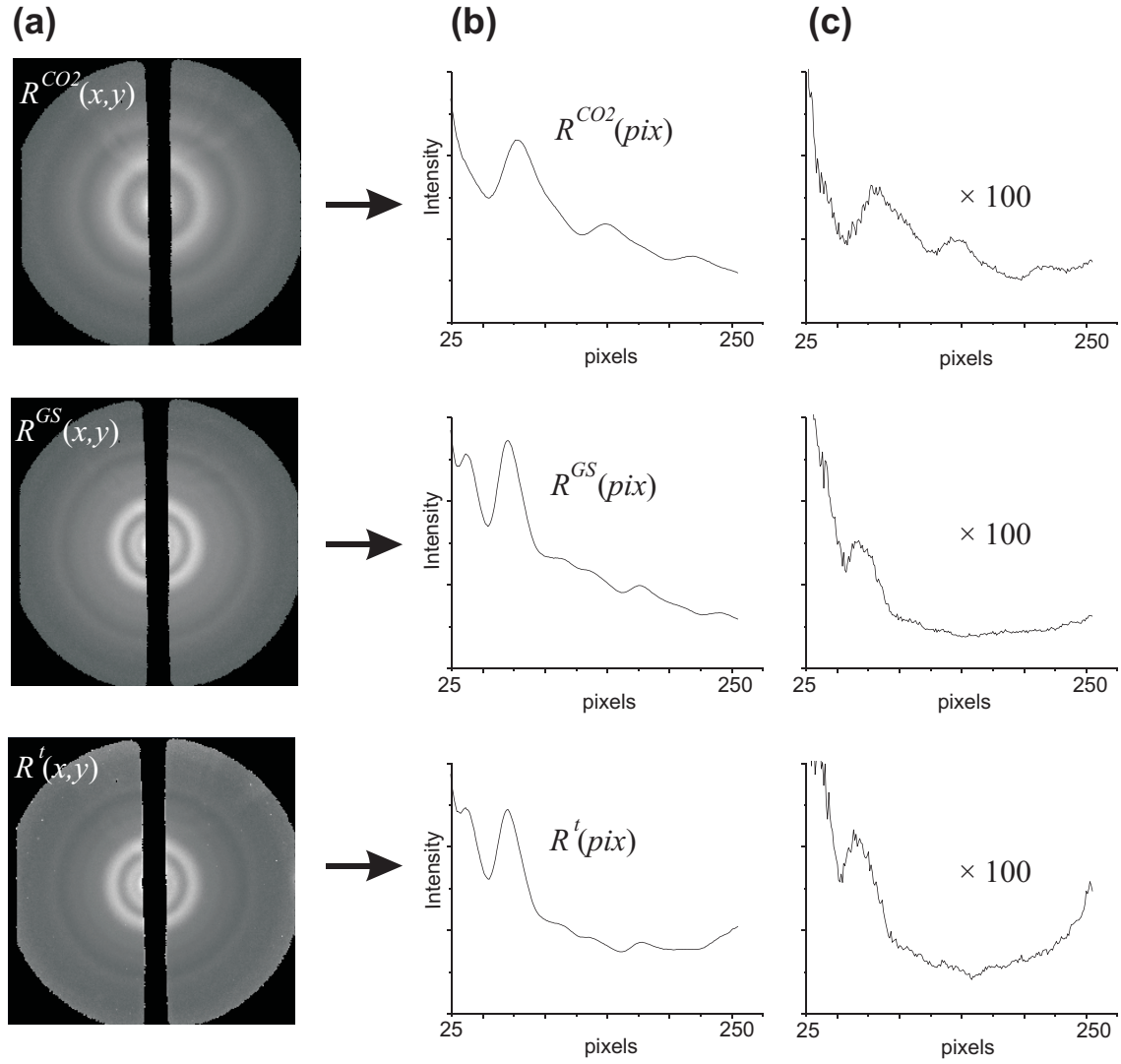
Fig. 4-5. At the correct center position, ratio images (a) are radial averaged to obtain the 1D ratio intensity data (b) in terms of pixels from the center, $R(x,y)$. The radial average also is used to calculate the error at each pixel value, shown in (c) as 3 .
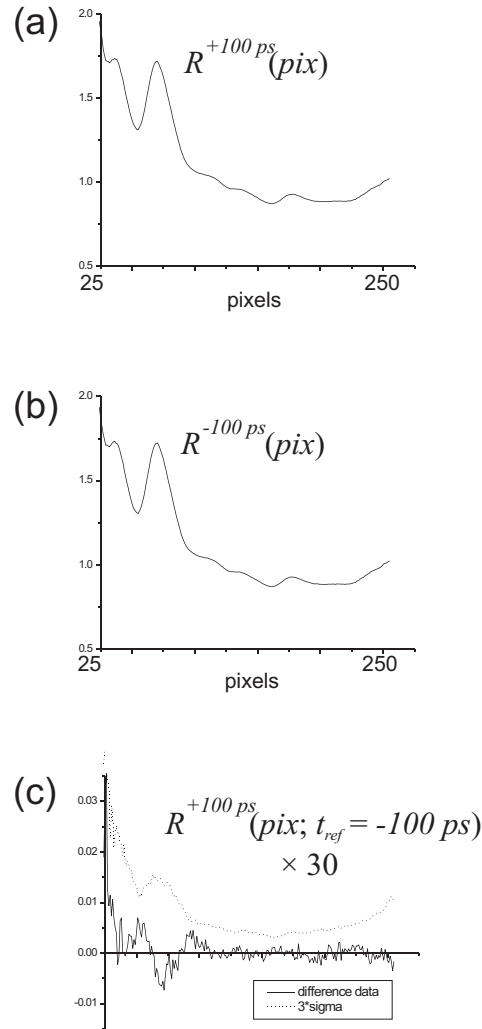
(a) $R^{+100\,ps}(pix)$

(b) $R^{-100\,ps}(pix)$

(c) $R^{+100\,ps}(pix; t_{ref} = -100\,ps) \times 30$

difference data
3*sigma

Fig. 4-6. Following radial average of the time-resolved diffraction ratio patterns, $R^t(x,y)$, data from a reference time (a), $R^{tref}(x,y)$, is subtracted from the remaining time points (b) to generate the difference data (c), $R^t(pix; t_{ref})$.
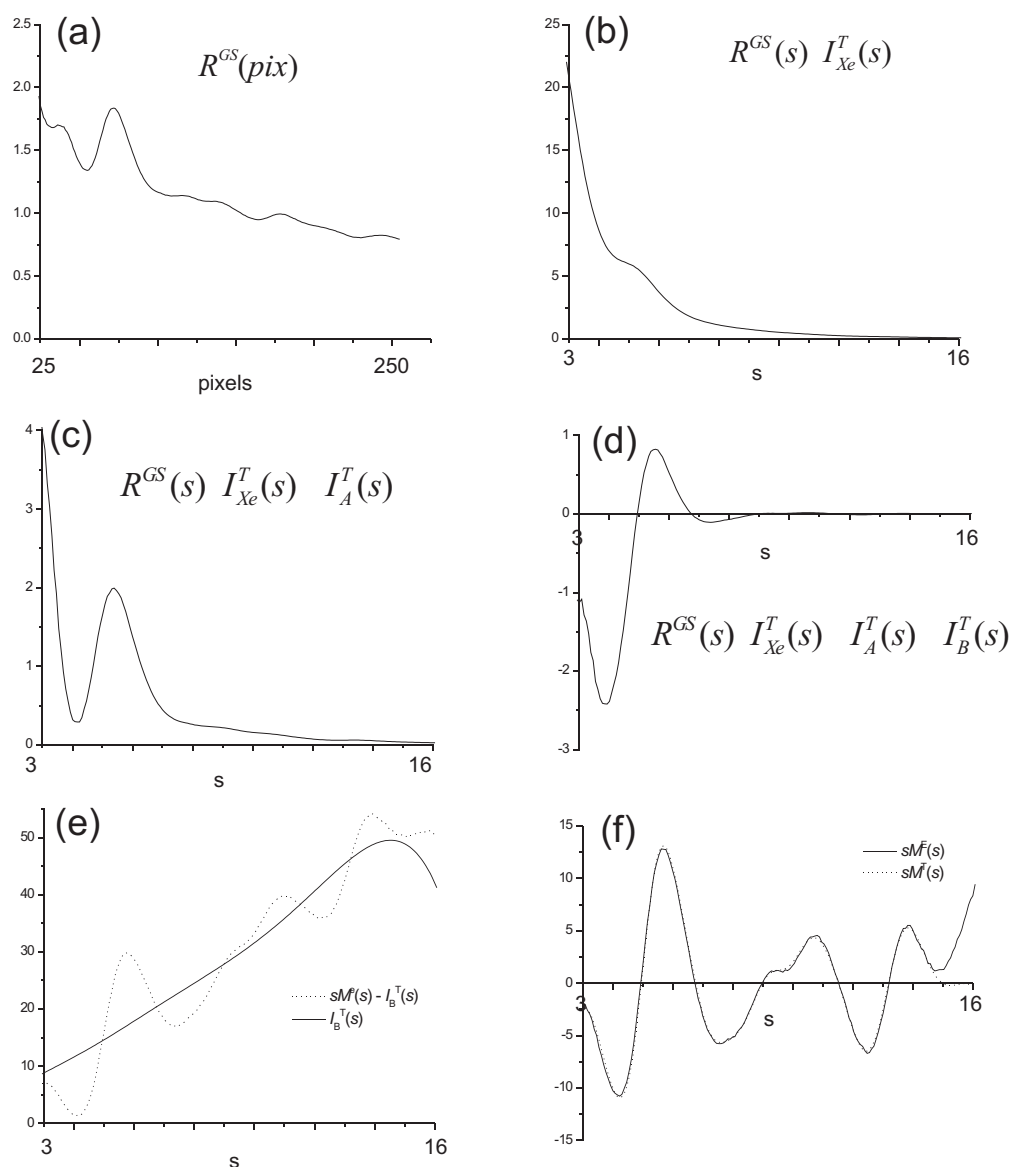
Fig. 4-7. A graphical representation of the steps needed to obtain the experimental modified molecular scattering curve, $sM(s)$, from the ratio data. In this example, data from the ground state of benzaldehyde is used. 1D ratio data in terms of pixels (a) is converted to data in momentum transfer space and multiplied by the simulated atomic scattering of xenon (b) after which the simulated atomic scattering of the molecule is subtracted (c). Using the theoretical molecular scattering intensity of ground state benzaldehyde the polynomial background coefficients are determined (see text) and the background is subtracted to produce the experimental molecular scattering curve, $I^e_M(s)$, (d). (e) Shows the polynomial background, $I^T_B(s)$, and the $sM^e(s)$ without the background. (f) shows the experimental and theoretical $sM(s)$ curves after the linear parameters have been calculated.
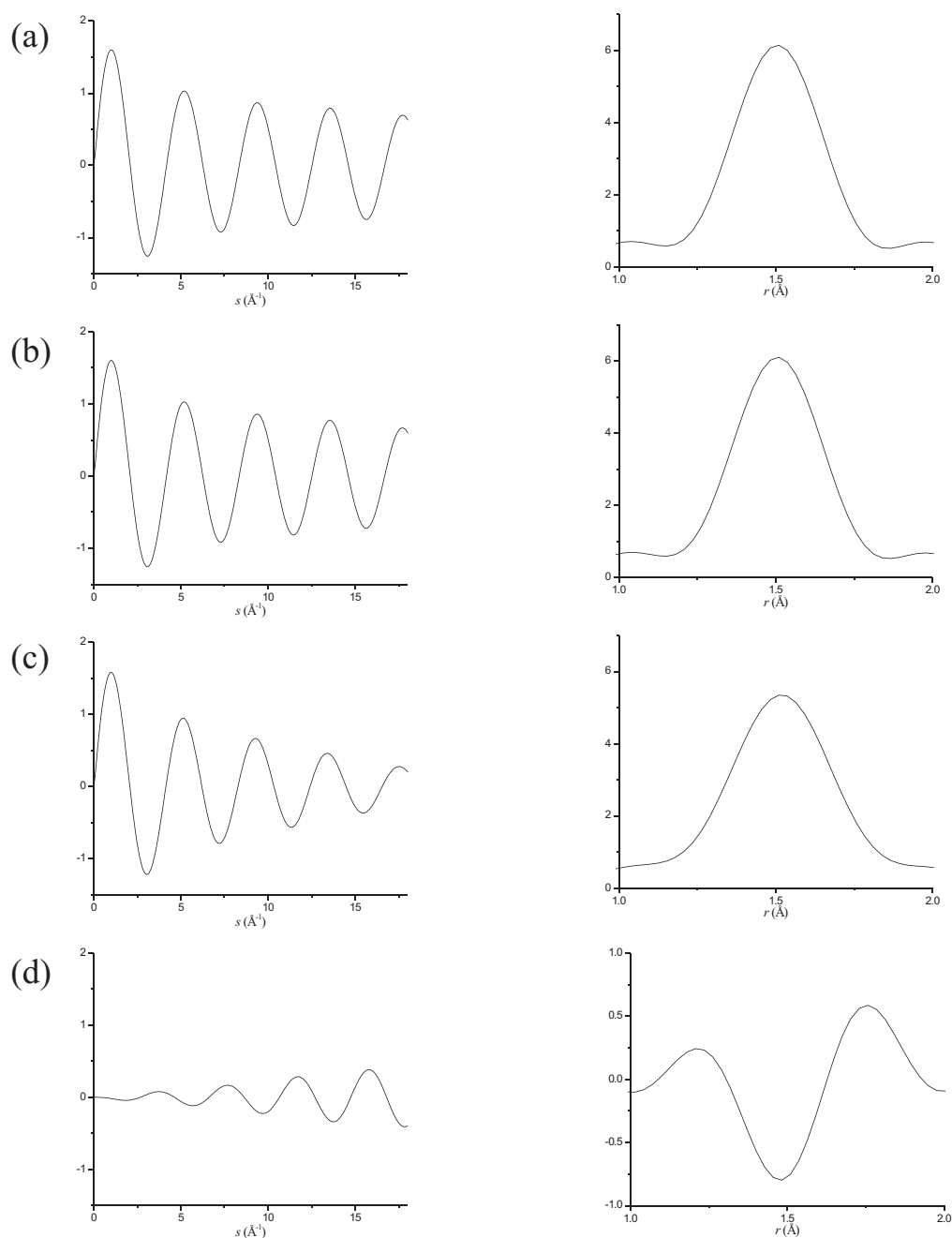
Fig. 4-8. The temperature dependence of a single C–C distance ($r = 1.5$ Å). The left column shows the theoretical $sM(s)$ curves and the right column shows $f(r)$ for the mean amplitude of vibration calculated at $T =$ (a) 5 K, (b) 500 K, (c) 2500 K. The difference in diffraction signal between molecules of very different temperature has a major effect on the molecular signal in the form of dispersive curves. Here, (d) is the difference between the above data (2500 K–500 K).