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G. Baciocco, P. Calvani, and S. Cunsolo

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Weak infrared bands in solid CH₄-II

G. Baciocco, P. Calvani, and S. Cunsolo

Dipartimento di Fisica, Università "La Sapienza," 00185 Roma, Italy

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The spectrum of solid methane in its partially ordered phase II was studied between 1000 and 3500 cm⁻¹ with improved sensitivity. The librational band of D_{2d} molecules associated with the ν_3 and ν_4 mode could be observed in detail, and evidence of induced absorption was found in the region of the infrared inactive ν_2 mode. The first infrared spectra in solid CH₄ of the overtone $2\nu_4$ and of the combination band $\nu_2 + \nu_4$ are also reported.

INTRODUCTION

The energy levels of a CH₄ molecule in the solid phase II were calculated by Yamamoto, Kataoka, and Okada¹ on the basis of an extended James and Keenan (EJK) model. Six of the eight molecules in the primitive cell are oriented by the anisotropic field of symmetry D_{2d} (which results from the superposition of the O_h crystal field with the T_d molecular field). They have three sets of states: a (tunneling levels), b (librations), and c (nearly free rotations). The last two molecules are nearly free rotors in the crystal field of symmetry O_h : their energy spectrum is similar to that of isolated CH₄, provided that the rotational constant B is assumed to be slightly smaller (4.2 cm⁻¹ instead of 5.253 cm⁻¹). The long-range order of phase II disappears at 20.4 K ($p = 0$) and gives place to the orientationally disordered phase I.

The results of the EJK model were quantitatively confirmed by several techniques, ranging from NMR² to inelastic neutron scattering.³ Early infrared⁴ and Raman⁵ spectra of phase II were also shown to be in agreement with them.⁶ Spectra in the far infrared, where translational absorption is dominating,⁷ gave instead little information on the orientational order of phase II. More recently, Medina and Daniels⁸ reported the first Raman observations of the D_{2d} molecules librational band—whose energy had already been measured by NMR⁹—and of the combination bands $2\nu_4$ and $\nu_2 + \nu_4$. Later, Medina¹⁰ measured the width of librations as a function of temperature at a pressure of 1.4 kbar, and determined an activation energy of 59 cm⁻¹. This value was related to the height of potential barriers for molecular reorientation, under the assumption that such a mechanism might cause the libration decay.

In this paper, we propose new vibration-libration infrared spectra at zero pressure. Peak widths which are larger and less dependent on temperature than those in the low-frequency Raman spectra¹⁰ are discussed. We then report the first infrared observation in phase II of the overtone $2\nu_4$ and of the combination band $\nu_2 + \nu_4$ which show a full (rotation/libration)-vibration spectrum. The assignment of O_h and D_{2d} lines is discussed in connection with corresponding Raman spectra.⁸ Finally, we show evidence of induced infrared absorption in the region of the inactive mode ν_2 and in combination bands at frequencies corresponding to the forbidden transition $S(0)$ of O_h molecules.

EXPERIMENTAL

Our samples were prepared from research grade CH₄ supplied by Società Italiana Ossigeno. After condensation

into the measuring cell they were slowly solidified under saturated vapor pressure. The cell, sealed by Irtran-2 windows, was mounted on the coldest flange of a two-stage Galileo Mk-2 cryogenerator, in such a way that the heat would flow downward. This procedure allowed growth of crystals of high optical quality, having a thickness d of either 0.5 or 1 mm. The samples were then cooled to the desired temperature, which was measured by platinum and germanium thermometers and kept stable by heaters. A schematic drawing of the apparatus will be published elsewhere.¹¹ The cryogenic system was inserted into a Bomem DA3.01 Fourier transform spectrometer, so that radiation was propagating in a vacuum for its full path.

RESULTS AND DISCUSSION

We first studied the weak side band of the two infrared active modes of CH₄, ν_3 , and ν_4 . The former is shown at a temperature of 14 K in Fig. 1, where as usual we plotted in arbitrary units,

$$A(\sigma) = (1/d) \ln [I_0(\sigma)/I(\sigma)], \quad (1)$$

where σ is the frequency, $I_0(\sigma)$ is the background intensity, and $I(\sigma)$ the intensity of the radiation transmitted through the sample. In Fig. 1, the high value of d prevents the observation of both the O_h vibration-rotation lines and the D_{2d}

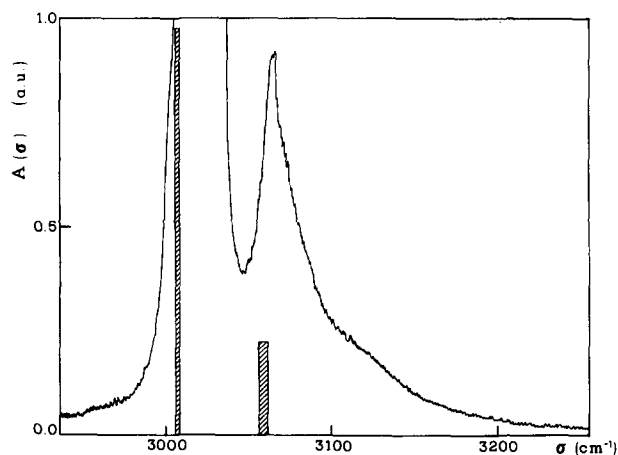


FIG. 1. The infrared librational band associated to the ν_3 mode: the sample thickness was 0.5 mm and the resolution was 0.5 cm⁻¹. Histograms give the position, the width at 0 K, and the relative intensity of the $|0a\rangle \rightarrow |1a\rangle$ and $|0a\rangle \rightarrow |1b\rangle$ transitions, as calculated in Ref. 6.

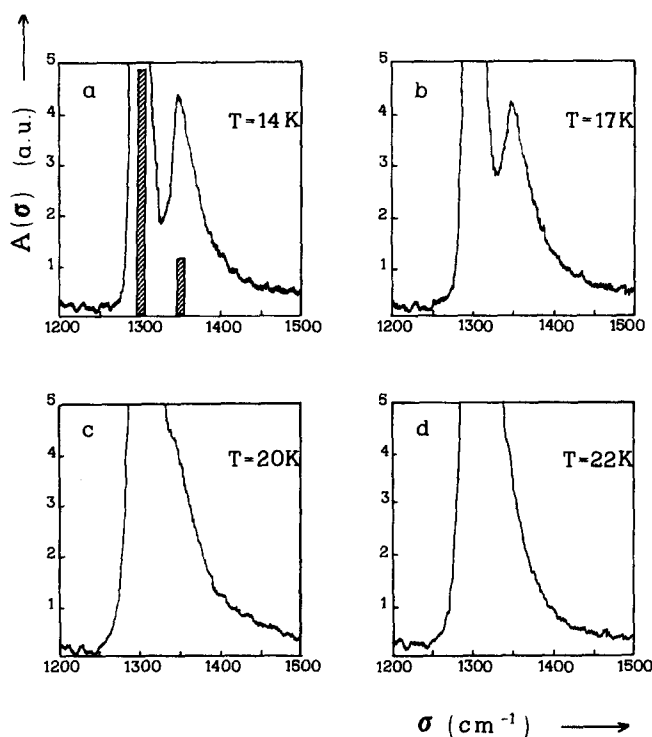


FIG. 2. The infrared side band associated to the ν_4 mode in phase II [(a),(b),(c)] disappears in phase I [(d)]: Sample thickness and resolution as in Fig. 1. In (a), histograms give the frequencies and relative intensities of $|0a\rangle \rightarrow |1a\rangle$ and $|0a\rangle \rightarrow |1b\rangle$ transitions of D_{2d} molecules, as calculated in Ref. 6.

$|0a\rangle \rightarrow |1a\rangle$ transitions, which correspond to a vibrational jump $0 \rightarrow 1$ within the set of tunneling levels a . On the other hand, Fig. 1 clearly shows a broad peak at 3065 cm^{-1} . This value is close to the frequency expected for transitions $|0a\rangle \rightarrow |1b\rangle$, which excite the librations of D_{2d} molecules. In Fig. 1, the bandwidth of librations at 0 K and their integrated intensity, as calculated by the EJK model,⁶ are represented, respectively, by the width and the height of the corresponding histogram. The shaded area at 3007 cm^{-1} yields for comparison the width and intensity of $|0a\rangle \rightarrow |1a\rangle$ transitions.

The corresponding spectrum for the ν_4 mode is shown at

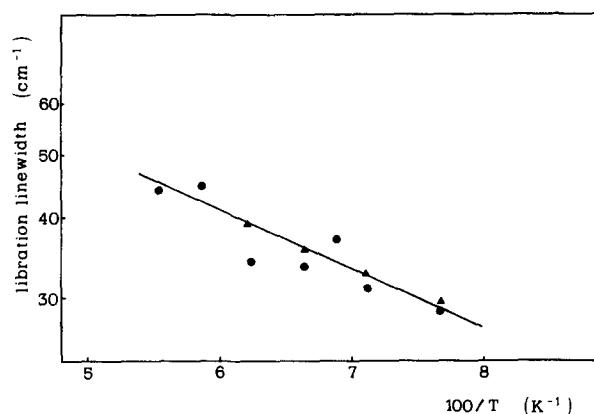


FIG. 3. The full linewidth of ν_3 (triangles) and ν_4 (dots) librational bands as a function of temperature in phase II of solid CH_4 .

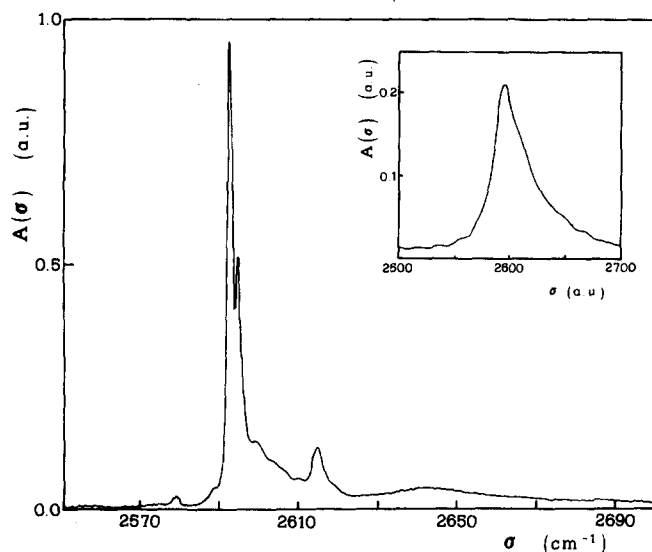


FIG. 4. Infrared spectrum of the overtone $2\nu_4$ for $d = 0.5 \text{ mm}$ at $T = 13 \text{ K}$ in phase II and at 25 K in phase I (insert). The intensity scale is the same for both spectra.

four different temperatures in Fig. 2. In Fig. 2(a) the histograms at 1300 and at 1350 cm^{-1} correspond as in Fig. 1 to the predictions of the EJK model.⁶ Here also the broadband observed at 1350 cm^{-1} is identified with the vibration-libration transition $|0a\rangle \rightarrow |1b\rangle$. When increasing the temperature in phase II, one gets the spectra of Figs. 2(b) and 2(c), which show a broadening of both the fundamental and the librational mode. Finally, in Fig. 2(d), at a temperature corresponding to the sample in phase I, the librational mode has disappeared.

The behavior with temperature of the vibration-libration linewidth is plotted for both the ν_3 and the ν_4 mode in Fig. 3, from which we extracted an activation energy of about 15 cm^{-1} . We could not compare this value with analogous results of previous observations. In the Chapados and Cabana⁴ infrared spectra the librational band was too weak, and no librations were observed by Medina and Daniels⁸ in their high-frequency and low-pressure Raman spectra of phase II. The linewidth of librations was measured instead in the low-frequency Raman spectrum by Medina¹⁰ at a pressure of 1.4 kbar and at temperatures ranging from 20 to 26 K . He found absolute values varying between 5 and 13 cm^{-1} with an activation energy of 59 cm^{-1} . As shown in Fig. 2, in our experiment the linewidth turns out to be much larger and less dependent on temperature. This is true also after subtraction of the fundamental vibration linewidth, which one can extract from the $|0a\rangle \rightarrow |1a\rangle$ transitions of D_{2d} molecules. These are much narrower than the vibration-libration band, as one can check in Figs. 4 and 5 where both types of transitions are observable. Even when allowance is made for the effect of pressure on the data of Ref. 10, it appears that if a libration is associated with a molecular vibration its lifetime is shortened considerably and is less sensitive to the lattice temperature. This leads to two possible formulations of the same result, depending upon our choice between localization and propagation of the librational excitation. If the libration decay is due to molecular reorientation, as considered in Ref. 10, the potential barriers created by the aniso-

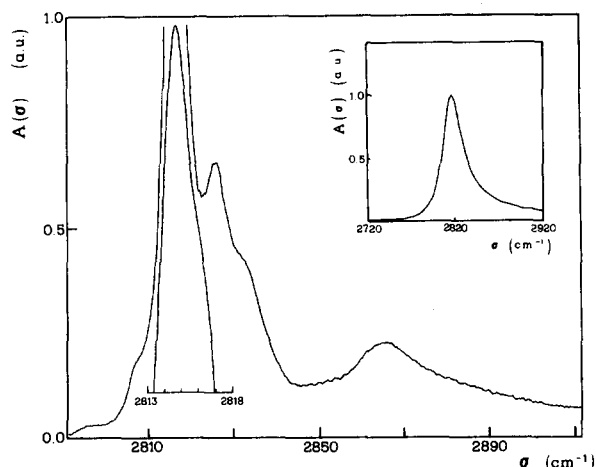


FIG. 5. Infrared spectrum of the combination band $\nu_2 + \nu_4$ for $d = 0.5$ mm in phase II at $T = 13$ K and in phase I at 25 K (insert). For both spectra, the intensity scale is the same as in Fig. 4, and the top of the peak would be at 3.4.

tropic field of phase II should be much lower for vibrating rather than rigid D_{2d} molecules. It would be interesting to include this effect in the EJK model. If on the other hand the librational excitation can propagate in the crystal (libron), its decay will be more rapid when the orientational lattice undergoes a distortion caused by molecular vibration. Our data show the effect of vibration on the librational linewidth but they do not yield an unambiguous interpretation of its origin. We are planning further investigations on librons in phase II, a problem which is still open in the panorama of solid methane research.

In Figs. 4 and 5 are, respectively, shown the overtone $2\nu_4$ and the combination band $\nu_2 + \nu_4$, which we have recently observed also for CH₄ molecules vibrating in a solid Kr matrix.¹² The spectra of Figs. 4 and 5 look similar, even if in the latter case the absorption is higher (both figures have the same scale) and the central peak is not fully resolved. In fact, even if the symmetry of the $2\nu_4$ mode is $(A_1 + E) + F_1 + F_2$ while that of $\nu_2 + \nu_4$ is $F_1 + F_2$, only the F_2 mode is infrared active. In spite of the similarities, the intraband spacings will in general not be the same due to different values of the Coriolis coupling.

When the sample is at 25 K in phase I (inserts of Figs. 4 and 5) the rotovibrational structure of combination bands cannot be resolved any more and all molecules are expected to undergo hindered rotations about randomly oriented axes.

The frequencies of lines observed in Figs. 4 and 5 are listed in Table I and assigned on the basis of the considerations which follow. Let us first examine the contribution of oriented D_{2d} molecules. The overtone $2\nu_4$ (Fig. 4), as we already mentioned, has symmetry $(A_1 + E) + F_1 + F_2$; then, in view of the selection rules for the CH₄ group T_d ,¹³ one may expect that $|0a\rangle \rightarrow |2a\rangle$ transitions produce either two Raman lines of symmetries $A_1 + E$ and F_2 , respectively, or a single infrared line of symmetry F_2 . Medina and Daniels⁸ did indeed observe two strong lines (at 2571 and 2592 cm⁻¹) which could be attributed to D_{2d} molecules. In our

TABLE I. Observed infrared frequencies in the $2\nu_4$ and $\nu_2 + \nu_4$ combination bands.

Mode	IR frequency ^a (cm ⁻¹)	Assignment
$2\nu_4$	2578 w	$P(1) O_h$
	2588 sh	$Q(1) O_h$
	2591.5 s	$a \rightarrow a D_{2d}$
	2594.0 sh	$R(0) O_h$
	2599 sh	$R(1) O_h$
	2614 m	$Q(1) + S_0(0) O_h$
	2641 b	$a \rightarrow b D_{2d}$
$\nu_2 + \nu_4$	2794 w	$P(1) O_h$
	2805 sh	$Q(1) O_h$
	2814.5 s	$a \rightarrow a D_{2d}$
	2816.5 sh	$R(0) O_h$
	2824 m	$R(1) O_h$
	2831 sh	$Q(1) + S_0(0) O_h$
	2864 b	$a \rightarrow b D_{2d}$

^a s = strong, m = medium, w = weak, b = broad, sh = shoulder.

$2\nu_4$ spectrum the former line is absent, while a strong absorption was detected at 2591 cm⁻¹. Therefore, we can attribute F_2 symmetry to the latter and, consequently, $A_1 + E$ symmetry to the Raman line at 2571 cm⁻¹. In turn, the $\nu_2 + \nu_4$ combination band (Fig. 5) has symmetry $F_1 + F_2$: so the D_{2d} tunneling molecules are expected to show, both in the infrared and in the Raman spectrum, a single F_2 line. This latter can be identified with the strong line observed by us at 2812 cm⁻¹ and by the authors of Ref. 8 at 2813 cm⁻¹. Finally, both the $2\nu_4$ and $\nu_2 + \nu_4$ infrared spectra exhibit a weak librational band. Its width (about 30 cm⁻¹ at 13 K) and its spacing from the lowest D_{2d} line are the same, within errors, as for the ν_4 mode.

Let us now turn to the contribution of free-rotating molecules to overtone and combination bands. In the ν_4 infrared spectrum four lines: $P(1)$, $Q(0)$, $R(0)$, and $R(1)$ were observed for CH₄ free rotating molecules, both in phase II⁴ and in a noble-gas matrix.¹² We assume that the same rotovibrational structure and similar intensity ratios hold for $2\nu_4$ and $\nu_2 + \nu_4$ infrared bands, which have the same F_2 symmetry as the ν_4 mode. This leads to the assignments given in Table I. They differ from those proposed in Ref. 8 where the two Raman lines observed at 2578 and 2587 cm⁻¹ ($2\nu_4$ band) were, respectively, identified as $Q(1)$ and $R(1)$. When applied to the infrared results, these assignments do not identify the strongest O_h lines in $2\nu_4$ and $\nu_2 + \nu_4$, as $R(0)$ lines, in contrast with the usual result for F_2 symmetry modes.^{4,6} In turn, the assignment $P(1)$ for the infrared line at 2578 cm⁻¹ is not consistent with the observation of a Raman peak at the same frequency. One is then led to suppose that these weak and broad lines, even if they occur at similar frequencies in the infrared and Raman spectra, do not correspond to the same transition.

A fifth line is clearly evident in Fig. 4 at 2614 cm⁻¹ and in Fig. 5 as a shoulder at 2831 cm⁻¹. In view of its position it could be identified either as a $R(2)$ or as a $S(0)$ transition [a strong Raman $S(0)$ line⁸ was observed at 2832 cm⁻¹], but the former is too weak at 13 K and the latter is forbidden in

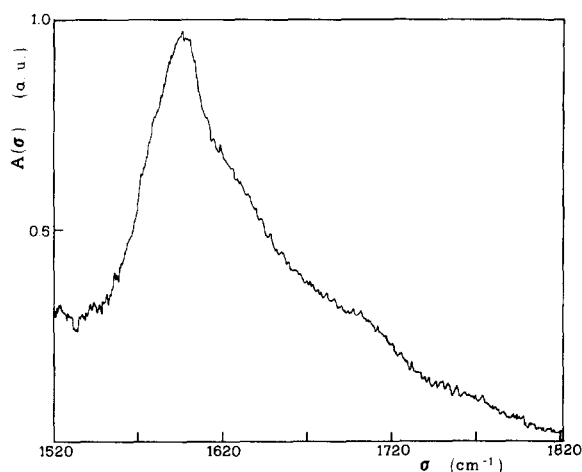


FIG. 6. Infrared spectrum in the region of the inactive mode ν_2 and of the combination band $\nu_3 - \nu_4$ for $d = 1$ mm, at $T = 13$ K.

the infrared. In both combination bands these lines have considerable intensity and are spaced at 26 cm^{-1} from $Q(1)$. One possible interpretation is the following: while a molecule i undergoes a $2\nu_4 + Q(1)$ transition, a $S_0(0)$ excitation is present (and eventually propagates) on molecules $j \neq i$. This could explain the observed intensity because in such case an induced absorption at $S(0)$ would not undergo any cancellation caused by the fcc lattice inversion symmetry. Moreover, in the absence of Coriolis coupling on j , the frequency separation from the rotovibrational transition on i would be the same for all combination bands.

The existence of induced infrared absorption in phase II of solid CH₄ is shown by our observations in the spectral region of the ν_2 vibrational mode which is not infrared active.¹³ Its Raman spectrum extends from about 1500 to 1600 cm^{-1} . Approximately in the same range of frequencies we observed a broad and weak absorption band (Fig. 6) in a sample having a thickness of 1 mm. In spite of an instrumental resolution of 0.5 cm^{-1} , no rotovibrational structure could be identified. The maximum of the band is at 1590 cm^{-1} , while the shoulder which appears in Fig. 5 at about 1700 cm^{-1} is likely to be the F_2 symmetry $\nu_3 - \nu_4$ combination band, which has never been observed in solid phase before.

SUMMARY AND CONCLUSIONS

Weak absorption bands were observed in the infrared spectrum of solid CH₄-II. The overtone $2\nu_4$ and the combination band $\nu_2 + \nu_4$ showed the full rotovibrational structure which is expected for both free-rotating O_h molecules and oriented D_{2d} molecules. Assignments were discussed in connection with previous Raman results.⁸ Associated with both combination bands was a line which does not correspond to any infrared active transition of the required intensity. This line was tentatively interpreted as a $S_0(0)$ excitation either localized on nearest neighbors of the molecule which undergoes the vibrational jump, or propagating in the crystal. This could explain the intense induced absorption at

the frequency of a Raman $S(0)$ line in the $\nu_2 + \nu_4$ region and also the detection, at the same spacing from $Q(1)$, of a well-defined absorption in the overtone $2\nu_4$ region.

The vibration-libration of oriented molecules was observed in four different bands: ν_3 , ν_4 , $2\nu_4$, and $\nu_2 + \nu_4$. The libration linewidth is always much larger than the fundamental band of D_{2d} molecules: between 13 and 19 K it increases with temperature, but more slowly than in the low-frequency Raman spectrum, where its absolute values are also smaller. In a single-molecule approach, if the libration decay is to be attributed to molecular reorientation, such a result would indicate that the potential barriers of the anisotropic field for a vibrationally excited CH₄ molecule are considerably lower than for a molecule in the ground state. If on the contrary one assumes a libron model, the broadening would be attributed to the distortion of orientational periodicity produced by molecular vibrations. Our data do not support one model rather than the other but we hope to get more experimental information on the eventual propagation of librons in the crystal by studying the librational band in CH₄-Kr alloys at high CH₄ concentration. These systems, where one can introduce both translational and orientational disorder under controlled conditions, have been recently studied by NMR¹⁴ and neutron scattering¹⁵ techniques. Infrared spectroscopy is sensitive to the highest energy states of CH₄ molecules and therefore seems to be particularly suitable for such investigation.

Finally, in our spectra we found evidence of induced infrared absorption in the region of the inactive mode ν_2 . This band is produced by the octupole and hexadecapole moments of nearest neighbors and, as expected, is broadened by their molecular motions.

ACKNOWLEDGMENT

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