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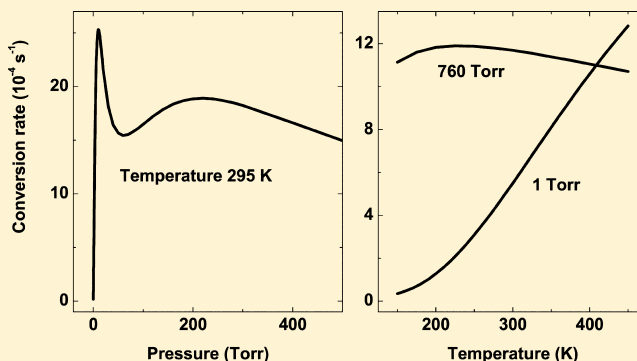
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ABSTRACT: A theoretical model of the nuclear spin isomer conversion in C_2H_4 induced by the intramolecular spin–spin interaction between hydrogen nuclei has been developed. In the ground electronic state, C_2H_4 has four nuclear spin isomers in contrast to two isomers in the molecules studied so far in this field of research. At the gas pressure of 1 Torr, the rate of conversion between isomers with the nuclear spin symmetries B_{1u} and B_{2u} was found to be $5.2 \times 10^{-4} s^{-1}$, which coincides within experimental uncertainties with the rate recently measured by Sun et al. (*Science* **2005**, *310*, 1938). It was determined that at low gas pressures the conversion is induced mainly by the mixing of only one pair of rotational states. The calculated pressure dependence of the conversion rate predicts that conversion slows down with increasing pressure at pressures higher than 300 Torr.



I. INTRODUCTION

Nuclear spin isomers of molecules (spin isomers, for short) were discovered in the late 1920s when the famous ortho and para hydrogen isomers were first separated.¹ Nuclear spin isomers of molecules occupy an important place in physics and chemistry. They have large scientific significance because they are the consequence of the fundamental physical phenomenon, the quantum statistics of identical nuclei in symmetric molecules.

New applications developed recently increased the interest in spin isomers. The use of parahydrogen in nuclear magnetic resonance spectroscopy and imaging is rapidly gaining popularity in the context of the so-called hyperpolarization techniques that can boost the sensitivity of NMR applications by several orders of magnitude. Parahydrogen-induced polarization (PHIP or PASADENA)^{2–6} provides the signal enhancement essential for the studies of the mechanisms and kinetics of homogeneous⁴ and heterogeneous^{7,8} catalytic processes by NMR. Furthermore, injection of a hyperpolarized substance in a lab animal provides the high sensitivity necessary to perform the in vivo spectroscopic and imaging studies of blood flow, tissue perfusion,^{9,10} and even cellular metabolism.¹¹ The recent introduction of the SABRE technique^{12,13} expands the range of substances that can be hyperpolarized using parahydrogen, including amino acids and peptides.¹⁴

Another interesting application of spin isomers is the measurement of hyperfine interactions in molecules. It was demonstrated that, by measuring the conversion rates in the arrangement of the level-crossing resonances,¹⁵ one can measure the hyperfine nuclear spin–spin and spin–rotation interactions.^{16,17} It is important that these types of experiments provide information about the off-diagonal tensor components

of the hyperfine interactions, in contrast to the standard measurements in spectroscopy that are sensitive to the diagonal terms of these interactions which shift the level energies.

Various physical and chemical properties of the spin isomers of molecular hydrogen were studied in detail in the 1930s.¹⁸ The striking feature of hydrogen spin isomers is their anomalously high stability. Enriched hydrogen isomers can survive for months at 1 atm pressure and room temperature. This high stability is the consequence of a weak coupling of the protons' spin with the environment, the high molecular symmetry and the large energy gaps between ortho and para states of H_2 .^{19,20}

From the time of the discovery of ortho- and parahydrogen, the existence of nuclear spin isomers in other symmetrical molecules was widely accepted and their existence was experimentally confirmed by the spectroscopic line intensity alternation effect.²¹ This effect is based on the nuclear statistical weights of different spin isomers and characterizes the static properties of the spin isomers. On the other hand, kinetic properties of isomers of molecules heavier than H_2 , e.g., spin isomer conversion, were not possible to study for a long time because of the difficulties in the enrichment of spin isomers (see, e.g., ref 22). Note that stability of nuclear spin isomers is a key issue for many applications of the isomers.

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To study the isomer conversion, one needs to create a nonequilibrium concentration of spin isomers. Enrichment of hydrogen spin isomers is easily performed at low temperatures because of the anomalously large rotational constant of H_2 .^{1,18} For molecules heavier than H_2 the cryogenic method fails and this significantly complicates the investigation of spin isomers. Nevertheless, in recent years new methods for the isomer enrichment were developed that made it possible to study spin isomers in a number of polyatomic molecules (see the review²³): $^{13}\text{CH}_3\text{F}$ and $^{12}\text{CH}_3\text{F}$,^{17,23,24} CH_2O ,²⁵ H_3^+ ,²⁶ and $^{13}\text{CCH}_4$.²⁷ In this paper we concentrate on the isomer conversion in the gas phase where properties of spin isomers are easier to understand and describe because of the free molecular rotation. We also restrict our consideration to the conversion at ambient temperature at which almost all molecules are in the ground electronic and vibrational state. Most of the experimental data for the isomer conversion under such conditions were obtained using the light-induced drift (LID) effect²⁸ as an isomer enrichment method.

Important experimental data were obtained recently by Sun et al.²⁹ for the spin isomers of ethylene (C_2H_4). The symmetry of this molecule is such that it has four different nuclear spin isomers in contrast to two spin isomers for the molecules studied so far. The authors²⁹ achieved the enrichment of spin isomers using the LID effect and measured the conversion rate between the spin isomers of negative spatial parity. The experiment showed also that there was no conversion between the spin isomers having positive and negative spatial parity. Note that the C_2H_4 molecule has the inversion symmetry that causes an interesting interplay between the molecular spatial parity and nuclear spin symmetry, first of this kind in the experimental studies of spin isomers of polyatomic molecules.

As was pointed out by Hougen and Oka,³⁰ it is important to develop a theoretical model of the spin isomer conversion in ethylene, C_2H_4 . The goal of the present paper is to analyze the role of the intramolecular spin–spin interactions in the C_2H_4 isomer conversion. Previously, the theoretical investigations of the nuclear spin isomers of the isotopically substituted ethylene, $^{13}\text{CCH}_4$ have been performed.³¹ However, the symmetry and the number of spin isomers in these two molecules are different.

The paper is organized as follows. In section II we give a short overview of the current situation in the investigations of the conversion of spin isomers of polyatomic molecules. In section III we consider the symmetry of ethylene rotational states and calculate the rotational energies and wave functions. In section IV we identify the nuclear spin isomers of C_2H_4 and analyze the symmetry of the rotational and spin states in the molecular symmetry group $D_{2h}(M)$ allowed by the symmetrization postulate. Section V contains the qualitative picture of the spin isomer conversion induced by a specific mechanism, quantum relaxation. We give also an expression for the isomer conversion rate calculated using a rigorous theory based on the density matrix formalism. In section VI the intramolecular mixing of ethylene states by hyperfine interactions is considered. The main attention is devoted to the state mixing by the spin–spin interactions between the hydrogen nuclei. In section VII we numerically calculate the conversion rates of ethylene isomers induced by the nuclear spin–spin interactions. Discussion and conclusions are given in section VIII.

II. CONVERSION OF SPIN ISOMERS OF POLYATOMIC MOLECULES

It is useful to summarize briefly the most significant points in our current understanding of the nuclear spin isomers of polyatomic molecules that appeared after their experimental investigations became possible. First of all it was proven experimentally that the conversion of polyatomic isomers can be induced by nonmagnetic collisions in the gas phase.³² This was an unexpected result because such a phenomenon was not known for hydrogen isomers for which conversion is caused either by magnetic collisions, or by collisions with the container walls. The conversion of polyatomic isomers appeared to be much faster than the hydrogen isomer conversion. Thus the assumption that the nuclear spin isomers can be considered as stable species (see, e.g., such statement about the spin isomers of ethylene, C_2H_4 , in the textbook³³) had to be discarded. On the other hand, it was verified experimentally that stability of spin isomers of polyatomic molecules is still extremely high. The isomers can survive more than 10^9 – 10^{10} gas kinetic collisions, thus being the most stable quantum states of molecules. This conclusion is valid for the molecules in the ground electronic states in which there is no electronic angular momentum. For the excited electronic states having angular momentum, the spin isomer conversion is predicted to be very fast.³⁴

Another unexpected result was the observation of the anomalously large (almost 2 orders of magnitude) isotope effect in the isomer conversion in the gas phase.³² To the best of our knowledge it is the only known gas-kinetic process having such a large isotope effect. For a conventional gas-kinetic process that can be described by a cross-section, one would expect that the isotope substitution in the molecule would affect its thermal velocity, polarizability, collision cross-section, etc., which would result in a much smaller isotope effect than was observed for the isomer conversion.

A very important result was the observation and study of the level crossing resonances in the isomer conversion, which appeared as the significant speed-up of the conversion if the molecular rotational levels were shifted and crossed by an external electric field.^{15,17} The shifts of the energies produced in these experiments were negligible in comparison with the thermal kinetic energy of the molecule but nevertheless increased the conversion rates by orders of magnitude. This is a very unusual behavior for a gas-kinetic process.

One more point that deserves to be mentioned is the nonconventional dependence of the isomer conversion rate on the gas pressure.³⁵ The rate of a conventional gas-kinetic process grows linearly with the gas pressure. Such dependence appears because the conventional process is based on a collisional cross-section. On the other hand, it was proven experimentally that the spin isomer conversion in the gas phase behaves differently. At low gas pressures the isomer conversion rate grows linearly with pressure, similar to a conventional process, but at high pressures the conversion rate slows down, demonstrating that frequent gas collisions trap the molecule in its spin state.

The current physical picture of the polyatomic spin isomers contains also an interesting theoretical model consistent with the experimental data. The model is based on the theoretical prediction, made first by Curl et al.,³⁶ that the isomer conversion can be induced by nonmagnetic collisions if the molecular isomer states are mixed by the intramolecular

interactions. The importance of such intramolecular interactions for the isomer conversion was proposed by Wigner.¹⁹ The useful insight to this theoretical model of isomer conversion was provided by Oka.²⁰

The theoretical model of the isomer conversion is rather unusual in molecular physics. Because of that, it was proposed to name it *quantum relaxation*³⁷ to distinguish it from the conventional gas-kinetic processes. The consistent description of spin isomer conversion by quantum relaxation in the framework of the density matrix formalism is given in ref 38. The model has two main ingredients, the intramolecular perturbation that mixes the energetically close spin isomer states of the molecule thus creating the quantum coherence between these states, and the relaxation process that destroys this coherence. Both these components of the quantum relaxation were addressed theoretically.

First, the intramolecular perturbations able to mix the spin isomer states in the molecules were identified as the spin–spin intramolecular interactions between the molecular nuclei^{36,38} and the spin–rotation interaction.^{17,36,39} Theoretical investigation of the second ingredient of quantum relaxation, the decoherence process, is presently less advanced. We refer here to the theoretical study of this process by Cacciani et al.⁴⁰ We note also that the level-crossing resonances mentioned above can serve as an experimental tool to measure the decay rate of the quantum coherence between the spin isomer states created by the hyperfine intramolecular interactions.^{15–17}

III. ROTATIONAL STATES OF ETHYLENE

Ethylene (C₂H₄) is a planar and nearly symmetric top molecule in its ground electronic and vibrational state. We address in this paper only such ethylene molecules because of the conditions of the experiment performed by Sun et al.²⁹ The molecular structure of C₂H₄ together with the molecular system of coordinate axes are presented in Figure 1. Molecular structure

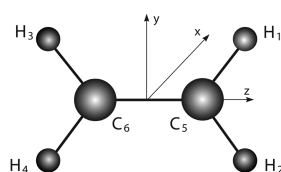


Figure 1. Numbering of atoms and the molecular right-handed system of coordinates in C₂H₄. The structure parameters are $r_{\text{CH}} = 1.087$ Å, $r_{\text{CC}} = 1.339$ Å, the angle $\alpha_{\text{HCH}} = 117.4^\circ$.

parameters are taken from ref 41. This choice of the molecular system of coordinates with the quantization axis directed along the C–C bond allows one to bring the description of C₂H₄ rotation closer to the theory of symmetric tops because of the small difference of rotational constants $B - C$ in comparison with the much larger rotational constant A (see Table 2 for the exact values of ethylene rotational constants). Note that such choice of molecular system of coordinates made our notations for the quantum states of C₂H₄ different from the notations used by Sun et al.²⁹ where different orientation of the molecular system of coordinates was chosen.

Conversion of spin isomers by quantum relaxation relies on the energetically close rotational pairs of levels belonging to the interconverting spin species. Because the mixing of these level pairs is performed by a weak (10 kHz) intramolecular hyperfine interactions, one needs rather accurate data on the level energies. The description of C₂H₄ as a rigid asymmetric rotor

does not provide sufficient accuracy and one has to account for the molecular distortion effects. As demonstrated by Rusinek et al.,⁴² a very precise description of C₂H₄ in the ground electronic and vibrational state can be performed with the help of the effective Watson's Hamiltonian having up to the sextic centrifugal distortion terms:⁴³

$$\begin{aligned} \hat{H}_0 = & \frac{1}{2}(B + C)\hat{J}^2 + \left(A - \frac{1}{2}(B + C)\right)\hat{J}_z^2 - \Delta_J(\hat{J}^2)^2 \\ & - \Delta_{JK}\hat{J}^2\hat{J}_z^2 - \Delta_K\hat{J}_z^4 + H_J(\hat{J}^2)^3 + H_{JK}(\hat{J}^2)^2\hat{J}_z^2 \\ & + H_{KJ}\hat{J}^2\hat{J}_z^4 + H_K\hat{J}_z^6 + \frac{1}{4}(B - C)\hat{E}_0 - \delta_J\hat{J}^2\hat{E}_0 \\ & - \delta_K\hat{E}_2 + h_J(\hat{J}^2)^2\hat{E}_0 + h_{JK}\hat{J}^2\hat{E}_2 + h_K\hat{E}_4 \end{aligned} \quad (1)$$

where \hat{J} , \hat{J}_x , \hat{J}_y , and \hat{J}_z are the molecular angular momentum operator and its projections on the molecular axes. A , B , and C are the effective rotational constants for the ground vibrational state of C₂H₄, which characterize the rotations around z , y , and x molecular axes, respectively (Figure 1). The rest of parameters in eq 1 account for the distortion effects.⁴³ In eq 1 the following notation was used

$$\hat{E}_n \equiv \hat{J}_z^n(\hat{J}_y^2 - \hat{J}_x^2) + (\hat{J}_y^2 - \hat{J}_x^2)\hat{J}_z^n \quad (2)$$

The Hamiltonian \hat{H}_0 can be diagonalized with the help of the symmetric-top quantum states $|J, k, M\rangle$, where J , k , and M are the quantum numbers of the angular momentum and its projections on the molecular quantization z -axis and on the laboratory quantization axis, respectively (see, e.g., ref 33). Diagonalization of \hat{H}_0 is simplified because \hat{H}_0 has non-vanishing matrix elements diagonal in J , M and with $\Delta k = 0, \pm 2$. An additional simplification can be achieved if one diagonalizes \hat{H}_0 using Wang's basis:^{44,45}

$$\begin{aligned} |\alpha, p\rangle &= f_K[|\alpha\rangle + (-1)^{p+J}|\bar{\alpha}\rangle] \quad 0 \leq K \leq J \\ f_K &= 1/\sqrt{2} \quad \text{if } K \neq 0; \quad f_K = 1/2 \quad \text{if } K = 0 \end{aligned} \quad (3)$$

Here, the sets of quantum numbers are $\alpha \equiv \{J, K, M\}$, $\bar{\alpha} \equiv \{J, -K, M\}$, and $K = |k|$, $p = 0, 1$.

The rotational states $|\alpha, p\rangle$ can be classified using the irreducible representations of the D_2 point group.³³ These states undergo the following transformations under the symmetry operations of the D_2 group,

$$\begin{aligned} R_z^\pi|\alpha\rangle &= (-1)^K|\alpha\rangle & R_y^\pi|\alpha\rangle &= (-1)^{K+J}|\bar{\alpha}\rangle \\ R_x^\pi|\alpha\rangle &= (-1)^J|\bar{\alpha}\rangle \end{aligned} \quad (4)$$

Consequently, the basis states $|\alpha, p\rangle$ have the transformation rules

$$\begin{aligned} R_z^\pi|\alpha, p\rangle &= (-1)^K|\alpha, p\rangle & R_y^\pi|\alpha, p\rangle &= (-1)^{K+p}|\alpha, p\rangle \\ R_x^\pi|\alpha, p\rangle &= (-1)^p|\alpha, p\rangle \end{aligned} \quad (5)$$

Depending on whether p and K values are even or odd, the states $|\alpha, p\rangle$ generate four irreducible representations of the group D_2 , as summarized in Table 1. The matrix elements of \hat{H}_0 between the states of different symmetry vanish. Thus the diagonalization of the Hamiltonian \hat{H}_0 in the basis $|\alpha, p\rangle$ is reduced to the diagonalization of four independent matrices, each for the states of a particular symmetry of D_2 group. Consequently, the eigenstates of the Hamiltonian \hat{H}_0 for each J

Table 1. Character Table of the Symmetry Group D_2 and Classification of the Basis States $|\alpha, p\rangle$ ^a

	E	R_z^π	R_y^π	R_x^π	K -even	K -odd
A	1	1	1	1	$p = 0$	
B ₁	1	1	-1	-1	$p = 1$	
B ₂	1	-1	1	-1		$p = 1$
B ₃	1	-1	-1	1		$p = 0$

^a E is the identity operation and the operations R_z^π , R_y^π , and R_x^π are the molecular rotations by π around the corresponding molecular axes.

and M values can be expanded over the basis states $|\alpha, p\rangle$ of the same symmetry,

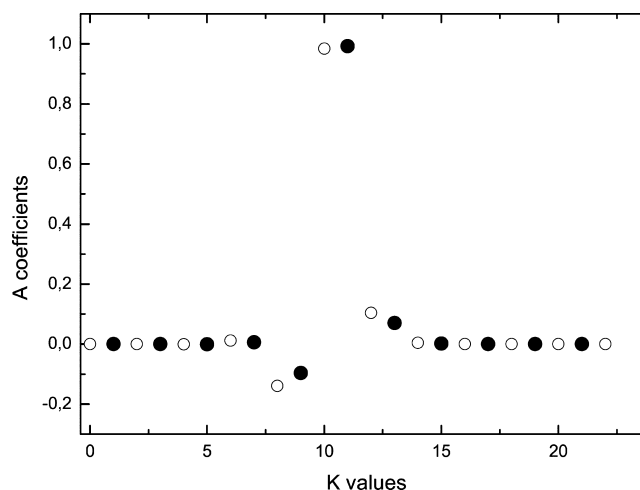
$$|\beta, p\rangle = \sum_K A_K |\alpha, p\rangle \quad (6)$$

where A_K are the expansion coefficients. The summation index, K , is given explicitly in (6), although A_K depends on the other quantum numbers as well. All coefficients in (6) are real numbers because the Hamiltonian \hat{H}_0 is symmetric in the basis $|\alpha, p\rangle$.

Quantum numbers J and p alone do not specify unambiguously the rotational states of an asymmetric top. To do it consistently, one would need to use the whole set of A_K coefficients from the expansion (6) for each rotational state. Clearly, this is not practical. There are a few schemes for abbreviated notations for the rotational states of asymmetric tops.⁴⁶ In this paper we will use the scheme³¹ that is somewhat better adapted to the description of nuclear spin isomers. We will designate the rotational states of C_2H_4 by indicating quantum numbers p and J and prescribing the allowed K values to the eigenenergies keeping both in ascending order. For example, the rotational state having $p = 1$, $J = 21$, and $K = 1, 3, 5, \dots, 21$ in the expansion (6) and being the sixth in the ascending order of rotational state energies of this family will be designated by $\mathcal{K} = 11$. (Note the difference between the two characters K and \mathcal{K}). It gives the unambiguous notation of the rotational states for each of the four species A, B₁ (\mathcal{K} -even) and B₂, B₃ (\mathcal{K} -odd). This classification establishes a clear correlation with the states of prolate symmetric top for which the expansion (6) would contain just one K -term for each rotational state. The application of the proposed scheme to such “accidentally symmetric top” would result in $\mathcal{K} = K$.

Insight to the proposed scheme of the rotational state notations is given in Figure 2, where A_K coefficients for the two rotational states ($p = 1$, $J = 21$, $\mathcal{K} = 11$) and ($p' = 1$, $J' = 23$, $\mathcal{K}' = 10$) are plotted. One can see from this figure that these states have significant A_K coefficients only for $K = 11$ and $K = 10$, which are used for the notations of these rotational states. The sharp peaks in the A_K dependencies on K are the consequence of the fact that C_2H_4 is a nearly symmetric top and confirm the correctness of our choice of the molecular quantization axis along the C–C bond.

In the numerical calculations of the rotational wave functions and energies with the Hamiltonian \hat{H}_0 we used the rotational parameters determined in ref 42. For the convenience of the reader, these parameters are given in Table 2. The energies of rotational states calculated with these parameters are presented in Figure 3. The calculations were done with the help of the computer software specially written for this purpose. The program calculates the eigenfunctions and the eigenenergies of the Hamiltonian \hat{H}_0 from eq 1 using the basis states $|\alpha, p\rangle$. The accuracy of this calculation was tested by comparing our

**Figure 2.** Values of the A_K coefficients from the expansions (6) for the rotational states ($p' = 1$, $J' = 23$, $\mathcal{K}' = 10$) (O) and ($p = 1$, $J = 21$, $\mathcal{K} = 11$) (●).**Table 2. Rotational Parameters of the C_2H_4 Molecule in the Ground Electronic and Vibrational State^{42,a}**

A	4.86462016(4)
B	1.00105650(1)
C	0.82804599(1)
$\Delta_J \times 10^6$	1.470224(41)
$\Delta_{JK} \times 10^6$	10.23214(36)
$\Delta_K \times 10^6$	86.4798(16)
$\delta_J \times 10^6$	0.281684(15)
$\delta_K \times 10^6$	10.1590(14)
$H_J \times 10^9$	0.002501(54)
$H_{JK} \times 10^9$	0.1845(39)
$H_{KJ} \times 10^9$	-0.424(14)
$H_K \times 10^9$	6.196(13)
$h_J \times 10^9$	0.001098(17)
$h_{JK} \times 10^9$	0.1138(23)
$h_K \times 10^9$	3.46(12)

^aAll values are in cm^{-1} . Uncertainties in unit of the last digits are given in parentheses.

rotational energies with the rotational energies in the ground electronic and vibrational state of C_2H_4 determined in ref 42. The coincidences were found to be at the level of 0.1 MHz, which is sufficient for our purpose.

IV. NUCLEAR SPIN ISOMERS OF ETHYLENE

Symmetrization postulate requires that the molecular wave functions are antisymmetric (symmetric) if two identical nuclei fermions (bosons) are interchanged (see, e.g., refs 20 and 47). The symmetrization postulate assumes an interchange of both spatial and spin coordinates of identical particles and thus leads to the correlations between spatial and spin quantum states of the molecule. Stable nuclear spin isomers appear if the nuclear spin states of different symmetries have different energies.

The symmetry of the quantum states of C_2H_4 and determination of nuclear spin modifications were analyzed in many textbooks. Here, we will use the description based on the molecular symmetry group, $D_{2h}(M)$, which is the symmetry group of C_2H_4 in the ground electronic state.⁴⁷ The numbering of nuclei in C_2H_4 and the orientation of the molecular coordinate axes are shown in Figure 1 and are the same as in ref

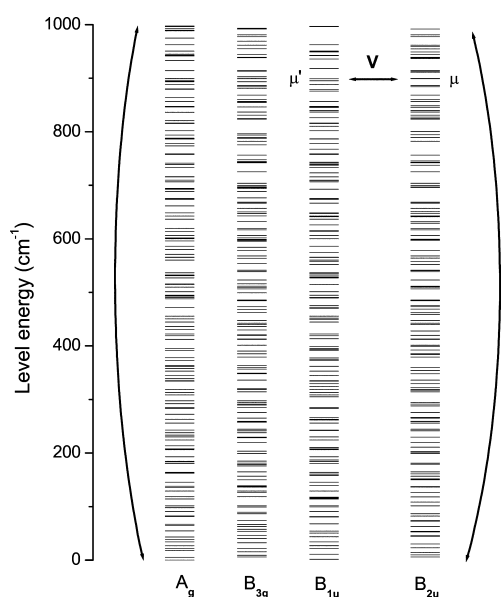


Figure 3. Rotational states of the four nuclear spin isomers of ethylene. The bent lines indicate the rotational relaxation inside each subspace of rotational states. At the figure bottom, the symmetries of the nuclear spin wave functions in the $D_{2h}(M)$ group are given.

47. The symmetry operations of the $D_{2h}(M)$ group and their characters are listed in Table 3. Here the inversion operation,

Table 3. Character Table of the Symmetry Group $D_{2h}(M)$ ^{47,a}

$D_{2h}(M)$:	E	a	b	c	E^*	a^*	b^*	c^*
D_{2h} :	E	C_2^z	C_2^y	C_2^x	σ_{yz}	σ_{xz}	σ_{xy}	i
equiv. rot.:	R^0	R_z^π	R_y^π	R_x^π	R_x^π	R_y^π	R_z^π	R^0
A_g	1	1	1	1	1	1	1	1
A_u	1	1	1	1	-1	-1	-1	-1
B_{1g}	1	1	-1	-1	-1	-1	1	1
B_{1u}	1	1	-1	-1	1	1	-1	-1
B_{2g}	1	-1	1	-1	-1	1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1
B_{3g}	1	-1	-1	1	1	-1	-1	1
B_{3u}	1	-1	-1	1	-1	1	1	-1

^a E^* is the inversion of the coordinates in the laboratory frame of all nuclei and electrons in the molecular center of mass. The operations of the molecular point group, D_{2h} ⁴⁷ are acting on the vibrational coordinates only. The abbreviations for the nuclei permutations are given by eq 7.

E^* , denotes the inversion of the space-fixed coordinates of the electrons and nuclei in the molecular center of mass. The abbreviations for the permutations of the nuclei in C_2H_4 are

$$\begin{aligned} a &= (12)(34) & b &= (13)(24)(56) & c &= (14)(23)(56) \\ a^* &= E^*a & b^* &= E^*b & c^* &= E^*c \end{aligned} \quad (7)$$

Labels g and u of the irreducible representations are determined, respectively, by the +1, or -1 characters of the operation c^* of the group $D_{2h}(M)$.

Also in Table 3 the operations of the *molecular point group* D_{2h} are given.⁴⁷ The operation i denotes the inversion of the molecular vibronic coordinates in the molecular frame. Equivalent rotations in Table 3 are the rotations of the molecular frame under operations of the $D_{2h}(M)$ group.

The symmetries of rotational states in the group $D_{2h}(M)$ are determined by the equivalent rotations. By comparing Table 1 and Table 3, one concludes that the rotational states are A_g , B_{1g} , B_{2g} , and B_{3g} species in accordance with their +1 characters for the operation c^* . The states A_g and B_{3g} have positive parity but the states B_{1g} and B_{2g} have negative parity in accordance with their characters for the operation E^* . These conclusions are consistent with the results of ref 48.

To construct the nuclear spin wave functions of the C_2H_4 with ^{12}C isotopes, we need to consider only the spins of four protons. There are $2^4 = 16$ nuclear spin wave functions that are different in the orientation of 4 proton spins in the C_2H_4 molecule relative to the laboratory quantization axis. These 16 nuclear spin wave functions form the representation having the following characters for the $D_{2h}(M)$ symmetry operations,

E	a	b	c	E^*	a^*	b^*	c^*
16	4	4	4	16	4	4	4

Note that the nuclear spin states remain unchanged under operation E^* .

Reducing this representation into irreducible representations of the $D_{2h}(M)$ group one can combine these 16 nuclear spin wave functions into four sets having the symmetries A_g , B_{3g} , B_{1u} , and B_{2u} of the $D_{2h}(M)$ group. Following the method explained in ref 33, one can determine that the A_g states have the total spin of 4 protons $I = 2$ or $I = 0$. There are two states with $I = 0$. Consequently, the states A_g have nuclear statistical weight equal to 7. The nuclear spin functions of B_{3g} , B_{1u} , and B_{2u} symmetries have the total spin of four protons $I = 1$. Each of these isomers has nuclear statistical weight equal to 3.

Each of the symmetry operations a , b , c exchanges an even number of proton pairs, and due to the symmetrization postulate, the total wave functions have the characters +1 for these operations. The parity of states is not determined by the symmetrization postulate. Consequently, the total states can be A_g or A_u species depending on the positive or negative parity of the total state. The symmetrization postulate allows the following total functions equal to the products of the spin wave functions and the rotational wave functions,

$$\begin{aligned} |A_g\rangle &= |A_g\rangle_{\text{nuc}} |A_g\rangle_{\text{rot.}} & |A_g\rangle &= |B_{3g}\rangle_{\text{nuc}} |B_{3g}\rangle_{\text{rot.}} \\ |A_u\rangle &= |B_{1u}\rangle_{\text{nuc}} |B_{1g}\rangle_{\text{rot.}} & |A_g\rangle &= |B_{2u}\rangle_{\text{nuc}} |B_{2g}\rangle_{\text{rot.}} \end{aligned} \quad (8)$$

From Tables 1 and 3, we see that for our choice of the rotational functions $|\alpha, p\rangle$ given by eq 3, the evenness of the quantum number p coincides with the spatial parity of the quantum states of the C_2H_4 molecule.

To conclude this section, we introduce the total wave functions, $|\mu\rangle$, of C_2H_4 as a product of the nuclear spin wave function and the spatial wave function of the asymmetric top as

$$|\mu\rangle = |I, \sigma, \mathcal{R}\rangle |\beta, p\rangle = |I, \sigma, \mathcal{R}\rangle \sum_K A_K |\alpha, p\rangle \quad (9)$$

Here, I and σ are the total spin of four hydrogen nuclei and its projection on the laboratory quantization axis, respectively. \mathcal{R} indicates the irreducible representation of the nuclear spin state. The rotational state $|\beta, p\rangle$ has the symmetry prescribed by eqs 8. It is important to note that the μ -states from eq 9 are the eigenstates of the molecular Hamiltonian \hat{H}_0 . The energies of the rotational states of four nuclear spin isomers of C_2H_4 are presented in Figure 3.

V. QUANTUM RELAXATION OF NUCLEAR SPIN ISOMERS

For the qualitative explanation of the essence of quantum relaxation, we will use the ethylene isomers as an example. The quantum states of the spin isomers of C_2H_4 are the eigenstates of the molecular Hamiltonian \hat{H}_0 . Let us assume now that the total molecular Hamiltonian contains an extra term and can be written as

$$\hat{H} = \hat{H}_0 + \hbar\hat{V} \quad (10)$$

where $\hbar\hat{V}$ is a small perturbation able to mix the states corresponding to different nuclear spin isomers of C_2H_4 molecule. For the qualitative description of quantum relaxation, we assume that the perturbation $\hbar\hat{V}$ mixes only two states, $|\mu'\rangle$ and $|\mu\rangle$, indicated in Figure 3. Suppose that initially the molecule was placed in the subspace of rotational states belonging to the B_{2u} nuclear state. Rotational relaxation induced by the nonmagnetic collisions will force this molecule to shuttle between the rotational states within the B_{2u} subspace. This will continue until the molecule arrives at the state $|\mu\rangle$. Then during the free flight the intramolecular interaction $\hbar\hat{V}$ will admix the state $|\mu'\rangle$ to the state $|\mu\rangle$. Consequently, the next collision will be able to transfer the molecule to other rotational states within the B_{1u} subspace and the spin conversion will occur.

The quantum relaxation of spin isomers takes place only between the states mixed by intramolecular perturbations. The quantum states in C_2H_4 molecules with positive parity $|A_g\rangle_{\text{nuc}}|A_g\rangle_{\text{rot}}$ and $|B_{3g}\rangle_{\text{nuc}}|B_{3g}\rangle_{\text{rot}}$ cannot be mixed with the states with negative parity $|B_{1u}\rangle_{\text{nuc}}|B_{1g}\rangle_{\text{rot}}$ and $|B_{2u}\rangle_{\text{nuc}}|B_{2g}\rangle_{\text{rot}}$ by any intramolecular perturbation. Consequently, the isomer relaxation in C_2H_4 is reduced to the relaxation between the states of the same parity: $|A_g\rangle_{\text{nuc}}|A_g\rangle_{\text{rot}} \rightleftharpoons |B_{3g}\rangle_{\text{nuc}}|B_{3g}\rangle_{\text{rot}}$ and $|B_{1u}\rangle_{\text{nuc}}|B_{1g}\rangle_{\text{rot}} \rightleftharpoons |B_{2u}\rangle_{\text{nuc}}|B_{2g}\rangle_{\text{rot}}$. It allows one to describe the spin isomer conversion in C_2H_4 by the theory developed for the molecules having only two isomers.³⁸

Let us consider the relaxation between the states of B_{1u} and B_{2u} symmetries of nuclear spin functions. This particular case was studied experimentally by Sun et al.²⁹ (in the work,²⁹ the notations for the nuclear spin states were different because of the different choice of the molecular axes). Suppose that at the initial moment the concentrations of the isomers were $\rho_{B_{1u}}(0)$ and $\rho_{B_{2u}}(0)$. Then, the concentration of B_{2u} molecules will relax exponentially in time toward the equilibrium value $\bar{\rho}$,

$$\begin{aligned} \rho_{B_{2u}}(t) - \bar{\rho} &= (\rho_{B_{2u}}(0) - \bar{\rho})e^{-\gamma t} \\ \bar{\rho} &= \frac{1}{2}(\rho_{B_{1u}}(0) + \rho_{B_{2u}}(0)) \end{aligned} \quad (11)$$

with the rate,

$$\gamma = \sum_{\mu' \in B_{1u}, \mu \in B_{2u}} \frac{2\Gamma_{\mu'\mu} |V_{\mu'\mu}|^2}{\Gamma_{\mu'\mu}^2 + \omega_{\mu'\mu}^2} (W_{\mu'} + W_{\mu}) \quad (12)$$

Here, $\hbar\omega_{\mu'\mu}$ is the energy gap between the states μ' and μ ; $\Gamma_{\mu'\mu}$ is the decay rate of the off-diagonal density matrix element, $\rho_{\mu'\mu}$ induced by the intramolecular perturbation $\hbar\hat{V}$. Note that here (and further) the μ -states form an uncoupled basis, i.e., the basis determined by neglecting the perturbation $\hbar\hat{V}$.

The Boltzmann factors determine the populations of the quantum states,

$$\begin{aligned} \rho_{\mu'\mu'} &= \rho_{B_{1u}} W_{\mu'} & \rho_{\mu\mu} &= \rho_{B_{2u}} W_{\mu} \\ \mu' &\in B_{1u}; \mu &\in B_{2u} \end{aligned} \quad (13)$$

Expression 12 shows that the contribution to γ from each pair of states has a different dependence on Γ (and thus on the gas pressure) in the two limiting cases: $\gamma \propto \Gamma$ at $\Gamma^2 \ll \omega^2$, but $\gamma \propto 1/\Gamma$ at $\Gamma^2 \gg \omega^2$. Note that we do not arrive at very large conversion rates, γ , for low Γ and degenerate states having $\omega = 0$ because the solution (12) is obtained in the first-order perturbation theory and is valid only under the following condition³⁷

$$|V|^2 \ll \frac{\nu_{\text{rot}}}{4\Gamma} \max\{\Gamma^2, \omega^2\} \quad (14)$$

where ν_{rot} is the rotational relaxation rate. Consequently, the solution (12) is not valid for the degenerate states and low Γ (low gas pressure).

VI. STATES MIXING BY HYPERFINE INTERACTIONS IN C_2H_4

Quantum states of nuclear spin isomers of C_2H_4 can be mixed by the nuclear spin–spin interactions. The nuclear spin of ^{12}C is zero and only the interactions between four protons contribute. The spin–spin interaction between two particles is described by the magnetic dipole–dipole interaction of their magnetic moments. For example, the interaction of the protons 1 and 4 (spin operators $\hat{\mathbf{I}}^{(1)}$ and $\hat{\mathbf{I}}^{(4)}$) in C_2H_4 has the form

$$\begin{aligned} \hat{V}_{\text{SS}}^{(1,4)} &= P_{14} \sum_{i,j} \hat{I}_i^{(1)} \hat{I}_j^{(4)} T_{ij}^{(1,4)} \\ T_{ij}^{(1,4)} &= \delta_{ij} - 3n_i^{(1,4)} n_j^{(1,4)} & P_{14} &= \frac{4m^2}{r_{14}^3 \hbar} \end{aligned} \quad (15)$$

Here summation is performed over Cartesian components in the laboratory frame, m is the proton's magnetic moment, r_{14} is the distance between the protons, and $\mathbf{n}^{(1,4)}$ is the unit vector directed from the proton 1 to proton 4. For further calculations it is convenient to express the operators in eq 15 through the spherical tensors,³³

$$\hat{V}_{\text{SS}}^{(1,4)} = P_{14} \sum_q (-1)^q (\hat{\mathbf{I}}^{(1)} \hat{\mathbf{I}}^{(4)})_{2,-q} T_{2,q}^{(1,4)} \quad (16)$$

Note that for the traceless and symmetrical tensor $T_{ij}^{(1,4)}$ the spherical components of ranks 0 and 1 vanish. The spin operator $(\hat{\mathbf{I}}^{(1)} \hat{\mathbf{I}}^{(4)})_{2,-q}$ can be expressed through the operators $\hat{I}_{1q_1}^{(1)}$ and $\hat{I}_{1q_4}^{(4)}$ as

$$(\hat{\mathbf{I}}^{(1)} \hat{\mathbf{I}}^{(4)})_{2,-q} = (-1)^q \sqrt{5} \sum_{q_1, q_4} \begin{pmatrix} 1 & 1 & 2 \\ q_1 & q_4 & q \end{pmatrix} \hat{I}_{1q_1}^{(1)} \hat{I}_{1q_4}^{(4)} \quad (17)$$

The total spin–spin interaction in C_2H_4 has to account for all proton pairs:

$$\hat{V}_{\text{SS}} = \sum_{m < n} \hat{V}_{\text{SS}}^{(m,n)} \quad m, n = 1, 2, 3, 4 \quad (18)$$

\hat{V}_{SS} has the symmetry A_g in the $D_{2h}(M)$ group which is the only allowed symmetry for the intramolecular Hamiltonian of C_2H_4 .

For the determination of the conversion rate, γ , using (12) one needs to calculate the matrix elements (see the expansion (9)),

$$\langle \mu' | \hat{V}_{SS} | \mu \rangle = \sum_{K', K} A_{K'} A_K \langle I', \sigma', \mathcal{R}' | \langle \alpha', p' | \hat{V}_{SS} | \alpha, p \rangle | I, \sigma, \mathcal{R} \rangle \quad (19)$$

With the help of eq 3 and the symmetry considerations, the matrix elements $\langle \alpha', p' | \hat{V}_{SS} | \alpha, p \rangle$ can be expressed through the symmetric top matrix elements $\langle \alpha' | \hat{V}_{SS} | \alpha \rangle$ as

$$\begin{aligned} \langle \alpha', p' | \hat{V}_{SS} | \alpha, p \rangle \\ = 2f_{K'} f_K \delta_{p', p} [\langle \alpha' | \hat{V}_{SS} | \alpha \rangle + (-1)^{p'+J'} \langle \alpha' | \hat{V}_{SS} | \alpha \rangle] \end{aligned} \quad (20)$$

As will be proven below by direct calculations, only the part of \hat{V}_{SS} that is equal to

$$\hat{V}_1 = \hat{V}_{SS}^{(1,4)} + \hat{V}_{SS}^{(2,3)} \quad (21)$$

contributes to the B_{1u} – B_{2u} conversion. The perturbation \hat{V}_1 has the correct symmetry A_g in the $D_{2h}(M)$ group. One can prove, either by direct calculations or by symmetry considerations, that matrix elements of the two perturbations, $\hat{V}_{SS}^{(1,4)}$ and $\hat{V}_{SS}^{(2,3)}$, are equal. Thus, one needs to determine the following matrix elements:

$$\begin{aligned} \langle I', \sigma', \mathcal{R}' | \langle \alpha' | \hat{V}_{SS}^{(1,4)} | \alpha \rangle | I, \sigma, \mathcal{R} \rangle \\ = P_{14} \sum_q (-1)^q \langle I', \sigma', \mathcal{R}' | (\hat{\mathbf{I}}^{(1)} \hat{\mathbf{I}}^{(4)})_{2,-q} | I, \sigma, \mathcal{R} \rangle \langle \alpha' | T_{2,q}^{(1,4)} | \alpha \rangle \end{aligned} \quad (22)$$

For the particular case of the conversion between B_{1u} and B_{2u} isomers, the matrix elements of the spin operator in eq 22 are given by the Wigner–Eckart theorem³³ as

$$\begin{aligned} \langle I'=1, \sigma', B_{1u} | (\hat{\mathbf{I}}^{(1)} \hat{\mathbf{I}}^{(4)})_{2,-q} | I=1, \sigma, B_{2u} \rangle \\ = (-1)^{\sigma'} \begin{pmatrix} 1 & 2 & 1 \\ -\sigma' & -q & \sigma \end{pmatrix} \langle B_{1u} || (\hat{\mathbf{I}}^{(1)} \hat{\mathbf{I}}^{(4)})_2 || B_{2u} \rangle \end{aligned} \quad (23)$$

Here $(:::)$ stands for the Wigner's 3j-coefficient and $\langle ||...|| \rangle$ is the reduced matrix element. One can prove that

$$\langle B_{1u} || (\hat{\mathbf{I}}^{(1)} \hat{\mathbf{I}}^{(4)})_2 || B_{2u} \rangle = -\sqrt{5} \frac{3}{4} \quad (24)$$

The symmetric top matrix elements were calculated in ref 33

$$\begin{aligned} \langle \alpha' | T_{2,q}^{(1,4)} | \alpha \rangle = (-1)^{K'-M'} \sqrt{(2J'+1)(2J+1)} \\ \times \begin{pmatrix} J' & 2 & J \\ -K' & K'-K & K \end{pmatrix} \begin{pmatrix} J' & 2 & J \\ -M' & q & M \end{pmatrix} \mathcal{J}_{2,K'-K}^{(1,4)} \end{aligned} \quad (25)$$

Here, $\mathcal{J}_{2,K'-K}^{(1,4)}$ are the spherical components of the $T^{(1,4)}$ -tensor calculated in the molecular frame. For the conversion between B_{1u} and B_{2u} spin isomers, the $K' - K$ values are odd, and only the tensor components $\mathcal{J}_{2,\pm 1}^{(1,4)}$ contribute. Their expression through the Cartesian components of the unit vector $\mathbf{n}^{(1,4)}$ reads³³

$$\mathcal{J}_{2,\pm 1}^{(1,4)} = -i3n_z^{(1,4)} n_y^{(1,4)} \quad (26)$$

This expression explains why only the spin–spin interaction of proton pairs (1, 4) and (2, 3) contributes to the relaxation between B_{1u} and B_{2u} spin isomers in C_2H_4 . For all other pairs of nuclei the tensor components $\mathcal{J}_{2,\pm 1}$ vanish. One can check also that for the pair (2, 3) of the hydrogen nuclei, the reduced matrix element for the spin operator similar to eq 24 and the $\mathcal{J}_{2,\pm 1}^{(2,3)}$ similar to that defined by eq 26 both have an opposite

sign as compared with the case of (1, 4) nuclei. Consequently, the two interactions $\hat{V}_{SS}^{(1,4)}$ and $\hat{V}_{SS}^{(2,3)}$ have equal matrix elements.

The magnitude of the spin–spin interaction is determined by the C_2H_4 spatial structure. Using the structure parameters provided in the caption of Figure 1 and the tabulated value for the proton magnetic moment, one has

$$P_{14} \mathcal{J}_{2,\pm 1}^{(1,4)} = -i5.88 \times 10^3 \text{ Hz} \quad (27)$$

The selection rules for the spin–spin mixing of the B_{1u} and B_{2u} spin isomer states read

$$|J' - J| \leq 2 \quad J' + J \geq 2 \quad K' - K = \pm 1 \quad (28)$$

The selection rules for J values follow from the properties of 3j-coefficients in eq 25. The selection rule for K follows from the evenness of K -numbers allowed for the B_{1u} and B_{2u} spin isomers and from the fact that the $\mathcal{J}_{2,q}^{(1,4)}$ tensors have $q \leq 2$.

In addition to the direct spin–spin interactions considered above, there are the so-called indirect interactions between molecular nuclei through the electronic states (see, for example, ref 49). These indirect spin–spin interactions have the similar tensorial form as the direct interactions given by eq 15. Because of that it would be easy to account for this type of spin–spin coupling. But in fact, this is not necessary to do at the present level of accuracy of the theoretical model because of the weakness of the indirect nuclear spin–spin interactions in C_2H_4 . The off-diagonal terms of such interactions in C_2H_4 are on the order of a few hertz,⁵⁰ which is negligible in comparison with the much stronger direct spin–spin interactions (see eq 27).

Another interaction that can cause the isomer conversion is the spin–rotation coupling. It results from the interaction of the nuclear spins with the magnetic field induced by the molecular rotation. The spin–rotation perturbation relevant to the spin isomer conversion in C_2H_4 can be written as^{39,51}

$$\hat{V}_{SR} = \frac{1}{2} \sum_n [\hat{\mathbf{J}} \cdot \mathbf{C}^{(n)} \cdot \hat{\mathbf{I}}^{(n)} + \text{HC}] \quad n = 1, 2, 3, 4 \quad (29)$$

where $\mathbf{C}^{(n)}$ is the spin–rotation tensor for the n th hydrogen nucleus. The selection rules for the spin–rotation mixing of the B_{1u} and B_{2u} spin isomers read^{39,51}

$$|J' - J| \leq 1 \quad J' + J \geq 1 \quad K' - K = \pm 1 \quad (30)$$

The selection rules (28) and (30) show that there are pairs of states that can be mixed by the spin–spin interaction but cannot be mixed by the spin–rotation interaction. Mixing of the C_2H_4 states by spin–rotation interaction is not considered in this paper.

VII. ISOMER CONVERSION RATES

For the calculation of the conversion rate γ using eq 12, one needs to know the relaxation rates $\Gamma_{\mu'\mu}$. For these parameters we will use the approximation verified in the previous studies with other molecules (see, for example, refs 17 and 23), $\Gamma_{\mu'\mu} = (\Gamma_{\mu'\mu'} + \Gamma_{\mu\mu})/2$, where $\Gamma_{\mu'\mu'}$ and $\Gamma_{\mu\mu}$ are the population decay rates in the states $|\mu'\rangle$ and $|\mu\rangle$. In further calculations we assume all $\Gamma_{\mu'\mu}$ to be equal to the line broadening rate measured for gaseous ethylene in ref 52

$$\Gamma_{\mu'\mu}/P \equiv \Gamma/P \simeq 3 \times 10^7 \text{ s}^{-1}/\text{Torr} \quad (31)$$

Table 4. Rotational Levels Most Important for the Conversion in C₂H₄ between the Nuclear Spin Isomers |B_{1u}⟩_{nuc}|B_{1g}⟩_{rot.} and |B_{2u}⟩_{nuc}|B_{2g}⟩_{rot.}^a

level pair (<i>p'</i> , <i>J'</i> , <i>K'</i>)–(<i>p</i> , <i>J</i> , <i>K</i>)	energy ^b (cm ^{−1})	ω/2π ^c (MHz)	<i>F</i> _{<i>a'a</i>} ^d (Hz ²)	<i>W</i> _{<i>a</i>} ^e	γ ^f (10 ^{−4} s ^{−1})
(1, 23, 10)–(1, 21, 11)	898.886	−46.2	1.4 × 10 ⁹	6.4 × 10 ^{−6}	4.9
(1, 14, 4)–(1, 15, 3)	255.885	1252.2	7.8 × 10 ⁸	1.5 × 10 ^{−4}	0.09
(1, 37, 0)–(1, 37, 1)	1192.606	−3.4	1.1 × 10 ⁶	1.5 × 10 ^{−6}	0.06
(1, 35, 0)–(1, 35, 1)	1070.404	−7.1	1.2 × 10 ⁶	2.8 × 10 ^{−6}	0.05
(1, 6, 4)–(1, 8, 3)	101.617	942.4	1.1 × 10 ⁸	3.1 × 10 ^{−4}	0.05
				total rate:	5.2

^aThe conversion rates are calculated at the gas pressure of 1 Torr and the gas temperature of 295 K. ^bThe energy of the rotational level (*p'*, *J'*, *K'*).

^cThe energy difference, *E*(*p'*, *J'*, *K'*) − *E*(*p*, *J*, *K*). ^dThe strength of mixing, eq 33. ^eThe Boltzmann factor. ^fContribution to the conversion rate from each pair of levels.

The validity of this approximation is justified by the physical picture of the line broadening of the rovibronic spectra. The broadening is mainly caused by the population decay of the rotational states due to the rotational relaxation.

The approximation (31) significantly simplifies the calculations. Let us split the summation in eq 12 into quantum numbers (*v'*, *v*) and (*a'*, *a*) of degenerate and nondegenerate states, respectively. For the case under consideration the quantum numbers of degenerate states are the projections of the angular momentum (*M'*, *M*) and the projections of the nuclear spins (*σ'*, *σ*) on the laboratory axis of quantization. It transforms eq 12 to the form³¹

$$\gamma = \sum_{a' \in B_{1u}, a \in B_{2u}} \frac{2\Gamma F_{a'a}}{\Gamma^2 + \omega_{a'a}^2} (W_{a'} + W_a)$$

$$F_{a'a} = \sum_{v'v} |V_{\mu'\mu}|^2 \quad (32)$$

where the *strength of mixing* *F*_{*a'a*} was introduced. In expression (32), *W*_{*a'*} ≡ *W*_{*a'v'*}; *W*_{*a*} ≡ *W*_{*av*}; and it is taken into account that the Boltzmann factors for all degenerate substates are equal.

Combining together the calculations performed in the previous sections, one has the strength of mixing for the B_{1u}–B_{2u} isomer conversion as

$$F_{a'a} = P_{14} \frac{2^9}{4} (2J' + 1)(2J + 1)$$

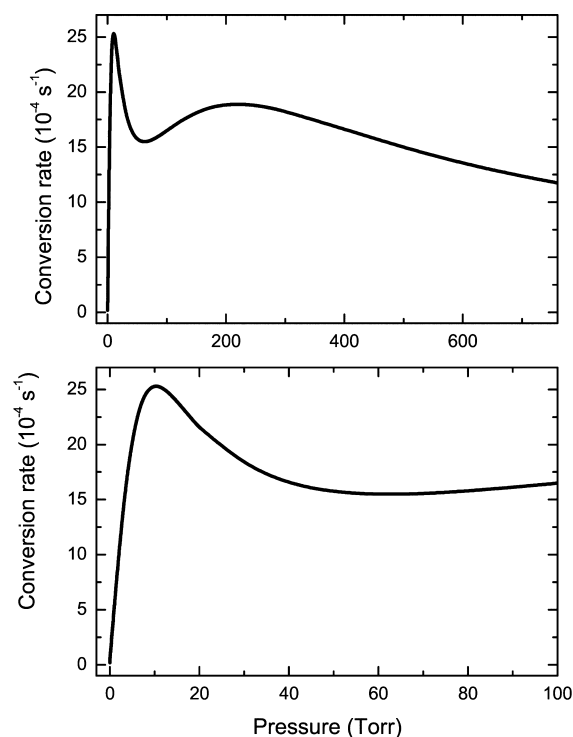
$$\times \sum_{K', K} A_{K'} A_K \begin{pmatrix} J' & 2 & J \\ -K' & K' - K & K \end{pmatrix}^2 |\mathcal{J}_{2, K' - K}^{(14)}|^2 \quad (33)$$

The contributions from both interactions *V*_{SS}⁽¹⁴⁾ and *V*_{SS}⁽²³⁾ were accounted for in eq 33, which gives an extra factor of 4 because of the constructive interference of *V*_{SS}⁽¹⁴⁾ and *V*_{SS}⁽²³⁾. The conversion rates, γ, calculated with the help of eqs 32 and 33 are summarized in Table 4. In these calculations we took into account all level pairs having *J* values up to 48 and the level pair gaps ≤3 GHz. The calculations were performed with the help of computer program specially written for this purpose.

As one can see, the most important contribution to the rate γ comes from just one pair of states. Note that this pair of states is not mixed by the spin–rotation interaction because of the restrictions in *J'* − *J* imposed by eq 30. The calculated total conversion rate induced by the nuclear spin–spin interactions coincides within experimental uncertainties with the rate measured by Sun et al.²⁹ It allows one to suggest that the spin–rotation contribution to the spin isomer conversion in ethylene is small. Assuming the nuclear spin–spin interactions being the main contribution to the conversion in ethylene, one

can calculate the pressure and temperature dependencies of the isomer conversion rate.

The pressure dependence of the rate γ is presented in Figure 4. The conversion rates in this figure were calculated for the

**Figure 4.** Spin isomer conversion rate dependence on gas pressure in two pressure ranges at room temperature.

level pairs having *J* values up to 48 and the level pair gaps ≤90 GHz. The smallness of the energy gap between the mixed states of the main level pair creates an interesting pressure dependence. The rate grows linearly with pressure only at low gas pressures. At high pressures, the conversion rate becomes low again and even decreases further as the gas pressure grows. The decreasing isomer conversion rate with increasing gas pressure was experimentally observed earlier for the spin isomers of CH₃F.³⁵

The temperature dependencies of the conversion rates at the gas pressures equal to 1 and 760 Torr are presented in Figure 5. The difference between these curves can be understood because at low and high gas pressures the main contributions to the conversion rate come from the mixing of the level pairs situated at significantly different energies. At the gas pressure of

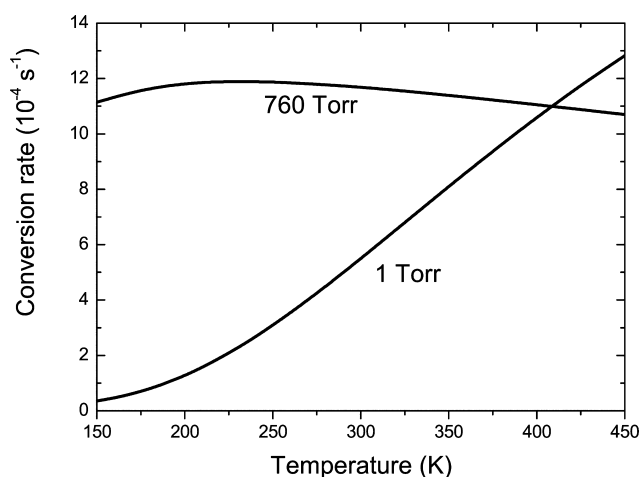


Figure 5. Spin isomer conversion rate dependence on gas temperature for the gas pressures of 1 and 760 Torr.

1 Torr, the main level pair (1, 23, 10)–(1, 21, 11) has the energy 899 cm^{-1} (Table 4). At 760 Torr, the main contribution to the conversion rate comes from the level pair (1, 14, 4)–(1, 15, 3) having the energy 256 cm^{-1} .

VIII. DISCUSSION AND CONCLUSIONS

We have calculated the energies and the nuclear spin and rotational wave functions of the asymmetric top molecule, C_2H_4 . Using these data, we determined the spin–spin mixing of the states of nuclear isomers in C_2H_4 having the B_{1u} and B_{2u} symmetries. This has allowed us to calculate the $B_{1u} \rightleftharpoons B_{2u}$ spin isomer conversion rate in C_2H_4 in the framework of the quantum relaxation model.

Our calculations determine that at low gas pressures the isomer conversion rate grows linearly with pressure as

$$\gamma_{\text{theor}} = 5.2 \times 10^{-4} P \text{ s}^{-1} \quad (34)$$

where P is the gas pressure in Torr units. This dependence is in very good agreement with the conversion rate dependence on pressure measured in a recent paper by Sun et al.,²⁹

$$\gamma_{\text{exp}} = (5.5 \pm 0.8) \times 10^{-4} P \text{ s}^{-1} \quad (35)$$

Our calculations show that the isomer conversion in C_2H_4 between the spin states with B_{1u} and B_{2u} symmetries is determined by the spin–spin mixing of just one pair of states having the rotational numbers $p' = 1, j' = 23, K' = 10$ and $p = 1, j = 21, K = 11$. The nuclear spin–rotation interaction was not taken into account in this paper. Note that the pair of states (1, 23, 10) and (1, 21, 11) is not mixed by the spin–rotation coupling because of the selection rules (30).

To avoid any confusion, we remind once again that our choice of the molecular coordinate axes made the notations of the spin states and rotational states different from that used in the paper by Sun et al.²⁹ We also used notations for the rotational levels different from the notations used in ref 29. On the other hand, one can check that the symmetries of rotational levels and their energies in the present paper are in complete agreement with Sun et al.²⁹

Although our calculations gave the value of conversion that is rather close to the measured one, there are many sources of uncertainties in the calculations, as is normally the case for the physical problem of this complexity. One source of uncertainty

comes from the approximation made in our estimation (31) of the rate Γ , which determines the decay rate of the coherence between spin isomer quantum states induced by the intra-molecular interactions. The rate Γ was assumed in our calculations to be equal to the population decay rate of the rotational states and thus equal to the ethylene spectral line broadening coefficient.

It is rather difficult to perform theoretical calculations of the rate Γ at the sufficient level of accuracy. Instead, one can measure the rate Γ experimentally by using for this purpose the level crossing resonances in isomer conversion. These phenomena were studied in refs 15 and 17 using CH_3F molecules and an external electric field for splitting and crossing the rotational levels of CH_3F . Ethylene molecules C_2H_4 have no permanent electric dipole moment and thus have a very small Stark effect. However, one can use the Zeeman effect for the observation of the level crossing resonances in the spin conversion of C_2H_4 . Magnetic fields on the order of 1–10 T would be sufficient for this purpose.

In our calculations we did not account for the spin–rotation interaction in C_2H_4 . The main reason for that is the difficulties in the calculations of the spin–rotation tensor for polyatomic molecules. The spin–rotation tensor can be determined by ab initio calculations similar to those of the theoretical work⁵³ devoted to the spin isomer conversion in NH_3 . On the other hand, our calculations show that the spin–spin coupling in C_2H_4 alone gives the conversion rate value close to the one experimentally determined in ref 29. It can happen that the spin–rotation contribution to the isomer conversion in C_2H_4 is suppressed because of the high symmetry of the molecule. If one assumes that all spin–rotational tensors in eq 29 are equal because of the symmetry of C_2H_4 , then the spin–rotation perturbation becomes proportional to the spin operator $\hat{I}^{(1)} + \hat{I}^{(2)} + \hat{I}^{(3)} + \hat{I}^{(4)}$. Such a spin operator has the symmetry A_g and cannot mix different spin isomers in the C_2H_4 . We will address the spin–rotation contribution to the isomer conversion in C_2H_4 elsewhere.

The calculated pressure dependence of the conversion rate shows that, at high gas pressures ($P \approx 300$ Torr), the conversion rate is small, $\gamma \approx 10^{-3} \text{ s}^{-1}$, and decreases even further with increasing pressure. In the pressure range 1–100 Torr the conversion rate behavior appears to be rather complicated.

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Notes

The authors declare no competing financial interest.

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