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Step-Scan Fourier-Transform Infrared Absorption Spectroscopy of Cubic Solid Acetylene Clusters

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Step-scan Fourier-transform infrared (FTIR) absorption spectroscopy has been used to study large clusters of C_2H_2 and C_2D_2 formed in pulsed supersonic jets. The ν_3 stretching bands in the infrared spectra of C_2H_2 and C_2D_2 have been measured near 3230 and 2400 cm^{-1}, respectively. The band positions show the formation of acetylene nanoclusters with the cubic solid structure. The deuterium isotopic shift is in good agreement with the predictions based on the harmonic oscillator model and confirms the assignment of the observed features to cubic C_2H_2 and C_2D_2. This is the first infrared observation of cubic solid C_2D_2, and the ν_3 C−D stretching band was observed at 2399 cm^{-1}. Furthermore, deconvolutions of C_2H_2 spectra into Lorentzian components reveal a new feature at 3241 cm^{-1} attributable to large amorphous clusters.

Introduction

The structure of molecular clusters is a problem of considerable interest because they are intermediate matter between isolated gas-phase molecules and the bulk condensed matter. Acetylene clusters have been the subject of several spectroscopic studies. Small C_2H_2 clusters generated by free jet expansion have been studied extensively by various spectroscopic methods, in particular, infrared laser spectroscopy.[1−8] Miller et al.[1] first obtained the infrared predissociation spectra of the small clusters using an optothermal molecular-beam color-center laser spectrometer and assigned the band system in the 3250−3290 cm^{-1} region to the C−H stretching ν_3 mode of C_2H_2 dimer and large clusters. This study was followed by the observation of infrared predissociation spectra under different source pressures, showing that these bands were due to different clusters, the specific size of which remained unclear.[2] These unidentified bands have been rotationally analyzed subsequently by high-resolution infrared laser spectroscopy and assigned to the dimer, trimer, and tetramer of C_2H_2. In another infrared active C−H bending ν_5 mode, only spectral data concerning the dimer is available.[7] From theoretical studies in addition to these spectroscopic data, the most stable structures of the dimer, trimer, and tetramer are known to be T-shaped, cyclic, and cyclic, respectively. For the pentamer, a cyclic structure has been suggested.[8] Spectra of large clusters with $n > 5$ are too complex to be resolved rotationally even by high-resolution infrared spectroscopy. Therefore, the spectroscopic determination of whether these clusters have liquid, amorphous, cubic, or orthorhombic structure is limited to information concerning the position and shape of the band. In the case of acetylene, the factor group splitting allows the discrimination of crystal phase when the clusters have a structure similar to crystal.

C_2H_2 and C_2D_2 undergo phase transitions at 133[9] and 149 K,[10] respectively. X-ray and neutron diffraction studies show acetylene to be orthorhombic in the low-temperature phase with *Acam* symmetry[11] and cubic in the high-temperature phase with *Pa*3 symmetry.[9,12] Most infrared spectra of solid acetylene have been measured on a cold substrate or in a low-temperature gas cell.[13−17] These studies provide information on only the low-temperature orthorhombic form of solid acetylene. On the other hand, the infrared spectroscopic studies of cubic acetylene have been limited owing to the high vapor pressure of acetylene above the phase transition temperature. The first infrared spectrum of solid C_2H_2 clusters in the cubic phase has been reported by Dunder and Miller[18] using a low temperature (∼95 K) gas cell and Fourier-transform infrared (FTIR) spectroscopy. They have indicated that the particles were formed in the high-temperature cubic phase of solid, even below the phase transition temperature.

Useful information on the structure and size of large C_2H_2 clusters has been obtained from electron diffraction studies[19] and coherent anti-Stokes Raman spectroscopy (CARS).[20] Bartell et al.[19] have indicated from electron diffraction patterns that C_2H_2 clusters have both orthorhombic and cubic structures when formed at various experimental conditions. Lee et al.[20] have used CARS for the study of large C_2H_2 clusters in the ν_1 and ν_2 regions, showing that they underwent the phase transitions from liquid to orthorhombic through cubic phase as the clusters cool along the flow axis of the expansion.

In contrast, only limited information on large clusters of acetylene has been obtained in the infrared region. Fischer et al.[2] have obtained infrared multiple predissociation spectra of large C_2H_2 clusters formed in a continuous cluster source. In their experiment, the band position was shifted from those of the small clusters as the source pressure increased, and the most red-shifted band position did not vary at pressures higher than 1000 kPa. Because the band position was not coincident with that of the solid in the low-temperature orthorhombic phase, even at the highest pressure of 1890 kPa, they concluded that the structure of these clusters was different from that of the solid. However, they later have shown that this most red-shifted band can be assigned to solid C_2H_2 in the cubic phase.[18]

In an earlier paper, we have first applied pulsed supersonic jet FTIR absorption spectroscopy to the study of C_2H_2 clusters in the 800−5000 cm^{-1} region using several different concentra-

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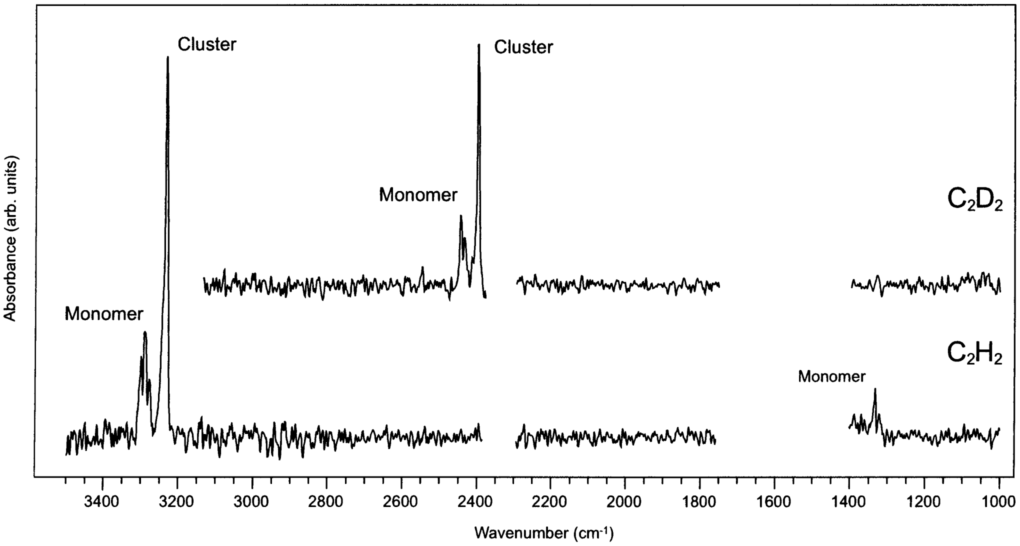

Figure 1. FTIR spectra of acetylene clusters. The top and bottom traces are obtained with 7% C_2D_2−Ar and 7% C_2H_2−Ar at the stagnation pressure of 350 kPa, respectively. The 1400−1750 and 2300 cm^{-1} regions are excluded because of the artifacts due to atmospheric H_2O and CO_2, respectively.

tions of C_2H_2 diluted in Ar.[21] The position of infrared absorptions was consistent with the peak of the solid C_2H_2 in the cubic phase. Unlike Fischer et al.,[2] we have observed only one dominant band corresponding to the large C_2H_2 clusters. In this study, infrared spectra of C_2D_2 clusters, as well as C_2H_2 clusters, were observed. This new experimental information allows the definite identification of large clusters as the cubic solid from the band position, the band shape, and the frequency isotopic shift. The cluster size is estimated on the basis of the experimental conditions and the behavior of another feature at 3241 cm^{-1}.

Experimental Approach

The experimental apparatus used in the present study has been described in detail elsewhere.[21] Acetylene clusters were generated in a molecular beam in the throat of a pulsed nozzle with an orifice of 0.8 mm diameter prior to supersonic expansion into a vacuum chamber. To increase the number of collisions, a channel extension with full length of 20 mm and circular holes of 3−5 mm diameter is attached to the nozzle head. C_2H_2 was obtained commercially and was used without further purification, while C_2D_2 was synthesized in our laboratory from the reaction of CaC_2 and D_2O. The isotopic constitution of the sample obtained after the reaction was found to be 78% C_2D_2, 21% C_2HD, and less than 1% C_2H_2 from the relative integrated band intensities for ν_3 band.

The commercial FTIR spectrometer (Bio-Rad, FTS-6000) equipped with step-scan mode, which allows us to collect time-resolved spectra, operates between 800 and 5000 cm^{-1} with a ceramic lamp, a liquid-nitrogen-cooled MCT detector, and a KBr beam splitter. Two spectral resolutions of 0.25 and 4 cm^{-1} were applied to obtain high- and low-resolution infrared spectra, respectively. The infrared probe beam intersected the free jet seven times in the region roughly 1−2 cm downstream from the nozzle with a multipass configuration composed of two slightly off-parallel plane mirrors. The operation of the pulsed nozzle is synchronized to the A/D converter trigger control signal of the FTIR spectrometer. To enhance S/N ratio, the data obtained at 2.5 μs sampling intervals are averaged within each scan step by the in-scan co-addition method. The interferograms were taken at 1000 μs time intervals and then Fourier-transformed to obtain the spectra at each time. The absorbance spectrum is obtained from the sample and background data recorded at 1000 and 2000 μs, respectively, after the trigger pulse.

For a typical experiment, ~10% acetylene in Ar was expanded using a stagnation pressure of 350 kPa and a gas pulse duration of ~1500 μs at a repetition rate of 10 Hz. These conditions are similar to those that optimized the production of cubic C_2H_2 clusters in our previous study.[21] For C_2H_2 clusters, the stagnation pressure was varied in the region of 200−450 kPa, while several different concentrations of C_2H_2 in Ar have been applied in our previous study.[21] Experiments using He and Ne instead of Ar as carrier gases were also performed.

Results

The low-resolution infrared absorption spectra are shown in Figure 1. These spectra were measured using 7% acetylene diluted in Ar with 4 cm^{-1} spectral resolution and 40 scans, which allows the observation of the wide wavenumber range of the infrared bands associated with the acetylene clusters formed in the supersonic free jet. A stagnation pressure of 350 kPa was applied. The dominant absorption features near 3230 and 2400 cm^{-1} in the C_2H_2 and C_2D_2 spectra, respectively, are assigned to the ν_3 fundamental mode. For C_2H_2, the feature at 3234 cm^{-1}, which is red-shifted from the monomer bands, is consistent with the band position of the solid in the cubic phase, as reported in our previous study.[21] In the case of C_2D_2, three absorption bands were observed in the region 2380−2460 cm^{-1}. Clearly, the two features at higher wavenumber represent the contours of P and R branch transitions of C_2D_2 monomer. The band shift and band shape of the strongest 2399 cm^{-1} feature are similar to those of the 3234 cm^{-1} feature in the C_2H_2 spectrum shown in Figure 1, indicating that the 2399 cm^{-1} band is likely associated with the ν_3 C−D stretch of solid C_2D_2. The blue-degraded profile with a steep red edge demands another component, as does the 3234 cm^{-1} feature in the C_2H_2 spectrum.

To investigate the absorption bands of C_2D_2 in more detail, a high-resolution infrared spectrum was measured as shown in Figure 2. The spectrum was recorded at a resolution of 0.25 cm^{-1} using 8% C_2D_2 in Ar at 350 kPa. The absorption band of C_2D_2 monomer was resolved into the rovibrational spectral lines. Based on the relative intensity of the rovibrational lines restricted to low-*J* transitions owing to adiabatic cooling in the supersonic

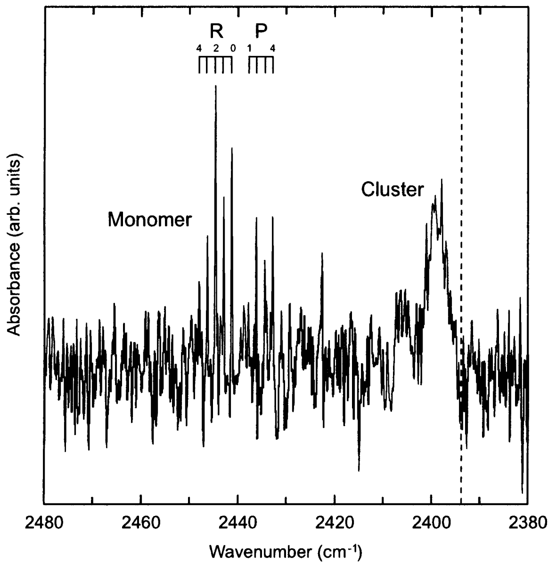

Figure 2. FTIR spectra for the ν_3 band of C_2D_2 monomer and clusters observed near 2400 cm^{-1} at high resolution of 0.25 cm^{-1}. P- and R-branch transitions up to $J = 4$ were measured for the monomer. The vertical dashed line indicates the band position of the orthorhombic phase of solid C_2D_2.

jet, the rotational temperature was calculated as 12 K, which is below the cubic−orthorhombic phase transition temperature of 133 K. The strong 2399 cm^{-1} feature remained broad and a weak broad absorption band was also observed at 2406 cm^{-1}.

Discussion

Comparison to Bulk Solid. According to the correlation diagrams of vibration modes for acetylene between gas phase and both orthorhombic and cubic phases of solid, the infrared spectra in solid phases are expected to consist of two infrared-active vibrational modes.[18,22,23] For the high-temperature cubic phase, the ν_3 band consists of a single component, while it splits into two components in the low-temperature orthorhombic phase. The splittings in the infrared spectra for the solid acetylene reported previously are consistent with those predicted by the correlation diagrams. In the ν_3 band of C_2H_2, two spectral components for the orthorhombic phase are centered at 3227 and 3243 cm^{-1},[17] while a single component for the cubic band occurs as a peak at 3232 cm^{-1}.[18] In the spectrum of large C_2H_2 clusters measured by Fischer et al.,[2] the cubic band was found near 3234 cm^{-1}. The agreement of the wavenumber of our 3234 cm^{-1} band with that of cubic solid C_2H_2 strongly suggests that the band can be assigned to solid C_2H_2 in the cubic phase. We note that the relative absorbance of the ν_3 mode to the $\nu_4 + \nu_5$ combination mode is not inconsistent with the assignment of the cubic solid. In the present experiments, no bands for the clusters were observed in the $\nu_4 + \nu_5$ region near 1300 cm^{-1}, while the absorbance for the ν_3 band for the clusters is stronger than that for the monomer under most experimental conditions. This is consistent with the fact that the absorbance ratio $I(\nu_3)/I(\nu_4+\nu_5)$ for the solid in both orthorhombic and cubic phases[17,18] is significantly larger than that for the monomer.

Although the dominant peak of orthorhombic C_2D_2 at 2394 cm^{-1} has been reported,[13,15] no infrared data for the cubic phase is available. It is obvious that our 2399 cm^{-1} band was red-shifted from the peak position of the orthorhombic solid by 5 cm^{-1}. Because the experimental conditions for C_2D_2 are the same as those for C_2H_2, in which cubic C_2H_2 was formed, we assume that the 2399 cm^{-1} band is due to cubic C_2D_2. To confirm the identification of cubic C_2H_2 and C_2D_2, we discuss the deuterium isotopic frequency shift in the orthorhombic, cubic, and gas phases using the harmonic oscillator model for the ν_3 infrared mode. For the theoretical value of acetylene monomer, $[\mu(C_2D_2)/\mu(C_2H_2)]^{1/2}$ is 0.734, where μ is the reduced mass, while the experimental ratio is 0.740. This value for the measured cubic peaks is 0.742, which is in good agreement with the experimental ratio for the orthorhombic acetylene calculated from the previous data,[15,17] as well as that of acetylene monomer. This agreement in the deuterium isotopic shift confirms that the 3234 and 2399 cm^{-1} features are assigned to solid C_2H_2 and C_2D_2, respectively, in the high-temperature cubic phase. This is the first infrared spectroscopic detection of the cubic solid C_2D_2.

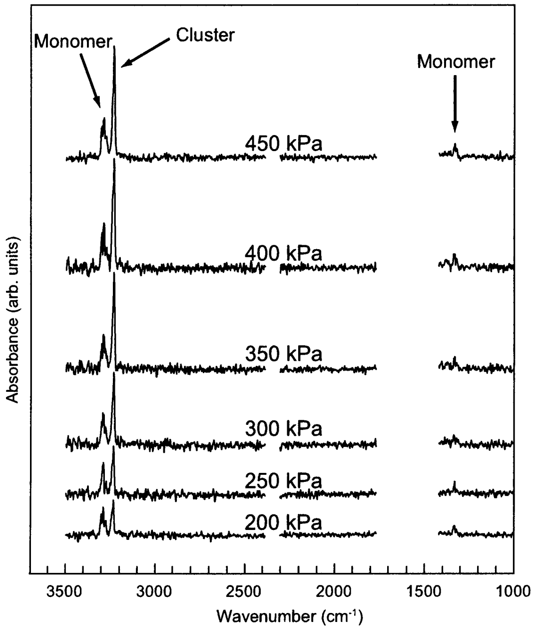

Figure 3. FTIR spectra observed with 10% C_2H_2 in Ar at stagnation pressures of 200, 250, 300, 350, 400, and 450 kPa.

Pressure Dependence. The infrared spectra recorded with 10% C_2H_2 in Ar at several different stagnation pressures are presented in Figure 3. The stagnation pressures applied in these experiments are 200, 250, 300, 350, 400, and 450 kPa. All spectra show the ν_3 asymmetric stretch and $\nu_2 + \nu_4 + \nu_5$ combination bands near 3300 cm^{-1} and the $\nu_4 + \nu_5$ combination band near 1300 cm^{-1}. The bands of both C_2H_2 monomer and clusters were observed in the ν_3 region, while only the monomer feature could be discerned in the $\nu_4 + \nu_5$ region because of the low S/N ratio (see Figure 3). In the present paper, therefore, attention is paid to the strong bands near 3300 cm^{-1}. Although the stagnation pressure was varied up to 450 kPa, the peak wavenumber of cubic bands was invariant at 3234 cm^{-1}, which is in good agreement with that reported by previous studies with different C_2H_2 concentration. Absorbance of the cubic feature becomes stronger as the stagnation pressure increases. Even at the highest pressure, no absorption bands of orthorhombic C_2H_2 were detected near 3227 cm^{-1}. Higher stagnation pressure may lead to the formation of the orthorhombic solid clusters.

Our previous work[21] has shown that two Lorentzians can produce the ν_3 band shape for C_2H_2 clusters. Here the measured infrared bands of C_2H_2 clusters were also fitted to two Lorentzian profiles as shown in Figure 4. Table 1 presents the peak positions, full widths at half-maximum (fwhm's), and relative intensities of these spectral features obtained in our earlier and present studies under a wide range of experimental

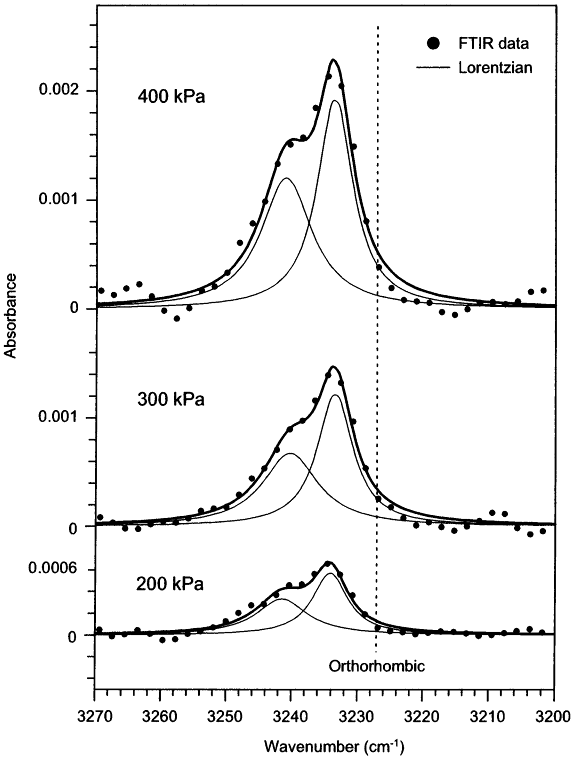

Figure 4. Lorentzian fits to the infrared absorption band of C_2H_2 clusters between 3200 and 3260 cm^{-1} at stagnation pressures of 200, 300, and 400 kPa. The vertical dashed line indicates the band position of the orthorhombic phase of solid C_2H_2.

TABLE 1: Wavenumbers, fwhm's, and Relative Intensities of Infrared Absorption Bands for C_2H_2 Clusters Measured under Various Experimental Conditions

$P_0 = 350$ kPa[a]

	cubic solid			large cluster			
C_2H_2/Ar (%)	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	I_{rel}	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	I_{rel}	$I_{cubic}/I_{cluster}$
5	3232.5	7.2	0.91	3243.8	11.0	0.18	5.1
10	3233.6	6.3	1.00	3241.5	11.8	0.40	2.5
15	3234.5	7.2	0.68	3241.6	9.0	0.68	1.0
20	3234.2	7.9	0.38	3241.4	9.8	0.44	0.9

10% C_2H_2 in Ar[b]

	cubic solid			large cluster			
P_0 (kPa)	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	I_{rel}	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	I_{rel}	$I_{cubic}/I_{cluster}$
200	3234.2	6.4	0.35	3241.5	9.4	0.20	1.8
250	3233.9	6.2	0.49	3240.8	10.1	0.29	1.7
300	3233.5	6.6	0.75	3240.3	10.3	0.41	1.8
350	3233.7	6.4	1.00	3240.3	9.7	0.56	1.8
400	3233.6	6.6	1.18	3241.0	9.5	0.73	1.6
450	3233.7	6.8	1.23	3241.2	10.3	0.57	2.2

Average

cubic solid		large cluster	
ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})
3233.7	6.8	3241.3	10.1

[a] Reference 21. [b] This work.

conditions. All spectra were reproduced well by two Lorentzian profiles centered at 3234 and 3241 cm^{-1} with fwhm's of about 7 and 10 cm^{-1}, respectively. The peak wavenumbers of these two bands remain essentially unchanged, while the intensities tend to increase steadily with stagnation pressure. These results indicate that two phases including the cubic phase of solid are consistently formed in our supersonic jet, regardless of the concentration of C_2H_2 and the stagnation pressure.

TABLE 2: Comparison between the Peak Wavenumber in FTIR Spectra for Acetylene Clusters and Previous Spectroscopic Results of Clusters and Solid in the Region of the ν_3 Band

	C_2H_2		C_2D_2		
cluster	ν (cm^{-1})	$\Delta\nu^a$ (cm^{-1})	ν (cm^{-1})	$\Delta\nu^a$ (cm^{-1})	I_H/I_D
monomer	3295		2439		0.740
dimer (slipped-parallel)	3285^b	−10			
	3282^b	−13			
	3279^b	−16			
dimer (T-shaped)	3272.5^b	−22.5			
trimer	3266^b	−29			
tetramer	3262.2^c	−32.8			
	3261.3^c	−33.7			
pentamer	3260.4^c	−34.6			
solid (cubic)	3232^d	−63			
solid orthorhombic)	3227^e	−68	2394.5^f	−44.5	0.742
	3241^e	−54			
this work (cubic)	3233.7	−61.3	2399	−40	0.742
	3241.3	−53.7			

[a] Wavenumber shifts relative to the monomer band. [b] Reference 2. [c] Reference 8. [d] Reference 18. [e] Reference 17. [f] Reference 15.

We turn next to the assignments of the unknown absorption features at 3241 cm^{-1}. Table 2 summarizes the wavenumber shifts relative to the monomer band for the ν_3 mode. The 3241 cm^{-1} band in the present spectra cannot be due to the orthorhombic C_2H_2 because of the absence of the more intense band reported near 3227 cm^{-1}. Clearly, this wavenumber is also different from those of small C_2H_2 and C_2H_2−Ar clusters.[1,3−6,8,24] Band positions of small $(C_2H_2)_n$ clusters ($n = 2−5$) slightly shift to the red as the cluster size increases. Infrared spectra of tetramer and pentamer are observed near 3260 cm^{-1}.[8] In the case of the ν_3 band, the band position converges toward the crystal band position as the cluster size becomes larger. As shown in Table 1, the relative absorbance of the cubic band at 3234 cm^{-1} to the 3241 cm^{-1} band decreases at higher C_2H_2 concentration. This may be due to reduction of the effectiveness of the carrier gas in extracting the heat of condensation from clusters, leading to inefficient production of solid via small and large clusters. The infrared band observed at 3241 cm^{-1} is attributed to large-sized clusters that are intermediate between gas and solid state, that is, the precursor to the formation of solid. As the stagnation pressure increases, the 3241 cm^{-1} band becomes more intense, as does the cubic band at 3234 cm^{-1}. It may be that these large-sized (amorphous) clusters could have a stable geometric structure with magic numbers. Another possibility is that the carrier gas Ar is included in the C_2H_2 cluster. When Ne and He are used instead of Ar as a carrier gas, however, the band at 3241 cm^{-1} does not disappear entirely, although the band intensities decrease by a factor of 2−6 because of the weaker cooling rate. Also, the bandwidth of ~10 cm^{-1} is not as broad as that found for the amorphous solid.

Cluster Size. In supersonic jet expansions, clusters with different sizes are produced simultaneously, which does not allow us to determine a precise cluster size. However, electron diffraction studies in supersonic jets have provided information on the mean size and indicated that the clusters are 10 nm in diameter.[19] CARS studies at high stagnation pressures have deduced that the mean cluster diameter was about 140 nm,[20] which is larger than that obtained by Bartell et al.[19] Here, we estimate the cluster size based on the comparison of the experimental conditions such as nozzle geometry, stagnation pressure, and sample concentration, which limit time for large clusters to assemble.

As mentioned above, the band position clearly suggests that the clusters consist of more than five acetylene molecules. Theoretical studies by Shuler and Dykstra[25] have shown that the structure of clusters with 13 molecules resembles the cubic solid structure and not the orthorhombic form. In the previous infrared spectroscopy of cubic C_2H_2 clusters,[1] infrared multiple absorption bands corresponding to the clusters with various sizes have been measured simultaneously. In our experiments, the only dominant band included two Lorentzian components, which arise from cubic solid and large clusters. This difference is likely due to the nozzle diameter. Despite the small nozzle diameter of 0.04 mm in the experiment by Miller's group,[1] the high stagnation pressures ($>$10 atm) would lead to the formation of cubic acetylene clusters. Although a difference of cluster size range may exist between these experiments, acetylene clusters with both the crystal and amorphous forms will be produced in both supersonic jets.

Bartell et al.[19] used a 0.1 mm diameter Laval nozzle of 30 mm length, and clusters in both the orthorhombic and cubic phases were detected when the stagnation pressure was more than 3 atm. From electron diffraction patterns, they have indicated that the clusters are 10 nm in diameter. In contrast, the spectra observed in the ν_1 and ν_2 regions by Lee et al.[20] show the three phases, liquid, orthorhombic, and cubic, but no small clusters were detected even near the nozzle throat because of the high stagnation pressure of $\sim$20 atm. In our experiments, the existence of the 3241 cm^{-1} spectral feature having an amorphous structure suggests cubic clusters formed are not as large as those in the CARS study.[20] Thus, the size of cubic solid clusters formed in the present experiment is most likely comparable to that in the electron diffraction study.[19] Also, from comparison of the experimental conditions, we believe that the size range for large acetylene clusters showing the 3241 cm^{-1} band is likely to be $<$10 nm.

Conclusion

Step-scan FTIR direct absorption spectroscopy of large C_2D_2 clusters formed in the pulsed supersonic free jet has resulted in the first infrared spectroscopic detection of the solid C_2D_2 in the cubic phase, which has been observed at 2399 cm^{-1}. The deuterium isotopic shift is in good agreement with the predictions based on the harmonic oscillator model and strongly supports the assignment of the observed features to cubic C_2H_2 and C_2D_2. Also, infrared absorption spectra have been obtained for clusters formed from C_2H_2 under various different supersonic jet conditions. The ν_3 band of C_2H_2 clusters was reproduced well by two Lorentzian profiles peaked at 3234 and 3241 cm^{-1}, which were assigned to the high-temperature cubic phase of the solid and to large amorphous clusters, respectively. Although the experimental data do not allow us to estimate the precise size of cubic acetylene clusters, the mean cluster size is likely to be $\sim$10 nm.

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