W(CO)$_6$ in cryogenic solids: A comparative study of vibrational properties

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A comparative study of the vibrational properties of W(CO)$_6$ has been performed in different solids at cryogenic temperatures focusing on the IR absorption and the vibrational dynamics of the CO stretching mode of the organometallic compound. Guest-host interactions are investigated in doped solids through the linear IR spectroscopy and four-wave mixing techniques at different temperatures. We show how the host nature, the trapping site, the crystallographic ordering affect the properties of the guest molecule and in particular its vibrational dynamics.

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1. Introduction

The advent of picosecond (ps) and femtosecond (fs) laser sources in the IR domain has enabled the study of the vibrational dynamics of a wide variety of systems spanning from biological molecules [1–5] to material sciences [6–8] through nonlinear four-wave mixing techniques such as IR photon echo [9] or two-dimensional IR spectroscopy [10]. Thanks to the very large transition dipole moment (μ=1D) of the asymmetric CO stretch vibrational mode (T$_{1u}$ mode near 2000 cm$^{-1}$) W(CO)$_6$ organometallic complex is highly interesting since it yields a large nonlinear response. In this sense W(CO)$_6$ has been widely studied by means of nonlinear processes in various condensed media [11–14]. In particular W(CO)$_6$ represents a very sensitive probe to characterize guest-host interactions and allows a very detailed insight into environment effects induced by the nature of the host on the molecular dynamics of W(CO)$_6$. We have investigated the environment effects on the vibrational properties of W(CO)$_6$ in the condensed phase in different cryogenic lattices such as rare gas crystals (argon [13], krypton [15]) and molecular hosts (nitrogen [15], methane [16]).

The vibrational properties of W(CO)$_6$ have been measured by linear and non-linear (pump-probe and photon echo techniques) IR spectroscopy at different temperatures. We thus have access to $T_1$ population relaxation time and $T_2$ dephasing time. $T_2$ is related to the homogeneous broadening $\gamma_{\text{homo}}$ through the relation:

\[
\frac{1}{\gamma_{\text{homo}}} = \frac{1}{2\pi T_1} + \frac{1}{\pi T_2} 
\]

where $T_2$, called pure dephasing time, is especially sensitive to the environment. In order to get an overview of the vibrational behavior of W(CO)$_6$ in cryogenic lattices, we performed additional experiments in neon (for probing a third rare gas host), in para-hydrogen (a specific host with quantum properties) and in carbon tetrafluoride (following the series of methane solids CH$_4$ and CD$_4$). This paper is thus dedicated to the comparison of these various results allowing for conclusive remarks on the host dependence of W(CO)$_6$ vibrational properties. After a description of the experimental procedures, the results in the different hosts are summarized. They are discussed in the last part before the conclusions in terms of host effects on the absorption features, vibrational population relaxation and dephasing processes. We show how the host nature, the trapping site, the crystallographic ordering affect the properties of the guest molecule and in particular its vibrational dynamics. The conclusions highlight the main tendencies obtained from the comparison of all the results.

2. Experimental procedure and methods

The detailed experimental set-ups have been extensively described in our previous papers [15–17] and only the main descriptions related to new results are presented.

In the case of CF$_4$, as for the experiments described in Refs. [15,16] the matrix samples have been obtained by continuous deposition of a gaseous mixture onto a cold CaF$_2$ window of the cryostat. Gaseous samples are prepared at room temperature by
mixing W(CO)$_6$ (Sigma Aldrich) with the carrier gas with W(CO)$_6$/[Host] ratio varying from $10^{-5}$ to $10^{-3}$. Matrix thickness is kept below 100 μm. Concentration and deposition times are adapted to keep an optical density of the T$_{1u}$ mode of W(CO)$_6$ of ≈ 1. Deposition temperatures can vary between 15 and 30 K depending on the host (30 K for CF$_4$).

Nonlinear measurements are obtained using an IR OPA source for fs pulses (see ref.[15] for details). The fs IR OPA is combined to a 3-pulse photon echo set-up. It is pumped by a 800 nm Ti:Sa laser/amplifier system and delivers an IR pulse centered at 1980 cm$^{-1}$, bandwidth 150 cm$^{-1}$, duration 145 fs, output ≈ 3μJ. Resulting IR beam is then split into three beams ($k_1$, $k_2$, and $k_3$ wave vectors) of equivalent intensities using two coated ZnSe beamsplitters. The echo signal is emitted in a well-defined direction given by phase-matching such as $k_s$ = $k_3$ + $k_2$ - $k_1$. The signal beam is focused on an MCT (mercury cadmium telluride) detector. There are two independent delay stages giving access to two delay times $\tau$ and $T$, called coherence time and waiting time and corresponding to the delay between the first two pulses and the last two pulses, respectively. The detected signal (quadratic detection) is:

$$S(\tau, T) = \int_0^\infty dt |P^{(3)}(\tau, T, t)|^2$$

$P^{(3)}(\tau, T, t)$ is the third order polarization created in the sample with the wave vector $k_s$. In a rough way, the $S(T)$ signal at fixed $\tau$ gives access to T$_1$ population lifetime and $S(\tau)$ signal at fixed $T$ to dephasing processes through the measure of T$_2$ dephasing time.

Absorption spectra have been recorded using an FTIR Mattson spectrometer at 0.25 cm$^{-1}$ spectral resolution to check the quality of the sample and its evolution with temperature and time. 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 have been measured using the nitrogen-cooled MCT detector.

Additional experiments in neon and parahydrogen (pH$_2$) have been performed with another set-up dedicated to pH$_2$ experiments. Hydrogen is converted to parahydrogen in a first cryostat kept at 17 K and parahydrogen vapor is directly condensed onto a cold diamond window of a second cryostat (IceOxford) at the lowest temperature of 3 K. W(CO)$_6$/pH$_2$ samples are obtained by flowing pH$_2$ over a tube containing W(CO)$_6$ and carrying its vapor before the deposition. The experimental procedure to produce doped pH$_2$ samples is the same as that described in ref. [17]. W(CO)$_6$/Ne samples are obtained in the same manner, replacing hydrogen by neon and keeping the first cryostat at 40 K to avoid any neon condensation. In this case, the first cryostat is used to trap all residual impurities. IR spectra of the samples are recorded by means of a Nicolet FTIR spectrometer at 0.125 cm$^{-1}$ spectral resolution. No time-resolved measurements have been conducted with this cryogenic set-up.

3. Results

3.1. Rare gas matrices: Ar, Kr, Ne

W(CO)$_6$ has been isolated in Ar, Kr and Ne solids. The IR spectra have been recorded in the three hosts and photon echo experiments have been performed in Ar and Kr. The IR spectrum in Kr, Ar and Ne in the region of the asymmetric $\nu_{CO}$ stretch of W(CO)$_6$ is displayed in Fig. 1. Spectra reveal a complex absorption spreading over 10 cm$^{-1}$ in contrast to the gas phase where there is only one line at 1998 cm$^{-1}$ [18]. The complex structure reflects the complexity of the trapping sites. With a diameter around 0.78 nm, W(CO)$_6$ is a huge impurity to trap in these crystallographic lattices. Rare gas solids have an fcc structure with a nearest neighbors distance $d$ of 0.40, 0.38 and 0.32 nm for Kr, Ar and Ne respectively, i.e. much smaller than the size of W(CO)$_6$. Consequently, the guest molecule is trapped in multi-vacancy sites. The structure of the absorption spectra can result from two effects: the presence of
many different trapping sites (differing for example by the number of hosts removed), and the possible degeneracy removal of the T1u mode (triplly degenerated in the isolated molecule) in trapping sites of lower degree of symmetry than O8 group (the group of symmetry of the isolated molecule).

Because Kr, Ar and Ne have different lattice parameters, trapping sites should be different in the three hosts. Nevertheless spectra in the three rare gas solids, depicted in Fig. 1, show a major structure in the red side and a minor one in the blue side. The energy gap between these two bands is roughly 4 ± 1 cm⁻¹ with no obvious correlation with the lattice parameter. In Ne, the absorption spectrum spreads only over 8 cm⁻¹ and this gap is reduced below 3 cm⁻¹ (Fig. 1). The frequency shift between matrix and gas phase (1998 cm⁻¹) is also the smallest. This is a well-known consequence of the lowest polarizability of Ne which induces the smallest matrix effect on the transition frequencies of guest molecules.

No significant change is observed when varying the temperature in Ar [13], Kr [15] and Ne in terms of band position or line-width. A small change in the relative intensities of the bands has been observed in Kr after annealing at 60 K, due to a slight re-organization of the trapping sites. We have also observed slight differences in W(CO)6/Ar spectra when varying the experimental deposition conditions; however the relative intensities of the two main features remain constant.

Despite complex band structures, the vibrational dynamics in Kr and Ar occur to be rather simple. Table 1 reports the main characteristic times of these dynamics, together with spectroscopic data. Time-resolved signals measuring T1 and T2 always exhibit long decay times in the hundreds of ps. Of course, since the IR laser pulses are spectrally broad, the time-resolved signals correspond to the nonlinear response of the entire absorption spectrum. In Kr, there is no variation in the population decays when changing the temperature. The decay is not in fact mono-exponential and the S(T) signals are better fitted with two exponential contributions that take into account two different dynamics linked to the population relaxation from ν = 1 excited state (T1) and recovery to the ground state (T8), suggesting a long-lived intermediate level in the vibrational relaxation [15] (Table 1).

In Ar, a single exponential is found but the signal has not been recorded until the end of the relaxation, suggesting that the long T8 time has not been actually measured. It gives a T9 population relaxation time which slightly shortens when temperature increases [13] (Table 1).

Similarly to S(T), the S(r) signals in Kr show no temperature effects between 25 and 50 K. The decay of the signal yields 100 ± 20 ps, equivalent to a γhomogeneous broadening (0.106 cm⁻¹) smaller than the width of the narrowest lines of the absorption spectrum (FWHM ≈ 0.5 cm⁻¹). It means that the absorption structure is not composed of homogeneous substructures. In Ar, T8 values are slightly longer than in Kr, they are not constant with temperature but they remain in the same order of magnitude (see Table 1). Corresponding γhomogeneous are much less than the line-widths of the absorption structures (≈2.3 cm⁻¹). In both rare gas solids we find T2 comparable to twice T1, meaning that dephasing processes are essentially governed by population relaxation.

Table 1
Summary of the results on the vibrational properties for the main features of W(CO)6 in different environments.

<table>
<thead>
<tr>
<th>Host</th>
<th>Characteristic times [ps]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr</td>
<td>5–50 1982</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>7–20 1986</td>
<td></td>
</tr>
<tr>
<td>Ne</td>
<td>3–8 1995.5</td>
<td></td>
</tr>
<tr>
<td>N2</td>
<td>6–22 1984</td>
<td></td>
</tr>
<tr>
<td>CH4</td>
<td>8 1980.5 1987.5</td>
<td></td>
</tr>
<tr>
<td>CD4</td>
<td>10–30 1980 1987</td>
<td></td>
</tr>
<tr>
<td>CF4</td>
<td>8 1989 1987.5</td>
<td></td>
</tr>
<tr>
<td>rh3</td>
<td>3 1992.2 1992.8</td>
<td></td>
</tr>
<tr>
<td>CCl4</td>
<td>300 1980</td>
<td></td>
</tr>
<tr>
<td>dibutyl -phthalate</td>
<td>80 1976 1975</td>
<td></td>
</tr>
<tr>
<td>xerogel MTEOS</td>
<td>5–300 1982</td>
<td></td>
</tr>
</tbody>
</table>

3.2. Molecular matrices

3.2.1. Nitrogen and methane

We have studied nitrogen and methane solids because the crystals also adopt an fcc structure similar to rare gas solids. Moreover, nearest neighbors distances d are of the same order of magnitude, and in particular close to that of Kr lattice: d = 0.401 nm and 0.417 nm in N2 and CH4 respectively. It is thus expected that the geometry of the trapping sites are similar between these molecular solids and Kr solids. In the case of CH4, our experimental conditions allow the exploration of different phases. CH4 solid presents two crystalline phases (both of fcc structure) with a temperature of phase transition at 20.4 K at zero pressure. From 20.4 K to 90.7 K phase I is orientationally disordered and molecules occupy O8 symmetry sites. Below 20.4 K in phase II, there is partial ordering of CH4 molecules due to octupole-octupole interactions with 3/4 of molecules undergoing hindered rotation in D2d symmetry and 1/4 free rotation in O8 symmetry [21].

The IR absorption of W(CO)6 in N2 and CH4 is quite complex.
and displays structured bands as in the case of Ne, Ar and Kr. As previously, spectra show two main features exhibiting a frequency gap $E_{5c,m}-1$, as in Kr (see Table 1). Main differences from rare gas matrices stem from the strong temperature dependence of the IR spectra (Fig. 2). Temperature effects have been of great help to assign the different substructures. In both molecular solids, four bands or substructures can be distinguished (numbered 1 to 4 in Fig. 2). In N$_2$ only band 2 exhibits a strong and reversible temperature effect while intensities of the three other bands remain almost constant. These characteristics suggest that bands 1, 3 and 4 correspond to sites of low symmetry. Band 2 would then correspond to sites of high symmetry where the molecule keeps its Oh symmetry [15].

In spite of a more complex absorption structure in CH$_4$, the comparison with N$_2$ also leads to assign bands 1, 3 and 4 to low symmetry sites and band 2 to high symmetry sites [16]. Populations of high and low-symmetry sites are comparable in N$_2$ and CH$_4$ with a ratio of 40:60 and 45:55 respectively. The temperature broadening of band 2 in N$_2$ could be due to an expected homogeneous broadening and time-resolved measurements confirm this assumption (see below). Very surprisingly, the temperature behavior seems reversed in CH$_4$ as highlighted in Fig. 2. In fact, bands 1, 2 and 3 are found to coalesce from phase II to phase I, leading to a global narrowing when temperature increases [16]. This effect is assigned to a motional narrowing due to the complete rotational disorder and the large motional fluctuations of CH$_4$ hosts in phase I, which for this reason is also named plastic phase [22].

There is no obvious temperature effect on the vibrational population relaxation of W(CO)$_6$ in N$_2$ and the decay times are in the hundreds of ps, similarly to the case of Kr (Fig. 3a). As in Kr two times in the population decay can also be considered, a $T_1$ time around 180 ps and a very long recovery time $T_g$ ($>1\text{ ns}$) [15]. They represent averaged population decay times for all the sites as in Kr and Ar. On the contrary, a strong temperature effect is observed in CH$_4$ in the $S(T)$ signals corresponding to distinct dynamical behaviors above and below phase transition of CH$_4$ (Fig. 3b); there is one long component at all temperatures (same order of magnitude as $T_1$ in N$_2$) but there is an additional shorter decay of 10 ps in phase I (red trace in Fig. 3b). The weight of the short component corresponds to the weight of high symmetry sites obtained in the analysis of the absorption spectra suggesting that the short 10 ps component reflects $T_1$ time of W(CO)$_6$ molecules in these high symmetry sites [16]. In these sites, W(CO)$_6$ does not significantly perturb the CH$_4$ lattice and fast relaxation involving a methane vibron can occur in phase I because of the strong broadening of methane modes in this crystallographic phase. Note that, whatever the temperature no very long ( $>400\text{ ps}$) decay has been measured in CH$_4$ precluding the existence of a very long $T_g$ time.

Photon echo measurements in N$_2$ and CH$_4$ both exhibit temperature effects. Fig. 4 shows signals recorded at two temperatures in N$_2$ and in CH$_4$. Experimental curves in N$_2$ are correctly modelled when considering $T_2$ times that depend on the family of sites. Only $T_2$ times of high symmetry sites are strongly temperature dependent, as reported in Table 1. It is in perfect agreement with the temperature broadening of band 2 in the absorption, leading to a significant homogeneous contribution at 20 K. In low symmetry...
sites, $T_2$ is almost constant, around 50 ps, i.e. shorter than in rare gas matrices. The temperature dependence in high symmetry sites can be described as an enhancement of the homogeneous width by coupling with a libration mode of the nitrogen lattice [15].

In CH$_4$, beside the large shortening of the population relaxation time in phase I assigned to high symmetry sites, $T_2$ is found to decrease with temperature increase in all sites. It is well depicted in Fig. 4b where $S(\tau)$ signals have been measured with long waiting times ($T > 30$ ps) to get rid of this short 10 ps component in $T_1$ in phase I. $T_2$ times are found to decrease smoothly from 120–140 ps at 6 K to 25–30 ps at 30 K. The latter value is very close to twice $T_1$ of high symmetry sites, where dephasing is governed by the loss of population in phase I. The corresponding homogeneous width of $E_0 = 0.4$ cm$^{-1}$ at 30 K for all sites is consistent with a predominant homogeneous broadening with a bandwidth of 0.5 cm$^{-1}$ measured on the main component of the absorption spectrum at 30 K. In both N$_2$ and CH$_4$ solids, the $S(\tau)$ signal becomes more symmetric with respect to $\tau$ (Fig. 4) reflecting the increase of the homogeneous contribution to broadening but one can notice that, whereas the rise of the signal (at $\tau < 0$) does not depend on temperature in N$_2$, it is longer at high temperature in CH$_4$ indicating that the inhomogeneous contribution is simultaneously reduced, which is a signature of the motional narrowing [16].

Experiments have also been conducted in heavy methane (CD$_4$) for which two phase transitions can be explored. In fact, the $T_{1u}$ mode of W(CO)$_6$ is found in resonance with the $2v_4$ overtone mode of CD$_4$ [16]. The consequence is a very fast population relaxation at all temperatures ($\approx 10$ ps) which prevents any analysis of environment effects on pure dephasing processes in this solid. The absorption spectrum shows the same global structure as in CH$_4$ with broad features in all the phases, suggesting a similar analysis based on low and high symmetry sites with a high/low ratio in CD$_4$ of 55:45.

### 3.2.2. Carbon tetrafluoride CF$_4$

In order to probe another crystallographic environment with molecular “spherical” hosts, we have studied CF$_4$ solid after CH$_4$ and CD$_4$. CF$_4$ carbon tetrafluoride presents a phase transition at 76.2 K (at zero pressure) [24], the high- and low-temperature phases are respectively designated by I and II. Phase I (or $\beta$) is also named “plastic” phase due to orientational disorder of CF$_4$ molecules [25], similarly to CH$_4$. It corresponds to a rhomboedric structure. Phase II (or $\alpha$) is a well-ordered crystal and the lattice structure changes to monoclinic [26]. It is therefore an interesting medium for trapping W(CO)$_6$ in terms of lattice structure and orientation of molecules.

In fact, only phase II has been explored in our experiments. Attempts to measure spectra above 50 K failed due to low optical density of the sample because of evaporation of the CF$_4$ matrix at 55 K despite a melting point at 89.5 K. This can be due to local heating of the matrix by the light sources. The IR spectrum is temperature dependent, as shown in Fig. 5. At low temperature (8 K) it exhibits two main bands centered at 1987.5 and 1989 cm$^{-1}$ (bands 1 and 2 respectively). The temperature dependence of the two main bands is especially pronounced. Band 1 broadens and shows a more and more obvious structure from 8 to 20 K. It seems to contain a substructure that shifts to the blue, reaching the middle of the two bands around 22 K and joining band 2 at higher temperatures. The consequence is a red shift and an increase of band 2 with temperature. At 35 K, there is only one main band at 1988.7 cm$^{-1}$. It is found to narrow slightly from 8 to 20 K and to broaden because of the previous effect. Spectral changes observed when varying the temperature are reversible. CF$_4$ forms a larger “sphere” (0.43 nm diameter) than methane but as in the other solids studied, W(CO)$_6$ (0.78 nm diameter) replaces more than one host in the lattice. Because of the monoclinic structure in phase II, the $C_3$ symmetry of W(CO)$_6$ cannot be preserved and band splitting due to degeneracy
removal is expected. It is thus not surprising that the spectral behavior is different in CF$_4$. Anyway, the comparison with the observations in N$_2$ and CH$_4$ suggests that the most intense band 2 at 1989 cm$^{-1}$ contains the main components of highest symmetry sites. The frequency shift of some components in the absorption spectrum toward the main one when temperature increases looks like the band coalescence observed in CH$_4$ from phase II to phase I [16], although 35 K is rather far from the temperature of phase transition in CH$_4$. One must remind that a lowering of this temperature was observed in methane when the solid was doped with W(CO)$_6$ [16] and such effect can also occur in CF$_4$.

Unfortunately, time-resolved measurements have been very difficult to obtain due to high scattering of the samples. The best signals have been recorded in a short temperature range only (30–45 K) corresponding to the best quality samples so only global behaviors can be extracted from the signals. Nevertheless a clear shortening of $T_2$ upon temperature increase is observed. $T_2$ of 50 ± 10 ps is obtained between 10 and 20 K, and this value continuously decreases to ≈ 20 ps at 50 K. The $S(T)$ signal at 30 K is shown in Fig. 6a. The asymmetric profile indicates a predominant inhomogeneous contribution to broadening. The deduced value of $T_2$=38 ps is an average for all bands. It corresponds to a homogeneous broadening of 0.27 cm$^{-1}$, which is lower than the linewidth of the substructures (0.5–1 cm$^{-1}$) measured in the absorption spectra. The $S(T)$ profile seems obviously more symmetric at 50 K (not shown), corresponding to the IR spectrum involving only one main band. $T_1$ is measured in the hundreds of ps in the explored temperature range, without any clear temperature effect. An example is given in Fig. 6b at 35 K, yielding $T_1=240 ± 30$ ps. No obvious long component can be extracted from the $S(T)$ curves, suggesting that there is no long $T_6$ recovery time as in CH$_4$.

Similarly to the case of N$_2$, no population relaxation enhancement takes place in CF$_4$ while a pure dephasing time $T_2$ in the tens of ps as given by Eq. (1) is present, that is temperature dependent. The molecular nature of the host could be at play in pure dephasing process, as in N$_2$ and CH$_4$ but data are too scattered for a more precise conclusion.

3.3. Quantum matrix: parahydrogen pH$_2$

Only IR measurements are available in solid parahydrogen (pH$_2$). Parahydrogen is a very attractive environment as it possesses unique properties. It is a quantum crystal thanks to its light pH$_2$ mass and to the significant translational zero-point motion of the pH$_2$ molecules about their equilibrium positions within the solid. The weak pH$_2$–pH$_2$ intermolecular forces, the $J=0$ rotational state at cryogenic temperatures for all molecules, the spherical symmetry of the ground state, the minimal cage effect contribute to the “softness” of the matrix and result in weak perturbations on the guest molecules [27]. By trapping W(CO)$_6$ molecules in pH$_2$, we thus expect that its spectroscopy and dynamics will qualitatively differ from the other solids studied so far. Solid pH$_2$ adopts a hcp lattice structure with nearest neighbors distance $d=0.379$ nm, i.e. a value very close to that of solid Ar. W(CO)$_6$ should thus replace a similar number of pH$_2$ hosts as Ar atoms in the respective lattices. Because of its softness, site effects are usually strongly reduced in this quantum solid and absorption bands are expected to be homogeneously broadened [28–30].

The IR spectrum of W(CO)$_6$ isolated in pH$_2$ at 3 K is displayed in Fig. 1d, allowing a direct comparison with spectra in rare gas solids. It is simpler than in the other solids and the global feature is much narrower than in other hosts. However, it does not show a unique band, as in the isolated molecule but two doublets. The most intense doublet absorbs at 1992.2 and 1992.5 cm$^{-1}$ and the weakest one is located at 1992.8 and 1993.3 cm$^{-1}$. The absorption spectrum exhibits a very slow time evolution, with a decrease of the bands at 1993.3 and 1992.5 cm$^{-1}$ meaning that they correspond to metastable sites. The two weaker bands have half intensities of the two stronger ones. We conclude that the two doublets correspond to two sites where the triply degenerated $T_{1u}$ mode gives rise to two components, one being doubly degenerated (the strongest one). Such degeneracy removal is consistent with the hcp structure. Bands are very narrow and their actual linewidth cannot be reached with our FTIR resolution (FWHM < 0.125 cm$^{-1}$). It gives a 0.1 cm$^{-1}$ limit to the value of $\gamma_{\text{hom}}$. The corresponding $T_2$ dephasing time is thus longer than 100 ps. Time-resolved experiments are necessary to obtain more accurate values.

4. Discussion

4.1. Spectroscopy

The complex structures in the absorption spectra in the crystalline cryogenic solids mainly reflect site effects. In amorphous solids, like xerogels or glasses, only a non structured and broad absorption band has been observed [14,31,32]. Since this band is inhomogeneously broadened, it corresponds to a continuum of different sites. Results in different environments are summarized in Table 1. The analysis of the structures in N$_2$ and CH$_4$ suggests the existence of high symmetry sites where the O$_6$ symmetry of W(CO)$_6$ is preserved [15,16]. In fcc lattices, with nearest neighbors distances around 0.4 nm, O$_6$ (or T$_{1u}$) trapping sites large enough to contain the guest molecule are obtained when removing 13 hosts (one and its 12 nearest neighbors). The size of this big hole has a diameter of around 0.77 nm, which is well adapted to W(CO)$_6$. Therefore, these O$_6$ trapping sites should also exist in Ar and Kr.
matrices and possibly in Ne. Similarly to the case of N2 and CH4, we can also conclude that in all these fcc solids the weaker feature in the blue part of the spectra is assigned to a non degenerated component of the T1u mode of W(CO)6 in low symmetry sites. A rough estimation of the integrated absorption of the weak and the strong bands (separated by few wavenumbers) can give an idea of the ratio of high/low symmetry sites. We find 40:60, 45:55, 45:55 in Kr, Ar and Ne respectively, it is as expected very similar to the 40:60 and 45:55 ratios obtained in the spectral analysis in N2 and CH4 respectively. The hcp structure of pH2 is very close to the previously described fcc structure and with a nearest neighbors distance d of 0.379 nm, a hole of 13 pH2 could also fit for the trapping of W(CO)6. The symmetry of such trapping site is D3h in the hcp structure, explaining the splitting of the T1u mode in two components. The results in pH2 in that sense confirm the previous assignment.

Fig. 7a shows the IR spectra of W(CO)6 recorded in the region of T1u mode in, from top to bottom, CH4, Kr, N2, Ar, CF4, pH2 and Ne. The gas phase is 20 K for all solids except in pH2, and Ne where it is 3 K. The gas phase frequency (1998 cm−1) is marked with a dotted line. (b) α a wavenumber (in cm−1) of the T1u mode of W(CO)6 in the gas phase, Ne, pH2, Ar, Kr, N2, CH4 and CF4 plotted as a function of the polarizability α of the host (Å3).

Fig. 7. (a) IR spectra of W(CO)6 recorded in the region of T1u mode in, from top to bottom, CH4, Kr, N2, Ar, CF4, pH2 and Ne. Temperature is 20 K for all solids except in pH2 and Ne where it is 3 K. The gas phase frequency (1998 cm−1) is marked with a dotted line. (b) α a wavenumber (in cm−1) of the T1u mode of W(CO)6 in the gas phase, Ne, pH2, Ar, Kr, N2, CH4 and CF4 plotted as a function of the polarizability α of the host (Å3).

4.2. Population relaxation

Vibrational relaxation of W(CO)6 in liquids was found to be strongly solvent dependent [20] because the vibrational pattern of the solvent can give intermediate levels in the vibrational relaxation depending on the vibrational energies of its modes compared to the probed T1u mode of W(CO)6. The same is observed in cryogenic solids. In CD4 a vibrational mode of the host is in quasi-resonance with the T1u mode yielding a reduced T1 value of 10 ps. We also suggest that the vibron of CH4 at 1538 cm−1 can be efficiently involved in the population relaxation of W(CO)6 in high symmetry sites because this energy corresponds to the energy gap between the probed T1u mode and low energy modes of W(CO)6 around 400 cm−1, leading also to a strongly reduced T1 time [16]. In all the other cases studied, T1 of 100–200 ps has been measured. In particular, T1 is not shortened in phase II of CH4 nor in low symmetry sites despite a rich vibrational pattern below 1900 cm−1. At low temperature, the population relaxation pathway needs to include vibrational levels of the host of rather precise energies to be efficient. The same remark is verified in the case of CF4. The solid possesses indeed only vibrational fundamental modes of low energies (≤1320 cm−1) [25] which cannot fill the gap between the T1u mode and low energy modes of W(CO)6 [33].

The temperature dependence of the long T1 (100–200 ps) has been difficult to measure, with very weak changes in the short temperature range accessible in the experiments. Because of the experimental difficulties to obtain precise measurements (low laser and sample stabilities in long acquisitions of hundreds of ps), signal changes are usually in the measurement errors. A slight effect has been measured in Ar without the possibility to extract a temperature law. It means that lattice phonons are rather inefficient in the relaxation pathway, which is expected since the order of magnitude of their energy is once or twice lower than the probed vibration.

On the other hand, 100–200 ps values are short compared with T1 = 700 ps obtained in CCl4 at room temperature [19]. There is no obvious reason for T1 times to be shorter in matrices at temperatures below 20 K, especially in rare gas solids or N2 with no vibrational levels below 1900 cm−1. In these solids, a longer time (>1 ns) has been measured and assigned to T2 recovery time. This value compares well with the long T1 recorded in CCl4. Assuming that this T2 time would correspond to the lifetime of ν = 1 in these cryogenic solids, the shorter T1 would then be assigned to the population relaxation time of the component of the T1u mode probed in the four wave mixing experiment, i.e. the time to leave the level probed by the first pulse and probably to reach another component of the T1u mode (through intra molecular energy transfer). There are in fact two other CO stretching modes close to T1u, but at higher energies: modes Eg and A1g. As noted in ref. [13], population of these states by phonon induced excitation from T1u is not efficient at the cryogenic temperatures and these states should not be at play in our experiments, contrary to the case of experiments in the liquid phase at room temperature [34,35]. On
the other hand, in cryogenic matrices, components of the $T_{1u}$ mode differ by less than few wavenumbers, which is lower than energies of phonons. It explains that vibrational energy transfer between these components is itself inefficient. Considering that $T_1$ times are $T_{1u}$ lifetimes in rare gas and $N_2$ solids, our experiments therefore show that the lifetime in $CH_4$ and in $CF_4$ is reduced (no long $T_1$ has been detected) as expected because of the existence of vibrational mode of medium energies. The $T_1$ value ($<100$ ps) found in xerogels at low temperature is consistent with this latter assumption [14].

4.3. Dephasing processes

Photon echo experiments give a direct access to the vibrational dephasing times. Thanks to the measurements of the population relaxation times, pure dephasing times are extracted by means of Eq. (1). From the results reported in cryogenic solids, there are two kinds of environments where dephasing processes are governed by population relaxation. The first one is rare gas solids (Ar and Kr). Both $T_1$ and $T_2$ times are in the hundreds of ps in the explored temperature range. Because of quite large measurement errors, it is not possible to extract valuable values of $T_1^v$ times, but in any case, at any temperature, we can conclude that $T_2^v$ is longer than twice $T_1$. Population relaxation is fast in the second kind of environment as in $CD_4$, where $T_1 \leq 10$ ps and $T_2 \approx 10$ ps, giving $T_2^v$ longer than 20 ps, i.e. longer than twice $T_1$. In the high symmetry sites of $CH_4$ in phase I, $T_2$ cannot be measured separately from the response of low symmetry sites but our signals are in full agreement with estimations of $T_2$ and $T_2^v$ equal to the above values in $CD_4$. Otherwise, $T_2$ and $T_2^v$ in $CH_4$ out of these specific environments are always longer than 20 ps. In the other cryogenic environments, $T_2$ is found shorter than $T_1$ and efficient pure dephasing processes occur ($T_2^v < T_1$) due to the environment. The first important remark is that it happens only with molecular hosts.

The temperature dependence of $T_2$ and $T_2^v$ documents the processes at play in the vibrational dephasing. This temperature dependence is clearly observed in $N_2$ and $CH_4$. In $N_2$, it concerns the temperature evolution of dephasing time in high symmetry sites. It has not been possible to extract a clear temperature dependence of $T_2$ or $T_2^v$ in the other sites whereas $T_1$ and $T_2$ values clearly indicate that pure dephasing processes occur also in these sites. In contrast in $CH_4$, the temperature behavior can be followed in low symmetry sites because fast population relaxation at high temperatures in high symmetry sites hides pure dephasing processes. As in $N_2$ and $CH_4$, pure dephasing processes are also at play in $CF_4$ solid. Fig. 8 displays the evolution of $\gamma_{homo}$ linked to $T_2$, against temperature in high symmetry sites of $N_2$ and low symmetry sites of $CH_4$ compared with $CF_4$ and Kr. In the latter increase of $\gamma_{homo}$ with temperature is very weak, being more or less included in the error bars (not shown). It means that phonons related to the hosts translational motion are hardly coupled with the vibrational motion of the guest. In contrast, the strong temperature dependence in high symmetry sites of $N_2$ where the dephasing processes at play are due to coupling with a librational mode of the solid. The behavior observed in $CH_4$ and $CF_4$ lies between the two cases, showing the clear influence of the molecular motions in the dephasing processes.

5. Conclusions

By probing the vibrational properties of a guest molecule (W(CO)$_6$) in diverse cryogenic lattices, we have obtained several results highlighting the specificities of the different environments explored. The IR absorption of W(CO)$_6$ always exhibits a structured feature. It is a signature of the limited number of families of trapping sites due to the crystalline environment. The simplest case is observed in solid pH$_2$, a solid with specific properties minimizing site effects. Band broadening of each structure in pH$_2$ is expected to be homogeneous but no time-resolved experiment has yet been performed to confirm this assumption. In other cryogenic matrices, some substructures possess narrow linewidths (\(\approx 0.5 \text{ cm}^{-1}\)) but time-resolved experiments always show a significant inhomogeneous contribution to broadening. However, strong homogeneous broadening is clearly observed in the absorption when temperature increases in a fraction of $N_2$ trapping sites.

Relaxation processes are found to be host-dependent and they are moreover site dependent as proved in $N_2$ or $CH_4$. Except in the case of resonances between the probed vibration and the energy levels in the host + guest system, $T_1$ population relaxation times are long. In fact, values of 100–200 ps may reflect vibrational energy transfers between components of the $T_{1u}$ mode of W(CO)$_6$ when a very long time in the ns range is detected, that would correspond to the $v=1$ lifetime (as observed in rare gas and $N_2$ solids). Dephasing is enhanced in molecular hosts probably because of coupling between molecular motions. Acoustic phonons turn out to be very inefficient in the dephasing process, in contrast with phonons coming from rotational or vibrational motions of the molecular hosts. Librons and vibrons affect the vibrational dynamics and their effect appears to be strong in sites where the lattice is weakly perturbed, i.e. high symmetry sites.

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