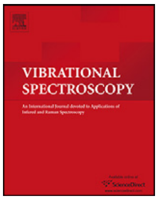
Vibrational Spectroscopy 57 (2011) 196–206

Contents lists available at ScienceDirect

Vibrational Spectroscopy

journal homepage: www.elsevier.com/locate/vibspec



Mid-infrared spectra of methane dispersed in solid neon and argon

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ARTICLE INFO

Article history:
Received 21 December 2010
Received in revised form 12 July 2011
Accepted 12 July 2011
Available online 23 July 2011

Keywords:
Spectra at high resolution
Dispersion in solid host
Molecular rotation
Quantitative spectrometry

ABSTRACT

We have recorded, in absorption, infrared spectra of samples of methane, CH_4 and CD_4, dispersed at molar fraction 0.0001–0.005 in solid neon, in solid argon and in their equimolar solid mixture in the temperature range 3–21 K and in the spectral domain 5000–500 cm^{-1} at resolution 0.04–0.2 cm^{-1}. We undertook quantitative fitting of the spectral profiles with components of gaussian and lorentzian shapes. Comparison of our spectra in regions of fundamental modes both ν_3 and ν_4 with published spectra of CH_4 and CD_4 in either crystalline para-dihydrogen or droplets of liquid helium indicates evidence for hindered rotation of CH_4 molecules in Ar but not for rotation of CH_4 or CD_4 in Ne or in a mixture of Ne and Ar. For CD_4 in solid Ar, the evidence for even hindered rotation is ambiguous. We make new assignments of lines to $^{13}CH_4$ and $^{13}CD_4$ in their environments in solid Ne and Ar.

1. Introduction

In conjunction with experiments on the photolysis of methane using radiation in the vacuum ultraviolet region from a synchrotron, we recorded, in the mid-infrared region, absorption spectra of methane, dispersed in solid neon, argon and their mixture at temperatures above 2.9 K. Although several authors have reported wavenumbers of lines due to absorption and Raman scattering from methane in relation to various experiments at temperatures less than 25 K with solid noble gases [1–12], crystalline para-dihydrogen [13] and droplets of liquid helium [14], we observed much fine structure and its dependence on temperature that greatly enhance the available information pertinent to the state of methane molecules under these conditions, which we present in this article. Experiments on neutron scattering of samples of methane in solid Ne [15] or solid Ar [16] have been interpreted for a similar purpose. A continuing concern is whether methane molecules can rotate, freely or otherwise, in these environments surrounded by atoms of noble-gas elements [17]. Free rotation of a molecule implies negligible interaction with its environment and a distribution over rotational states populated according to the temperature of a sample, with the corresponding ramifications for states of nuclear spin. If rotation be significantly hindered, the rotation might acquire a sense of a vibration, with occasional non-radiative transmission between possible equivalent geometries in which that libration occurs. These recorded infrared spectral lines in absorption attributed to either vibrational or vibration-rotational transitions provide a basis for an inquiry into the nature of the state of a solid sample comprising atoms of a noble gas with molecules of size comparable with the diameters of those atoms as a dilute component. For an accurate assessment of such states, spectra of great optical resolution are required, because both the widths of spectral lines, pertaining to samples at temperatures near 0 K, and their separations might be comparable with those characteristics of spectral lines observed for gaseous samples. Our interferometric spectrometer provides optical resolution far superior to that of instruments used by most preceding investigators of spectra of methane in solid samples prepared from noble gases, and our refrigerator enables the setting of temperature down to 2.9 K; these conditions are optimal for a critical reinvestigation of the possibility of rotation of methane molecules in solid Ne or Ar.

We have recorded spectra of CH_4 and CD_4 separately dispersed in solid Ne, solid Ar and equimolar mixtures of Ne and Ar, within the wavenumber domain 5000–500 cm^{-1}. That domain contains absorptions attributed to modes of vibration in modes attributed to either the degenerate deformation, designated ν_4, or the degenerate stretching vibration, ν_3, of these two isotopic species; only these two fundamental modes are regarded as intrinsically active in infrared spectra of these methanes. Our sensitivity is such that we measured absorption signals of $^{13}CH_4$ and $^{13}CD_4$ in natural abundance with a satisfactory ratio of signal to noise; that information is valuable in facilitating the analysis of the dominant spectra of $^{12}CH_4$ and $^{12}CD_4$. Our spectra of CH_4 and CD_4 dispersed in a mixed host of Ne and Ar in equimolar proportions at 3 K have no reported precedent.

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doi:10.1016/j.vibspec.2011.07.006

Information published about these systems began with Cabana et al. [1–3] who recorded both infrared [1,2] and Raman [3] spectra of CH_4 and CD_4 dispersed in solid Ar, Kr and Xe, and separately of solutions in liquid noble-gas elements [4]. Frayer and Ewing [5,6] made measurements of the relaxation of nuclear spin in solid samples prepared by freezing solutions from the liquid phase. Nelander [7] claimed to find evidence of rotation of methane in solid dinitrogen. At much superior optical resolutions 0.012–0.06 cm^{-1}, Jones et al. [8] deduced slightly hindered rotation of CH_4 in Ar, Kr and Xe, but not in Ne, based on measurements of only vibrational mode ν_4 of CH_4; in their similar experiments on CD_4 in solid Ar and Kr at resolution 0.04–0.06 cm^{-1}, Jones and Ekberg claimed a similar interpretation [9]. Regitz et al. [10] and Sagara and Ikezawa [11] made further measurements of Raman spectra at only moderate resolution. On the basis of spectra recorded at great resolution with light from a diode laser, Dubs alluded [12] to multiple lines associated with infrared absorption of only CH_4 in solid Ar near 1300 cm^{-1} but provided neither spectra nor details. For CH_4 and CD_4 [13] in solid para-dihydrogen and for CH_4 in droplets of liquid helium [14], nearly free rotational motion of methane is amply proven, as for other small molecules. Inelastic scattering of neutrons yielded data that were claimed to imply the free rotation of methane in Ar [16] and a nearly free rotation in Ne [15]. The complicated nature of spectra of absorbing molecules dispersed in crystalline deposits of noble gases is attributed to various factors, of which an important consideration for methane is that the symmetry of free space for the free molecule is lost when a molecule becomes constrained within a rigid environment imposed by a lattice of atoms of noble-gas elements. An aspect that Govender and Ford explored [17] is the effect of proximity of two or more methane molecules, both in solid Ar and in solid N_2, which is significant for molar fractions of methane greater than 0.005.

As a basis of a critical assessment of the abundant structure recorded in our spectra, we combine our experimental facilities that enable the measurement of mid-infrared spectra at effective spectral resolution 0.04 cm^{-1} for samples maintained at controlled temperatures greater than 2.9 K with quantitative spectrophotometric analysis that yields accurate specifications of absorption features. The results indicate that greatly hindered rotation of CH_4 and CD_4 might occur for its dispersions in solid Ar but not in mixed Ar and Ne, nor in solid Ne despite the many spectral lines distinguished in the regions of fundamental modes both ν_3 and ν_4.

2. Experiments

In a manifold designed for the purpose [18–21], we prepared gaseous mixtures of methane with Ar and Ne with conventional manometric techniques. CH_4 (nominal purity 99.999%, Matheson Gases), CD_4 (isotopic purity ~98%, Cambridge Isotope Laboratories), Ar (99.999%, Matheson Gases) and Ne (99.999%, Scott Specialty Gases) were used without further purification. A gaseous mixture of methane in Ne or Ar, or in an equimolar mixture of Ne and Ar, at a molar ratio selected in a range 0.0001–0.005 was deposited over 5–16 h onto a transparent crystalline plate (CsI, cooled to ~3.0 K) that serves as a substrate for a solid sample. A closed-cycle cryogenic refrigerator (Janis RDK-415) employed to cool the target is mounted on a sealed rotary plate; the cold CsI window is thereby rotatable to face a jet for sample deposition, or a port for infrared detection, or radiation from the beam line of the synchrotron. The cryo-chamber is evacuated with a turbomolecular pump (BOC-Edwards STC-451C) backed in turn by a scroll pump (Varian EXPPTS 06001); the pressure is typically less than 1.3 μPa before or after deposition, but might increase slightly during annealing of a sample. The rate of deposition was regulated in a range/$\mu mol\,s^{-1}$ 0.7–4.4, monitored with a flow controller (MKS 179A11CS1BV); for most experiments reported here the rate was 0.7 $\mu mol\,s^{-1}$. Infrared absorption spectra in transmission through the sample were recorded at various further stages of experiments with an interferometric spectrometer (Bomem DA8; SiC source, KBr beamsplitter) equipped with a HgCdTe detector (Belov Technology Co., Inc., IPH4800L) to cover the spectral range 5000–500 cm^{-1} and an InSb detector (IPH5000L) for the range 5000–1900 cm^{-1}; 400–1000 scans at resolution 0.04–0.2 cm^{-1} with Hamming apodization were recorded at each stage of the experiment. In Figs. 1–4, the effective optical resolution is 0.04 cm^{-1}, but 0.2 cm^{-1} for Figs. 5 and 6.

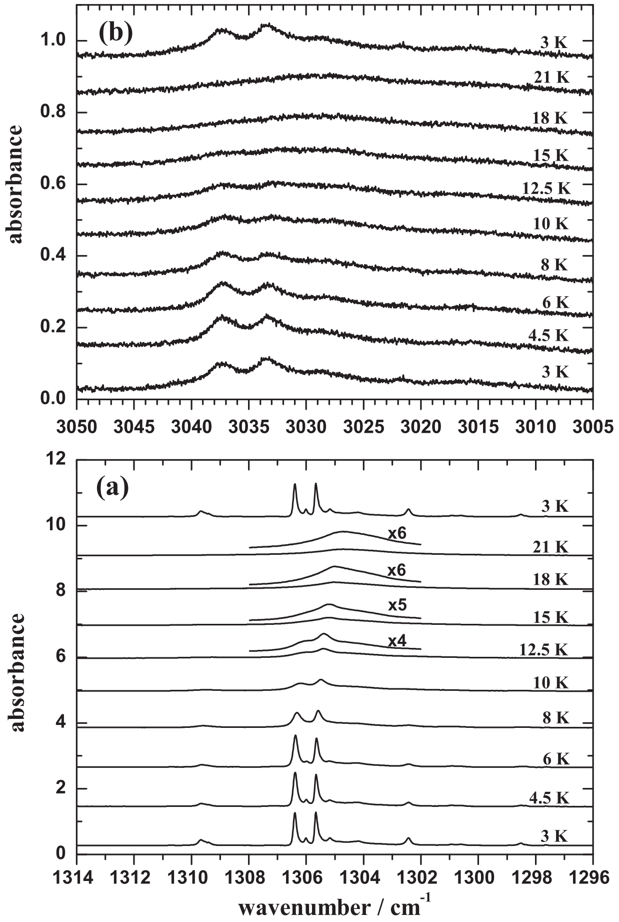

Fig. 1. Absorption spectrum of CH_4 dispersed in Ar (molar ratio 1000) at temperature/K 3, 4.5, 6, 8, 10, 12.5, 15, 18, 21 and returned to 3; (a) 1314–1296 cm^{-1}, (b) 3050–3005 cm^{-1}.

After deposition of the gaseous sample, we recorded spectra at the minimum temperature and then after increasing the temperature to selected values. An annealing operation consisted of holding the sample in darkness at a temperature below that of a significant volatility, up to about 9 K for Ne as a dispersant and 21 K for Ar. Selected spectra were fitted quantitatively (Grams software, Thermo-Galactic) to reduce the spectral lines or their deduced components to these characteristics: wavenumber at maximum absorbance, net maximum absorbance or stature, full width at half maximum absorbance and integrated area; for the shape of each measured line, we tested both gaussian and lorentzian profiles, and their combination.

3. Results

Figs. 1–6 show portions of the mid-infrared spectra of CH_4 and CD_4 in absorption associated with fundamental vibrational modes

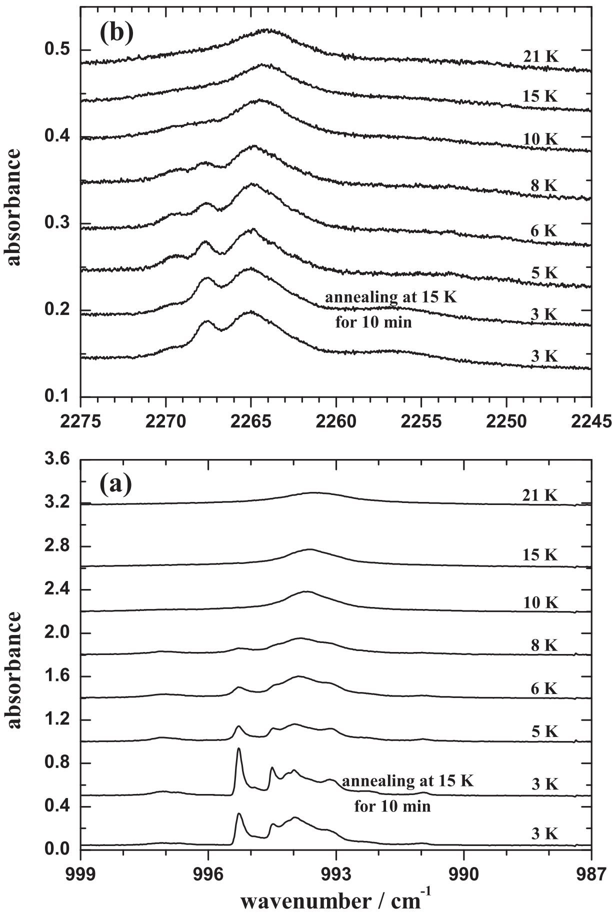

Fig. 2. Absorption spectrum of CD_4 dispersed in Ar (molar ratio 1000) at temperatures/K 3, 3 after annealing at 15 K for 10 min, 5, 6, 8, 10, 15, 21; (a) 999–987 cm^{-1}, (b) 2275–2245 cm^{-1}.

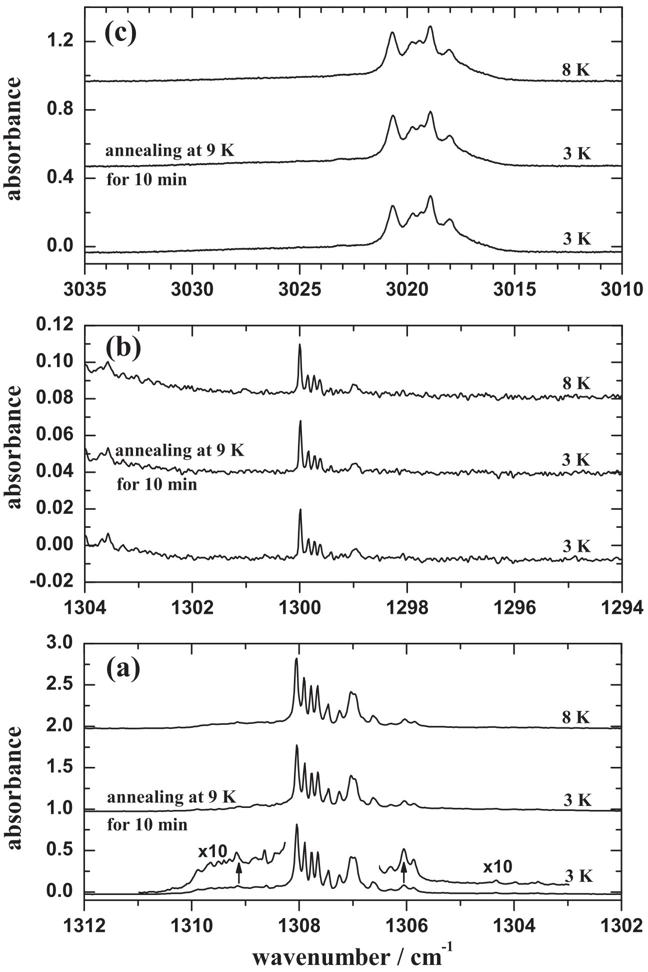

Fig. 3. Absorption spectrum of CH_4 dispersed in Ne (molar ratio 1000) at temperature 3 K after deposition, at 3 K after further annealing at 9 K for 10 min, and at 8 K; (a) 1312–1302 cm^{-1}, (b) 1304–1294 cm^{-1}, and (c) 3035–3010 cm^{-1}.

below 1500 cm^{-1} and above 2000 cm^{-1}. The vibration-rotational bands of gaseous $^{12}CH_4$ have centres near 1305.5 cm^{-1}, assigned to deformation mode ν_4, and near 3018.8 cm^{-1}, associated with C–H stretching mode ν_3; the corresponding wavenumbers for gaseous $^{12}CD_4$ are 996 and 2259.2 cm^{-1}, respectively. Both fundamental vibrational modes involve triply degenerate motions of symmetry class F. Other lines were recorded for both isotopic species associated with combination modes of vibration but are of peripheral interest; weak lines near 1625 and 3750 cm^{-1} are due to adventitious H_2O and near 2342 cm^{-1} to CO_2, both in vestigial proportions. In descriptions of our analysis of the spectra to follow, we discuss the spectral lines of carriers CH_4 and CD_4 in the two specified regions characteristic of their fundamental modes of vibration.

Fig. 1 presents, for a sample of CH_4 dispersed in solid Ar at molar ratio 10^{-3}, infrared absorption spectra in two selected regions as a function of temperature from 3 K to 21 K; these spectra demonstrate the dependence of the absorption profile in both regions on temperature. After the sample was deposited at rate 0.74 $\mu mol\, s^{-1}$ for 6 h at 2.9 K in darkness, the temperature of the sample in the dark was increased to 21 K for 1200 s, before the first spectrum was recorded. On an entirely empirical basis employing purely gaussian or mixed gaussian and lorentzian functions, a quantitative fit of the absorption profile between 1297 and 1311 cm^{-1} requires at least 26 component lines with gaussian shape and widths/cm^{-1} mostly in a range 0.08–0.3, with a hint of a further weak line near 1312.57 cm^{-1}. As temperature was increased from 2.9 K to 21 K, all these lines broadened, and eventually merged into a feature with a lorentzian profile, having a single maximum at 1304.428 ± 0.002 cm^{-1} and width 3.43 ± 0.01 cm^{-1}. Near 15 K three components with gaussian profiles are identifiable. An analogous fit of the absorption profile near 3020 cm^{-1} for the sample at 3 K, measured accurately with the InSb detector, required at least seven component lines of gaussian shapes with widths/cm^{-1} in a range 3–6.2; at 21 K only two components with gaussian shapes – at 3014.13 ± 0.28 cm^{-1} with width 14.8 ± 0.4 cm^{-1} and at 3029.7 ± 0.13 cm^{-1} with width 16.6 ± 0.15 cm^{-1} – suffice to characterize the net absorption; for spectra in both regions recorded with the HgCdTe detector, the ratio of their respective areas is 1:2.5. This thermal behavior is reversible in that, after cooling a sample from 21 K to 3 K, the subsequent spectrum greatly resembles the original spectra recorded immediately after deposition and annealing of the sample; explicitly, the two spectra in the region near 1300 cm^{-1} recorded 56 h apart were indistinguishable within the (small) level of noise, whereas either a general shift of the baseline occurred or a broad line (width ~70 cm^{-1}) arose between 3040 and 2970 cm^{-1}, with no relative effect on component lines.

Fig. 2 shows the corresponding spectra of CD_4 in Ar, again recorded at resolution 0.04 cm^{-1}, at several temperatures that demonstrate the dependence of the absorption profile in both fundamental modes on temperature. The reversibility of the variation of the absorption patterns is illustrated through annealing operations according to which the temperature of the sample was increased to 15 K and then decreased to 3 K for the recording of further spectra. As the temperature was increased to 21 K, the multiple

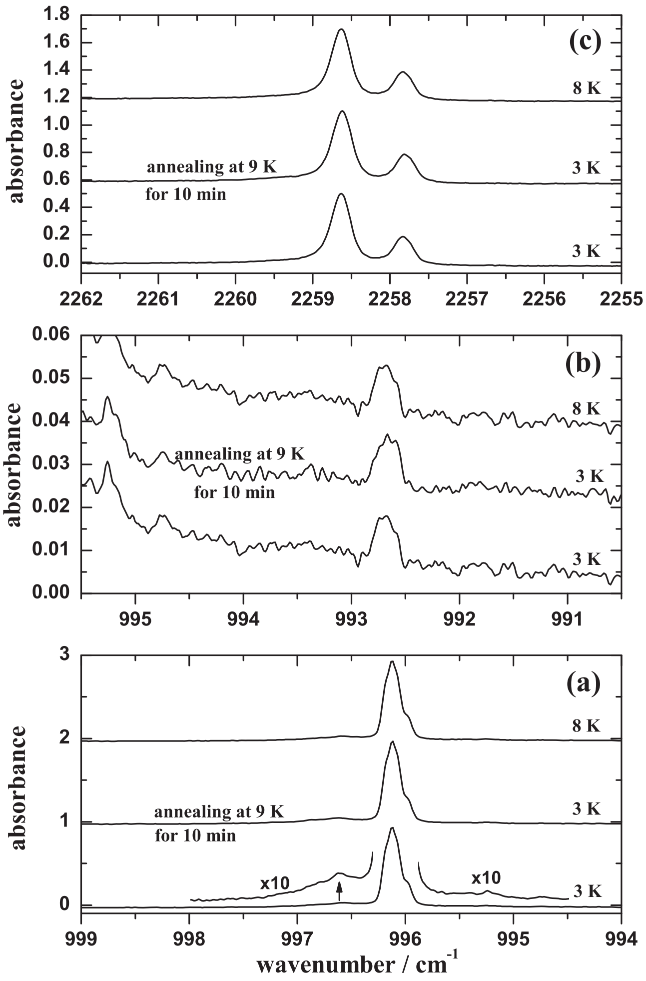

Fig. 4. Absorption spectrum of CD_4 dispersed in Ne (molar ratio 1000) at temperature 3 K after deposition, at 3 K after further annealing at 9 K for 10 min, and at 8 K; (a) 999–994 cm^{-1}, (b) 995.5–990.5 cm^{-1}, and (c) 2262–2255 cm^{-1}.

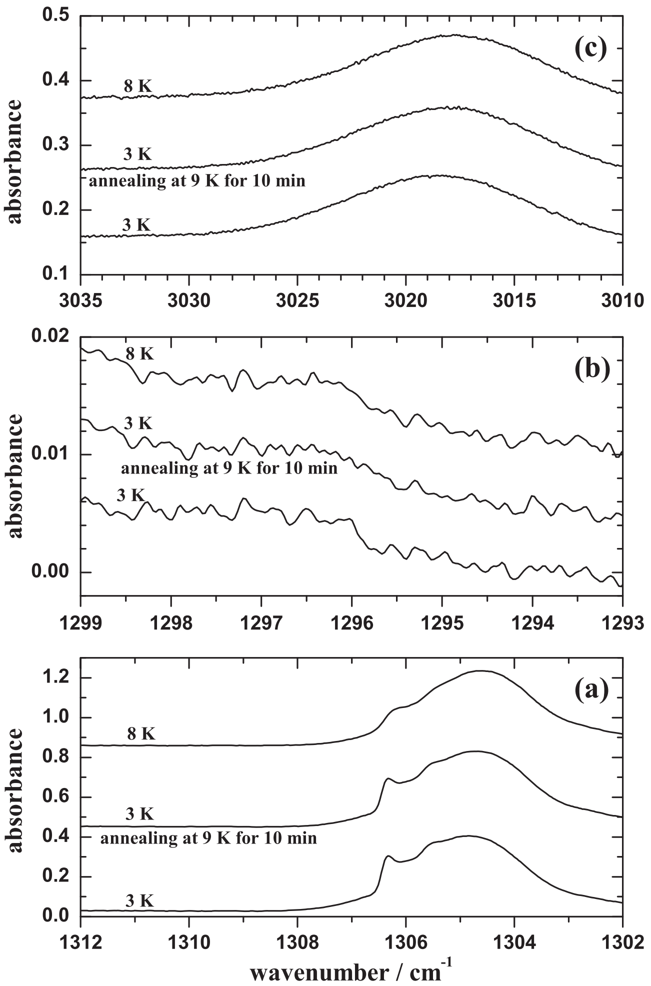

Fig. 5. Absorption spectrum of CH_4 dispersed in solid mixed Ar and Ne (molar ratios 500) at temperature 3 K after deposition, at 3 K after further annealing at 9 K for 10 min, and at 8 K; (a) 1312–1302 cm^{-1}, (b) 1299–1293 cm^{-1}, and (c) 3035–3010 cm^{-1}.

contributions to the pattern of absorption about 994 cm^{-1} blended into a single feature with maximum at 993.486 ± 0.003 cm^{-1} and a nearly lorentzian profile with width 2.54 ± 0.01 cm^{-1}, whereas at 3 K at least fifteen components, each of gaussian profile, contribute to the absorption between 999 and 990 cm^{-1}, with widths in a range 0.10–0.7 cm^{-1}. Comparison of a spectrum recorded at sample temperature 3 K directly after deposition in the dark and another spectrum recorded at sample temperature also 3 K but after annealing of the sample at 11 K for 300 s showed that the absorption features between 993.45 and 994.15 cm^{-1} gained intensity whereas other features on either side lost intensity. The relative intensities of weak lines near 1620 cm^{-1} due to vestigial H_2O likewise altered perceptibly. At 3 K at least five components of gaussian profile contribute to the absorption near 2265 cm^{-1}, with widths in a range 1.0–2.5 cm^{-1}; in contrast, at 21 K only two gaussian components were required, with lines at 2264.28 ± 0.02 cm^{-1} of width 6.65 ± 0.06 cm^{-1} and at 2253.75 ± 0.09 cm^{-1} of width 6.30 ± 0.22 cm^{-1}. The effect of the annealing operation at 11 K on absorption features in this region about 2265 cm^{-1} was imperceptible.

Because neon is more volatile than argon, an upper limit of temperature for samples held in an evacuated environment to avoid loss of sample through evaporation is 10 K. For this reason we annealed samples of CH_4, for spectra in Fig. 3, and CD_4, for spectra in Fig. 4, each separately dispersed in solid Ne at molar ratio 10^{-3}, to only 9 K before decreasing the temperature to 3 K to record further spectra. Fig. 3 for CH_4 in Ne presents traces at two temperatures, 3 K and 8 K, that demonstrate the essential lack of dependence of the absorption profile in both fundamental modes on temperature within that range. To reproduce the experimental profile within a range 1311–1305 cm^{-1} for CH_4 in Ne, the spectrum shown in Fig. 3a requires not less than 38 components, with a further seven lines in a range 1300–1299 cm^{-1}, all having fitted widths as small as 0.05 cm^{-1} that is comparable with the effective instrumental resolution. Among these 45 lines, most have widths less than 0.10 cm^{-1}, which is slightly greater than the optical resolution of our interferometric instrument. In the region near 3020 cm^{-1}, at least eleven components, with widths as small as 0.4 cm^{-1} for the intense components, are required to fit the profile, shown in Fig. 3c. The most notable feature of this profile is a long tail to wavenumbers greater than those of the intense lines in the group; in lieu of evidence of identifiable components of this tail, two lines with widths about 2.4 and 8 cm^{-1} were applied in the fit, in contrast to the analogous absorption above the most intense line at 1308.04 cm^{-1} that requires at least 15 distinct components.

Fig. 4 for CD_4 in Ne presents traces also at two temperatures, 3 K and 8 K, that likewise demonstrate the lack of dependence of the absorption profile in both fundamental modes on temperature. In Fig. 4c the traces near 2260 cm^{-1} are practically superimposable without distinction, whereas near 997 cm^{-1} in Fig. 4a the intensities of two weak lines near 996.6 and 996.9 cm^{-1} decreased

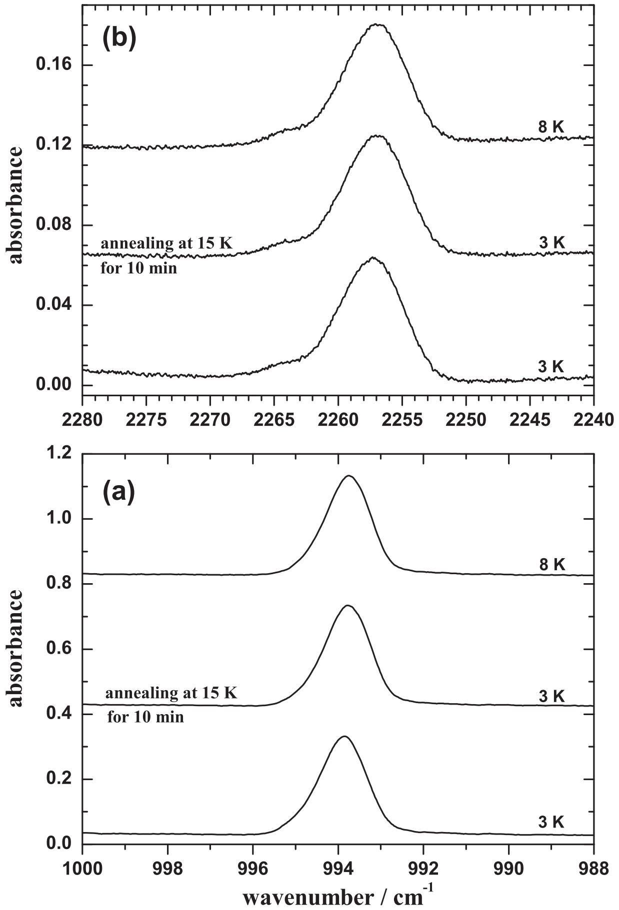

Fig. 6. Absorption spectrum of CD_4 dispersed in solid mixed Ar and Ne (molar ratios 500) at temperature 3 K after deposition, at 3 K after further annealing at 15 K for 10 min, and at 8 K; (a) 1000–988 cm^{-1}, (b) 2280–2240 cm^{-1}.

at increased temperature. In a profile with only one prominent maximum, the absorption near 996 cm^{-1} requires nine components, plus a separate line near 987.5 cm^{-1}, whereas the absorption near 2259 cm^{-1} exhibits two separate prominent maxima and a tail at greater wavenumbers, as for CH_4. Most components near 2259 cm^{-1} have widths near 0.2 cm^{-1} whereas some components near 996 cm^{-1} have widths less than 0.08 cm^{-1}.

Fig. 5, for CH_4, and Fig. 6, for CD_4, each show two selected regions of infrared absorption spectra of samples dispersed in Ne and Ar in equimolar mixtures, with molar ratio 10^{-3} of methane; because these spectra contain no narrow lines due to those samples, an effective spectral resolution 0.2 cm^{-1} sufficed for these measurements. For some samples the spectra in Fig. 5 of CH_4 in mixed Ar and Ne show only two prominent absorption lines, both slightly asymmetric. Their profiles conform closely to a gaussian shape, with only minor contributions from lorentzian functions; for this reason gaussian profiles were enforced. In other samples of CH_4 in mixed Ne and Ar of the same composition and deposited at the same rate and temperature of the substrate, some structure appears on the side of the line above 1304.8 cm^{-1}, as shown in Fig. 5, but neither the prominent line of CH_4 near 3000 cm^{-1} nor either prominent line of CD_4 in the two pertinent regions ever exhibited any such resolvable structure for samples in mixed Ne and Ar. Fitting the recorded profile of absorption required, however, a few components to reproduce the total absorption. Fig. 5a for CH_4 in mixed Ar and Ne near 3 K requires four components near 1300 cm^{-1} – one broad line with centre near 1304.8 cm^{-1} and three nearly resolved and narrower lines at 1305.6, 1306.05 and 1306.35 cm^{-1} for $^{12}CH_4$ plus a weak satellite line near 1296.6 cm^{-1} attributed to $^{13}CH_4$. In Fig. 5b, of another line near 3018.5 cm^{-1} and its prominent shoulder about 3033 cm^{-1}, both have widths from 7 to 9 cm^{-1}. In photolysis experiments, to be reported elsewhere, the spectrum obtained on subtraction of these methane signals after photolysis from the same signals before photolysis, which corresponds to a depletion spectrum, showed that these line shapes remained essentially constant; there was no evidence of inhomogeneous broadening of the lines due to absorbers in distinct environments.

Fig. 6 for CD_4 in mixed Ar and Ne near 3 K likewise exhibits only one prominent line near 995 cm^{-1} plus a weak satellite line near 987.4 cm^{-1}, and another single line near 2257 cm^{-1}. Both prominent lines possess weak shoulders at greater wavenumbers; such a tail extends to 989 cm^{-1} for the former line, and a single broad tail extends to 2270 cm^{-1} for the latter line. All these lines were fitted satisfactorily with generally only gaussian functions, but widths varied from about 1.3 cm^{-1} for intense components near 994 cm^{-1} to about 5 cm^{-1} for the two components near 2257 cm^{-1}. Annealing a sample to 9 K altered the spectrum in both regions inappreciably, but warming the sample progressively to 25 K caused the prominent lines to shift to near 993 and 2263 cm^{-1}; the total intensity of each feature decreased to about one third the initial value, indicating loss of part of the sample during that warming. Unlike the case of CH_4, no variation of the shapes and widths of lines of CD_4 in mixed Ar and Ne was found in the several experiments, each with a fresh sample.

Four further figures presented in supplementary information facilitate comparison and contrast of spectra of separate samples, although information therein is available in Figs. 1–4. Fig. S1 shows that for CH_4 in Ne the lines associated with a degenerate stretching mode designated ν_3 are clustered closely about the band centre at 3018.8 cm^{-1} for the gaseous compound, whereas for CH_4 in Ar the corresponding lines are spread more widely about 3035 cm^{-1}. For the degenerate deformation designated as ν_4 the lines of CH_4 in Ne are clustered about 1308 cm^{-1} whereas the lines for CH_4 in Ar are clustered about 1306 cm^{-1}, to be compared in either case with 1305.5 cm^{-1} for the band centre of a gaseous sample. In Fig. S2 we compare spectra of CD_4 in Ne and Ar; for the Ne sample two prominent lines arise with maxima near 2257.8 and 2258.6 cm^{-1} shifted slightly from the band centre at 2259.2 cm^{-1} for the gaseous sample, whereas for CD_4 in Ar the pattern has a single maximum of absorption near 2268 cm^{-1}. Near 1000 cm^{-1}, absorption of CD_4 in Ne exhibits only one prominent feature, but there are several lines for CD_4 in Ar. Fig. S3 enables a comparison between absorption patterns of CH_4 and CD_4, both in Ar, with the features of CD_4 shifted to facilitate that comparison, and Fig. S4 analogously between CH_4 and CD_4 in Ne. Supplementary tables S1–S6 present the characteristics of the components that contribute to the total absorption of CH_4 and CD_4 in Ar and Ne in modes ν_3 and ν_4 at selected temperatures.

4. Analysis and discussion

In the accumulated literature, the proffered explanations of absorption features of infrared spectra of methane dispersed in solid deposits at a small molar fraction relative to Ne, Ar, krypton or xenon as solid host include almost free or significantly hindered rotation, multiple sites within a crystalline environment defined by species only other than methane, and multiple sites including two or more methane molecules in proximity. We exclude the latter possibility as being responsible for a significant fraction of the total infrared absorption of methane in our samples at molar fraction 10^{-3} or smaller; to account for most absorption in each region, an explanation in terms of an association between methane molecules would be statistically unlikely because of the great dilution [22]. Govender and Ford [17] endeavoured to make some assignments to associated CH_4 molecules on the basis of quantum-chemical calculations on two adjacent methane molecules and of their spectra of methane in solid dinitrogen at temperatures in a range 17–35 K, but only for molar fractions of CH_4 greater than 0.005, and not for samples in solid Ar; the calculations of these authors [17] indicated that two adjacent methane molecules absorb light in vibrational modes, both ν_3 and ν_4, at wavenumbers slightly smaller than for methane molecules surrounded by host atoms.

After a summary account of the influence of rotational motions on vibrational transitions, we consider in turn spectra of CH_4 and CD_4 dispersed in Ne and Ar in equimolar proportions, in Ne and in Ar.

4.1. *Rotational motion*

For free rotation of a molecule of type spherical rotor, such as CH_4 or CD_4, B denotes the single primary rotational parameter. If this parameter vary only slightly between combining vibrational states, the interval between adjacent rotational lines, neglecting multiplet structure, within branches P and R is roughly 2 B; the same separation 2 B is applicable also between the head of branch Q and the first line in branch either P or R. In the absence of coupling between vibrational and rotational motions, B has the significance of a reciprocal moment of inertia, but, when such coupling occurs, an effective value of B becomes applicable; its value is then typically less than that implied by the reciprocal moment of inertia. For free CH_4, that reciprocal moment of inertia implies 2 $B \sim 10.5\,cm^{-1}$ and for free CD_4 2 $B \sim 5.2\,cm^{-1}$, for comparison with kT equivalent to $\sim 2.1\,cm^{-1}$ at 3 K.

As examples of spectra that have been claimed to demonstrate unequivocally the rotation of methane molecules in a crystalline environment, we recall the absorption spectra of CH_4 and CD_4 in crystalline para-dihydrogen at 4.5 K [13]. Because a transition, designated Q(0) that implies $\Delta J = 0$, from the ground vibration-rotational state, for which $J = 0$, is lacking in absorption, the only transition from this ground state has $\Delta J = 1$, corresponding to branch R, so R(0), and thus up to 2 B above the band centre that implies the formally purely vibrational transition. Once the first excited rotational state, for which $J = 1$, becomes populated, transitions in each of branches P, Q and R, with $\Delta J = -1, 0, +1$ respectively, become observable. For CH_4 and CD_4 in para-dihydrogen and both ν_3 and ν_4 [13], well resolved and separate lines are assigned to transitions from not only the ground rotational state but also the first excited rotational state; with roughly equal separations between adjacent lines, these four lines are designated P(1), Q(1), R(0) and R(1) in order of increasing wavenumber. The intensities of lines P(1), Q(1) and R(1) relative to that of line R(0) are expected to be sensitive to temperature, according to the Boltzmann factor for a population at thermal equilibrium of the state for which $J = 1$. The separation between each two adjacent lines, among those four, is 2 B, in which B would be the effective rotational parameter; the total extent of the pattern would thus be 6 B. As in the spectrum of a gaseous sample of CH_4, this effective parameter is affected by the extent of Coriolis coupling with other vibrational modes. For this reason, the quantity 2 B for gaseous CH_4 is effectively about $10\,cm^{-1}$ for the upper state of transition ν_3 near $3000\,cm^{-1}$ but about $5\,cm^{-1}$ for the upper state of ν_4 near $1300\,cm^{-1}$; for gaseous CD_4, the corresponding values of 2 B are approximately $5\,cm^{-1}$ for ν_3 near $2260\,cm^{-1}$ but $2.5\,cm^{-1}$ for ν_4 near $1000\,cm^{-1}$. The effective rotational parameters for CH_4 and CD_4 in solid para-dihydrogen average about 0.88 times the corresponding values in the gaseous phase [13], attributed to an effect of the environment that increases the effective moment of inertia. Splittings of the lines for samples in para-dihydrogen are attributed to effects of the anisotropic crystalline host, which has mostly an hexagonally close-packed lattice, although regions of a cubic close-packed lattice occur to a minor extent [13]. For CH_4 and CD_4 in droplets of liquid helium at 0.37 K [14], no prominent line P(1), Q(1), R(0) and R(1) is split, and line P(2) was also observed, attributed to slow conversion of states of nuclear spin of protons, of symmetry classes A, F and E; the effective rotational parameters for states combining to produce bands v_3 of both CH_4 and CD_4 in liquid helium are similar to the values for the free molecules. For methane in droplets of liquid helium, an appreciable variation of the temperature of samples is impracticable, but, for CD_4 in solid para-dihydrogen, increasing the temperature from 4.5 K to 8 K caused broadening of the lines, with or without a slight shift of wavenumber depending on the particular transition [13]. As a model or criterion to assess our own spectral observations, we take these conditions for samples in solid para-dihydrogen and droplets of liquid helium to be characteristic of methane molecules undergoing only slightly hindered, or nearly free, respectively, rotation at temperatures less than 10 K. The detection of transitions other than R(0) at temperatures near 0.37 K for dispersions in liquid helium or even 4.5–8 K in solid para-dihydrogen is attributed to the failure of relaxation to the ground state because of lack of conversion of nuclear spin [13,14]. All these spectra of CH_4 and CD_4 show narrow lines in regions of both ν_3 and ν_4.

Frayer and Ewing reported experiments in which solutions of only CH_4 in liquid Ar were cooled to a crystalline phase [5,6]; spectra were then recorded as a function of time, without or with O_2 added to their initial samples. A half-life about 5400 s for relaxation from states associated with $J = 1$ to the ground state $J = 0$ was deduced [6] for samples of CH_4 in Ar, but 200 s when O_2 was added at a proportion comparable with that of CH_4. Jones et al. reported a corresponding half-life about 9000 s for their samples of CH_4 in Ar prepared with pulsed gaseous deposition [8]. For our samples of CH_4 in solid Ar prepared with slow continuous deposition at 3 K, the rate of relaxation at that temperature was sufficiently small that we could increase the temperature of a sample to 9 or 21 K for several hours; when we decreased the temperature to 3 K, the spectral profiles remained characteristic of the elevated temperature for a sufficient interval to record the spectrum. A difference spectrum between the spectrum of a sample maintained at 3 K for 16 h and another spectrum recorded immediately after returning to 3 K from a greater temperature hence indicated the altered features characteristic of the elevated temperature, equivalent to a difference spectrum between spectra recorded of samples at the two temperatures. For CD_4 in Ar the rate of relaxation was much greater than for CH_4, in agreement with reported findings [9]; for this reason we recorded spectra of samples of CD_4 in Ne or Ar at the elevated temperature of interest and performed direct spectral subtraction to observe the effect of temperature.

4.2. *CH_4 and CD_4 dispersed in solid mixed Ar and Ne*

Providing that each molecular absorber has an identical environment and lacks significant interaction with another absorber, the simplest infrared spectrum of a molecular entity present as a dilute component in a mixture held rigidly with atoms of a noble gas in a polycrystalline deposit would presumably arise from a single line, not composite, for each active vibrational mode of a particular isotopic variant; the effects of preferential alignment that might be observed in measurements with polarized light [8] are here ignored. This condition of a single maximum of absorption for each vibrational mode seemed to prevail for some samples of CH_4, and all samples of CD_4, dispersed in solid Ar and Ne in equimolar proportions at 3 K, with CH_4 or CD_4 at molar fraction 10^{-3}. This single absorption feature and the lack of dependence of its shape on temperature provide no evidence for rotational motion of CH_4 or CD_4 dispersed in solid mixed Ar and Ne. For CH_4, one prominent line has its centre at $3018.17\,cm^{-1}$, with stature 0.132, full width $8.9\,cm^{-1}$ at half maximum net absorbance and area $1.331\,cm^{-1}$, but requires a weak gaussian component at $3025.0\,cm^{-1}$ and of area $0.0885\,cm^{-1}$

to reproduce satisfactorily the profile; both components conform closely to a gaussian shape – allowing a lorentzian component in the shape of the major component produced a contribution only a tenth of the total area, thus insignificant. The wavenumber of this feature practically coincides with that of the band centre for mode ν_3 of gaseous $^{12}CH_4$ near 3018.8 cm^{-1}; any shift due to the effect of the solid solvent or environment is hence small relative to typical displacements of order 15–30 cm^{-1} for molecular species dispersed in solid Ar [23]. If we assume that, dispersed within solid mixed Ar and Ne, a molecule of methane essentially preserves its molecular identity, we attribute the observed absorption feature centred at 3018.17 cm^{-1} to an isolated molecule of CH_4 and its fundamental vibrational mode ν_3. The other prominent line at 1304.7 cm^{-1} that displayed a single maximum in the absorption spectrum of CH_4 required, to yield a satisfactory reproduction of the total profile of absorption, three gaussian components as listed in Table S5. For this feature associated with mode ν_4 of $^{12}CH_4$ for which the band centre in the gaseous state is near 1305.5 cm^{-1}, the total integrated absorption for this particular sample is thus 1.28 cm^{-1}; the ratio of this area to that for the other prominent absorption near 3019 cm^{-1} is 0.95. For comparison, for gaseous CH_4 the ratio of the strengths of the corresponding bands is about one half [24]. The wavenumbers of these absorption maxima clearly correspond to those of the centres of vibration-rotational bands of gaseous $^{12}CH_4$ associated with fundamental modes of vibration active in infrared absorption. With those two prominent lines appears a minor line centred at 1296.60 ± 0.01 cm^{-1} of stature 0.0034 ± 0.00004, width 1.98 ± 0.01 cm^{-1} and area 0.0071 cm^{-1} is assigned to $^{13}CH_4$ in its mode ν_4 on the basis of the known isotopic shift and the ratio of that area with the total area of the three components listed above, which is somewhat less than the known relative natural abundance 0.011 of ^{13}C. For mode ν_3 of $^{13}CH_4$, the predicted isotopic shift is comparable with the width of the line of $^{12}CH_4$, precluding its detection in this spectrum under our conditions. We recorded also a weak line near 2821.9 cm^{-1}, attributed to combination $\nu_2 + \nu_4$, and two weak lines at 4213.8 and 4313.0, attributed to combinations $\nu_1 + \nu_4$ and $\nu_3 + \nu_4$, respectively; although each such line has a slightly asymmetric shape and a width at half maximum stature in a range 1.3–9.5 cm^{-1}, there is no convincing evidence of distinct multiple components.

Although these spectra of CH_4 and CD_4 dispersed in solid mixed Ar and Ne show generally only broad lines, for CH_4 three nearly resolvable components about 1305.6, 1306.05 and 1306.35 cm^{-1}, in order of increasing intensity, appeared in some experiments beside the dominant and reproducible prominent feature near 1304.7 cm^{-1}. These three lines appear to constitute a sequence, but an interpretation is lacking. No counterpart of those three lines appeared in any spectrum of CD_4 in solid mixed Ar and Ne. Fitting of all lines with gaussian profiles invariably indicated a necessity of multiple components for which either no distinct maximum was discernible or only a point of inflexion might be deduced along the curve of total absorbance; fitting a line as a single feature of either gaussian or lorentzian shape, or their combination, yielded a poor reproduction of these profiles. These spectra seem to be compatible with methane molecules experiencing diverse environments with neighbouring atoms comprising Ar and Ne in varied proportions. There is no evidence of separate crystallites of nearly pure Ar or Ne, due to phase separation, with methane as impurity therein, which might yield approximately a superposition of spectra of methane in Ar and in Ne separately. Measurements with X-ray diffraction of samples prepared on deposition of a mixture of methane in Ar at a small molar fraction, under conditions similar to those commonly employed for experiments involving infrared spectra of those deposits, indicated that deposits comprised crystallites of mean diameter 40–50 nm [25]. Such crystallites cause significant Rayleigh or Mie scattering of the incident infrared light that is readily discernible for our deposits of Ar, and of mixed Ar and Ne, but was much less pronounced for Ne; this scattering caused significant deterioration of the ratio of signal to noise in the region of mode ν_3 of CH_4 relative to the region of mode ν_4, for instance. The spectra thus indicate an approximately homogeneous mixture of solid Ar and Ne, consistent with a depletion spectrum recorded after photolysis of methane with vacuum ultraviolet light.

For CH_4 samples, a weak but distinct additional signal near 1309 cm^{-1} requires, for its quantitative description, two gaussian components, at 1308.9 cm^{-1} as a shoulder and at 1309.4 cm^{-1} and of total area 0.0051 cm^{-1} for the same sample as above; we suggest no assignment. Whereas a line at 1623.57 cm^{-1} due to trace adventitious H_2O had a well defined lorentzian profile, of width 1.66 cm^{-1}, a weaker line that was occasionally observable at 1607.81 cm^{-1} exhibited a gaussian profile of width 1.39 cm^{-1}; another faint line at 2340.6 cm^{-1} due to CO_2 had a purely gaussian profile of width 3.5 cm^{-1}.

The corresponding spectrum of CD_4 in mixed Ne and Ar contains two major features, one at 993.57 cm^{-1} with shoulders near 992 and 995 cm^{-1} for ν_4 and another at 2256.55 cm^{-1} with a shoulder at 2264.0 cm^{-1} for ν_3, all fitted satisfactorily with gaussian profiles. A weak line at 987.43 cm^{-1} is assigned to $^{13}CD_4$ on the same basis as the line at 1296.6 cm^{-1} to $^{13}CH_4$. Although such a simple spectrum comprising essentially a single absorption feature for each vibrational mode might be taken as a limiting case, the breadth of these measured lines much exceeds what is typically encountered for samples of various small molecular species dispersed in either solid Ne or solid Ar separately, as our other spectra illustrate. The lack of pronounced structure of these spectra precludes a meaningful analysis of the nature of a possible molecular motion in these samples, but direct evidence for rotation is certainly absent.

4.3. CH_4 and CD_4 dispersed in solid Ne

For CH_4 and CD_4 dispersed in solid Ne at temperatures 3–8 K, Figs. 3 and 4 show that the relative intensities of the absorption lines in a particular region vary inappreciably with temperature and time; the ranges of prominent contributions to the absorption patterns associated with both vibrational modes ν_3 and ν_4 are much less than 2 B for molecules in the gaseous phase, and the centres of those regions lie at almost the same wavenumbers as the corresponding band origins of the respective carriers in the gaseous phase. We hence conclude that methane, CH_4 or CD_4, undergoes neither free nor hindered rotation in solid Ne. In the region for ν_4 of CH_4 in Ne, the most intense line lies near 1308 cm^{-1}, for comparison with the band centre near 1305.5 cm^{-1} for a gaseous sample, but weak and poorly resolved features have gradually diminishing relative intensities until 1310.5 cm^{-1}. Jones et al. made no mention of such structure, but reported “broad absorptions at lower frequencies” (i.e. smaller wavenumbers) [8]; in our spectra several irregular features are discernible down to 1305.8 cm^{-1} and even further, below the prominent lines at 1308–1307 cm^{-1}. All these lines are assigned to $^{12}CH_4$, whereas a further seven lines in a range 1300–1299 cm^{-1} are assigned to $^{13}CH_4$ on the basis of the shift and the intensity relative to corresponding lines near 1308 cm^{-1}. That the region between 1300 and 1306 cm^{-1} is nearly devoid of perceptible absorption is remarkable. The resemblance of the lines at 1300–1299 cm^{-1} in Fig. 3b to those of $^{12}CH_4$ in a range 1308–1307 cm^{-1} is also remarkable, considering that $^{13}CH_4$ is present in nominally natural abundance, corresponding to a ratio one part in 10^5 of Ne and measured with a ratio ∼15 of signal to noise for the line near 1300 cm^{-1}. We concur with Jones et al. [8], whose conclusion was based on infrared absorption spectra of quality similar to ours, that this multiplet structure, in either domain, fails to convey evidence for rotation, although greatly hindered rotation is not excluded, but we disagree with Prager et al.

[15] whose opinion was based on inelastic scattering of neutrons. A scrutiny of the latter report indicates that the evidence of those authors [15] for rotational motion is flimsy at best; their conclusion was based on a single experiment with a molar ratio 0.0204 of CH_4, much larger than in our experiments at ratios 0.0001–0.005 and in those of Jones et al. at ratio 0.0002 [8]; at molar ratio 0.02, most methane molecules are unlikely to have only Ne atoms in their immediate vicinity. The fit [15] by Prager et al. of their measured points involved an "arbitrary parametrization" of some assumed distribution to reproduce a single and poorly defined distribution of "energy transfer"; such meagre experimental data and perfunctory theoretical analysis appear inadequate for the substantive conclusion. The origin or cause of the abundant structure documented for our solid samples in the vicinity of the wavenumbers characteristic of the respective band centres for a gaseous sample remains mysterious; if combination with lattice modes of Ne were involved, one might expect a dependence on temperature that is unobserved. For ν_3 of CH_4 in solid Ne, the absorption lines are in a cluster from 3020 to 3018 cm^{-1}, about the centre of the band of a gaseous sample near 3018.8 cm^{-2}. A line at 3009.1 cm^{-1} with shoulders at 3007.9 and 3010.3 cm^{-1} corresponds to ν_3 of $^{13}CH_4$, at almost the position of the band centre of a gaseous sample. Similarly for CD_4, two prominent lines associated with ν_3 of $^{12}CD_4$ straddle 2258 cm^{-1}, just below the centre of the band for a gaseous sample near 2259.7 cm^{-1}, and their counterparts with the same pattern are observed at 2243.3 and 2244.1 cm^{-1}. The latter, assigned to $^{13}CD_4$, exhibit an intensity pattern practically identical with the two prominent lines at 2257.8 and 2258.6 cm^{-1} assigned to $^{12}CD_4$. The main feature at 996 cm^{-1} for ν_4 of CD_4 in Ne, which requires nine components for $^{12}CD_4$, is almost exactly at the corresponding band centre of the gaseous sample of $^{12}CD_4$; a weak line at 992.7 cm^{-1} has no evident assignment, but another line at 987.5 cm^{-1} is appropriate for ν_4 of $^{13}CD_4$. On the basis of only spectra of CH_4 recorded only near 1300 cm^{-1}, Jones et al. [8] postulated "trapping cages" of "five or six distinct types" corresponding to their measured six distinct lines, but our spectra exhibit, for both $^{12}CH_4$ and $^{13}CH_4$ in association with mode ν_4 and for $^{12}CH_4$ in association with ν_3, at least seven such sites on the basis of prominent features, neglecting 31 other weak components fitted to reproduce the total pattern of absorption for ν_4; in contrast, for CD_4 and its vibrational mode ν_3 only two such principal sites in the Ne lattice seem indicated, and for mode ν_4 perhaps only one site. The inconsistency of the apparent number of "trapping cages" between CH_4 and CD_4 indicates that that explanation might be a great oversimplification. To avoid speculation, we proffer no alternative explanation.

We investigated in two ways whether the multiple weak features on either side of the prominent lines of CH_4 and CD_4 dispersed in solid Ne might be artefacts arising from apodization in the transformation of the interferogram: the known first side lobes due to Hamming apodization are much less intense than our weak features, relative to the prominent lines, and scrutiny of a spectrum of gaseous $^{12}C^{16}O$ under analogous conditions of measurements showed no such weak satellites between the separate vibration-rotational lines other than those due to isotopic variants at known wavenumbers. The latter test is consistent with a physical basis for the multiple lines and components that we report, rather than their being instrumental artefacts.

4.4. CH_4 and CD_4 dispersed in Ar

Figs. 1 and 2 show that the spectral features of samples of CH_4 or CD_4 in solid Ar vary with temperature between 3 and 21 K in a reversible manner. For CH_4 in solid Ar, the profile of the spectrum recorded for a sample at 3 K immediately after deposition differs from that of the same sample maintained at 3 K for a further 16 h, clearly demonstrated in a difference spectrum, whereas for CD_4 the relaxation to what appears to be a condition of thermal equilibrium at a particular temperature is much more rapid, as previously noted [9]. This temperature dependence and the evident distribution of absorption features has been taken to indicate that rotational motion of methane molecules occurs within their environment of Ar atoms. As the span of the profiles of absorption for modes both ν_3 and ν_4 of CH_4 is substantially less than what is observed for the interval between P(1) and R(1) of gaseous CH_4, or even for these species in solid H_2 or liquid He, rotation must be appreciably hindered. On the basis of the lines in difference spectra, Fig. 7, near the centres of patterns that exhibit a depletion, relative to adjacent features, with increased temperature being associated with R(0) or its equivalent, we deduce correlations between spectra of gaseous methane [26] and of methane in solid Ar as presented in Table 1.

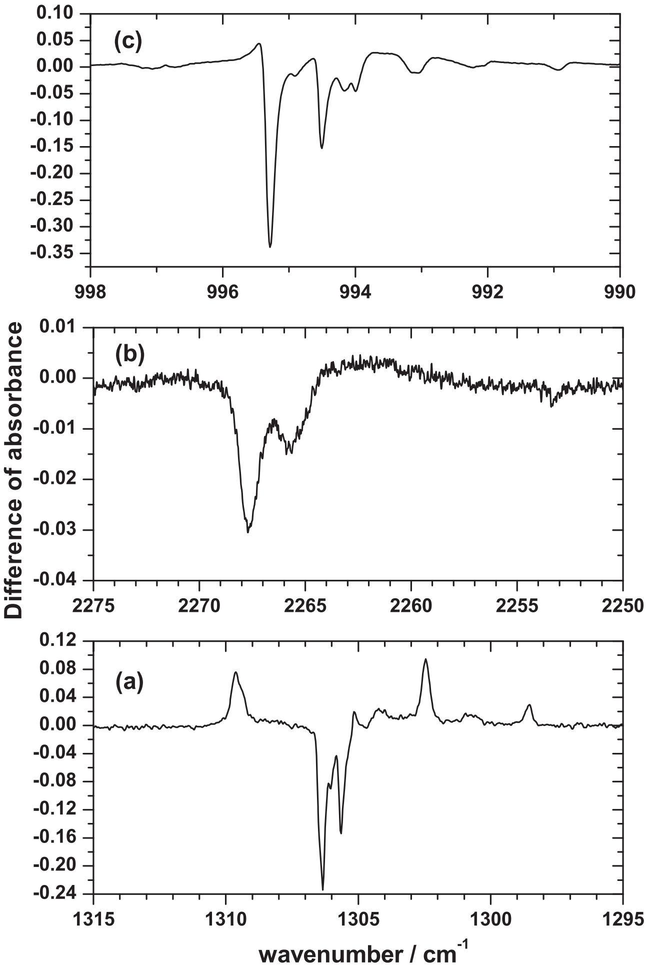

Fig. 7. Difference spectra showing depletion and enhancement of lines between spectra of samples at disparate temperatures. (a) CH_4 in Ar, spectrum of a sample at 9 K minus a spectrum of the same sample at 3 K, 1315–1295 cm^{-1}; (b) CD_4 in Ar, spectrum of a sample at 6 K minus a spectrum of the same sample at 3 K, 2275–2250 cm^{-1}; (c) same as (b) except 998–990 cm^{-1}.

For CH_4 these correlations indicate a shift of the band centres, i.e. the hypothetical transition Q(0), by −3 cm^{-1} for ν_4 and +9.9 cm^{-1} for ν_3; these shifts are contrary to typical trends for stretching and deformation modes [23], but not anomalously so. The effective rotational parameter appears to be decreased by about one third from the gaseous value. The difference spectra clearly exhibit two lines for R(0) of each mode of CH_4 in solid Ar; for the region of ν_3 see Fig. 7a. Jones et al. [8] claimed two lines to be associated with ν_4 R(1), but our line requires only one component. In contrast, Jones et al. [8] attributed a line near 1305.6 cm^{-1} to the

Table 1
Vibration-rotational transitions for methane gaseous and dispersed in solid Ar.

Line	Gas, ν_4/cm^{-1}	Ar, ν_4/cm^{-1}	Gas, ν_3/cm^{-1}	Ar, ν_3/cm^{-1}
$^{12}CH_4$				
P(1)	1300.28	1298.4	3009.01	3022.2
Q(1)	1305.51	1302.5	3018.83	3027.6
R(0)	1311.42	1305.6, 1306.3	3028.76	3033.5, 3037.0
R(1)	1316.82	1309.6	3038.50	3041.2
$^{12}CD_4$				
P(1)	992.61	–	2254.82	–
Q(1)	996.01	992.7	2259.18	2261.9
R(0)	999.49	995.3	2263.59	2265.5, 2267.7
R(1)	1002.82	–	2267.94	2271.5

carrier being in a site other than that of the carrier of the line at 1306.3 cm^{-1}; according to our measurements, the two lines that we associate with ν_4 R(0) exhibit the same dependence on temperature. We observe, moreover, an equivalent phenomenon for lines of ν_3, in that both lines at 3037.0 and 3033.5 cm^{-1} exhibit the same dependence on temperature; Jones et al. made no analysis of this region [8]. Our direct spectral subtractions demonstrate these effects unambiguously. According to its temperature dependence, the line near 1298.4 cm^{-1} appears appropriately assigned to P(1), consistent with Jones et al. [8] and with our parallel observations for CH_4 in solid Ne; the area of this composite line, with unresolved components at 1298.4 and 1298.6 cm^{-1}, is about twice as great, relative to the absorption near 1306 cm^{-1}, as the natural proportion of ^{13}C. A weaker line at 1297.6 cm^{-1}, of which the dependence on temperature is immeasurable because of its weakness, is appropriate as R(0) of $^{13}CH_4$. The precision of our values in the columns for samples in solid Ar in Table S2 reflects that a reduction of the difference spectrum yields wavenumbers of features slightly varied from those of the direct absorption spectrum because the spectral features are incompletely resolved; the listed values represent a composite assessment of data from the two sources.

The situation for CD_4 in solid Ar is less clear than for CH_4. The spectra of our samples of CD_4 in Ar above 10 K contain one principal absorption feature in each region of ν_4 and ν_3 that has in each case a definitely lorentzian profile; for a sample at 10 K the line at 993.66 cm^{-1} has only one weak shoulder at 996.6 cm^{-1} whereas the line at 2264.3 cm^{-1} has two pronounced shoulders at 2255.6 and 2269.0 cm^{-1}. Our spectrum, recorded at 3 K, near 995 cm^{-1} of the sample annealed at 15 K resembles that of CD_4 in Ar reported by Jones and Ekberg at 5 K [9], but our quantitative analysis reveals additional features. In our spectrum the stature of a line at 994.51 cm^{-1} is only half that of the principal line at 995.29 cm^{-1}, whereas the former line in the spectrum of Jones and Ekberg is more intense than the latter, assigned as R(0), despite claimed annealing of the sample to 60 K. On the basis of an irreproducible spectrum [9], those authors assigned four lines as P(1), Q(1), R(0) and R(1). Our difference spectrum in Fig. 7c, recorded with an excellent ratio of signal to noise, between spectra of the same sample at 6 K, after a preceding annealing at 15 K, and at 3 K, exhibits a depletion of not only the line at 995.29 cm^{-1} but also lines at 990.95, 993.09 cm^{-1} (previously assigned [9] as Q(1)), and the intervening lines at 994.00, 994.21 and 994.49 cm^{-1}, previously assigned [9] to CD_4 occupying a hexagonally close-packed site. All lines in our direct absorption spectrum and in the indicated difference spectrum are fitted adequately with purely gaussian profiles of each component. The difference spectrum, Fig. 7b, exhibits depletions of lines at 2251.3, 2265.7 and 2267.6 cm^{-1} in the region of ν_3; if the latter line be assigned as R(0) of $^{12}CD_4$, the first and weak member of those three features is appropriate for R(0) of $^{13}CD_4$ – otherwise no assignment is obvious.

Other authors presented spectra of poor optical resolution as a basis of advocating rotational motion to some extent, except Dubs [12] who, on the basis of only measurements near 1300 cm^{-1} for only CH_4 dispersed in only Ar, suggested hindered rotation as a partial explanation of the complicated undisclosed structure, with no justification of that assertion. No preceding author of papers on methane dispersed in solid Ne or Ar had available the incontrovertible spectra of CH_4 and CD_4 in solid para-dihydrogen [13] and liquid helium [14] as models of incontestable rotation of these molecules in a condensed phase based on well defined lines and appropriate intensities and intervals. Jones et al. [8] not only speculated that CH_4 had comparable populations in two distinct sites in Ar, Kr and Xe undergoing transition ν_4 R(0), but even assigned the two sites to be substitutional within hexagonally close-packed and cubic close-packed lattices; even though an hexagonally close-packed structure is known for crystalline Ar in addition to the dominant cubic close-packed lattice, the former is metastable and present at a minute fraction of the lattice content, but the extent is sensitive to the presence of impurities [27]. Direct examination of samples of CH_4 in solid Ar with X-ray diffraction indicated retention of the cubic close-packed structure even up to molar fraction 0.1 of methane, with little or no indication of hexagonally close-packed Ar [25]. Similar speculation [9] about the nature of sites for CD_4 in solid Ar is based on a single and irreproducible experiment from which was presented a spectrum for only the ν_4 region, again ignoring the disparate structure in the ν_3 region, with an unknown influence of the "overcoat" of krypton on the solid Ar. In that irreproducible experiment [9], annealing to 62 K was claimed to have been effected in an open system, whereas raising the temperature to 25 K of our sample of methane in Ar in an open system resulted in a significant partial loss of that sample. The analogous evidence for an invocation of a specific second site is much less strong for spectra of CD_4 than for CH_4 in the ν_4 region, and for both CH_4 and CD_4 in their ν_3 regions.

The explanation of Jones et al. [8,9] in terms of hindered rotation of CH_4 or CD_4 in solid Ar applicable for vibrational motion in mode ν_4, but ignoring ν_3, is questionable. The abundant fine structure in the spectra of CH_4 and CD_4 in Ne, for which there is agreement about no implication of rotation, except from one discredited experiment on neutron scattering [15], demonstrates that multiple adjacent lines in a region for a particular vibrational mode need not imply a particular molecular motion. Such interpretation should take into account not only the dependence of intensity on temperature but also the nature of the samples resulting from the method of their preparation, such as slow continuous deposition, or pulsed deposition, or slow freezing from a liquid phase, and the temperature of the substrate. The structure of a free complex between CH_4 and Ar [29] yields no clue to the nature of the interaction between CH_4 and surrounding Ar atoms in a crystalline environment.

Further evidence pertinent to this issue might arise from the widths of lines according to our quantitative fitting of absorption profiles. For all lines of CH_4 and CD_4 in solid para-dihydrogen at temperatures less than 8 K and in droplets of liquid helium, the widths lie within a range 0.015–0.4 cm^{-1} with solid para-dihydrogen as host [13] and 0.24–1.1 cm^{-1} for liquid helium as host [14]. For our spectra of CH_4 and CD_4 dispersed in solid Ne, likewise the widths of prominent lines are small, typically less than 0.5 cm^{-1} for both ν_3 and ν_4 regions, even though there is conclusive evidence against free or nearly free rotation of these molecules in this environment. In contrast, the widths of lines of both CH_4 and CD_4 in solid Ar in the ν_3 region are much larger, typically greater than 2 cm^{-1}; this condition might reflect relaxation through transfer of vibrational energy among vibrational modes at similar or smaller wavenumbers. For some – but not all – samples of CH_4 and CD_4 in solid Ne or in solid Ar, weak spectral lines were recorded due to H_2O

present in the solid sample in vestigial proportions; in both ν_2 and ν_3 regions, these lines exhibited widths in a range, varying slightly with sample, such as 0.6–0.8 cm^{-1} for the line at 1623.66 cm^{-1} and up to 1.55 cm^{-1} for the line at 3756.40 cm^{-1}. Even in solid mixed Ar and Ne a line at 1623.58 cm^{-1} has width 1.45 cm^{-1} and a line at 3756.4 cm^{-1} has width 4.4 cm^{-1}. For the latter lines of H_2O, a lorentzian shape is strongly favoured over a gaussian shape according to statistical indicators of the goodness of fit. For comparison, in a spectrum of one of our solid samples a weak line due to atmospheric water vapour outside the cryostat had a measured width 0.081 cm^{-1} and a preferred gaussian shape; this value simply provides an upper bound of our spectral resolution. For samples of H_2O in solid Ar, the absorption spectra have been interpreted to indicate that H_2O rotates almost freely under these conditions [28]. The width of a line attributed to an absorbing species in a liquid or solid sample is a measure of the interactions of that absorber with its environment and of the relaxation of excited states; if the width of a single isolated line be much greater than that typical of molecules for which rotational motions are not greatly hampered, that condition likely indicates a significant interaction with the environment, which is consistent with a lack or impediment of rotational degrees of freedom. This information about line widths appears insufficient to resolve an ambiguity about the nature of the molecular motions in these solid phases.

With regard to a physical interpretation of both our and preceding spectral observations, the relative sizes of the species involved are worthy of consideration; according to kinetic-molecular properties, the diameters/10^{-10} m of effectively spherical entities are approximately Ne 2.75, Ar 3.42, Kr 4.0, N_2 3.75 and CH_4 3.8. Although such classical descriptors of atomic and molecular size are semiquantitative at best, and as methane is intrinsically not spherical, the large discrepancy between these values for Ne and CH_4 might signify that free rotation of a methane guest within a single substitutional site would be greatly hampered, even if nearly free rotation might occur when CH_4 or CD_4 occupies a substitutional site in a regular crystalline lattice of Ar or Kr. Such a substitutional site is favoured by measurements of X-ray diffraction [25]. The molecular diameter might be smaller than the extent of available space in the solid lattice, as pertains, for instance, to para-dihydrogen [13] that has large cavities; in that environment the rotation of methane molecules occurs, but still with modified rotational parameters. Another aspect of this dimensional argument is that the exact nature of the site or sites in which methane is located is unknown; a substitutional site is the most likely possibility if the nominal dimensions of host and guest are commensurate [25], but replacement of more than one host atom must be involved in a case that the size of the guest molecule is much greater than that of the host atom, as found for SF_6 in Ar or even Kr [25], and possibly analogously for CH_4 in Ne.

The conditions of preparation of our samples for these experiments include slow and continuous deposition in darkness with a substrate near 2.9 K; there was no indication of a significantly increased temperature at the surface of the sample during prolonged deposition as a result of the gas incoming from a reservoir through connecting tubing near 298 K. These conditions of deposition, whether of Ne or of Ar or of their mixture, with methane in minute proportion in each case, seem most conducive to preparation of a homogeneous sample, without separation of immiscible solid phases [25], and without a thin intermediate liquid film on the surface as the deposit increased in thickness.

5. Conclusion

Based on a comparison of our quantitatively fitted spectra of methane in solid neon or solid argon with published spectra of methane in crystalline para-dihydrogen and in droplets of liquid helium, we find no evidence for free, or nearly free, rotation of molecules of CH_4 or CD_4 dispersed in solid Ne at a small molar fraction, contrary to a preceding claim [15]. For samples of CH_4 in solid Ar, molecular rotation is hindered more than for CH_4 in solid para-dihydrogen or liquid helium, according to effective values of the rotational parameter, unlike the nearly free rotation in a manner postulated by preceding authors. The dependence on time and temperature of the relative intensities for samples of CH_4 at 3 K within the region attributed to both fundamental vibrational modes ν_3 and ν_4 is consistent with some such rotational motion, like the analogous variations of lines of H_2O that we detected and that have been associated with molecular rotation [28]. Consistent with the disparity between the absorption patterns and rates of relaxation of nuclear spin of CH_4 and of CD_4 in Ar, there is a possibility that the motions of these two isotopically related species might differ appreciably, such as hindered rotation for CH_4 in Ar but either no rotation or much more strongly hindered rotation for CD_4 in Ar. According to our measurements at optical resolution 0.04 cm^{-1}, the abundant features, which are discernible through quantitative fitting of the total spectral profile and which comprise collectively the absorption in regions associated with modes ν_3 and ν_4, require further theoretical treatment for their elucidation. A theoretical investigation by Kobashi et al. [30] of the Raman spectra of methane dispersed in solid Ar or krypton or xenon provides no explanation applicable to the numerous components of our recorded spectra.

Our spectra as a function of temperature, shown in Figs. 1 and 2, prove that merely to attribute some spectral lines of CH_4 and CD_4 in solid Ar as rotational fine structure accompanying vibrational transitions of molecules surrounding by Ar atoms in a crystalline lattice at 3–5 K is a gross oversimplification. Not only are there additional lines, extraneous to this explanation, as conceded by Jones and coworkers [8,9] who published spectra of comparable resolution, but also the spectra of the same samples at temperatures above 8 K fail to conform even to this partial explanation. Whereas the increased relative intensities of lines assigned to transitions originating in states with $J = 1$ and the appearance of further lines originating in states with $J = 2$ would be consistent with this rotational phenomenon, the observed rotational structure instead coalesces above 8 K into essentially a single line, which reversibly reverts to its split components on decreasing the temperature; in contrast the line at 1623 cm^{-1} attributed to H_2O rotating in an Ar lattice [28] persists, slightly broadened, beyond 15 K in our experiments. For methane in crystalline H_2 the absorption lines likewise maintained their identities up to 8 K, at which temperature the crystals became unsuitable as a host because of molecular diffusion [13]. Do CH_4 molecules in solid Ar cease to rotate at 8 K, even though the expanding Ar lattice and increased thermal energy might facilitate such motion? Our spectra of not just one vibrational mode and of samples at not just one temperature, unlike in preceding reports [8,9], leave significant questions about this system unanswered. Further experimental and computational strategies are required to resolve this problem, for which purpose our spectra furnish a concrete basis on which to progress; a lack of knowledge of the exact nature of the solid sample remains a formidable impediment.

Acknowledgements

We thank Dr. Yu-Jong Wu for assistance with preliminary experiments and for helpful comments, Professor M. Quack for information about spectra of gaseous methane and Professor T. Momose for helpful discussion about spectra of methane in solid dihydrogen. National Science Council of Republic of China (grant

99-2113-M-213-003-MY3) and National Synchrotron Radiation Research Centre in Taiwan supported this project.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.vibspec.2011.07.006.

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