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Isolation of CH_3• rotor in thermally stable inert matrix: first characterization of the gradual transition from classical to quantum behaviour at low temperatures

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Matrix isolation is a method which plays a key role in isolating and characterizing highly reactive molecular radicals. However, the isolation matrixes, usually composed by noble gases or small diamagnetic molecules, are stable only at very low temperatures, as they begin to desegregate already above few tens of Kelvin. Here we report on a successful isolation of CH_3• radicals into the cages of a nearly inert clathrate-SiO_2 matrix. This host is found to exhibit a comparable inertness with respect to that of most conventional noble gas matrixes but it is characterized by a peculiar thermal stability. This latter property is related to the covalent nature of the host material and gives the opportunity to study the confined radical from few degrees Kelvin up to at least room temperature. Thanks to this advantage we were able for the first time to explore with continuity the CH_3• rotor properties by electron paramagnetic resonance spectroscopy, starting from the quantum rotations which are observable only at the lowest temperatures ($T \approx 4$ K), going through the gradual transition to the classical motion (4 K $< T < 30$ K), and ending with the properties of the fully classical rotor ($T > 30$ K). The method of isolation presented here is found to be very effective and promising, as it is expected to be applicable to a large variety of different molecular radicals.

Introduction

Many fundamental chemical processes take place through the formation of highly reactive transient radicals.[1, 2] Due to the high reactivity of these radicals, their characterization is typically a major problem and deserves special techniques to be accomplished. To overcome this difficulty, the freshly produced radicals are typically studied very rapidly before reaction (flash photolysis (FP))[3, 4] or by isolating them into an inert environment (matrix isolation) to prevent any reaction.[5] The main drawback of the first technique is that, since the measurements have to be completed in a very short time interval, it requires very sensitive properly designed equipments.[3,4] On the other hand, the matrix isolation technique, which usually makes use of noble gas matrixes to achieve nearly inert confinement of the radicals, is typically applicable solely at very low temperature ($T<20$ K).[5,6] In fact, already at temperatures of about few tens of Kelvin, many undesirable processes take place, as the diffusion of the radicals between adjacent vacancies and their consequent reaction, the rotation and the diffusion of the inert gas atoms (which influence the properties of the radical), the desegregation of the matrix and so on. [5,6]

In particular, many efforts have been devoted up to now to fully characterize the $CH_3^{\bullet}$ radicals, which represent one of the most relevant and studied organic radicals involved in many fundamental photochemical reactions.[1] Its optical absorption has been characterized in gas phase (by FP)[7] and in less inert water (by pulse radiolysis),[8] whereas its vibrational properties have been investigated in gas phase (by FP)[9,10] and in noble gas matrixes.[11] The properties of the electron paramagnetic resonance (EPR) spectrum of the radical have been extensively investigated in a wide variety of inert gas matrixes.[12-25] Notwithstanding, many fundamental aspects remain at the moment unclear and continue to motivate a strong research activity in this field.[12-25] A large number of EPR studies have been also devoted to methyl radical in less inert or invasive environments, as in liquid methane,[26] in aqueous solution,[27] in organic media,[28-30] in interstitial position in bulk amorphous silica,[31-33] adsorbed on the surface of porous amorphous silica[34-38] or of alluminosilicate zeolite[39-41] and clathrate hydrate materials.[42] The $CH_3^\bullet$ molecule involves an unpaired electron interacting with three nearly equivalent protons and consequently (in the coupled representation) it is described by two J=1/2 (A states) and one J=3/2 (E states).[17,23,43] By considering the Zeeman Hamiltonian of the system, limiting ourselves to the first order perturbative treatment, the pair of lines arising from each of the A states superimposes to the inner pair of lines of the quartet arising from E states.[17,23,43] At room temperature, A and E states are almost equally populated and the EPR spectrum consists of four lines with a relative multiplicity 1:3:3:1, being the separation among adjacent lines of about 2.3 mT.[17,23,43]

Isolated $CH_3^\bullet$ radicals at very low temperature (T<7 K) are expected to exhibit a purely quantum effect related to the Pauli's anti-symmetry principle.[17,23,43] This effect originates when the molecule reaches its fundamental electronic, vibrational and rotational state. Due to the high symmetry of the molecule, this ground state has a fixed symmetry for exchange of a pair of protons of the molecule.[17,23] In particular, it can be shown that the rotational (J=0) and the vibrational (ν=0) components of the ground state wavefunction are symmetric, whereas the electronic component is anti-symmetric, resulting in an overall anti-symmetric behavior.[17,23] This circumstance, together with the Pauli's principle, imposes to the remaining part of the wave function, which concerns the magnetic levels of the radical, to be necessarily symmetric. Since A states are anti-symmetric whereas E states are symmetric, only the transitions related to E states are allowed, giving rise to an EPR spectrum consisting in a quartet of lines with a relative multiplicity of 1:1:1:1, instead of the usual 1:3:3:1.[17,23] This quantum effect has been actually observed experimentally at liquid helium temperature, but *exclusively* for methyl radicals trapped in the most inert matrixes, as those composed by N_2, Ar, Kr, H_2, He, CO, CO_2, N_2O.[14-25] In all the other less inert environments, the interaction of the radical with the environment is typically strong enough to inhibit quantum rotations and, in some cases, to completely immobilize the molecule at low temperature.[14,42] These latter results give further support to the expectation that, since the occurrence of quantum rotations is strictly related to the high symmetry of the molecule and to its isolation from the environment (which guarantee nearly free rotation of the molecule), it can be considered an extraordinary efficient probe of the inertness of the matrix.[17,23]

In the present experimental investigation we report on a new successful method of isolation of the $CH_3^\bullet$ radicals. We induced them into the cages of the SiO_2-clathrate structure of natural Melanophlogite by β-ray irradiation of the pristine material. Melanophlogite is a naturally occurring SiO_2-based clathrate structure which shares the same crystalline structure of type I gas hydrates.[44] Two types of voids are involved in the structure of Melanophlogite (Cage I and Cage II), which are typically occupied by guest CH_4, CO_2 and N_2 molecules, weakly interacting with the host structure by van der Waals interaction.[44-47] Typically, each cage is occupied by just one guest molecule. The free space within Cage I can be approximately described by a sphere-like void with diameter d~5.7 Å and a volume V~97 Å^3,whereas that within Cage II can be approximated by an ellipsoid with d_1=d_2=5.8 Å, d_3~7.7 Å and a volume of 136 Å^3.[44-47]

Our experiments indicate that a large number of $CH_3^\bullet$ radicals are generated by β-ray irradiation of Melanophlogite, presumably from CH_4 molecules through the process of C-H bonds breaking. Furthermore, we have found that $CH_3^\bullet$ radicals are reasonably singly trapped into the cages of Melanophlogite, fully stable in time (at room temperature) and experiencing an environment with inertness comparable with that of many conventional inert gas matrixes. However, at variance to any previous attempt, the isolation matrix presented here is thermally stable from 0 K up to at least room temperature,[47] allowing to investigate with continuity the properties of the $CH_3^\bullet$ in such a wide range of temperatures.

Experimental

The material considered here consists in a sample of natural Melanophlogite from Fortullino (Italy) with size of about 3x3x3mm^3.[45,46]

β-ray irradiation has been carried out by using a linear accelerator at the dose rate of 120 kGy/h. The accelerator operating conditions were: 6 MeV mean electron energy; 2 μA mean electron beam current; 100 Hz pulse frequency; 3 μs pulse duration; ±5% spot uniformity over an area with a diameter of about 12 mm. The irradiation dose accumulated in the sample of Melanophlogite considered was about 10^4 kGy.

EPR measurements were carried out with a Bruker EMX spectrometer working at a frequency of about 9.8 GHz (X-band) and with magnetic-field modulation frequency of 100 kHz. The spectra were acquired in the temperature range from T=4 K to T=300 K by using a standard Oxford He cryostat.

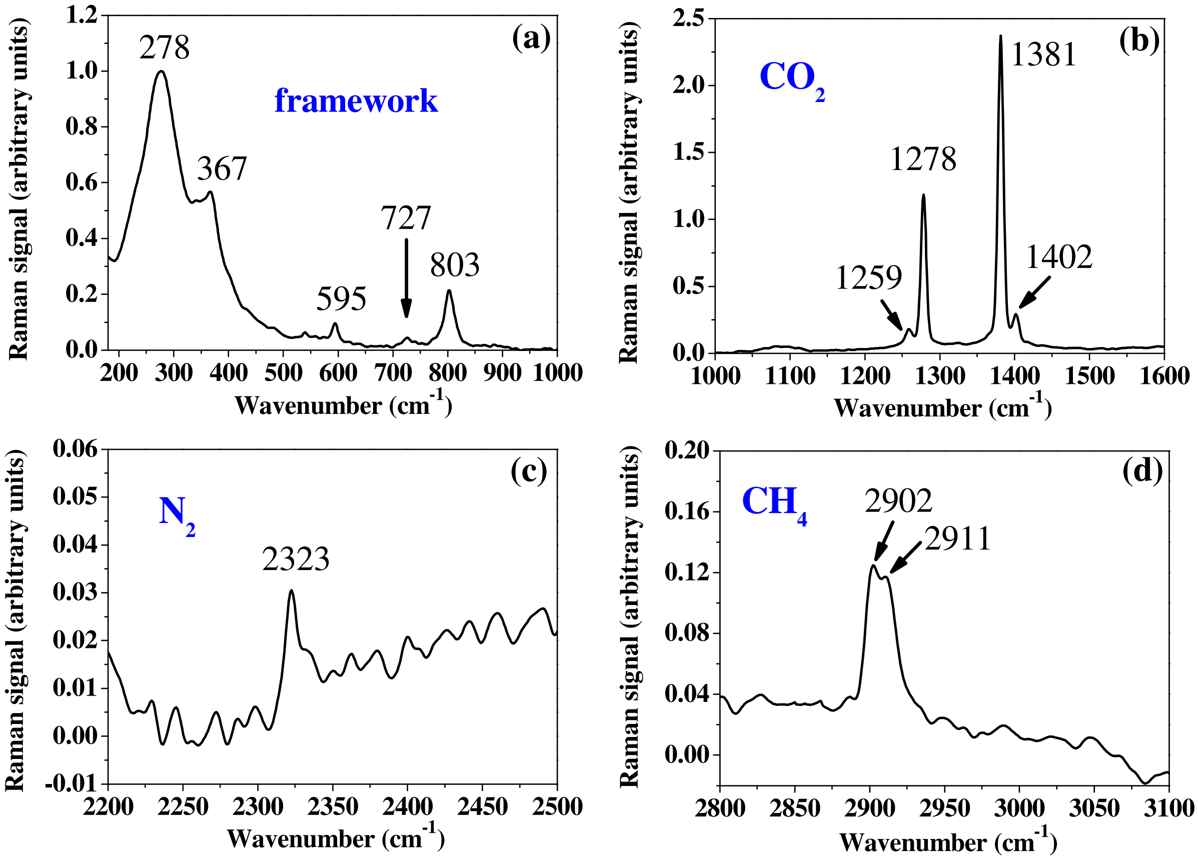

Fig. 1 Raman spectrum obtained at T=300 K before β-ray irradiation for the sample of Melanophlogite considered in the present work. The four panels single out the spectral regions in which the lines attributed to the host network (a) and to CO_2 (b), N_2 (c) and CH_4 (d) trapped molecules are located.

Raman spectra were acquired at room temperature by using a Fourier Transform Raman spectrometer Bruker RAMII equipped with a 500 mW Nd:YAG laser at 1064 nm. The applied experimental conditions lead to a spectral resolution of 5 cm^{-1}.

Results and discussion

The natural sample of Melanophlogite considered in the present work, once received, was subjected to a preliminary characterization aimed to verify its composition and structure. In line with previous experimental investigations,[45,47-48] this first study was performed by Raman spectroscopy, as it is able to easily identify both the intrinsic lines (due to SiO_2 host matrix) and those related to the gases trapped in the cages of the network (guest molecules). The main features of the Raman spectrum obtained for our sample are summarized in Fig. 1. In the four panels of this figure we single out the four regions of the experimental spectrum in which the Raman lines attributed to the host network and to CO_2, N_2 and CH_4 trapped molecules are located, Fig. 1 (a)-(d) respectively. By comparing the main spectroscopic features of these lines with those reported in literature,[45,47-48] we were able to conclude that our sample actually consists of a high-purity Melanophlogite with the ordinary cage like host structure and containing the commonly observed guest molecules: CO_2, N_2 and CH_4. A similar study was also performed in the same sample after irradiation, but no detectable change of the properties of the material was recognized. This result indicates that the host structure of the material is stable upon irradiation and that only a small fraction of the CH_4 molecules contained in the material are eventually transformed into CH_3 radicals by irradiation.

No paramagnetic centers were detected in the Melanophlogite sample before irradiation. At variance, an EPR signal was observed after β-ray irradiation, as shown in Fig. 2(a) where we report the EPR spectrum acquired at T=300 K. In this figure a multiplet of four lines with relative multiplicity of 1:3:3:1 and average separation among adjacent lines of 2.27±0.01 mT is easily recognized, which can be properly attributed to $CH_3^\bullet$ radicals.[17,23,43] By double integral of the multiplet a concentration of methyl radicals of about 10^{18} spins/cm^3 was

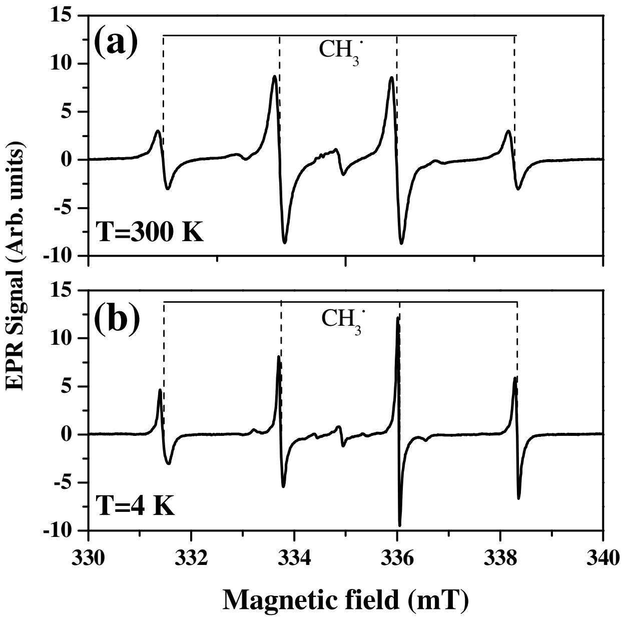

Fig. 2 EPR spectra obtained at (a) T=300 K and (b) T=4 K for β-ray irradiated Melanophlogite.

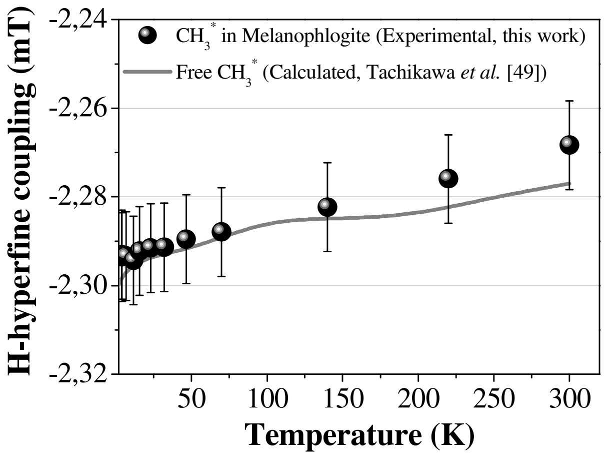

Fig. 3 H-hyperfine coupling of the $CH_3^{\bullet}$ multiplet observed in β-ray irradiated Melanophlogite as a function of temperature.

estimated. Other EPR signals are also recognizable in the spectrum in the regions among the main lines attributed to the methyl radical, see Fig. 2(a). These resonances have significantly lower amplitude with respect to that of methyl radicals and are of unknown origin, at the moment. Further experimental investigations are required in order to assign these signals to specific paramagnetic centers. In Fig. 2(b) we report the EPR spectrum acquired for the same sample at T=4 K. In this case we have estimated an average separation among adjacent lines of the $CH_3^{\bullet}$ radicals of 2.29±0.01 mT, which is a little wider than at T=300 K. Furthermore, the quantitative analysis of the double integral of each of these lines have pointed out that they share almost equal intensity, indicating the occurrence of nearly free quantum rotations.[17,23] Finally, by comparing Fig. 2(a) and (b), it is evident that the four lines of the $CH_3^{\bullet}$ hyperfine multiplet are narrower at T=4 K than at T=300K and that the peak-to-peak width at T=4 K is different for the various components. It is worth to note that no detectable variation of the amplitude of the EPR spectra reported in Fig. 2 was recognized in two years of observations, indicating that at room temperature methyl radicals are stable and unable to escape from the cages in which they are trapped.

By taking advantage of the strong thermal stability of radicals in the host matrix used, it was possible for the first time to investigate their dynamical thermal properties with continuity from T=4 K up to room temperatures. All the features observed in these experiments, which are described in the following, were found to be completely reversible by reversing the temperature changes.

In Fig. 3 (circles) we report the H-hyperfine coupling of the $CH_3^{\bullet}$, which is estimated as the opposite of the average separation among adjacent lines of the multiplet,[14] as a function of temperature. As shown, it changes almost linearly on increasing the temperature, but the overall change remains small, about 0.02 mT. In the same figure we report the results obtained by using *ab-initio* molecular dynamics (MD) calculations by Tachikawa *et al.*[49] for the *free* $CH_3^{\bullet}$ molecule, for comparison. As shown, a very good agreement is found between experimental and calculated data, indicating that as far as the H-hyperfine coupling is considered, the methyl radicals trapped in the cages of Melanophlogite behave as they were almost isolated. Since, as discussed above, inert gas matrixes are very poorly stable with temperature, similar studies cannot be undertaken in those systems in a suitable temperature range. Some useful experimental results have been reported by Garbutt *et al.*[37] for methyl radicals adsorbed on the poorly inert porous silica surface in the temperature range from 77 K to 300 K. In that work the H-hyperfine coupling of the $CH_3^{\bullet}$ multiplet was found to be almost constant for temperatures lower than about 150 K, whereas it underwent a gradual increase for higher temperatures.[37] These features differ significantly with respect to those reported in Fig. 3, in which the H-hyperfine coupling increases almost linearly with temperature. This comparison suggests that the interaction involved in the adsorption process of $CH_3^{\bullet}$ on silica surface is able to affect the

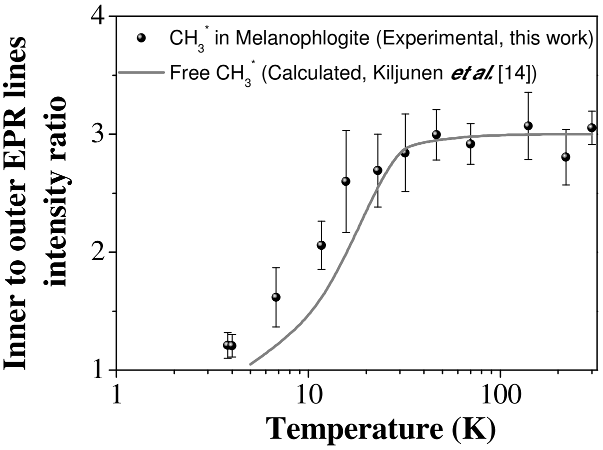

Fig. 4 Intensity ratio between the inner and the outer pairs of the $CH_3^{\bullet}$ hyperfine multiplet observed in β-ray irradiated Melanophlogite as a function of temperature.

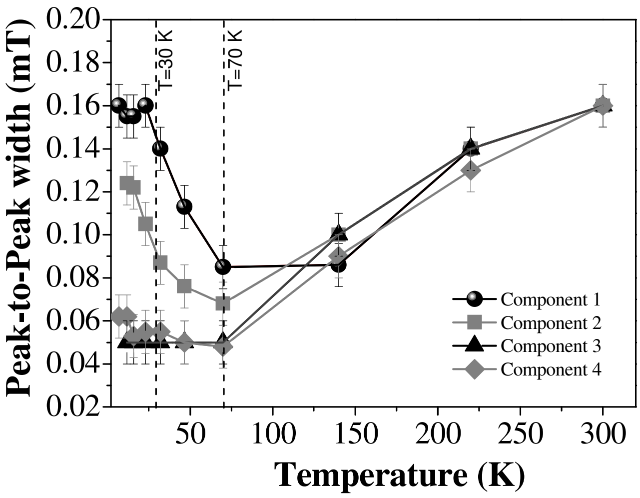

Fig. 5 Peak-to-peak width of the four components of the $CH_3^{\bullet}$ hyperfine multiplet observed in β-ray irradiated Melanophlogite as a function of temperature.

H-hyperfine coupling of the paramagnetic center, giving further support to our conclusion that the same molecule trapped inside Melanophlogite cages behaves almost freely.

In Fig. 4 we report the intensity ratio between the inner and the outer pairs of the hyperfine multiplet as a function of temperature. As shown, this ratio is almost equal to about 1.2 for T=4 K and it increases on increasing the temperature up to T=30 K, where it assumes the value of about 3. No further changes take places for higher temperatures up to T=300 K. These results are very interesting as they allow to evidence for the first time the progressive onset of quantum behavior of the $CH_3^{\bullet}$ rotor on decreasing the temperature below about 30 K. In the same figure we also report the intensity ratio between the inner and the outer pairs of the hyperfine multiplet calculated for *free* $CH_3^{\bullet}$ radical, for comparison.[12] As shown, for temperatures lower than about 30 K, the experimental values are systematically larger than the calculated ones, unveiling the existence of some degree of interaction between the $CH_3^{\bullet}$ rotor and the cages of the host material. Notwithstanding, the relative ratio between outer and inner components of the multiplet of about 1.2 at T=4 K, indicates that the interactions of the rotor with the surrounding is very limited.

The peak-to-peak width of the four components of the $CH_3^{\bullet}$ hyperfine multiplet as a function of temperature is reported in Fig. 5. As shown, most of the components of the multiplet have different widths for T< 70 K. This feature is recognizable also at liquid Helium temperature, indicating that the radical wave function is not fully isotropic even at T=4 K. This result has very relevant physical consequences, as discussed in the following. If $CH_3^{\bullet}$ radical were completely isolated from the environment, it would live in the overall ground state at T=4 K.[17] This state is characterized by a zero orbital magnetic moment and consequently it involves an isotropic wave function. This isotropy does not arise from an average related to the rotational motion of the molecule, but it is a "quantum" property of the molecular orbital in its ground state.[17] This inference is in contrast with our experimental observations on the $CH_3^{\bullet}$ in Melanophlogite and points out that methyl radicals actually experience an interaction with the cages of the host material.[17] This interaction has the effect to reduce the energy separation between the ground state and the first excited ones, so enabling a significant population of the first excited levels already for temperatures as low as 4 K.[17] The anisotropy of the peak-to-peak width of the components of the hyperfine multiplet measured at T=4 K is a very common feature. In fact, a completely isotropic $CH_3^{\bullet}$ hyperfine multiplet was reported in just two experimental investigations in which Ar[23] and para-H_2[15] isolation matrixes were considered. At variance, in many other works devoted to methyl radicals trapped in Ne,[15,20] Ar,[15,21] Kr,[15,20-22] CO[14,22], N_2O,[25] CO_2[14] and N_2[22] matrixes, the EPR spectrum was found to exhibit anisotropic features. By comparing quantitatively the anisotropy observed in our system with that found in other isolating matrixes, it emerges that the degree of inertness of Melanophlogite network is comparable to that commonly observed in ordinary inert gas matrixes.[15]

The experimental data reported in Fig. 5 also show that the widths of the components of the $CH_3^{\bullet}$ multiplet decrease gradually on increasing the temperature in the range from 30 K to 70 K, also reducing their relative differences. As discussed above and shown in Fig. 4, the quantum behavior of methyl radicals trapped in Melanophlogite disappears for T>30 K. As a consequence, the features observed in this range of temperature fall in the classical regime. In line with this inference, the narrowing effect observed for temperatures in the range from 30 K to 70 K and shown in Fig. 5 can be reasonably attributed to the rapid rotation and/or stochastic reorientation of the radical. In fact, when such a motion is sufficiently rapid, it is able to influence the EPR spectrum so that this latter reflects just the average values of both the spectroscopic splitting factor and the hyperfine matrixes, **g** and **A**, respectively.[17] In this respect, it is worth to note that it has been well established that the $CH_3^{\bullet}$ at-rest is characterized by a very anisotropic hyperfine matrix with principal values of about 1 mT, 3÷4 mT and 2÷3 mT.[50-52] Furthermore, in agreement with our picture, it has been also shown that most of this anisotropy can be averaged out by a fast rotation of the molecule around its C3 symmetry axis.[17]

As shown in Fig. 5, for temperatures higher than about 70 K, all the components of the multiplet broaden on increasing the temperature and they promptly assume comparable widths. This effect is reasonably attributable to the relaxation mechanism related to the coupling between the electron spin magnetic moment and that associated to rotational angular momentum.[53] This interaction increases on increasing the rotational energy of the molecule and consequently it becomes more and more effective on increasing the temperature. Furthermore, this mechanism is expected to broaden uniformly the four components of the multiplet.[53] Both these properties agree very well with the experimental results shown in Fig. 5, strongly supporting our attribution. In addition, the data reported in Fig. 5 indicate that for temperatures higher than about 70 K the broadening effect related to this process becomes dominant with respect to that of (motional) narrowing discussed above. Unfortunately, due to their intrinsic thermal instability, similar studies cannot be accomplished for $CH_3^{\bullet}$ radicals trapped in inert gas isolation matrixes. Notwithstanding, again, the features observed for T>70 K and shown in Fig. 5 can be compared with those obtained by Garbutt *et al.*[37] for $CH_3^{\bullet}$ radicals adsorbed on porous silica surface. However in that case, the study of the peak-to-peak width was possible only for the inner pair of components of the hyperfine multiplet, as it is three times more intense than the outer pair. [37] In that work it was found that the widths of the two components differ significantly between them and become narrower on increasing temperature up to about T=200 K. On increasing further the temperatures the peak-to-peak widths increase gradually and become comparable. These features are qualitatively similar to those reported in Fig. 5, but they differ significantly from the quantitative point of view. In fact, the minimum of the widths is observed at about T=200 K for $CH_3^{\bullet}$ adsorbed on silica surface, whereas it is observed at about T=70 K for the same radical in cages of Melanophlogite. Since, as discussed above, the mechanisms affecting the widths of the hyperfine components are related to the degree of mobility of the radical, the observed difference indicates that, at a fixed temperature, the radicals move more freely in Melanophlogite than when they are adsorbed on silica surface.

To summarize, the overall data we have reported here strongly suggest that the methyl radicals trapped in the clathrate host of Melanophlogite are just weakly interacting with the cages. The comparison, when possible, of this system with other standard matrix isolation methods indicates that the degree of interaction between the radical and the host in Melanophlogite is comparable to that observed in standard inert gases hosts. Since Melanophlogite offers a strongest thermal stability than conventional matrixes, it undoubtedly makes the former the isolation method of choice. In principle, the applicability of this isolation method is not limited to methyl radicals but it is expected to be extendable to a large variety of highly reactive species of interest. In fact, it has been already established that it is possible to empty the cages of Melanophlogite simply by thermal treatment at about T=380 K, while preserving the integrity of the host network.[48] Subsequently, other small molecules can be inserted into the cages of the material upon thermal treatments in high pressure of controlled atmosphere. Besides, it has been shown that a large variety of molecules can be trapped into the cages of Melanophlogite by simply introducing them during the synthesis procedure.[54] Furthermore, it has been also shown that by properly changing the synthesis conditions, different clathrate structures can be obtained with cages of different size.[54] This result indicates that the method of isolation presented here is not applicable solely to molecules whose size is comparable to that of the cages of Melanophlogite, but its potentialities are significantly wider.

As discussed in the Introduction, previous experimental investigations were already focused on $CH_3^{\bullet}$ trapped in alluminosilicate zeolite materials.[39-41] However, in all these cases a strong interaction between the radical and the host material was observed. The main difference between those cases and our approach consists in the fact that we have considered pure silica clathrate material, whereas in all the previous studies the Aluminium content of the host material was significant. This is a key point because Al sites of the network are usually negatively charged and consequently they are expected to adsorb methyl radicals by establishing a strong electrostatic bond. Such interaction is absent for pure silica clathrate/zeolite materials, giving them a high degree of inertness.

Conclusions

Here we presented an experimental investigation by EPR spectroscopy focused on $CH_3^{\bullet}$ radicals singly trapped in the cages of Melanophlogite. In particular, we have characterized the H-hyperfine coupling, the relative intensity of the four components of the hyperfine multiplet and their peak-to-peak widths. Thanks to the thermal stability of the trapping host, we were able to obtain a detailed characterization of these properties in the wide temperature range from 4 K up to 300 K. These studies have permitted us to observe the occurrence of the quantum rotations at the lowest temperature (T= 4 K), but also to follow for the first time the gradual transition from quantum to classical regime on increasing the temperature. The comparison of the inertness of the Melanophlogite host with respect to that of other standard inert gas matrixes indicates that they are almost comparable. However, since the former has an unparalleled thermal stability, it undoubtedly offers extraordinary advantages.

Typically, the properties of the systems consisting in matrix isolated radicals are strongly dependent on the details of the material synthesis. For this reason it is important in future works to compare the properties of similar systems but obtained with different routes. These studies could also help to unveil the nature and the properties of the weak interactions taking place between the radicals and the host materials.

We believe that the isolation method presented here and applied to methyl radicals has strong potentialities, as it is expected to be applicable to a large variety of strongly reacting molecular radicals with a large variety of sizes.

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Notes and references

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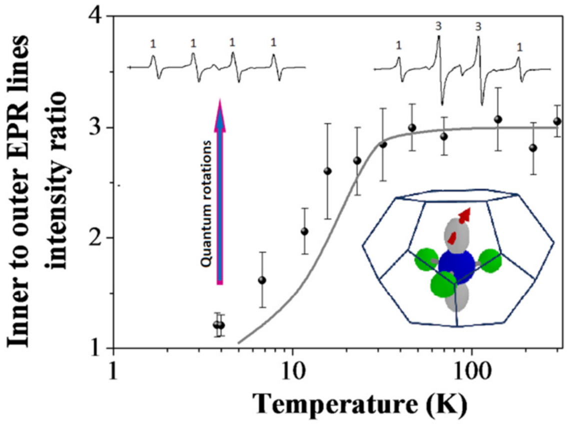
Table of contents entry:



By isolating the CH_3• rotor in a stable clathrate host the gradual transition from classical to quantum behavior was observed