Influence of Hot Bands on Vibrational Spectra of Shock Compressed Materials

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For polyatomic molecules, extracting vibrational frequency shifts from spectra recorded under shock loading conditions is complicated by anharmonic coupling of modes and thermal population of low lying vibrational levels, which produce hot bands in the vibrational spectra. Most vibrational frequency shifts with shock pressure reported in the literature have been extracted from inadequately resolved spectral bands fitted with single Gaussians. This paper shows that, in general, for polyatomic molecules, the effect of the hot bands is to push the centroid of the fitted Gaussian away from the frequency of the vibrational fundamental. The direction and magnitude of this effect requires knowledge of the anharmonic coupling coefficients (which are in all likelihood also pressure dependent). To completely characterize the intra- and intermolecular potentials, it is therefore necessary to use the highest spectral resolution possible, and to independently measure or calculate the pressure and temperature dependence of the anharmonic coupling coefficients for the molecules of interest.

Introduction

Raman spectroscopy is often used to interrogate the vibrational spectra of molecular materials under shock loading conditions.[1−14] Infrared absorption has also been used,[15−16] although until recently the technology for producing and detecting short broad-band infrared laser pulses has been inadequate for shock wave applications. The aim of such vibrational spectroscopic studies has been to provide information necessary to evaluate changes in the intramolecular potential energy surface caused by sudden increases in density, pressure, and energy, with the ultimate goal of understanding the intimate details of how shock waves cause chemistry, especially in energetic materials.

In studies of shock compressed diatomic molecular materials, hot bands have been observed and were found to be well resolved from the fundamental.[1−6,17−20] Experiments in liquid nitrogen,[4] oxygen,[5] carbon monoxide,[17] and their mixtures[18−20] could all be well explained using gas-phase anharmonicities and reasonable pressure and temperature shifts of the fundamental vibrational frequency.

The spectra of polyatomic molecules are more complicated because anharmonicity couples the normal modes, i.e., the wave equations have cross terms containing the vibrational quantum numbers of two or more normal vibrations.[21−24] These anharmonic coupling coefficients have been determined for few molecules, even in the gas phase.[21−23] In shock compressed condensed molecular materials, the thermal population of low lying vibrational levels will produce intensity in the hot bands in the vibrational spectra. However, we know of no data on the pressure and temperature dependence of anharmonicity coefficients, with the exception of the diatomics discussed above.[4,5,17−20] Such data are necessary to calculate the vibrational frequencies of the hot bands at an arbitrary shock state, to correctly fit experiment. By and large, vibrational spectroscopic studies in shock compressed larger molecules (such as water,[8] carbon tetrachloride,[14] benzene,[9] and nitromethane[9−13]) have ignored the effects of these hot bands in band shape and frequency shift analyses. This paper will demonstrate the consequences of such a choice and will outline the measurements and/or calculations needed to improve the analyses.

Theory

For polyatomic molecules, the vibrational energy $G(v_i)$ expressed in terms of anharmonic coupling coefficients x_{ij} (neglecting vibrational angular momentum interactions) can be expressed[21]

$$G(v_1,v_2 \cdots) = \sum_i \omega_i(v_i + g_i/2) + \sum_i \sum_{j \geq k} x_{ij}(v_i + g_i/2)(v_j + g_j/2) + \cdots \quad (1)$$

where v_i is the vibrational quantum number, ω_i the fundamental frequency, and g_i the degeneracy of normal mode i.

The frequency of a general transition originating in the state $(v_1,v_2, \cdots)$ and ending at the state $(v'_1,v'_2 \cdots)$ can be estimated (using eq 1)

$$G(v'_1,v'_2 \cdots) - G(v_1,v_2 \cdots) = \sum_i \omega_i(v'_i + g'_i/2) + \sum_i \sum_{j \geq i} x_{ij}(v'_i + g'_i/2)(v'_j + g'_j/2) - \sum_i \omega_i(v_i + g_i/2) - \sum_i \sum_{j \geq i} x_{ij}(v_i + g_i/2)(v_j + g_j/2) \quad (2)$$

The hot band $(\nu_i + \nu_j - \nu_j)$ [notation from ref 23] of this transition originating from the state $[v_j]$ will be at frequency[23]

$$\nu_i[v_j] = \nu_i + (g_i + 1)x_{ii}v_i + \sum_{j \neq i} x_{ij}v_j \quad (3)$$

Consider a fundamental ν_i which is accompanied by the hot band $(\nu_i + \nu_j - \nu_j)$. The separation between these two is x_{ij}. If x_{ij} is large enough to allow the bands to be resolved, there is no spectroscopic misunderstanding; the situation is like that described above for simple diatomic molecules.[17−20] In condensed-phase materials, however, the bandwidths can be comparable to or larger than typical x_{ij} leading to overlap, even with very

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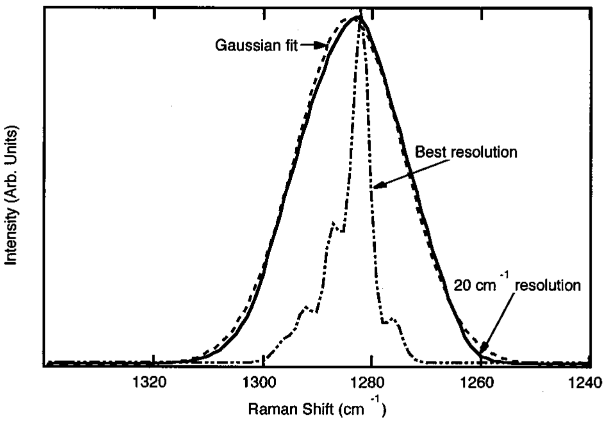

Figure 1. Gaussian fit of the calculated 900 K Raman spectrum for the ν_1 mode of N_2O convoluted with a 20 cm^{-1} triangular slit function.

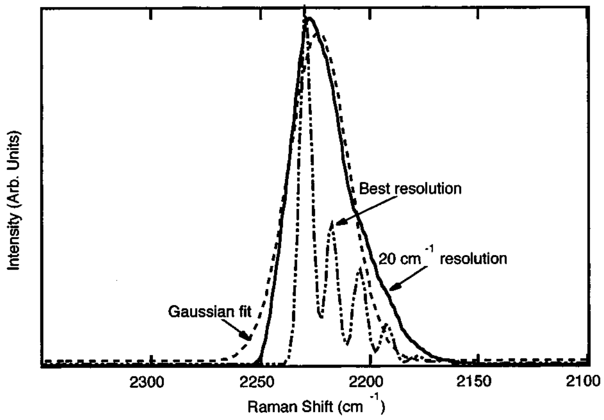

Figure 2. Gaussian fit of the calculated 900 K Raman spectrum for the ν_3 mode of N_2O convoluted with a 20 cm^{-1} triangular slit function.

high instrumental resolution.[24] The consequent obscuration of the hot bands has led to their neglect in the shock-compression literature to date.

Examples

Gas-phase anharmonic coupling coefficients for N_2O extracted from IR and Raman spectra are known.[21] These can be used to demonstrate the effect of increasing temperature for the case of inadequate resolution and spectral overlap in condensed phase materials, although, in real materials, increasing density at higher pressures and temperatures will cause the fundamental vibrational frequencies and probably also the anharmonic coupling coefficients (and therefore the frequencies of the hot bands) to shift. The point of these examples is to demonstrate the effect so that further experiments will someday be performed to obtain the pressure-induced shifts needed to analyze high-pressure spectra correctly.

The calculated ν_1 and ν_3 Raman bands of liquid N_2O at 900 K are shown in Figures 1 and 2, respectively. The "best resolution" calculated spectra assume collapsed Q-branch bandwidths of 2.3 cm^{-1} for the ν_1 mode and 4 cm^{-1} for the ν_3 mode.[25] Note the presence of hot bands on both the high and low-frequency sides of the ν_1 fundamental in Figure 1, because of the positive x_{ij} between the ν_1 and ν_2 modes and the negative x_{ij} between the ν_1 and ν_3 modes.

If an experiment could be performed in N_2O that had been heated suddenly to 900 K while the pressure remained constant (isochoric heating), and a Raman instrument of adequate resolution (<4 cm^{-1}) was used, something like the best resolution spectra shown in Figures 1 and 2 would be measured (assuming enough time for vibrational equilibration was allowed). However, such an experiment is extremely difficult (if not impossible) to achieve in practice. Typically, shock compression methods are used to achieve states of matter near or above liquid density at high temperature (a state sometimes known as "warm dense matter"). Some unique attributes of shock compression methods lead to quite severe requirements for measuring Raman spectra. The short time during which the sample can be kept at pressure and the destructiveness of typical shock compression apparatus imply single-shot experiments. The thickness of the sample (limited by the need for isobaric conditions) as well as laser damage and nonlinear optical considerations limit the incident laser intensity that can be used. Typically, Raman signal-to-noise ratios achieved have been 50 or less, but even those cases required quite low resolution (i.e., wide spectrometer entrance slits) Raman detection.

The effect on these N_2O bands of the typical spectrometer resolution (ca. 20 cm^{-1}) used in Raman experiments reported in the literature, can be estimated by convoluting the calculated infinite resolution spectrum with such a slit function. The results of the convolution of a 20 cm^{-1} triangular slit function with the calculated 900 K Raman spectrum for the ν_1 and ν_3 modes of N_2O are also shown in Figures 1 and 2. The hot bands are now just bumps on a broad envelope, and would not even be visible at a signal-to-noise ratio of 20 or less.

Extraction of Raman Shift

The Raman spectroscopic experiments in shock compressed polyatomic materials reported to date in the literature have obtained vibrational frequency shifts by (1) fitting the spectra using a single Gaussian band for each mode, and (2) assuming the centroid of the Gaussian is the frequency of the fundamental vibration at that shock pressure and temperature.

The effect of this procedure is illustrated in Figures 1 and 2 (for the ν_1 and ν_3 modes of N_2O at 900 K, respectively). Note that the centroid of the Gaussian fit is offset from the frequency of the vibrational fundamental in each case. The effect of the hot bands is to push the centroid of the fitted Gaussian away from the frequency of the vibrational fundamental. It can be reasonably stated that this effect is quite general for polyatomic molecules. However, the direction and magnitude of this effect requires knowledge of the anharmonic coupling coefficients. For experiments under shock compression, the extraction of fundamental frequency shifts, important for comparison with calculated potential energy functions, therefore requires knowledge of the effect of pressure on the anharmonic coupling coefficients, i.e., $x_{ij}(P)$.

A similar procedure could be used for Raman spectra of the CN-stretch mode (ν_4) of nitromethane, a molecule of much interest in the literature (refs 9−13), if the anharmonic coupling coefficients for the ν_4 mode with the other 14 vibrational modes were known. In a previous publication[7] we used a model for the anharmonic coupling coefficients to fit high-resolution nitromethane ν_4 mode Raman spectra taken at 283, 298, and 328 K and ambient pressure. The model assumed that the anharmonic coupling coefficient for a given vibrational band component is proportional to the amount of vibrational energy in the lower state. That is: $x_{44} = {}^1\!/_2 A\ \omega_4$ and $x_{4j} = A\omega_j$ where $j \neq 4$, and the three A parameters (one for each symmetry) were set from the measured frequency of the first overtone of ν_4. This model provided an adequate fit to the low-frequency tail of the ν_4 Raman band at all three temperatures, which could not be fit without inclusion of the hot bands.[7]

For the purposes of this paper, this model was used to calculate all the components (hot bands plus fundamental) of

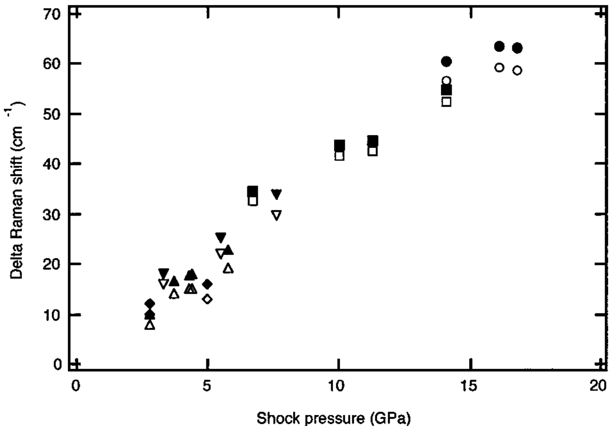

Figure 3. Corrections from the anharmonic coupling coefficient model for nitromethane (see text) applied to CN stretch (ν_4) mode vibrational frequency shift measurements in the literature. Note the corrections to single shock data are larger at a given pressure than those to step-wave loading data. Open symbols are the original data, and the solid symbols are corrected values. Circles: ref 11 (step wave); squares: ref 10 (step wave); diamonds: ref 13 (single shock); up triangles: ref 12 (single shock); down triangles: ref 9 (single shock − CARS measurements).

the ν_4 Raman mode of nitromethane as a function of temperature. These infinite resolution bands were then convoluted with a 20 cm^{-1} instrument function and fitted with a Gaussian. The resulting frequency of the centroid of the Gaussian fit was found to be increasingly offset from the vibrational fundamental with increasing temperature, due to the increasing contributions from the hot bands, similarly to the ν_3 mode of N_2O.

Effect on Experimental Data

There are a number of Raman and coherent anti-Stokes Raman (CARS) measurements of the ν_4 vibrational band of nitromethane under shock and stepwise loading conditions in the literature.[9−13] All of the reported frequency shifts in those references have been extracted from the data by using the centroid of a single Gaussian fit. As an illustration of the consequence of ignoring the hot bands, Figure 3 shows Gaussian centroid frequency shifts for the ν_4 mode Raman (and CARS) measurements of refs 9−13 as well as the frequency shifts of the fundamental using the anharmonic coupling coefficient model above. Any actual (not model) corrections will, of course, depend on the pressure-induced changes in the anharmonic coupling coefficients. However, for the purposes of this illustration, they are assumed not to change (as has been observed for several diatomic molecules).[4,5,17−20] The single-shock temperatures are those given in refs 9, 12, and 13 (which were calculated from the Lysne−Hardesty equation of state for nitromethane[26]) and the step-wave temperatures are those given in refs 10 and 11. Note that the correction for single shock data is larger than that for step-wave data (see Figure 3 caption) at the same final pressure because of the lower temperature achieved in the latter. Still, in all cases the corrections are nonnegligible and would have a deleterious effect on potential energy functions benchmarked by such frequency shift data.

Granted, the actual anharmonic coupling coefficients for nitromethane and other larger polyatomic molecules are very difficult to measure, especially at high pressure. However, recent calculational methods could be used to estimate their values in the condensed phase at ambient pressure, and also possibly their density dependence.[27] These values could (and should) then be used to more adequately correct Raman vibrational frequency shift measurements.

It is clear that the actual (not model) corrections depend on knowing the anharmonic coupling coefficients as a function of pressure. Conversely, if these coefficients are known (or could be calculated with sufficient accuracy) and adequate spectral resolution is used so that the actual band shape is measured, then the vibrational temperature can be extracted from Raman spectra. Methods to measure temperatures *in situ* in shock compressed materials are rare, but extremely important to benchmark equations of state. Vibrational temperatures can be and have been used to evaluate the accuracy of equations of state and the intermolecular potential energy functions used in their calculation.[18]

Conclusions

The molecular level behavior of dense fluids is often investigated using vibrational spectroscopic techniques in conjunction with shock compression methods. Vibrational frequency shifts can be used to benchmark potential energy surfaces used in equation of state models. For polyatomic molecules, extracting vibrational frequency shifts from spectra recorded under shock loading conditions is complicated by anharmonic coupling of modes and thermal population of low lying vibrational levels, which produce hot bands in the vibrational spectra. For experiments in which these hot bands are not spectrally resolved, the spectra give little evidence for their presence. Therefore, the bands in such spectra have usually been fit with a single Gaussian and the shift of the centroid of the Gaussian with shock pressure has been reported as the vibrational frequency shift. We have shown in this paper that, in general, for polyatomic molecules, the effect of the hot bands is to push the centroid of the fitted Gaussian away from the frequency of the vibrational fundamental. The direction and magnitude of this effect requires knowledge of the anharmonic coupling coefficients, (which are in all likelihood also pressure dependent). It is therefore important to use the highest resolution possible for these types of experiments. It will ultimately be necessary to measure the pressure and temperature dependence of anharmonic coupling coefficients directly using high-temperature static high-pressure techniques, or to calculate them with the most accurate means possible. Then, vibrational spectra can be used to extract the vibrational temperature, providing an additional benchmark for equations of state.

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