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Molecular Dynamics

Nuclear Spin Conversion to Probe the Methyl Rotation Effect on Hydrogen-Bond and Vibrational Dynamics**

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Intramolecular hydrogen bonds play a key role in the structure and dynamics of many molecules because of their intermediate strength between covalent and long-range polarization forces. Their weakness enables large-amplitude motions, whereas their strength hinders movements about otherwise very weak torsion modes. These effects combine and compete in a very subtle way in intramolecular H-atom transfers (labeled hereafter as H_{int} transfer), which are one of the most important reactions in biochemistry and material sciences. Enol tautomers of β-diketones and dialdehydes often appear as benchmarks systems for investigating structural and dynamical effects associated with intramolecular hydrogen bonds. The multidimensional nature of the H_{int} transfer process has been well-established, even in a simple molecule such as the enol form of malonaldehyde, the prototypical dialdehyde, ($HCOCH_2COH$; hereafter labeled as MA).[1] In the enol tautomer of 2-methylmalonaldehyde, the interplay between H_{int} transfer and methyl rotation was reported.[2] These two latter processes involve large-amplitude motions, and their coupling can induce complex behaviors. For example, it was predicted theoretically[3] and confirmed experimentally[4] that the transfer of the H-bonded H-atom in 5-methyltropolone can drive the rotation of the remote methyl group through long range chemical interactions. The present study is focused on acetylacetone, a prototypical β-diketone with two methyl groups. Hindered methyl-group rotation is investigated with the aid of nuclear spin conversion (NSC) observed through the time evolution of the IR spectrum at low temperature. As methyl torsions are entangled with the H_{int} transfer, IR bands provide information on the large-amplitude motions and especially on their coupling with high-frequency modes.

Acetylacetone (2,4-pentanedione, hereafter labeled as Hacac) is mostly present in the enol form when isolated in the gas phase and in matrices.[5] Most experimental results support a C_s structure with the H-bonded H-atom in unsymmetrical position with respect to the central oxygen atoms, placing it in proper position for an H_{int} transfer process[6] (shown as the C_s equilibrium structure in Figure 1). Our calculations and those of others[5,7,8] suggest that the hindered rotations of the methyl groups couple with the H_{int} transfer, as in 2-methylmalonaldehyde. The resulting change in the methyl positions owing to the H_{int} transfer appears in the two C_s equilibrium structures at the bottom of Figure 1.

Calculations also conclude that the two methyl groups are associated with very different torsional barriers in Hacac. The hindered rotation of a methyl group around its C_3 axis creates a ground torsional tunneling splitting in two states of A (nondegenerate) and E (doubly degenerate) symmetries, the A being the lowest.[9] The two tunneling splittings have been measured in solid acetylacetone as 40 μeV (0.32 cm^{-1}) and 0.5 μeV (4.0×10^{-3} cm^{-1}) for the methyl on the C=O group

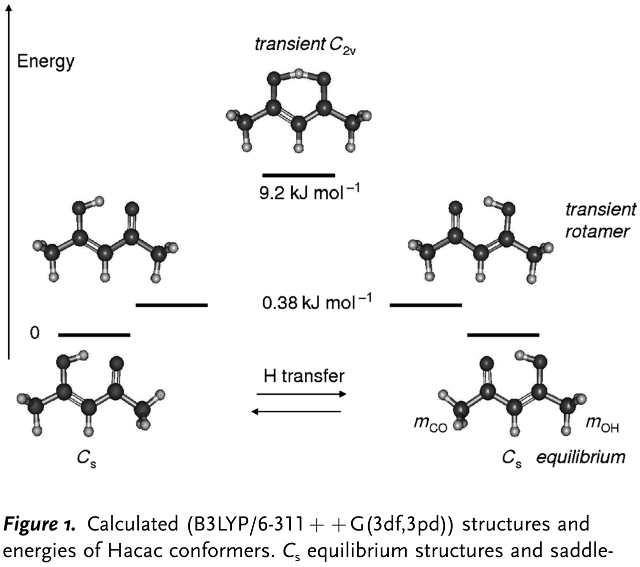

Figure 1. Calculated (B3LYP/6-311++G(3df,3pd)) structures and energies of Hacac conformers. C_s equilibrium structures and saddle-point structures: the transient rotamer, a saddle-point in the methyl m_{CO} rotation, and the transient C_{2v}, a saddle-point in the H_{int} transfer. The bottom right structure also defines the labels m_{CO} and m_{OH} used herein for the methyl groups.

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side (m_{CO}) and for the methyl on the COH side (m_{OH}), respectively.[10] We performed DFT B3LYP/6-311++G-(3df,3pd) calculations on the isolated molecule, using the Gaussian 03 package.[11] The predicted relevant structures and energetics are shown in Figure 1. Geometrical structures and energetics of the stable C_s tautomers and of several transients were also calculated at the MP2 level, using the same basis functions. DFT calculations predict torsional barriers of 32 and 411 cm^{-1} for m_{CO} and m_{OH}, respectively, whereas they are found at 77 and 466 cm^{-1} at the MP2 level. Such an order of magnitude and differences between the two barriers are in qualitative agreement with previous theoretical estimations.[12] A large tunneling splitting (of a few wavenumbers) is thus expected in the torsional levels of m_{CO} in the isolated molecule.

Therefore, enolic Hacac exhibits three coupled large-amplitude motions involving hydrogen atoms with different barriers, the H_{int} transfer between the two oxygen atoms and the two non-equivalent methyl torsions. A complex energy level pattern is thus expected, as recently theoretically investigated by Chou.[13] This provides impetus to investigate experimentally the hierarchy of couplings between the vibrational levels involved in the H_{int} transfer process. Ultrafast nonlinear and 2D IR spectroscopy appear to be ideal methods for this purpose. Herein we present a very simple alternative to nonlinear spectroscopy for documenting the dynamics related to the three entangled large-amplitude motions of Hacac in the ground electronic state. This alternative is based on IR spectroscopy of Hacac trapped in a solid parahydrogen (p-H_2) matrix.

The experimental setup and the operating conditions are described in Ref. [5]. p-H_2 is a quantum crystal and its weak interaction with the Hacac guest should 1) reduce the inhomogeneous broadening owing to the p-H_2 host below that due to the intrinsic dynamics of the Hacac guest; and 2) preserve large amplitude intramolecular motions of Hacac. The weak effect of this host on the methyl torsion or rotation has already been confirmed in the study of small molecules carrying a single methyl group (methanol,[14] methylfluorine[15]) in p-H_2. Moreover, nuclear spin conversion (NSC) in the methyl group was clearly observed in those studies, a phenomenon which will be at play in the present work. The nuclear spin of a methyl group is fully coupled to its rotation by symmetry reason. The A state is associated with the totally symmetric nuclear spin wavefunction ($I=3/2$), whereas the E state corresponds to the nonsymmetric case ($I=1/2$). Consequently, the A–E transfer of population implies NSC, a slow process compared to thermalization.[9] Thus, immediately after trapping the molecules in p-H_2, in the case of a large A–E splitting (that is, slightly hindered rotation), A and E state populations differ from the Boltzmann distribution at the low matrix temperature (4 K).

Indeed, a slow NSC process is observed in Hacac through the evolution in time of its IR spectrum in solid p-H_2. Its analysis can be used to compare the dynamics of the ground vibrational state with that of an excited state related to torsional motion in a methyl hindered rotation. The key point here is that the extra energy in the excited state is not sufficient to overcome the barrier of H_{int} transfer (see energetics in Figure 1). Nevertheless, it is deposited in a mode which is expected to trigger the reaction. This offers the possibility to probe the efficiency of such triggering when exciting other vibrational modes that turn on the H_{int} transfer by comparing the width of the IR bands for both the ground and torsionally excited states.

The IR spectrum recorded immediately after Hacac was trapped in p-H_2 contains broad bands belonging to the enolic form (average width of the order of 10 cm^{-1}) and a few narrow bands which were assigned to the keto form.[5] The most interesting spectral range is reproduced in Figure 2a. Some bands are surprisingly broad in comparison with the Hacac spectrum recorded in a neon matrix (Figure 2c). Importantly, annealing at 6 K does not modify the spectrum. Figure 2b shows the spectrum of the same sample 24 h after deposition. It reveals the time evolution of the broad bands, especially in the low-frequency range. Actually, spectra have been recorded every 90 min, allowing us to extract two components in these bands. One increases as a function of time whereas the other decreases (Supporting Information, Figure S1). The full spectrum is then separated in two components related to two "species", labeled as the most stable (ms) and less stable (ls) in Figure 3.

The total amount of enol (ms + ls) is constant along the experiment and the time evolution of the ms and ls "species" can be fitted by an exponential growth and decay, respectively, with a common rate constant of 0.043 h^{-1}. This value is of the same order of magnitude as the NSC rates measured in solid p-H_2 on other molecules carrying a methyl group.[14,15] The o-H_2 impurities in p-H_2 broaden the IR absorption bands of both ms and ls components. Thus, the o-H_2→p-H_2 NSC would correspond to reducing linewidths in the spectra of both ms and ls components, whereas the linewidths in the ms and ls spectra remain constant as a function of time in the present experiment. The spectral evolution observed is thus assigned to NSC in Hacac.

In Hacac, the splitting associated with the m_{CO} torsion, the less hindered methyl rotor, is larger than the other splittings, and can be greatly enhanced owing to the coupling with the H_{int} transfer.[13] In a simple approach, its A and E symmetries can be used for ordering this complex level landscape. Accordingly, ms documents the spectrum of the ground

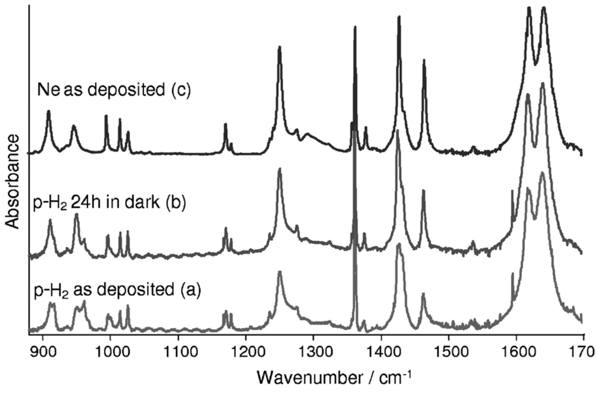

Figure 2. IR spectra (selected spectral range) of Hacac isolated at 4 K in solid p-H_2 just after sample deposition (a), 24 h after deposition (b), and in solid neon (c)

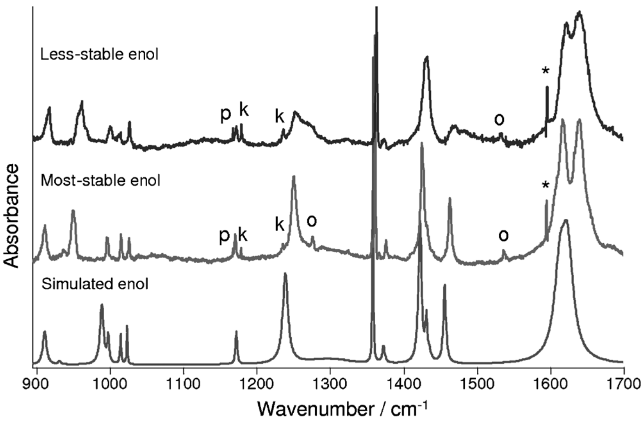

Figure 3. IR spectra (selected spectral range) of the ms (middle panel) and ls (top panel) species extracted from IR spectra of Hacac/p-H_2 (Figure 2). The bottom panel reproduces a simulated spectrum obtained with anharmonic frequency values (o = overtones; k = keto line; p = parahydrogen line; ⋆ = water impurity).

vibrational and torsional state of the m_{CO} rotor; that is, the "A" state, whereas ls corresponds to the "E" states of the same rotor.

Accurate calculations of the tunneling splitting related to the m_{CO} rotor are lacking, but the "E" levels, higher in energy than the "A" one, are closer to the levels of the transient rotamer, which is drawn in Figure 1 (this statement is substantiated in the Supporting Information, Table S1). The frequencies of ms (ν_{ms}) and the frequency shifts ($\nu_{\mathrm{ms}}-\nu_{\mathrm{ls}}$) between ms and ls provided by the experiment are compared in the Table S1 to the calculated frequencies of the stable C_s structure of Hacac (ν_s and ν_s anh) and to the difference $\nu_s-\nu_r$ between frequencies of the latter species and those of the transient rotamer (both calculated at the same level of theory: B3LYP, harmonic). The experimental shifts ($\nu_{\mathrm{ms}}-\nu_{\mathrm{ls}}$) are strongly mode-dependent, and follow essentially the theoretical difference ($\nu_s-\nu_r$). In particular, the largest shifts are observed for the OH out-of-plane bending mode (γ_{OH}), which is explained well by the simplified picture of the transient rotamer: the hydrogen bond is stronger in this structure than in the C_s stable form, and an almost pure OH bending mode, such as γ_{OH}, has consequently a higher frequency.

As the tunneling splitting Δ("A"–"E") in the Hacac ground state is the same for all vibrational transitions, the IR spectra also reveal those that are due to proton tunneling or a change in the methyl torsion in the various vibrational excited states. $|\nu_{\mathrm{ms}}-\nu_{\mathrm{ls}}|$ values can reach few wavenumbers (up to 12 cm^{-1}). This suggests that the observed shifts reflect couplings which perturb the tunneling splittings of the m_{CO} torsions, highlighting the influence of the H_{int} transfer and coupling with the other methyl torsion. In fact, the influence of the H_{int} bond on the m_{CO} methyl rotor was already observed experimentally in solid Hacac, where deuteration of the OH group decreases strongly the tunneling splitting of the weaker hindered methyl rotor, but not of the other.[10]

The bottom panel of Figure 3 shows the simulated spectrum obtained from the anharmonic vibrational frequencies,[5,16] combined with calculated intensities in the harmonic approach and experimental bandwidths from the ms spectrum (Supporting Information, Table S1). The average mismatch between the calculated and the experimental frequencies for ms is 3.3 cm^{-1}, and the mode assignment provided by the calculation can be considered reliable. The two significant frequency mismatches concern the specific γ_{OH} mode, which is very sensitive to the internal H-bond (the mismatch is very large: +39 cm^{-1}), and the doublet around 1630 cm^{-1}, which does not appear in the calculations because the two components collapse in the bandwidth. Note that this doublet was also badly reproduced in similar calculations of open enol conformers of Hacac.[16] The in-plane bending motion (δ_{OH}) of the hydroxy group is included in many modes between 1650 and 1200 cm^{-1}. One, predicted at 1298 cm^{-1}, has an abnormally large width of 80 cm^{-1}. This observation is consistent with previous works in matrices and in the gas phase.[17,18] The corresponding mode is the only one with δ_{OH} motion in phase with C=C, C–C, C–O and C=O stretches (Supporting Information), thus making the electronic π delocalization in the pseudo cycle easier, which is a substantial hint to the H_{int} transfer.[19] Moreover, the equivalent mode in MA, at 1364 cm^{-1}, exhibits the largest vibrationally excited-state tunneling splitting (69 cm^{-1}) in jet experiments.[20] In the corresponding $v=1$ level, the barrier to hydrogen transfer is significantly lowered. The same is expected in Hacac. We thus assign the large bandwidth to a strong coupling between the hydrogen and ring motions. Modes predicted near 1620 cm^{-1} also involve δ_{OH} and stretches of the O–C–C–C–O pseudo ring (Supporting Information), but not in-phase as in the previous case. This lack of concerted motions toward a hydrogen transfer likely induces a smaller broadening, as it reduces the proton tunneling in the equivalent mode at 1594 cm^{-1} in MA.[21]

A striking difference between the ms and ls spectra concerns the width of the bands, which are narrower in ms. A first origin is that ls may include several levels. Nevertheless, the H_{int} transfer is likely involved also. The corresponding line broadening is expected to be mode-dependent, thus probing the vibrational dynamics in torsionally excited levels. The barrier height to H_{int} transfer can be estimated as the energy difference between the stable C_s structure and the transient (saddle-point) C_{2v} structure (see Figure 1). The value of 1359.2 cm^{-1} obtained for MA in CCSD(T)/aug-cc-pVTZ calculations[22] can be compared to 1276.7 cm^{-1} for Hacac in CCSD(T)/aug-cc-pVDZ calculations.[8] In spite of a lower barrier height, tunneling splitting owing to hydrogen transfer in Hacac is expected to be smaller than in MA because of the presence of methyl groups, which makes the reaction coordinate heavier. Assuming as above that ls has similarities with transient rotamer, the hydrogen transfer in the "E" state should mimic that in MA and has a smaller energy barrier than in the "A" state, thus allowing promoted transfer with vibrational excitation on other modes than the previously described δ_{OH} mode at 1290 cm^{-1}. Actually, two bands at 1250 cm^{-1} and 1460 cm^{-1} have a very large width in the ls spectrum (see Figure 3 and the Supporting Information, Table S1). The first involves δ_{OH} bending and stretching deformation of the pseudo ring (Supporting Information), whereas the m_{OH} motion, which is the second rotor coupled with the H_{int} transfer, participates to the second band

(Supporting Information). Finally, the δ_{OH} mode at 1290 cm^{-1} does not show up in the ls spectrum; either it is too broad to be detected, or it is hidden by the very broad 1250 cm^{-1} mode. All of these broadening origins reflect the delocalization of the hydrogen atom on the vibrationally excited PES, coupled with low-frequency motions, inducing fast vibrational dephasing.

No clear evidence of a tunneling splitting owing to the internal hydrogen bond can be observed from the IR spectra. Either 1) the tunneling splitting in the vibrational ground state is negligible, as suggested by Chou[13] to explain microwave experiments,[23] and its possible enhancement with vibrational excitation is hidden by the bandwidths, or 2) it is large enough to get only the lower state of the doublet populated at the matrix temperature (4 K) and all the vibrational bands originate from this level alone. Alternatively, the H_{int} tunneling process could be quenched by coupling with phonon in the matrix environment. Such process was observed for MA in inert gas matrices[24,25] and Ar clusters,[21] but it is unlikely in the present soft para-hydrogen environment: as H_{int} transfer is coupled with methyl torsions, this quenching should also affect "A"–"E" tunnelling splitting and it is obviously only a weak effect in solid p-H_2. Hacac spectra in solid neon (Figure 2 c) and solid xenon[17] are very similar to the ms spectrum (Figure 3). NSC is more efficient in these hosts containing magnetic isotopes, and the fact that only the "A" state is populated explains the spectroscopic similarities. Nevertheless, the "E" state can be thermally populated when the matrix temperature is increased, but no temperature effect was observed in these classical hosts, thus revealing the important "heavy" matrix effect on large amplitude motions in a complex molecule such as Hacac. Note that such a thermal effect was observed in the case of methanol isolated in neon.[26]

In summary, isolation of acetylacetone in solid para-hydrogen has revealed new vibrational behavior directly related to the complex dynamics of intramolecular H-atom (H_{int}) transfer. This works confirms the pertinence of isolation in solid p-H_2 which, on the contrary to classical hosts, preserves subtle intrinsic dynamical properties of the guest molecule, such as the large-amplitude motions that are at play in Hacac. In particular, the present work brings experimental evidence of proton tunneling within the less-hindered methyl group of Hacac, and related nuclear spin conversion (NSC) is clearly observed. All of the results are in full agreement with a C_s stable structure of the enol form with a nearly free rotation of one methyl group.

Experimental evidence was brought that the H_{int} transfer is mediated by the torsion of the less-hindered methyl group. This was revealed using NSC in this methyl group as a tool to disentangle two IR absorption spectra corresponding to the ground vibrational state (ms species) and a torsional excited state of enolic Hacac (ls species). The present work thus appears as a case study showing that NSC in solid p-H_2 is a dedicated tool for investigating the spectroscopy of molecular species carrying energy in internal methyl torsion. Such event is very common in biomolecules.

Finally, this work shows directly, with almost no host effect, which vibrational modes are coupled to promote the H_{int} transfer in a concerted fashion. The observed band widths and positions, by providing information on the intrinsic properties of the molecule, offer a quantitative benchmark for future calculations of the H_{int} transfer process. These will be certainly very challenging (but manageable) as they will need to consider the two methyl torsions and the pseudo cycle deformation modes that both host the H_{int} transfer coordinate and interplay with the simultaneous change of the electron configuration.

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