Infrared spectra and structure of methane – noble gas mixed crystals: the influence of temperature and methane concentration on the v_3 vibration band of methane[1]

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The infrared spectra of CH_4, at low concentrations in the noble gases, were obtained at temperatures ranging from 4 °K up to the respective boiling points of argon, krypton, or xenon. It is concluded from this study that methane occupies substitutional cavities in these lattices. Furthermore, it is established that the potential hindering the rotation of the molecules perturbs the higher rotational levels to a greater extent than the low lying levels.

In a second series of experiments, the methane concentration was varied from 0.06 to 55% for krypton; narrower ranges were used for argon and xenon. The experimental results clearly demonstrate that the influence of the CH_4 concentration is different for the three systems and that the fine structure does not result from molecular aggregation.

The spectrum of 0.06% CD_4 in solid krypton shows fine structure which confirms the rotational origin of the four components observed for CH_4. The CD_4 spectra previously published were complicated with additional lines that probably arose from the nonhomogeneity of the samples.

Les spectres infrarouges du CH_4 en faibles concentrations dans les gaz nobles furent enregistrés à des températures allant de 4 °K jusqu'aux points d'ébullition de l'argon, du krypton ou du xénon. Cette étude nous a permis de conclure que le méthane occupe des cavités substitutionnelles dans ces réseaux. On a de plus constaté que le potentiel s'opposant à la rotation des molécules se manifeste à un plus haut degré sur les niveaux de rotation élevés que sur les premiers niveaux.

La concentration de méthane fut ensuite variée de 0.06 à 55% pour le krypton; des domaines moins étendus furent utilisés pour l'argon ou le xénon. Les résultats expérimentaux obtenus démontrent clairement que l'effet de la concentration en CH_4 est différent pour les trois systèmes et que la structure fine n'est pas causée par l'agglomération des molécules.

Le spectre du CD_4 en solution à 0.06% dans le krypton montre une structure fine qui confirme la nature rotationnelle des quatre composantes observées pour le CH_4. Les spectres de CD_4 publiés antérieurement étaient compliqués par des raies additionnelles probablement attribuables à l'inhomogénéité des échantillons.

Introduction

Since the first report of molecular rotation of HCl in solid argon (1), the problem of the fine structure observed on the vibrational bands of small molecules isolated in noble gas crystals has been of considerable interest. The present work is an extension of the research on the infrared absorption spectra of CH_4 or CD_4 trapped in inert gas matrices (2) and in liquid solutions with the noble gases (3). The spectral features observed on the v_3 and v_4 bands were previously ascribed to the quantized molecular rotation. The Raman spectrum of a mixed crystal, grown from a melt, was also found to be consistent with the concept of rotation, although the resolution achieved was insufficient to permit a detailed analysis (4). The time dependence of the intensities of the spectral features of CH_4 in crystalline

argon has been taken as evidence of equilibration between the three possible spin species of CH_4 (5). These experimental studies have aroused interest in theoretical investigations on the nature of rotation in these solids, particularly for tetrahedral molecules trapped in octahedral cavities (6). All these studies are based on the assumption that the host molecules replace noble gas atoms in undistorted face-centered cubic (f.c.c.) lattices. Although it is known that, at least in the low concentration range, CH_4 forms solid solutions with krypton (7) or argon (8), it appeared desirable to obtain additional data which could yield information on the nature of the sites occupied and on the distribution of the molecules over the available cavities.

Two different sets of experiments seemed appropriate to the solution of the problem. In the first series, the effect of the temperature on the fine structure of the v_3 band was investigated in the range extending from 4 °K up to the boiling points of the noble gases used. In the second, the

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influence of the solute concentration of the v_3 band was studied. The concentration was varied from 0.06 up to 55% in the case of the CH_4–krypton system; fewer solutions and narrower ranges were investigated for the argon and xenon systems. The present study should bring support to the interpretation of the nature of the fine structure presented by Cabana et al. (2) and thus to the reported spin equilibration discussed by Frayer and Ewing (5).

Experimental

All the spectra were taken with a Perkin–Elmer Model 125 prism–grating spectrometer; under the experimental conditions prevailing, the actual resolving power varied from 0.5 to 1.5 cm^{-1}, depending upon the spectral regions and the optical quality of our samples. The factory calibration was checked during each run by recording appropriate gas-phase spectra and comparing with the values given in the Tables of Wavenumbers (9). The frequencies quoted later are accurate to ± 0.3 cm^{-1} for sharp peaks which are relatively free of overlapping. A conventional cryostat equipped with a variable pressure gas exchanger was used to obtain any selected temperature in the range 4 to 170 °K with liquid helium or nitrogen as the coolant. The control thus achieved was relatively rough but it could be improved by introducing small electrical heaters around the filling tube and the sample cell. The heater around the filling tube was found particularly useful to prevent clogging if the tube inadvertently touched the nitrogen shield; it also created a temperature gradient through the cell diameter and prevented the formation of bubbles in the middle of our samples. The temperature was measured with a copper–constantan thermocouple and a carbon resistor, both embedded in the cell body; the accuracy is better than $\pm 1°$ above 50 °K, but considerably worse at the lowest temperatures, where it can be of the order of $\pm 5°$.

The gaseous mixtures were prepared in a Pyrex system previously pumped down to pressures lower than 1×10^{-5} mm Hg and outgassed. Research-grade methane and noble gases (Matheson of Canada, Ltd.) were used. The samples were prepared by condensing the mixture to the liquid phase in the experimental cell and, whenever necessary, cooling through the freezing point. Various cooling rates were tried without any noticeable difference in the observed spectra. The samples were often kept for rather long periods of time at temperatures close to their melting points; spectra recorded at different intervals were found identical. The crystals, which were perfectly transparent at 77 °K, had a tendency to crack upon further cooling.

The thickness of the sample cell was of the order of a few microns for high methane concentrations and 2 mm for the low concentrations; the small spacings were determined approximately by counting the interference fringes (10). The window material was either sapphire or Irtran-2 and the seals were achieved with 0.010 in. diameter indium wire squeezed between the windows and the cell body, which was copper. The design was such that the coolant surrounded the sample, thus providing lower temperatures. In addition, KBr windows were placed in the beam holes of the nitrogen shield and narrow-band-pass filters were used on the outside window; these two additional precautions helped in obtaining lower sample temperatures.

Results

The spectra of the 0.06% CH_4–argon mixed crystal, 0.1% CH_4–krypton crystal, and 0.06% CH_4–xenon crystal are shown in Fig. 1; the frequencies are collected in Table 1. The temperatures at which the spectra were recorded are indicated on each tracing. The bottom spectrum of each set is that of the liquid solution. Only the v_3 vibration region was scanned. The low-temperature spectra of the three systems exhibit similar patterns, contrary to those reported previously (2). As the temperature is raised, the four lines gradually blend together and finally they form a continuous band more typical of the liquid state or of disordered crystals. It is observed that the intensities of the various components do not vary the same way as the temperature is raised. In particular, this effect gives rise to a shift of the band at temperatures, T, approaching 40 or 50 °K. At higher temperatures, the shifts are smooth up to the melting points, where discontinuities occur: a sudden high-frequency displacement for the xenon system, a slight low shift for krypton, and a larger downward shift for argon.

The spectra of CH_4 at various concentrations in argon are given in Fig. 2; in krypton, Fig. 3; and in xenon, Fig. 4; the temperature during the runs was kept as close as possible to that of liquid helium. The frequencies at maximum intensity are collected in Table 2. In argon, the CH_4 concentration ranged from 0.06 to 35%; in krypton, concentrations up to 55% were used; while in xenon only two solutions were prepared: 0.06 and 20% CH_4. It is readily seen that the influence of the solute concentration was very different for the three systems. Figure 5 summarizes the effect of the concentration on three lines of the v_3 vibration band of methane in krypton. The low-temperature spectrum ($T < 10$ °K) of 0.06% CD_4 in solid krypton is shown in Figs. 6 and 7.

Discussion

A. The Influence of Temperature on the v_3 Absorption Band
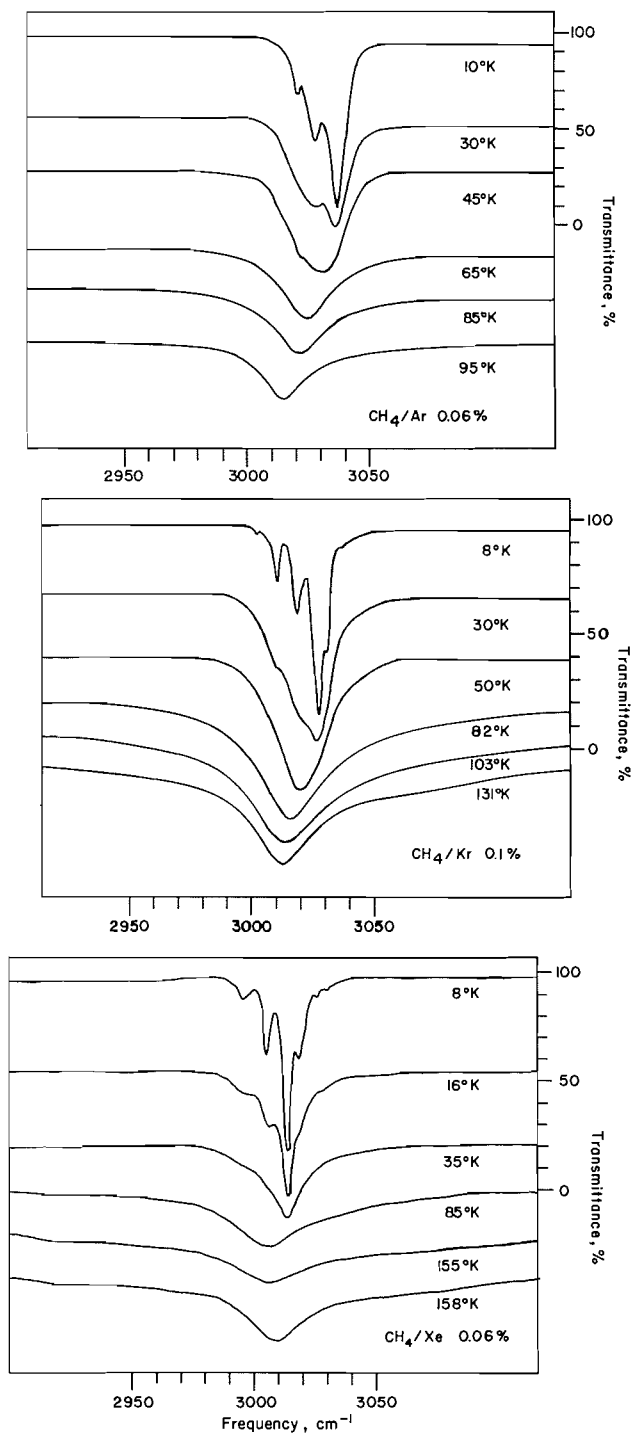
The spectra recorded at low temperatures have

FIG. 1. (*Upper*) Infrared spectra of 0.06% CH₄ in crystalline argon at various temperatures; at 95 °K, the solution is liquid. (*Middle*) Infrared spectra of 0.1% CH₄ in crystalline krypton at various temperatures; at 131 °K, the solution is liquid. (*Lower*) Infrared spectra of 0.06% CH₄ in crystalline xenon at various temperatures; at 158 °K, the solution is liquid.

TABLE 1

Frequencies of the components of the ν_3 vibration band of methane*

Matrix	Temperature (°K)	Frequency, cm^{-1}			
		P(1)	Q	R(0)	R(1)
Xe	8	2995.6	3005.3	3013.3	3018.3
Xe	16	2996	3005.9	3013.2	3019
Xe	35			3012.9	
Xe	85		3004.8		
Xe	155		3004.9		
Xe	158†		3007.4		
Kr	8	3010.1	3018.3	3026.5	3030.0
Kr	30			3026.1	
Kr	50		3017.0		
Kr	82		3016.0		
Kr	103		3014.1		
Kr	131†		3011.7		
Ar	10	3021.6	3028.6	3037.4	‡
Ar	30		3028.4	3036.5	
Ar	45			3033.0	
Ar	65		3025.5		
Ar	85		3022.3		
Ar	95†		3015.1		

*CH_4 concentration was 0.06% for the argon and xenon systems and 0.10% for the krypton system.
†Liquid state.
‡Shoulder.

TABLE 2

Frequencies of the components of the ν_3 vibration band of methane; temperature lower than 10 °K

% concentration	System	Frequency, cm^{-1}				
		P(1)	Q		R(0)	R(1)
0.06	CH_4–Xe	2995.6	3005.3		3013.3	3018.3
20	CH_4–Xe	2997	3005.3		3013.4	†
0.06	CH_4–Kr	3010.1	3018.3		3026.5	3030.0
0.1	CH_4–Kr	3009.8	3017.7		3026.1	3029.6
5.0	CH_4–Kr	3009.4	3018.4		3024.7	†
10	CH_4–Kr	3009.4	3017.3		3024.7	†
13	CH_4–Kr	3009.2	3016.4		3022.9	†
15	CH_4–Kr	3009.6	3016.0		3021.1	†
18	CH_4–Kr	3009.1	3015.3		3020.6	†
24	CH_4–Kr	3008.9	3015.2		3020.6	†
35	CH_4–Kr	3009.4	3014.7		3019.5	†
55	CH_4–Kr*	3008	3013		3016	
0.06	CH_4–Ar	3021.6	3028.6		3037.4	†
3.0	CH_4–Ar			3026		
6.0	CH_4–Ar			3026		
20	CH_4–Ar			3017		
35	CH_4–Ar			3016		

*Three lines are observed; their nature is uncertain.
†Shoulder.

shown the time dependence ascribed by Frayer and Ewing (5) to spin equilibration. Our results agree with this; thus no further discussion regarding this particularity will be carried out here.

Three aspects of these experimental results inevitably draw attention: (a) The observation of opposite shifts for the ν_3 vibration of CH_4 in xenon and in argon upon melting of the mixed crystals. (b) The different behavior of the intensities for the various components as the temperature is increased. (c) The rapid broadening of the individual lines with increasing temperature. These observations will now be discussed in
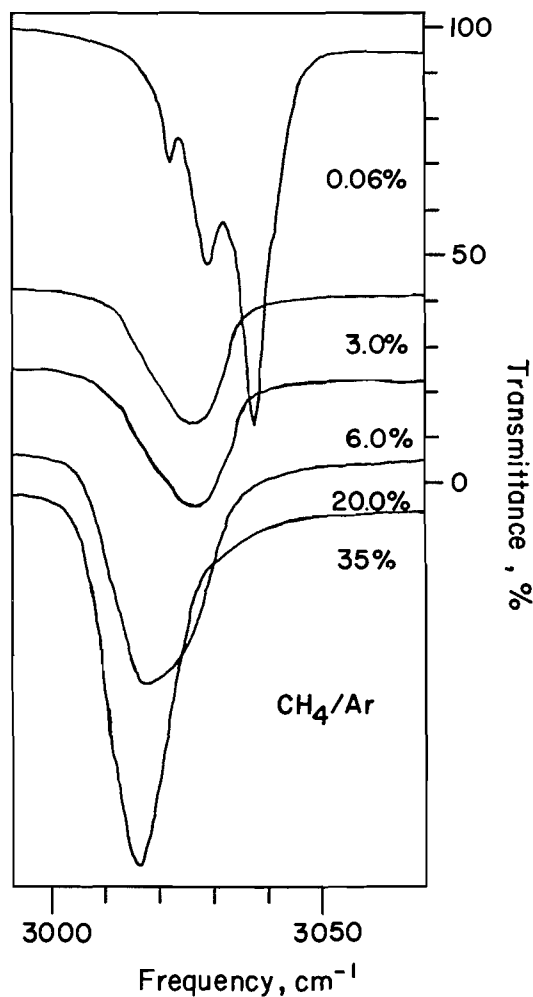

FIG. 2. Infrared spectra of CH_4 in solid argon at 8 °K. The concentrations, ranging from 0.06 to 35% CH_4, are indicated on each spectrum.
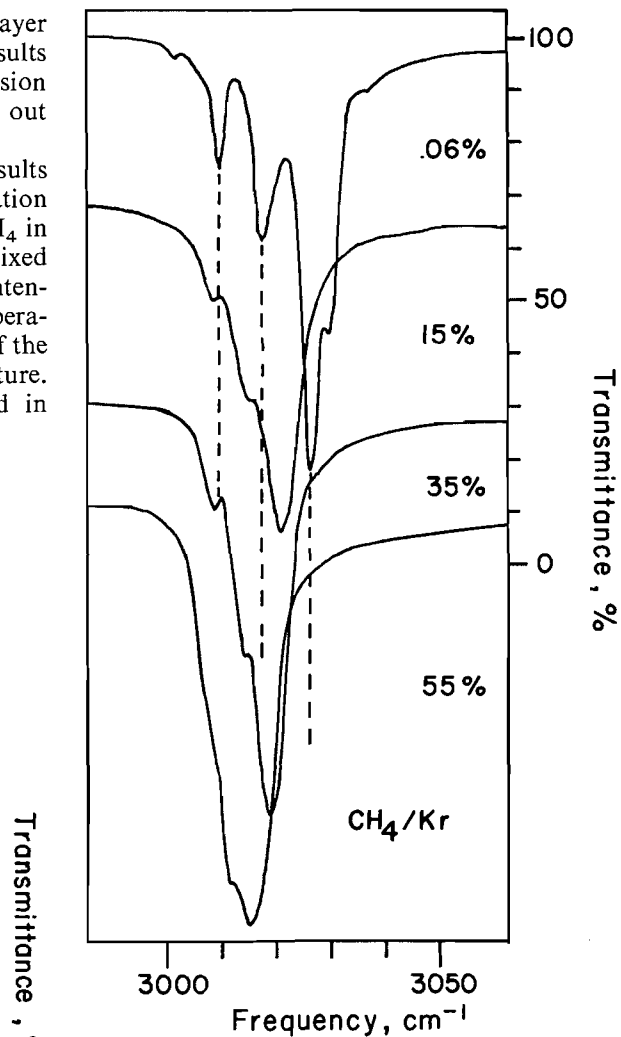

FIG. 3. Infrared spectra of CH_4 in solid krypton at 8 °K. The concentrations, ranging from 0.06 to 55% CH_4, are indicated on each spectrum.

terms of the nature of the fine structure of the unsymmetrical stretching vibration band of methane and of the kinds of sites occupied by the molecules.

The low-frequency displacements of the ν_3 vibration band of CH_4 dissolved in liquid argon (-3 cm^{-1}), krypton (-7 cm^{-1}), and xenon (-11 cm^{-1}) indicate that the predominant interaction between the molecules and the atoms is attractive. Upon solidification of these solutions, shifts of $+7.2$, 2.3, and -2.5 cm^{-1} are measured for the band in argon, krypton, and xenon, respectively. Thus, upon formation of the
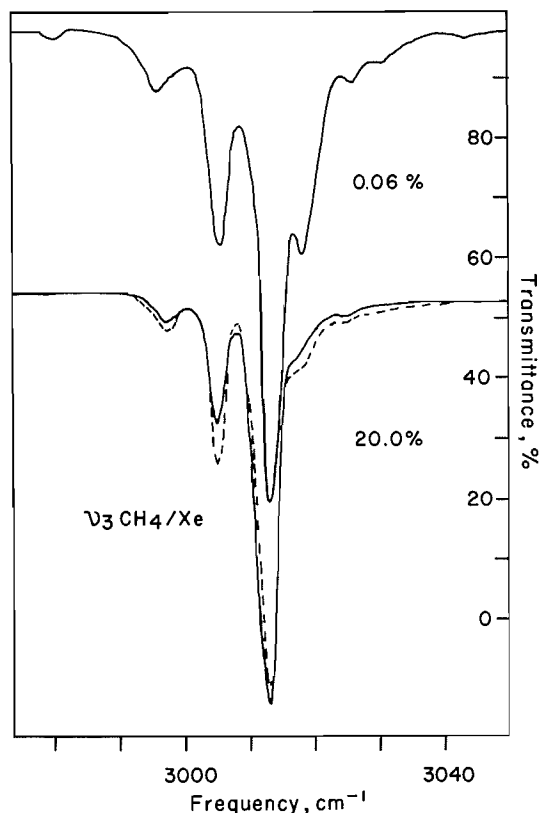
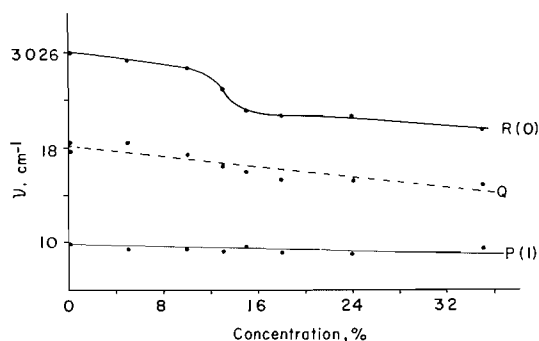FIG. 4. Infrared spectra of 0.06 and 20% CH₄ in solid xenon at 8 °K.

FIG. 5. Frequencies of the R(0), Q, and P(1) lines of methane in crystalline krypton as a function of the methane concentration, at 8 °K.

withdrawing an atom from a lattice site are 3.8 Å for argon, 4.0 Å for krypton, and 4.4 Å for xenon (11), as compared to 4.1 Å, the diameter of the stationary CH_4 molecule. Thus, while the molecule inherits a larger cavity as xenon crystallizes, it is squeezed into smaller cavities in krypton and even more so in argon. Additional support for this arrangement of the molecules in the crystals is provided by the frequency shifts of the stretching vibration, which occur upon contraction of the lattice as the temperature is lowered: $+6$ cm^{-1} for 75° lowering of temperature in argon, $+4$ cm^{-1} for 100° in krypton, and no shift in xenon over 120°.

The relative intensity of the four lines observed in the v_3 vibration band at low temperature is altered as the temperature is raised (see Fig. 1). At the lowest temperature, the line labelled R(0) is the strongest component; gradually the line labelled Q, on the low-frequency side of R(0), gains intensity and finally around 50 °K it becomes the predominant feature. After the fine structure is lost, some information may still be gained from the spectra by studying the band

lattice, the repulsive forces acting on the molecule augment in argon and in krypton, but diminish in xenon. *This is precisely what is predicted for these mixed crystals if a molecule occupies a substitutional cavity created by the displacement of a noble gas atom.* The diameters of the holes formed by
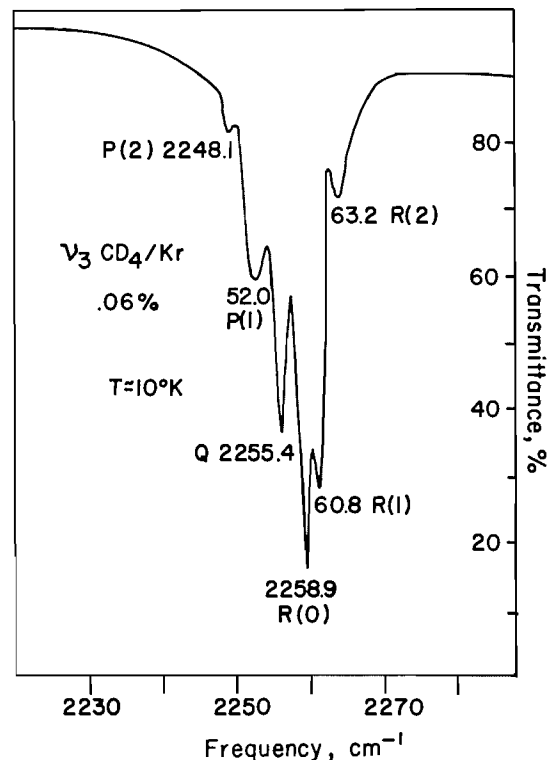

FIG. 6. The v_3 vibration band of 0.06% CD_4 in crystalline krypton, at 8 °K.

TABLE 3

Intensities of the vibration–rotation transitions of freely rotating
methane molecules

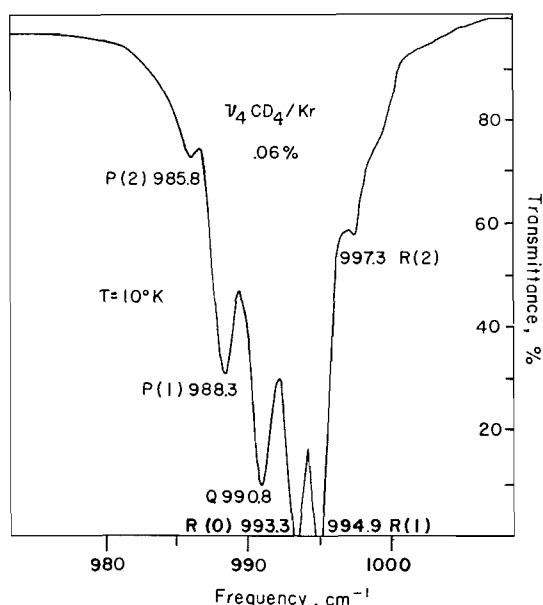|	Intensity					
	With spin equilibration			Without spin equilibration		
	4.4 °K	8.8 °K	17.6 °K	17.6 °K	40.0 °K	75 °K
R(8)						0.1
R(7)						0.5
R(6)					0.1	2.0
R(5)					0.5	3.1
R(4)			0.1		3.8	8.4
R(3)			1.8	1.7	11.1	13.0
R(2)		3.0	13.3	11.6	12.6	8.4
R(1)	13.2	33.0	30.6	29.8	10.7	5.3
R(0)	77.0	36.0	14.3	29.9	15.3	6.5
Q	7.7	21.0	27.4	23.4	28.0	31.1
P(1)	2.6	7.0	6.1	4.6	2.1	1.1
P(2)		1.0	5.6	3.0	5.4	3.6
P(3)			1.0	1.0	6.2	7.2
P(4)			0.1	0.3	2.7	5.3
P(5)					0.4	3.1
P(6)					0.1	1.5
P(7)						0.4
P(8)						0.1

FIG. 7. The ν_4 vibration band of 0.06% CD_4 in crystalline krypton, at 8 °K.

shape. At the higher temperatures, the bands are unsymmetrical, the high-frequency side being wider and more intense. Such an observation is consistent with the concept of rotation, since the R branch is always more intense than the P branch

(see Table 3). There is, however, a difficulty: the band center grows too rapidly in comparison with the wings. There does not seem to be an easy answer to this problem, but several factors may contribute to this phenomenon if a barrier opposing rotation exists in these solids as indicated from earlier studies (2, 5). For example, theoretical calculations for a tetrahedral molecule undergoing rotation in an octahedral field indicate that the splitting of the rotational levels increases with increasing J and that some sublevels converge to the $J = 0$ state (6). Also of importance is the fact that, as the temperature is raised, the vibrational amplitude of the lattice increases, possibly modifying the interactions between the atoms and the molecules. *Thus we can summarize by stating that the molecules trapped in crystals of the noble gases undergo some type of quantized rotational motion; the departure from free rotation is certainly much more evident at the higher temperatures, indicating that the levels having high J numbers are more perturbed than those with low J.* Agreement between experimental and theoretical (6) data is only qualitative.

B. The Influence of the CH_4 Concentration

Argon, krypton, xenon, and CH_4 all crystallize in the f.c.c. lattice, although it has been shown that the close-packed hexagonal structure can be

obtained as a metastable phase for pure argon, or as a stable phase, near the melting point, in certain argon-based solid solutions (12). For the methane–argon system, it was recently shown that the crystal structure is f.c.c. (8). At least for the mixed crystals with low CH_4 concentrations discussed in the previous section, it can be considered established that the structure is f.c.c. and that the molecules occupy substitutional cavities. We wish now to find out what happens to the f.c.c. lattice when the concentration of methane is increased and if possible find out something about the distribution of the molecules within the mixed crystal. The three systems under investigation have shown widely different behavior with respect to the concentration, as shown in Figs. 2 to 5, although their spectra at low concentration have revealed identical structures.

In the argon–methane system, the v_3 vibration band of CH_4 clearly demonstrates that at concentrations of CH_4 as low as 3%, the solid has modified its structure; the lines resolved at 0.06% have collapsed. The band shape and the frequency at maximum intensity coincide with those of an amorphous solid of very low solute concentration, easily obtained with the spray technique by slow deposition at very low temperature without annealing. At 20% CH_4, and even more so at 35%, the band narrows and the frequency at maximum intensity moves close to that of pure solid CH_4. It seems that microcrystals of pure CH_4 are being formed and that a two-phase system is obtained; this deduction is consistent with the results obtained from X-ray diffraction studies (8).

The methane–krypton system shows a more intricate behavior. As the CH_4 concentration is increased in the range 0.06 to 10%, no modification of the spectrum was observed except for a small low-frequency shift (see Fig. 5). This shift arises from lattice expansion resulting from the introduction of slightly larger species in the matrix. In the range 10–14% CH_4, the line labelled R(0) undergoes a very rapid displacement, while the three other lines are simply subjected to the low-frequency shift just discussed; it may seem that the Q line is subjected to a larger shift than R(1) or P(1), but closer examination reveals that this effect results from an increased overlapping of that line with the very strong R(0) component. In the range from 14 to 35% (and very likely up to 50%), all lines are again shifted slowly to lower

frequencies as the lattice expands. An additional experiment with a crystal containing 55% CH_4 has yielded a spectrum showing major modifications.

We now have to justify why the R(0) line was influenced differently from the others. The answer to this question lies in the fact that this line and only this line (since the 0–0 transition is forbidden) originates from nonrotating molecules in the ground vibrational state. It seems reasonable to believe that these nonrotating molecules will interact with the surroundings differently from those in the $J = 1$ or higher states. In other words, these molecules may orient themselves in the direction of maximum interaction. Thus, a modification of the structure of the mixed crystal may very well manifest itself differently on R(0) than on R(1), Q(1), or P(1).

For a random distribution of the molecules over the lattice sites, major modifications of the v_3 vibration band are expected in the low concentration range. This is contrary to our findings. It has already been shown that while very few molecules are located on adjacent sites at a concentration of 0.06% CH_4, 25% of them are paired at 5% CH_4 (13). Molecules on adjacent sites would certainly have a different spectrum than those truly isolated. *We are led to conclude that the distribution is not random and we have to find an array consistent with the observed spectral changes.* It need not surprise us to find that the molecules are distributed in an ordered manner in these crystals since intuitively it appears to be an arrangement that minimizes the strain energy. Let us consider what happens when molecules enter the krypton crystal: the molecule, larger than the available substitutional cavities, will displace the surrounding atoms, creating strain in a given region of the crystal. If another molecule is introduced in the immediate vicinity of the first one, the strain introduced is expected to be larger than that created by the first molecule, since the crystal was already distorted in that region. On the contrary, if the molecule migrates to an undistorted portion of the solid, it will create a repetition of the first phenomenon. It seems that the lowering of the repulsive forces obtained by this regular distribution is high enough to compensate for the loss in entropy.

Something may be learned about the "organized distribution" of the molecules over the lattice sites from a discussion of the observed

irregular displacements of the CH_4 R(0) line in the krypton crystal. Several arrays of the molecules could produce the spectral changes found at a 12.5% CH_4 concentration, but if the structure of the mixed crystal remains f.c.c. at these concentrations, the molecules have to occupy fourth nearest neighbor sites separated by a distance $2\sqrt{2}a_0$ (where a_0 is the length of the cube edge of the primitive cell). After 12.5% of the sites are filled, the spectrum is expected to be very sensitive to the introduction of more CH_4, since each additional molecule creates six next-nearest neighbors which interact with each other. Such a model, although very attractive, has to be abandoned for the higher concentrations, since it predicts additional spectral changes at 25% CH_4 and it fails to account for those observed at 50%. Amongst the structures consistent with a change at a concentration of 50% CH_4, the most appealing ones seem to be the sodium chloride and cesium chloride lattices, where the anions are the molecules and the cations the atoms or vice versa. In the sodium chloride lattice, the anions occupy a set of f.c.c. sites and the cations another set. The structure of the "mixed crystal" is simple cubic. The most usual way to look at it is to consider the chloride ions on a f.c.c. lattice and the sodium ions in its octahedral cavities. In the methane–krypton system, since both species have about the same diameter, the noble-gas lattice has to be expanded in order to accommodate the molecules or a structural transformation occurs and the structure becomes simple cubic or body-centered cubic. In both cases, there are no pairs formed at concentrations as high as 50%, but in the first case at exactly 50% CH_4 the molecules are surrounded by six atoms, while they are surrounded by eight in the second. These suggestions may be regarded as highly speculative; nevertheless the observed spectral changes taking place upon increasing the methane concentration require structural modifications. X-Ray diffraction studies of the CH_4–Kr system seem most desirable and promise to be more informative than those on the CH_4–Ar (8) or CH_4–Xe mixed crystals.

The CH_4–Xe system was not as thoroughly investigated as the other two; nevertheless, the results obtained are interesting. The spectrum of the 0.06% CH_4 solution was identical to that of the 20%, except for a slight broadening of the lines which seems at least partly responsible for the loss of the R(1) feature. It is therefore believed that no major changes of structure occurred within that range of methane concentration. However, this spectrum is possibly less sensitive to structural modifications because the molecules fit loosely into the substitutional cavities.

C. The "Additional Lines" Observed for Microcrystals Formed by the Spray Technique

In an earlier paper (2), "additional lines" were reported to be found in the v_3 vibration band of methane dispersed in argon and krypton crystals. In argon, a line was found at 3033 cm^{-1} and a band with some structure appeared on the low-frequency side of the main components; in the krypton crystal, only one "additional line" was seen, at 3022 cm^{-1}. None of these was ever detected when the crystals were grown slowly from the liquid, but instead the four-line pattern always showed up exclusively.

We wish to discuss the origin of the additional features, starting with the prominent band of the argon system that develops (2) during the annealing process and which was believed to be caused by diffusion inside the matrix. In view of the results reported in this paper, it becomes clear that this interpretation is erroneous. Since this band is never found with closed cells, it appears to result from preferential sublimation of the most volatile component (argon) from the surface of the film when the temperature is raised to the temperatures of annealing. Thus we conclude that this band results from microcrystals at the surface of the film.

The nature of the 3022 cm^{-1} line found in krypton and the 3033 cm^{-1} line found in argon is certainly different from that of the prominent band. These two lines are likely to have the same origin. Their intensities and positions are not exactly reproducible from run to run (ref. 14 and unpublished data from this laboratory). We have shown, in a previous section, that only the line labelled R(0) was highly sensitive to the methane concentration (see Fig. 5). Few experiments were carried out with the argon system, but a large number with the krypton system; the position of the additional lines was always in the range of the R(0) frequencies found with various CH_4 concentrations. Since the spectrum of the xenon system has been shown to be insensitive to methane concentration in the range 0.06–20%, it should not show the additional line when the

crystals are prepared from a spray. This is precisely what is observed. It is thus concluded that the microcrystals obtained with the spray technique are inhomogeneous, some portions having high concentrations of molecules while others will have low concentrations.

D. The Vibration–Rotation Band of CD_4 in the CD_4–Krypton System

The crystals grown from liquid solutions yielded reproducible spectra of higher quality than those resulting from films prepared from a spray. v_3 and v_4 now show identical features (Figs. 6 and 7), labelled from high to low frequencies, R(2), R(1), R(0), Q, P(1), and P(2). The measured intensities of the seven lines agree rather well with those calculated for a free rotator assuming complete spin equilibration and a temperature close to 5 °K. The discrepancies probably result from incomplete equilibration. These spectra confirm the rotational nature of the fine structure proposed earlier. For this reason, it may be interesting to compare the frequency spacings observed in the matrix to those between the rotational levels of CD_4 in the gas phase.

The gas-phase spacing for v_3 of CD_4 is about $2B(1 - \xi_3) = 4.5 \text{ cm}^{-1}$, while that for v_4 is $2B(1 - \xi_4) = 3.5 \text{ cm}^{-1}$ (15). The measured values for v_3 of CD_4 in solid krypton are: $R(2) - R(1) = 2.4 \text{ cm}^{-1}$, $R(1) - R(0) = 1.9 \text{ cm}^{-1}$, $R(0) - Q = 3.5 \text{ cm}^{-1}$, $Q - P(1) = 3.4 \text{ cm}^{-1}$, and $P(1) - P(2) = 3.9 \text{ cm}^{-1}$. In v_4, $R(2) - R(1) = 2.4 \text{ cm}^{-1}$, $R(1) - R(0) = 1.6 \text{ cm}^{-1}$, $R(0) - Q = 2.5 \text{ cm}^{-1}$, $Q - P(1) = 2.5 \text{ cm}^{-1}$, and $P(1) - P(2) = 2.5 \text{ cm}^{-1}$. Hence it is clear that the matrix does decrease the separations between successive rotational levels. However, it seems appropriate to correct for the effects of the Coriolis coupling in order to compare directly the gas-phase spacings to those observed in the matrix for the v_3 and v_4 vibration–rotation bands. This correction will be carried out in the usual manner (16) with the approximation used previously (5). The following combination differences, written in a form appropriate for the gas phase are needed

$$R(2) - Q(2) = F_1^{(-)}(3) - F_1^{(0)}(2)$$

$$R(1) - Q(2) = F_1^{(-)}(2) - F_1^{(0)}(2) \\ + F_0(2) - F_0(1)$$

$$R(0) - Q(1) = F_1^{(-)}(1) - F_1^{(0)}(1) \\ + F_0(1) - F_0(0)$$

$$Q(2) - P(2) = F_1^{(0)}(2) - F_1^{(+)}(1)$$

$$Q(1) - P(1) = F_1^{(0)}(1) - F_1^{(+)}(0)$$

From these combination differences, appropriate corrections to the observed spacings in the matrix can be made and thus one obtains the energy-level differences for CD_4 in the matrix, free from Coriolis interaction. Table 4 summarizes the results. It can be seen that the energy-level differences as determined from either v_3 or v_4 are roughly equal for both vibrational states. The crystal field reduces all the spacings and it seems to be more important for the excited vibrational state than for the ground state.

TABLE 4

Rotational energy-level differences for CD_4, corrected for Coriolis coupling

| | Energy-level difference, cm^{-1} | | |
| | Gas phase | Matrix | |
$F_v(J + 1) - F_v(J)$	v_3 and v_4	v_3	v_4
$F_1(3) - F_1(2)$	$6B = 15.9$	10.3	11.8
$F_1(2) - F_1(1)$	$4B = 10.6$	7.1	7.7
$F_1(1) - F_1(0)$	$2B = 5.3$	4.3	4.3
$F_0(2) - F_0(1)$	$4B = 10.6$	9.0	8.0
$F_0(1) - F_0(0)$	$2B = 5.3$	4.2	4.3

Conclusions

The methane molecules occupy substitutional cavities in any of the solid noble gases when the concentration of methane is low enough; the limit of solute concentration is different for the three noble gases used. The temperature-dependence study shows that the motion of the molecules is more complex than free rotation and that the high rotational levels $J \geqslant 2$ are more highly perturbed than the two lowest ones. The aggregation of the molecules as a possible cause of the fine structure has to be definitively ruled out. The influence of the methane concentration on the structures of the three systems is different; this is likely the result of the strain energy, which is highly different in the three different mixed crystals. X-Ray diffraction studies of the methane–krypton system are needed; more information about intermolecular forces should be obtained from this system than from the

methane–argon or methane–xenon mixed crystals. As regards the thin films deposited on a cold plate suspended in vacuum, it has been shown that their composition or structure, or both, are not uniform over the entire sample. Raman spectra of solutions with low CH_4 concentrations will be reinvestigated. Using the high-power lasers now available, it should be possible to obtain spectra of much higher quality than those reported previously (4). Because of the different selection rules, such spectra would certainly be very useful to the solution of the problems discussed in this paper.

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