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Vibrational spectroscopy and dynamics of W(CO)$_6$ in solid methane as a probe of lattice properties

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Methane solids present more than one accessible crystalline phase at low temperature at zero pressure. We trap W(CO)$_6$ in CH$_4$ and CD$_4$ matrices between 8 and 35 K to probe the interaction between an impurity and its surrounding molecular solid under various physical conditions. Linear and nonlinear vibrational spectroscopies of W(CO)$_6$ highlight different kinds of interaction and reveal new and remarkable signatures of the phase transition of methane. The structures in the absorption band of the antisymmetric CO stretching mode exhibit a clear modification at the transition between phase II and phase I in CH$_4$ and motional narrowing is observed upon temperature increase. The vibrational dynamics of this mode is probed in stimulated photon echo experiments performed with a femtosecond IR laser. A short component around 10 ps is detected in the population relaxation lifetime in the high temperature phase of solid CH$_4$ (phase I) and disappears at lower temperatures (phase II) where the vibrational lifetime is in the hundreds of ps. The analysis of the nonlinear time-resolved results suggests that the short component comes from a fast energy transfer between the vibrational excitation of the guest and the lattice in specific families of sites. Such fast transfers are observed in the case of W(CO)$_6$ trapped in CD$_4$ because of an energy overlap of the excitation of W(CO)$_6$ and a lattice vibron. In solid CH$_4$, even when these V-V transfers are not efficient, pure dephasing processes due to the molecular nature of the host occur: they are temperature dependent without a clear modification at the phase transition. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4968561]

I. INTRODUCTION

Solid methane is an interesting medium for numerous reasons. In particular, as methane is cosmochemically abundant, its ices are especially important for astrophysics and planetology science.1–3 From a fundamental point of view, it offers a very nice example of a van der Waals solid exhibiting quantum effects and phase transitions (e.g., Refs. 4 and 5). CH$_4$ solid exists in two crystalline phases at zero pressure with phase transition occurring at $\Theta = 20.4$ K. In phase I, between 20.4 K and 90.7 K, there is no orientational ordering of the methane molecules in the lattice. In phase II, below 20.4 K, partial ordering affects three quarters of the molecules. The two phases differ consequently by the possibilities of rotational molecular motions. The aim of the present paper is to investigate the influence of the host molecular motions and of the phase transition on the molecular properties of a guest species trapped in solid methane.

In previous studies, we used tungsten hexacarbonyl (W(CO)$_6$) to examine weak interactions with a cryogenic solid4,5 by probing the vibrational dynamics of the antisymmetric CO stretching mode ($T_{1u}$ mode $\sim 2000$ cm$^{-1}$). W(CO)$_6$ is a benchmark molecule for nonlinear IR experiments and its vibrational dynamics was extensively studied, especially in solutions (see, e.g., Ref. 8). In a recent time-resolved study at the femtosecond time scale,9 we demonstrated the sensitivity of its vibrational coherence upon molecular motion of the lattice host by comparing nonlinear results in rare gas and in nitrogen (N$_2$) matrices where the vibrational dephasing time is reduced at 20 K from hundreds to tens of ps respectively. These experiments also enabled to distinguish the vibrational dynamics upon the trapping site in N$_2$ matrices: for instance, the $T_{1u}$ mode of W(CO)$_6$ was found to be specifically coupled with a librational mode of the host in one type of trapping site. This stretching mode is thus a remarkable tool for probing the environment effects. In solid methane, both librational and rotational motions of the molecular hosts can occur; thus, the study of W(CO)$_6$ embedded in such solid can be rich and informative and we expect in particular strong temperature dependence due to the phase transition.

The structure and properties of solid methane were widely investigated both experimentally and theoretically. In both crystalline phases of CH$_4$ solid, the carbon atoms of methane molecules occupy the centers of an fcc lattice. The distance $d$ between nearest neighbors is around 0.417 nm, showing a slight increase with temperature.10 Solid methane shows great similarities with Kr or N$_2$ fcc lattices where $d = 0.399$ nm.
and $d = 0.401$ nm, respectively. In phase I, methane molecules exhibit random reorientations due to thermal orientational fluctuations (orientational diffusion) and occupy $O_h$ symmetry sites whereas in phase II, electrostatic octupole-octupole interactions induce partial ordering.\(^1\!\!^,\!\!^5,\!\!^11,\!\!^12\) The crystal structure then contains eight sublattices of which six are orientationally ordered with molecules occupying $D_{2d}$ symmetry sites. The two remaining sublattices show no such ordering and the molecules occupy $O_h$ symmetry sites.\(^4\) Methane molecules in $O_h$ positions rotate almost freely.\(^4,\!\!^13\) With heavy methane ($CD_4$), a third crystalline phase can be reached at low temperature (phase III) at zero pressure. Phase transitions occur at $22.1$ K (III $\leftrightarrow$ II) and $27.0$ K (II $\leftrightarrow$ I).\(^14\) Phase III exists only at high pressure in the case of CH$_4$. The structure is orthorhombic\(^14\) and the molecules do not rotate anymore. Although the structure of solid methane was mainly explored through neutron scattering experiments,\(^14\!\!^–\!\!^17\) phase transitions were also clearly observed by spectroscopic methods.\(^11,\!\!^12,\!\!^18–\!\!^20\) Positions, intensities, and shapes of Raman and IR bands differ with the phase. In phase I, the very broad vibrational bands (linewidth up to 100 cm$^{-1}$) can be explained by considerable motion of methane molecules in the lattice, including rotation\(^12,\!\!^20\) — phase I is considered as a plastic phase\(^21\) because of the large motional fluctuations. In phase II the existence of $D_{2d}$ sites induces specific libration-vibration sharp features\(^19\) and some vibrational transitions are only clearly observed in phase II.

We performed experiments in CH$_4$ and in CD$_4$. In order to get a complete insight into the vibrational behavior of the W(CO)$_6$ guest molecule, we combined linear and nonlinear vibrational spectroscopies. The former is obtained by IR absorption spectra and the latter by IR stimulated photon echoes at the femtosecond time scale, similar to our previous study in nitrogen matrices.\(^9\) IR spectra were also used to control the vibrational bands of methane. In the condensed phase, absorption bands are often mainly inhomogeneously broadened and the homogeneous bandwidth (γ$_h$), directly related to the vibrational dephasing time ($T_2 = 1/\pi\gamma_h$), needs to be measured by nonlinear techniques. Stimulated photon echoes give direct access in the time domain to $T_2$ and to the population relaxation time $T_1$. Both characteristic times are linked by the relation,

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*},$$

where $T_2^*$ is the “pure” dephasing time depending on the environment of the guest. In rare gas matrices and in solid nitrogen, the $T_{1a}$ mode of W(CO)$_6$ was found to exhibit a $T_1$ value of 100–200 ps.\(^7,\!\!^9\) In nitrogen a value in the tens of ps for $T_2$ time was thus the signature of dephasing processes due to the molecular lattice. In solid methane we obtained new and complex behaviors with $T_1$ and $T_2$ times varying from tens to hundreds of picoseconds and strong temperature dependence.

A short description of the setup and the photon echo process is given in Sec. II. Experimental results are presented in Sec. III, with a detailed description of the temperature effects on the absorption spectra and on the characteristic times extracted from photon echo experiments in solid CH$_4$. A brief overview of the results obtained in CD$_4$ solid is also given. Time-resolved results are discussed in Sec. IV and their analysis is supported by simulations of the photon echo signal. The simulation allows one to extract the main trends and main conclusions and to compare the various cryogenic environments we have explored so far. A summary highlighting the original behaviors obtained in solid methane ends the paper (Sec. V).

II. METHODS

A. Experimental setup

1. Matrices

The complete setup has already been described elsewhere.\(^9\) The matrix samples were obtained by continuous deposition of the gaseous mixture onto a CaF$_2$ window kept at 20 K of a helium-flow cryostat (Janis). Gaseous samples were prepared at room temperature by mixing W(CO)$_6$ (Sigma Aldrich), degassed by several freeze-pump-thaw cycles with methane in proportions varied from $10^5$ to $10^3$ (W(CO)$_6$/methane ratio). The deposition rate was typically 30 mmol/h. Matrix thickness was kept below 100 µm. Concentration and deposition times were adapted so as to keep an optical density of the $T_{1a}$ mode of W(CO)$_6$ of $\sim$1.

2. IR spectroscopy

Absorption spectra were recorded using an FTIR Mattson spectrometer at 0.25 cm$^{-1}$ spectral resolution. A switching gold coated mirror brings the FTIR Globar beam to probe the same matrix region as in photon echo experiments. Linear and nonlinear data were measured using the same nitrogen cooled MCT (mercury cadmium telluride) detector.

3. Time-resolved measurements

Photon echo experiments originated from a supercontinuum seeded BBO optical parametric amplifier (OPA) (Spectra Physics) pumped by a 800 nm Ti:Sapphire laser/amplifier system (Coherent-Thales): duration 120 fs, repetition rate 1 kHz, and energy 800 µJ/pulse. Briefly, the tunable mid-IR fs pulse used for photon echoes was generated by difference frequency mixing of signal and idler pulses of the OPA in an AgGaS$_2$ crystal (center frequency: 1980 cm$^{-1}$; bandwidth 150 cm$^{-1}$; duration 145 fs; output $\sim$3 µJ). Detailed description of the laser system is given in Ref. 22. The output was split into three beams ($k_1$, $k_2$, and $k_3$ wave vectors) of equivalent energies using two coated ZnSe beam splitters. $k_2$ and $k_3$ beams were delayed with respect to $k_1$ by two optical delay stages. The three beams were made parallel and were focused at the sample by a 150 mm reflected focal length off-axis parabolic mirror in a boxcar geometry. The photon echo signal ($k_s$ wavevector) was generated in the $k_s = k_3 + k_2 - k_1$ phase matching direction (see Figure 1). The four beams were reflected by a second 150 mm focal length off-axis parabolic mirror. An iris was used to select $k_s$ and discard any light contribution from $k_1$, $k_2$, and $k_3$ beams. Photon echo signal was focused into the MCT detector by a 60° off-axis parabolic mirror.

This setup corresponds to a stimulated photon echo setup where two delay times are used. The typical pulse sequence
of photon echoes is pulse “$k_1$” coming first followed by pulse “$k_2$” which is delayed by $\tau$ called coherence time, then by pulse “$k_3$” which is delayed by $T$ called waiting time. The detected signal (quadratic detection) is

$$S(\tau, T) = \int_0^{\infty} dt |P(\tau, T, t)|^2.$$  

$P(\tau, T, t)$ is the third order polarization created in the sample with the wave vector $k_i$. In a simplified view, the $\tau$ dependence of $S$ gives access to dephasing processes ($T_2$) whereas the $T$ dependence gives access to population lifetimes ($T_1$). Consequently, two kinds of signals are recorded: $S(\tau)$ obtained by scanning $\tau$ at a fixed delay $k_2$-$k_3$ and $S(T)$ by varying the $k_1$-$k_3$ delay, keeping $\tau$ fixed. Speed and use of the delay lines are the same as in Ref. 9.

**B. Theoretical modelling of nonlinear signals**

The experimental signals were simulated following the model described in Ref. 9. The third order polarization created in the sample comes from the molecules trapped in different sites which can be classified by families of sites (see Sec. III A). The third order polarization $P_f(\tau, T, t)$ coming from each family ($f$) is calculated and $\rho_f(\tau, T, t)$ is obtained by a weighted sum of $P_f(\tau, T, t)$, the weights ($\alpha_f$) being given by the populations of families. Simulation of $P_f(\tau, T, t)$ takes into account all the Feynman pathways explored by the sequence of the three pulses (wave vectors $k_1$, $k_2$, and $k_3$) giving rise to $P_f(\tau, T, t)$ in the direction $k_n$. Two of these pathways are shown in Figure 1. Since the spectral bandwidth of the femtosecond laser is large compared to the anharmonicity of the vibrational mode that is probed, the pathways can involve $v = 0, 1$, and 2 vibrational levels. The $T_{1u}$ mode of W(CO)$_6$ is triply degenerated and this degeneracy can be removed in the crystal environment, so that the pathways can also involve vibrational modes of different frequencies.

In summary, $P_f(\tau, T, t)$ results from 7 pathways in the $k_1, k_2, k_3$ sequence described previously (Sec. II A, Figure 1) corresponding to the so-called rephasing case. There are also 7 paths in the $k_2, k_1, k_3$ sequence corresponding to $\tau < 0$ and the non-rephasing case, and there are 6 paths when $k_1$ is the last pulse. In the latter case, all the paths involve overtone or combination of modes. The paths are numbered as $F_k$ with $k = 1-7$ for the first case, $k = 8-14$ for the second case, and $k = 15-20$ for the last case. The corresponding polarizations are noted $P_f^{(3)}[F_k](\tau, T, t)$ for each path and each family. Paths and polarizations are described in the supplementary material. We used the same assumptions and notations as in our previous work, following the calculations detailed by Ge et al. in Ref. 24. In particular, the model describes the vibrational frequency fluctuations in the limit of Bloch dynamics, i.e., in the case of a clear separation between homogeneous and inhomogeneous broadenings. The former part is characterized by the $T_2$ time and the latter by a time noted $T_1$. Inhomogeneous broadening is usually depicted by a Gaussian profile. As a matter of fact, the absorption bands of interest in cryogenic matrices were often much better reproduced by Lorentzian profiles. Consequently, we phenomenologically substituted the Gaussian profiles used in the calculations by Lorentzian profiles in the model (see the supplementary material). We obtain

$$P^{(3)}(\tau, T, t) = \sum_f \alpha_f \sum_m P^{(3)}_{f,m}[F_k](\tau, T, t)$$  

with $n$ and $m$ depending on the sequence of the pulses. The photon echo signal is calculated by applying Eqs. (2) and (3) and compared with the recorded signals.

**III. EXPERIMENTAL RESULTS**

Linear and nonlinear spectroscopy experiments were performed on W(CO)$_6$/CH$_4$ and W(CO)$_6$/CD$_4$ samples. The results in light methane are fully described in Secs. III A–III C. A summary of the observations in heavy methane is reported in Sec. III D.

**A. IR absorption spectroscopy**

W(CO)$_6$ is a large molecule (~0.78 nm diameter) of high symmetry. It takes the place of several hosts in the cryogenic lattice and can be trapped in different sites, depending at least on the number of host atoms or molecules it replaces. A large inhomogeneous broadening, more or less structured, of its absorption spectrum is thus expected in cryogenic matrices. Its modes are described in the O$_h$ symmetry group. The $T_{1u}$ vibrational mode of interest corresponding to the carbonyl antisymmetric stretches is triply degenerated. This degeneracy is lifted in sites of lower symmetry. Consequently, the IR spectrum of this mode alone can be quite complex, as reported in rare gas or N$_2$ matrices. Its spectra in solid methane at two temperatures are displayed in Figure 2 and their characteristics are summarized in Table I. At 8 K, the spectrum contains indeed several structured bands (black curve) whereas it is much simpler at 25 K (red curve).

This remarkable temperature effect especially affects the low frequency range of the spectrum, below 1984 cm$^{-1}$.
only one band is observed at high temperature. Its temperature evolution is shown in Figure 3(a) and the frequencies of the main components versus temperature are plotted in Figure 3(b). One can distinguish three main bands at low temperature. They clearly coalesce to one main band around 19 K (Figure 3(b)). In fact, no dramatic modification is observed above 19 K. The total absorption intensity from 1978 to 1984 cm\(^{-1}\) is found constant whatever the temperature. Spectral changes are reversible and decreasing the temperature of the sample yields the split bands of the low-temperature spectra back. These changes are thus clearly correlated to the phase transition in solid methane. Black and red curves represent the spectral features in phase II and phase I, respectively, in Figs. 2 and 3(a). As mentioned in the Introduction, the main difference between the two crystalline phases concerns the orientational ordering of methane molecules. The spectral evolution depicted in Figure 3 can be explained by a motional narrowing effect: part of the static interactions at low temperature are no more static at high temperature due to the orientational fluctuations of all methane molecules so that W(CO)_6 is sensitive to an “averaged” and a more homogeneous environment. Inhomogeneity and/or lack of symmetry induced by the partial ordering of host molecules in phase II are reduced in phase I. One can also notice a slight shift to higher frequencies with temperature growth in phase I (Figure 3(b)) which can be related to the increase of the lattice parameter.\(^{10}\)

In our previous work, analysis of the IR spectra of W(CO)_6/N\(_2\) samples, reinforced by size considerations, led us to assume that a large part of W(CO)_6 molecules were embedded in sites of O\(_h\) symmetry, replacing 13 host molecules.\(^9\) The lattice parameter of solid methane is slightly higher than that of nitrogen but remains very close (0.417 nm compared to 0.401 nm) and we assume that this kind of sites also exists in methane. In N\(_2\) as well as in Ar and Kr matrices, a smaller band was observed, \(\sim 5\) cm\(^{-1}\) blue-shifted from the main feature. It was assigned to one non-degenerated component of the vibrational transition in sites of a lower symmetry (B\(_{1u}\) band in Ref. 9). Similarly, we make the same assumption for the band near 1987 cm\(^{-1}\) in CH\(_4\) (band 4). Its integrated intensity represents 19\% \pm 1\% of the total absorption whatever the temperature (see Table I). It means that lower symmetry sites related to this band represent roughly 57\% (3\% \times 19\%) of the total sites, thus yielding a population of 43\% \pm 3\% for high symmetry sites.

We can thus begin the analysis by considering that the three branches (1, 2, and 3) of Figure 3(b) at low temperature are the equivalent of the B\(_{3u}\), T\(_{1u}\), and B\(_{2u}\) bands observed in nitrogen, respectively. It is however more complex in the case of methane since the three “B\(_{iu}\)” bands (1, 3, and 4) have different intensities. In order to get a better insight into the absorption, the spectra were fitted with several Lorentzian lines (up to fifteen lines to correctly reproduce the whole structure of IR spectra in phase II). Table I reports the average

**TABLE I.** Frequency, width (FWHM), and area in cm\(^{-1}\) of the CO stretching bands of W(CO)_6 in methane at 8 K (phase II) and 25 K (phase I) (main components).

<table>
<thead>
<tr>
<th>8 K</th>
<th>25 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu)</td>
<td>Width</td>
</tr>
<tr>
<td>1979.3</td>
<td>0.27</td>
</tr>
<tr>
<td>1979.7</td>
<td>0.35</td>
</tr>
<tr>
<td>1980.6</td>
<td>0.41</td>
</tr>
<tr>
<td>1981.1</td>
<td>0.53</td>
</tr>
<tr>
<td>1982.7</td>
<td>0.32</td>
</tr>
<tr>
<td>1983.0</td>
<td>0.32</td>
</tr>
<tr>
<td>1987.0</td>
<td>Structured</td>
</tr>
<tr>
<td>1988.0</td>
<td></td>
</tr>
</tbody>
</table>

**FIG. 2.** IR spectra of W(CO)_6/CH\(_4\) at 8 K (black) and 25 K (red). W(CO)_6 is displayed in the figure. The spectrum at 8 K can be analysed in four (more or less) structured bands marked (1, 2, 3, 4). At 25 K, only two bands are observed, one above 1984 cm\(^{-1}\), and one below.

**FIG. 3.** Temperature-dependence of the low-frequency feature of the spectrum of W(CO)_6 in methane: (a) IR spectra between 5 and 30 K, (b) frequency evolution of the bands 1, 2, 3 against temperature; each band exhibits a clear doublet structure and the two main frequencies are reported for each band (see Table I). The dashed line represents the highest temperature (18 K) with three distinct bands.
frequencies of the main components taking into account the weight of the various lines involved in each band. An estimation of the intensities of the four bands can thus also be obtained from the fits. The 45% ± 2% intensity of the middle band 2 is in agreement with our estimation of high symmetry sites (43% ± 3%). Band 3 has the lowest intensity (10% ± 1%), meaning that the amount of sites with complete degeneracy removal is ∼30%. Consequently, band 4 (intensity of 19%, see above) includes this kind of sites (10%) and also sites where degeneracy is partially removed (9%). Band 1 represents ∼26% of the total area: it is less than the sum of complete (10% from band 3) and partial (18% ± 2% × 9% from the remaining part of band 4) degeneracy removal, but remains consistent with all the data taking into account the measurement errors. Band 4 is highly structured at all temperatures, and especially in phase II. It reflects the large number of different sites of low symmetry, in agreement with the previous analysis of bands 1 and 3. Band 2, related to high symmetry sites, is also obviously structured in phase II, probably because of different trapping sites. Moreover, the O₈ symmetry is probably not preserved in phase II due to different behaviours of the neighbouring methane molecules, but can be restored in phase I.

The present analysis is fully consistent with our analysis of W(CO)₆/N₂ spectra. In both cases, four bands can be distinguished with one band assigned to high symmetry sites (the second band in increasing frequency order) and the three others to low symmetry sites, with very similar frequencies distribution. High and low symmetry sites are present at a very similar ratio: 40/60 in N₂ and 45/55 in CH₄. A slightly larger ratio in favour of high-symmetry sites in CH₄ is consistent with the slightly higher lattice parameter in this solid. The temperature dependence is however very different in the two lattices⁹ and low symmetry sites in CH₄ are separated into two groups: 30% of sites show complete degeneracy removal of the T₁u mode and 25% of sites show a partial removal. In phase I, the lack of well-defined structures in the main band which is composed of high and low symmetry sites underlines the similarities between the trapping sites despite their different symmetries.

Of interest is the temperature of the onset of coalescence highlighted in Figure 3. Although the phase transition of methane is at 20.4 K, bands 1, 2, and 3 converge at 18-19 K. It is confirmed by the IR bands of methane for the same sample in the region of the 2ν₄ band and the ν₄ + ν₂ combination band (2591 and 2814 cm⁻¹, respectively) which show that the phase transition occurs between 18 and 19 K (Figure 4). We ran similar experiments in a pure methane matrix and we checked that phase transition occurred at ∼20 K, as expected (see Figure S1 in the supplementary material). This temperature downshift could be due to the large size of the W(CO)₆ impurity that strongly perturbs the lattice and prevents partial ordering of methane molecules at long distance scales. To our knowledge, this is the first observation of the phase transition of methane through the IR spectroscopy of an impurity isolated in the solid.

B. Nonlinear signals: Dependence on waiting time

In photon echo experiments, the signal versus waiting time (S(T)) should reflect the evolution of the vibrational
populations (see Sec. II). Figure 5 shows $S(T)$ population relaxation signals recorded at $\tau = 0$ ps between 8 and 25 K. A short component in the time decay is clearly observed at the highest temperatures, i.e., in phase I (red curves in Figure 5). This component seems to disappear in phase II (black curves), so it can be used as a signature of the phase transition.

In fact, the third order polarization can be fitted by a bi-exponential decay versus time $T$ whatever the temperature, with a long and a short component. Note that due to the quadratic detection, the $S(T)$ signal is fitted with the square of a bi-exponential decay (Figure 5(b)). The long component is very similar at all the temperatures explored with corresponding fits of $\sim 240$ ps. The short component is $\sim 7$ ps. Its value is not well defined in phase II, because the weight of the short component decreases drastically from phase I to phase II: the short component is the dominant one at $\Theta > 20$ K and its weight decreases with temperature in phase II, with less than 30% at $\Theta = 18$ K, and disappears below 10 K.

The temperature behaviour of $S(T)$ suggests that the short component is related to the crystalline phase of methane and thus to the motion of methane molecules. Its characteristic time, shorter than 10 ps, cannot reflect the population relaxation time ($T_1$) of all W(CO)$_6$ molecules in phase I since we have the following: (i) $T_2$ must be shorter than $2 \times T_1$ (cf. Eq. (1)) and (ii) $T_2$ values larger than 20 ps are obtained in phase I (see Sec. III C). The short component may be assigned to only a fraction of the trapped W(CO)$_6$ molecules, or to another process. This puzzling point will be discussed later in Sec. IV B. On the contrary, the long component is comparable to the results of $S(T)$ obtained in argon and nitrogen matrices where $T_1$ values were in the order of 100-200 ps.\textsuperscript{7,9} This simplified analysis involves no long recovery time ($T_g$) linked to relaxation back to the ground state, while it was considered in N$_2$. On the other hand, the long component can be decomposed in two steps, one ($T_1$) of $\sim 100$ ps and a second ($T_g$) $\sim 400$ ps.

C. Nonlinear signals: Dependence on the coherence time

Stimulated photon echo signals $S(\tau)$ at different waiting times $T$ were recorded from 5 K to 35 K. In Figure 6(a) $S(\tau)$ signals are plotted at 24 K and 8 K and at $T > 15$ ps to get rid of the short component in the population relaxation signal. They show strong temperature dependence. The most obvious change occurs for $\tau > 0$, i.e., in the rephasing part of the signal, with much shorter decays at high temperatures, where dephasing processes are more efficient, as expected. Less evident is the effect of temperature in the non-rephasing part of the signal ($\tau < 0$). It shows a slower rise at high $\Theta$ than at low $\Theta$, and the whole $S(\tau)$ signal looks more symmetric in $\tau$ at high $\Theta$. It means that rephasing processes take less important parts, i.e., that inhomogeneous broadening is less significant. It is a direct consequence of the motional narrowing observed in the absorption spectra (see Sec. III A). In order to quantify this effect in a simple way, the signals $S(\tau)$ are fitted with an expression of the third order polarization taking into account a global effective $T_2$ time ($T_2^{\text{eff}}$) and a global effective inhomogeneous width through a time constant $T_1^{\text{eff}}$, as was used in

\begin{equation}
S(\tau) \propto e^{-\frac{\tau}{T_2}} \times e^{-\frac{\tau}{T_1}}.
\end{equation}

The temperature dependence of $T_2^{\text{eff}}$ and $T_1^{\text{eff}}$ is reported in Figure 6(b). $T_2^{\text{eff}}$ continuously diminishes when temperature increases and displays no dramatic change near phase transition. On the contrary, one can distinguish two temperature ranges in the evolution of $T_1^{\text{eff}}$. It is nearly constant in each phase and shows a sudden increase at phase transition from phase II to phase I. At high temperature, $T_2^{\text{eff}}$ and $T_1^{\text{eff}}$ have similar values. For example, at 32 K $T_2^{\text{eff}} = 25$ ps and $T_1^{\text{eff}} = 18$ ps which means that homogeneous and inhomogeneous broadenings are of the same order of magnitude. These broadenings will be discussed in Sec. IV C where the model of Sec. II B is used to reproduce the experimental data.

The $S(\tau)$ signals often present oscillations, more or less visible depending on the experimental conditions. They can be identified in the Fourier transform of the time-resolved signal. Two oscillations are in particular well observed and well-defined. The first one with a frequency of $14.5 \pm 0.3$ cm$^{-1}$ corresponds to the anharmonicity of the CO antisymmetric stretch mode. Figure 7(a) shows an example of signal with an inset blowing up the part where these oscillations are more visible. The anharmonicity was especially well characterized in W(CO)$_6$/N$_2$ samples\textsuperscript{9} with a value of $14.7 \pm 0.1$ cm$^{-1}$. Very similar values were measured in solutions\textsuperscript{30,31} and in xerogels\textsuperscript{6} highlighting the weakness of the perturbation induced on the
These oscillations appear at all temperatures and can be seen in $S(\tau)$ signals recorded at waiting times longer than tens of ps. As they come from a coherent excitation of both $0 \leftrightarrow 1$ and $1 \leftrightarrow 2$ vibrational transitions, it means that the population relaxation time $T_1$ of $v = 1$ must be longer than these tens of ps for a large part of the trapped W(CO)$_6$ at all temperatures, in agreement with the measurement of the long component of $S(T)$.

The other clear oscillations corresponding to a frequency of $\sim 6 \text{ cm}^{-1}$ appear only at high temperatures (see Figure 7(b)). They well match the spectral difference between the intense band at $\sim 1981 \text{ cm}^{-1}$ and band 4 at $\sim 1987 \text{ cm}^{-1}$ in the absorption spectra in phase I (Figure 2). They come from the coherent excitation of all the absorption frequencies. At low temperature, in phase II, more than two frequencies are involved in the non-linear response and the related oscillations can be scrambled. The observation of oscillations will be discussed in Sec. IV with the modelling of the nonlinear signals.

D. W(CO)$_6$ embedded in solid CD$_4$

The rationale for studying solid CD$_4$ is to have a direct comparison of the behaviour of W(CO)$_6$ in the two methane matrices which display strong similarities, in particular for phase transitions, and to investigate the effects of host rotation. Moreover, phase III of CD$_4$ is accessible under our experimental conditions ($\Theta_{I-II} = 27 \text{ K}, \Theta_{II-III} = 22 \text{ K}$): comparing the vibrational dynamics of the guest molecule in the three phases of CD$_4$ has motivated this work.

The study begins with the IR spectra of W(CO)$_6$ in CD$_4$ and it immediately appears that there is a spectral overlap of the $T_{1u}$ mode of W(CO)$_6$ with the $2\nu_4$ overtone mode of CD$_4$ at $1976 \text{ cm}^{-1}$. Figure 8(a) depicts the absorption spectra at 24 K in this spectral range of a W(CO)$_6$/CD$_4$ sample (black), a “pure” CD$_4$ matrix (grey), and the corresponding difference spectrum (dots) which highlights the absorption profile of W(CO)$_6$ alone. The latter spectrum shows a broad structure for which we can tentatively extract three bands at $1976.8$, $1980.5$, and $1986.3 \text{ cm}^{-1}$, each one with bandwidths larger than $2.5 \text{ cm}^{-1}$. Following the same assumptions as for the analysis of W(CO)$_6$/CH$_4$ IR spectra, the highest frequency band has been assigned to low symmetry sites, giving a ratio of $\sim 55/45$ of high/low symmetry sites. The lowest frequency band is especially broad and less defined because of the overlap with the CD$_4$ mode. The ratio between high and low symmetry sites is thus badly measured and a deeper comparison with CH$_4$ cannot be specified at this point.

In contrast with CH$_4$ samples, the absorption of W(CO)$_6$ in CD$_4$ does not show any strong variations with temperature. As such, it cannot be used to probe the phase transitions of CD$_4$. Comparing Figure 8(a) and Figure 2 highlights the overall broadening of the spectrum in CD$_4$. Figure 8(b) shows quite comparable absorption patterns in the three phases and differences consist mostly of band broadening at low temperature (phase III) corresponding to a large inhomogeneity in the trapping sites. Band narrowing is observed for the middle
band with temperature increase, where it varies from $\sim 3$ cm\(^{-1}\) at 10 K to 2.4 cm\(^{-1}\) at 30 K, and can be assigned to a weak *motional narrowing* effect. In contrast, phase transitions are well observed in the spectral bands of the CD\(_4\) host as well as CH\(_4\) which is always present as traces (Figure S2 in the supplementary material). When following the phase transition with the trapping of W(CO)\(_6\), similarly to the case of CH\(_4\) samples. The temperature of phase transition II-III is $\Theta_{II-III} = 20\, K$ when CD\(_4\) contains W(CO)\(_6\) impurities, while it is 22 K in pure CD\(_4\) (Figure S3 in the supplementary material). The latter value is consistent with the work of Calvani and Lupi.\(^{32}\)

The previously mentioned resonance between guest and host vibrational excitations causes the broadening of W(CO)\(_6\) bands, preventing the observation of phase transitions. It implies a great efficiency of vibrational energy transfer between the guest and the host. The time-resolved signals directly reflect this property: $S(T)$ and $S(\tau)$ show fast decays corresponding to $T_1$ and $T_2$ of few picoseconds. Figure 9 shows the results at 30 K. No temperature effect has been evidenced. From $S(T)$ and $S(\tau)$ data, $T_1 \leq 10\, ps$ and $T_2 = 10-12\, ps$ are extracted whatever the temperature. A very short component is detected in $S(T)$, especially at high temperature, corresponding to a relaxation time of $\sim 1.5\, ps$ which could reflect the lifetime of the vibrational excitation in perfect resonance with the CD\(_4\) vibron. At lower temperatures, $T_1$ remains very short but the fact that $T_2 \leq 2 \times T_1$ indicates that pure dephasing processes are also at play in spite of the fast population relaxation. The shortness of the signals prevents any further analysis of the data in terms of families of sites or more precise environment effects. The above effective dephasing time $T_2$ corresponds to a homogeneous broadening around 1 cm\(^{-1}\), which is much smaller than the bandwidths measured in the IR spectra. Therefore there is an inhomogeneous contribution to the broadening.

**IV. DISCUSSION**

**A. Modelling photon echoes in solid CH\(_4\)**

The model described in Sec. II B has been applied in order to extract more information from the time-resolved data. The analysis of IR spectra (Sec. III A) evidences the presence of various kinds of sites of different symmetries. The simplest model considers three families of sites described by their temporal characteristics $T_1$, $T_2$, and $T_1$ (population relaxation time, dephasing time, and “inhomogeneous” time, respectively) related to the three symmetry types described in Sec. III A: (1) a high symmetry family, where the $T_{1u}$ mode remains triply degenerated, described by one frequency; (2) a lower symmetry family, where the $T_{1u}$ mode is split into two bands, with one being doubly degenerated, described by two frequencies; (3) a family with the lowest symmetry where the degeneracy of mode $T_{1u}$ is totally removed, described by three frequencies. This model includes a maximum of four frequencies to describe bands 1, 2, and 3 of the absorption spectra whereas doublets of bands 1 and 2 are well-resolved at low temperature (Figures 2 and 3). Band 2 corresponding to the high symmetry family is then described by two frequencies assigned to two different high symmetry sites in phase II. The doublet of band 1 can be assigned to the sites of lowest symmetry for its weaker component (lowest frequency) and to the sites of intermediate symmetry for its stronger component (at highest frequency). A set of 3 or 4 families of sites is thus used in the model, depending on the doublet resolution of band 2, which is temperature dependent, to describe the absorption features. The weights $\alpha_i$ as well as band frequencies (parameters $\omega_i$) in equations Sn of the supplementary material are extracted from the absorption spectra at all temperatures. Inhomogeneous times $T_i$ are also estimated from the absorption profiles (bandwidths) taking into account the homogeneous part related to $T_2$. Only a small number of independent frequencies have been used in the model, so it cannot reflect all the structures observed in the IR spectra. The band frequencies as well as $T_1$ can be varied in order to use only one band to simulate several close structures. In particular, the description of the highly structured band 4 cannot reproduce well the absorption result within the present approximation. Consequently, $T_1$ related to the high frequency components of the two sites of low symmetry is reduced in the model, compared to the other components (in bands 1 and 3). The other parameters of the model ($\epsilon_{ij}$, $T_{corr}$, $D_{ij}$) are related to the correlation between bands, overtones, and combination modes. At each temperature, a whole set of parameters is obtained to reproduce all the different recorded signals ($S(T)$ and $S(\tau)$ with varying $T$ and $\tau$). Despite the simplifications described above, a lot of parameters are still involved. Further assumptions are applied in order to extract the physical meaning of the modelling. The major one is to apply the same parameters—except frequencies—to all families, when there is no evidence of other site effects. All the experimental signals are then well reproduced with the model.

It is of course important to take into account the structure of the IR spectrum and the different pathways to simulate the oscillations observed in the non-linear signals. These simulations bring new information. The oscillations at frequencies around 6 cm\(^{-1}\) are well reproduced by the model (see Figure 7(b)), but to get the oscillation magnitude observed experimentally, non-diagonal anharmonicities $D_{ij}$ (cf. Eqs S5–S20 in the supplementary material) must be $\neq 0$ in the low symmetry sites. It means that the modes obtained after the
T_{1u} degeneracy removal are coupled. It is also a proof that band 4 of the absorption spectra corresponds to a component of T_{1u} and does not belong to specific sites with specific frequency shifts. Oscillations around 14.5 cm\(^{-1}\) can only be well simulated when sites with a large inhomogeneous broadening (>20 cm\(^{-1}\)) are introduced in the model. A similar behavior was noted in the simulations of photon echoes in W(CO)\(_6\)/N\(_2\) samples.\(^3\) These oscillations appear when there is a spectral overlap between the 0 \leftarrow 1 and 1 \leftarrow 2 vibrational bands,\(^3\) i.e., with large inhomogeneous broadening. The broadening deduced from the absorption spectra and modelled by Lorentzian profiles is not large enough to obtain visible broadening deduced from the absorption spectra and modelled overtones and combination levels (see Eqs. S15–S20 in the supplementary material). These oscillations could help evaluate the D_{ij} parameters. Unfortunately, we have not succeeded in rationalizing the experimental results with a small set of D_{ij} values in the simulations and the conclusion was similar as previously: D_{ij, i\neq j} \neq 0 in low symmetry sites. The exact values of D_{ij, i\neq j} are not crucial for modelling the most significant parts of the photon echo signals. Similarly, the experimental signals do not inform on the correlation parameters (c_{ij} and T_{corr} in Eqs. S1–S20 of the supplementary material).

B. S(T) and vibrational population relaxation

No temperature dependence of the long component of S(T) is observed in the explored temperature range (5–35 K). As explained above, this long component must include a T\(_1\) time and a value of T\(_1\)\(_{\text{long}}\) = 180 ± 30 ps can be adjusted for all cases. S(T) exhibits a puzzling short component in phase I (see Sec. III B). In order to take into account this behavior, we consider that T\(_1\) is strongly reduced in one family of sites. This hypothesis will be discussed below. This short value of T\(_1\) should concern the high symmetry family because oscillations related to beats between components of low symmetry sites are observed in S(\tau) signals recorded with T > 40 ps, i.e., signals coming mainly from sites with long T\(_1\). The weight of the short component is correctly reproduced in phase I considering that it concerns the whole high symmetry family and that T\(_g\) = T\(_1\) in these sites. We obtain T\(_1\)\(_{\text{short}}\) = T\(_g\)\(_{\text{short}}\) = 10 ± 2 ps. The assumption of T\(_1\)\(_{\text{short}}\) \neq T\(_g\)\(_{\text{short}}\), i.e., a long T\(_g\) time combined with T\(_1\)\(_{\text{short}}\), would have led to significantly increase the weight of short-T\(_1\) sites in order to reproduce the S(T) signals, meaning that the slow decay would have been only governed by a T\(_g\) time in phase I, in contradiction with the results deduced from S(\tau). In phase II, the weight of the short component is correctly reproduced when considering that only part of the high symmetry sites has a short population relaxation time. This part decreases with a temperature decrease (22% at 14 K and nil below 10 K).

Because of the large energy gap between the T\(_{1u}\) mode and vibrational levels of lower energy,\(^3\) the lifetime of the excited vibration is intrinsically long in W(CO)\(_6\). Long T\(_1\) times were also measured in solvents such as CCl\(_4\) at room temperature (700 ps)\(^5\) because of the lack of vibrational levels of intermediate energy in the vibrational manifold of the solvent. Similarly, T\(_1\) values of hundreds of picoseconds were found in rare gas and nitrogen matrices.\(^7,9\) In CH\(_4\) the long 180 ± 30 ps component measured in the present experiments corresponds to a similar relaxation process. A much longer time, assigned to a recovery time (T\(_g\) ~ 1 ns), was observed in nitrogen matrices\(^9\), highlighting the inefficiency of the vibrational relaxation in this cryogenic matrix. Unfortunately our measurements of S(T) in CH\(_4\) were not long enough to extract accurate T\(_g\) times and a value of 300 ps has been taken in the model. From the analysis of S(T), T\(_g\) cannot be longer than 500 ps. In fact, T\(_1\)\(_{\text{long}}\) and T\(_g\) have the same order of magnitude (respectively 180 ps and 300 ps) and it is not clear whether we can distinguish between two cases: (i) distinct T\(_1\) and T\(_g\) times and (ii) different sites displaying different long T\(_1\) times. In contrast with rare gas and nitrogen, the methane host has vibrational energy levels in the energy gap of the vibrational pattern of the W(CO)\(_6\) guest which can help in the vibrational relaxation, which would suggest that T\(_1\) = T\(_g\) is at play in most of the sites, in favor of the second possibility. The present modelling cannot distinguish between both assumptions which lead to similar evaluations of the other parameters. When a vibrational level of the host is in resonance with the guest excited vibration, T\(_1\) and T\(_g\) are found to be strongly reduced, as it is observed in CD\(_4\) leading to T\(_1\) = T\(_g\) ≤ 10 ps.

The population decay at low temperature is mainly composed of long components and the relaxation process in CH\(_4\) thus resembles those in rare gas and nitrogen matrices. When Θ increases, in phase I, a new process occurs with the appearance of the short component in S(T). The signals are well reproduced assuming that a fraction of the sites in CH\(_4\) experiences very fast vibrational relaxation, similarly to the case of CD\(_4\). The closest fundamental mode of CH\(_4\) below the excited vibration of W(CO)\(_6\) is ν\(_{2}\) at 1538 cm\(^{-1}\) in crystal phase I.\(^20\) Because of rotational and translational motion of CH\(_4\) in this phase, vibrational bands are very large.\(^19\) Phonon bands extend up to 160 cm\(^{-1}\).\(^36\) We thus suspect that above phase transition, a new efficient relaxation path is at play: a vibron assisted relaxation could enhance the population relaxation rate either to the ground state or to a low frequency mode of W(CO)\(_6\) in the 400–500 cm\(^{-1}\) frequency range.\(^34\) In our model, the fast relaxation process occurs for high symmetry sites. The lattice order is better preserved around these sites, so that coupling with lattice vibrons and phonons should be stronger. We found in the same manner that W(CO)\(_6\) vibration was more coupled with N\(_2\) librions in this kind of sites in the study of W(CO)\(_6\)/N\(_2\) samples.\(^9\) Assuming that T\(_1\)\(_{\text{short}}\) of few ps corresponds to this process, T\(_g\) cannot be much longer, justifying T\(_g\) = T\(_1\) for this family of sites. We found that the short decay in S(T) does not disappear completely below phase transition. Based
on these assumptions, it could come from a fraction of the high symmetry sites remaining in phase I, because of possible temperature shift of the phase transition around an impurity, as remarked in Sec. III A.

C. Vibrational coherence

In CD$_4$, $T_2$ is mainly limited by the population relaxation time $T_1$. The same conclusion is applied in the short-$T_1$ sites in phase I and we assume $T_2$(short) = $2 \times T_1$(short). Further decrease of $T_2$(short) would lead to broadening of the absorption bands which is not observed. A final adjustment of dephasing process is obtained by modelling $S(T)$ signals at various waiting times $T$. We have clearly observed that the decay of $S(T)$ is faster at $T = 0$ than at $T > 10$ ps (not shown): sites with short $T_1$ do not contribute to the signal at long $T$.

Consequently, we here discuss the longer dephasing times, referred to as $T_2^1$, coming mostly from the low symmetry sites in phase I. $T_2^1$ are preferably deduced from the simulations of $S(T)$ data recorded with $T > 30$ ps in order to minimize the influence of sites with fast population relaxation. In phase II, $T_2^1$ values still correspond to “average” values including high and low symmetry sites. In any case, clear temperature dependence is observed, in contrast with the case of the long $T_1$.

The temperature dependence of the related homogeneous bandwidth $\gamma_h (\Theta = 1/\tau_T)$ is reported in Figure 10 (red squares) showing a quasi-linear dependence with $\Theta$. The solid red line is a fit of the experimental points at $\Theta < 20$ K, i.e., in phase II, with the formula,

$$\gamma_h^1 (\Theta = 0) = A \times \Theta.$$  

(5)

$\gamma_h^1 (\Theta = 0)$ is governed by the population relaxation time and $T_1$ deduced from the fit is $190 \pm 30$ ps, in perfect agreement with the measurement of $T_1$(long). Figure 10 shows that, as mentioned previously, there is no sudden change in the $\gamma_h^1$ behavior at the phase transition. However, at $\Theta > 25$ K, the homogeneous broadening deviates from the linear behavior observed in phase II, revealing more efficient processes in phase I. The explored temperature range is not large enough in the present study to discuss more precisely the pure dephasing in phase I.

The linear dependence observed in CH$_4$ differs strongly from the temperature dependence measured in nitrogen matrices for vibrational relaxation of the same molecule. The measured homogeneous bandwidths of N$_2$ sites exhibiting temperature dependence are reported in Figure 10 for comparison (black open squares). In solid N$_2$, a dephasing process due to the coupling with a librational mode of nitrogen was suggested. In solid CH$_4$, the temperature dependence is much softer and a similar process is not at play. Such linear dependence was observed in the case of vibrational relaxation of RuTTPCOPy in glasses and was expected in the frame of the theories involving the frequency fluctuations due to the solvent such as the model of two-level systems (TLS) in amorphous solids. The static orientational disorder of methane around W(CO)$_6$ in sites with long $T_1$ could induce properties similar to those of an amorphous solid. On the other hand, linear temperature dependence can also result from coupling with local phonons in specific cases. In rare gas matrices, no important pure dephasing process was observed meaning that acoustic phonons are quite inefficient. A deeper insight is necessary to analyze the dephasing process in solid methane which differs definitely from the nitrogen solid and from the rare gas matrices.

V. CONCLUSIONS

Vibrational dynamics of W(CO)$_6$ trapped in solid methane highlights various effects. First, the $T_{1u}$ absorption band around 1800 cm$^{-1}$ shows structured features in CH$_4$ which are temperature dependent and correlated with the crystalline phase of CH$_4$ so the IR spectrum of W(CO)$_6$ can be used as a probe of the phase transition. The absorption structures are assigned to families of sites with different site symmetries and come partly from band splitting due to degeneracy removal in low symmetry sites. Nonlinear IR spectroscopy helps understand the vibrational behavior hidden behind such complex absorption spectra.

The coalescence of the absorption structures with increasing temperature corresponds to a motional narrowing effect from phase II to phase I. This is due to large rotational fluctuations of all methane molecules in phase I, leading to an orientational disorder, whereas three quarters of CH$_4$ have hindered rotation in phase II. Photon echoes point out that motional narrowing is expressed by two complementary behaviors: increased homogeneous broadening and decreased inhomogeneous contribution. The former corresponds to the increase of dephasing processes with temperature and can lead to predominant homogeneous widths. In the present case, the inhomogeneous part itself, responsible for the structures, shows temperature dependence with a clear change at phase transition.

The phase transition of methane is also clearly detected in the temperature evolution of the $S(T)$ population relaxation signal. It seems that the vibrational lifetime of a substantial fraction of W(CO)$_6$ trapped in CH$_4$ is suddenly reduced from phase II to phase I. It could come from a quasi-resonance between an intramolecular transition of the guest and a vibron of the lattice appearing only in phase I, considered as a plastic phase close to liquid, where vibrational transitions of CH$_4$ are very broad. In contrast, the vibrational lifetime of

FIG. 10. Temperature dependence of the homogeneous bandwidths in CH$_4$ sites with long $T_1$ (red full squares) and in N$_2$ sites of high symmetry (black open squares—data from Ref. 9). The solid red line corresponds to a linear fit of CH$_4$ data below 20 K.
the other trapped W(CO)$_6$ remains very long at all temperatures, in both phases. The involvement of a host vibrational transition in the shortening of $T_1$ is still to be proved, for example, with the study of other guest molecules. On the other hand, the consequences of vibrational resonance between guest and host vibrations can be clearly seen in the case of W(CO)$_6$ trapped in CD$_4$ by the broad absorption features and the fast decays in the time-resolved signals at all temperatures.

The absorption spectrum of the W(CO)$_6$ $T_{1u}$ mode in all the cryogenic matrices we have studied so far shows great similarities. Moreover, the comparison between nitrogen and methane reinforces the assignment to different families of sites, suggesting similar analysis in Ar and Kr. A clear effect of the host molecular motion on the dephasing process is observed when comparing the vibrational coherence in rare gas solids with nitrogen and methane. In Ar and Kr, vibrational dephasing is mainly due to population relaxation.$^7$ In nitrogen, $T_2$ is reduced in all trapping sites meaning that pure dephasing processes due to molecular motions occur. The homogeneous broadening in a part of the trapping sites has been explained by a coupling with a librational mode of nitrogen.$^8$ The homogeneous broadening cannot be directly detected in linear spectroscopy in the case of methane because the decrease of the inhomogeneous broadening is the major effect observed in absorption spectra. However, dephasing times are also shortened in all trapping sites in methane compared to rare gas matrices, either because of pure dephasing processes which are temperature dependent (low symmetry sites of solid CH$_4$) or because of fast population relaxation (solid CD$_4$ and high symmetry sites of solid CH$_4$). Note that a specific shortening of relaxation times is assigned to high symmetry sites in both molecular lattices (N$_2$ and CH$_4$). It suggests a stronger coupling with molecular lattice motion in these sites, affecting vibrational coherence in the case of N$_2$ and vibrational population relaxation in the case of CH$_4$.

Physical properties of methane solids are revealed for the first time by probing linear and nonlinear spectroscopic features of a guest molecule. The phase transition is clearly inferred through observation of the molecular properties of the guest. Questions are still to be solved, especially in terms of specific behaviors of families of sites. The photon echo experiment could be upgraded to 2D-IR spectroscopy and W(CO)$_6$/CH$_4$ could be an interesting system to probe for a direct observation of site effects on the dynamical properties of the guest, if a good spectral resolution can be achieved.

SUPPLEMENTARY MATERIAL

See supplementary material for additional information: The detailed calculation of the third order polarization is provided together with the assumptions used and a scheme of the Feynman diagrams. Three additional figures are presented. Fig. S1: effect of the W(CO)$_6$ impurity on the temperature of the phase transition in CH$_4$; Fig. S2: absorption spectra of W(CO)$_6$/CD$_4$ in the three phases of solid CD$_4$; Fig. S3: effect of the W(CO)$_6$ impurity on the temperature of the phase transitions in CD$_4$.

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