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Phase transitions and hindered rotation in dimethylacetylene at high pressures probed by Raman spectroscopy

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We present Raman spectroscopy experiments in dimethylacetylene (DMA) using a sapphire anvil cell up to 4 GPa at room temperature. DMA presents phase transitions at 0.2 GPa (liquid to phase I) and 0.9 GPa, which have been characterized by changes in the Raman spectrum of the sample. At pressures above 2.6 GPa several bands split into two components, suggesting an additional phase transition. The Raman spectrum of the sample above 2.6 GPa is identical to that found for the monoclinic phase II ($C2/m$) at low temperatures, except for an additional splitting of the band assigned to the fourfold degenerated asymmetric methyl stretch. The global analysis of the Raman spectra suggests that the observed splitting is due to the loss of degeneracy of the methyl groups of the DMA molecule in phase II. According to the above interpretation, crystal phase II of DMA extends from 0.9 GPa to pressures close to 4 GPa. Between 0.9 and 2.6 GPa, the methyl groups of the DMA molecules rotate almost freely, but the rotation is hindered on further compression. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1814353]

I. INTRODUCTION

Spectroscopic experiments provide important information about the changes on molecular interactions produced by applying pressure to molecular crystals, and offer interesting results concerning the nature of both intermolecular and intramolecular forces.

Under extreme pressure conditions the distinction between intramolecular and intermolecular interactions is more and more diffuse and interesting chemical reactions may occur. This phenomenon is particularly interesting in systems containing unsaturated bonds.[1–10] Thus, in the last few years, new chemical processes have been discovered in high-pressure experiments on molecular systems, leading to the synthesis of new classes of novel materials.

An important issue to understand the mechanisms that govern high-pressure chemical reactivity concerns the initial relative orientation of the reacting molecules.[11] Since most pressure-induced reactions develop in the solid state, the study of the high-pressure phases of potentially reactive systems is crucial to understand the kinetic mechanisms that govern high-pressure reactivity.

Ab initio molecular dynamics calculations[12,13] provide a reasonable interpretation of the experimental results,[7,9,10] however, knowledge of the high-pressure phases involved in pressure-induced reactions is still a prerequisite. An additional complication is that molecular systems often show a rich phase diagram in a narrow range of pressures. So far, there is a need of structural information of molecular systems at high pressure to take advantage of the new synthetic routes discovered.

Information about the nature of solid phases and chemical processes that take place by the application of pressure can be gained from the analysis of the vibrational spectroscopy experiments.[14] However, in most cases, the assignment of internal vibrational modes after a phase transition is not straightforward, because the different molecular interactions present in the new phase may induce important changes in the geometry of the molecules. If this occurs, the spectroscopic activity of the internal vibrations must be also affected, and the vibrational assignment is increasingly difficult in complex polyatomic samples (in addition to crystal field effects). In other words, spectral changes are quite valuable to detect phase transitions, but their origin is sometimes difficult to be certainly known. More often than desirable, the presence of Fermi resonance effects changes in the activities of both fundamentals and overtones, or modifications of the intramolecular anharmonic interactions lead to different interpretations. In other words, interpretations based solely on the analysis of a single spectral window (CH stretches, CH bendings, etc.) should be taken with care. Some of these difficulties can only be resolved with a careful analysis of the pressure evolution of the whole vibrational spectrum, because the analysis of the pressure slopes of the bands can be used as a double check for vibrational assignment. In this sense, a subsidiary goal of this paper is to show that high-pressure vibrational spectroscopy experiments are a valuable tool in their own right to perform vibrational analysis of polyatomic molecules.

We present here a detailed Raman spectroscopic study of dimethylacetylene (DMA, or 2-butyne) up to 4 GPa. This system can be considered as a prototypical for high-pressure reactivity studies for its relation with acetylene and its polymeric derivatives.

As in most molecular systems, the structures of the high-pressure phases of DMA and the transition pressures are not known. Two stable phases (I and II) are known at low temperatures,[15,16] and a low-temperature neutron powder dif-

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fraction study[16] on DMA indicates that phase II was monoclinic (space group $C2/m$), with two molecules per unit cell. There also exists a low-temperature Raman study of thin solid DMA films in the solid phase II.[17]

In this work we provide information about the high-pressure phase transitions deduced from the pressure evolution of our Raman spectra, together with the available structural[16] and spectroscopic[17] results. Our measurements reveal that DMA presents phase transitions at 0.2 and 0.9 GPa, which have been characterized by changes in the Raman spectrum of the sample. On further compression, several Raman bands split into two components above 2.6 GPa, suggesting an additional phase transition. We conclude that the splitting can be in fact attributed to the loss of degeneracy of the DMA methyl groups in the monoclinic ($C2/m$) phase II. Our results indicate that rotation of the methyl groups along the molecular axis is hindered by application of pressure. Between 0.9 and 2.6 GPa the methyl groups of the DMA molecules rotate almost freely along the molecular axis, but the rotation is hindered on further compression. Thus, phase II of DMA extends from 0.9 up to 4 GPa. This conclusion is quite interesting because preliminary experiments performed in our laboratory[18] indicated that DMA reacted at pressures above 4 GPa.

II. EXPERIMENT

Our high-pressure Raman spectra were measured using a sapphire anvil cell described elsewhere.[19] The cell and the liquid used in the experiments were cooled a few degrees due to the high vapor pressure of liquid DMA at room conditions (liquid DMA has a very narrow existence range between 241 and 300 K at room pressure). The anvil cell was therefore loaded with liquid DMA (Fluka spectroscopic grade) together with a few microcrystalline diamonds used as pressure markers.[19] Sample dimensions were 250 μm in diameter and 100 μm thick, and copper gaskets were used. Two samples were prepared and measured along 20 points below 4 GPa. The second sample was prepared and measured to check that metastable high-pressure phases of DMA were absent during our experiments, as will be discussed later.

The Raman spectra were excited using the 488 nm line of an ILT air-cooled Ar-ion laser. The scattered radiation was spatially filtered and collected in backscattering, and the Raman spectra were recorded with an ISA HR460 spectrograph coupled to a liquid nitrogen cooled charge-coupled device multichannel detector. Raman shifts were calibrated using minimum slit widths and a several lines from an emission neon lamp.[19] Measurements were performed at room temperature, laser-induced heating being negligible as revealed by the frequencies of the main bands of DMA at room conditions.[20,21] An infrared absorption spectrum of liquid DMA was also measured at room conditions using a Nicolet 750 Magna Fourier transform infrared (FTIR) spectrophotometer with a 1 cm^{-1} resolution. The FTIR spectrum was used to check the quality of the samples, and to perform a preliminary vibrational analysis of liquid DMA.

At each pressure, Raman spectra were collected at two different spectral resolutions. An initial middle resolution spectrum (4 cm^{-1} spectral resolution) was measured to detect general changes in the pressure evolution of the whole Raman spectrum of DMA. Middle-resolution spectra were collected between 400 and 3500 cm^{-1}. High-resolution spectra (1 cm^{-1} spectral resolution) were subsequently measured in three selected spectral windows about 500 cm^{-1} wide. All the spectra presented here result from spectral accumulations of at least 10 min. to obtain the desired signal to noise ratio. In general, sample 2 spectra showed poorer signal to noise ratios than those obtained from sample 1.

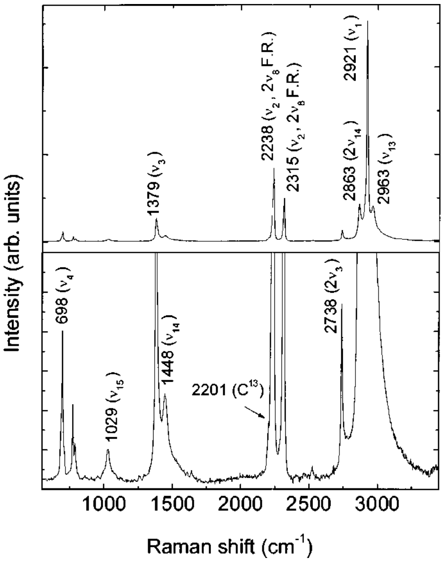

FIG. 1. Middle-resolution Raman spectrum of liquid dimethylacetylene obtained at room conditions. Frequencies and vibrational assignment are included for the relevant Raman features of the spectrum. The weakest bands are expanded at the bottom.

The pressure on the sample was determined by measuring the shift of the Raman band of the microcrystalline diamonds spread into the sample chamber. The diamond signal was recorded using the 2400 lines/mm grating with minimum slits, which allows determination of the pressure with an absolute uncertainty of 0.09 GPa. Hydrostatic conditions were maintained in our measurements as revealed by the measured linewidth (2–3 cm^{-1}) and high symmetry of the Lorentzian diamond signal. In most cases the diamond signal was recorded together with the spectrum of the sample in order to minimize pressure uncertainties due to pressure gradients on the sample.[19] At the highest pressure reached in our present experiments the pressure gradient observed was less than 0.2 GPa.

III. RESULTS AND DISCUSSION

For the sake of clarity the general changes observed in our samples will be discussed first. Both Raman and IR frequencies of liquid DMA recorded at room conditions agree to within 2 cm^{-1} with those compiled by Herzberg[20] and Sverdov *et al.*[21] The relevant features of the Raman spectrum of liquid DMA are detailed in Fig. 1. We have used the band assignment of Herzberg,[20] which is the one used in force field,[22] Fermi resonance studies,[23] and in the Raman study of phase II of DMA by Mohaček and Furić referred to in the Introduction.[17] The frequencies reported here are obtained

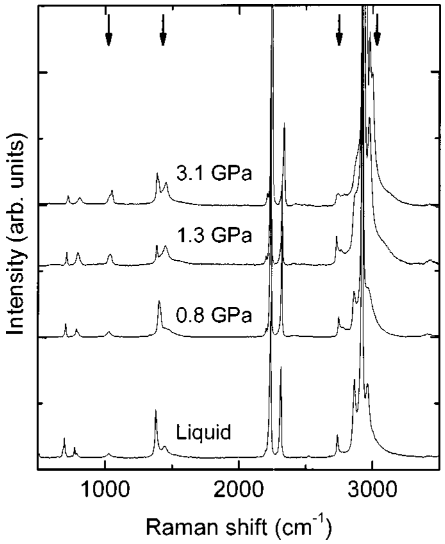

FIG. 2. Selected middle-resolution Raman spectra of dimethylacetylene at room temperature. The spectra are labeled by the appropriate pressure value in GPa. These spectra were obtained in sample 1 (see text) at room temperature in increasing pressure. The Raman spectrum of the liquid was measured under room conditions. Arrows indicate those spectral features where major changes are observed, which correspond to vibrational modes assigned to the terminal methyl groups.

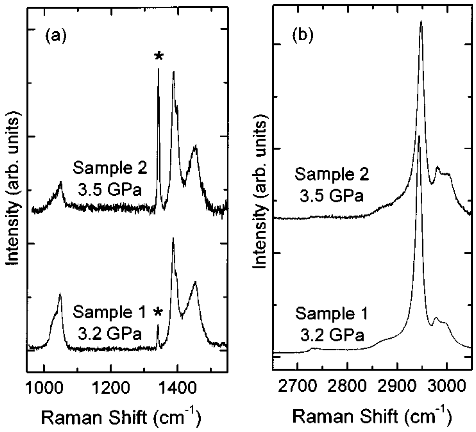

FIG. 3. Comparison of the high-resolution Raman spectra obtained for sample 1 and sample 2 in two relevant spectral windows: (a) methyl deformation and rocking fundamentals, (b) methyl stretching fundamentals and deformation overtones. The Raman band of the diamond pressure marker is indicated in (a) with an asterisk.

from the band profile analysis of the Raman spectra using both Lorentzian and Gaussian functions depending on the nature of the sample. For instance, the bands appearing on the Raman spectrum of the disordered phase I are often better represented with Gaussian profiles.

The existence of the methyl rotation makes the symmetry analysis of the DMA molecule controversial,[20,24] because the trivial D_{3h} and D_{3d} symmetries fail to describe the observed vibrational spectra at room conditions. Duncan,[22] who assumed a staggered configuration of the methyl groups, already recognized that the point group for DMA should be of higher order than D_{3d}, but he stated that the global interpretation would not be affected too much by assuming free internal rotation, as later emphasized by Lichene *et al.*[25] However, although this approximation is good enough to interpret most of the spectral features found in our spectra, recent high-resolution experiments[26,27] indicate that methyl fundamentals of the DMA molecule are each better described as fourfold degenerated vibrations using the extended G_{36} symmetry group.[28] Thus, to analyze the degenerate methyl stretching (ν_9/ν_{13}), deformation (ν_{10}/ν_{43}), and rocking (ν_{11}/ν_{15}) modes, we shall refer to the discussion given in Ref. 17 when needed; we also include the symmetry notation used by these authors. An additional observation is that diffraction experiments[15] suggest that rotation of the methyl groups in adjacent molecules are synchronized in the solid, so the degeneration is likely to persist in crystalline phases, as confirmed in Ref. 16.

Selected middle-resolution Raman spectra of DMA measured at room temperature are compared at four representative pressures in Fig. 2. The spectral changes consist of (a) pressure shifts of the bands to higher frequencies, (b) broadening of bands with increasing pressure, (c) appearance (disappearance) of bands, and (d) splitting of some bands into several components. These are the typical signatures used to detect pressure-induced phase transitions.[14] In general, if a phase transition takes place, the selection rules, which depend on both crystal and molecular symmetries, will also change and new features may appear. In general, our results indicate that the main spectral changes are observed on the fourfold degenerate vibrational fundamental modes and overtones assigned to the methyl groups. These changes are particularly important in the methyl deformation and rocking modes appearing in the 1000–1500 cm^{-1} range. Arrows in Fig. 2 indicate the relevant spectral regions that will be analyzed in detail below.

From the results collected in Figs. 2–9 we first observe a

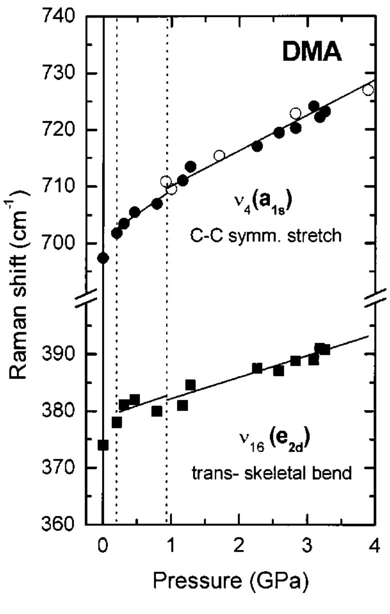

FIG. 4. Pressure shifts of the Raman bands ν_4 and ν_{16} of dimethylacetylene assigned to fundamental modes involving the carbon skeletal. Filled symbols correspond to measurements on sample 1, and opened symbols to those on sample 2. Symmetry assignment is given into parenthesis. Vertical broken lines at 0.2 and 0.9 GPa indicate transitions pressures for the liquid to phase 1, and phase I to phase II, respectively.

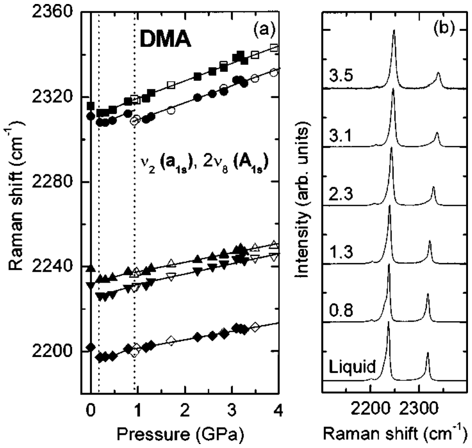

FIG. 5. (a) Pressure shifts of the Raman bands of dimethylacetylene assigned to the Fermi resonance between ν_2 (triple bond stretch) and $2\nu_8$ (asymmetric single carbon stretch overtone). Symmetry assignment is given into parenthesis. Filled symbols correspond to measurements on sample 1, and opened symbols to those on sample 2. Vertical broken lines at 0.2 and 0.9 GPa indicate transitions pressures for the liquid to phase I, and phase I to phase II, respectively. (b) High-resolution Raman spectra of dimethylacetylene in the spectral window corresponding to bands assigned to the triple bond stretch at different pressures. Pressure is given in GPa units. The Raman spectrum of the liquid was measured under room conditions.

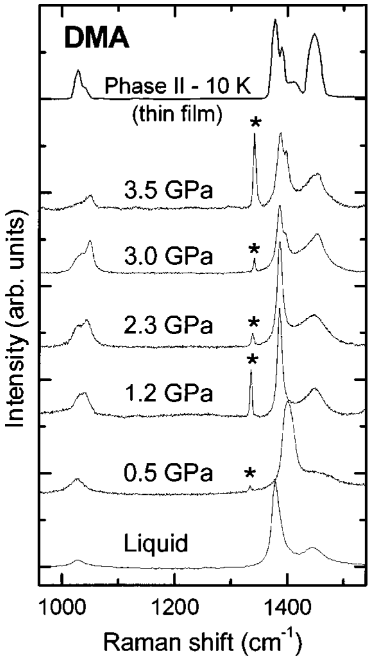

FIG. 6. High-resolution Raman spectra of dimethylacetylene in the spectral window corresponding to bands assigned to the methyl deformation (ν_3 and ν_{14}) and rocking (ν_{15}) fundamentals at different pressures. Pressure is given in GPa units. The Raman spectrum of the liquid was measured under room conditions. The band of the diamond pressure marker is indicated with an asterisk. A Raman spectrum of a thin film of DMA in the monoclinic phase II recorded at 10 K is included on the top. This spectrum has been adapted from Fig. 5 of Ref. 17.

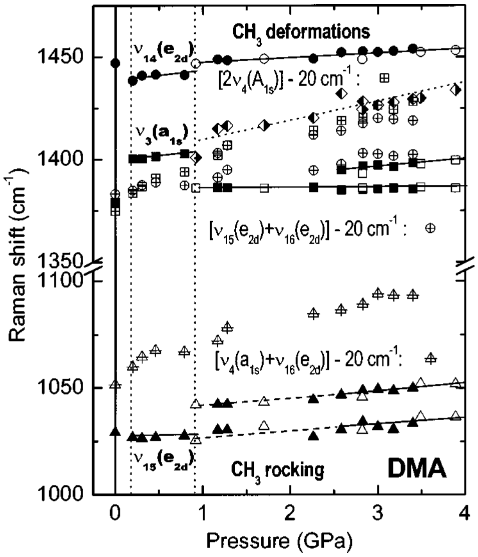

FIG. 7. Pressure shifts of the Raman bands of dimethylacetylene assigned to the methyl deformations (ν_3 and ν_{14}) and rocking (ν_{15}) fundamentals of dimethylacetylene. Symmetry assignment is given into parenthesis. Filled symbols correspond to measurements on sample 1, and opened symbols to those on sample 2. Straight lines correspond to fittings to fundamentals. Half filled symbols correspond to other bands obtained in the profile analysis that may be assigned to overtones and combination bands (see text); dotted lines are used to fit these bands. Crossed symbols are included to compare the overtones and combination bands obtained from the results plotted on Fig. 4 for ν_4 and ν_{16}, together with those of ν_{15} plotted at the bottom of the figure. The corresponding symbols are explained in the figure, together with the band assignment and the anharmonicity used for calculations (see text). Vertical broken lines at 0.2 and 0.9 GPa indicate transitions pressures for the liquid to phase I, and phase I to phase II, respectively. The two dashed lines between 0.9 and 2.6 GPa are used to indicate a partial split of the ν_{15} methyl rocking mode (see text).

transition at 0.2 GPa (liquid to crystal phase I), which agrees with the result (0.23 GPa at 300 K) obtained from the Simon-Glatzel equation reported in Ref. 29. Between 0.2 and 0.9 GPa most bands show significant frequency changes. A clear broadening is also observed in that pressure range, which is indicative of a highly disordered phase.[15] The symmetry of this phase has not been fully determined, although Ibberson and Prager[15] stated that it is most likely rhombohedral with three molecules per unit cell. Above 0.9 GPa there is clear indication of a second phase transition, very likely due to the transformation into the crystal phase II (see discussion below), in accordance with the phase sequence found with decreasing temperature.[15,17]

Both phases I and II are found to be stable crystal phases for DMA, but there is evidence of al least two metastable phases at temperatures below 120 K.[17,30] These metastable phases may appear when rapid cooled rates are applied on the sample, so it is conceivable that a metastable phase could be promoted by a sudden application of pressure.[17] In order to rule out this possibility we performed the second set of experiments in sample 2. This second sample was rapidly compressed from room pressure up to 1 GPa, and subsequently pressurized up to 4 GPa in 0.5–0.7 GPa steps. We compare in Fig. 3 the two spectral windows (methyl stretch and bending bands) where the most significant changes are expected to occur if a metastable phase is quenched. The similarity of the spectral features of the two samples (except for the different signal to noise ratio discussed before) indicates the absence of pressure-induced metastable phases in our experiments.

Now we shall describe the changes observed in our high-

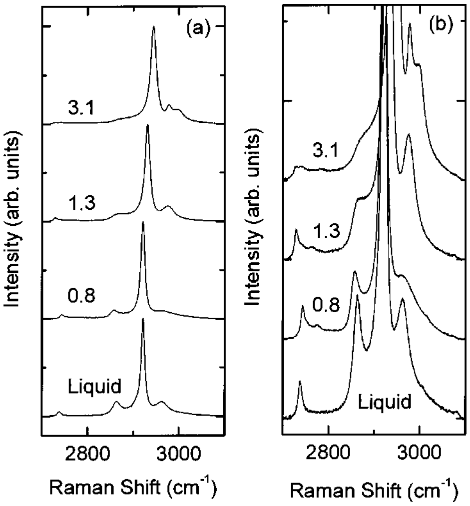

FIG. 8. (a) High-resolution Raman spectra of dimethylacetylene in the spectral window corresponding to bands assigned to the methyl stretch fundamentals (ν_1 and ν_{13}) and deformation overtones at different pressures. Pressure is given in GPa units. The Raman spectrum of the liquid was measured under room conditions. (b) Expanded view of the weaker bands of the spectra plotted in (a).

resolution spectra. In general, those modes assigned to the rigid carbon skeletal: ν_2 (triple bond stretch), ν_4 (single bond symmetric stretch), and ν_{16} (trans-skeletal bend), are less sensitive to phase transitions. We show in Fig. 4 the evolution of the bands assigned to the singled bonded carbons of the molecule; no splitting or significant frequency changes are observed in these bands.

The Raman features assigned to the triple bond stretch, those appearing between 2200 and 2400 cm^{-1}, do not exhibit significant variations either, except for their relative intensities. Let us say in passing that the interpretation of this part of the spectrum is controversial because of mixed Fermi resonance and isotopic effects.[17,20,21,23,24,30] The changes observed in the relative intensities reflect the effect of pressure on the Fermi interaction, and will be the subject of a forthcoming publication. We observe five components at the following wave numbers (in cm^{-1}) and intensities at room conditions: 2201 (w), 2231 (ms, sh), 2239 (vs), 2310 (m, sh), and 2315 (s). The 2310 cm^{-1} band has not been previously reported to the best of our knowledge, and its existence is revealed with increasing pressure.

The evolution with pressure of the five bands involving the triple bond stretch is analyzed in Fig. 5. There is a generalized decrease on the frequencies in going from the liquid phase to phase I, but the frequency jumps are not so important in subsequent transitions. Fermi resonance does not seem to affect the pressure evolution of these frequencies in great extent, i.e., all the bands exhibit a linear dependence with pressure. Of course, the slopes and relative intensities of the nonperturbed bands are modified by the Fermi interaction, but, for current purposes, this part of the spectrum does not indicate the occurrence of further phase transitions between 0.9 and 4 GPa, in agreement with the analysis of the modes assigned to the single bonded carbons of the molecule.

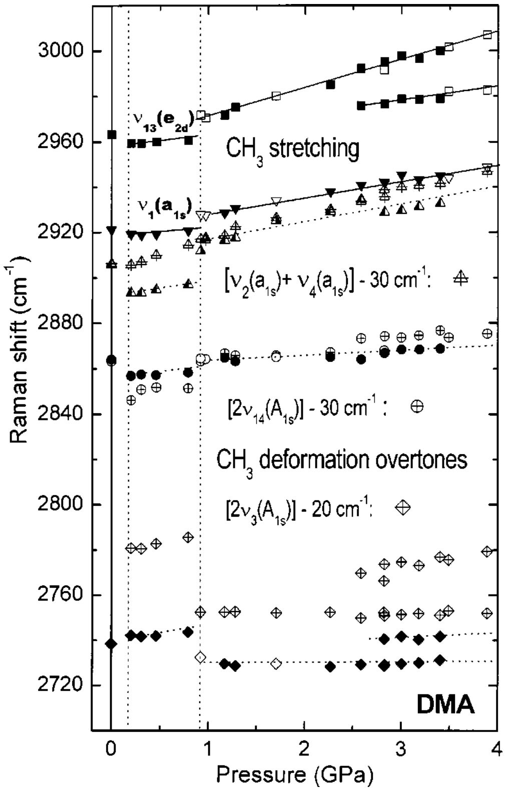

FIG. 9. Pressure shifts of the Raman bands of dimethylacetylene assigned to the symmetric methyl stretch fundamentals (ν_1 and ν_{13}) and methyl deformation overtones of dimethylacetylene. Symmetry assignment is given into parenthesis. Symbol explanation as in Fig. 7. Overtones and combination bands are obtained from the results plotted on Fig. 4 for ν_4, Fig. 5 for ν_2, and Fig. 7 for ν_3 and ν_{14}. Since ν_2 is in Fermi resonance with $2\nu_8$, our results correspond only to those obtained using the band appearing at 2239 cm^{-1} in the liquid. Those corresponding to the resonance band appearing at 2315 cm^{-1} appear at higher frequencies than those considered in the figure. Anharmonicities are calculated to match the frequencies of the bands obtained from the profile analysis in the liquid (see text). Two broken lines at 0.2 and 0.9 GPa indicate transitions pressures for the liquid to phase I, and phase I to phase II, respectively.

The spectral region corresponding to the methyl bending is shown in Fig. 6 at six selected pressures. The diamond pressure-marker Raman band appears in this spectral region, and it is signaled in the figure with an asterisk. In addition, a Raman spectrum of DMA adapted from Fig. 5 of Ref. 17 is included on top of Fig. 6. Since this spectrum was collected on a thin film at 10 K,[31] the relative intensities of the bands differ from those of the crystalline phase. On the other hand, all the frequencies are of course shifted due to the pressure and temperature differences existing between both experiments. In any case, there exist obvious similarities between the thin film Raman spectrum and those recorded in our samples above 2.6 GPa. For instance, the fourfold degenerated band ν_{14} is broad, and no splitting is observed. The number and positions of the rest of the bands also agree in both experiments, including the breaking of the fourfold degenerate methyl mode ν_{15} into two bands. Similar coincidences are observed when the whole Raman spectrum shown in Fig. 4 of Ref. 17 is compared, for instance, with our Raman spectra recorded at 1.3 and 3.1 GPa (see Fig. 2). However, as will be discussed later, we observe additional splitting of the band assigned to the fourfold degenerated methyl stretch ν_{13}. Anyway, according to this spectral window, our experiments support the conclusion that phase II could be the stable phase above 2.6 GPa, so we need to clarify whether an additional crystalline phase exists between 0.9 and 2.6 GPa or not. This issue can be clarified from a detailed analysis of the degenerate bands related to methyl groups where splitting is observed, namely (Raman active) ν_3 and ν_{15}.

The pressure evolutions of ν_3, ν_{14}, and ν_{15} are shown in Fig. 7. A splitting is already observed for the methyl rocking band ν_{15} at 0.9 GPa, however, as indicated by dashed lines in Fig. 7, the splitting is not complete after 2.6 GPa, when splitting of the methyl deformation band ν_3 (and the methyl stretch ν_{13}) takes place.

To explain the complex pressure evolution of the spectra, we have included in Fig. 7 the overtones and combination bands of ν_4 (C–C symmetric stretch) and ν_{16} (trans-skeletal bend), as calculated from results shown in Fig. 3. Since bond anharmonicities are unknown, and might be affected after a phase transition, a direct comparison is not possible. However, to a good approximation, anharmonicities can be derived from existing spectroscopic results in the gas phase.[26]

In a recent study, di Lauro *et al.*[26] found that the $(\nu_4+\nu_{16})$ combination band significantly perturbs the fundamental ν_{15}. Thus, we have used the 21 cm^{-1} difference observed between ν_{15} and $(\nu_4+\nu_{16})$ in the gas phase[26] to fix the zero pressure value of $(\nu_4+\nu_{16})$. This yields an anharmonicity of about 20 cm^{-1}, which is a reasonable value, as typical anharmonicities found in hydrocarbons vary from 10 to 40 wave numbers.[20,21] The pressure evolution of the $(\nu_4+\nu_{16})$ combination band indicates that Fermi resonance effects might be present because the perturbation is allowed by symmetry. However, our results indicate that Fermi resonance has no significant effect on the splitting of ν_{15}, as it should be already observed at low pressures. Mohaček and Furić already reported the breaking of the fourfold degenerate (ν_{11}/ν_{15}) mode into two modes in phase II of DMA.[17] We believe that the possibility that steric interactions would be involved in the partial split of the ν_{15} methyl rocking mode cannot be disregarded, but such pressure effect would not change the entire lattice symmetry but simply limit or reduce the motion of the methyl groups.

We have used the same anharmonicity value to estimate the position of the $2\nu_4$ and the combination band $(\nu_{15}+\nu_{16})$, including the observed splitting for ν_{15}.

Mohaček and Furić assigned the two bands around 1390 cm^{-1} to ν_3 and $2\nu_4$.[17] This assignment disagrees with our results plotted in Fig. 7, because the pressure evolutions of the bands suggest a quite different assignment. Our results indicate that the $2\nu_4$ overtone has no significant effect on the splitting of ν_3, because it should be already observable at low pressures, in contrast to our findings.

The pressure evolution of the $(\nu_{15}+\nu_{16})$ combination band indicates that Fermi resonance might be also involved in the splitting observed in ν_3. However, as in previous cases, we do not observe band splitting at low pressures. Thus, although it is difficult to give an unambiguous explanation of this complex spectral window, our results do not seem to support the existence of Fermi resonance for this band, and the splitting of ν_3 at 2.6 GPa is most likely directly related to the hindered rotation by the interaction of the methyl groups with the surrounding molecules.

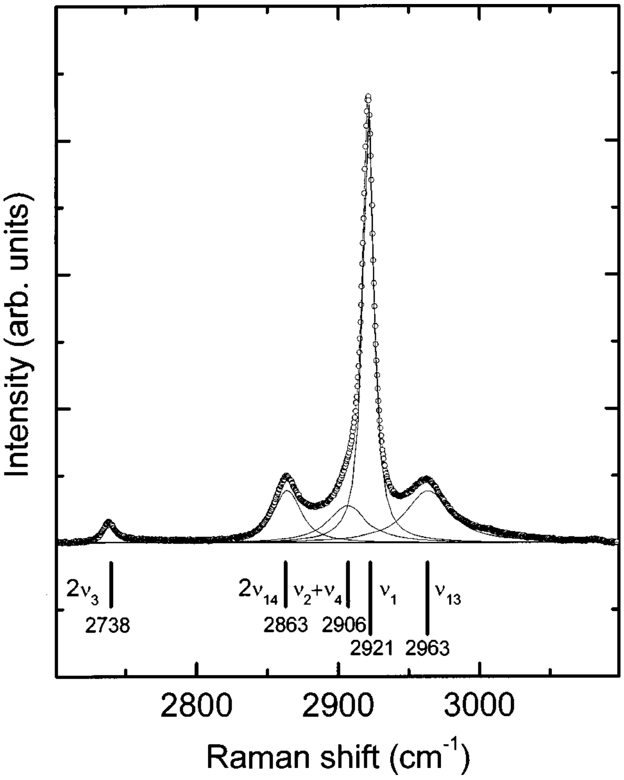

FIG. 10. High-resolution Raman spectra of liquid dimethylacetylene in the spectral window corresponding to bands assigned to the methyl stretch fundamentals and deformation overtones. Band profile analysis is included together with the symmetry assignment for the bands. The weak band that appears around 3000 cm^{-1} is not included into the profile analysis. Assignment of the 2906 cm^{-1} is deduced from the pressure evolution of the bands plotted in Fig. 9.

In order to confirm the above observations, we have performed a similar analysis of the methyl stretch region of the Raman spectrum of DMA. Some results are depicted in Figs. 8–10. Figures 8(a) and 8(b) show four representative spectra of this spectral region. Above 2.6 GPa there is a clear splitting of the ν_{13} Raman active mode (see Fig. 9), in agreement with our previous observations. Simultaneously, as shown in Fig. 9, the spectral features assigned to the methyl deformation overtones are strongly modified above 2.6 GPa. The pressure dependencies of all these bands are plotted in Fig. 10, together with the methyl bending overtones and combination bands obtained from the results plotted in Fig. 4 for ν_4, Fig. 5 for ν_2, and Fig. 7 for ν_3 and ν_{14}. In this case, we can estimate the bond anharmonicities of the overtones and combination bands by fixing the zero pressure values of the overtones to our observed Raman features in the liquid. The resulting anharmonicities are 30 cm^{-1} for $2\nu_{14}$, 20 cm^{-1} for $2\nu_3$, and 30 cm^{-1} for $(\nu_2+\nu_4)$.

Although it is evident that the analysis of the CH-stretch spectral is rather complex, we may extract some interesting conclusions from our analysis. First, the assignment of $2\nu_{14}$ is readily confirmed by the pressure shift of this overtone over the whole pressure range. These results also confirm that there exist small anharmonicity changes in going from the liquid to the disordered phase I, and again after the phase transition above 0.9 GPa. This observation is also in accordance with the profile changes observed in Fig. 8(b) in the vicinity of 2900 cm^{-1}.

Another interesting result from our analysis (see Fig. 10) is that the $(\nu_2+\nu_4)$ combination band can be unambiguously assigned to the shoulder appearing in the CH-stretch region, which must be included in the band profile analysis to fit the experimental Raman spectra. Our results indicate that the anharmonicity of this combination band is about 30 cm^{-1}. Although ν_2 is in Fermi resonance with $2\nu_8$, we plot only the results obtained using the band appearing at 2239 cm^{-1} in the liquid. The results corresponding to the band in resonance at 2315 cm^{-1} appear at higher frequencies, and very likely are responsible for the weak band appearing around 3000 cm^{-1} (see Fig. 10).

Finally, although the frequencies calculated for the $2\nu_3$ overtone does not match those observed in our experiments, the strong changes and the complex background observed in the methyl deformation overtone region between 2700 and 2900 cm^{-1} are clearly consequence of the splitting of the methyl deformation fundamentals. Furthermore, the pressure slopes and the splitting observed in the experiments are also consistent with this view, and confirm, at least qualitatively, the present analysis.

In summary, the analysis of the overtones and combination bands obtained from the corresponding fundamentals measured in different spectral windows support the conclusion that crystal phase II of DMA extends from 0.9 GPa to pressures close to 4 GPa. Between 0.9 and 2.6 GPa, the methyl groups of the DMA molecules rotate almost freely, and the rotation is subsequently hindered on further compression at pressures around 2.6 GPa.

IV. CONCLUSIONS

The high-pressure phase transitions of DMA at room temperature have been studied by Raman spectroscopy. Our analysis provides evidence for two phase transitions occurring at 0.2 (liquid-phase I) and 0.9 GPa (phase I-phase II). We also observe changes in the Raman spectra at pressures above 2.6 GPa that we interpret as a consequence of a hindered rotation of the terminal methyl groups. This effect is very likely due to the collapse of the DMA molecules by the effect of pressure. According to that interpretation, crystal phase II of DMA extends from 0.9 GPa to pressures close to 4 GPa. Between 0.9 and 2.6 GPa, the methyl groups of the DMA molecules rotate almost freely, but the rotation is hindered on further compression.

The previous conclusion is supported by the analysis of the overtones and combination bands obtained from the corresponding fundamentals measured in different spectral windows. The pressure evolution of the bands allows us to assign most of the complex features observed in the Raman spectra, and to explain the peculiar pressure changes observed during our experiments.

According to our present interpretation, crystal phase II of DMA extends from 0.9 GPa to pressures close to 4 GPa. This information is crucial to understand the reactivity of the DMA molecule at higher pressures, because a pressure-induced reaction is expected to develop in phase II.[18] In fact, the spectral background of sample 2 measurements above 3.5 GPa might indicate the onset of such a process. Since the orientation of the DMA molecules in phase II is substantially different to that found in solid acetylene, a completely different kinetic mechanism is expected to occur. Work in this direction is in progress.

Finally, in spite of the interest of our study within the high pressure framework, we believe that our results can be significant for their relation to rotation tunneling studies,[32] for which DMA is a model molecule.

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