

Vibron propagation and localization determined from infrared combination bands of molecular crystals

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Infrared spectra of CH_4II , SiH_4II , and GeH_4IV show that localized overtones are produced in the crystal by strongly anharmonic transitions, pairs of propagating vibrons by weakly anharmonic transitions. In CH_4II , rotons are also detected. A comparison between these results and unpublished overtone spectra of solid $p\text{-H}_2$ is proposed.

Theory¹ shows that rotational and vibrational excitations give rise in molecular crystals to propagating modes, similar to Frenkel excitons in the insulators. No direct evidence of exciton propagation is reported in the literature for the solid phases of XH_4 compounds ($X = \text{C}, \text{Si}, \text{Ge}$), even if they are suitable for extended studies of low-energy excitons, with their variety of vibrational modes $\nu_1 (A_1)$, $\nu_2 (E)$, $\nu_3 (F_2)$, and $\nu_4 (F_2)$ and with their orientationally ordered, low-temperature structures. Moreover, solid CH_4 is the only pure crystal, together with solid hydrogens, where rotational excitons can be observed at low T (in CH_4II , free rotating molecules at O_h sites coexist with oriented molecules at D_{2d} sites).

In this Brief Report it is our aim to show that vibron propagation and localization can be usefully studied in the weak infrared overtone and combination bands of molecular crystals. Let us consider, for instance, a vibrational transition $0 \rightarrow \nu_i + \nu_j$, where i and j label the normal modes. It may take place (a) on the same molecule (overtone); (b) simultaneously on different molecules (dou-

ble transition). The excitation will then propagate in the crystal with momentum \mathbf{k} . In case (a) absorption will take place at $\mathbf{k}_{i+j} = 0$ as for the fundamental vibrations, and narrow spectral features are expected at low T . Such features will reflect the crystal translational and orientational symmetry. In case (b), absorption will take place for any $\mathbf{k}_i = -\mathbf{k}_j$ and the observed spectrum will be broad, being substantially determined by the joint density of states of bands $E_i(\mathbf{k}_i)$ and $E_j(\mathbf{k}_j)$. Finally, it may also happen that the overtone will not propagate as in (a), thus producing a "localized exciton" (c). In case (c), the infrared combination bands will exhibit a lower number of lines than in (a), and resemble those observed for a "host" molecule of the same species, in a solid matrix. An analysis of well-resolved infrared combinational spectra will then be able to discriminate between cases (a), (b), and (c).

Two examples of combination bands showing different mechanisms of excitation in solid CH_4II , are reported in Fig. 1. Data of Fig. 1 were taken in a 0.18-mm-thick,

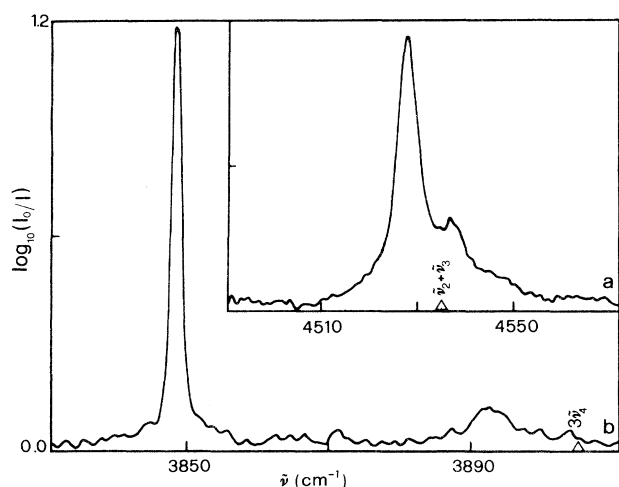


FIG. 1. The $\nu_2 + \nu_3$ (a) and $3\nu_4$ (b) infrared bands of solid CH_4II at 13 K are plotted on the same vertical scale. Here and in the next figures, I is the intensity of radiation transmitted by the sample, I_0 is that of background, and the triangle indicates the sum of the corresponding fundamental frequencies, as measured in the solid phase.

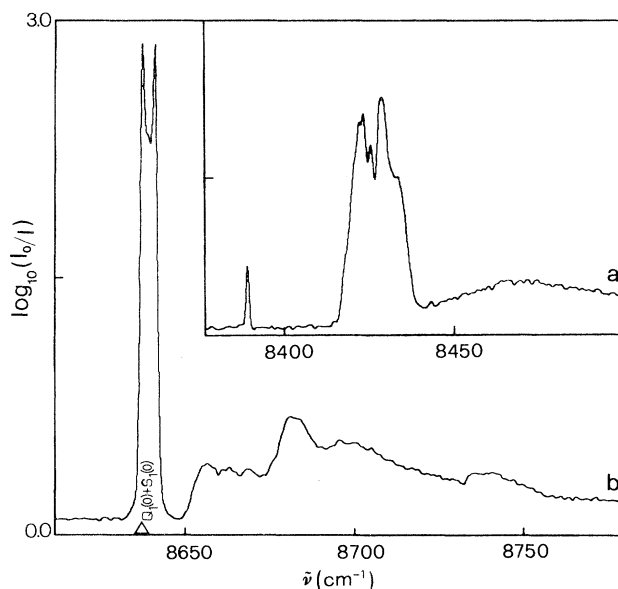


FIG. 2. The regions of first overtone (a) and of double vibrational transition (b) in pure solid $p\text{-H}_2$ at 1.6 K (Ref. 4). (a) and (b) are on the same vertical scale.

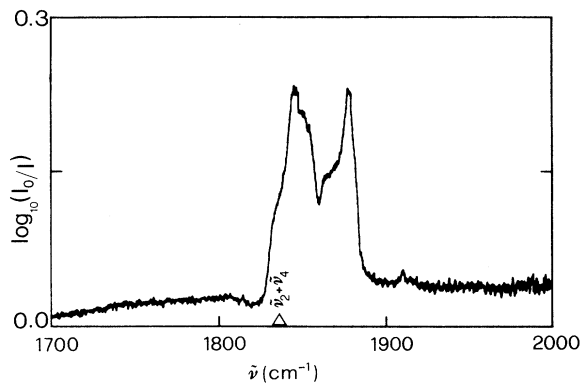


FIG. 3. The region of the combination band $\nu_2 + \nu_4$ in solid SiH_4II at 17 K.

solid CH_4 sample, at 13 K and with a resolution of 0.5 cm^{-1} . The band $\nu_2 + \nu_3$ in Fig. 1(a) shows a vibrational peak at 4527 cm^{-1} with a linewidth of 5.5 cm^{-1} , a value which is by an order of magnitude larger than the fundamental vibrational lines observed in the same system at $\mathbf{k}=0$. This suggests that two vibrons ν_2 and ν_3 are propagating in the crystal, as in the above case (b). In the gas, the shift of the $\nu_2 + \nu_3$ $Q(0)$ line² with respect to $\tilde{\nu}_2 + \tilde{\nu}_3$ is $(\Delta_{2,3})_{\text{gas}} = -2.6 \text{ cm}^{-1}$, suggestive of a weak anharmonic interaction between these modes. The peak at 4536 cm^{-1} is rotational by comparison with the fundamental bands. Its shift of $9 \pm 1 \text{ cm}^{-1}$ fits with the $R(0)$ frequency of O_h molecules in CH_4II (9.0 cm^{-1}), in absence of Coriolis coupling. This is what expected for a $R_0(0)$ exciton, propagating in CH_4II in spite of 40% ortho ($J=1$) O_h molecules, distributed at random in the crystal at 13 K. This also confirms that two lines, previously observed³ in CH_4II , could indeed be attributed to $S_0(0)$ rotors.

The spectrum of the overtone $3\nu_4$ in solid CH_4II [Fig. 1(b)] exhibits a single line at 3847 cm^{-1} . With a linewidth smaller than 1.5 cm^{-1} , it can be reasonably assigned to case (c) discussed above. As the D_{2d} field of phase II results from a weak dihedral perturbation on a T_d site symmetry, a singlet (or unresolved doublet) is indeed expected for a localized vibrational exciton. It should be noted that the $3\nu_4$ overtone is considerably displaced ($\Delta_{4,4,4} = -57 \text{ cm}^{-1}$) with respect to $3\tilde{\nu}_4$.

The above results can be usefully compared to the infrared spectra of solid $p\text{-H}_2$, a system where both vibrons and rotors are known to exist.¹ Figure 2 shows unpublished induced absorption spectra⁴ in the region of the first overtone. Data were taken at 1.6 K in a 5-cm-thick $p\text{-H}_2$ solid sample ($o\text{-H}_2 < 0.5\%$), with a resolution of 0.1 cm^{-1} . The line at 8389.0 cm^{-1} in Fig. 2(a), whose width is instrumental, is assigned to a localized $S_2(0)$ transition. The broad band around 8425 cm^{-1} is in turn attributed⁵ to a $Q_2(0) + S_0(0)$ transition, where the roton only is propagating. The shift $\Delta_{Q_2, S_0} = E[S_2(0)] - E[Q_2(0) + S_0(0)]$ ($\approx -35 \text{ cm}^{-1}$ at midband) measures the vibron-roton interaction energy. The spectrum in

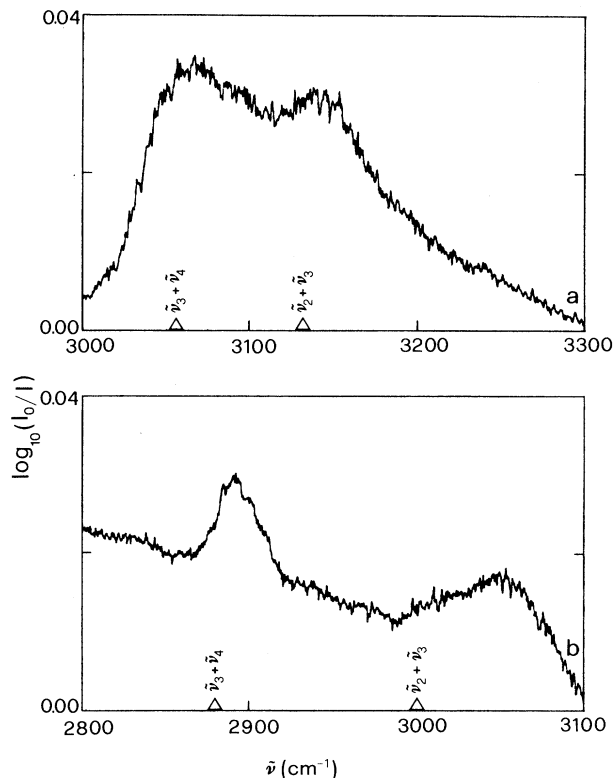


FIG. 4. The spectral region of $\nu_3 + \nu_4$ and $\nu_2 + \nu_3$ combination bands in SiH_4II (a) and GeH_4IV (b) at 17 K.

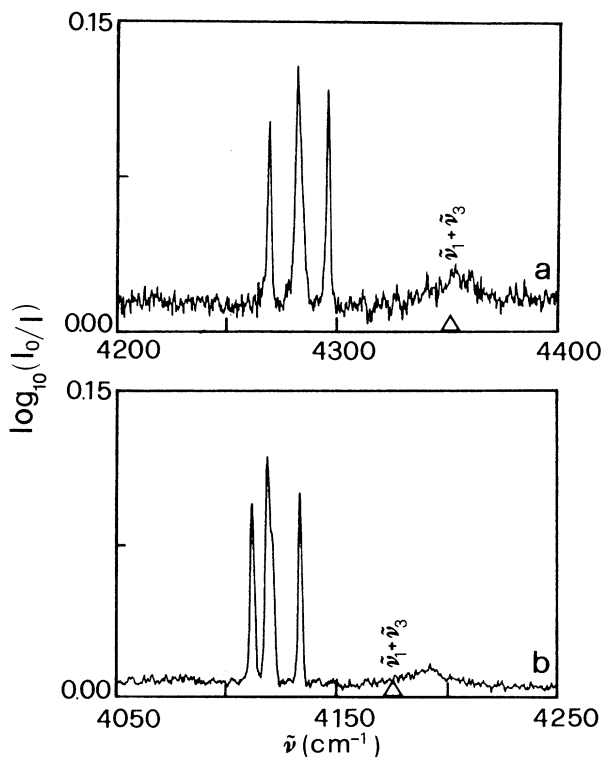


FIG. 5. The $\nu_1 + \nu_3$ combination band in SiH_4II (a) and GeH_4IV (b) at 17 K.

TABLE I. The peak frequencies $\tilde{\nu}_{\text{solid}}$ of the infrared combination bands observed in CH_4II at 13 K, in SiH_4II , and GeH_4IV at 17 K, are compared with the corresponding $\tilde{\nu}_{\text{gas}}$ when available, as reported for the $Q(0)$ branch by various authors. Preliminary CH_4II data had been published in Ref. 3. The fundamental frequencies utilized to calculate the anharmonic frequency shifts Δ_{sol} and Δ_{gas} are also listed. For broad bands, both the lower and higher absorption edges of the band are reported, together with the corresponding shifts. Data are expressed in cm^{-1} . Superscripts 2, 9, 10, 12, and 14 refer to references.

Band	CH_4				SiH_4				GeH_4			
	$\tilde{\nu}_{\text{solid}}$	Δ_{solid}	$\tilde{\nu}_{\text{gas}}$	Δ_{gas}	$\tilde{\nu}_{\text{solid}}$	Δ_{solid}	$\tilde{\nu}_{\text{gas}}$	Δ_{gas}	$\tilde{\nu}_{\text{solid}}$	Δ_{solid}	$\tilde{\nu}_{\text{gas}}$	Δ_{gas}
ν_4	1301.3		1310.8 ²		880		913.3 ¹²		791		821.0 ¹⁴	
ν_2	1526		1533.5 ²		956.5		972.1 ¹²		911		930.7 ¹⁴	
ν_1	2901		2918 ²		~2170		2186.9 ¹³		~2085		2110.6 ¹⁴	
ν_3	3008.5		3019.2 ²		2176		2189.2 ¹³		2089		2111.7 ¹⁴	
$2\nu_4$	2591.5	-11	2618.5 ²	-3.1								
$\nu_2 + \nu_4$	2814.5	-13	2830.4 ¹¹	-13.7	1830 ± 1890	-6 ± 54			1680 ± 1800	-22 ± 98		
$\nu_1 + \nu_4$	4190 ± 4220	-12 ± 18	4223.5 ²	-5.3								
$\nu_3 + \nu_4$	4300	-10	4319.2 ²	-10.8	3035 ± 3110	-21 ± 54			2860 ± 2950	-20 ± 70		
$\nu_2 + \nu_3$	4510 ± 4555	-25 ± 20	4549.9 ²	-2.6	3115 ± 3155	-17 ± 23			2995 ± 3015	-5 ± 15		
$\nu_1 + \nu_3$					4269.6	-77 ± 5			4111.9	-66 ± 5		
					4282.9	-64 ± 5			4119.1	-59 ± 5		
					4296.5	-51 ± 5			4133.9	-44 ± 5		
					4330 ± 4370	-22 ± 18	4309.4 ⁹	-66.7	4180 ± 4205	+2 ± 27	4154.1 ¹⁰	-68.2
$2\nu_3$	5990	-28	6004.6 ²	-34.4								
$3\nu_4$	3847	-57										
$\nu_2 + 2\nu_4$	4090 ± 4140	-38 ± 12										
$\nu_3 + 2\nu_4$	5566	-45										
$\nu_2 + \nu_3 + \nu_4$	5801	-34			3955	-67			3727	-64		

Fig. 2(a), which also shows a broad phonon branch, is similar in shape to the fundamental band,⁶ where in turn one gets $\Delta_{Q_1, S_0} = E[S_1(0)] - E[Q_1(0) + S_0(0)] = -25 \text{ cm}^{-1}$. At higher frequencies [Fig. 2(b)], two narrow lines at 8637.5 and 8641.4 cm^{-1} , and a broad roton-phonon band, are shown. The doublet has the frequency of a $Q_1(0) + S_1(0)$ transition [triangle in Fig. 2(b)], and its splitting $\Delta_1 = 3.9 \text{ cm}^{-1}$ is due to the quadrupole-quadrupole interaction E' , which removes the degeneracy of the $Q_1(0)$ vibron propagating in the hcp phase (two molecules per unit cell). At $\mathbf{k}=0$ one gets¹ $\Delta_1 = (\frac{1}{2})E'S_6 = 3.5 \text{ cm}^{-1}$, with $S_6 = 14.4359$ and $E' = 0.49 \pm 0.01 \text{ cm}^{-1}$, in excellent agreement with Fig. 2(b).

The separation $E[S_2(0)] - E[Q_1(0) + S_1(0)] = -250 \pm 2 \text{ cm}^{-1}$, measures in turn the binding energy Δ_{Q_1, Q_1} of the two vibrons in solid $p\text{-H}_2$, when $\Delta_{Q_2, S_0} - \Delta_{Q_1, S_0} \approx -10 \text{ cm}^{-1}$ is deducted. The resulting value (-240 cm^{-1}) is close to the anharmonic contribution to the first overtone of a H_2 molecule in the gas (-236 cm^{-1}).⁷ In summary, Fig. 2 shows that as in Fig. 1 rotors and vibrons with $\Delta v = 1$ are propagating in molecular crystals, while the overtones are localized. However, in CH_4II the infrared roton bands are narrower than in solid $p\text{-H}_2$. Indeed, in the former system the anisotropic interaction among nearly free rotors is weaker, both because the leading term is of higher order (octupole-octupole), and because the nearest neighbors of any O_h molecule are all D_{2d} 's.

The combination bands of solid SiH_4 and GeH_4 at low T , allow to study the propagation of vibrons in low-symmetry crystal fields. Figure 3 shows the $\nu_2 + \nu_4$ band in a 0.1-mm-thick SiH_4II sample at 17 K. In solid SiH_4II , $\bar{\nu}_2 + \bar{\nu}_4$ falls inside the band, which in turn is

broad and structured. This indicates that a pair of propagating vibrons are produced in the $0 \rightarrow \nu_2 + \nu_4$ transition. The spectrum in Fig. 3 should then reproduce minima and maxima in the joint density of states of ν_2 and ν_4 vibron bands. Analogous explanations hold for the combination bands $\nu_3 + \nu_4$ and $\nu_2 + \nu_3$ of SiH_4II [Fig. 4(a)] and GeH_4IV ⁸ [Fig. 4(b)]. The F_2 -symmetry combination band $\nu_1 + \nu_3$ exhibits quite a different shape both in SiH_4II [Figs. 5(a)] and in GeH_4IV [Fig. 5(b)]. Three narrow lines, considerably shifted with respect to the sum of the fundamental frequencies, are detected. This shows that the F_2 overtone is localized (case c). If it were propagating, nine lines would instead be observed.⁸ In the gaseous phase, the $\nu_1 + \nu_3$ band displays a strong anharmonic shift both in SiH_4 (-66.7 cm^{-1})⁹ and in GeH_4 (-68.2 cm^{-1}).¹⁰ Figure 5 then yields further evidence that anharmonic transitions produce in the crystal localized vibrons. Such a conclusion is confirmed by Table I, where our observations are compared with those in the gaseous phase. Broad bands, suggestive of propagating excitons, contain the "zero shift" frequency and correspond in the isolated molecule to transitions with small negative shifts $\Delta_{i,j}$. On the other hand, narrow peaks, as produced by localized excitons, correspond in most cases to strong anharmonic shifts both in the solid and the gaseous phase.

In conclusion, we have studied the infrared combination bands in molecular crystals characterized by different structures, intermolecular interactions, and site symmetries. Strongly anharmonic transitions produce localized overtones, while multiple transitions give rise to propagating vibrons and rotors. In the case of $p\text{-H}_2$, the existing theories¹ yield quantitative agreement with the observations. It is hoped that similar calculations will be carried out for XH_4 molecular crystals.

¹J. Van Kranendonk, *Solid Hydrogen* (Plenum, New York, 1983).

²D. L. Gray and A. G. Robiette, *Mol. Phys.* **37**, 1901 (1979).

³G. Baciocco, P. Calvani, and S. Cunsolo, *J. Chem. Phys.* **87**, 1913 (1987).

⁴S. Cunsolo and H. P. Gush (unpublished).

⁵G. Varghese, R. D. G. Prasad, and S. Paddi Reddy, *Phys. Rev. A* **35**, 701 (1987).

⁶H. P. Gush, W. F. J. Hare, E. J. Allin, and H. L. Welsh, *Can. J. Phys.* **38**, 176 (1960).

⁷A. Watanabe, J. L. Hunt, and H. L. Welsh, *Can. J. Phys.* **49**, 860 (1971).

⁸P. Calvani, C. Ciotti, S. Cunsolo, and S. Lupi, *Solid State Commun.* **75**, 189 (1990).

⁹R. Bregier and P. Lepage, *J. Mol. Spectrosc.* **45**, 450 (1973).

¹⁰L. Halonen and M. S. Child, *Mol. Phys.* **46**, 239 (1982).

¹¹J. Lolck and A. G. Robiette, *Chem. Phys. Lett.* **64**, 195 (1979).

¹²H. W. Kattenberg and A. Oskam, *J. Mol. Spectrosc.* **49**, 52 (1974).

¹³A. Owyong, P. Esherrick, A. G. Robiette, and R. S. McDowell, *J. Mol. Spectrosc.* **86**, 209 (1981).

¹⁴H. W. Kattenberg, W. Gabesc, and A. Oskam, *J. Mol. Spectrosc.* **86**, 209 (1981).