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Communication: Observation of homonuclear propensity in collisional relaxation of the $^{13}C^{12}CD_2$ ($v_2 = 1$) isotopologue of acetylene by stimulated Raman spectroscopy

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We report the first experimental observation of homonuclear propensity in collisional relaxation of a polyatomic molecule. A pump-probe stimulated Raman setup is used to pump population to a single rotational level of the $v_2 = 1$ vibrationally excited state in $^{13}C^{12}CD_2$ and then monitor the redistribution of the rotational population that has taken place after a fixed delay. The *Q*-branch of the $2\nu_2-\nu_2$ band shows a pattern of intensity alternation between the even and the odd rotational components, with the greater intensities always corresponding to the rotational levels with the same parity as the one where all the population was initially deposited. The effect can be explained by the existence of a propensity rule that favors collisional relaxation between rovibrational levels of the same parity. © *2011 American Institute of Physics*. [doi:10.1063/1.3602916]

INTRODUCTION

Early experimental studies in molecular collision dynamics led to the widespread adoption of the concept of "propensity rules."[1] As opposed to the strict selection rules that govern radiative transitions, propensity rules provide just a probabilistic account of the outcome of molecular collisions. These probabilities can be quantified, for a specific collisional system, through both theoretical calculations and experimental measurements.

The observation of propensity rules often reflects the fact that the outcome of a single atom-molecule or molecule-molecule collision is a function of a large number of parameters (angles, relative velocities, initial states of the colliders, etc.), and different initial values of these parameters can result in different final states for the collisional products. Given the difficulty to isolate and control all the parameters simultaneously, experimental measurements are typically averages over very large numbers of individual collisions with different initial conditions, resulting in the observation of a mixture of collisional products in different states. When some of these states are clearly preferred over others, propensity rules are often said to exist for the collisional process. Some propensity rules, however, stem not from the variability of the initial parameters of the collision but directly from the quantum nature of the process, so that a certain distribution of products would be observed even if the experiment could be performed with total control over the parameters (e.g., a single collision carried out repeatedly under the exact same conditions). The propensity rule observed in this work is of this latter type, and appears in collisional relaxation of molecules which can be loosely described as *quasi*-centrosymmetric. This term refers to species whose intramolecular potential energy surface and/or mass distribution, while not centrosymmetric, are still close to those of a centrosymmetric molecule.

The rule can be described as an alteration of the rotational relaxation probabilities such that collisions in which the molecule gains or loses an even number of rotational quanta ($\Delta J = \pm 2, \pm 4, \ldots$) are more likely than those in which an odd number of quanta is exchanged. From an empirical point of view this propensity rule can be viewed as a remnant of the strict $\Delta J = even$ selection rule for collisional transitions in homonuclear diatomic molecules, which in turn stems from the negligible probability of interconversion between their different nuclear spin species by collisions. It is for this reason that this kind of propensity has been named "homonuclear propensity."[2] In quantum and semiclassical scattering calculations, it arises naturally as an interference effect.[3] The interest of these interpretations resides in the fact that they are able to explain both homonuclear propensity and the strict homonuclear selection rule as different degrees of the same interference phenomenon, without resorting to nuclear spin arguments. For example, in the semiclassical S-matrix framework the amplitude of a given collisional transition is calculated as a sum of the amplitudes of the different paths that lead from the same initial to the same final state. When the amplitude is squared to calculate the cross section of the transition, some of these paths can interfere and even completely cancel each other to produce a zero probability (forbidden) transition. This in turn can be explained because the anisotropic part of the collisional potential, responsible for the inelastic collisions, consists of an even and an odd parts. In homonuclear diatomic or centrosymmetric molecules the odd part is zero, and this translates into total cancellation of the interfering terms for $\Delta J = odd$ transitions. If the symmetry of the molecule is now broken (for example, through isotopic substitution of one atom) the odd part of the anisotropic potential is no longer zero and the

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cancellation of the interfering terms is not complete, which results in a nonzero probability for $\Delta J = odd$ transitions. This probability tends to grow rapidly, and differences between $\Delta J = even$ and $\Delta J = odd$ transitions are washed out, as the molecular geometry strays further apart from the symmetric case. Propensity rules such as the one observed in this work are seen when the molecular geometry is still very close to the symmetric case and $\Delta J = odd$ collisional transitions, while not forbidden, have a small cross section.

Homonuclear propensity was predicted for the first time in 1974 (Refs. 4 and 5) and later studied in detail through semiclassical calculations.[3] However, it was not verified experimentally until 1982.[6] Since then it has been observed in collisions involving NO,[6,7] CO,[8] CN,[9,10] ^{6}Li^{7}Li,[11] and SiS (Ref. 12) with diverse partners, typically noble gases. In the present study we report the observation, for the first time, of homonuclear propensity in a polyatomic molecule, ^{13}C^{12}CD$_2$. It must be mentioned that the observation was not being sought, but made in the course of a spectroscopic study of the $2\nu_2-\nu_2$ hot band of this isotopologue of acetylene.

EXPERIMENTAL

The experimental setup used in this work is based on an apparatus originally used for high resolution Raman spectroscopy of vibrationally excited states,[13–15] that later evolved into a more elaborate setup for the determination of state-to-state rotational energy transfer rate coefficients.[16] For the observations described in this communication a simplified version of the latter setup has been used. The experiment follows a similar scheme to the ones used in the works of Orr (Ref. 17 and references therein) and Zacharias,[18] consisting of a stimulated Raman pumping stage for sample preparation followed by a probing stage, which in our case also relies on the use of stimulated Raman spectroscopy. We will just provide a brief overview of the technique and refer the reader to Ref. 16 for a much more detailed description of the experimental apparatus.

The experiment populates the first vibrationally excited state of a suitable mode of the molecule under study, in this case the ν_2 vibrational mode of ^{13}C^{12}CD$_2$, by optically pumping population from the ground vibrational state through a single rovibrational transition of a Raman Q-branch. It then registers the high resolution rovibrational Raman spectrum of the Q-branch of the $2\nu_2-\nu_2$ vibrational hot band before the rotational population reaches a state of thermal equilibrium. The setup uses a pump-probe arrangement in which the stimulated Raman effect is used for both the pump stage (stimulated Raman pumping) and the probe stage (stimulated Raman spectroscopy). Figure 1 shows a schematic representation of this arrangement. Each one of the main laser beams used in the experiment is depicted as an arrow. The two arrows on the left side of the figure represent the two laser beams responsible for the stimulated Raman pumping, that promotes population from the ground state to the first vibrationally excited state of the molecule under study. The linewidths of the lasers are narrow enough to allow rotational selectivity, that is, population is pumped through a single Q-branch rovibrational transition and thus a single rotational level is initially populated in

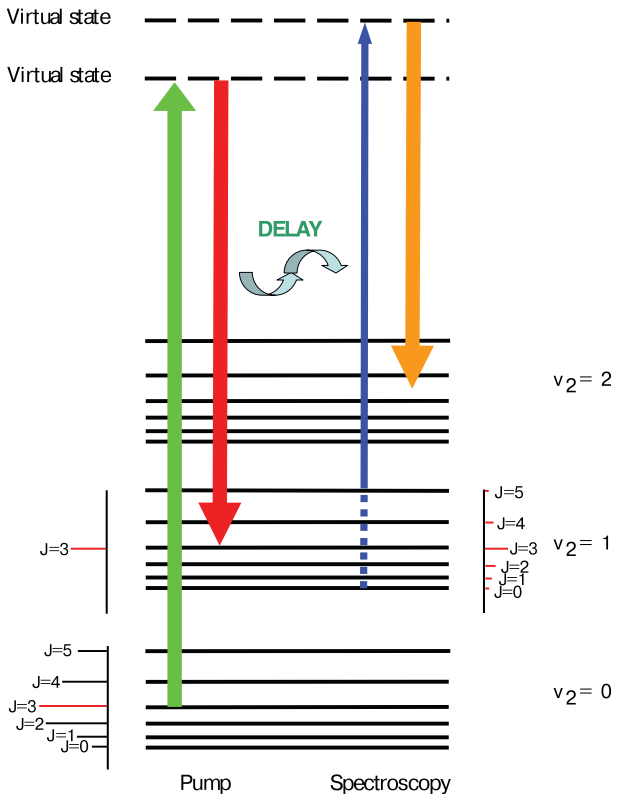

FIG. 1. Scheme of the pump-probe stimulated Raman setup.

$v_2 = 1$. The two arrows on the right side of the figure represent the laser beams that probe, by stimulated Raman spectroscopy, the population that has been deposited in $v_2 = 1$ by the pump stage and that is being redistributed among the different rotational states through collisional relaxation. A delay is introduced between pump and probe so that a few collisions have already taken place when the probe pulses arrive, and in this way rotational states other than the one initially pumped are already populated and thus visible.

The pump and probe stages of the experiment are similar to those described in our latest setup,[16] with one fixed frequency beam (in the pump stage it is a Nd:YAG laser and in the probe stage a frequency-locked Ar^+ ion laser, both represented as upward arrows in Fig. 1) and one tunable beam (the downward arrows, provided in both stages by pulsed amplification of tunable cw seeds in pulsed dye amplifiers, in turn pumped by Nd:YAG lasers). The only relevant modification introduced for the present experiment is the use of a single Nd:YAG laser to drive both the pump and probe stages, which allows considerable simplification of the setup at the expense of having to set a fixed pump-probe delay by adjusting the optical paths of the laser beams. For this experiment the delay was set to 15 ns.

The sample of ^{13}C^{12}CD$_2$ containing D^{13}C^{12}CH and H^{13}C^{12}CD as impurities was prepared by the base-catalyzed H/D exchange of H^{13}C^{12}CH with D$_2$O (99.75 at.% D, Merck) following the method reported in Ref. 19. The precursor H^{13}C^{12}CH was prepared starting from ^{12}CH$_3$^{13}CH$_2$OH (99 at.% ^{13}C, CortecNet) as detailed in Ref. 20. The ^{13}C^{12}CD$_2$ concentration in the synthesized mixture, estimated by IR

spectroscopy, was found to be >70%. The $H^{13}C^{12}CH$ concentration in the mixture was negligible. The concentrations of the symmetric isotopologues of acetylene ($^{12}C_2H_2$, $^{13}C_2H_2$, $^{12}C_2D_2$, and $^{13}C_2D_2$) were also estimated by IR and Raman spectroscopy and found to be below 1% in all cases. This is of particular importance in our experiment, given that the symmetry restrictions for ortho/para conversions in these species may also create hindered relaxation if they are present in significant amounts as collision partners.

The temperature of the coolable sample cell was set to 160 K in order to concentrate the rotational population of the ground vibrational state in a few low-J levels, thus increasing the amount of population promoted to the $v_2 = 1$ state. The experiments were conducted at pressures of 5 and 8 mbar.

RESULTS AND DISCUSSION

Figure 2(a) presents a Raman spectrum of the Q-branch of the $2\nu_2-\nu_2$ band of $^{13}C^{12}CD_2$ recorded with our setup at a pressure of 8 mbar. The asterisk indicates the rotational level of $v_2 = 1$ where all the population promoted by Raman pumping is initially deposited, in this case $J = 8$. This is also the level where a Boltzmann distribution of population has its maximum at 160 K for this molecule. While population can be observed in levels up to $J = 25$, the most striking feature of the spectrum is the fact that the intensities follow an alternating pattern for transitions departing from $J = even$ and $J = odd$ states, with the $J = even$ states favored to such an extent that this spectrum resembles that of a centrosymmetric molecule with a certain ratio of *ortho* to *para* spin varieties. However, this cannot be the case here: the rupture of the central symmetry by the introduction of an atom of ^{13}C implies that *ortho* and *para* varieties do not exist for this isotopologue. The other possibility is that 15 ns after the pumping has taken place, when the spectrum is recorded, rotational relaxation is still incomplete. To verify that this is indeed what is happening in this case, Fig. 3 presents in its upper field (a) a blowup of the most intense lines of Fig. 2(a). The lower field (b) of Fig. 3 shows the same region of the spectrum when the experiment is performed at a pressure of 5 mbar in order to decrease the number of collisions with respect to the previous measurement and obtain a picture of the system at an earlier stage of collisional relaxation. It can be seen that the overall even/odd intensity ratios are different from those in the previous spectrum, with less population having reached the $J = 9$ state. It is thus clear that the intensity alternation that appears in the spectrum is not stationary but just a consequence of incomplete rotational relaxation that is progressing at very different rates for the even and odd rotational states.

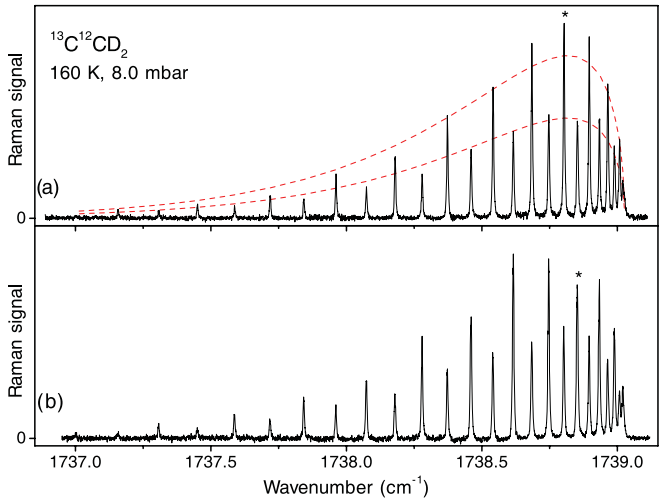

FIG. 2. Stimulated Raman spectra of the Q-branch of $2\nu_2 - \nu_2$ at 8 mbar with population pumping in (a) $J = 8$ and (b) $J = 7$. The transitions departing from the rotational levels where population is initially deposited by Raman pumping are marked with an asterisk. The dashed lines represent the intensities that would correspond to a spectrum in Boltzmann equilibrium with different scaling factors.

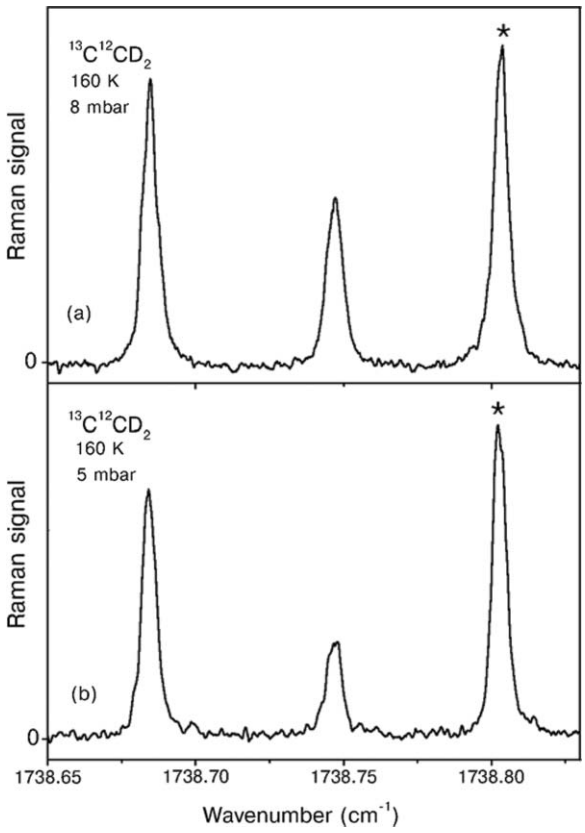

FIG. 3. Stimulated Raman spectra of a section of the Q-branch of $2\nu_2-\nu_2$ with population pumping in $J = 8$ and pressures of 8 mbar (a) and 5 mbar (b). The $Q(8)$ line is marked with an asterisk.

The dashed lines in Fig. 2(a) represent the intensities that would correspond to a Boltzmann distribution of population for $^{13}C^{12}CD_2$ at 160 K with two different normalization factors. While the overall distribution of population in the spectrum is marked by the intensity alternation, if each subset of rotational levels, even and odd, is considered separately it can be seen that the population within each one of the two subsets is already converging towards a Boltzmann distribution. It is the relative populations of the two subsets of levels the ones that are still far from equilibrium. This is a clear evidence of the existence of some sort of bottleneck in the collisional relaxation process that hinders its efficiency for collisions in which there is a change of the rotational parity, so that the time it takes for the molecules to reach thermal equilibrium within one subset of rotational levels is much shorter than the

time it takes for the two subsets to reach a state of equilibrium with each other.

In order to verify whether the even and odd rotational states are affected differently, Fig. 2(b) presents another spectrum recorded at the same pressure as the one in Fig. 2(a) but under different pumping conditions. An odd rotational level, $J = 7$, has been initially populated for comparison. The result after 15 ns is a Raman spectrum that shows a distribution of rotational population that favors the $J = odd$ states. The comparison with the spectrum in Fig. 2(a) clearly demonstrates that the favored rotational levels are always those who have the same rotational parity, whether $J = even$ or $J = odd$, as the one initially populated.

To put the different rates of relaxation in perspective one can use *ortho*-acetylene ($^{12}C_2H_2$), for which there exist accurate rotational relaxation data at 155 K, and extrapolate and compare these data to $^{13}C^{12}CD_2$. For example, the total depopulation rate for $J = 7$ in *ortho*-$^{12}C_2H_2$ has been measured to be 37.08 μs^{-1} $mbar^{-1}$.[16] When corrected for the reduced mass of $^{13}C^{12}CD_2$, this figure becomes 35.1 μs^{-1} $mbar^{-1}$. At a pressure of 8 mbar and for a pump-probe delay of 15 ns, this would equate to 4.2 effective collisions. As previous works in $^{12}C_2H_2$ show, this number of collisions should be enough to reach, from the single initially populated level, a distribution of population that already approaches a Boltzmann distribution. This is indeed what the spectra in both fields of Fig. 2 show for each subset of rotational levels when they are considered independently. While this is only a rough numerical estimate, it would appear that rotational relaxation between levels of the same parity in $^{13}C^{12}CD_2$ is taking place at rates that are similar to (or at least not much slower than) those of *ortho*-$^{12}C_2H_2$. Relaxation between states of different parity, on the other hand, is anomalously slow when compared to *ortho*-$^{12}C_2H_2$.

The conclusion of these observations is that there exists a bottleneck in collisional relaxation that has the form of a $\Delta J = even$ propensity rule, making relaxation between levels with different rotational parity much less efficient than relaxation between levels of the same parity. This constitutes, to our knowledge, the first observation of homonuclear propensity in a polyatomic molecule.

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