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Theory of nuclear-spin conversion in ethylene

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A theoretical analysis of nuclear-spin conversion in ethylene $^{13}CCH_4$ has been performed. The conversion rate was found to be $\simeq 3\times10^{-4}$ s^{-1}/Torr, which is in qualitative agreement with the recently obtained experimental value. It was shown that the ortho-para mixing in $^{13}CCH_4$ is dominated by spin-rotation coupling. Mixing of only two pairs of ortho-para levels was found to contribute significantly to the spin conversion.

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I. INTRODUCTION

Nuclear-spin isomers of molecules were discovered nearly 70 years ago when ortho and para hydrogen isomers were separated for the first time. Although it was realized already at the time of that discovery that many other symmetrical molecules have nuclear-spin isomers too, until recently almost nothing was known about isomers of molecules heavier than hydrogen. This is because of the lack of practical separation methods. The separation method based on deep cooling was applicable to hydrogen (and deuterium) but failed in the case of heavier molecules. Presently, a few new methods for spin isomer separation have been proposed and successfully tested, which has advanced this field significantly. Yet we are at the very early stage of this research. The list of molecules for which the nuclear-spin isomers have been separated is rather short: H_2 [1], CH_3F [2], H_2O [3], CH_2O [4], Li_2 [5], H_3^+ [6], and C_2H_4 [7].

The CH_3F molecule occupies a special place in this list because it is the only polyatomic molecule for which the isomer conversion mechanism has been identified. The CH_3F spin isomers appeared to be extremely stable, surviving $\sim 10^9$ gas collisions. Nevertheless, the isomer conversion was found to be based on ortho-para state mixing induced by tiny intramolecular hyperfine interactions and interruption of this mixing by collisions. This specific type of relaxation was referred to as quantum relaxation. It is essential for the physics of molecular spin isomers to understand which processes are responsible for the spin conversion in other molecules.

Recently the first separation of nuclear-spin isomers of ethylene $^{13}CCH_4$ has been performed [7]. The conversion rate has been determined and it was shown that the rate increases proportional to the gas pressure, $\gamma/P \simeq 5\times10^{-4}$ s^{-1}/Torr. An understanding of the mechanism of the conversion in ethylene needs theoretical investigation of the process.

In the present paper, we perform a theoretical analysis of the spin conversion in ethylene molecules. The purpose is to verify the consistency of the experimental data on isomer conversion in ethylene with the conversion by quantum relaxation. We consider the same isotope species, $^{13}CCH_4$, for which the experiment was done [7]. An essential difference of the present study from the well-understood case of CH_3F molecules is that now we have to work with an asymmetric-top molecule. This appeared to be much more complicated than the case of symmetric-top molecules. We would like to point out that spin conversion in asymmetric tops was considered theoretically previously for the CH_2O and H_2O molecules [8].

II. ISOMER CONVERSION BY QUANTUM RELAXATION

Although the spin conversion in molecules by quantum relaxation is explained in other publications, we will describe briefly its essence here for the convenience of the reader. At room temperature, almost all molecules are in their ground electronic and vibrational states. Suppose that these states are separated into two subspaces, namely the nuclear-spin ortho and para states, as is shown in Fig. 1 for the particular case of $^{13}CCH_4$. Note that some molecules may have more than two nuclear-spin isomer forms, e.g., methane or normal ethylene. On the other hand, many molecules, e.g., H_2, CH_3F, and $^{13}CCH_4$ too, have just two type of spin species.

The relaxation process that we are going to consider has two main ingredients. First, the ortho and para quantum states of the test molecules are not completely independent. There is a small *intramolecular* perturbation, $\hat{V}$, which is able to mix the ortho and para states. This perturbation can mix, in general, many ortho-para level pairs. But in Fig. 1, the mixing is important just for one pair of states, as will be the case for $^{13}CCH_4$ (see below). Second, the test molecules are embedded in an environment that is able to induce fast relaxation inside the ortho or para subspace, but is not able to produce direct transitions between these subspaces. This implies that the relevant cross section $\sigma(\text{ortho}|\text{para})=0$. The relaxation by direct transitions is the process opposite to the quantum relaxation.

The isomer conversion by quantum relaxation consists of the following. Suppose that at the instant $t=0$ a test molecule is placed in the ortho subspace. Due to collisions with surrounding particles, the test molecule starts to perform fast migration among rotational states inside the ortho subspace. This is the familiar rotational relaxation. This running up and down along the ladder of the ortho states con-

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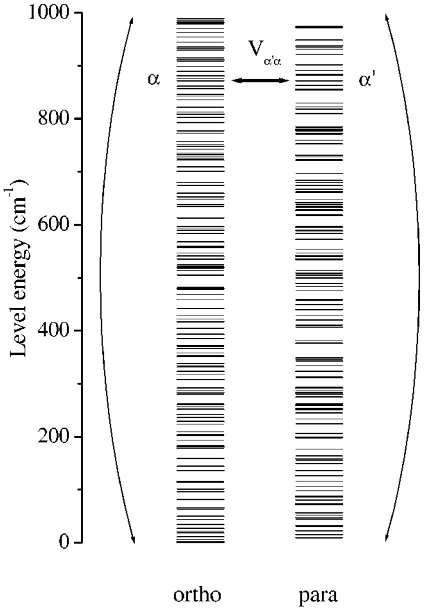

FIG. 1. The ortho and para states of the $^{13}CCH_4$ molecules. The bent lines indicate the rotational relaxation inside the two subspaces. $V_{\alpha'\alpha}$ refers to the intramolecular mixing of the ortho and para states. The indicated pair of states is the most important one for the spin conversion in $^{13}CCH_4$.

tinues until the molecule jumps in the state α, which is mixed by an *intramolecular* perturbation with the energetically close para state α'. During the free flight after this collision, para state α' will be admixed to the ortho state α. Consequently, the next collision can transfer the molecule to other para states and thus localizes it inside the para subspace. Such a mechanism of spin isomer conversion was proposed in the theoretical work by Curl *et al.* [8] (see also [9]).

The quantum relaxation of spin isomers can be quantitatively described in the framework of the kinetic equation for the density matrix [9]. One needs to split the molecular Hamiltonian into two parts,

$$\hat{H}=\hat{H}_0+\hat{V}, \tag{1}$$

where the main part of the Hamiltonian, $\hat{H}_0$, has pure ortho and para states as the eigenstates; the perturbation $\hat{V}$ mixes the ortho and para states. If initially a nonequilibrium concentration of, say, ortho molecules $\delta\rho_o(t=0)$ is created, the system will relax then exponentially, $\delta\rho_o(t)=\delta\rho_o(0)e^{-\gamma t}$, with the rate

$$\gamma=\sum_{a'\in p,a\in o}\frac{2\Gamma F(a'|a)}{\Gamma^2+\omega_{a'a}^2}[W_p(\alpha')+W_o(\alpha)],$$

$$F(a'|a)\equiv\sum_{\nu'\in p,\nu\in o}|V_{\alpha'\alpha}|^2. \tag{2}$$

The sets of quantum numbers $\alpha'\equiv\{a',\nu'\}$ and $\alpha\equiv\{a,\nu\}$ consist of the degenerate quantum numbers ν',ν and the quantum numbers a',a, which determine the energy of the states. In Eq. (2), Γ is the decay rate of the off-diagonal density-matrix element $\rho_{\alpha'\alpha}(\alpha'\in\text{para};\alpha\in\text{ortho})$ assumed here to be equal for all ortho-para level pairs; $\omega_{a'a}$ is the gap between the states a' and a; $W_p(\alpha')$ and $W_o(\alpha)$ are the Boltzmann factors of the corresponding states. For the following, it is convenient to introduce the *strength of mixing*, $F(a'|a)$, which sums the intramolecular couplings over all degenerate states.

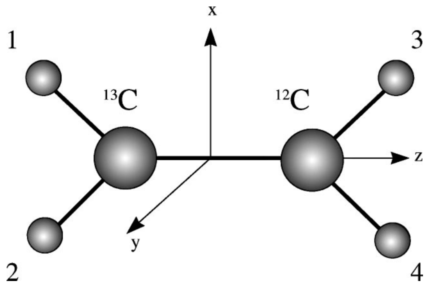

FIG. 2. Numbering of atoms in $^{13}CCH_4$ and orientation of the molecular system of coordinates.

III. ROTATIONAL STATES OF ETHYLENE

Ethylene is a popular object in high-resolution infrared spectroscopy. This fortunate circumstance made available rather accurate data on molecular parameters and position of molecular rotational levels. The molecular structure, numbering of hydrogen atoms, and orientation of the molecular system of coordinates are presented in Fig. 2. $^{13}CCH_4$ is a plane, prolate, nearly symmetric top having the symmetry point group C_{2v}. The characters of the group operations and the irreducible representations are given in Table I. We give in Table I also two isomorphic groups, molecular symmetry group $C_{2v}(M)$[10] and the point group D_2. The bond lengths and angles that were used in our calculation are as follows: $r_{\text{CH}}=1.087$ Å, $r_{\text{CC}}=1.339$ Å, and the angle $\alpha_{\text{H-C-H}}=117.4°$ [11].

The fact that the ethylene molecule is an asymmetric top complicates in two aspects the theoretical analysis of the isomer conversion. First, the energy levels and wave functions for asymmetric tops can be found only numerically but not analytically, as is possible for symmetric-top molecules. Second, the rotational quantum number k (projection of molecular angular momentum on the molecular symmetry axis)

TABLE I. The character table for the symmetry groups C_{2v}, $C_{2v}(M)$, D_2 and classification of the basis states (5).

$C_{2v}(M)$	E	$(12)(34)$	E^*	$(12)(34)^*$	ortho	ortho	para
C_{2v}	E	C_2	σ_v	σ'_v			
D_2	E	R_z^π	R_y^π	R_x^π	K even	$K=0$	K odd
A_1	1	1	1	1	$p=0$	J,p-even,	
B_2	1	-1	-1	1			$p=1$
A_2	1	1	-1	-1	$p=1$	J,p-odd	
B_1	1	-1	1	-1			$p=0$

becomes an approximate quantum number in asymmetric tops. Consequently, one should calculate numerically more ortho-para matrix elements than in the conversion of symmetric-top molecules; see, e.g., [9].

Rotational states of ^{13}CCH$_4$ can be determined using the Hamiltonian of Watson [12] and the set of molecular parameters from Refs. [13,14]. The rotational Hamiltonian up to sixth-order terms has the form [12]

$$\begin{aligned}\hat{H}_0 = {} & \tfrac{1}{2}(B+C)\mathbf{J}^2+[A-\tfrac{1}{2}(B+C)]J_z^2-\Delta_J(\mathbf{J}^2)^2-\Delta_{JK}\mathbf{J}^2J_z^2-\Delta_K J_z^4\\ & +H_J(\mathbf{J}^2)^3+H_{JK}(\mathbf{J}^2)^2J_z^2+H_{KJ}\mathbf{J}^2J_z^4+H_K J_z^6\\ & +\tfrac{1}{4}(B-C)F_0-\delta_J\mathbf{J}^2F_0-\delta_K F_2+h_J(\mathbf{J}^2)^2F_0+h_{JK}\mathbf{J}^2F_2+h_K F_4,\end{aligned} \tag{3}$$

where $\mathbf{J}$, J_x, J_y, and J_z are the molecular angular momentum operator and its projections on the molecular axes. The B, C, and A are the parameters of a rigid top that characterize the rotation around the x, y, and z molecular axes, respectively (see Fig. 2). The rest of the parameters account for the centrifugal distortion effects [12]. In Eq. (3), the following notation was used:

$$F_n \equiv J_z^n(J_x^2-J_y^2)+(J_x^2-J_y^2)J_z^n. \tag{4}$$

The Hamiltonian (3) can be diagonalized for each value of J and M in the basis of the symmetric-top quantum states $|J,k,M\rangle$ $(-J\leqslant k\leqslant J)$, where J, k, and M are the quantum numbers of the angular momentum, its projection on the molecular symmetry axis, and on the laboratory quantization axis, respectively. The Hamiltonian (3) has matrix elements diagonal in k due to the first two lines and matrix elements having $|\Delta k|=2$. The calculations of the rotational eigenstates can be simplified if one uses the Wang basis [15] with $K=|k|$:

$$|\alpha,p\rangle=\frac{1}{\sqrt{2}}[|\alpha\rangle+(-1)^{J+K+p}|\overline{\alpha}\rangle],\quad 0<K\leqslant J,$$

$$|\alpha_0,p\rangle=\frac{1+(-1)^{J+p}}{2}|\alpha_0\rangle,\quad K=0. \tag{5}$$

Here $p=0,1$ and the sets of quantum numbers are $\alpha \equiv\{J,K,M\}$, $\overline{\alpha}\equiv\{J,-K,M\}$, and $\alpha_0\equiv\{J,K=0,M\}$. Depending on the parity of J, K, and p, the states (5) generate four different irreducible representations of the molecular symmetry group D_2 (Table I). The molecular Hamiltonian is fully symmetric (symmetry A_1). Consequently, the matrix elements between the states of different symmetry disappear. Thus diagonalization of the total Hamiltonian in the basis of Eqs. (5) is reduced to the diagonalization of four independent submatrices, each for the states of particular symmetry. The rotational states of asymmetric top can be expanded over the basis states (5),

$$|\beta,p\rangle=\sum_K A_K|\alpha,p\rangle, \tag{6}$$

where A_K stands for the expansion coefficients. The summation index, K, is given explicitly in Eq. (6), although A_K depends on the other quantum numbers as well. All coefficients in the expansion (6) are real numbers because the Hamiltonian (3) is symmetric in the basis $|\alpha,p\rangle$.

There are a few schemes for practical classification of the rotational states of asymmetric tops [16]. In this paper, we will use the scheme that is somewhat better adapted to the description of nuclear-spin isomers. We will designate the rotational states of the asymmetric top by indicating p, J, and prescribing the allowed K values to the eigenstates keeping both in ascending order. For example, the eigenstate having $p=0,J=20$, and $K=0,2,4,\ldots,20$ in the expansion (6) and being the third in ascending order will be designated by $\mathcal{K}=4$. (Note the difference between the two characters K and $\mathcal{K}$.) It gives unambiguous notation of rotational states for

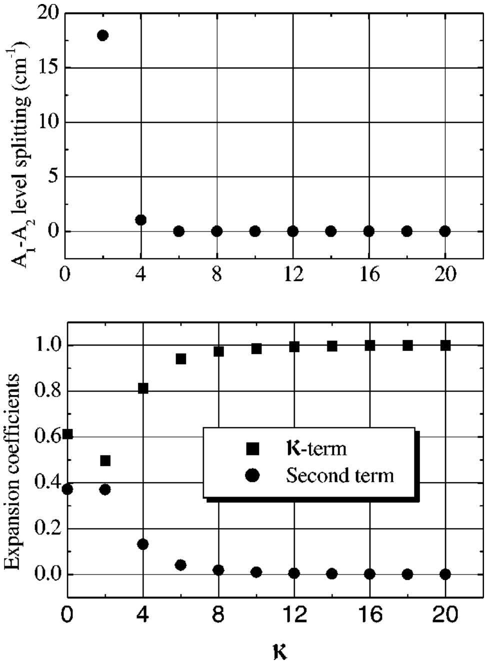

FIG. 3. Properties of asymmetric-top rotational states. The upper panel gives splitting between the states $(0,J=20,\mathcal{K})$ and $(1,J=20,\mathcal{K})$. The lower panel gives squared values of the two terms in the expansion (6) for the state $(0,J=20,\mathcal{K})$. "$\mathcal{K}$ term" is $A^2_{K=\mathcal{K}}$. "Second term" is the second biggest coefficient in each expansion.

each of the four species A_1, A_2 ($\mathcal{K}$ even) and B_1,B_2 ($\mathcal{K}$ odd). This classification establishes the connection with the prolate symmetric top for which $\mathcal{K}=K$. One should remember that the physical meaning of the quantum number $\mathcal{K}$ is clearly limited. To illustrate this, we consider as an example the rotational states of A_1 and A_2 symmetry ($\mathcal{K}$ even) for $J=20$. The upper panel in Fig. 3 shows that the energy of the rotational states is not determined solely by $\mathcal{K}$, as it would be for a rigid symmetric top. The graph shows the difference in energy between rotational states A_1 and A_2 having the same $\mathcal{K}$ number but different quantum numbers *p*. The states A_1, $\mathcal{K}=0$ and A_2, $\mathcal{K}=0$ are omitted from the graph because the latter state does not exist. As is seen from the data, the splitting is significant for low values of $\mathcal{K}$ and rapidly disappears as $\mathcal{K}$ increases. Note that the A_1 and A_2 states for a rigid symmetric-top molecule would be degenerate for all $\mathcal{K}$.

The low panel in Fig. 3 illustrates the property of the eigenstate expansions over the basis states (5). In this panel, the squared magnitude of the two A_K coefficients in each eigenstate of the symmetry A_1 ($J=20$) is given. The first one (''$\mathcal{K}$-term'' in Fig. 3) is A_K^2 having $K=\mathcal{K}$. These coefficients appear to be the biggest coefficients in each expansion. This adds some physical insight to the proposed classification scheme. The ''second term'' is the second biggest coefficient in the expansion. Again, at low $\mathcal{K}$ values there is more than one significant term in the expansion (6). As $\mathcal{K}$ grows, the contribution from just one term becomes predominant. Note that the same graph for a symmetric-top molecule would show only one significant term, $A_{K=\mathcal{K}}$, in the expansions of all eigenstates.

IV. ORTHO AND PARA ISOMERS OF ETHYLENE

The total molecular wave function is a product of spatial wave function and spin wave function. The nuclear-spin states in ^{13}CCH$_4$ are of A_1 and B_1 species, having the statistical weights 20 and 12, respectively. The ortho spin states (symmetry A_1) have the two hydrogen pairs (H_1-H_2 and H_3-H_4) either both in the triplet state or both in the singlet state. The para species (symmetry B_1) have one pair of protons in the singlet state but the other pair in the triplet state. Each symmetry operation of the C_{2v} group interchanges an even number of protons in ^{13}CCH$_4$. Consequently, the total wave function must be unchanged under all operations, thus belonging to the representation A_1. In order to have the total wave function of species A_1, one has to have the spatial wave function of symmetry A_1 and B_1 as the spin wave functions are. This implies that the rotational states A_1 and B_1 should be only positive (even in parity) but the rotational states A_2 and B_2 should be only negative (odd in parity).

Summarizing this discussion, we can write all possible nuclear-spin–rotational states in the ^{13}CCH$_4$ molecules. The ortho states can be represented as

$$|\mu\rangle=|\beta,p\rangle|i_{12},i_{34},i_C\rangle,\quad i_{12},i_{34}=t,s,\quad \mathcal{K}\ \text{even}. \tag{7}$$

Here i_{12}, i_{34}, and i_C designate the spin states of the two pairs of protons and the nucleus ^{13}C (Fig. 2). For ortho molecules, the spin states of the proton pairs should be either both triplet, $|t,t\rangle$, or both singlet states, $|s,s\rangle$.

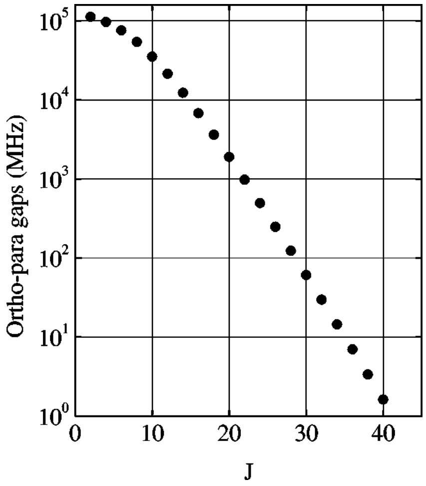

FIG. 4. Collapse of the energy gap between the ortho and para states in ethylene as a function of *J*. The figure shows the energy gaps between the ortho states $(0,J,\mathcal{K}=0)$ and the para states $(0,J,\mathcal{K}'=1)$.

The para states can be represented as

$$|\mu'\rangle=|\beta',p'\rangle|i'_{12},i'_{34},i'_C\rangle,\quad \mathcal{K}'\ \text{odd}. \tag{8}$$

For para molecules, one pair of protons is in the singlet, but the other pair is in the triplet state; thus the proton spin states are $|t',s'\rangle$ or $|s',t'\rangle$. In Eqs. (7) and (8) and below, we use unprimed parameters for ortho species and primed parameters for para species; $p=0,1$ indicates a positive or a negative sign of the state, respectively. Equations (7) and (8) imply that the ortho-para state mixing in ethylene needs coupling of states having different parity of $\mathcal{K}$.

The relative position of ortho and para states is important for the calculation of the conversion rate [see Eq. (2)]. In the case of a symmetric-top molecule, the ortho-para energy gaps can be expressed as a polynomial of *J* and *K*. This gives ''accidental'' (isolated) resonances between the ortho and para states in a symmetric top. Note that relaxation through ''accidental'' resonances is known to be important in small molecules, e.g., for singlet-triplet interconversion in Na$_2$ [17]. In the case of an asymmetric top, one has a phenomenon that can be called collapse of ortho and para states [8]. It appears in ethylene as a progressive decrease of the ortho-para energy gaps between the states of identical rotational momenta, *J*, as *J* increases. This is illustrated in Fig. 4, which shows the gaps between the ^{13}CCH$_4$ ortho states, $\mathcal{K}=0$, and the para states, $\mathcal{K}'=1$, both having positive sign $(p=0)$ and the same *J*. If such ortho-para level pairs would exist for symmetric tops, they would dominate the conversion. In the case of asymmetric tops, the situation is different. We will see below that this sequence of closed ortho-para level pairs does not produce a significant contribution to the isomer conversion in ^{13}CCH$_4$.

The Boltzmann factors $W_o(\alpha)$ and $W_p(\alpha')$ in Eq. (2) determine the relative population of rotational states in the ortho and para families,

$$\rho_\alpha = \rho_o W_o(\alpha), \quad \rho_{\alpha'} = \rho_p W_p(\alpha'), \tag{9}$$

where ρ_o and ρ_p are the total densities of ortho and para molecules, respectively. Equations (9) imply equilibrium distributions inside the ortho and para subspaces. This is fulfilled with high accuracy even if the ratio ρ_o/ρ_p is out of equilibrium because rotational relaxation is many orders of magnitude faster than the ortho-para conversion. The partition functions for ortho and para molecules at room temperature ($T = 295$ K) are found to be equal to

$$Z_{\text{ortho}} = 2.66\times 10^4, \quad Z_{\text{para}} = 1.60\times 10^4. \tag{10}$$

In the calculation of these partition functions, we took into account the degeneracy over M, nuclear spins, including also spin of nucleus ^{13}C, parity of states, as well as the restrictions imposed by quantum statistics.

V. ORTHO-PARA STATE MIXING

In the present paper, we will consider the ortho-para conversion induced by the two hyperfine interactions, viz., magnetic dipole-dipole interaction between the molecular nuclei (spin-spin interaction, $\hat{V}_{\text{SS}}$) and the nuclear-spin-rotation interaction, $\hat{V}_{\text{SR}}$. Thus the total intramolecular perturbation able to mix the ortho and para states is

$$\hat{V} = \hat{V}_{\text{SS}} + \hat{V}_{\text{SR}}. \tag{11}$$

All matrix elements of $\hat{V}$ are diagonal in parity p.

A. Nuclear–spin-spin coupling

The ortho-para conversion in molecules induced by nuclear–spin-spin coupling were investigated in [8,9] (for other references, see the review [18]). The spin-spin Hamiltonian for the two magnetic dipoles μ_1 (having spin $I^{(1)}$) and μ_2 (having spin $I^{(2)}$) separated by the distance r has the form [15]

$$\hat{V}_{12} = P_{12}\mathbf{T}^{(12)} \quad : \quad \hat{\mathbf{I}}^{(1)}\hat{\mathbf{I}}^{(2)},$$

$$T^{(12)}_{ij} = \delta_{ij} - 3n_i n_j, \quad P_{12} = \mu_1\mu_2/r^3 I^{(1)} I^{(2)}, \tag{12}$$

where $\hat{\mathbf{I}}^{(1)}$ and $\hat{\mathbf{I}}^{(2)}$ are the spin operators of the particles 1 and 2, respectively, $\mathbf{n}$ is the unit vector directed along $\mathbf{r}$ and i and j are the Cartesian indices. The second-rank tensor $\mathbf{T}^{(12)}$ in Eqs. (12) represents a spatial part of the spin-spin interaction. The second-rank tensor $\hat{\mathbf{I}}^{(1)}\hat{\mathbf{I}}^{(2)}$ acts on spin variables.

The total spin-spin interaction in ^{13}CCH$_4$ is composed from the interactions between all pairs of molecular nuclei. One can show that the spin-spin interactions between the protons 1-3, 2-4, 1-2, and 3-4 have a spatial part that can mix the quantum states only if they have K numbers of the same parity. Consequently, these terms do not contribute to the ortho-para state mixing in ethylene. The complete nuclear–spin-spin interaction in ^{13}CCH$_4$ able to mix the ortho and para states reads

$$V_{\text{SS}} = V^{(14)}_{\text{SS}} + V^{(23)}_{\text{SS}} + V^{(C1)}_{\text{SS}} + V^{(C2)}_{\text{SS}} + V^{(C3)}_{\text{SS}} + V^{(C4)}_{\text{SS}}. \tag{13}$$

Here the upper indices refer to the hydrogen nuclei in the molecule 1, . . . , 4 and to the nucleus ^{13}C, which has a spin equal to $\frac{1}{2}$ (see Fig. 2). Calculation of the spin-spin matrix elements can be simplified by a few observations, which we discuss in more detail for the perturbations $V^{(14)}_{\text{SS}}$ and $V^{(23)}_{\text{SS}}$. First, one can prove by applying the proper symmetry operation that

$$\langle \mu' | V^{(14)}_{\text{SS}} | \mu\rangle = \langle \mu' | V^{(23)}_{\text{SS}} | \mu\rangle. \tag{14}$$

Next, the two out of four matrix elements between the ortho and para spin states vanish,

$$\langle t', s' | V^{(14)}_{\text{SS}} | s, s\rangle = \langle s', t' | V^{(14)}_{\text{SS}} | s, s\rangle = 0, \tag{15}$$

because in these two cases one has the matrix elements of a vector (spin operator) between the states both having zero spin. On the other hand, the remaining two matrix elements are equal to each other,

$$\langle t', s' | V^{(14)}_{\text{SS}} | t, t\rangle = \langle s', t' | V^{(14)}_{\text{SS}} | t, t\rangle. \tag{16}$$

To summarize, one can conclude that the variety of matrix elements for the operators $V^{(14)}_{\text{SS}}$ and $V^{(23)}_{\text{SS}}$ is reduced to one matrix element, e.g., $\langle \beta', p, t', s' | V^{(14)}_{\text{SS}} | \beta, p, t, t\rangle$. Obviously, the carbon spin state, which is omitted in this expression for simplicity, should be unchanged in this matrix element.

Further, we write this matrix element using an expansion over symmetric-top states (6),

$$\langle \beta', p, t', s' | V^{(14)}_{\text{SS}} | \beta, p, t, t\rangle = \langle t', s' | \left[\sum_{K',K} A'_{K'} A_K \langle \alpha', p | V^{(14)}_{\text{SS}} | \alpha, p\rangle \right] | t, t\rangle. \tag{17}$$

This expression reduces the calculation of the spin-spin matrix elements in asymmetric tops to the calculation of symmetric-top matrix elements. Solution for the latter can be found in [9], which allows one to express the strength of mixing in ethylene by $\hat{V}_{\text{SS}}$ as

$$F_{\text{SS}}(a'|a) = (2J'+1)(2J+1)\mathcal{T}^2 \times \left| \sum_{K>0,q} q A'_{K+q} A_K \begin{pmatrix} J' & 2 & J \\ -K-q & q & K \end{pmatrix} + \frac{1+(-1)^{J+p}}{\sqrt{2}} A'_1 A_0 \begin{pmatrix} J' & 2 & J \\ -1 & 1 & 0 \end{pmatrix} \right|^2. \tag{18}$$

Here $q = \pm 1$; $(:::)$ stands for the $3j$ symbol, and the following notation was used:

$$\mathcal{T}^2 = 2|P_{14}\mathcal{T}^{(14)}_{2,1}|^2 + 2|P_{C1}\mathcal{T}^{(C1)}_{2,1}|^2 + 2|P_{C3}\mathcal{T}^{(C3)}_{2,1}|^2,$$

$$\mathcal{T} = 45.4 \text{ kHz}, \tag{19}$$

where P factors are equivalent to the similar factor in Eq. (12); $\mathcal{T}^{(mn)}_{2,1}$ are the spherical components of the corresponding $\mathbf{T}$ tensor calculated in the molecular frame. The numerical value of $\mathcal{T}$ was found using molecular structure from [11]. The selection rules for the spin-spin mixing in ethylene read

$$\Delta p = 0, \quad |\Delta J| \leqslant 2, \tag{20}$$

and, in addition, the parity of $\mathcal{K}'$ and $\mathcal{K}$ is opposite.

B. Spin-rotation coupling

Ortho-para conversion in molecules induced by spin-rotation coupling was studied in [8,19,20] (more references can be found in [18]). Nuclear–spin-rotation coupling in molecules is due to magnetic fields produced by the molecular electrical currents. The spin-rotation perturbation can be represented as [21,16,20]

$$\hat{V}_{\mathrm{SR}} = \frac{1}{2}\left(\sum_i \hat{\mathbf{I}}^{(i)} \cdot \mathbf{C}^{(i)} \cdot \hat{\mathbf{J}} + \mathrm{H.c.} \right), \quad i = 1,2,3,4. \tag{21}$$

For the spin-rotation perturbation relevant to the ortho-para mixing, the index i should refer only to the hydrogen nuclei.

The calculation of the second-rank spin-rotation tensor $\mathbf{C}$ is rather a complicated problem that is not yet solved completely. We will use the following estimation of $\mathbf{C}$. First we note that contribution to the spin-rotation coupling arising from the electric fields in the molecule has been shown to be very small compared to the part having ‘‘magnetic’’ origin and can be neglected [22]. Then, we split the $\mathbf{C}$ tensor arising from magnetic fields of the moving charges into two parts,

$$\mathbf{C} = {}^{e}\mathbf{C} + {}^{n}\mathbf{C}, \tag{22}$$

produced by the molecular electrons and nuclei, respectively. The nuclear contribution, ${}^{n}\mathrm{C}$, is obtained as a first-order average in the vibrational ground state, and depends only on the nuclear coordinates. In contrast, the electron part, ${}^{e}\mathrm{C}$, is a second-order series expansion that involves the full electronic spectrum. Fortunately, the xz and zx components, which are responsible for the mixing of states having $\Delta K = 1$ in C_2H_4 vanish by symmetry [20].

Therefore, the $\mathbf{C}$ tensor effective in ortho-para conversion can be approximately written (in Hz) for the ith proton as [22]

$$\mathrm{C}^{(i)} = \sum_{k \neq i} b_k [(\mathbf{r}_k \cdot \mathbf{R}_k)\mathbf{1} - \mathbf{r}_k \mathbf{R}_k] \cdot \mathbf{B},$$

$$b_k = 2\mu_p q_k / c\hbar R_k^3, \tag{23}$$

where $\mathbf{R}_k$ is the radial distance from the proton $\mathrm{H}^{(i)}$ to the charge k, $\mathbf{r}_k$ is the radial from the center of mass to the particle k, q_k are the nuclei charges, and $\mathbf{B}$ is the inverse inertia tensor. $\mathbf{B}$ is a diagonal matrix having the elements $B_{xx} = 58.6$ GHz, $B_{yy} = 48.7$ GHz, and $B_{zz} = 291.9$ GHz. The index k runs here over all nuclei in the molecule except for the proton i.

The spherical components of the spin-rotation tensor of the rank $l (l = 1,2)$ for the ith proton calculated in the molecular frame, $\mathcal{C}^{(i)}_{l,q}$, can be determined using Eq. (23). For the ethylene molecular structure from Ref. [11] and bare nuclear charges, these components are

$$\mathcal{C}^{(1)}_{2,1} = 3.8 \ \mathrm{kHz}, \quad \mathcal{C}^{(1)}_{1,1} = -2.9 \ \mathrm{kHz},$$

$$\mathcal{C}^{(3)}_{2,1} = -4.1 \ \mathrm{kHz}; \quad \mathcal{C}^{(3)}_{1,1} = 3.2 \ \mathrm{kHz}. \tag{24}$$

The differences between the absolute values of $\mathcal{C}^{(1)}_{l,q}$ and $\mathcal{C}^{(3)}_{l,q}$ appear because of the shift of the molecular center of mass caused by the bigger mass of ${}^{13}\mathrm{C}$ in comparison with ${}^{12}\mathrm{C}$.

Similar to the preceding section, one can reduce the calculation of the matrix elements of the spin-rotation coupling in asymmetric tops to the calculation of the symmetric-top matrix elements. The latter can be found in [19,20,23]. Thus one has the strength of mixing due to the spin-rotation coupling in ethylene,

$$F_{\mathrm{SR}}(a'|a) = 2(2J'+1)(2J+1) \times \sum_i \left| \sum_{K>0,q} A'_{K+q} A_K \Phi(i;J',K+q|J,K) + \frac{1+(-1)^{J+p}}{\sqrt{2}} A'_1 A_0 \Phi(i;J',1|J,0) \right|^2. \tag{25}$$

Here $q = \pm 1$; $i = 1,3$ denotes the hydrogen nuclei 1 and 3. Note that the protons 2 and 4 were also taken into account because they produce mixing equal to that of protons 1 and 3. In Eq. (25), the following notation was used:

$$\Phi(i;J',K'|J,K) = \sum_l \sqrt{2l+1}\, \mathcal{C}^{(i)}_{l,q} \begin{pmatrix} J' & l & J \\ -K' & q & K \end{pmatrix} \times \left[y(J)(-1)^l \begin{Bmatrix} J' & J & l \\ 1 & 1 & J \end{Bmatrix} + y(J') \times \begin{Bmatrix} J & J' & l \\ 1 & 1 & J' \end{Bmatrix} \right], \tag{26}$$

where $\{: \ : \ :\}$ stands for the $6j$ symbol and $y(J) = \sqrt{J(J+1)(2J+1)}$. The selection rules for the ortho-para mixing by the spin-rotation perturbation in ethylene read

$$\Delta p = 0, \quad |\Delta J| \leqslant 1. \tag{27}$$

And again, the parity of $\mathcal{K}'$ and $\mathcal{K}$ is opposite.

VI. CONVERSION RATES

The decoherence rate Γ is another important parameter for the isomer conversion by quantum relaxation [see Eq. (2)]. This parameter is rather difficult to calculate or to measure. Due to its physical meaning, the value of Γ is close to the rotational state population decay, which determines the line broadening in microwave rotational spectra. Unfortunately, ethylene does not have pure rotational spectra be-

TABLE II. The most important ortho-para levels and their contributions to the spin conversion in ethylene. In calculations, the molecular parameters from [14] and molecular structure from [11] were used. The total rate combines the contributions from all ortho-para level pairs having $J \leqslant 40$.

Level pair $p',J',\mathcal{K}'$-$p,J,\mathcal{K}$	Energy (cm^{-1})	$\omega/2\pi$ (MHz)	F_{SS} (MHz^2)	F_{SR} (MHz^2)	γ/P (10^{-4} s^{-1}/Torr)
1,27,7-1,28,6	871.53	1006.7	4.0×10^{-2}	4.4	2.49
0,27,7-0,28,6	871.69	-3435.5	4.0×10^{-2}	4.4	0.21
0,4,3-0,6,2	53.72	-3180.6	1.1×10^{-3}	0	3.3×10^{-3}
1,26,3-1,24,6	680.68	944.3	3.3×10^{-4}	0	5.3×10^{-4}
0,20,1-0,20,0	356.02	1894.4	6.9×10^{-8}	2.4×10^{-6}	4.8×10^{-6}
Total rate					2.70

cause it has no permanent electric dipole moment, or, to be precise, a very small dipole moment in the case of $^{13}\mathrm{CCH}_4$.

In the present calculations, we take the estimation of Γ from the line broadening in infrared spectra, for which the information is available. Recently, the line broadening was accurately measured for $\mathrm{C_2H_4}$ embedded in nitrogen [24]. One should not expect a big difference for the line broadening between the isotopic species $\mathrm{C_2H_4}$ and $^{13}\mathrm{CCH}_4$. From the data [24] one can estimate the decoherence rate as

$$\Gamma/P = 2\times10^{7}\ \ \mathrm{s}^{-1}\mathrm{Torr}. \tag{28}$$

This rate is 10 times smaller than the Γ determined for the isomer conversion in $\mathrm{CH_3F}$ [25]. This is because ethylene is not a polar molecule and thus has slower rotational relaxation. Probably, the estimation (28) is too low for the case of pure ethylene gas because ethylene has a polarizability larger than nitrogen. For the buffer gases having a large polarizability, like Kr or $\mathrm{SF_6}$, nearly three times bigger line broadening was found [26]. Nevertheless, we will use the estimation (28), which can be considered as a lower limit for Γ.

Now we are ready to calculate the conversion rate in ethylene. The final expression for the conversion rate, γ, is again given by Eq. (2), which has the strength of mixing, $F(a'|a) = F_{\mathrm{SS}}(a'|a) + F_{\mathrm{SR}}(a'|a)$. The results of the calculations are given in Table II. From these data, we note that there is no appreciable contribution to the conversion from the collapsing ortho-para level pairs presented in Fig. 4. Another observation is that the contribution from the mixing of states having $|\Delta\mathcal{K}|\rangle 1$ is also small. This is the consequence of the fact that the ethylene molecule is rather close to a symmetric top. The main contributions to the conversion come from just two level pairs, both having the same quantum numbers $(J',\mathcal{K}')$-$(J,\mathcal{K})$, but different p. The most important ortho-para level pair (1,27,7)-(1,28,6) has the frequency gap $\simeq 1.0$ GHz. This level pair is indicated in Fig. 1, from which one can see that this pair of states is situated at rather high energies. Nearly 10% of the conversion rate is due to the pair (0,27,7)-(0,28,6). This level pair has the same strength of mixing as the first pair but a three times bigger level splitting, ω. The properties of the states $(1,J=28,\mathcal{K}=6)$ and $(1,J=27,\mathcal{K}=7)$ are illustrated in Fig. 5, which presents the expansion coefficients, A_K, for these states. One can note that the biggest coefficient in both expansions has the value of K equal to the value of $\mathcal{K}$ chosen for the designation of the eigenstate in our classification scheme.

The total conversion rate in $^{13}\mathrm{CCH}_4$, which is the sum over all ortho-para level pairs having J' and J up to 40, was found to be equal to

$$\gamma/P = 2.7\times10^{-4}\ \ \mathrm{s}^{-1}/\mathrm{Torr}. \tag{29}$$

This rate is close to the experimental value $(5.2\pm0.8)\times10^{-4}$ s^{-1}/Torr [7]. Note, however, that the value for Γ used [see Eq. (28)] was considered a lower limit. A somewhat higher value of Γ would make the agreement with experiment even better.

The calculations of the conversion rates were repeated using less accurate molecular parameters from [13]. We obtained essentially the same results. The conversion is again determined by the same two level pairs and the value of the total conversion rate is 3.5×10^{-4} s^{-1}/Torr, which is close to the more precise value (29).

Our model allows us to determine the pressure dependence of the conversion rate in $^{13}\mathrm{CCH}_4$ at the conditions of the experiment [7]. By comparing the level splitting of the most important ortho-para level pair (1,27,7)-(1,28,6), which is $\sim$1.0 GHz, with the decoherence rate (28), one can conclude that the case corresponds to the limit $\Gamma \ll \omega$. From Eq.

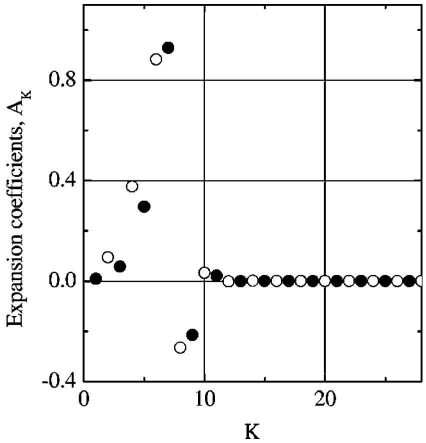

FIG. 5. The expansion coefficients, A_K, for the states most important for the spin conversion in $^{13}\mathrm{CCH}_4$. ○, ortho state $(1,J=28,\mathcal{K}=6)$; (●) para state $(1,J=27,\mathcal{K}'=7)$.

(2), one can see that in this limit the conversion rate, γ, should grow linearly with increasing gas pressure. (Note that Γ is proportional to the gas pressure.) This dependence was indeed observed in the experiment [7].

The magnitude of the calculated conversion rate relies heavily on the determination of the ortho-para level splitting. The gap of the most important level pair appeared to be rather large, $\simeq 1.0$ GHz, and it is unlikely that it has been determined with significant error. This can be proven by comparing this splitting with the one calculated using less accurate molecular parameters [13]. These parameters give the gap 0.914 GHz, which is close to the value given in Table II.

The two sources of the ortho-para mixing have been analyzed. The spin-spin interaction between the molecular nuclei could be calculated rather accurately. The uncertainty of this perturbation is mainly due to small errors in the knowledge of the molecular structure. On the other hand, our analysis has shown that the spin-spin coupling contributes less than 1% to the ethylene conversion and is thus negligible. There are a few reasons for this reduction. First, the spin-spin tensor has a relatively small value due to the big distances between the interacting nuclei and the small magnitude of the magnetic moment of the carbon nucleus. Second, due to high symmetry of the molecular structure, interactions between many pairs of protons do not contribute to the ortho-para mixing. Moreover, there are no close ortho-para level pairs at small J, where spin-spin coupling can compete with the spin-rotation coupling.

We have taken into account also the spin-rotation perturbation. The magnitude of the spin-rotation tensor was estimated and it was demonstrated that the main contribution to the ethylene conversion comes from the spin-rotation mixing. The strong contribution from the spin-rotation coupling is due to the fact that the strength of the mixing F_{SR} grows as J^3 in comparison with the slower (J^2) growth of the spin-spin strength of mixing F_{SS}. This makes the ''accidental'' resonance at big J $(1,27,7)$-$(1,28,6)$ so important. An extra cause of the efficiency of the spin-rotation coupling is that the spin-rotation tensors of first and second rank both contribute to the conversion. On the other hand, not all close ortho-para level pairs contribute to the conversion. In the particular case of the collapsing ortho-para levels (Fig. 4), there is no strong mixing mainly because of interferences between many symmetric-top components with different quantum numbers K, and also because for these $J'=J$ pairs, the first-rank spin-rotation tensor does not contribute.

Error in the estimation of Γ introduces a systematic uncertainty into the final result. But it does not undermine the model as a whole. First, one can turn around the approach and determine which decoherence rate Γ should be chosen in order to fit the experimental data. In order to reproduce the experimental rate of conversion, one should take the decoherence rate, $\Gamma/P = 3.9\times 10^7\ \mathrm{s}^{-1}/\mathrm{Torr}$, which is less than two times different from our rough estimation (28). Of course, such an approach will be justified only when the spin-rotation perturbation in ethylene is known from an independent source. There is another point that is worth mentioning. Recently, a new approach was proposed for isomer conversion in which the knowledge of Γ is not necessary at all [27]. It is based on a fast linear sweep of the molecular levels through the ortho-para resonance. Nuclear-spin conversion in such an experimental arrangement is dependent only on the strength of ortho-para mixing and the population of the mixed states.

Finally, it seems interesting to emphasize the difference between the conversion rates produced by the two pairs of identical rotational quantum numbers (27,7)-(28,6) but with different parity. This peculiarity arises from the asymmetric top properties, where the energy of states depends on parity. This in turn has the dynamical consequence that the spin isomers equilibrate first in one parity manifold (here the odd one).

VII. CONCLUSIONS

A theoretical model for the nuclear-spin conversion in ethylene ($^{13}\mathrm{CCH}_4$) has been developed. The theory of the spin isomer conversion in asymmetric tops could be compared with experimental data for isomer conversion. We have found that the two experimental results [7], namely the magnitude of the ethylene ($^{13}\mathrm{CCH}_4$) isomer conversion rate and its pressure dependence, are consistent with the spin conversion governed by quantum relaxation. The ortho-para state mixing is caused in this molecule mainly by the coupling between the protons' spins and the molecular rotation. We have identified also the two pairs of ortho-para states which almost completely determine the spin conversion in $^{13}\mathrm{CCH}_4$.

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