Photoacoustic Detection of Weak Absorption Bands in Infrared Spectra of Calcite

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Abstract

Photoacoustic spectroscopic detection of infrared absorption often produces spectra with enhanced intensities for weaker peaks, enabling the detection of features due to overtones and combinations, as well as less-abundant isotopic species. To illustrate this phenomenon, we present and discuss photoacoustic infrared spectra of calcite. We use linearization of rapid-scan spectra, as well as comparing step-scan and rapid-scan spectra, to demonstrate that saturation is not the driving force behind these enhanced intensities. Our results point to a significant knowledge gap, since a theoretical basis for the enhancement of these weak bands has not yet been developed.

Introduction

In the field of materials characterization, infrared (IR) spectroscopy can be used to assess structural differences in materials based on differences in the fundamental bands, as well as in the overtones, combinations, and isotopic peaks. The latter three band types are generally much weaker than fundamental bands, making it difficult to obtain information regarding all of the desired peak locations and intensities from a single spectrum. In traditional absorption spectroscopy, weak peaks can be intensified by increasing the quantity of sample that is examined, but this may cause the stronger peaks to become saturated. The identification of weak bands is even more problematic when sample quantities are limited. Alternative methods for the acquisition of IR spectra are needed in these circumstances. In this work, we discuss one such alternative method, photoacoustic spectroscopy (PAS), and its application to the mineral calcite ($CaCO_3$).

The PAS variant of Fourier transform IR (FT-IR) spectroscopy is based on the detection of thermal waves induced in a sample as it absorbs modulated IR radiation.[1–3] PAS is less common than other IR sampling techniques that are based on transmission measurements for samples embedded in alkali halide pellets or solutions, or others based on attenuated total reflection (ATR) of powders, solutions, or films. Nevertheless, PAS is the preferred option for strongly absorbing solid materials, as well as viscous liquids and semi-solids that may consist of multiple phases, which are not amenable to grinding or are insoluble in common solvents. Furthermore, PAS can enable depth profiling of layered or inhomogeneous samples, under specialized experimental conditions. The advantage that PAS offers is based on the fact that the modulated IR energy absorbed by a sample within an enclosed cell produces thermal waves, which in turn create corresponding pressure waves in a carrier gas that surrounds the sample. These pressure (acoustic) waves can be detected by a sensitive microphone or cantilever. The signals produced by these transducers are amplified and then processed by the FT-IR spectrometer, yielding an absorptive PAS spectrum.

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Calcite, the material under investigation in the present work, has been widely studied using FT-IR transmission and ATR techniques, but very little by PAS.[4–8] Calcium carbonate polymorphs, including CaCO₃, appear naturally in many instances and are of importance to materials scientists, archaeologists, and those who study biomineralization.[9–11] FT-IR spectroscopy offers distinct advantages relative to diffraction-based techniques because calcium carbonate polymorphs can be easily differentiated from each other even when they are poorly crystallized. This is particularly important in the context of biomineralization, wherein newly mineralized tissues typically form from amorphous calcium carbonate, which then crystallize as they mature.[9,11] In archaeological contexts, calcium carbonate can be poorly crystalline when it originates from wood ash or lime plaster binder, but is well crystallized in the form of limestone.[10,12,13] Thus, the ability to monitor transitions between amorphous and crystalline CaCO₃—as well as intermediate levels of crystallinity—offers great insights with regard to material identification and transformation.

The FT-IR spectra acquired using different variants (ATR, transmission or PAS) are not identical, even when the spectra are acquired for the same sample. Previous work on strongly absorbing samples has shown that differences in peak widths and shapes are sometimes observed when comparing PAS and transmission FT-IR spectra. These differences are often attributed to partial saturation in the PAS spectra; this phenomenon limits maximum intensities while increasing the apparent widths of the strong bands. In these situations, the intensities of weaker bands, such as those arising from combinations and overtones, are enhanced with respect to the more prominent features in the spectrum.

Previous studies, whether experimental or theoretical, have not fully discussed the origins or implications of these differences. In the present context, the accurate analysis of calcium carbonate materials requires the recognition of which differences in the spectra can be attributed to structural differences within the minerals themselves. If differences occur in spectra due to the use of alternative measurement methods (ATR, PAS, transmission), then there is a risk that these differences could be erroneously attributed to variations or changes in the materials under study. In this way, materials scientists require a solid working knowledge of the characterization methods on which they rely for structural data.

We show here—and cite examples from other work in the literature—that differences in peak widths, shapes, and relative intensities can occur among PAS, ATR, and transmission IR spectra of CaCO₃. This includes a systematic investigation of saturation-related effects in PAS data.

Methods

We used CaCO₃ (analytical grade CaCO₃, Merck) as our benchmark material in this study. CaCO₃ has been studied extensively in our laboratory and shown to give rise to a number of distinct mid-IR absorption bands, including isotopic (^{12}C, ^{13}C) peaks, combination modes, and overtones. The assignments of these bands are well known.[14] Prior to each measurement, the CaCO₃ powder was manually ground using a mortar and pestle for approximately 2 minutes to sharpen the spectral features, as described in detail elsewhere.[15]

All experiments were carried out with vacuum FT-IR spectrometers with thermal infrared (globar) sources. Initial PAS measurements used a spectrometer (Bruker IFS 66v/S) and a microphone-based PAS cell (MTEC PAC300) located at the mid-infrared beamline of the Canadian Light Source. More extensive experiments were carried out at Memorial University with a cantilever-based cell (Gasera PA301) with a different spectrometer (Bruker Vertex 70v). For PAS data collection, a few milligrams of ground powder were loaded directly into an aluminum sample cup that sits inside the PAS cell. Data were collected either under ambient conditions (Memorial) or after the PAS cell was purged with dry helium gas (Canadian Light Source). Carbon black standards (MTEC and Gasera, respectively) were employed to acquire background (reference) spectra. Rapid-scan (continuous scan) and step-scan data were collected with both spectrometers. Rapid-scan spectra were acquired at different frequencies (specified at 15 800 cm⁻¹, the wavenumber of the internal He–Ne laser) ranging from 1.6 kHz to 18.0 kHz. For this range of scan frequencies, the thermal diffusion length of CaCO₃ falls in the 60–20 μm range. The physical sample depth is much larger than this, on the order of millimetres, when using 2–5 mg of sample. The intensity scale is labeled as arbitrary units; sample spectra were ratioed against reference spectra recorded under like conditions.

Transmission and ATR IR spectra were also collected (Bruker Vertex 70v). For each ATR measurement, a few milligrams of powder were pressed directly onto the ATR crystal (Bruker Platinum ATR, single reflection diamond, 45° incidence angle), and the data were collected under ambient conditions. Assuming an index of refraction $n = 1.6$ for CaCO₃, the resulting effective penetration depth ranges between 1.8 and 18 μm, for 4000 and 400 cm⁻¹, respectively.

Transmission measurements required diluting the sample (~1:100) with potassium bromide (KBr) to allow sufficient transparency. The CaCO₃–KBr mixture was ground and repressed into a 5 mm pellet using a hand press (Pike Technologies) several times before measurement, in order to minimize particle scattering effects that broaden IR peaks.[16] Transmission measurements were carried out under vacuum conditions. The illumination spot is about 4 mm across, and scattering does not increase the heated area. Diluted samples refer only to transmission measurements (using KBr pellets), not ATR or PAS measurements.

Results

Figure 1 compares rapid-scan PAS, ATR, and absorption spectra collected for the same $CaCO_3$ powder sample. The weakest peaks in the ATR and absorption spectra (middle and bottom, respectively) are greatly enhanced—relative to the strongest (ν_3) band—in the PAS spectrum. As mentioned earlier, the assignments of these bands are well documented in the literature.[14,17,18] The weak peaks above 1500 cm^{-1} have been attributed to overtones or combinations.[14] At lower wavenumbers, the ν_2 and ν_4 bands are also intensified in the PAS spectrum. Furthermore, there is a narrow band at 860 cm^{-1} (the ν_2 vibration of the ^{13}C isotopic species) that is resolved from its ^{12}C counterpart at 878 cm^{-1}. We note that our data show that instrumental broadening is unlikely to have much influence on the width of ν_2 and ν_3. Figure 1 shows that ν_4 is narrower; hence, the instrumental resolution must be lower than the observed width of these two tallest bands, and their widths are genuine. Indeed, previous work has shown that the ν_3 band is a series of four to five over-lapping peaks.[14,17,18] In contrast, the ν_2 band has only one contributor. This helps to explain why the ν_3 band displays a high-frequency shoulder in the PAS spectrum. Thus, the PAS spectrum shows many enhanced weak spectral features that are less evident in the ATR and absorption spectra.

The intensification of the weak overtone and combination bands in the PAS data is a general result that occurs for many solid materials. Indeed, Natale and Lewis noted this tendency nearly four decades ago in near-IR PAS data for carbonyl compounds.[19] More recent studies show this effect in mid-IR PAS data for aromatic hydrocarbons and soils.[20–22] Although this intensification is beneficial for analyzing weak peaks, the effect that causes it is poorly understood. Below, we demonstrate that saturation alone cannot explain the enhancement of the weak peaks in the PAS data. In doing so, we describe how we process the data to eliminate any "artificial" contributions to the data, in accordance with best practices described in the literature.[3]

Linearization of Rapid-Scan Spectra

The striking differences between the PAS data and the ATR and absorption spectra in Fig. 1 deserve further comment. Given the differences in the overall shape of the strong broad ν_3 band in the PAS data, it is reasonable to suspect some degree of saturation. To investigate this possibility, we compared a series of rapid-scan PAS data at progressively higher scan frequencies ranging from 3.0 to 18.0 kHz. This experiment relies on the fact that greater scan velocities (modulation frequencies) lead to the reduction—and eventually elimination—of saturation. We note that this series of spectra are adversely affected by cantilever cell resonances at modulation frequencies near 820 and 1640 Hz: these resonances produce nonlinear responses, making some of these spectra unreliable in particular wavenumber regions. We provide a detailed list of the wavenumber ranges we avoided due to the cell resonances—which vary for different scanner velocities (mirror speeds)—as Supplemental Material.

Figure 2 displays rapid-scan PA spectra acquired at 3.0, 10.0, and 18.0 kHz. As described above, these frequencies refer to radiation at 15 800 cm^{-1}. In a Michelson
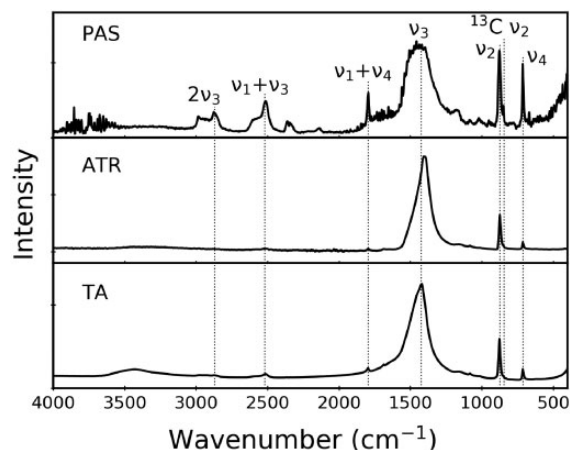

Figure 1. Representative FT-IR spectra of calcite acquired using three different techniques: PAS (top), ATR (middle), absorption (bottom). Peaks are labeled as fundamentals (ν_2, ν_3, and ν_4), overtone ($2\nu_3$), or combination modes ($\nu_1 + \nu_3$, $\nu_1 + \nu_4$). A fundamental peak for a minority isotopic species (^{13}C ν_2) is also visible. These spectra represent 27 scans for PAS, and eight scans for ATR and absorption.
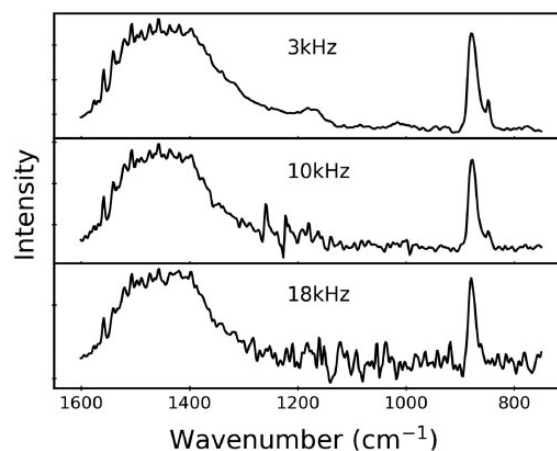

Figure 2. Representative rapid-scan PAS data for calcite acquired at 3.0 kHz (top), 10.0 kHz (middle), and 18.0 kHz (bottom) with 2 minutes collection time for each. The bottom two spectra show significant noise resulting from the intrinsically weaker spectra at these higher scan frequencies. A wider spectral range for the 3.0 kHz (top) spectrum is provided in Fig. 3.

interferometer such as those used in this work, modulation frequency f (Hz) and wavenumber ν (cm^{-1}) are related by $f = 2V\nu$, where V is mirror velocity (cm/s). For the 3.0 kHz spectra discussed in Figs. 2 to 5, $V = 0.095$ cm/s and f varies from 76 Hz at 400 cm^{-1} to 760 Hz at 4000 cm^{-1}. The breadth of this frequency range is particularly relevant, since PAS intensity varies approximately as $1/f$.[3] As a consequence, low wavenumber bands such as ν_2 and ν_4 are intensified relative to those at higher wavenumbers in rapid-scan PAS data.

Still referring to Fig. 2, we note that the relative peak intensities of the ν_2 band (878 cm^{-1}) and the ν_3 band (centred near 1450 cm^{-1}) are nearly the same in all three spectra. If the ν_3 band were saturated at lower frequencies, the ν_2/ν_3 intensity ratio would decrease at higher frequencies. The consistency of this relative intensity ratio even at different scan frequencies is a very significant point: it implies that the ν_3 band is not saturated to a significant extent in these spectra. Further comparisons of peak heights and widths, in table form, are provided as Supplemental Material. Taken as they are, these data strongly support the idea that saturation is not a dominant effect in our spectra.

To make our case for the lack of saturation more quantitative, we linearize the rapid-scan PAS data. This calculation produces spectra that are linear over one or more orders of magnitude of absorption intensity; put simply, this reduces saturation effects in PAS data.[3] In conventional PAS data treatment, a single-channel spectrum from the sample is divided by a carbon black spectrum acquired under like conditions. In contrast, linearization uses a numerical method developed a number of years ago by Burggraf and Leyden that has been used effectively in several PAS studies.[23–25] The linearization calculation utilizes amplitude and phase information for both sample and reference. The procedure uses real and imaginary spectra derived from Fourier transformation of the two interferograms, rather than the more common Mertz phase correction. We emphasize that linearization can correct for intensity saturation effects, but it does not compensate for lineshape differences that occur between PAS and transmission IR spectra.

Figure 3 compares linearized and conventional PAS data for CaCO$_3$. The spectra are quite similar. There is slight narrowing of the broad ν_3 band in the linearized spectrum, but only slight changes in the relative peak intensities. We emphasize that we employed linearization as a check for saturation, yet this process hardly changes the spectrum. This result is in stark contrast to data from others that showed significant changes (peak intensity enhancements) after linearizing PAS spectra that were affected by saturation.[24,25] Because of the similarities between the conventional and linearized PAS data, there is little reason to suspect that saturation measurably affects the CaCO$_3$ PAS data reported in this work. This conclusion is
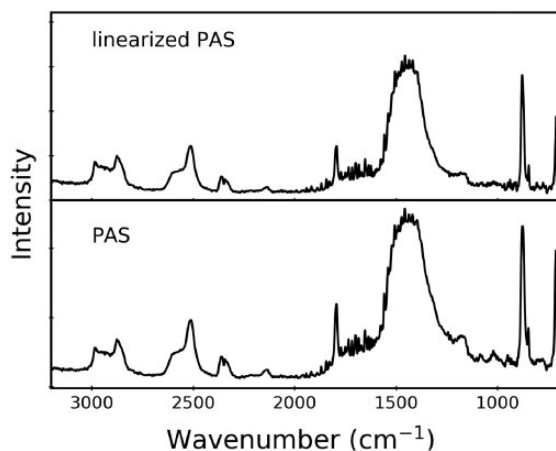

Figure 3. Comparison of linearized (top) and standard (bottom) rapid-scan PAS data for calcite, recorded at 3.0 kHz for 27 scans. The intensity scales are different due to the calculation details in the two methods, so we report the intensities in arbitrary units and comment only on relative peak intensity changes. We note that at this scan frequency, the first detector resonance (820 Hz) would occur well above the spectral range shown here at 3000 cm^{-1} is equivalent to 570 Hz.

consistent with the fact that different rapid-scan modulation frequencies also show very little change in relative peak intensities, even at the highest scan velocities.

Step-Scan Versus Rapid-Scan Spectra

A cleaner way to avoid saturation effects is to perform a different FT-IR experiment that uses step-scan mirror movement. In step-scan (step-and-integrate) spectroscopy, the incident radiation is modulated either by chopping the IR beam (amplitude modulation) or by dithering the mirror at each resting position (phase modulation). Amplitude modulation with a chopper modulates the entire spectrum at a single frequency, but with a trade-off that half of the incident intensity is blocked by the chopper blade. Nevertheless, either strategy will ensure that all PAS data are collected at a single frequency, and eliminate the low-wavenumber bias of the rapid-scan spectra. Our experiments employed phase modulation, thereby utilizing all of the available incident intensity.

Figure 4 compares representative step-scan and rapid-scan PAS data for CaCO$_3$. Band intensities above 2000 cm^{-1} are significantly increased in the step-scan spectrum, as expected. We note that the intensity in this kind of phase modulation spectrum is proportional to a first-order Bessel function, which rises from zero at 0 cm^{-1} to a maximum whose location varies with modulation amplitude and frequency. A representative example of this effect is provided as Supplemental Material. The Bessel function profile therefore reduces band intensities at low wavenumbers.[3] However, this affects both sample and reference, so it is largely eliminated when the CaCO$_3$ spectrum is ratioed
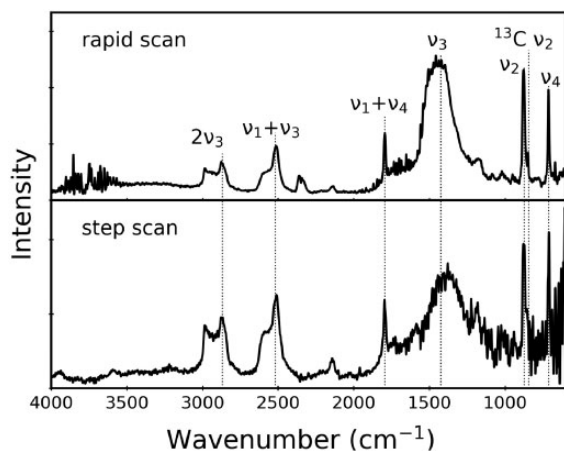
Figure 4. Comparison of rapid-scan (top) and step-scan (bottom) PAS data for calcite. The rapid-scan spectrum was obtained at 1.6 kHz for 27 scans, while the step-scan spectrum was acquired using phase modulation at 227 Hz and a modulation amplitude of 2λ ($\lambda = 633$ nm) for 64 scans.

Figure 5. Representative rapid-scan PAS data for calcite that compare: cantilever transducer (top), cantilever transducer with repacked sample (middle), microphone transducer (bottom). These spectra represent 8, 32, and 512 scans, respectively.

against the carbon black reference spectrum. Any difference in modulation frequency between the two spectra contributes to the relative intensity reduction for the ν_2, ν_3, and ν_4 bands in the step-scan spectrum.

We note that Fig. 4 compares a rapid-scan result obtained at a scan frequency of 1.6 kHz, while the step-scan modulation frequency was 227 Hz. This means that the ν_3 band occurs at a frequency near 150 Hz in the rapid-scan spectrum, which is slightly lower than the 227 Hz frequency that applies throughout the entire step-scan spectrum. If saturation were affecting this ν_3 band, the rapid-scan spectrum should have a reduced amplitude and increased width; this is the opposite of what we observe. Thus, what is very significant for the discussion here is that, even though there are some inherent differences, both the step-scan and rapid-scan PAS data show enhancement of the weak peaks at higher wavenumbers.

Transducer Effects

The relative peak intensities in PAS data for $CaCO_3$ samples are not affected by transducer type (cantilever versus microphone) nor by repacking the powdered sample used for the measurement. Figure 5 shows illustrative data that support this assertion. The top and middle spectra compare the same $CaCO_3$ powder, loaded in the sample cup and packed on different days. The similarity in the resulting spectra is consistent with earlier reports that show PAS data are usually insensitive to the amount of solid, likely because the penetration depth limits how much of the material is probed.[3] For the bottom panel of Fig. 5, a spectrum collected with a microphone-based transducer is virtually identical to the cantilever-based spectra shown above it. We note that all PAS data in Figs. 1 to 4 were collected with a cantilever-based cell.
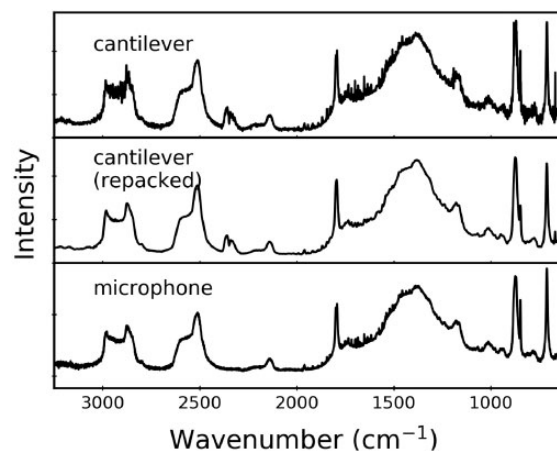
It is worth clarifying our assumptions about optical and thermal penetration depths. According to Rosencwaig-Gersho theory, for optically transparent and thermally thick samples (the case that could be said to apply for the weak bands), only the light absorbed within the first thermal diffusion length contributes to the PAS signal, even though the light is also absorbed at greater depths.[1] The thermal diffusion length is given by $\mu_s = (\alpha/\pi f)^{1/2}$ where α is thermal diffusivity and f is frequency. For optically opaque and thermally thick samples (the case for the strong bands), as long as the thermal diffusion length is less than the optical path length, it is again the light absorbed within the thermal diffusion length that produces the PAS signal. In other words, the same thermal diffusion length pertains to both the weak and strong bands. We provide additional details in the Supplemental Material.

Discussion

Our experiments and subsequent analyses, as laid out above, do not point to a reasonable cause for enhanced weak peaks in PAS data for $CaCO_3$. These effects are not associated solely with either rapid-scan or step-scan data. We demonstrate that our sample is substantially thicker than the optical penetration depth or thermal diffusion length. We compare two different kinds of transducers, and find no clues there. Finally, we present a large number of comparisons (including different mirror speeds, collection times, and linearization corrections) that show that the intensity enhancements are not consistent with saturation effects.

Existing theories do not help us understand these intensity enhancements. Transmission IR data for $CaCO_3$ have been simulated by many groups using quantum chemical density-functional theory calculations.[14,16,18,26] In these

instances, calculations provide energy values for the fundamental vibrational modes, and the IR spectra are then simulated based on initial user-specified broadening parameters and intensities. Relative changes in peak widths and intensities are qualitatively meaningful, but all are based on initial user-specified input, which is based on experimental trends. In this way, the IR peak intensities are not calculated from first principles in the same way that the energies of the vibrational modes are calculated. Furthermore, there are always discrepancies between the calculated and experimentally observed band energies due to anharmonicity. We are not aware of any PAS-specific calculations or simulations for IR spectra of solids.

It is conceivable that scatter-induced enhanced absorption could be a candidate for the anomalous behavior as it would cause unusual and enhanced saturation behavior around ν_3 and strong enhancement of weak bands. Since our beam covers almost all of our 5 mm samples, scattering could not significantly increase the effective sampled area. However, lateral scattering into the thermally probed region would dramatically increase the effective path length seen by each photon, especially at weakly absorbed bands. This could be investigated by diluting the sample with a non-absorbing solid such as KBr, which would reduce the path length pertaining to the absorbing sample.

Conclusion

The PAS spectra show persistent, repeatable enhancement of weak peaks due to combination modes, overtones, and isotopic species in $CaCO_3$ relative to transmission and ATR spectra of this material. We have shown that this enhancement is intrinsic to the detection method (PAS) and note that an adequate theoretical explanation for this long-standing phenomenon has not yet been developed.

Declaration of Conflicting Interests

Funding

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Supplemental Material

The supplemental material mentioned in the text, consisting of figures and tables, is available in the online version of the journal.

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